TECHNISCHE UNIVERSITÄT WIEN
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Diplomarbeit

Synthesis and Characterization of PN-supported Mn(I) Alkyl Complexes

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Diplom-Ingenieurs

unter Leitung von

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Wien, im April 2022 _____

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Abstract

The replacement of noble metals by earth abundant metals is of fundamental importance in organometallic chemistry and a challenge in terms of reactivity and stability. Over the last few years various manganese(I)-complexes were established and implemented for catalytic approaches.

This work presents the synthesis and characterization of novel Mn(I) alkyl carbonyl complexes, bearing PN-ligand. In this context, the influence of steric and electronic effects were investigated. At first, three different pathways for PN-ligand synthesis were optimized, utilizing HPR_2 or $LiPR_2$ and the desired amine.

Later on, complexation was achieved upon treatment with $[Mn(CO)_5Br]$. These tricarbonyl complexes were used as starting material for the synthesis of PN-based manganese(I) carbonyl alkyl complexes. In fact, alkyl complexes were successfully synthesised upon treatment of the triflate congener complexes with MeLi or MeMgCl. In this context, the novel Mn(I) complexes $[Mn(P^{iPr}N^{Me}\text{-Et})(CO)_3(CH_3)]$, $[Mn(P^{Cy}N^{Me}\text{-Et})(CO)_3(CH_3)]$ and $[Mn(P^{Ph}N^{Me}\text{-Et})(CO)_3(CH_3)]$ were received.

Moreover, preliminary catalytic investigation in the dimerization of alkynes confirmed PN-based Mn(I) alkyl complexes as potential catalysts.

Kurzfassung

Homogene Katalyse stellt einen der wichtigsten Bereiche der modernen metallorganischen Chemie dar. Hierbei basieren die meisten Katalysatoren nach wie vor auf Edelmetallen wie etwa Ruthenium oder Palladium. Der Ersatz durch unedle Metalle spielt eine immer wichtigere Rolle in der heutigen Zeit. Übergangsmetallen wie Mangan haben sich in den letzten Jahren als vielversprechende Kandidaten erwiesen.

Diese Arbeit behandelt die Synthese und Charakterisierung neuer Mangan(I) Alkylkomplexe und legt einen besonderen Fokus auf den Einsatz verschiedener PN-Liganden.

Zu Beginn dieser Arbeit wurden drei verschiedene Synthesewege für PN-Liganden präsentiert. Hierbei wurde das entsprechende Phosphin mit dem jeweiligen Amin., in einer Einstufensynthese umgesetzt. Anschließend konnte die Komplexierung mit $[Mn(CO)_5Br]$ durchgeführt werden.

Die Einsetzbarkeit der synthetisierten Tricarbonyl-Bromid Komplexe als Ausgangsverbindungen für Alkylkomplexe wurde untersucht. Hierbei stellte sich heraus, dass der Bromidligand durch einen Triflatliganden substituiert werden musste. Durch Umsetzung mit MeLi oder MeMgCl konnten drei neue Alkylkomplexe $[Mn(P^{iPr}N^{Me}\text{-}Et)(CO)_3(CH_3)]$, $[Mn(P^{Cy}N^{Me}\text{-}Et)(CO)_3(CH_3)]$ und $[Mn(P^{Ph}N^{Me}\text{-}Et)(CO)_3(CH_3)]$ hergestellt werden.

Darüber hinaus wurden erste Vorversuche getätigt um die katalytische Aktivität der Komplexe zu untersuchen. Hierfür wurde die Dimerisierung von Phenylacetylen gewählt.

1 Introduction

Industrial and technological advancement have a major impact on our everyday lives. Chemical processes are the basis of many developments in these areas and often require the use of catalysts.[1] A catalyst may accelerate a reaction, lower the required reaction temperature and/or increase productivity. Moreover, side product formation can be avoided, eliminating purification steps and thus reducing energy consumption.[2]

In the last century, organometallic catalysis played a major role as important industrial processes such as the Fischer-Tropsch[3] synthesis[3] or the Monsanto acetic acid process[4] were developed. In 1938, Roelen introduced hydroformylation[5] reactions and within that he laid the foundation for the industrial use of homogeneous organometallic catalysts.[6]

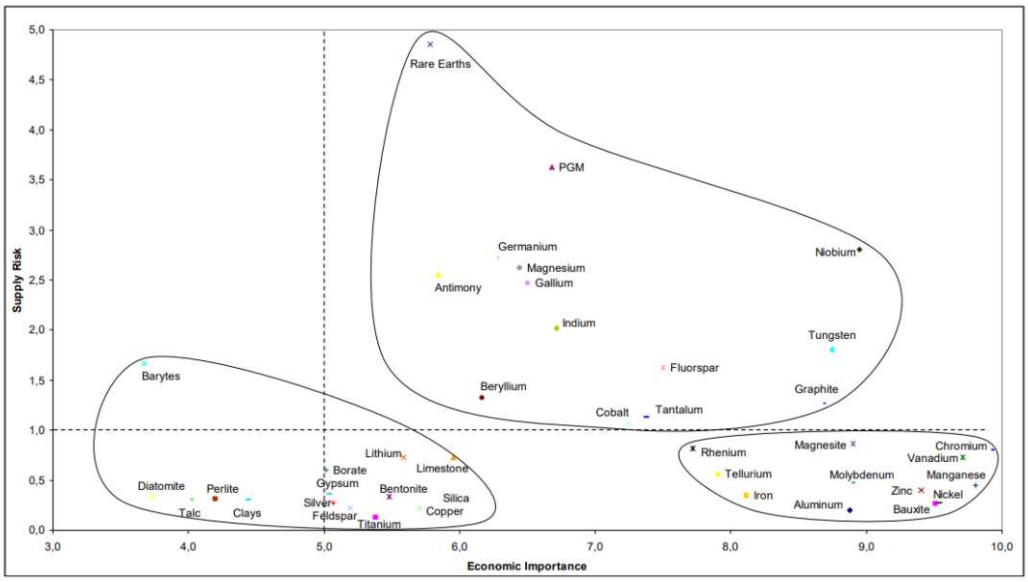


Figure 1. Overview of Crucial Materials and Their Supply Risks.[7]

Thus far, the most efficient and widely used catalysts are usually based on noble metals such as Ru, Pd or Pt.[7] As the supply risk (Figure 1) for these metals increases, it stands to reason that replacing these precious and expensive metals is of great interest. Fortunately, utilizing manganese as the third most abundant non-precious metal in earth's crust grew in popularity in the last few years.[8]

The following sections will give an insight into synthesis and catalytic application of manganese(I)-based complexes. In this context, the crucial role of appropriate ligands will be emphasized.

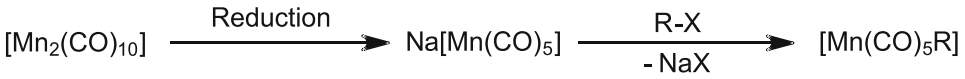
1.1 Manganese Carbonyl Alkyl Complexes

In 1957, Coffield *et al.*[9] described the first stable transition metal carbonyl alkyl compound $[Mn(CO)_5(CH_3)]$ (**I**). Since then, numerous researches established three different routes to synthesise this well-studied alky complex. Additionally, not only methyl, but also various alkyl or aryl congeners were successfully synthesized.

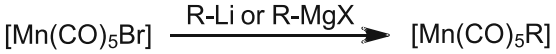
The first synthesis, reported in 1957 by Coffield[9], covers reduction of $[Mn_2(CO)_{10}]$ with an excess of 1% sodium amalgam to form $Na[Mn(CO)_5]$ (Scheme 1, I). After treatment with the alkyl halide MeI or dimethyl sulfate, $[Mn(CO)_5(CH_3)]$ could be isolated and purified by means of sublimation, yielding colourless crystals.

Another possibility represents the utilization of $[Mn(CO)_5(Br)]$ as starting material (Scheme 1, II). Upon treatment with the nucleophilic alkylation reagents phenyl lithium[10] or benzylmagnesium chloride[11] the alkylated complexes $[Mn(CO)_5(Ph)]$ or $[Mn(CO)_5(Bn)]$ were received. The main drawback of this route is massive formation of $[Mn_2(CO)_{10}]$ as side product. In addition, nucleophilic attack of the carbanions at the carbon atom of a carbonyl ligand may occur.

I) Reaction of Nucleophilic $Na[Mn(CO)_5]$ with Electrophilic Carbon

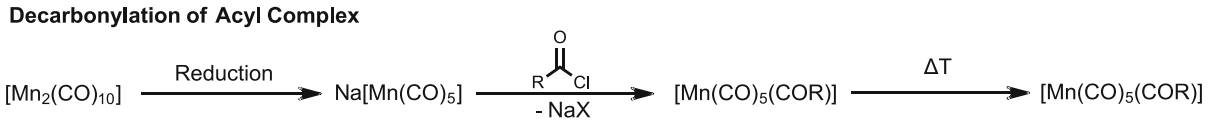


II) Reaction of Electrophilic $[Mn(CO)_5Br]$ with Nucleophilic Carbon



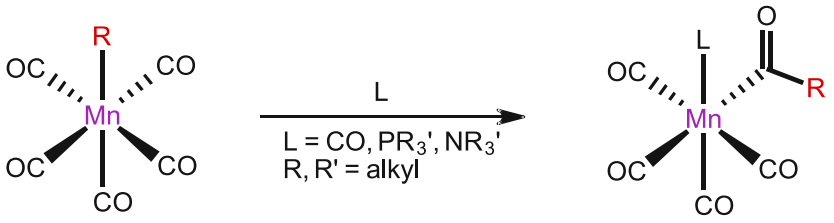
Scheme 1. Synthesis of Manganese Carbonyl Alkyl Complexes.

In order to get alkylated manganese(I) complexes a third route was developed (Scheme 2).[12] First, a THF solution of $NaMn(CO)_5$ was reacted with AcCl or BnCl. Once $[Mn(CO)_5Ac]$ had formed, decarbonylation due to thermal treatment took place to give $[Mn(CO)_5Me]$. Since this reaction is reversible, carbonylation is preferred at room temperature, thus increased reaction temperatures and long reaction times are required to receive an alkyl complex *via* this route. Thermal treatment of $[Mn(CO)_5Bz]$ resulted in the formation of $[Mn(CO)_5Ph]$.



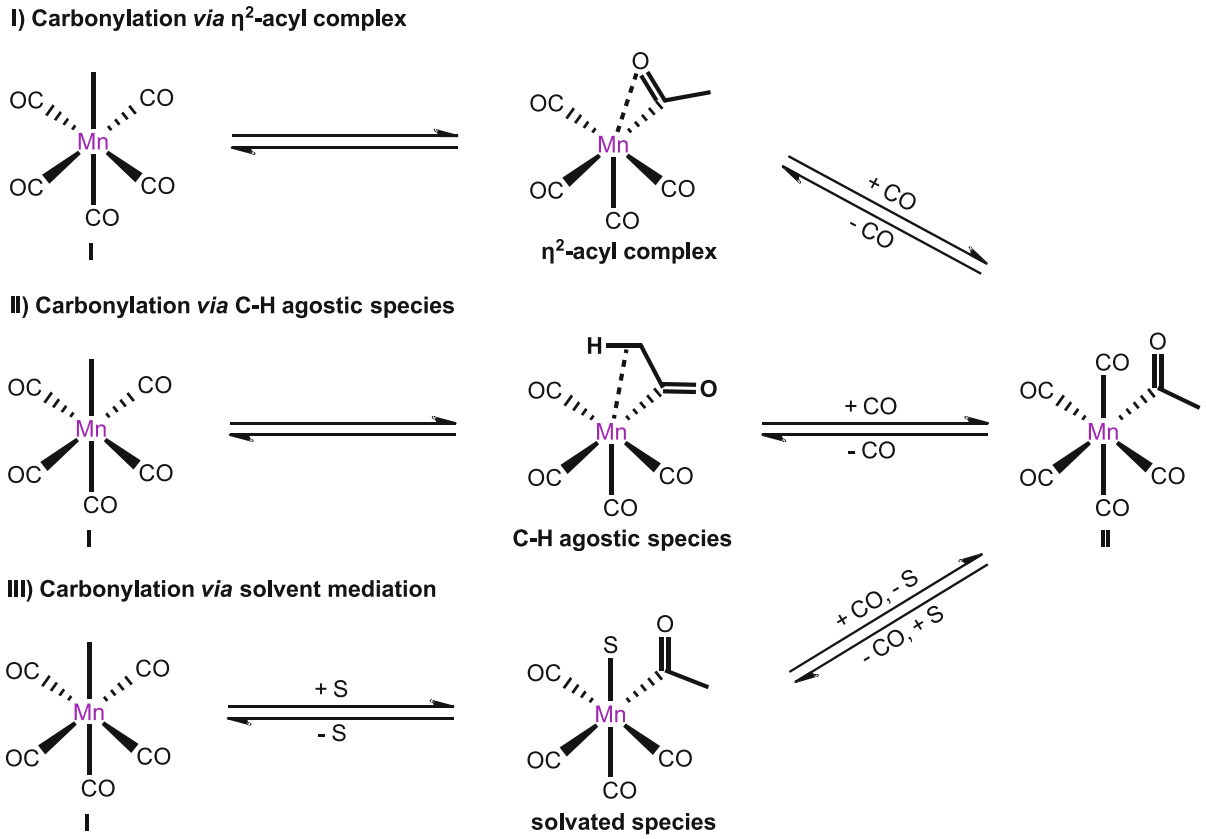
Scheme 2. Synthesis of Mn-Alkyl Complexes by Decarbonylation.

The reversible decarbonylation/carbonylation, described by Coffield and coworkers, is among the most studied migratory insertion reaction. The entering neutral ligand (L) induces the migration of the alkyl group to the positively polarized carbonyl. Thus, the alkyl metal carbonyl is converted to the corresponding acyl complex (Scheme 3). Calderazzo and coworkers demonstrated for the carbonylation reaction that the carbonyl inserts into the Mn-alkyl and not *vice versa*.[13]



Scheme 3. General Reaction Pattern of Migratory Insertion in Mn-Alkyl Complexes.

For the description of the reaction pathway, theoretical studies[14] indicated at least two different non solvent assisted intermediates. The fist intermediate (Scheme 4, I) involves a coordinatively saturated complex with an η^2-acyl group. In contrast, a coordinatively unsaturated species, stabilized by an agostic interaction between C-H and manganese (Scheme 4, II) is possible. Since migratory insertion is a twostep process, a CO molecule attacks the intermediate to form the acyl-product (**II**). In scenario II, the agostic intermediate is formed first, followed by conversion to **II**. Further work presented a solvent-coordinated acyl complex (Scheme 4, III) as a third potential pathway to achieve migratory insertion.[15]

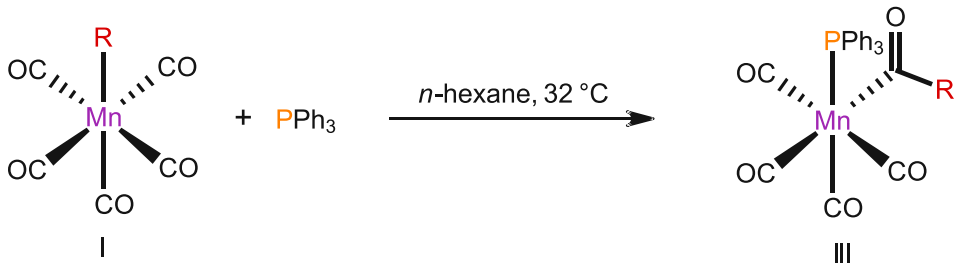


Scheme 4. Reaction Pathways for the Conversion of I to II.

The influence on the reaction rates depends on various parameters. One of them is the effect of the solvent. Cotton and coworkers pointed out that polar solvents may enhance the carbonylation rates of $[Mn(CO)_5(Me)]$.[16] It was found that electron-donating solvents e.g., THF increase the rate of alkyl insertion in $[Mn(CO)_5CH_2C_6H_{5-n}X_n]$ compounds. Even the effective size of the solvent is crucial, hence the rate constant k decreases with increasing solvent size.[17]

However, a far greater influence on the rate of alky migration refer to the nature of the alkyl or aryl ligand coordinated to metal centre. The following trend for carbonylation reactions was found *n*-Pr > Et > $CH_2C_6H_5$ > Ph > Me ≫ CF_3.[18,19]

Since other entering ligands apart from CO may be utilized to trigger migratory insertion, the nature of the entering ligand also plays a role. In fact, phosphines are commonly used as incoming ligands. As for carbonylation reactions, Moss and Anderson figured out a rate dependency for the alkyl group R in respect to reactions of $[Mn(CO)_5R]$ (R = CH_3 to *n*-$C_{18}H_{37}$) with PPh_3 (Scheme 5).[20,21]



Scheme 5. Reaction of I with Triphenylphosphine.

The kinetic data revealed strong increase for the rate from R = CH_3 to R = *n*-propyl, followed by a rapid decrease until R = *n*-heptyl. Steric and electron effects influence the reaction rates, which becomes clear as the rate-determining step in the CO-insertion is the migration of R. Again, electron-donating substituents facilitate this kind of reaction. It should be mentioned that when R becomes larger than *n*-propyl, steric effects start to take over until R = *n*-heptyl. From then on, rates stay almost constant.

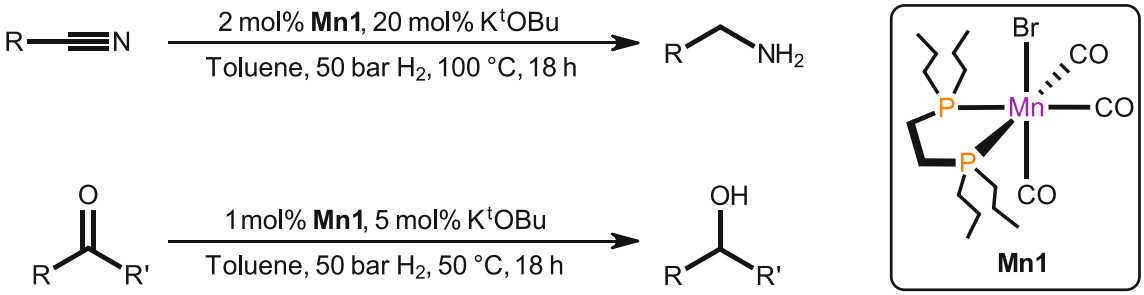
Furthermore, various research works have been carried out to study reactions with manganese-pentacarbonyl-alkyl complexes.[22] Anionic nucleophiles e.g., OCH_3^-, SCN^- or CN^- were also capable of insertion reactions, as well as LiI salt, forming anionic complexes.[23] Reactions with alkenes, alkynes and azobenzene gave cyclometalated products.[24,25]

In this context, a wide range of catalytic transformations have been studied in the last decades and selected examples, relevant for this thesis, are briefly presented in the following section.

1.2 Bisphosphine-Based Manganese(I) Complexes

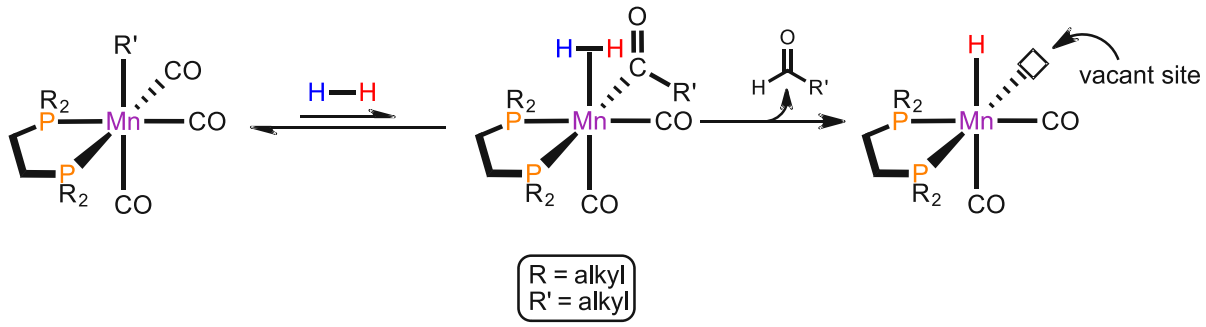
1.2.1 Hydrogenation Reactions

In 2018, the research group of Kirchner presented the highly productive complex *fac*-[Mn(dpre)(CO)$_3$Br] (**Mn1**) which is capable of hydrogenating (hetero)aromatic or aliphatic nitriles and ketones in the presence of a base (K^{t}OBu) (Scheme 6). Reduction of nitriles to primary amines required a reaction temperature of 100 °C and 50 bar hydrogen pressure. Excellent yields could be achieved for various electron-donating and electron-withdrawing substituents e.g., halides, ethers, esters, alcohols, alkynes or pyridine moieties. In contrast to that, the hydrogenation of ketones to alcohols took place with a smaller amount of catalyst (1 mol%) and fewer base (5 mol%). Additionally, the reaction was performed at 50 °C. Again, excellent yields for selected aromatic and aliphatic substrates were observed.[26]



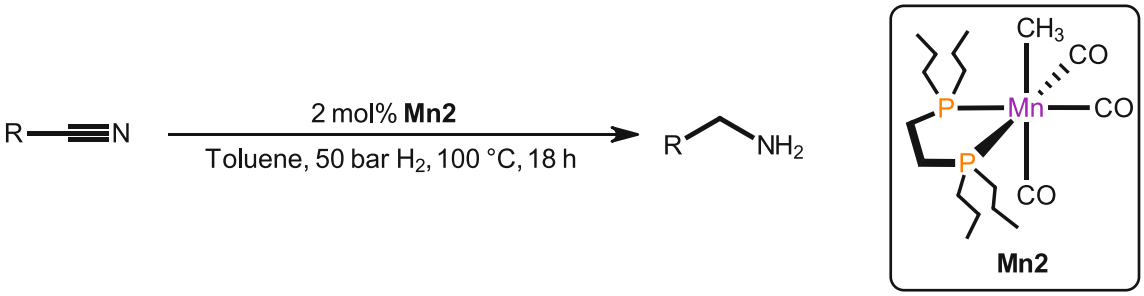
Scheme 6. Hydrogenation of Nitriles and Ketones by Mn1.

One may suggest, that a substitution of bromide by *t*-BuO$^-$ takes place, upon which the nucleophile attack of *t*-BuO$^-$ on the electrophilic adjacent CO ligand may occur, followed by an inner-sphere mechanism. Thus, if the anionic ligand is exchanged with an alkyl group, migratory insertion can occur. In this context, molecular hydrogen can activate the alkyl migration while forming an acyl intermediate. This acyl ligand is capable of H-H bond cleavage. Hydrogenolysis liberates the *n*-aldehyde, whereby the unsaturated 16 e$^-$ complex is formed. This catalytically active complex is now capable of reduction *via* inner sphere mechanism (Scheme 7).



Scheme 7. Activation of PP-supported Mn(I) Carbonyl Akyl Complex by H_2.

Following works focused on the alkylated species for catalytic applications. Soon after explorations with **Mn1**, Kirchner and coworkers introduced the methylated complex *fac*-[Mn(dpre)$(CO)_3CH_3$] (**Mn2**) (Scheme 8).[27] Catalytic activity was shown for the hydrogenation of nitriles. One important difference to **Mn1** was the absence of base, which represents an atom-economic improvement. No activity was detected for the corresponding hydride complex *fac*-[Mn$(CO)_3$(dpre)H]. Additionally, the performance of 2,2'-bipyridine (bpy)-based complex *fac*-[Mn(bpy)$(CO)_3CH_3$] was investigated,[28] giving no conversion. This may be a consequence of the less donating bipyridine ligand, highlighting the importance of the bisphosphine ligands.

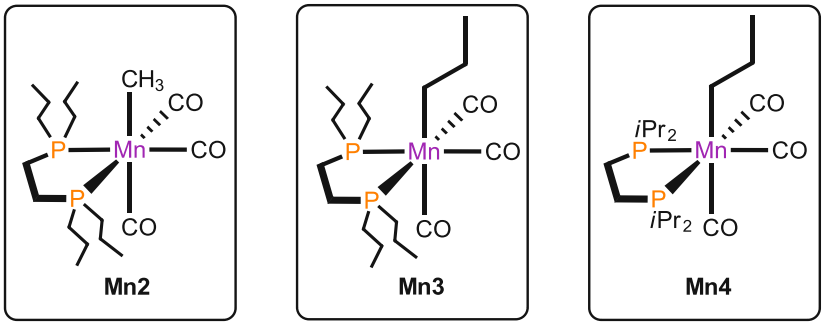


Scheme 8. Additive-Free Hydrogenation of Nitriles by Mn2.

Since previous results in hydrogenation reactions were satisfying, further studies involved modifications related to the number of carbon atoms of the alkyl ligand and the substituents on the bisphosphine ligand.[29] In this context, **Mn2**, *fac*-[Mn(dpre)(CO)$_3$(CH$_2$CH$_2$CH$_3$] (**Mn3**) and *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$] (**Mn4**) (Scheme 9) were investigated for catalytic applications.[30] Interestingly, chemoselective reduction toward *α,β*-unsaturated carbonyls was found.

The reactions were conducted with catalyst loading of 3 mol% and a hydrogen pressure of 10 bar. At room temperature the C-C double bond of *α,β*-unsaturated carbonyls stayed intact, whereby heating up to 60 °C fully saturated systems were achieved. Several aromatic substrates, tolerating halides, ethers, amines and pyridine motives, were reduced to the corresponding alcohol. The right choice of bidentate ligand and alkyl ligand seems to be crucial, since no or only traces of conversion were observed for **Mn2** and **Mn3**.

As described in the section before, a *n*-propyl alkyl ligand facilitates migratory insertion due to electron-donating properties. In this case the sterically more demanding *iso*-propyl based bisphosphine ligand played a more dominant role, as **Mn4** was the only one to exhibit good catalytic activity.

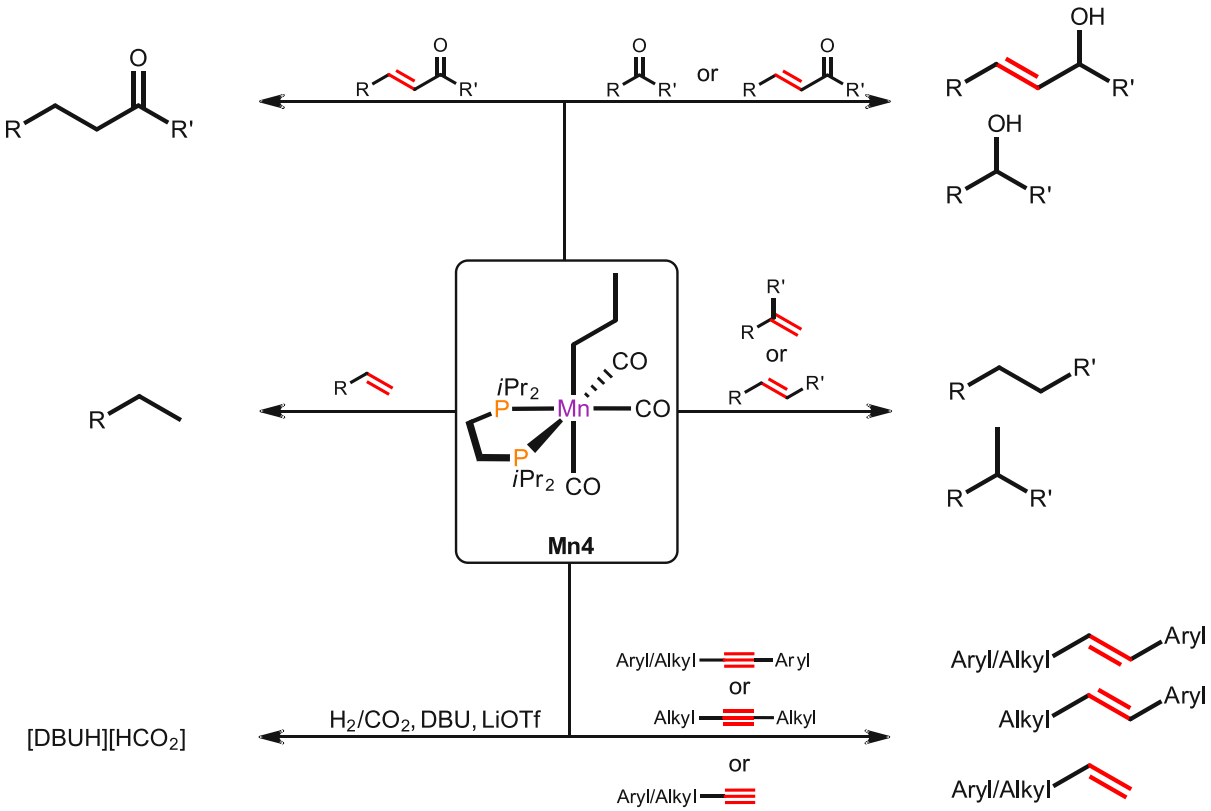


Scheme 9. Investigated Complexes for the Hydrogenation of Ketones.

Further investigations of Kirchner[31] and coworkers concerned the hydrogenation of unactivated C=C double bonds. A catalyst loading of 2 mol% **Mn4** and a hydrogen pressure of 50 bar was applied. Within this work mono and 1,1-disubstituted alkenes were reduced at room temperature, whereas disubstituted alkenes required a reaction temperature of 60 °C. On the other hand, trisubstituted alkenes stayed intact. Substrates bearing halides, alcohols, acetals or anhydride functionalities as well as dienes gave moderate to excellent yields. Nitriles or acidic carboxylic moieties were not tolerated under these reaction conditions. It should be mentioned, that no reaction occurred if $[Mn(CO)_5CH_3]$, *fac*-$[Mn(bpy)(CO)_3CH_3]$ or *fac*-$[Mn(dippe)(CO)_3H]$ were employed as catalyst.

In addition, **Mn4** was proven to be capable of reducing CO_2 to formate in the presence of base (DBU) and a Lewis acid (LiOTf). The ideal conditions were found to be 80 °C, 75 bar H_2/CO_2. Interestingly, DFT calculations revealed that the κ^2-*O*,*O*-formate is the most stable intermediate, which is an off-cycle species. To keep the equilibrium on the side of the productive κ^2-*CH*,*O*-formate complex, LiOTf was added, hence lewis acids are known to enhance reactivity.[32]

Recently, the selective semihydrogenation of alkynes with **Mn4** was reported by Kirchner.[33] Two different options for the hydrogen source were described, both of which resulted in selective reduction to *E*-alkenes. The first option included 1 mol% catalyst loading, hydrogen pressure at 30 bar and reaction temperature at 60 °C in toluene. The second one was conducted with a catalyst loading of 0.5 to 2 mol% at 90 °C. In this case the dihydrogen was generated *in situ* by combining MeOH and $K[BH_4]$. The borohydride undergoes alcoholysis to form $K[BOR_4]$ and H_2. A broad scope of aryl-aryl, alkyl-aryl and terminal alkynes were investigated. Functional groups on the substrate such as halides, phenols, nitriles, unprotected amines and heterocycles were tolerated. Interestingly, aliphatic alkynes gave excellent conversions, but showed moderate *E*-selectivity. An overview of all hydrogenation reactions catalysed by **Mn4** is depicted in Scheme 10.



Scheme 10. Overview of Hydrogenation Reactions, Catalysed by Mn4.

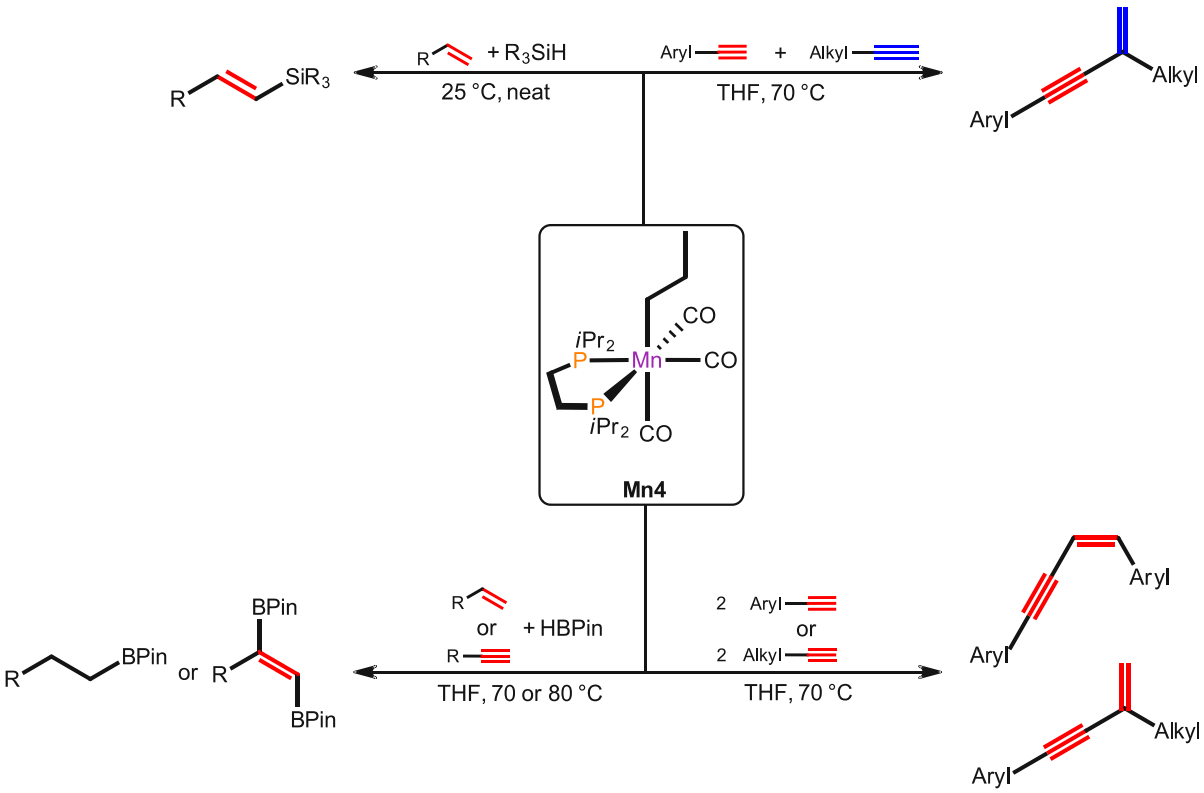
1.2.2 Hydrofunctionalization Reactions by Manganese Alkyl Complexes

Another area that shall be discussed are Mn(I)-catalysed hydrofunctionalizations. In this context, polarized E-H (E = C, B, Si) bonds induce migratory insertion, whereby the activated 16 e^- complex Mn-E is formed. Interestingly, the hydrogen can be seen as a proton (for alkynes) or as a hydride (for boranes and silanes).

In 2021 Kirchner and coworkers described the dimerization of terminal alkynes catalysed by **Mn4**.[34] Remarkable results in terms of conversion and selectivity were pointed out. All reactions were performed at 70 °C within 18 hours and a catalyst loading of 1 mol%. For aromatic substrates mainly *Z*-1,3-enynes (head-to-head) products were observed. Electron-withdrawing groups gave excellent yields and moreover good *E*:*Z-ratio*. No conversion was observed for substrates bearing aniline or pyridine moieties, probably due to the coordinating properties of the nitrogen. Interestingly, dimerization of aliphatic alkynes mainly gave *geminal*-1,3-enynes (head-to-tail) products with a certain content of *Z*-1,3-enynes, perhaps as consequence of rotating coordinated alkyne during the catalytic process. Additionally, cross-coupling of aromatic and aliphatic alkynes was possible, with moderate to good yields for electron-rich aryl systems with aliphatic alkynes.

Further investigations verified catalytic activity of **Mn4** towards hydroboration reactions with pinacolborane (HBPin).[35] Monosubstituted aromatic and aliphatic alkenes were converted with HBPin in THF at 60 °C within 24 hours and a catalyst loading of merely 0.25 mol% to the respective hydroborated-alkane. Substrates bearing halides, ethers, amines and esters were well tolerated. Rising catalyst loading up to 0.5 mol% enabled diboration of terminal acetylenes to *trans*-1,2-diborated products. Until now, this is the only transition metal complex known to catalyse this type of transformation.

Later on, Kirchner and coworkers presented investigations in respect to Mn(I)-supported dehydrogenative silylation of alkenes.[36] Again, **Mn4** appears to be capable of this transformation. Et_3SiH, $PhMe_2SiH$ and $(SiMe_3O)_2MeSiH$ were chosen as silylation agents. In the case of aromatic alkene substrates, the reaction yielded *E*-vinylsilanes. In contrast to that, aliphatic alkenes were transformed to *E*-allylsilanes. Electron-withdrawing and electron-donating groups on the aromatic substrates achieved excellent *E*-selectivity and yields. It was figured that the highest reactivity was observed for $PhMe_2SiH$ with 0.5 mol% catalyst, followed by Et_3SiH with 2 mol% catalyst and $(SiMe_3O)_2MeSiH$ with 2 mol% catalyst and elongated reaction times. It should be emphasized that all reactions were conducted without solvent and at room temperature. Since the ratio of alkene and silane was approximately 3:2, at least partial acceptorless dehydrogenative silylation (ADS) took place.

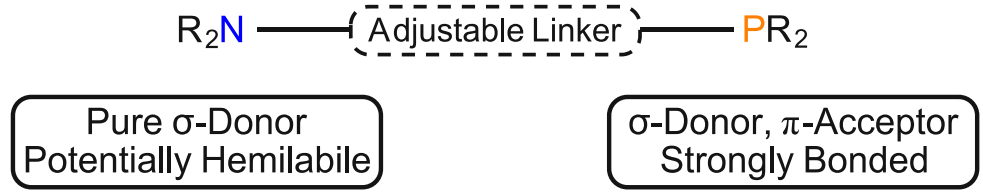


Scheme 11. Overview of Hydrofunctionalization Reactions, Catalysed by Mn4

1.3 Aminophosphine Bidentate Ligands (PNs)

Neutral chelating ligands such as aminophosphines (PNs) represent an interesting class of 4 e^- donors and are widely used as bisphosphine surrogates and often outperform them.[37] In the following, selected properties and applications of PN-based systems shall be sketched.

One attribute of PN ligands is the combination of two different donors. Phosphines are considered to be σ-donors as well as π-acceptor ligands. As a consequence, phosphines are known to be soft Lewis bases. Thus, phosphines typically form strong bonds with electron rich transition metals in low oxidation states. In contradiction to that, amines, being pure σ-donors, represent hard donors and often bind strongly to hard Lewis acids.[37] The combination of these properties in one ligand set (Scheme 12) may result in the formation of an unsymmetrical electronic situation around the metal centre. Thus, various reactions may be facilitated e.g., selective ligand substitution.[38] Apart from electronic parameters, the steric demand of amine ligands is significantly higher, then the demand of phosphine donors with the same substituents. The combination of forming weaker nitrogen-metal bonds (at least for late transition metals) and the increased steric bulk, enables (hemi)lability of amine donors. Thus, hemilability is often characteristic for PN-based complexes.[39]



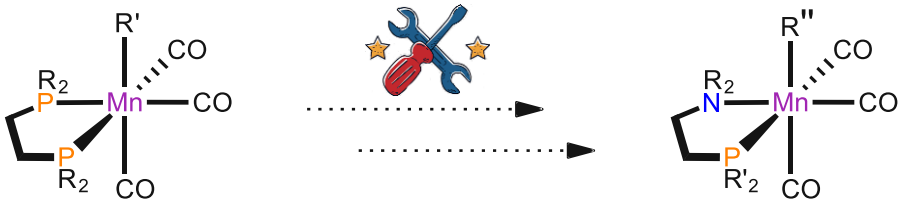
Scheme 12. Electronic and Steric Parameters of PN Ligands.

In fact, Moreno-Mañas and coworkers studied the isomeric equilibria for cationic PN-derived Pd-allyl complexes by means of NMR.[40] The hemilability of the N-donor was assigned to be the reason for the fluctional behavior of the allyl group. Furthermore, the donor properties of the amine *versus* the phosphine donor could be elucidated by ^{13}C-NMR.

In regard to catalytic applications, Schubert and coworkers employed [(PN)Pt(Me)(X)] (X = Me, Cl) complexes for a manifold of transformations. Such complexes were shown to be active for the chlorination of silanes with chloroform,[41] formation of cyclic siloxane from silanes under oxidative conditions[42] or the reductive coupling of stannanes accompanied by dihydrogen formation.[43]

2 Aim of the Thesis

In the recent years, various bisphosphine supported manganese(I) alkyl complexes were implemented as organometallic catalyst capable of hydrogenation and hydrofunctionalization reactions. Since, bidentate aminophosphines (PNs) as ligands combine different donor properties, the concept of hemilabilty may be exploited.



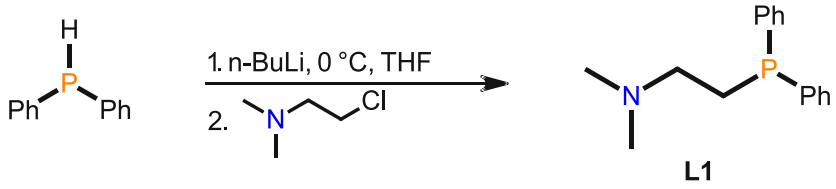
In this regard, the aim of the thesis was the synthesis and characterization of PN-based Mn(I) alkyl complexes, with the intention to outperform the PP-based systems in catalysis. PN bidentate ligands can readily be coordinated to manganese upon treatment with $[Mn(CO)_5Br]$. Afterwards, a suitable alkylation procedure shall be explored. The concluding purpose is the investigation of steric and electronic parameters in catalytic applications.

3 Results and Discussion

Various PN-ligand systems were chosen as potential surrogates for bisphosphine ligands. At first, the synthesis of such ligands will be elucidated and the results briefly discussed. Next, complexation of a manifold of PN-ligands with $[Mn(CO)_5Br]$ will be described. Furthermore, various approaches towards complexes of the type $[Mn(PN)(CO)_3(R)]$ will be compared. At last, the catalytic performance of the novel PN-supported in alkyne dimerization will be sketched.

3.1 Ligand Synthesis

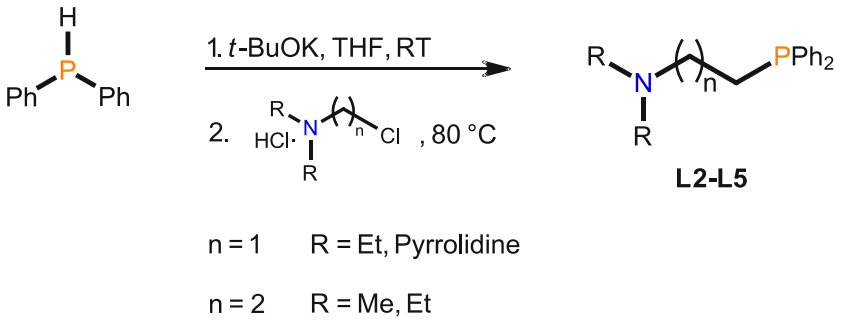
In order to obtain the PN-bidentate ligands three different routes were developed. **Route A** was found to be the most suitable way to synthesise **L1**. In this context, a modified procedure from literature was utilized (Scheme 13).[44] In the first step, $HPPh_2$was lithiation with *n*-BuLi at 0 °C, to form $LiPPh_2$ *in situ.*



Scheme 13. Synthesis of Ligand L1.

Subsequently, $Cl(CH_2)_2NMe_2$ was added dropwise and the reaction mixture was stirred at room temperature (RT) overnight. $^{31}P\{^1H\}$-NMR analysis showed the formation of several side products and residual PPh_2H (approx. 18 %). Upon work up, **L1** was isolated as a colourless oil in a moderate yield of 41 %.

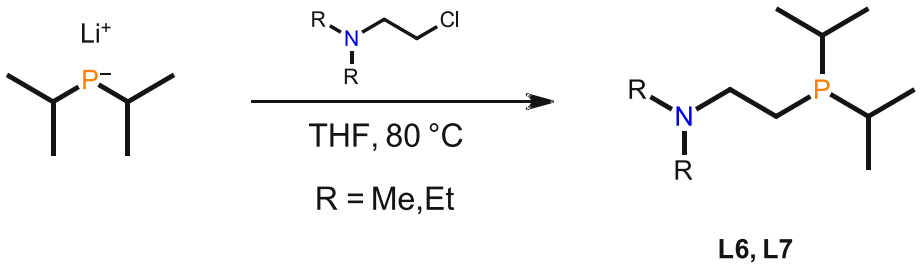
In order to improve the yield, **route B** was developed, which represents an adopted procedure from the literature (Scheme 14).[45]



Scheme 14. Synthesis of Ligands L2-L5.

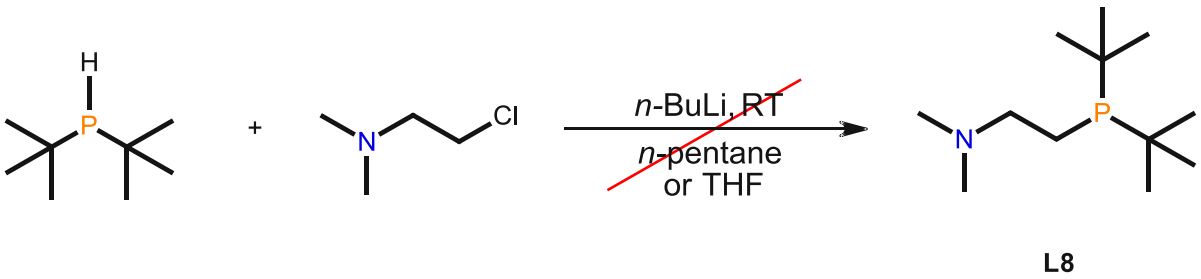
In this case *t*-BuOK was utilized to deprotonate the phosphine, followed by addition of the respective amine hydrochloride salt and refluxing overnight. During the reaction progress the orange suspension turned colourless. The reaction $^{31}P\{^{1}H\}$-NMR showed clean formation of the product, with no $HPPh_2$ left. This route contains the advantage of direct utilization of amine hydrochloride salt, compared to **route A**. With this approach the ligands **L2, L3**, **L4** and **L5** could be obtained *via* one step synthesis in moderate yields (Table 1).

The third **route C** (Scheme 15) has been designed according to **route A** and **B**. Readily, **L6** and **L7** could be obtained by treating *i*Pr_2PLi with the corresponding free amine. The crucial step was to add the free amine at reflux, otherwise low conversion and the formation of many side products was observed.



Scheme 15. Synthesis of Ligands L6 and L7.

Since this procedure worked well for the ligands **L6** and **L7**, the assumption was that it would also work for the corresponding ligand bearing *t*-butyl groups on the phosphine (**L8**) (Scheme 16). However, this was not the case. The first attempt was the *in situ* formation of *t*-Bu_2PLi by lithiation of *t*-Bu_2PH with *n*-BuLi in *n*-pentane. After stirring for 5 hours, the free amine $Cl(CH_2)_2NMe_2$ was added dropwise to the colourless suspension at RT, upon which the colour changed to yellow. This reaction mixture was stirred for 24 hours. The second attempt included THF instead of *n*-pentane and free amine was added dropwise at reflux temperature to *t*-Bu_2PLi. After 2 hours the reaction mixture was allowed to reach RT and stirred for another 24 hours. Both reactions resulted in a variety of side products, whereby no pure ligand could be obtained.



Scheme 16. Attempted Synthesis of L8.

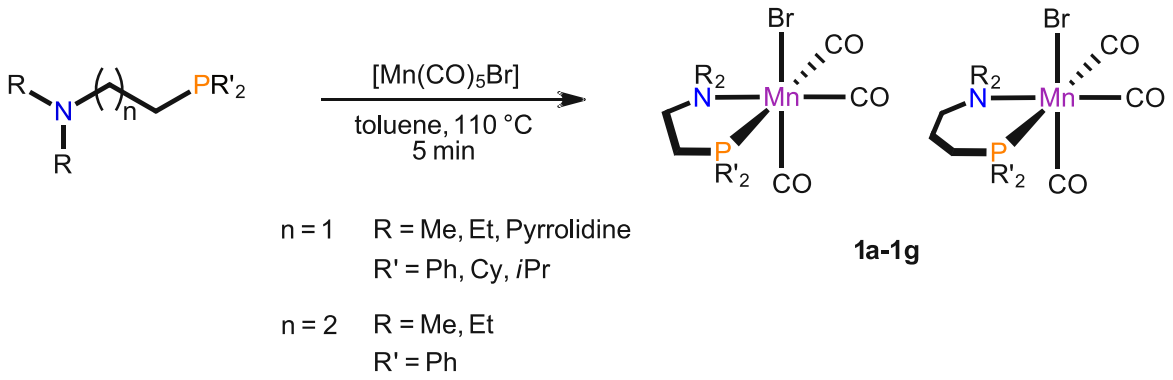
Ligands **L1**-**L7** were isolated as viscous oils with acceptable yields, which are depicted in Table 1. Although moderated yields were achieved, these three routes present one step syntheses for a broad scope of bidentate aminophosphine ligands with inexpensive starting materials. Additionally, scaling up was possible.

Table 1. Yields and ^{31}P-shifts of synthesized PN-ligands.

	Yield [%]	Colour	^{31}P-NMR shift [ppm]
$Ph_2P(CH_2)_2NMe_2$ **(L1)**	41	colourless	-19.7
$Ph_2P(CH_2)_2NEt_2$ **(L2)**	29	orange	-19.4
$Ph_2P(CH_2)_2N^{Pyrr}$ **(L3)**	41	colourless	-19.4
$Ph_2P(CH_2)_3NMe_2$ **(L4)**	44	colourless	-16.0
$Ph_2P(CH_2)_3NEt_2$ **(L5)**	38	orange	-16.1
$iPr_2P(CH_2)_2NMe_2$ **(L6)**	41	colourless	0.4
$iPr_2P(CH_2)_2NEt_2$ **(L7)**	46	colourless	0.5

3.2 Reaction of PN-Ligands with $[Mn(CO)_5Br]$

The next step was the complexation of all PN-synthesised ligands. In order to achieve this, the respective ligand was refluxed 5 minutes with $[Mn(CO)_5Br]$ in toluene as depicted in Scheme 17. Gas evolution indicated complexation, due to substitution of two CO-ligands by a PN-ligand. It was found that the choice of the solvent was crucial for product precipitation during work up. MeOH proofed to be suitable for **1a** and **1b**, whereas *n*-pentane was the solvent of choice for **1c**, **1d**, **1f**. After work up, the bromide complexes **1** were obtained as bench stable yellow or orange powders in good to moderate yields, as depicted in Table 2. However, **1b** could only be isolated in lower yield. Furthermore, it should be mentioned that **1e** was obtained as an orange oil. No tendency for crystallization was found for **1e**, perhaps due to the more flexible chain and ethyl groups.

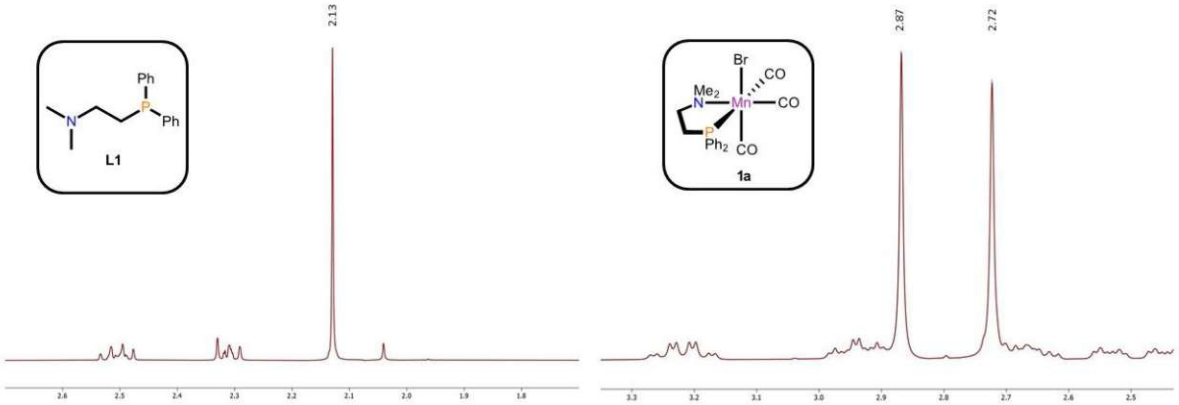


Scheme 17. Complexation of [Mn(CO)5Br] with PN-Ligands.

Table 2. Yields and Spectroscopic Data for 1a-1h.

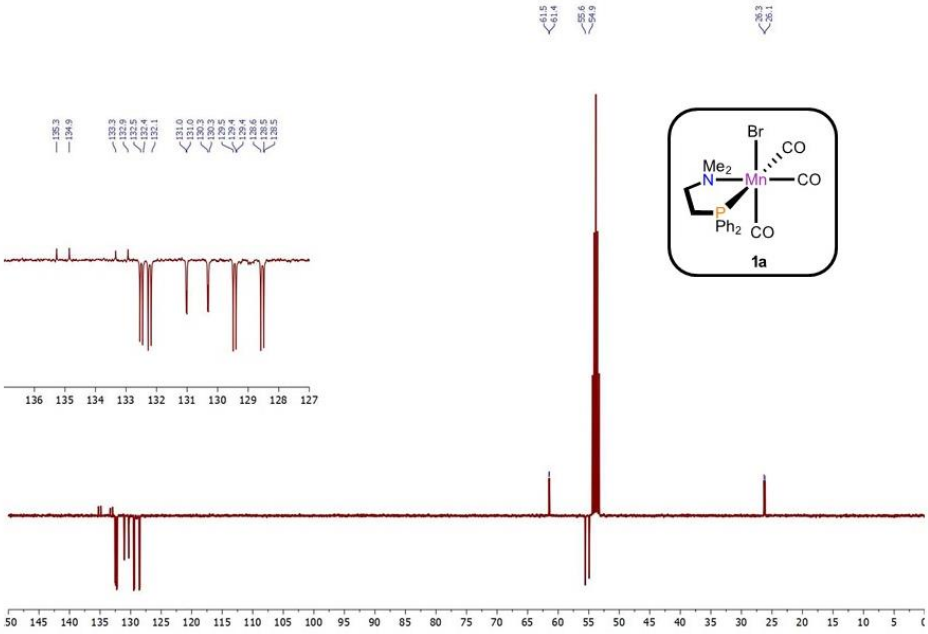
	Yield [%]	Colour	^{31}P }-NMR shift [ppm]
[Mn($P^{Ph}N^{Me}$-Et)$(CO)_3$Br] **(1a)**	63	yellow	59.9
[Mn($P^{Ph}N^{Et}$-Et)$(CO)_3$Br] **(1b)**	23	orange	55.2
[Mn($P^{Ph}N^{Pyrr}$-Et)$(CO)_3$Br] **(1c)**	77	yellow	57.5
[Mn($P^{Ph}N^{Me}$-Pr)$(CO)_3$Br] **(1d)**	70	orange	49.0
[Mn($P^{Ph}N^{Et}$-Pr)$(CO)_3$Br] **(1e)**	51	orange oil	37.1
[Mn($P^{iPr}N^{Me}$-Et)$(CO)_3$Br] **(1f)**	77	orange	49.0
[Mn($P^{iPr}N^{Et}$-Et)$(CO)_3$Br] **(1g)**	55	yellow	65.8

All products shown in Table 2 were characterized by ATR-IR- and NMR-spectroscopy. Whether the complex was formed or not, was easily determined by ^{1}H-NMR spectroscopy. As shown in Scheme 18, the methyl groups of ligand **L1** arise as one singlet. Due to the lack of symmetry upon complexation, the methyl groups arise as two singlets in complex **1a**.



Scheme 18. ^{1}H-NMR of Ligand L1 *versus* Complex 1a.

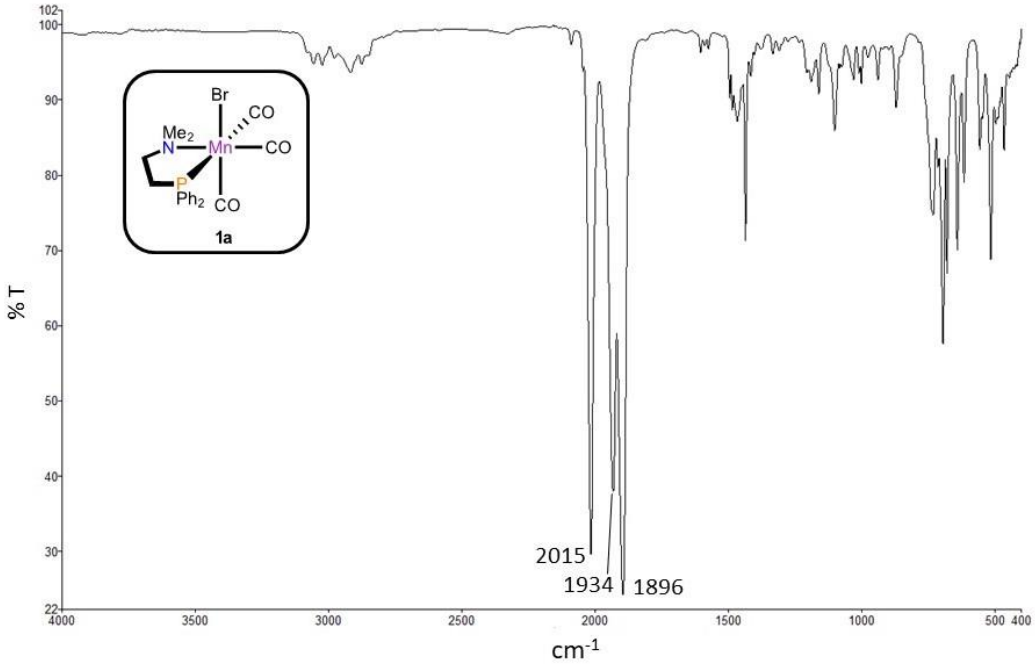
$^{13}C\{^{1}H\}$-NMR analysis of complex **1a** shows a carbon-phosphorus coupling for all carbon atoms except for -NMe_2. This is noticeable by the fact that these signals occur as doublets (Scheme 19). As described for the methyl groups in the ^{1}H-NMR, a separate set of signals appear in $^{13}C\{^{1}H\}$ spectra for the phenyl rings. The coupling constants of one phenyl ring in **1a** $^{1}J_{C\text{-}P}$ of 41.8 Hz, $^{2}J_{C\text{-}P}$ of 10.0 Hz, $^{3}J_{C\text{-}P}$ of 9.1 Hz and $^{4}J_{C\text{-}P}$ of 2.1 Hz follow the expected order of $^{1}J > {}^{2}J > {}^{3}J > {}^{4}J$.



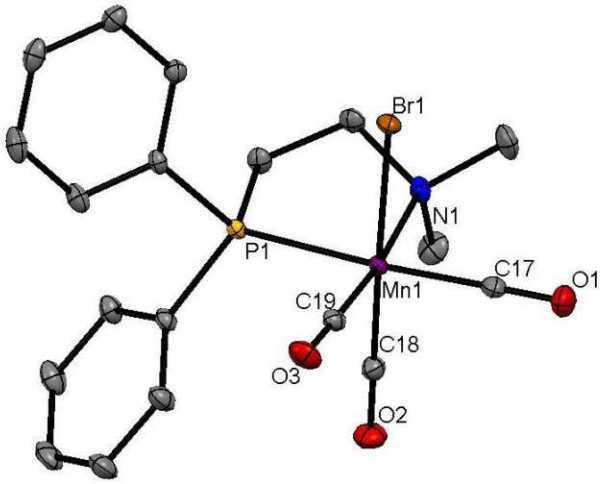
Scheme 19. $^{13}C\{^{1}H\}$-NMR of Complex 1a.

In principle it can be stated, that the linker signals in **1**, which is closer to the nitrogen, is shifted to lower field than the one closer to the phosphorous atom (Scheme 19). Unfortunately, no carbonyl resonances could be observed in all bromide complexes. In addition to that, the quaternary carbon atom of the phenyl groups in **1b** could not be detected.

Another important method to elucidate the coordination geometry is infrared analysis. Referring to the IR spectrum of **1a** (Scheme 20) three CO signals at 2015 cm^{-1}, 1934 cm^{-1} and 1896 cm^{-1}, one may predict *facial* arrangement of the CO-ligands. Furthermore, the molecule structure was confirmed by single crystal analysis of complex **1a** (Scheme 21) and **1b** (Scheme 22).



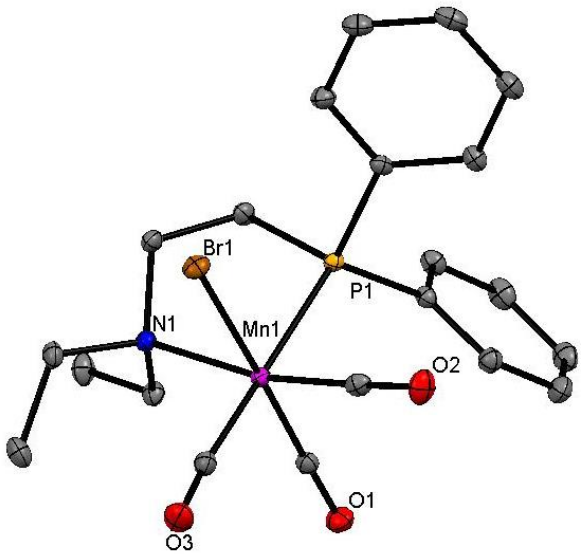
Scheme 20. ATR-IR Spectrum of 1a.



Scheme 21. Structural View of 1a with 50 % thermal ellipsoid. H omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mn1-Br1 2.5271(4), Mn1-P1 2.3214(5), Mn1-N1 2.204(1), Mn1-C17 1.847(2), Mn1-C18 1.791(2), Mn1-C19 1.793(2), P1-Mn1-C17 176.28(5), Br1-Mn1-C18 177.13(5), N1-Mn1-C19 174.31(6).

Delightfully, crystals suitable for X-Ray analysis were obtained by storing a saturated *n*-penatne solution of **1a** and **1b** at room temperature. Complex **1a** provides a slightly distorted octahedral coordination sphere with bond angles of 176.28° (P1-M1-C17), 177.13° (Br1-Mn1-C18) and 174.31° (N1-Mn1-C19). Hereby, the biggest deviation from perfect linear angle of 180° is seen for N1-Mn-C19. In Scheme 21 the *facial* arrangement of the carbonyl ligands is consistent with the IR spectrum. The Mn1-P1 distance of 2.321 Å and the Mn1-Br1 distance of 2.527 Å are longer than the bond distance Mn1-N1 of 2.204 Å. The shortest metal-carbonyl bond length is Mn1-C18 with 1.791 Å, the apical one. The basal CO lingand distances to the metal centre are 1.847 Å (Mn1-C17) and 1.793 Å (Mn1-C19).

In 2017 Pidko *et al.*[46] reported a similar system [Mn($P^{Ph}N^{H}$-Et)$(CO)_3$Br] with comparable bond distances in **1a**. The reported bond distances are 2.318 Å (Mn2-P2), 2.556 Å (Mn2-Br2), 2.115 Å (Mn2-N2), 1.795 Å (Mn2-C17(2)), 1.834 Å (Mn2-C16(2)) and 1.806 Å (Mn2-C15(2)). Bond lengths Mn2-P2 and Mn2-Br2, as reported by Pidko and coworkers, are comparable to those of complex **1a**, while Mn2-N2 is significant shorter then in **1a**. The metal ligand distances of the basal CO ligands are as well comparable to **1a**. The metal ligand bond of the apical CO is almost the same length as in **1a**.



Scheme 22. Structural View of 1b with 50 % thermal ellipsoid. H omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mn1-Br1 2.5291(5), Mn1-P1 2.3230(5), Mn1-N1 2.239(1) Mn1-C19 1.796(1), Mn1-C20 1.791(1), Mn1-C21 1.831(1), P1-Mn1-C21 176.03(4), Br1-Mn1-C19 174.50(4), N1-Mn1-C20 169.59(5).

Complex **1b** is also octahedral coordinated (Scheme 22), with more deviation from perfect linear angle of 180° compared to complex **1a**. Especially the bond angle between N1-Mn1-C20 in **1b** shows deviating angle apart from 180° with 169.59°. The bond distances are 2.320 Å (Mn1-P1), 2.529 Å (Mn1-Br1) and 2.239 Å (Mn1-N1). The comparison of Mn1-P1 and Mn1-N1 bond distances of complex **1a** and **1b** revealed an interesting aspect. The distances between manganese and phosphorus atom are approximately the same in comparison to **1a**. The situation is quite different for the bond distances between manganese and nitrogen. Here, the distance of complex **1a** (2.204 Å) is significantly shorter than of complex **1b** (2.239 Å). This implies, that the longer distance is a consequence of the sterically more demanding ethyl groups in complex **1b**. From the reported data, the bond distance between manganese and nitrogen increases in the order $-NH_2$, $-NMe_2$, $-NEt_2$ due to steric and electronic effects.

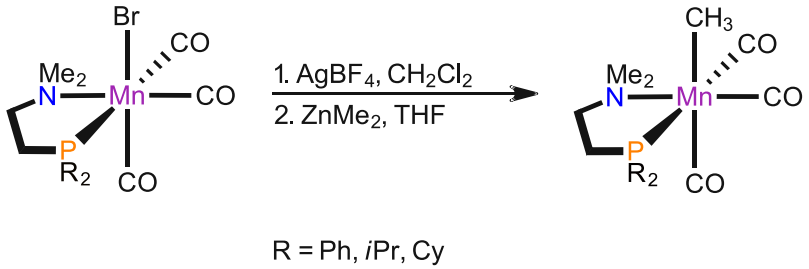
Unfortunately, thus far no single crystals with *iso*propyl or cyclohexyl on the P-donor were obtained.

3.3 PN-Supported Manganese Alkyl Complexes

Prior work has documented the efficiency of Mn(I) alkylated complexes for various catalytic transformations. Hence, PN-supported manganese alkyl complexes were targeted.

In analogues to the synthesis of PP-based systems,[31] reduction with Na-sand was tested to receive a nucleophilic Mn(-I), which was subsequently treated with electrophilic alkylation agents e.g., MeI or 1-bormopropane. All reaction *via* this method resulted in either in the formation of a hydride species (in case of 1-bromopropane) *via* tentative β-hydride elimination, or in decomposition. Furthermore, undesired tetracarbonyl side products occurred in virtually all reactions.

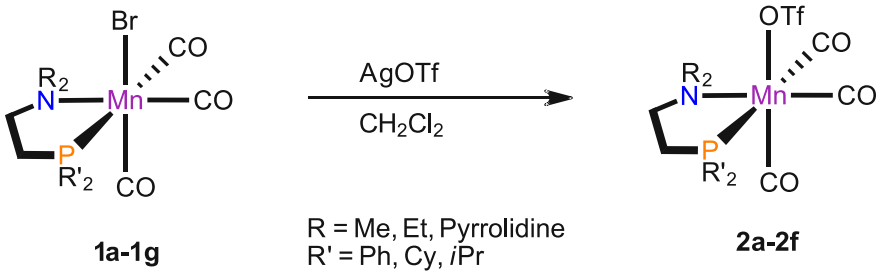
The next intention was to get from a nucleophilic to an electrophilic character of the manganese centre. In this case, manganese(I) complexes, bearing an electrophilic Mn-centre, should be reacted with carbon nucleophiles. The leaving group properties of the anionic ligand shall be increased, due to preliminary results within the Kirchner group. For this reason, tetrafluoroborate was chosen as weakly coordinating anion. Therefore complexes **1** were treated with $AgBF_4$ to introduce the tetrafluoroborate moiety. After filtration of the insoluble Ag-salts *via* syringe filter, the solvent was evaporated, the residue was redissolved in THF and either treated with $ZnMe_2$ or $ZnEt_2$ (Scheme 23). For alkylation of complex **1a**, **1f** and **1h** conversion to the desired products using $ZnMe_2$ was observed. However, similar impurities were observed as detected for the reactions with Na-sand. One of the major drawbacks, apart from long reaction times and low yields, was the removal of formed zincates from the product.



Scheme 23. Synthesis Plan for PN-Based Manganese Alkyl Complexes *via* $AgBF_4$ and $ZnMe_2$.

The method was adapted by utilization of AgOTf (Scheme 24). Here, the counterion may coordinate to the metal centre and represents a good leaving group for nucleophilic attack. The conversion was carried out with the corresponding precursor complexes **1** and AgOTf in DCM under light exclusion. At this point, the synthesis became tedious, as the precipitated silver salt

was difficult to separate. Separation was performed by filtration over a pad of Celite and *via* a syringe filter as many times as necessary, until no dark silver salt was observed anymore. Afterwards, the solvent was evaporated under reduced pressure and the crude product was washed with *n*-pentane. Compared to the first two attempts, this procedure was an excellent way to achieve halide abstraction and allowed isolation of complexes **2** in moderate to good yields (Table 3). All products were obtained as yellow or orange powders.

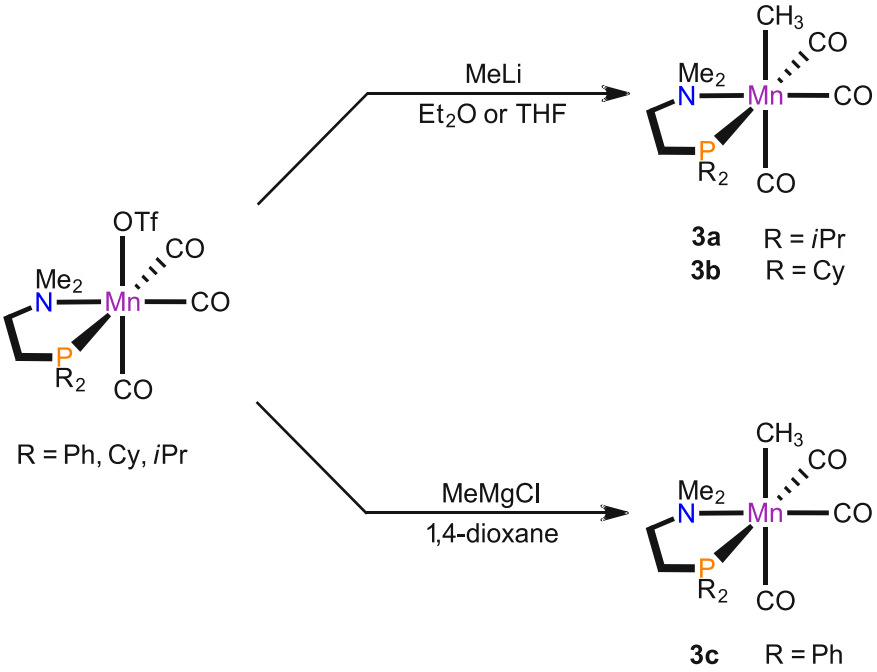


Scheme 24. Synthesis of Triflate-Coordinated Complexes 2.

Table 3. Yields and ^{31}P-NMR Shifts of Complexes 2.

	Yield [%]	**Colour**	**^{31}P-NMR shift [ppm]**
[Mn($P^{Ph}N^{Me}$-Et)$(CO)_3$OTf] **(2a)**	78	orange	60.3
[Mn($P^{Ph}N^{Et}$-Et)$(CO)_3$OTf] **(2b)**	61	orange	55.8
[Mn($P^{Ph}N^{Pyrr}$-Et)$(CO)_3$OTf] **(2c)**	66	yellow	58.2.
[Mn($P^{iPr}N^{Me}$-Et)$(CO)_3$OTf] **(2d)**	60	orange	75.6
[Mn($P^{iPr}N^{Et}$-Et)$(CO)_3$OTf] **(2e)**	58	orange	69.6
[Mn($P^{Cy}N^{Me}$-Et)$(CO)_3$OTf] **(2f)**	86	yellow	67.6

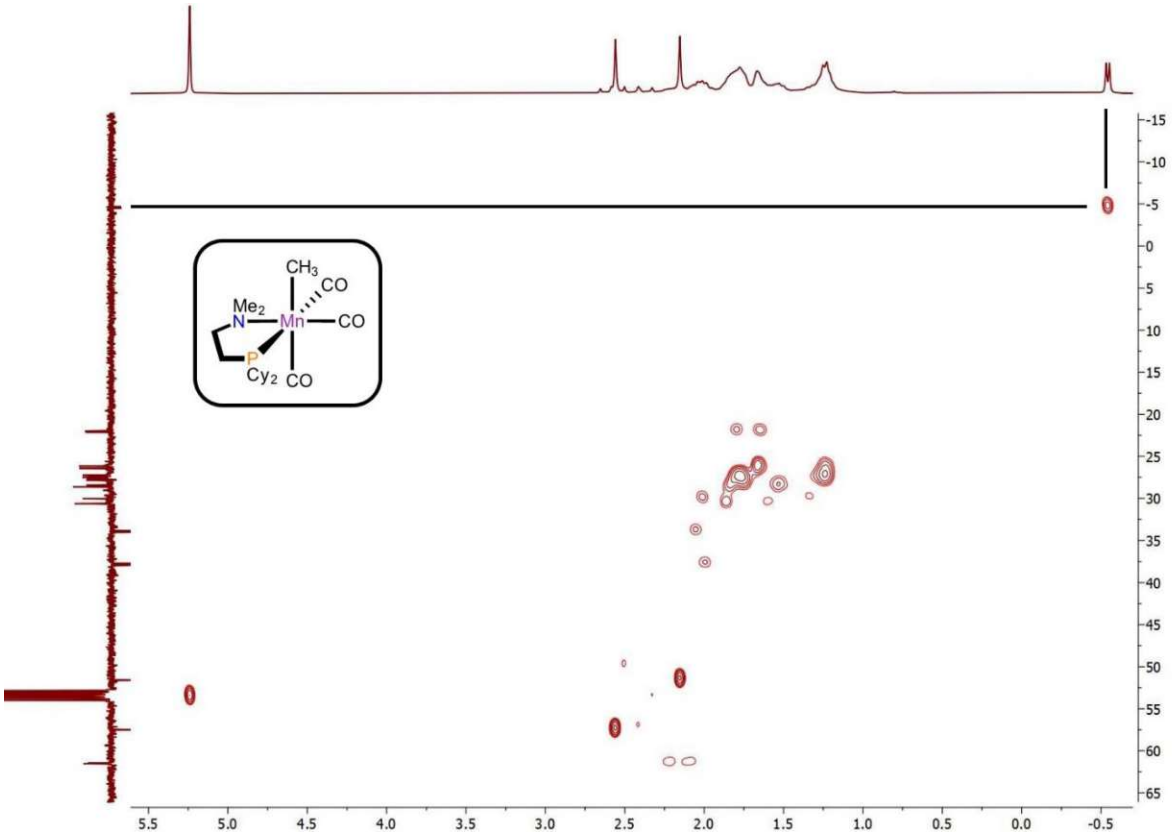
The isolated and bench stable triflate complexes proofed to be suitable candidates for consecutive alkylation. Again, organozinc reagents seemed to be a suitable alkylation agent. However, decomposition of the complexes as well as the formation of inseparable zincates did not allow product isolation.



Scheme 25. Synthesis of Alkyl Complexes 3 *via* Lithium- or Grignard-Reagents.

Since the modified precursors in combination with organozinc compounds almost gave the same results as with the bromide congeners, the alkylation reagent was substituted. Therefore, reactions of complexes **3** with MeLi or *n*-BuLi, utilizing different solvents, were investigated. Treatment of a suspension of **2d** in Et_2O with 1.51 equiv. MeLi (Scheme 25), stirring for 1 hour at -70 °C and for another 2 hours at RT afforded a brown mixture. An aliquot of the reaction mixture was evaporated and the residue was taken up in CD_2Cl_2 and $^{31}P\{H\}$- and ^{1}H-NMR was measured.

Delightfully, the only detectable complexes was found to be the alkylated complex **3a**. In addition to that, IR-spectroscopy was also found to be a suitable method for reaction control. Work up was done by evaporation of the solvent, followed by extraction with *n*-pentane and filtration *via* syringe filter. Finally, upon evaporation of the solvent, the alkylated complex **3a** was obtained as yellow powder in 15 % yield. The $^{31}P\{H\}$ NMR spectrum displayed a singlet at 80.0 ppm. The significant high field shifted doublet at -0.43 ppm ($J_{H\text{-}P}$ = 8.2 Hz) in the ^{1}H-NMR spectrum indicated the presence of a methyl group, being bonded to the Mn-center.



Scheme 26. $^{1}H/^{13}C$-HSQC of Complex 3b.

The same procedure was conducted with **2f** yielding **3b** as a pale yellow powder in 23 % yield. The $^{31}P\{^{1}H\}$ signal was detected at 71.3 ppm and the ^{1}H resonance, referring to the methyl group, was found at -0.45 ppm ($J_{H\text{-}P}$ = 8.1 Hz). The recorded $^{1}H/^{13}C$-HSQC spectrum showed a crosspeak of the alkyl ligand, which coordinates to the metal centre, at -4.2 ppm ($J_{C\text{-}P}$ = 18.4 Hz) (Scheme 26).

Unfortunately, reactions of a triflate complexes, bearing a phenyl moiety on the phosphine donor, were not successful neither with MeLi nor *n*-BuLi. In general, a coordinated butyl group to the metal centre has never been observed. Even when the tentative alkyl complex was formed, impurities from various species were present, preventing isolation and characterization of the expected compound. When THF was utilized as solvent, even worse results, in terms of conversion and side-product formation, were observed.

Sine no alkylated complex with phenyl moiety on the phosphine could be isolated if lithium reagents were employed, Grignard reagent were envisioned to be suitable surrogates. Thus, **2a** was suspended in 1,4-dioxane and 1.98 equiv. MeMgCl were added at RT. This led to change in colour of the suspension from yellow suspension changed brown.

Analysis of reaction mixture by $^{31}P\{^{1}H\}$- and ^{1}H-NMR as well as IR-spectroscopy indicated that the desired complex was formed. Although evaporation of the solvent was laborious, 1,4-dioxone was essential for precipitation of the formed magnesia salts. The solvent was evaporated under vacuum followed by extraction with *n*-pentane, followed by filtration *via* a syringe filter. Surprisingly, CO bands were not observed anymore. The assumption that perhaps only free ligand was extracted, was confirmed by $^{31}P\{^{1}H\}$ analysis. Therefore, the rection mixture was extracted with toluene. After evaporation of the solvent **3c** was obtained as a pale yellow powder in 28 % yield. **3c** gave rise to a singlet at 72.1 ppm in the $^{31}P\{^{1}H\}$-NMR. The signal referring to the methyl group on manganese displayed a doublet at -0.78 ppm ($J_{H\text{-}P}$ = 10.3 Hz) in the ^{1}H spectrum. Interestingly, utilizing MeMgBr, instead of MeMgCl, the corresponding bromide **1a** and not the expected methyl **3c** complex was obtained.

IR spectroscopy was not only a convenient method for reaction control, but also allowed the prediction of bond strengths relative to each other. When comparing **3a**, **3b** and **3c** with the corresponding bromide or triflate complexes, the highest wavenumber was observed for triflate complexes, the lowest for methylated complexes and for the bromide complexes in between. This implies the strongest metal-CO bond for the methylated complexes.

3.4 Catalytic Application

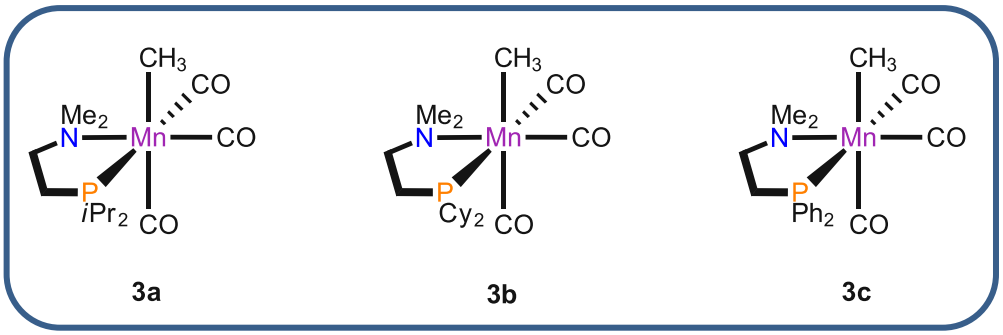
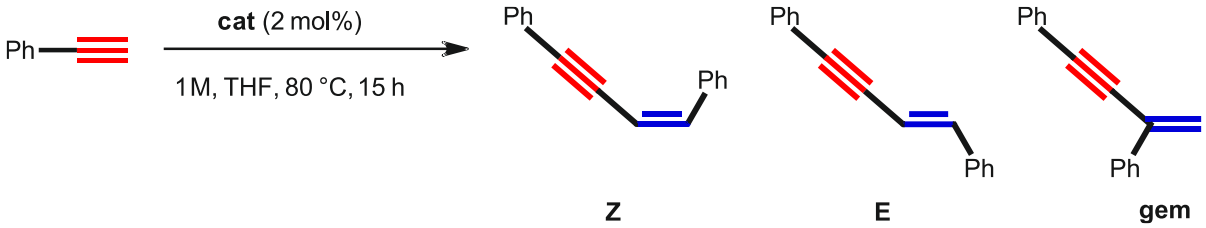


Figure 2. Investigated PN-Complexes for the Dimerization of Phenylacetylene.

In order to gain preliminary insights in the reactivity of PN-based alkyl complexes the dimerization of phenylacetylene with **3a**, **3b** and **3c** (Figure 2) was investigated. Therefore, dimerization reactions were conducted with a catalyst loading of 2 mol% at 80 °C for 15 hours in THF (1M) as it can be seen in Scheme 27. In fact, similar reaction conditions were found to give good to excellent results for related PP-based systems.[47] GC-MS as well as ^{1}H-NMR spectroscopy were used to determine the conversion and selectivity.

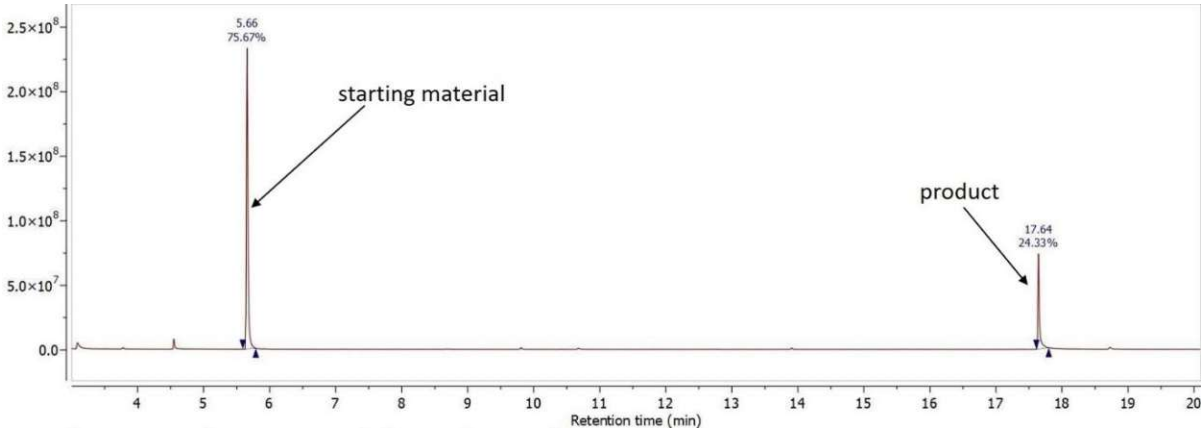


Scheme 27. Dimerization of Phenylacetylene Catalysed by 3a-3c.

Table 4. Catalytic Performance of PN-based Complexes for Phenylacetylene Dimerization.

Entry	Catalyst [mol%]	Conversion [%]	*Z:E ratio*
3a	2	61	81:19
3b	2	77	78:22
3c	2	-	n.d.

Since the molecular weight of the starting material is lower than the molecular weight of the products, phenylacetylene appears at lower retention times in GC-spectra (Scheme 28). The retention time for phenylacetylene was found to be 5.6 minutes, whereas the *Z*-product has a retention time of 17.7 minutes. Both catalysts (**3a**, **3b**) show a moderate conversion and similar *Z:E ratio* (Table 4).

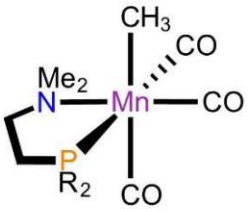


Scheme 28. Typical GC-Spectrum for the Dimerization of Phenylacetylene by 3.

Although the PP-bidentate bears two equal phosphines the results for dimerization are comparable to the PN-supported systems. As depicted in Scheme 29, the catalytic activity of **1** is superior in comparison to complex **3a-3c**. On the other hand, **3b** outperforms both **2** and **3a**

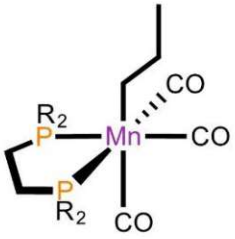
in terms of productivity. As a result, more sterically demanding groups on the phosphine affect better catalytic activity. In fact, no conversion was observed for **3c**. This may be attributed to the lower donor properties and deceased steric bulk in contradiction to alkyl phosphines. It is evident that the right choice of ligand is crucial to achieve high productivity and selectivity. However, further optimisation of reaction conditions shall be done to improve the reactivity and selectivity of the novel PN-supported complexes.

This work



R	Conversion [%]	*Z:E* ratio
*i*Pr **(Mn1)**	61	81:19
Cy **(Mn2)**	77	78:22

Previous report



R	Conversion [%]	*Z:E* ratio
*i*Pr **(1)**	>99	96:4
n-Pr **(2)**	67	79:21

Scheme 29. Catalytic Performance of PP- *versus* PN-Based Systems for Alkyne Dimerization.

4 Conclusion and Outlook

Within this work, novel PN-based Mn(I) carbonyl alkyl complexes were synthesised and characterised. Additionally, preliminary catalytic investigations in the dimerization of alkynes gave promising results.

Various routs for PN-ligand synthesis were developed and allowed fast synthesis of ligands, which are needed to fine-tune electronic and steric parameters in complexes. Furthermore, the synthesised PN-ligands were successfully coordinated with [$Mn(CO)_5Br$)] to give the corresponding bromide complexes in good yields. These complexes were fully characterised by multinuclear NMR analysis and infrared measurements. Two crystal structures were obtained to confirm a octahedral coordination sphere. Furthermore, the bromide ligand was exchanged with a triflate moiety to increase the leaving group properties.

In order to alkylate the triflate complexes, MeLi was found to be a suitable reagent for complexes bearing isopropyl or cyclohexyl groups on the phosphine. A quite different situation was observed for complexes with phenyl moieties on the phosphine, hence Grignard reagent was the best choice. In addition, preliminary investigations of the reactivity of PN-based systems in the dimerization of phenylacetylene with [$Mn(P^{iPr}N^{Me}\text{-Et})(CO)_3Me$] and [$Mn(P^{Cy}N^{Me}\text{-Et})(CO)_3Me$] revealed good activity and *Z:E* ratio*s*.

Future work will be dedicated to increase the yield in the synthesis of alkyl complexes as well as further investigations referring to different alky groups on the manganese centre for better catalytic activity as well as optimisation of already in this work reported catalysis.

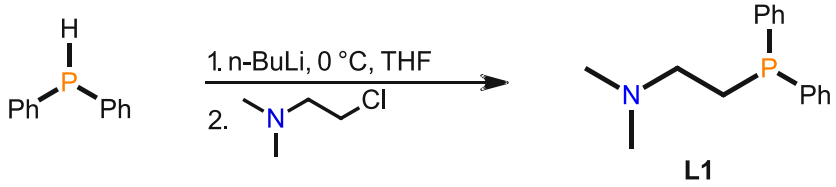
5 Experimental Part

General Information. All reactions were performed under inert atmosphere of argon using Schlenk techniques or in a MBraun inert-gas glovebox, unless otherwise noted. The solvents were purified according to standard procedures.[48] All used reagents and solvents were purchased from commercial suppliers and directly used without further purification, if not stated otherwise. Complex **1h** was provided by Dr. Stefan Weber. The deuterated solvents were purchased from Aldrich and dried over 3 Å molecular sieves. ^{1}H and $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra were recorded on Bruker AVANCE-250, AVANCE-400 and AVANCE-600 spectrometers. ^{1}H and $^{13}C\{^{1}H\}$-NMR spectra were reference internally to residual protio-solvent and solvent resonance, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). $^{31}P\{^{1}H\}$-NMR spectra were referenced externally to H_3PO_4 (85%) (δ = 0 ppm). All IR measurements were performed on a Bruker Tensor 27 with an ATR unit. GC-MS analysis was conducted on a ISQ LT Single quadrupole MS (Thermo Fisher) directly interfaced to a TRACE 1300 Gas Chromatographic systems (Thermo Fisher), using a Rxi-5Sil MS (30 m, 0.25 mm ID) cross-bonded dimethyl polysiloxane capillary column at a carrier flow of He 1.5 mL/min. Single crystals suitable for X-Ray analysis were measured on a Bruker SMART-CCD area diffractometer system with a Mo-K α-radiation and a graphite monochromator. The data were processed with the SADABS[49] algorithm and the crystal structures were solved and refined with SHELXTL software suite.[50]

5.1 Ligand Synthesis

5.1.1 Route A

2-(Diphenylphosphino)-*N*,*N*-dimethylethanamine (L1)



L1

L1 was synthesised by a modified procedure, which was reported previously. [44]

In a Schlenk flask, PPh_2H (1.70 mL, 9.72 mmol, 1.00 equiv.) was mixed with THF (25 mL). After cooling at 0 °C *n*-BuLi (6.10 mL, 1.6 M in *n*-hexane, 9.76 mmol, 1.00 equiv.) was added dropwise. Shortly afterwards, $NMe_2(CH_2)_2Cl$ (1.06 g, 9.85 mmol, 1.01 equiv.) was added slowly and the solution mixture was stirred overnight at RT. The colourless suspension was quenched with deoxygenated H_2O (5 mL) and the aqueous layer was separated. The organic layer was dried over Na_2SO_4, filtrated and the solvent was evaporated. The colourless residue was taken up in *n*-pentane (20 mL) and filtered over a pad of silica gel. After evaporation of the solvent, **L1** was obtained as colourless viscous oil (750 mg, 41 %).

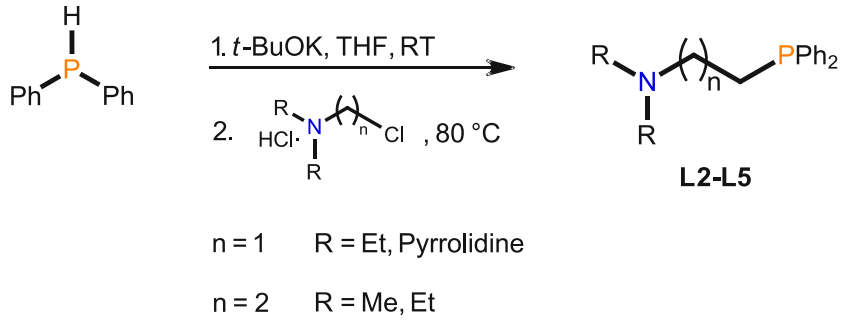
Analytical data is consistent with the literature.[44]

^{1}H NMR (400 MHz, C_6D_6): δ = 7.48 – 7.45 (m, 4H, $Ph^{2,6}$), 7.11 – 7.03 (m, 6H, $Ph^{3,4,5}$), 2.44 – 2.34 (m, 2H, NCH_2), 2.26 – 2.16 (m, 2H, PCH_2), 2.02 (s, 6H, NCH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 139.9 (C_q), 133.2 (d, *J* = 18.8 Hz, $Ph^{2,6}$), 128.7 (d, *J* = 6.5 Hz, $Ph^{3,5}$), 128.6 (Ph^4), 56.5 (NCH_2), 45.2 (NCH_3), 27.3 (d, *J* = 12.8 Hz, PCH_2).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = -19.7.

5.1.2 Route B



n = 1 R = Et, Pyrrolidine

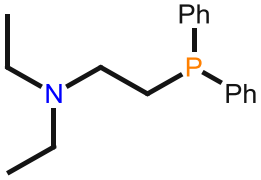
n = 2 R = Me, Et

L2-L5 were synthesised by a modified procedure, which was reported previously. [45]

General procedure

In a Schlenk flask, PPh_2H was added dropwise to a suspension of *t*-BuOK in THF and stirred for 30 minutes at RT. Afterwards the orange suspension was mixed with the respective amine salt $R_2N(CH_2)_nCl$ and refluxed overnight. During the reaction the colour changed from orange to white. The suspension was quenched with deoxygenated H_2O. The aqueous layer was separated and the organic layer was dried over Na_2SO_4. The product was extracted with *n*-pentane (3 x 7 mL) and filtered over a pad of silica. After evaporation of the solvent, the pure product was obtained as a colourless to orange oil.

2-(Diphenylphosphino)-*N*,*N*-diethylethanamine (L2)



L2

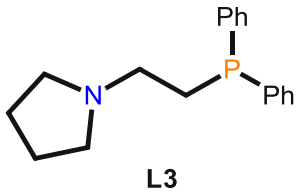
PPH_2H (1.70 mL, 9.77 mmol, 1.00 equiv.); *t*-BuOK (2.63 g, 23.4 mmol, 2.40 equiv.); $Ph_2P(CH_2)_2NEt_2$ (1.78 g, 10.3 mmol, 1.06 equiv.); solvent: 30 mL THF; quenched with 10 mL deoxygenated H_2O; 820 mg (29 %) as orange oil.

^{1}H NMR (400 MHz, C_6D_6) δ = 7.63 – 7.38 (m, 4H, $Ph^{2,6}$), 7.13 – 6.97 (m, 6H, $Ph^{3,4,5}$), 2.67 – 2.59 (m, 2H, $PCH_2C\underline{H_2}N$), 2.36 (q, *J* = 7.1 Hz, 4H, $NC\underline{H_2}CH_3$), 2.26 – 2.19 (m, 2H, $PC\underline{H_2}CH_2N$), 0.88 (t, *J* = 7.1 Hz, 6H, $NCH_2C\underline{H_3}$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ: = 140.0 (d, *J* = 14.8 Hz, C_q), 133.2 (d, *J* = 18.8 Hz, $Ph^{2,6}$), 128.7 ($Ph^{3,4,5}$), 128.6 (d, *J* = 3.3 Hz, $Ph^{3,4,5}$), 49.8 (d, *J* = 22.2 Hz, $PCH_2\underline{C}H_2N$), 46.9 ($N\underline{C}H_2CH_3$), 26.6 (d, *J* = 13.1 Hz, $P\underline{C}H_2CH_2N$)), 12.4 ($NCH_2\underline{C}H_3$).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: = -19.4.

1-[2-(Diphenylphosphino)ethyl]pyrrolidine (L3)



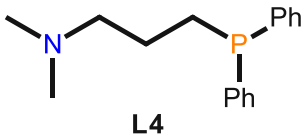
L3

PPh_2H (1.50 mL, 8.62 mmol, 1.00 equiv.); *t*-BuOK (2.38 g, 21.2 mmol, 2.46 equiv.); $Ph_2P(CH_2)_2N^{Pyrr}$ **(L3)** (1.82 g, 10.7 mmol, 1.24 equiv.); solvent: 30 mL THF; quenched with 10 mL deoxygenated H_2O; 922 mg (41 %) as colourless oil.

^1H NMR (400 MHz, C_6D_6) δ: = 7.51 – 7.44 (m, 4H, $Ph^{2,6}$), 7.11 – 7.02 (m, 6H, $Ph^{3,4,5}$), 2.71 – 2.54 (m, 2H), 2.40 – 2.22 (m, 6H), 1.61 – 1.48 (m, 4H).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: = -19.4.

3-(Diphenylphosphino)-*N*,*N*-dimethyl-1-propanamine (L4)



L4

PPh_2H (1.6 mL, 9.19 mmol, 1.00 eq.); *t*-BuOK (2.50 g, 22.3 mmol, 2.42 equiv.); $Me_2N(CH_2)_3Cl{\cdot}HCl$ (1.76 g, 11.1 mmol, 1.21 eq.); solvent: 25 mL THF; quenched with 7 mL deoxygenated H_2O; 1.11 g (44 %) as colourless oil.

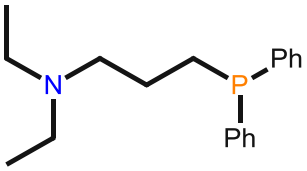
Analytical data is consistent with the literature.[44]

^1H NMR (400 MHz, C_6D_6) δ: = 7.50 – 7.41 (m, 4H, $Ph^{2,6}$), 7.12 – 7.02 (m, 6H, $Ph^{3,4,5}$), 2.17 (t, *J* = 6.8 Hz, 2H, $NC\underline{H_2}$), 2.12 – 2.04 (m, 2H, $PC\underline{H_2}$), 2.01 (s, 6H, $NC\underline{H_3}$), 1.64 – 1.53 (m, 2H, $NCH_2C\underline{H_2}CH_2P$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ: = 139.7 (d, *J* = 14.7 Hz, C_q), 132.8 (d, *J* = 18.6 Hz, $Ph^{2,6}$), 128.3 ($Ph^{3,4,5}$), 128.2 (d, *J* = 4.6 Hz, $Ph^{3,4,5}$), 60.3 (d, *J* = 13.3 Hz, NCH_2), 45.1 (NCH_3), 25.7 (d, *J* = 12.0 Hz, PCH_2), 24.3 (d, *J* = 16.3 Hz, $NCH_2\underline{C}H_2CH_2P$).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: = -16.0

3-(Diphenylphosphino)-*N*,*N*-diethyl-1-propanamine (L5)



L5

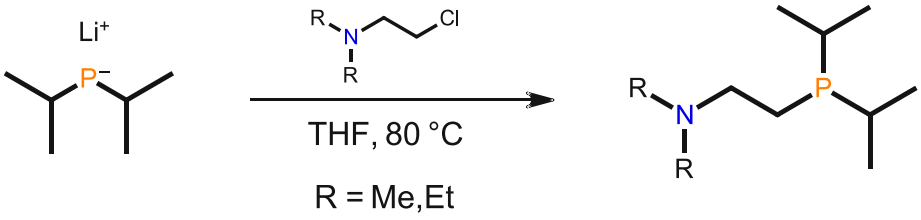
PPh_2H (1.5 mL, 8.62 mmol, 1.00 equiv.); *t*-BuOK (1.42 g, 12.7 mmol, 1.46 equiv.); $Et_2N(CH_2)_3Cl$ (as free amine) (1.54 g, 10.3 mmol, 1.19 equiv.); solvent: 20 mL THF; quenched with 5 mL deoxygenated H_2O; 970 mg (38 %) as orange oil.

^1H NMR (400 MHz, C_6D_6) δ: = 7.52 – 7.43 (m, 4H, $PH^{2,6}$), 7.13 – 6.99 (m, 6H, $Ph^{3,4,5}$), 2.38 (t, *J* = 6.9 Hz, 2H, NCH_2), 2.32 (t, *J* = 7.1 Hz, 4H, NCH_2CH_3), 2.13 – 2.03 (m, 2H, PCH_2), 1.66 – 1.54 (m, 2H, $NCH_2CH_2CH_2P$), 0.91 (t, *J* = 7.1 Hz, 6H, NCH_2CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ: = 140.1 (d, *J* = 14.5 Hz, C_q), 133.2 (d, *J* = 18.4 Hz, $Ph^{2,6}$), 128.7 ($Ph^{3,4,5}$), 128.6 (d, *J* = 5.7 Hz, $Ph^{3,4,5}$), 54.3 (d, *J* = 13.4 Hz, NCH_2), 47.2 (NCH_2CH_3), 26.2 (d, *J* = 12.4 Hz, PCH_2), 24.5 (d, *J* = 16.2 Hz, $NCH_2CH_2CH_2P$), 12.4 (NCH_2CH_3).

$^{31}P\{^1H\}$ NMR (162 MHz, C6D6) δ: = -16.1.

5.1.3 Route C

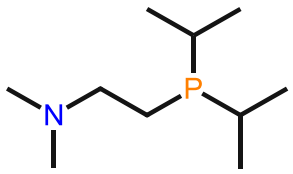


L6, L7

General procedure

Inside an argon flushed glovebox, the lithium salt was suspended in THF (25 mL) in a Schlenk flask and refluxed. The corresponding amine was added dropwise to the yellow solution over 10 minutes. After 1.5 hours, stirring was continued for another hour at RT. THF was evaporated under reduced pressure, *n*-pentane (10 mL) and H_2O (1.5 mL) were added. After addition of Na_2SO_4 the mixture was extracted with *n*-pentane (3 x 10 mL) and filtered over a pad of silica. The solvent was evaporated yielding a colourless viscous oil.

[2-(Dimethylamino)ethyl]diisopropylphosphine (L6)



L6

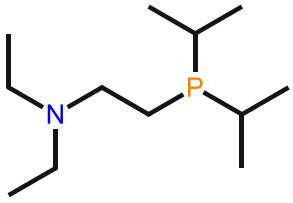
PPh_2Li (551 mg, 4.44 mmol, 1.00 equiv); $iPr_2P(CH_2)_2NMe_2$ (526 mg, 4.89 mmol, 1.10 equiv.); 260 mg (41 %) as colourless oil.

^1H NMR (400 MHz, C_6D_6) δ: = 2.51 – 2.43 (m, 2H, NCH_2), 2.12 (s, 6H, NCH_3), 1.64 – 1.49 (m, 4H, PCH_2CH_2N, $PCHCH_3$), 1.09 – 0.94 (m, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ: = 59.4 (d, J = 27.9 Hz, NCH_2CH_2), 45.3, (NCH_3), 23.7 (d, J = 14.1 Hz, NCH_2CH_2P), 20.3 (d, J = 16.6 Hz, $CHCH_3$), 19.0 (d, J = 10.0 Hz, $CHCH_3$).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: = 0.4.

[2-(Diethylamino)ethyl]diisopropylphosphine (L7)



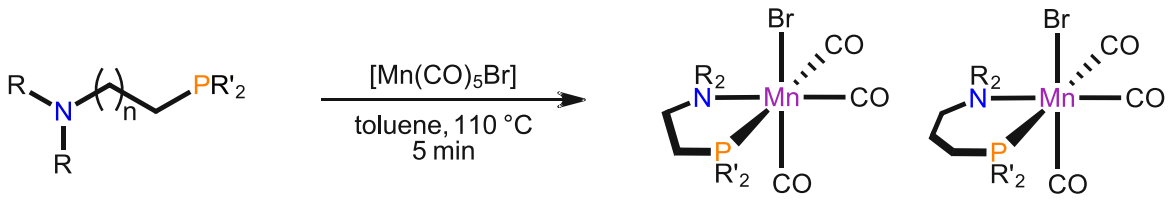
L7

PPh_2Li (580 mg, 4.67 mmol, 1.00 equiv.); $iPr_2P(CH_2)_2NEt_2$ (697 mg, 5.14 mmol, 1.10 equiv.); 466 mg (46 %) as colourless viscous oil.

^1H NMR (400 MHz, C_6D_6) δ: = 2.81 – 2.64 (m, 2H, NCH_2CH_2P), 2.45 (q, J = 7.2 Hz, 4H, NCH_2CH_3), 1.67 – 1.49 (m, 4H,CH_2PCHCH_3), 1.08 – 0.97 (m, 18H, $PCHCH_3$,NCH_2CH_3).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: = 0.5.

5.2 Reaction of PN-Ligands with $[Mn(CO)_5Br]$



n = 1 R = Me, Et, Pyrrolidine
R' = Ph, Cy, *i*Pr

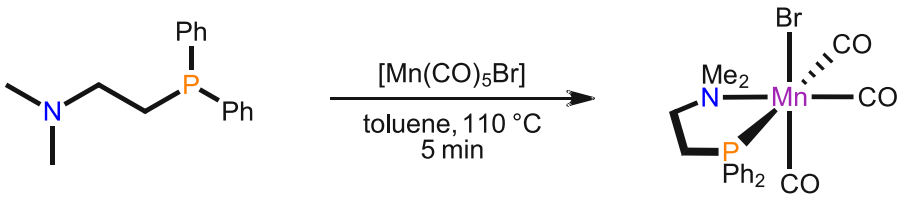
n = 2 R = Me, Et
R' = Ph

1a-1g

General procedure

In a Schlenk flask, the respective ligand was dissolved in toluene and mixed with $Mn(CO)_5Br$. The suspension was refluxed for 5 minutes, thereby releasing CO gas. The orange solution was concentrated to one third. Afterwards the complex was precipitated with MeOH or *n*-pentane and washed with the corresponding solvent (2 x 5 mL). Upon drying, the product was obtained as yellow or orange powder.

***fac*-[Mn($P^{Ph}N^{Me}$-Et)$(CO)_3Br$] (1a)**



L1 **1a**

L1 (1.62 g, 6.30 mmol, 1.00 equiv.); $Mn(CO)_5Br$ (1.73 g, 6.29 mmol, 1.00 equiv.), solvent: 35 mL toluene; precipitated and washed with MeOH; 1.90 g (63 %) of a yellow powder.

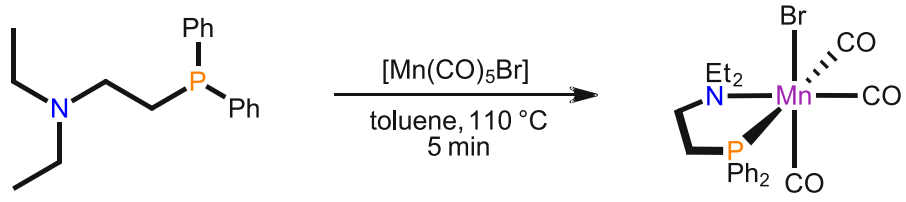
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.79 – 7.67 (m, 2H, $Ph^{2,6}$), 7.64 – 7.55 (m, 2H, $Ph^{2,6}$), 7.53 – 7.47 (m, 3H, $Ph^{3,4,5}$), 7.45 – 7.39 (m, 3H, $Ph^{3,4,5}$), 3.23 (qd, *J* = 12.4, 4.2 Hz, 1H, NCH_2CH_2P), 3.05 – 2.88 (m, 1H, NCH_2CH_2P), 2.88 (s, 3H, NCH_3), 2.73 (s, 3H, NCH_3), 2.71 – 2.61 (m, 1H, NCH_2CH_2P), 2.60 – 2.38 (m, 1H, NCH_2CH_2P).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ: = 135.1 (d, *J* = 41.8 Hz, C_q), 133.1 (d, *J* = 40.3 Hz, C_q), 132.5 (d, *J* = 9.1 Hz, $Ph^{3,5}$), 132.1 (d, *J* = 10.0 Hz, $Ph^{2,6}$), 131.0 (d, *J* = 2.1 Hz, Ph^4), 130.3 (d, *J* = 2.5 Hz, Ph^4), 129.5 (d, *J* = 9.3 Hz, $Ph^{3,5}$), 128.5 (d, *J* = 9.8 Hz, $Ph^{2,6}$), 61.5 (d, *J* = 7.8 Hz, NCH_2CH_2P), 26.25 (d, *J* = 18.8 Hz, NCH_2CH_2P).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 59.9.

IR (ATR, cm^{-1}) = 2015 (CO), 1927 (CO), 1890 (CO).

***fac*-[Mn($P^{Ph}N^{Et}$-Et)$(CO)_3$Br] (1b)**



L2 **1b**

L2 (153 mg, 0.536 mmol, 1.00 equiv.); $Mn(CO)_5Br$ (148 mg, 0.597 mmol, 1.11 equiv.); solvent: 5 mL toluene; precipitated and washed with MeOH; 63 mg (23 %) as orange powder.

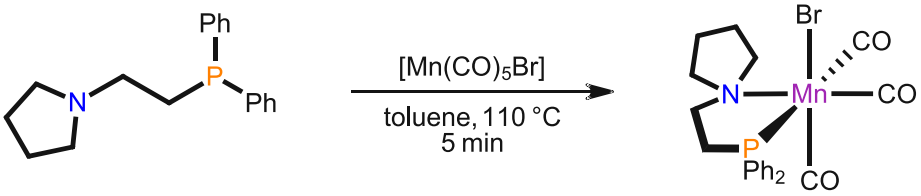
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.75 – 7.66 (m, 2H, $Ph^{2,6}$), 7.63 – 7.56 (m, 2$H^{2,6}$), 7.50 (d, *J* = 6.9 Hz, 3H, $Ph^{3,4,5}$), 7.41 (d, *J* = 4.5 Hz, 3H, $Ph^{3,4,5}$), 3.49 – 2.31 (m, 8H, NCH_2CH_2P, NCH_2CH_3), 1.30 (t, *J* = 7.1 Hz, 6H, NCH_2CH_3), 1.08 (t, *J* = 7.2 Hz, 3H, NCH_2CH_3).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ: = 132.5 (d, *J* = 8.7 Hz, $Ph^{3,5}$), 132.2 (d, *J* = 9.8 Hz, $Ph^{2,6}$), 131.0 (d, *J* = 2.1 Hz, Ph^{4}), 130.3 (d, *J* = 2.5 Hz, Ph^{4}), 129.4 (d, *J* = 9.3 Hz, $Ph^{3,5}$), 128.5 (d, *J* = 9.7 Hz, $Ph^{2,6}$), 56.0 (d, *J* = 8.1 Hz, NCH_2CH_2P), 53.7 (NCH_2CH_3), 51.4 (NCH_2CH_3), 25.5 (d, *J* = 18.8 Hz, NCH_2CH_2P), 11.0 (NCH_2CH_3), 9.0 (NCH_2CH_3). P-$C_{(Ph)}$ not observed.

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: 55.2.

IR (ATR, cm^{-1}) = 2007 (CO), 1923 (CO).

***fac*-[Mn($P^{Ph}N^{Pyr}$-Et)$(CO)_3$Br] (1c)**



L3 **1c**

L3 (152 mg, 0.536 mmol, 1.00 equiv.); $Mn(CO)_5Br$ (146 mg, 0.531 mmol, 1.00 equiv.); solvent: 5 mL toluene; precipitated and washed with *n*-pentane; 206 mg (77 %) as yellow powder.

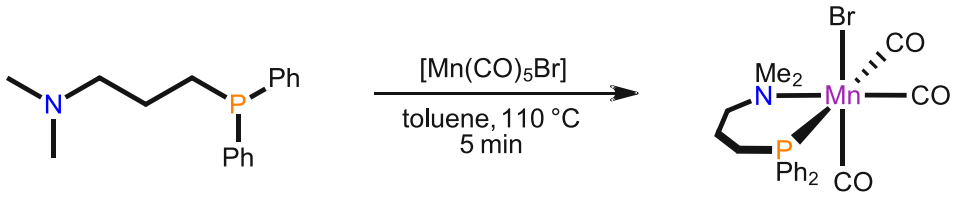
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 8.20 – 6.62 (m, 10H, Ph), 4.24 – 0.56 (m, 12H, NCH_2CH_2P, pyrrolidine).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ: = 134.3 (C_q), 132.7 (C_q), 132.3 (d, *J* = 8.7 Hz, $Ph^{3,5}$), 131.8 (d, *J* = 9.3 Hz, $Ph^{2,6}$), 130.6 (d, *J* = 2.2 Hz, Ph^4), 130.0 (d, *J* = 2.7 Hz, Ph^4), 129.1 (d, *J* = 9.1 Hz, $Ph^{3,5}$),128.2 (d, *J* = 9.5 Hz, $Ph^{2,6}$), 63.7 ($NCH_2CH_2CH_2CH_2$), 61.8 ($NCH_2CH_2CH_2CH_2$), 58.5 (d, J = 8.4 Hz, NCH_2CH_2P), 26.3 (d, J = 19.1 Hz, NCH_2CH_2P), 23.4 ($NCH_2CH_2CH_2CH_2$), 21.9($NCH_2CH_2CH_2CH_2$).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ: 57.5.

IR (ATR, cm^{-1}) = 2010 (CO), 1937 (CO), 1913 (CO).

***fac*-[Mn($P^{Ph}N^{Me}$-Pr)$(CO)_3$Br] (1d)**



L4 **1d**

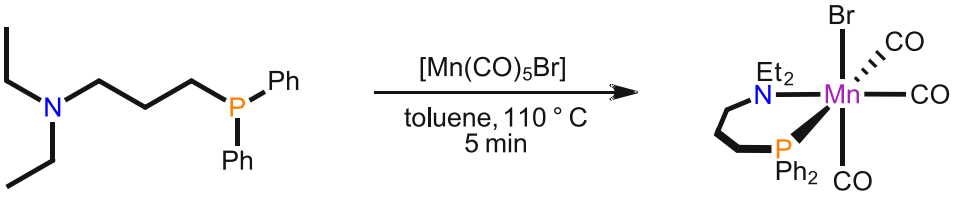
L4 (157 mg, 0.579 mmol, 1.10 equiv.); $Mn(CO)_3Br$ (146 mg, 0.531 mmol, 1.00 equiv.); solvent: 5 mL toluene; precipitated and washed with *n*-pentane; 183 mg (70 %) as orange powder.

^1H NMR (400 MHz, CD_2Cl_2) δ: = 7.79 – 7.58 (m, 2H, $Ph^{2,6}$), 7.58 – 7.11 (m, 3H, $Ph^{3,4,5}$), 2.73 – 2.58 (m, 2H, NCH_2), 2.24 – 2.16 (m, 2H), 2.03 (s, 6H, NCH_3), 1.46 – 1.33 (m, 2H, $NCH_2CH_2CH_2P$).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 49.0.

IR (cm^{-1}) = 2021 (CO), 1946 (CO), 1895 (CO).

***fac*-[Mn($P^{Ph}N^{Et}$-Pr)$(CO)_3$Br] (1e)**



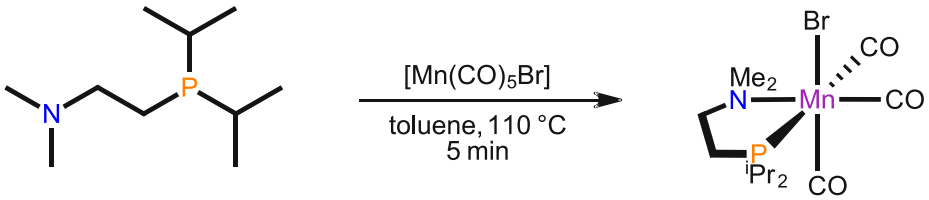
L5 **1e**

(L5) (149 mg, 0.498 mmol, 1.00 equiv.); $Mn(CO)_3Br$ (139 mg, 0.506 mmol, 1.02 equiv.); solvent: 5 mL toluene; 132 mg (51 %) as orange oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.00 – 6.77 (m, 10H), 2.97 – 1.99 (m, 6H), 1.65 – 0.62 (m, 8H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 37.0.

***fac*-[Mn(P$^{i\text{Pr}}$N$^{\text{Me}}$-Et)(CO)$_3$Br] (1f)**



L6 **1f**

L6 (260 mg, 1.37 mmol, 1.00 equiv.); $Mn(CO)_5Br$ (376 mg, 1.37 mmol, 1.00 equiv.); solvent: 10 mL toluene; precipitated and washed with *n*-pentane; 432 mg (77 %) as orange powder.

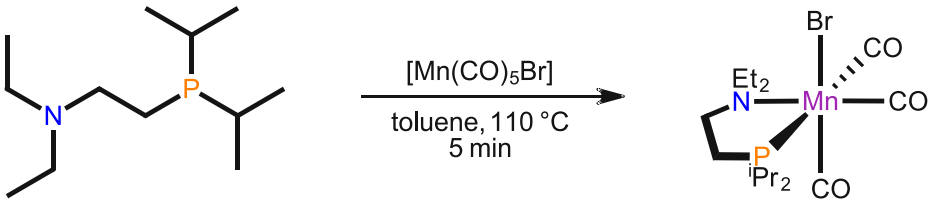
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 2.95 (d, J = 9.0 Hz, 2H, NC$\underline{H_2}$CH$_2$P, PC$\underline{H}$CH$_3$), 2.83 (s, 3H, NCH$_3$), 2.70 (s, 3H, NCH$_3$), 2.55 – 2.39 (m, 1H, PC$\underline{H}$CH$_3$), 2.38 – 2.20 (m, 1H, NC$\underline{H_2}$CH$_2$P), 2.12 – 1.97 (m, 1H, NCH$_2$C$\underline{H_2}$P), 1.98 – 1.84 (m, 1H, NCH$_2$C$\underline{H_2}$P), 1.56 – 1.27 (m, 12H, PCHC$\underline{H_3}$).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 61.5 (d, J = 6.4 Hz, N$\underline{C}$H$_2$CH$_2$P), 55.2 (NCH$_3$), 54.8 (NCH$_3$), 27.1 (d, J = 22.0 Hz, P$\underline{C}$HCH$_3$), 25.0 (d, J = 18.0 Hz, P$\underline{C}$HCH$_3$), 23.4 (d, J = 14.4 Hz, NCH$_2$$\underline{C}H_2$P), 20.3 (PCH$\underline{C}H_3$), 20.1 (d, J = 1.9 Hz, PCH$\underline{C}$H$_3$), 19.7 (d, J = 1.4 Hz, PCH$\underline{C}$H$_3$), 18.6 (d, J = 4.6 Hz, PCH$\underline{C}$H$_3$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 49.0.

IR (ATR, cm^{-1}) = 2010 (CO), 1930 (CO), 1884 (CO)

***fac*-[Mn(P$^{i\text{Pr}}$N$^{\text{Et}}$-Et)(CO)$_3$Br] (1g)**



L7 **1g**

L7 (466 mg, 2.14 mmol, 1.00 equiv.); $Mn(CO)_5Br$ (589 mg, 2.14 mmol, 1.00 equiv.); solvent: 15 mL toluene; precipitated and washed with *n*-pentane; 515 mg (55 %) as an yellow powder.

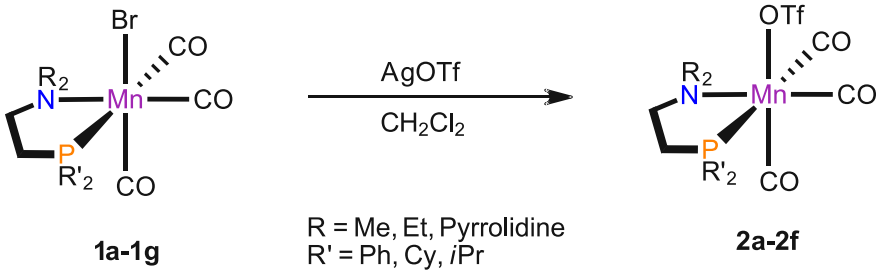
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 3.61 (s, 1H), 3.51 – 3.15 (m, 2H), 3.12 – 2.81 (m, 2H), 2.78 – 2.57 (m, 2H), 2.56 – 2.35 (m, 1H), 2.07 (dd, *J* = 15.4, 11.1 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.69 – 1.35 (m, 12H, PCHC$\underline{H}_3$), 1.33 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.02 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 55.8 (d, *J* = 7.1 Hz, N$\underline{C}H_2CH_2P$), 51.3 (N$\underline{C}H_2CH_3$), 27.2 (d, *J* = 22.3 Hz, P$\underline{C}HCH_3$), 25.0 (d, *J* = 18.5 Hz, P$\underline{C}HCH_3$), 23.0 (d, *J* = 14.7 Hz, $NCH_2\underline{C}H_2P$), 20.2 (PCH$\underline{C}H_3$), 20.1 (d, *J* = 1.9 Hz, PCH$\underline{C}H_3$), 19.6 (PCH$\underline{C}H_3$), 18.7 (d, *J* = 4.8 Hz, PCH$\underline{C}H_3$), 11.2 (PCH$\underline{C}H_3$), 8.6 ($NCH_2\underline{C}H_3$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 65.8.

IR (ATR, cm^{-1}) = 2004 (CO), 1918 (CO), 1979 (CO).

5.3 Triflate Complexes



1a-1g

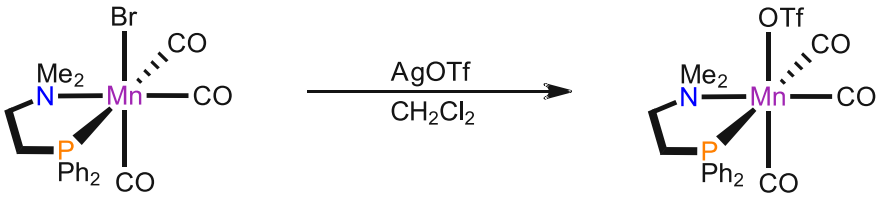
R = Me, Et, Pyrrolidine
R' = Ph, Cy, *i*Pr

2a-2f

General Procedure

In a Schlenk flask, covered with aluminium foil, the respective bromide complex **1** was dissolved in DCM and AgOTf was added. After stirring for 50 minutes at RT the reaction mixture was filtered over a pad of Celite as well as a syringe filter. This step was repeated until no dark precipitate was observed in the solution. The solvent was evaporated and the crude product was washed with *n*-pentane. The product was dried under vacuum, yielding a yellow or orange powder.

***fac*-[Mn(P^{Ph}N^{Me}-Et)(CO)$_3$OTf] (2a)**



1a **2a**

[Mn(P^{Ph}N^{Me}-Et)(CO)$_3$Br] **(1a)** (499 mg, 1.05 mmol, 1.00 equiv.); AgOTf (402 mg, 1.5 mmol, 1.49 equiv.); solvent: 15 mL DCM; washed with n-pentane (2 x 5 mL); 444 mg (78 %) as orange powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.72 – 7.63 (m, 2H, Ph^{2,6}), 7.63 – 7.56 (m, 2H, Ph^{2,6}), 7.57 – 7.50 (m, 3H, Ph^{3,4,5}), 7.50 – 7.36 (m, 3H, Ph^{3,4,5}), 2.84 (s, 3H, NCH_3), 2.67 (s, 3H, NCH_3), 3.02 – 2.48 (m, 4H).

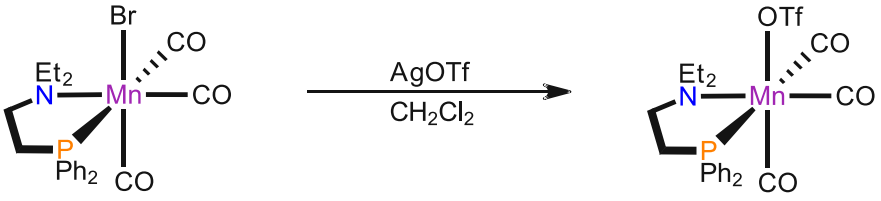
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 132.4 (d, *J* = 9.9 Hz, Ph^{2,6}), 132.1 (d, *J* = 10.0 Hz, Ph^{2,6}), 131.6 (d, *J* = 1.8 Hz, Ph^4), 131.2 (d, *J* = 2.5 Hz, Ph^4), 129.8 (d, *J* = 9.8 Hz, Ph^{3,4}), 129.5 (d, *J* = 9.9 Hz, Ph^{3,4}), 61.7 (d, *J* = 7.8 Hz, N$\underline{C}H_2CH_2P$), 55.4 (NCH_3), 26.3 (d, *J* = 19.2 Hz, $NCH_2\underline{C}H_2P$). P-C$_{(Ph)}$ not observed.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 60.3.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: = -77.9.

IR (ATR, cm^{-1}) = 2027 (CO), 1941 (CO), 1907 (CO).

***fac*-[Mn(P^{Ph}N^{Et}-Et)(CO)$_3$OTf] (2b)**



1b **2b**

[Mn(P^{Ph}N^{Et}-Et)(CO)$_3$OTf] **(1b)** (201 mg, 0.399 mmol, 1.00 equiv.); AgOTf (133 mg, 0.518 mmol, 1.30 equiv.); solvent: 5 mL DCM; washed with *n*-pentane (2 x 2 mL); 139 (61 %) as orange powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.76 – 7.33 (m, 10H, Ph$^{2-6}$), 3.37 – 3.07 (m, 4H), 3.07 – 2.66 (m, 4H), 1.43 – 1.34 (m, 3H), 1.15 – 1.07 (m, 3H).

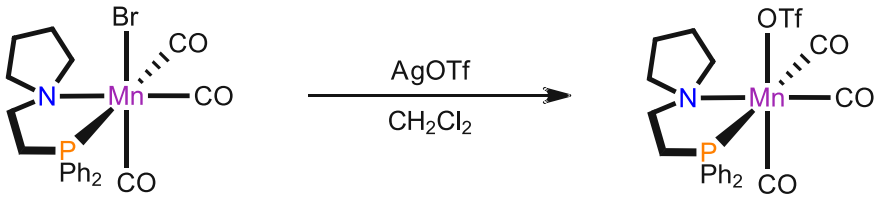
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ: = 132.4 (d, *J* = 9.5 Hz), 132.2 (d, *J* = 9.5 Hz), 131.6 (d, *J* = 2.4 Hz, Ph^4), 131.1 (d, *J* = 2.4 Hz, Ph^4), 129.8 (d, *J* = 9.6 Hz), 129.5 (d, *J* = 9.6 Hz), 55.9 (d, *J* = 8.0 Hz, NCH_2CH_2P), 51.0 (NCH_2CH_3), 47.9 (NCH_2CH_3), 25.8 (NCH_2CH_2P), 11.2 (NCH_2CH_3), 8.3 (NCH_2CH_3).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 55.8.

$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) δ: = -78.0.

IR (ATR, cm^{-1}) = 2028 (CO), 1947 (CO), 1903 (CO).

***fac*-[Mn($P^{Ph}N^{Pyr}$-Et)$(CO)_3$OTf] (2c)**



1c **2c**

[Mn($P^{Ph}N^{Pyrr}$-Et)$(CO)_3$Br] **(1c)** (300 mg, 0.597 mmol, 1.00 equiv.); AgOTf (232 mg, 0.903 mmol, 1.51 equiv.); solvent: 7 mL DCM; washed with *n*-pentane (2 x 3 mL); 224 mg (66 %) as yellow powder.

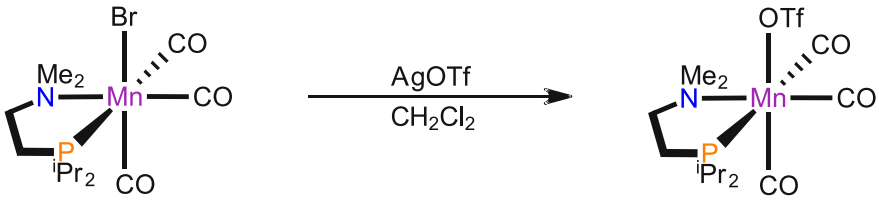
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.75 – 7.57 (m, 4H, $Ph^{2,6}$), 7.57 – 7.38 (m, 6H, $Ph^{3,4,5}$), 3.58 – 3.29 (m, 2H), 3.01 – 2.64 (m, 6H), 2.28 – 1.88 (m, 4H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 58.2.

$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) δ: = -77.9.

IR (ATR, cm^{-1}) = 2028 (CO), 1945 (CO), 1907 (CO).

***fac*-[Mn($P^{iPr}N^{Me}$-Et)$(CO)_3$OTf] (2d)**



1f **2d**

[Mn($P^{iPr}N^{Me}$-Et)$(CO)_3$Br] **(1f)** (432 mg, 1.06 mmol, 1.00 equiv.); AgOTf (400 mg, 1.55 mmol, 1.47 equiv.); solvent: 10 mL DCM; washed with *n*-pentane (2 x 3 mL); 301 mg (60 %) as orange sticky solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 2.82 (s, 3H, NCH_3), 2.61 (s, 3H, NCH_3), 2.59 – 2.48 (m, 3H, NCH_2CH_2P), 2.49 – 2.36 (m, 1H, $PCHCH_3$), 2.17 – 2.00 (m, 2H, NCH_2CH_2P), 1.54 – 1.32 (m, 12H, $PCHCH_3$).

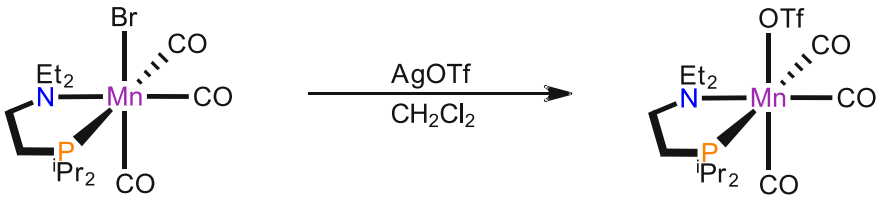
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 61.4 (d, *J* = 6.0 Hz, NCH_2CH_2P), 54.8 (NCH_3), 52.6 (NCH_3), 25.7 (d, *J* = 23.7 Hz, $PCHCH_3$), 23.3 (d, *J* = 15.2 Hz, NCH_2CH_2P, $PCHCH_3$), 23.2 (d, *J* = 15.5 Hz, NCH_2CH_2P, $PCHCH_3$) 19.8 ($PCHCH_3$), 19.2 ($PCHCH_3$), 18.1 (d, *J* = 4.4 Hz, $PCHCH_3$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 75.6.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: = -77.8.

IR (ATR, cm^{-1}) = 2071, 2029 (CO), 1945 (CO), 1907 (CO).

***fac*-[Mn(P$^{i\mathrm{Pr}}$N$^{\mathrm{Et}}$-Et)(CO)$_3$OTf] (2e)**



1g **2e**

[Mn(P$^{i\mathrm{Pr}}$N$^{\mathrm{Et}}$-Et)(CO)$_3$Br] **(1g)** (212 mg, 0.486 mmol, 1.00 equiv.); AgOTf (186 mg, 0.724 mmol, 1.49 equiv.); solvent: 5 mL DCM; washed with *n*-pentane (2 x 2 mL); 142 (58 %) orange powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 3.35 – 3.03 (m, 2H, NCH_2CH_3), 2.97 – 2.63 (m, 2H, NCH_2CH_3), 2.60 – 2.31 (m, 4H, NCH_2CH_2P, $PCHCH_3$), 2.24 – 1.94 (m, 2H, NCH_2CH_2P), 1.62 – 1.30 (m, 12H, $PCHCH_3$), 1.28 (s, 3H, NCH_2CH_3), 1.24 – 0.96 (m, 3H, NCH_2CH_3).

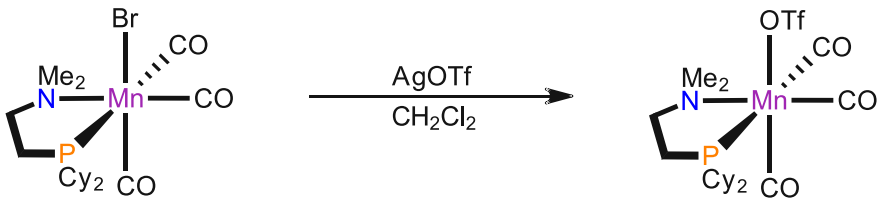
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 55.2 (d, *J* = 6.7 Hz, NCH_2CH_2P), 52.7 (NCH_2CH_3), 50.4 (NCH_2CH_3), 26.1 (d, *J* = 23.7 Hz, $PCHCH_3$), 23.1 (d, *J* = 15.1 Hz, $PCHCH_3$), 22.6 (d, *J* = 15.2 Hz, NCH_2CH_2P), 19.7 ($PCHCH_3$), 19.2 ($PCHCH_3$),18.2 (d, *J* = 3.8 Hz, $PCHCH_3$), 10.8 (NCH_2CH_3), 7.7 (NCH_2CH_3).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 69.6.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: = -77.9.

IR (ATR, cm^{-1}) = 2069, 2025 (CO), 1941 (CO), 1901 (CO).

***fac*-[Mn(P^{Cy}N^{Me}-Et)(CO)$_3$OTf] (2f)**



1h **2f**

[Mn(P^{Cy}N^{Me}-Et)(CO)$_3$Br] **(1h)** (300 mg, 0.614 mmol, 1.00 equiv.) AgOTf (238 mg, 0.926 mmol, 1.51 equiv.); solvent: 5 mL DCM; washed with *n*-pentane (2 x 3 mL); 283 mg (86 %) as yellow powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 2.8 (s, 3H), 2.6 (s, 3H), 2.5 – 2.3 (m, 2H, NC$\underline{H}_2$CH_2P), 2.2 – 1.1 (m, 24H).

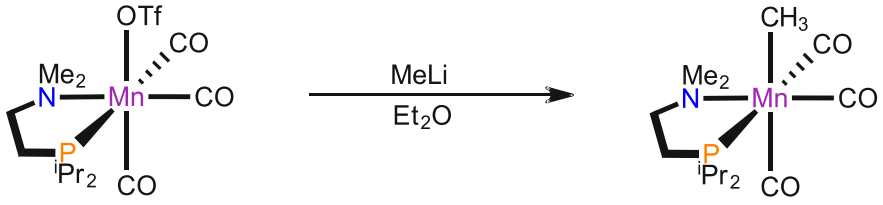
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 61.8 (d, *J* = 6.5 Hz, N$\underline{C}$H$_2$CH$_2$P), 55.3 (NCH$_3$), 52.8 (NCH$_3$), 37.5 (d, *J* = 22.1 Hz, P$\underline{C}$H), 34.0 (d, *J* = 13.9 Hz, P$\underline{C}$H), 30.7, 29.8, 29.7, 29.1 (d, *J* = 5.2 Hz), 28.0, 27.8, 27.8, 27.7, 27.7, 27.6, 27.6, 27.5, 26.3 (d, *J* = 5.0 Hz), 21.8 (d, *J* = 15.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 67.6.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: = -77.9.

5.4 Alkyl Complexes

***fac*-[Mn(P^{iPr}N^{Me}-Et)(CO)$_3$(CH$_3$)] (3a)**



2d **3a**

In a Schlenk flask, the triflate complex **2d** (192 mg, 0.402 mmol, 1.00 equiv.) was suspended in Et_2O (10 mL), cooled to -70 °C followed by dropwise addition of MeLi (0.38 mL, 1.6 M in Et_2O, 0.608 mmol, 1.51 equiv.). Stirring was continued for 1 hour and afterwards the suspension was allowed to reach RT, upon which the colour changed to red. During the reaction progress, the solution mixture turned brown. After 2 hours the solvent was evaporated, the

residue extracted with *n*-pentane (5 x 5 mL) and filtered *via* a syringe filter. The solvent was evaporated, yielding a yellow powder (22.0 mg, 15 %).

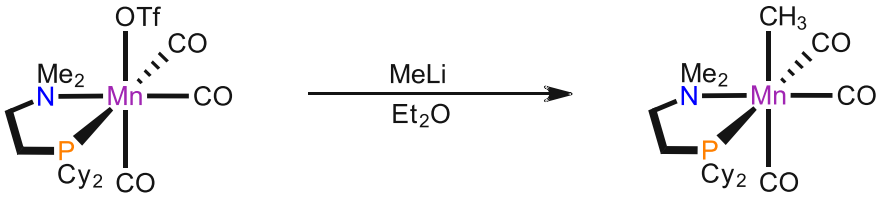
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 2.66 (s, 3H, NCH_3), 2.59 – 2.29 (m, 2H, $NC\underline{H_2}CH_2P$), 2.25 (s, 3H, NCH_3), 2.01 – 1.84 (m, 1H, $NCH_2C\underline{H_2}P$), 1.84 – 1.67 (m, 1H, $NCH_2C\underline{H_2}P$), 1.47 – 1.12 (m, 12H, $PCHC\underline{H_3}$), -0.43 (d, J = 8.2 Hz, 3H, Mn-CH_3).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 61.6 (d, J = 7.9 Hz, $N\underline{C}H_2CH_2P$), 57.5 (NCH_3), 51.7 (NCH_3), 26.0 (d, J = 20.1 Hz, $P\underline{C}HCH_3$), 24.0 (d, J = 12.2 Hz, $NCH_2\underline{C}H_2P$), 23.0 (d, J = 17.2 Hz, $P\underline{C}HCH_3$), 20.3 (d, J = 2.8 Hz, $P\underline{C}HCH_3$), 19.5 (d, J = 3.5 Hz, $P\underline{C}HCH_3$), 18.8 (d, J = 1.7 Hz, $P\underline{C}HCH_3$), 17.8 (d, J = 5.3 Hz, $P\underline{C}HCH_3$), -4.9 (d, J = 17.5 Hz, Mn-CH_3).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: = 80.0.

IR (ATR, cm^{-1}) = 1972 (CO), 1873 (CO), 1842 (CO).

***fac*-[Mn($P^{Cy}N^{Me}$-Et)(CO)$_3$(CH_3)] (3b)**



2f **3b**

In a Schlenk flask, the triflate complex **2f** (100 mg, 0.180 mmol, 1.00 equiv.) was suspended in Et_2O (5 mL), cooled to -70 °C and subsequently MeLi (0.11 mL, 1.6 M in Et_2O, 0.18 mmol, 0.98 equiv.) was added dropwise. During addition, the yellow suspension turned brown. After 50 minutes, the solution mixture was allowed to reach RT and stirred for 1.5 hours. The solvent was evaporated, the remained residue was extracted with *n*-pentane (3 x 5 mL) and filtered *via* a syringe filter. After evaporation of the solvent, the solid was digested in *n*-pentane (3 mL) for 10 minutes. Upon drying of the precipitate, **3b** was obtained as pale yellow powder(17.7 mg, 23 %).

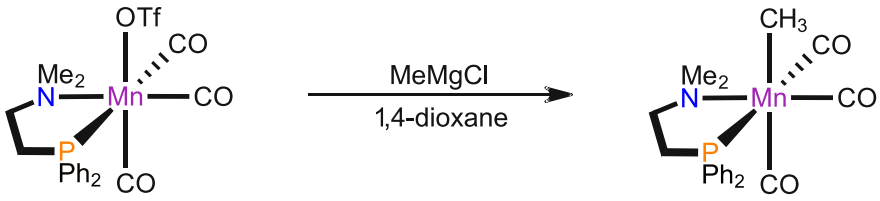
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 2.65 (s, 3H, NCH_3), 2.24 (s, 3H, NCH_3), 2.83 – 1.02 (m, 29H), -0.45 (d, J = 8.1 Hz, 3H, Mn-CH_3).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: = 61.9 (d, J = 7.9 Hz, $N\underline{C}H_2CH_2P$), 57.9 (NCH_3), 52.0 (NCH_3), 38.2 (d, J = 19.3 Hz, PCH), 34.3 (d, J = 15.8 Hz, PCH), 28.8 (d, J = 5.5 Hz), 28.3, 28.1, 28.1, 28.0, 27.9, 27.9, 27.7, 27.6, 26.7 (d, J = 26.6 Hz), 22.5 (d, J = 12.7 Hz), -4.2 (d, J = 18.4 Hz, Mn-CH_3).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 71.3.

IR (ATR, cm^{-1}) = 2018, 1978 (CO), 1886 (CO), 1855 (CO).

***fac*-[Mn($P^{Ph}N^{Me}$-Et)$(CO)_3(CH_3)$] (3c)**



2a **3c**

In a Schlenk flask, triflate complex **2a** (107 mg, 0.196 mmol, 1.00 equiv.) was suspended in 1,4-dioxane (6 mL) and MeMgCl (0.13 mL, 3.0 M in THF, 0.390 mmol, 1.98 equiv.) was added dropwise, upon which the yellow suspension changed to brown. After stirring for 2 hours and 15 minutes the solvent was evaporated under reduced pressure. The reaction mixture was extracted with toluene (3 x 5 mL) and filtered *via* syringe filter. After evaporation of the solvent and drying, a yellow residue remained. The residue was washed with *n*-pentane (1.5 mL), yielding a pale yellow powder (22.7 mg, 28 %).

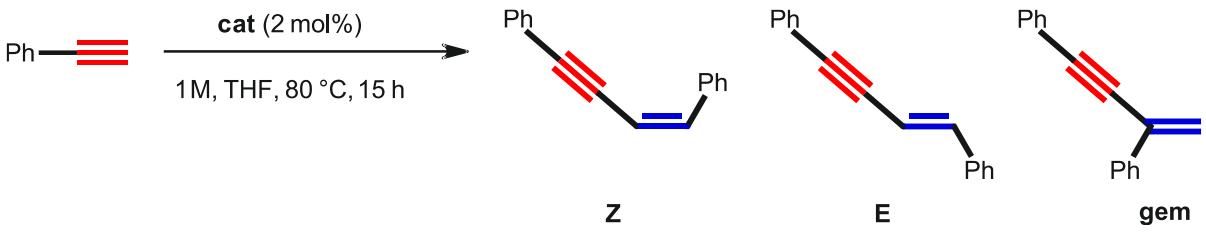
^{1}H NMR (400 MHz, CD_2Cl_2) δ: = 7.83 – 7.65 (m, 4H, $Ph^{2,6}$), 7.52 – 7.29 (m, 6H, $Ph^{3,4,5}$), 2.91 – 2.74 (m, 2H, $NC\underline{H_2}CH_2P$), 2.65 (s, 3H, NCH_3), 2.60 – 2.44 (m, 2H, $NCH_2C\underline{H_2}P$), 2.34 (s, 3H, NCH_3), -0.78 (d, J = 10.3 Hz, 3H, Mn-CH_3).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ: = 132.5 (d, J = 10.7 Hz, $Ph^{2,6}$), 131.4 (d, J = 9.2 Hz, $Ph^{2,6}$), 130.5 (d, J = 2.1 Hz, Ph^{4}), 129.7 (d, J = 2.2 Hz, Ph^{4}), 129.1 (d, J = 9.2 Hz, $Ph^{3,4}$), 128.8 (d, J = 9.2 Hz, $Ph^{3,4}$), 61.2 (d, J = 8.9 Hz, $N\underline{C}H_2CH_2P$), 57.9 (NCH_3), 52.8 (NCH_3), 26.5 (d, J = 17.2 Hz, $NCH_2\underline{C}H_2P$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: = 72.1.

IR (ATR, cm^{-1}) = 2024 (CO), 1890 (CO), 1852 (CO).

5.5 Catalytic Dimerization of Phenylacetylene



Inside an argon flushed glove box a screw cap vial was charged with phenylacetylene (72.5 mg, 77.9 µL, 0.710 mmol, 1.00 equiv.), catalyst (**3a-3c)** (2 mol%) and THF (0.70 mL). Subsequently, the solution turned red. The vial was transferred out of the glovebox and stirred for 15 hours at 80 °C. The solution was allowed to reach RT and exposed to air. An aliquot was analysed by GC-MS.

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