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Metal Template Controlled Formation of [11]ane-P_2C^{NHC} Macrocycles

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Abstract: The synthesis of N-heterocyclic carbene-diphosphine macrocycles by metal template assisted cyclization reactions has been explored. Attempts to prepare the *facial* tungsten tricarbonyl precursor complex containing an NH,NH-functionalized carbene and a suitable diphosphine resulted in displacement of the coordinated carbene and the isolation of the corresponding diphosphine tungsten tetracarbonyl [**3**]. The Re^{I} chloro tetracarbonyl complex bearing an NH,NH-functionalized carbene ligand [**5**] can be prepared and is a suitable precursor for the subsequent formation of the carbene-diphosphine tricarbonyl intermediate [H_2-**6**]Cl bearing reactive 2-fluoro substituents at the phosphine-phenyl groups. Two of these fluoro substituents are displaced by a nucleophilic attack upon deprotonation of the coordinated NH,NH-functionalized carbene resulting in new C−N bonds resulting in the partially coupled intermediate, [**10**], followed by the desired complex with the macrocyclic ligand [**8**]Cl. Compounds [H-**7**]Cl and [**8**]Cl are also formed during the synthesis of [H_2-**6**]Cl as a result of spontaneous HF elimination. Complex $[\mathbf{8}]^+$ may be converted to the neutral dicarbonyl chloro analog [**11**] by action of Me_3NO. Related chemistry with analogous manganese complexes is observed. Thus, from the NH,NH-functionalized carbene manganese bromo tetracarbonyl [**12**], the diphosphine manganese carbene tricarbonyl cation [H_2-**13**] may be readily prepared which provides the macrocyclic carbene-diphosphine tricarbonyl cation $[\mathbf{14}]^+$ following base promoted nucleophilic intramolecular displacement of fluoride. Again, $[\mathbf{14}]^+$ is converted to the neutral bromo dicarbonyl upon reaction with Me_3NO. All complexes with the exception of the reaction intermediate [**10**] have been characterized by spectroscopic and analytical methods in addition to X-ray crystallographic structure determinations for complexes [**3**], [**5**], [H_2-**6**]Cl, [H_2-**6**][**9**], [**8**]Cl, [**10**], [**11**], [**12**], and [**14**]Br.

1. Introduction

Although a large variety of tridentate N-donor macrocyclic ligands and their metal complexes are known,[1] their P-donor homologues have attracted only limited attention. This is mostly due to the lack of facile synthetic routes for the generation of macrocycles with P-donor groups. Nevertheless, the generation of tridentate P-donor macrocycles by a purely organic approach using high dilution methods has been demonstrated.[2] This approach, however, allows only few variations in the linkers between the phophorus atoms and the reaction products are always obtained as a mixture of all possible diastereomers including the thermodynamically more stable *syn*−*anti* isomer. Among these, only the *all-syn* isomer is able to bind to a metal ion as a tridentate ligand. Due to the high inversion barrier at the phosphorus atom (the inversion barrier for nitrogen is substantially lower), high temperatures (typically >150 °C) are necessary for the interconversion of isomers, enabling entrapment of the desired *all-syn* isomer in the coordination sphere of a suitable metal ion.[2b]

Alternatively, tridentate P-donor macrocycles can be prepared by metal template controlled procedures. Such syntheses are stereoselective allowing the exclusive formation of the *all-syn* isomer which remains, however, coordinated to the metal template after its formation. In selected cases it is possible to liberate the ligand from the metal center[3] whereupon the *all-syn* conformation is retained in the free macrocyclic triphosphines. The liberated tridentate P_3-macrocycles can then be coordinated to a variety of transition metals under mild conditions.[4]

Most commonly, the metal template controlled macrocyclization reaction proceeds via radical or base-induced intramolecular hydrophosphination of appropriately functionalized coordinated

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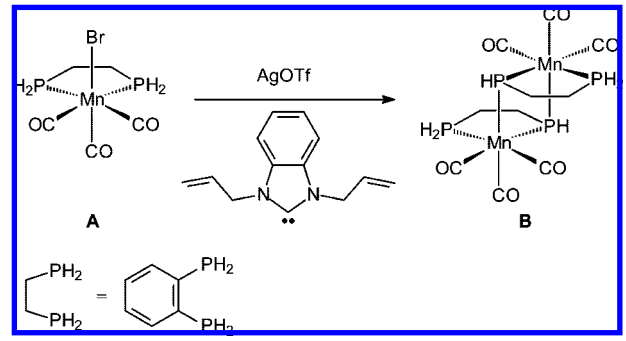
primary or secondary phosphines.[3,5] Besides this general method, a new metal template approach utilizing the nucleophilic attack of coordinated phosphides at coordinated *o*-fluorophenyldiphosphines has also been developed by us.[6] From these methods a number of triphosphine-macrocycles with ring sizes of 9,[5a−c,7] 10,[5d] 11,[2] 12,[3,5e−h,7,8] and 15 atoms[5g] have been prepared. Even larger macrocycles (45 ring-atoms) are accessible by ring-closing metathesis of coordinated tri(ω-octenyl)phosphines.[9]

The triphosphamacrocycles normally act as tridentate *facially* capping ligands and as six-electron donors and may be considered as neutral cyclopentadienyl analogs.[4] In addition, the resulting metal species are stabilized by the macrocyclic effect of the ligand. In 5- and 6-coordination geometries, a *facially* capping ligand leaves the remaining coordination sites mutually *cis* to each other and *trans* to the labilizing phosphine donors. These are potentially important features for homogeneous catalysis.

N-heterocyclic carbenes (NHCs)[10] have attracted interest as spectator ligands in catalytically active metal complexes[11a] and as organocatalysts.[11b] However, only few macrocyclic ligands with NHC donor groups are known. The first complex with a cyclic tetra-NHC ligand was reported in 2005.[12] This complex was obtained by the template controlled cyclization of four β-functionalized phenyl isocyanides followed by linkage of the four resulting NH,NH-stabilized benzimidazolin-2-ylidene ligands. Additional complexes of macrocyclic tetracarbene ligands derived from the corresponding imidazolium salts have also been reported.[13] So far, macrocyclic tridentate ligands containing NHC donor groups are unknown.

Depending on the nature of the substituents, tertiary phosphines and N-heterocyclic carbenes can exhibit similar σ-donor properties but phosphines tend to have a greater propensity for M → L back-donation. The incorporation of these two types of donors into a tridentate macrocyclic ligand therefore may impart interesting properties to a given metal complex. Such a ligand, when coordinated *facially* in an octahedral complex would potentially allow some discrimination of the remaining three ligands due to the differences in the *trans*-effects of phosphines and NHCs. Recently, we described briefly the template controlled preparation of a Re^I-coordinated [11]ane-P_2C^{NHC} macrocycle[14] containing two phosphine and one NHC donor groups. In this manuscript we present a comprehensive account of the synthetic methods employed for the generation and the resultant properties of tridentate macrocycles containing an NHC and two phosphine donor groups coordinated to Re^I and Mn^I.

Scheme 1. Formation of the Dinuclear Diphosphido Manganese Complex **B**



2. Results and Discussion

2.1. Reactions with *N,N′*-Diallylbenzimidazolin-2-ylidene. Initially we tried to use the hydrophosphination reaction[5a−c] for the template-controlled generation of a P_2C^{NHC} macrocycle (Scheme 1). The manganese(I) complex with a coordinated primary diphosphine **A** was selected as starting material. It was intended to substitute the bromo ligand in **A** for an *N,N′*-diallylbenzimidazolin-2-ylidene ligand.[15] In a second step the allyl groups would be used to link the NHC ligand to the diphosphine through known radical-induced hydrophosphination chemistry. Unfortunately, the benzimidazolin-2-ylidene acts as a Brønsted base in the attempted substitution reaction, deprotonating the diphosphine ligand and thus leading to the formation of the dinuclear diphosphido bridged manganese complex **B**.[15d] From this experiment it was concluded that a reactive NHC ligand has to be introduced before the reaction with a coordinated primary or secondary phosphine can take place. Alternatively, the use of primary or secondary phosphines has to be avoided altogether.

To avoid phosphines with P−H bonds in the synthesis of P_2C^{NHC} macrocycles we decided to study the intramolecular cyclization reaction of complexes of type **C** containing an NH,NH-stabilized NHC ligand and a chelating bidentate diphosphine bearing halogen functionalized substituents (Scheme 2). Complexes with NH,NH-stabilized NHC ligands are accessible through a template controlled cyclization of β-functionalized alkyl[16a,b] or aryl isocyanides.[16c−h] The *N,N′*-alkylation of the

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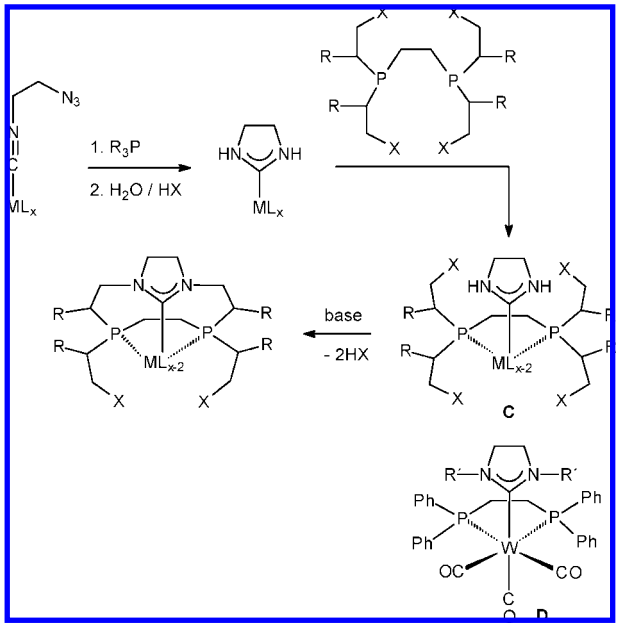
Scheme 2. Synthetic Strategy for the Preparation of P_2C^{NHC} Macrocycles



nitrogen atoms of a coordinated NH,NH-stabilized NHC ligand has been demonstrated.[16]

2.2. Tungsten as Template Metal. Tungsten(0) NHC complexes are known to act as carbene transfer agents.[17] It was therefore hoped that a P_2C^{NHC} macrocycle generated at tungsten as template metal could be removed from the metal center. A tungsten complex of type **C** namely *fac*-[$W(CO)_3$(NHC)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane, NHC = *N*,*N*′-dialkylimidazolidin-2-ylidene) **D** has been described.[17a] The NHC ligand in complex **D**, however, is unsuitable for macrocycle formation via the methodology depicted in Scheme 2 since both ring nitrogen atoms are alkylated. It was hoped that the published method used for the synthesis of **D** could be used for the synthesis of complexes of type **C** with a reactive NH,NH-stabilized NHC ligand.

Previously we have described the synthesis of complex [**1**] (Scheme 3) which was obtained from [$W(CO)_6$] and 2-azidoethyl isocyanide followed by cyclization of the coordinated isocyanide ligand by a Staudinger reaction and hydrolysis of the resulting phosphinimine.[16a] The desired complex [**4**] was not obtained from the reaction of [**1**] and 1,2-bis(di(*o*-fluorophenyl)phosphino)benzene **2**[14] under irradiation and/or reflux in various solvents (acetonitrile, benzene, toluene). The fluorinated diphosphine **2** is apparently much less basic than dppe used for the preparation of **D** and W^0 carbonyl complexes are generally less Lewis acidic then Mn^I or Re^I carbonyls which were used later (*vide infra*). Nevertheless, an increase of the reaction temperature by using boiling *o*-xylene at 140 °C led to the coordination of diphosphine **2** to [**1**] (Scheme 3).

The $^{31}P\{^1H\}$ NMR spectrum of the reaction product showed a signal at $\delta = 26.7$ ppm with characteristic satellites ($^1J_{P,W} = 237$ Hz). The ^{19}F NMR exhibits only one signal ($\delta = -98.0$ ppm) indicating the presence of a complex with higher symmetry than in the desired complex [**4**]. In addition the IR spectrum shows four carbonyl stretching absorptions at $\nu = 2029$, 1930, 1897 and 1879 cm^{-1} indicative of a tetracarbonyl complex with C_{2v} symmetry. From the spectroscopic data it was concluded that complex [**3**] was obtained (76% yield) rather than the desired complex [**4**].

The formation of complex [**3**] was confirmed by an X-ray diffraction study. Suitable crystals of [**3**] were obtained by slow evaporation of the solvent from a dichloromethane solution of the complex. The structure analysis confirmed the formation of the C_{2v}-symmetrical complex [$W(CO)_4$(**2**)] [**3**] (Figure 1). Liberation of the NH,NH-stabilized NHC ligand apparently occurs under the harsh reaction conditions employed for coordination of **2** to [**1**]. While compounds of the general formula [$W(CO)_4$(P−P)] (P−P = chelating diphosphine) can be obtained by more direct methods[18] the loss of the NHC ligand from [**1**] is still an interesting observation. Normally NHC ligands are known to displace phosphines from their metal complexes. During the synthesis of [**3**] we have therefore observed an example for the reverse reactivity, albeit involving an NH,NH-stabilized NHC ligand. The use of decarbonylizing agents like N-oxides to facilitate the coordination of **2** to [**1**] was not investigated due to the possible formation of the geometrically unfavorable *meridional* complex.

Complex [**3**] resides on a crystallographic mirror plane which passes through atoms O3/C3/W/O1/C1 thereby bisecting the phenyl ring of the diphosphine ligand. The fluoro substituent of one phenyl ring is disordered over positions F2 and F2A. No special features were observed in the bond lengths and bond angles of [**3**]. We assume that packing effects prevent the coplanarity of the P/W/P* plane and the phenyl ring bridging the two phosphorus atoms (dihedral angle $\delta = 11.8°$).

2.3. Rhenium(I) as Template Metal. Since our attempts to prepare a tungsten(0) complex exhibiting *facial* coordination of the diphosphine **2** and an NH,NH-stabilized NHC ligand were unsuccessful we investigated other template metals. The NH,NH carbene complex [**5**] (Scheme 4) has been synthesized from [$ReCl(CO)_5$] and the phosphinimine $H_2NCH_2CH_2N{=}PPh_3$ most likely by attack of the phosphinimine group at an electrophilic carbonyl group resulting in formation of $Ph_3P{=}O$ and the isocyanide ligand followed by intramolecular cyclization to give the NH,NH-stabilized carbene ligand.[14] This method has been previously employed for the preparation of a similar complex with a bromo instead of a chloro ligand.[16b] The $^{13}C\{^1H\}$ NMR spectrum of [**5**] exhibits the resonance of the carbene carbon atom at $\delta = 193.6$ ppm. The protons at the ring-nitrogen atoms were observed as a singlet at $\delta = 6.90$ ppm in the ^1H spectrum. Crystals of [**5**] were obtained by slow evaporation of the solvent from a concentrated dichloromethane solution. The X-ray

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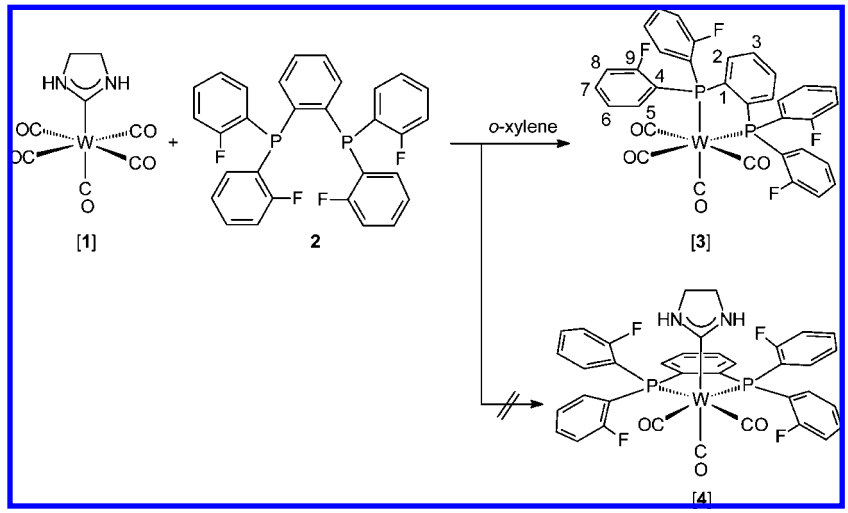
Scheme 3. Reaction of [**1**] with **2** to Give [**3**] Instead of [**4**][a]



[a] Numbering for [**3**] refers to the assignment of the NMR resonances in the Experimental Section.

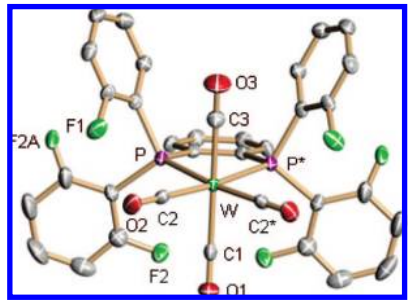


Figure 1. Molecular structure of complex [**3**]. Selected bond lengths (Å) and angles (deg): W−P 2.4934(8), W−C1 2.037(4), W−C2 1.993(3), W−C3 2.050(4), O1−C1 1.138(5), O2−C2 1.146(3), O3−C3 1.127(5); P−W1−P* 79.31(4), P−W−C1 94.88(9), P−W−C2 93.85(8), P−W−C3 89.26(9), P−W−C2* 172.85(8), C1−W−C2 87.75(11), C1−W−C3 174.6(2), C2−W−C3 88.55(12), C2−W−C2* 92.9(2).

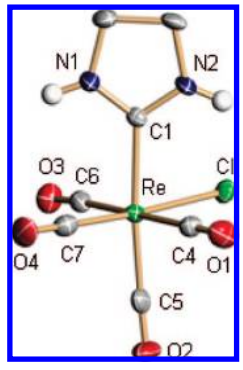


Figure 2. Molecular structure of complex [**5**]. Selected bond lengths (Å) and angles (deg): Re−Cl 2.4960(14), Re−C1 2.175(5), Re−C4 1.995(5), Re−C5 1.978(6), Re−C6 2.011(5), Re−C7 1.915(5); Cl−Re−C1 84.42(13), Cl−Re−C4 88.12(15), Cl−Re−C5 91.1(2), Cl−Re−C6 90.27(15), Cl−Re−C7 176.5(2), C1−Re−C4 88.7(2), C1−Re−C5 175.0(2), C1−Re−C6 92.2(2), C1−Re−C7 92.1(2), C4−Re−C5 88.9(2), C4−Re−C6 178.1(2), C4−Re−C7 91.5(2), C5−Re−C6 90.1(2), C5−Re−C7 92.4(2), C6−Re−C7 90.1(2), N1−C1−N2 108.2(4).

diffraction analysis shows a distorted octahedral rhenium(I) atom surrounded by the carbene, one chloro and four CO ligands. Apparently, the chloro ligand is the strongest π-donor followed by the NHC ligand as judged from the Re−C7 (1.915(5) Å) and Re−C5 (1.978(6) Å) bond distances (Figure 2).

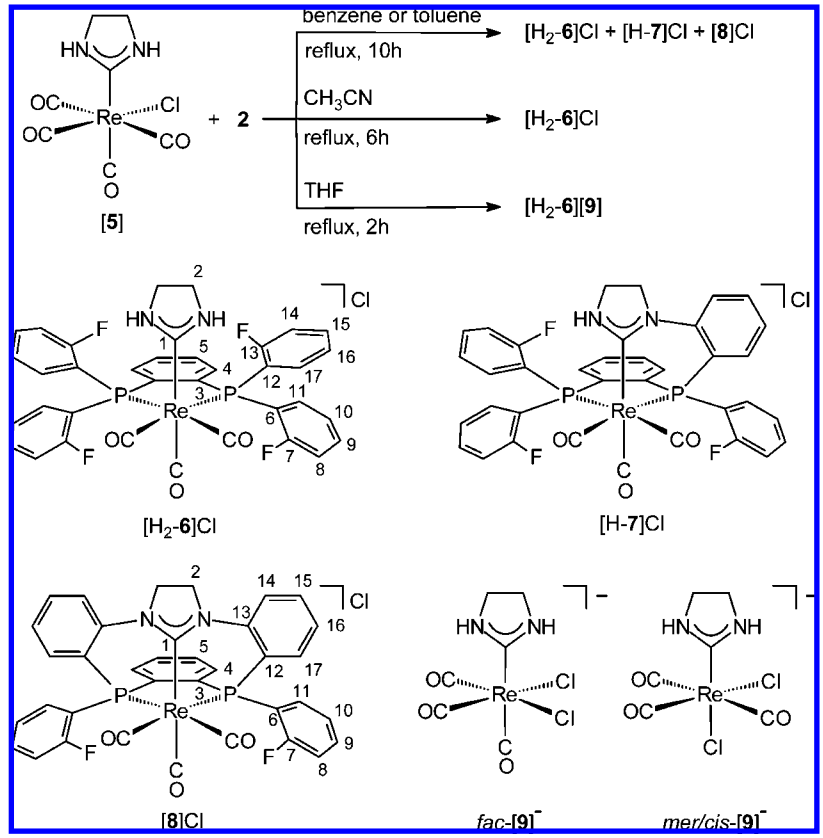
The reaction of the bromo derivative of complex [**5**] with dppbz (dppbz = 1,2-bis(diphenylphosphino)benzene) in refluxing benzene has been shown to yield *fac*-[Re(NHC)(dppbz)$(CO)_3]^+$.[19] We therefore decided to react complex [**5**] with the fluorinated diphosphine **2**. Contrary to the clean reaction of [**5**] with dppbz the same reaction with the fluorinated diphosphine **2** gave a mixture of reaction products depending on the solvent and temperature employed for the reaction (Scheme 4). When the reaction was carried out in benzene following the described protocol,[19] several resonances indicative of the formation of different complexes were observed in the $^{31}P\{^1H\}$ NMR spectrum. The mass spectrum also indicated the formation of different rhenium containing complexes that we assume arise from simultaneous CF and NH activation.

The desired cation $[H_2\text{-}\mathbf{6}]^+$ was identified in the reaction mixture by the presence of a resonance at $\delta = 21.8$ ppm with $^3J_{P,F} = 14.7$ Hz in the $^{31}P\{^1H\}$ NMR spectrum. Cation $[H_2\text{-}\mathbf{6}]^+$ was also identified in the ES mass spectrum at $m/e = 859$ ($[M]^+$). A doublet at $\delta = 15.8$ ppm with $^3J_{P,F} = 16.6$ Hz was tentatively assigned to cation $[\mathbf{8}]^+$ with two $N-C_{Ar}$ bridges. The formation of $[\mathbf{8}]^+$ was confirmed by a peak in the mass spectrum at $m/e = 819$ which corresponds to the mass of $[H_2\text{-}\mathbf{6}]^+ - 40$ amu (2 × HF). Two additional broad peaks were recorded in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 20.5$ and 18.2 ppm. These chemical shifts fall in between the values recorded for $[H_2\text{-}\mathbf{6}]^+$ and $[\mathbf{8}]^+$ and it is therefore reasonable to assume that these resonances are caused by the semibridged complex cation $[H\text{-}\mathbf{7}]^+$. This assumption is corroborated by the observation of a peak at $m/e = 839$ in the ES mass spectrum which corresponds to the value for $[\mathbf{6}]^+ - HF$. In addition to the $^3J_{P,F}$ coupling observed for the cations $[H_2\text{-}\mathbf{6}]^+$ and $[\mathbf{8}]^+$ additional $^2J_{P,P}$ coupling is operative in $[H\text{-}\mathbf{7}]^+$ leading to the observed line broadening.

We have been unable to separate the rhenium complexes obtained from the reaction in benzene. In addition, the relative amounts of the complexes in the reaction mixture varied between different runs. No preference for one of the three complexes was observed even in higher boiling solvents like toluene. We assume that this behavior is caused by the insolubility of the complexes in aromatic hydrocarbons. The HF generated during

(19) Xue, W.-M.; Chan, M. C.-W.; Su, Z.-M.; Cheung, K.-K.; Liu, S.-T.; Che, C.-M. *Organometallics* **1998**, *17*, 1622–1630.

Scheme 4. Products of the Reaction of [**5**] with **2** under Different Conditions[a]



[a] Numbering for [H_2-**6**] and [**8**]Cl refers to the assignment of the NMR resonances.

the C−F/N−H activation reacts with boron of the glass vessel leading to the formation of BF_4^- counterions which were detected in the ^{19}F NMR spectrum at $\delta = -153$ ppm. Similar reactions of HF with the glass of reaction vessels have been reported.[20] While the reaction of [**5**] and **2** in benzene or toluene did not lead to the selective formation of complex cation [H_2-**6**]$^+$ it showed that ligand **2** can substitute two ligands (CO and Cl^-) in [**5**]. In addition, the formation of [H_2-**6**]$^+$, [**H-7**]$^+$ and [**8**]$^+$ in this reaction constituted promising results regarding the preparation of macrocyclic P_2C^{NHC} ligands in a template controlled reaction at Re^I.

Since the formation of different rhenium complexes in the reaction of [**5**] with **2** in benzene or toluene is most likely due to the insolubility of the reaction products in these solvents it was decided to increase the solubility of the reaction products by the use of more polar solvents. The stoichiometric reaction of [**5**] and **2** in acetonitrile yields complex [H_2-**6**]Cl in nearly quantitative yield (Scheme 4). The complex was identified by the single resonance at $\delta = 21.8$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. The formation of [H_2-**6**]Cl was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography. The IR spectrum of [H_2-**6**]Cl exhibits three CO stretching frequencies

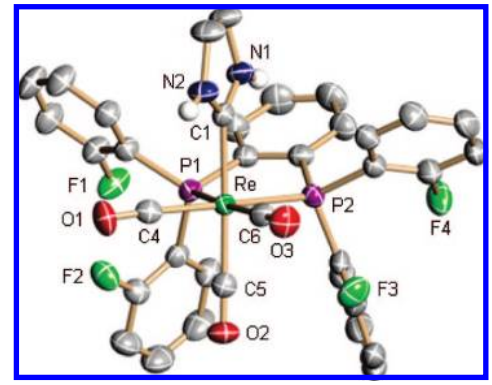


Figure 3. Molecular structure of the complex cation [H_2-**6**]$^+$ in [H_2-**6**]Cl·3THF. Selected bond lengths (Å) and angles (deg): Re−P1 2.428(2), Re−P2 2.420(2), Re−C1 2.188(5), Re−C4 1.971(5), Re−C5 1.950(5), Re−C6 1.975(6); P1−Re−P2 80.11(5), P1−Re−C1 90.60(13), P1−Re−C4 93.54(14), P1−Re−C5 90.50(15), P1−Re−C6 173.31(14), P2−Re−C1 90.43(13), P2−Re−C4 173.60(14), P2−Re−C5 91.53(15), P2−Re−C6 93.21(15).

at $\nu = 2043$, 1971 and 1949 cm^{-1}. This is in agreement with a *facial* tricarbonyl complex with C_S symmetry. The absorption for the N−H groups was observed at $\nu = 3460$ cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance for the carbene carbon atom at $\delta = 189.8$ ppm only slightly upfield from the value recorded for [**5**] ($\delta = 193.6$ ppm).

An X-ray diffraction analysis with crystals of [H_2-**6**]Cl·3THF (Figure 3) confirmed the *facial* arrangement of the ligands in a distorted octahedral complex. Bond lengths and angles of the cation [H_2-**6**]$^+$ fall in the expected range observed previously for similar Re^I NHC complexes.[19] The plane of the carbene

(20) (a) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C. *J. Organomet. Chem.* **1999**, *582*, 163–172. (b) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Organometallics* **2003**, *22*, 1802–1810. (c) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1996**, 3215–3220.

(21) (a) Hu, X.; Meyer, K. *J. Organomet. Chem.* **2005**, *690*, 5474–5484. (b) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Chem. Commun.* **2004**, 2164–2165. (c) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755–764.

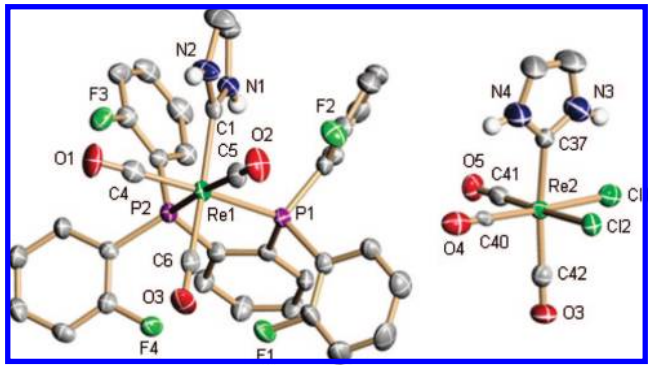


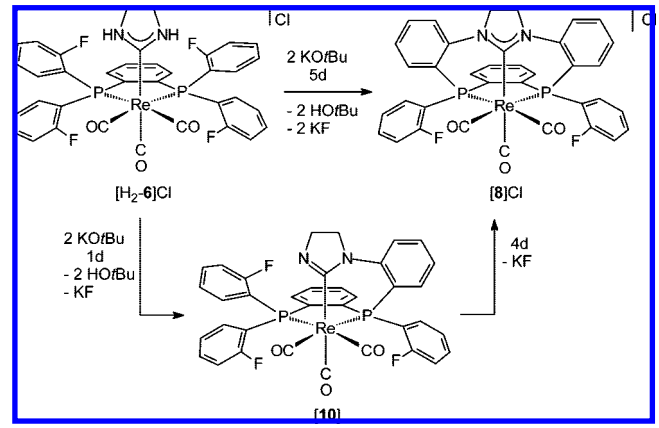
Figure 4. Molecular structure of cation $[H_2\text{-}\mathbf{6}]^+$ (left) and the anion *fac*-$[\mathbf{9}]^-$ (right) in $[H_2\text{-}\mathbf{6}]$*fac*-$[\mathbf{9}]\cdot CH_2Cl_2$. The metric parameters of the cation $[H_2\text{-}\mathbf{6}]^+$ match those found in $[H_2\text{-}\mathbf{6}]Cl\cdot 2THF$ (Figure 3). Selected bond lengths (Å) and angles (deg) for *fac*-$[\mathbf{9}]^-$: Re2−Cl1 2.502(2), Re2−Cl2 2.5135(13), Re2−C37 2.154(5), Re2−C40 2.000(6), Re2−C41 1.895(5), Re2−C42 1.964(5); Cl1−Re2−Cl2 88.95(5), Cl1−Re2−C37 86.30(14), Cl1−Re2−C40 177.3(2), Cl1−Re2−C41 93.1(2), Cl1−Re2−C42 89.78(15), Cl2−Re2−C37 85.12(14), Cl2−Re2−C40 89.9(2), Cl2−Re2−C41 176.67(15), Cl2−Re2−C42 90.48(15), C37−Re2−C40 91.1(2), C37−Re2−C41 92.4(2), C37−Re2−C42 174.2(2), C40−Re2−C41 88.0(2), C40−Re2−C42 92.7(2), C41−Re2−C42 92.2(2).

ligand is oriented between P1/P2 and C4/C6 in a fashion which allows for a minimal interaction with the coordinated diphosphine ligand.

A further compound was obtained when the reaction of [**5**] with **2** was carried out in boiling THF over a period of 2 h (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum shows the formation of $[H_2\text{-}\mathbf{6}]^+$ with a resonance at $\delta = 21.8$ ppm. The IR spectrum of the reaction product, however, exhibits the three CO stretching frequencies of the cation $[H_2\text{-}\mathbf{6}]^+$ (ν = 2043, 1971 and 1949 cm^{-1}) in addition to three CO stretching frequencies at ν = 2004, 1895 and 1849 cm^{-1}. This was taken as an indication for the formation of the unusual anion $[\mathbf{9}]^-$ which cocrystallized with $[H_2\text{-}\mathbf{6}]^+$. 2D NMR experiments with the reaction product revealed three carbene carbon signals at δ = 189.8 ($[H_2\text{-}\mathbf{6}]^+$), 208.6 and 203.6 ppm (most likely for two isomers of $[\mathbf{9}]^-$). The ^1H spectrum shows three singlets for the protons of the carbene NCH_2CH_2N group at δ = 3.60, 3.56 and 3.21 ppm with a relative intensity of 0.4:0.6:1.0. The resonance at $\delta = 3.21$ ppm was assigned to the protons of the cation $[H_2\text{-}\mathbf{6}]^+$ which is known from $[H_2\text{-}\mathbf{6}]$Cl, whereas the other two signals are due to two isomers of $[\mathbf{9}]^-$ which apparently are present in a 40:60 ratio. While the formula of the product obtained in the reaction between [**5**] and **2** in THF is apparently $[H_2\text{-}\mathbf{6}][\mathbf{9}]$, no absolute assignment of the isomers of $[\mathbf{9}]^-$ can be made from the NMR spectroscopy. It is reasonable to assume that anion $[\mathbf{9}]^-$ exists as *fac*-$[\mathbf{9}]^-$ and *mer/cis*-$[\mathbf{9}]^-$ isomers while the conceivable *mer/trans*-$[\mathbf{9}]^-$ isomer is thermodynamically unfavored. As expected, the spectroscopic data for the cation $[H_2\text{-}\mathbf{6}]^+$ are identical irrespective of the nature of the anions (Cl^- or $[\mathbf{9}]^-$). To our knowledge, $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ represents the first example of a compound containing both a cationic and an anionic carbene complex.

The conclusions drawn from the NMR spectra of $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ were confirmed by an X-ray diffraction study. Suitable crystals of $[H_2\text{-}\mathbf{6}][\mathbf{9}]\cdot CH_2Cl_2$ were obtained by slow evaporation of the solvent from a saturated dichloromethane solution of the salt. The structure determination confirms the formation of the salt $[H_2\text{-}\mathbf{6}][\mathbf{9}]$. The metric parameters of the cation $[H_2\text{-}\mathbf{6}]^+$ in $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ (Figure 4) match, within experimental error, those found for the cation in $[H_2\text{-}\mathbf{6}]$Cl.

Scheme 5. Synthesis of [**8**]Cl via the Intermediate [**10**]



The anion in $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ was found as *fac*-$[\mathbf{9}]^-$. No other isomers, proposed on the basis of the NMR spectra, were found in the crystal. Atoms Cl1 and the carbonyl group C40≡O4 in *fac*-$[\mathbf{9}]^-$ are disorderd and only one arrangement is depicted in Figure 4. The Re−C_{NHC} bond length in the anion *fac*-$[\mathbf{9}]^-$ (Re2−C37 2.154(5) Å) is shorter than the equivalent parameter in the neutral complex [**5**] (Re−C1 2.175(5) Å) and in the cation $[H_2\text{-}\mathbf{6}]^+$ (Re−C1 in $[H_2\text{-}\mathbf{6}]$Cl 2.188(5) Å; Re1−C1 in $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ 2.194(5)). Apparently, the number of π-donating chloro ligands bound to rhenium(I) and the charge of the complex determine the π-basicity of the metal atom. An increase of the metal to carbene π-backbonding could provide an explanation for the observed trend in the Re−$C_{carbene}$ bond lengths.[21]

The next step in the generation of an [11]ane-P_2C^{NHC} macrocycle is the connection of the carbene ligand in $[H_2\text{-}\mathbf{6}]^+$ to the phenyl groups of the coordinated diphosphine ligand via an S_N2_{Ar} type substitution with consequent elimination of two equivalents of HF. Initial results (see Scheme 4) indicated the feasibility of this approach. Compound $[H_2\text{-}\mathbf{6}]$Cl was used for the construction of the P_2C^{NHC} macrocycle. Compound $[H_2\text{-}\mathbf{6}]$Cl was suspended in THF and treated with KO*t*Bu to deprotonate the NH,NH-stabilized carbene ligand. The subsequent nucleophilic attack of the deprotonated nitrogen atoms at the C−F bonds of the diphosphine gave the cationic complex $[\mathbf{8}]^+$ with the [11]ane-P_2C^{NHC} macrocycle (Scheme 5).[14] After a reaction time of five days compound [**8**]Cl precipitates from the reaction mixture in 90% yield.

Compound [**8**]Cl was identified by the $^{31}P\{^1H\}$ NMR signal at δ = 15.8 ppm which was previously observed for $[\mathbf{8}]^+$ obtained from the reaction of [**5**] with ligand **2** in aromatic hydrocarbons (Scheme 4). Linkage of the diphosphine phenyl groups to the NHC ligand in $[\mathbf{8}]^+$ causes an upfield shift of the $^{31}P\{^1H\}$ resonance of about 6 ppm relative to the unbridged cation $[H_2\text{-}\mathbf{6}]^+$ ($^{31}P\{^1H\}$ NMR: $\delta = 21.8$ ppm). To date, no arylation of an NH,NH-stabilized NHC ligand comparable to the template controlled reaction $[H_2\text{-}\mathbf{6}]^+ \rightarrow [\mathbf{8}]^+$ has been reported and even the direct *N*-arylation of azoles has been described as being problematic.[10a]

In addition to the preparation of $[\mathbf{8}]^+$ we isolated an intermediate formed during its generation. Compound [**8**]Cl precipitates from the reaction mixture over a period of five days. Formation of a precipitate was already noted after a reaction time of only one day. Isolation of this precipitate revealed that it was composed of the salt [**8**]Cl and the neutral complex [**10**]. Only small amounts of [**10**], insufficient for a detailed spectroscopic investigation, could be isolated. The concentration of [**10**]

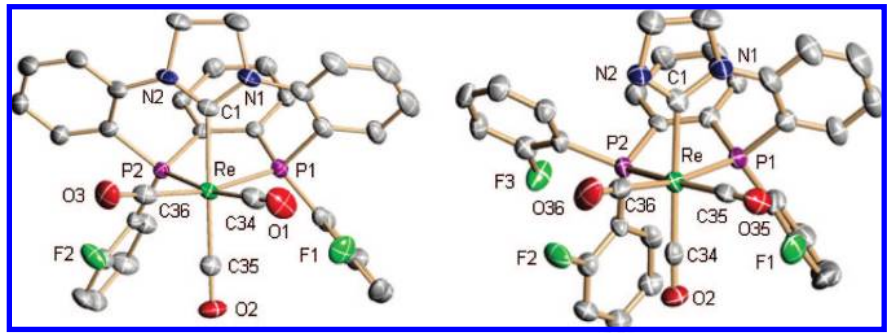
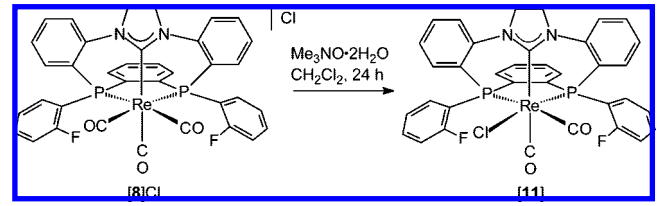


Figure 5. Molecular structures of $[\mathbf{8}]^+$ in $[\mathbf{8}]Cl{\cdot}3H_2O$ (left) and [**10**] (right). Selected bond lengths (Å) and angles (deg) for $[\mathbf{8}]^+$: Re−P1 2.3957(13), Re−P2 2.3895(14), Re−C1 2.172(4), Re−C34 1.966(4), Re−C35 1.950(4), Re−C36 1.966(4), N1−C1 1.350(5), N2−C1 1.342(5); P1−Re−P2 81.58(5), P1−Re−C1 77.96(10), P1−Re−C34 91.72(13), P1−Re−C35 97.93(12), P1−Re−C36 167.33(12), P2−Re−C1 79.12(10), P2−Re−C34 170.73(13), P2−Re−C35 96.60(11), P2−Re−C36 91.15(13), C1−Re−C34 93.3(2), C1−Re−C35 174.40(14), C1−Re−C36 90.52(15), C34−Re−C35 90.6(2), C34−Re−C36 94.2(2), C35−Re−C36 93.2(2), N1−C1−N2 108.6(3). [**10**]: Re−P1 2.3837(14), Re−P2 2.4518(14), Re−C1 2.191(6), Re−C34 1.937(6), Re−C35 1.947(6), Re−C36 1.954(6), N1−C1 1.448(7), N2−C1 1.290(6); P1−Re−P2 79.54(5), P1−Re−C1 80.10(15), P1−Re−C34 98.7(2), P1−Re−C35 90.4(2), P1−Re−C36 169.9(2), P2−Re−C1 90.04(14), P2−Re−C34 90.1(2), P2−Re−C35 169.6(2), P2−Re−C36 97.6(2), C1−Re−C34 178.7(2), C1−Re−C35 90.8(2), C1−Re−C36 90.3(2), C34−Re−C35 88.8(2), C34−Re−C36 90.9(2), C35−Re−C36 92.7(2), N1−C1−N2 109.7(5).

remained low in the reaction mixture due to its subsequent reaction to [**8**]Cl (Scheme 5). Compound [**8**]Cl was crystallized by slow diffusion of diethyl ether into a concentrated acetonitrile solution in air as $[\mathbf{8}]Cl{\cdot}3H_2O$. Crystals of [**10**] could be obtained by slow evaporation of the dichloromethane solvent from a solution containing [**8**]Cl and [**10**]. The X-ray diffraction analysis with crystals of $[\mathbf{8}]Cl{\cdot}3H_2O$ (Figure 5, left) confirms the formation of the coordinated macrocycle [11]ane-P_2C^{NHC}. All bond distances in $[\mathbf{8}]^+$ are shortened in comparison to equivalent bonds in $[H_2\text{-}\mathbf{6}]^+$. This is most noticeable for the Re−C1 and Re−P bonds. The bond angles in the cation $[\mathbf{8}]^+$ deviate more strongly from octahedral geometry than those found for cation $[H_2\text{-}\mathbf{6}]^+$. This effect is most pronounced for those angles involving donor groups of the macrocycle. For example, the P−Re−C1 bond angles in the cation $[H_2\text{-}\mathbf{6}]^+$ (P1−Re−C1 90.60(13)°, P2−Re−C1 90.43(13)°) measure about 90° whereas significantly smaller values for the equivalent angles were found in the cation $[\mathbf{8}]^+$ (P1−Re−C1 77.96(10)°, P2−Re−C1 79.12(10)°).

The neutral complex [**10**] differs from $[H\text{-}\mathbf{7}]^+$ (Scheme 4) because it was obtained from $[H_2\text{-}\mathbf{6}]^+$ by deprotonation of the NHC nitrogen atoms with a base while $[H\text{-}\mathbf{7}]^+$ was obtained from the same precursor by C−F and N−H activation in boiling aromatic solvents. In principle, [**10**] should be accessible from $[H\text{-}\mathbf{7}]^+$ by reaction with a base. However, it is difficult to isolate due to its subsequent reaction to yield [**8**]Cl. Since [**10**] can only be obtained as a reactive intermediate its isolation in large amounts has been impossible. The cation $[H\text{-}\mathbf{7}]^+$ contains an NH,NR-stabilized NHC ligand while [**10**] features an anionic N-heterocyclic carbon bound ligand. Similar deprotonated derivatives of benzannulated N-heterocyclic carbenes coordinated to transition metals have been described.[22] The structure analysis shows that the N-heterocycle in [**10**] (Figure 5, right) is different to those in the NHC complexes $[H_2\text{-}\mathbf{6}]^+$ and $[\mathbf{8}]^+$. Two distinctly different C1−N bond lengths (1.448(7) and 1.290(6) Å) corresponding to a single and a double bond were found. In addition, the N1−C1−N2 angle in [**10**] measures 109.7(5)° which is a significantly larger value than observed for the N−C−N angle in the rhenium NHC complexes [**5**], $[H_2\text{-}\mathbf{6}]^+$, $[\mathbf{8}]^+$ and *fac*-$[\mathbf{9}]^-$ where values smaller than 108.6° have been observed. Similarly to the situation found in complex $[\mathbf{8}]^+$ containing the [11]ane-P_2C^{NHC} macrocycle the introduction of only one $N_{heterocycle}-C_{aryl}$ bond causes the P1−Re−C1 angle to shrink to 80.10(15)° while the P2−Re−C1 angle (C2−Re−C1 90.04(14)°) remains larger. The introduction of the $N_{heterocycle}-C_{aryl}$ bond also leads to a shortening of the Re−P1 bond length (2.3837(14) Å) relative to the Re−P2 bond length (2.4518(14) Å).

Scheme 6. Synthesis of [**11**] from [**8**]Cl



Compound [**8**]Cl is stable toward water. It is also stable toward oxidation with sulfur, aerial oxygen or bromine. Since the *facially* coordinated P_2C^{NHC} macrocycle in $[\mathbf{8}]^+$ contained two different types of donor groups the carbonyl groups *trans* to these donors might be expected to exhibit different reactivity. We expected the weaker bound and thus the easier to oxidize CO ligands in *trans* position to the phosphine donors as phosphines are good π-acceptors in contrast to NHCs. Addition of N-oxides to [**8**]Cl leads to loss of one carbonyl ligand (Scheme 6). The vacated coordination site is then occupied by the chloride counterion leading to the neutral complex [**11**]. Complex [**11**] precipitates from the reaction mixture as a bright yellow solid which, once precipitated, was only sparingly soluble in common organic solvents limiting its spectroscopic characterization.

$^{31}P\{^1H\}$ NMR spectroscopy revealed a nonspecific reactivity of the carbonyl ligands in [**8**]Cl. Three resonances were observed corresponding to the complexes with the chloro ligand *trans* to the NHC (δ = 30.9 ppm, s) or *trans* to one of the phosphine donors (δ = 27.9, m, and 25.5 ppm, m, for the two different phosphorus atoms). Against our expectations the *trans*-influence of the donor groups in $[\mathbf{8}]^+$ is similar enough to prevent a selective substitution reaction.

Complex [**11**] was crystallized as $[\mathbf{11}]{\cdot}0.25H_2O{\cdot}CH_2Cl_2$ by slow evaporation of the solvent from a dilute solution of the complex in dichloromethane. The X-ray diffraction study

(22) (a) Hahn, F. E.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1995**, 569–570. (b) Hahn, F. E.; Klusmann, D.; Pape, T. *Eur. J. Inorg. Chem.* **2008**, 4420–4424.

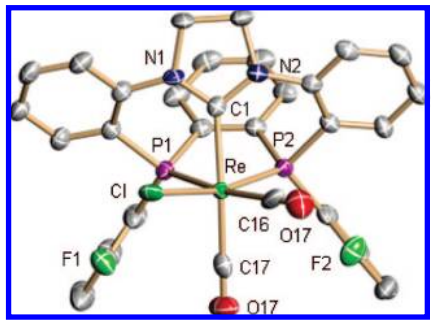
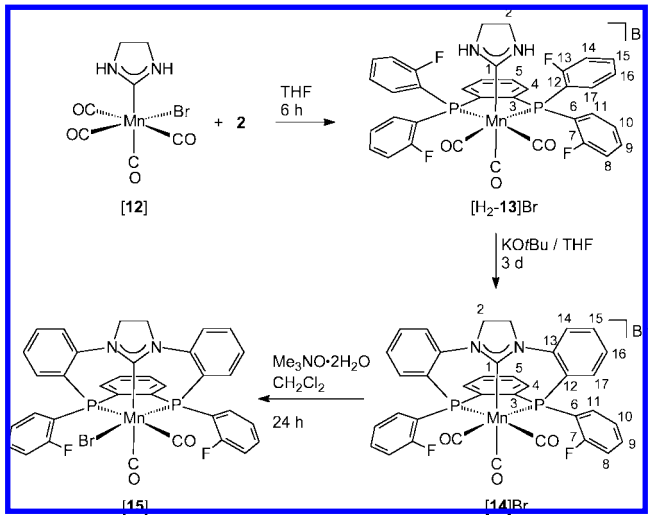


Figure 6. Molecular structure of complex [**11**] in [**11**]·0.25H_2O·CH_2Cl_2. Selected bond lengths (Å) and bond angles (deg): Re−P1 2.3732(11), Re−P2 2.2866(11), Re−Cl 2.5234(12), Re−C1 2.156(4), Re−C16 1.997(6), Re−C17 1.961(5); P1−Re−P2 82.96(4), P1−Re−Cl 95.68(4), P1−Re−C1 79.31(11), P1−Re−C16 172.68(14), P1−Re−C17 93.81(14), P2−Re−Cl 166.53(4), P2−Re−C1 80.63(11), P2−Re−C16 91.99(13), P2−Re−C17 95.34(12), Cl−Re−C1 85.94(11), Cl−Re−C16 88.00(13), Cl−Re−C17 98.13(12), C1−Re−C16 94.7(2), C1−Re−C17 172.4(2), C16−Re−C17 91.9(2), N1−C1−N2 107.0(4).

Scheme 7. Synthesis of Complexes [**12**], [**13**]Br, [**14**]Br, and [**15**][a]



[a] Numbering for [**13**]Br and [**14**]Br refers to the assignment of the NMR resonances.

revealed that the isomer with the chloro ligand *cis* to one carbene donor had been isolated in the crystal (Figure 6). The presence of the chloro ligand in [**11**] also becomes evident when the Re−P bond lengths are considered. In contrast to the carbonyl ligands the chloro ligand is a net π-donor. This property leads to a shortened Re−P bond *trans* to the chloro ligand (Re−P2 2.2866(11) Å) compared to the Re−P bond trans to the carbonyl (Re1−P1 2.3732(11) Å). Both the Re−$C_{carbonyl}$ and the Re−C_{NHC} distances are shorter in the neutral complex [**11**] compared to the cationic complex [**8**]$^+$.

2.4. Manganese as Template Metal. To demonstrate the general applicability of the template controlled synthesis of P_2C^{NHC} macrocyclic ligands the manganese(I) complexes [**12**], [H_2-**13**]Br, [**14**]Br and [**15**] were prepared (Scheme 7). Not only are manganese complexes with tridentate macrocyclic P_2C^{NHC} ligands currently unknown but manganese complexes bearing NHC ligands are generally rare. Most known manganese NHC complexes contain the unsaturated imidazolin-2-ylidene ligand.[23] Two examples of manganese complexes with the saturated imidazolidin-2-ylidene have been reported[24] but these complexes were isolated in low yield from the reaction of the entetraamine

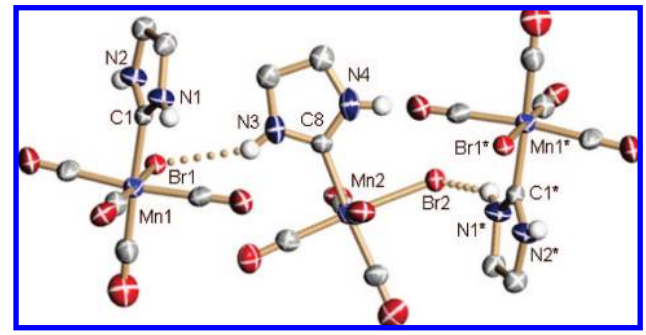


Figure 7. Molecular structures of three molecules of [**12**] illustrating the different hydrogen bonds. Selected bond length (Å) and angles (deg) for molecule **1**: Mn1−Br1 2.5429(6), Mn1−C1 2.035(3), Br1−Mn1−C1 88.71(7). For molecule **2**: Mn2−Br2 2.5345(8), Mn2−C8 2.040(2); Br2−Mn2−C8 89.88(7).

with Mn^I starting materials and have only been characterized by ^{1}H and/or IR spectroscopy.

The Mn^I complex [**12**] was prepared from H_2NCH_2-$CH_2N{=}PPh_3$ and [$MnBr(CO)_5$] using the method of Liu et al.[16b] After deoxgenation of one carbonyl group and formation of $O{=}PPh_3$, the intermediate 2-aminoisocyanide spontaneously cyclizes, resulting in the formation of [**12**] in good yield (65%). The $^{13}C\{^1H\}$ NMR spectrum shows the resonance for the carbene carbon atom at δ = 219.7 ppm shifted to lower field compared to its rhenium(I) analog [**5**] (δ = 193.6 ppm). A significant downfield shift was also observed for the $^{13}C\{^1H\}$ NMR resonances of the carbonyl carbon atoms in [**12**] (δ = 210.8, 212.1 and 212.6 ppm) relative to [**5**] (δ = 184.7, 184.9 and 186.8 ppm). The rhenium complex [**5**] exhibits two N−H stretching frequencies in the IR spectrum, which were attributed to intermolecular N−H···Cl hydrogen bonds[14] while the IR spectrum of complex [**12**] exhibits three N−H stretching vibrations at ν = 3451, 3388 and 3363 cm^{-1}. This has been attributed to different intermolecular N−H···Br hydrogen bonds which were identified in the solid state by a single-crystal X-ray structure analysis (*vide infra*).

Crystals of [**12**] which were suitable for an X-ray diffraction analysis could be obtained by slow evaporation of the solvent from a dichloromethane solution of the complex. The asymmetric unit contains two molecules of [**12**]. The molecular geometry of [**12**] (Figure 7) compares well to that of [**5**] (Figure 2). Two different type of intermolecular hydrogen bonds were found in [**12**] (N1*−H1*···Br2 = 2.650 Å, N3−H3···Br1 = 2.597 Å) explaining the observation of three N−H stretching vibrations in the IR spectrum. As expected, all bonds to the manganese atom in [**12**] are significantly shorter than equivalent bonds in the rhenium(I) complex [**5**]. The Mn−$C_{carbene}$ bond lengths measure 2.035(3) and 2.040(2) Å and thus fall in the range described previously for manganese NHC complexes. The Mn−CO bond *trans* to the bromo ligand is the shortest Mn−C bond in the complex. However, the differences in the Mn−C bond lengths is less pronounced for [**12**] in comparison to [**5**] which we attribute to the less effective π-donation of the bromo ligand in [**12**] compared to the chloro ligand in [**5**].

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(24) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172–2180.

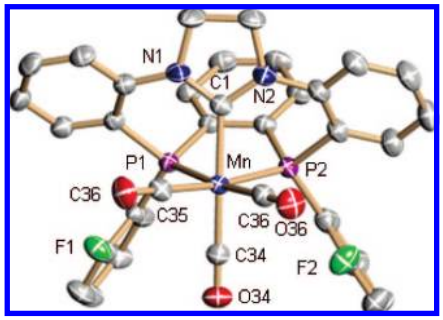

Figure 8. Molecular structures of $[\mathbf{14}]^+$ in $[\mathbf{14}]Br{\cdot}CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Mn−P1 2.2469(7), Mn−P2 2.2386(8), Mn−C1 2.033(2), Mn−C34 1.813(2), Mn−C35 1.823(2), Mn−C36 1.828(3), N1−C1 1.355(3), N2−C1 1.345(3); P1−Mn−P2 84.64(2), P1−Mn−C1 81.67(7), P1−Mn−C34 92.56(8), P1−Mn−C35 92.21(8), P1−Mn−C36 173.82(8), P2−Mn−C1 81.60(7), P2−Mn−C34 93.31(8), P2−Mn−C35 172.59(8), P2−Mn−C36 91.85(8), C1−Mn−C34 172.60(9), C1−Mn−C35 91.32(10), C1−Mn−C36 92.79(10), C34−Mn−C35 93.54(11), C34−Mn−C36 92.73(11), C35−Mn−C36 90.66(11), N1−C1−N2 107.2(2).

In contrast to the rhenium analog [**5**] (Scheme 4), the reaction of [**12**] with **2** in acetonitrile leads to a mixture of reaction products as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. Changing the solvent to THF allowed the preparation and isolation of the compound [H_2-**13**]Br in 39% yield (Scheme 7). The NMR spectra of [H_2-**13**]Br are similar to those of the rhenium analog [H_2-**6**]Cl with the exception of the chemical shifts of atoms directly bound to the manganese atom. The $^{31}P\{^1H\}$ NMR resonance in [H_2-**13**]Br was observed at $\delta = 70.3$ ppm and thus significantly downfield from the corresponding resonance in [H_2-**6**]Cl ($\delta = 21.8$ ppm). A downfield shift of 20−30 ppm relative to the values measured for [H_2-**6**]Cl was also observed for the carbonyl and carbene carbon resonances in [H_2-**13**]Br.

The formation of the [11]ane-P_2C^{NHC} macrocycle was induced by addition of two equivalents of KO*t*Bu to [H_2-**13**]Br (Scheme 7). Deprotonation of the NH function leads to a nucleophilic attack of the nitrogen atoms at the fluorine substituted aromatic carbon atoms and formation of the macrocyclic ligand in complex [**14**]Br. As expected only one $^{31}P\{^1H\}$ NMR resonance was observed for [**14**]Br. This resonance, however, is shifted downfield to $\delta = 73.4$ ppm relative to the value observed for [H_2-**13**]Br ($\delta = 70.3$ ppm). This behavior contrasts the observations made in the $^{31}P\{^1H\}$ NMR spectra of the analogous rhenium complexes where the reaction of [H_2-**6**]Cl ($\delta = 21.8$ ppm) to yield the complex with the macrocyclic ligand [**8**]Cl ($\delta = 15.8$ ppm) leads to an upfield shift for the $^{31}P\{^1H\}$ resonance.

Crystals of $[\mathbf{14}]Br{\cdot}CH_2Cl_2$ were obtained by slow evaporation of the solvent from a dichloromethane solution of complex [**14**]Br. The structure analysis (Figure 8) confirms the formation of the macrocyclic ligand.

As observed for the rhenium analog [**8**]Cl (Figure 5, left) the [11]ane P_2C^{NHC} macrocycle in [**14**]Br is coordinated in a *facial* manner to the manganese atom. The P−Mn−P and $C_{carbene}$−Mn−P angles deviate most strongly from 90°. The Mn−C1 bond distance (2.033(2) Å) compares well to the equivalent value in [**12**] and falls in the range reported for other manganese NHC complexes.[23]

In analogy to the behavior of [**8**]Cl one carbonyl group in [**14**]Br can be removed by reaction with $Me_3NO{\cdot}2H_2O$. The resulting complex [**15**] is again nearly insoluble in common organic solvents. We assume that the halogen counterion occupies the position vacated by the carbonyl ligand as was observed in the analogous rhenium complex [**11**]. The observation of three $^{31}P\{^1H\}$ NMR resonances indicates that in common with [**11**], [**15**] is obtained as a mixture of isomers with the bromo ligand in either the *cis* or *trans* position to the carbene donor.

Attempts were made to liberate the [11]ane-P_2C^{NHC} from the neutral rhenium or manganese complexes [**11**] or [**15**], respectively. Aerial oxidation of the complexes in dichloromethane over two weeks resulted for both complexes in the isolation of the free macrocycle as di(phosphine oxide)/imidazolidinium salt. This salt was identified by its peak at $m/e = 581$ in the mass spectrum. Liberation of the P-oxidized/C^{NHC}-protonated macrocycle appears not very useful particularly since it has been demonstrated that related [9]ane-P_3 macrocycles after liberation and oxidation to the tri(phosphine oxides) cannot be reduced to the free triphosphines.[5a]

3. Conclusions

We have prepared complexes with a *facially* coordinated [11]ane-P_2C^{NHC} ligand. The ligand was generated by the template controlled linkage of a coordinated diphosphine to an NH,NH-stabilized NHC ligand at Re^I and Mn^I centers. The preparation of the precursor diphosphine/NHC complex has been shown to be strongly dependent on the solvent which in one case led to the isolation of a salt comprised of NHC containing anions and cations. The template controlled synthesis of macrocyclic ligands containing NHC donor groups may be of general interest if the synthetic methodology can be transferred to catalytically active metals. In addition, the synthesis of $P(C^{NHC})_2$ macrocycles appears also possible. Current studies are directed toward the preparation of alkylidene ruthenium complexes with an [11]ane-P_2C^{NHC} ligand which might be useful in olefin-metathesis catalysis.[25]

4. Experimental Section

General. All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. The preparation of (1,2-bis(di(*o*-fluorophenyl)phosphino)benzene) **2**[14] and $[W(CO)_5(NHC)]$ [**1**][16a,b] have been described. All chemicals were used as received. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer and mass spectra were obtained with a Varian MAT 212 (MALDI) or a Bruker Daltonic Micro Tof (ES) spectrometer.

Synthesis of [3]. A solution of [**1**] (220 mg, 0.55 mmol) and **2** (285 mg, 0.55 mmol) in *o*-xylene (5 mL) was heated under reflux for 2 h. After cooling to ambient temperature the reaction mixture was filtered. The solution was taken to dryness and the solid residue was washed with *n*-hexane (20 mL). The crude solid was dissolved in dichloromethane and purified by column chromatography (SiO_2, dichloromethane). After removal of the solvent, complex [**3**] was isolated as a yellow solid. Yield: 340 mg (0.42 mmol, 76%). ^1H (400.1 MHz, [d_6]DMSO): $\delta = 7.70$ (m, 4H, Ar−H), 7.56 (m, 4H, Ar−H), 7.33 (m, 4H, Ar−H), 7.24 (m, 4H, Ar−H), 6.95 ppm (m, 4H, Ar−H). $^{13}C\{^1H\}$ NMR (100.6 MHz, [d_6]DMSO, assignment of resonances see Scheme 3): $\delta = 207.5$ (m, CO), 200.6 (m, CO), 162.9 (dd, $^1J_{C,F} = 248$ Hz, $^3J_{C,P} = 3.6$ Hz, C9), 141.5 (m, C1), 133.7 (m, C5), 132.2 (m, C2), 131.7 (d, $^3J_{CF} = 13.9$ Hz, C7), 128.7 (s, C3), 124.8 (m, C6), 121.6 (m, C4), 116.5 ppm (d, $^2J_{CF} = 22.5$ Hz, C8). $^{31}P\{^1H\}$ NMR (162.0 MHz, [d_6]DMSO): $\delta = 26.7$ ppm ($^1J_{P,W} = 237$ Hz). ^{19}F NMR (376.5 MHz, [d_6]DMSO): $\delta = -98.0$

(25) Kaufhold, O.; Flores Figueroa, A.; Pape, T.; Hahn, F. E. *Organometallics*, in press.

ppm. IR (KBr): ν = 2029 (s, CO), 1930 (s, CO), 1897 (s, CO), 1879 cm^{-1} (s, CO). MS (MALDI, positive ions): *m/e* (%): 814 (30) (calcd $[\mathbf{3}]^+$ 814.0288), 786 (100) (calcd $[\mathbf{3} - CO]^+$ 786.0339).

Synthesis of [5]. A solution of $[ReCl(CO)_5]$ (720 mg, 2.0 mmol) and $H_2NCH_2CH_2N{=}PPh_3$ (640 mg, 2.0 mmol) in THF (20 mL) was stirred for 24 h. After removal of the solvent the crude product was purified by column chromatography (dichloromethane, SiO_2) yielding a colorless powder. Yield: 670 mg (1.66 mmol, 83%). ^1H (400.1 MHz, $CDCl_3$): δ = 6.90 (s, br, 2H, NH), 3.72 ppm (s, 4H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 193.6 (NCN), 186.8 (CO), 184.9 (CO), 184.7 (CO), 44.2 ppm (NCH_2CH_2N). IR (KBr): ν = 3429 (s, NH), 3265 (s, br, NH), 2107 (s, CO), 2016 (s, CO), 1993 (s, br, CO), 1924 cm^{-1} (s, br, CO). MS (ES, positive ions): *m/e* (%): 426.9455 (100) (calcd $[\mathbf{5} + Na]^+$ 426.9457).

Reaction of Complex [5] with 2 in Benzene or Toluene. This reaction afforded a mixture of compounds $[H_2\text{-}\mathbf{6}]Cl$, [H-**7**]Cl, and [**8**]Cl in varying relative amounts. Typically a solution of [**5**] (150 mg, 0.40 mmol) and **2** (210 mg, 0.40 mmol) in benzene (20 mL) was heated under reflux for 10 h. After cooling to ambient temperatures, the formed white precipitate was isolated by filtration and washed with diethyl ether (2 × 10 mL). This solid contained a mixture of compounds. The NMR and mass spectra were collected using this mixture of compounds. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_3CN): δ = 21.8 (d, $^3J_{P,F}$ = 14.7 Hz, $[H_2\text{-}\mathbf{6}]^+$), 20.5 and 18.2 (br, $[H\text{-}\mathbf{7}]^+$), 15.8 ppm (d, $^3J_{P,F}$ = 16.6 Hz, $[\mathbf{8}]^+$). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −95 (br, Ar−F), −96 (br, Ar−F), −98 (Ar−F), −153 ppm (BF_4^-). MS (ES, positive ions): *m/e*: 859 (calcd $[H_2\text{-}\mathbf{6}]^+$ 859.0909)), 839 (calcd $[H\text{-}\mathbf{7}]^+$ 839.0852), 819 (calcd $[\mathbf{8}]^+$ 819.0784).

Synthesis of $[H_2\text{-}\mathbf{6}]Cl$. A solution of complex [**5**] (150 mg, 0.37 mmol) and ligand **2** (250 mg, 0.48 mmol) in acetonitrile (5 mL) was heated under reflux for 6 h. After cooling to ambient temperature the solvent was almost completely removed and diethyl ether (20 mL) was added to the oily residue. Complex $[H_2\text{-}\mathbf{6}]Cl$ precipitated and was isolated by filtration. Yield: 330 mg (0.36 mmol, 98%). ^1H (400.1 MHz, CD_3CN, assignment of signals see Scheme 4): δ = 8.02 (m, 2H, Ar−H4), 7.88 (m, 2H, Ar−H5), 7.67 (m, 2H, Ar−H15), 7.44 (m, 2H, Ar−H9), 7.39 (m, 2H, Ar−H16), 7.32 (m, 2H, Ar−H17), 7.27 (m, 2H, Ar−H14), 7.16 (m, 2H, Ar−H10), 7.10 (m, 2H, Ar−H8), 6.92 (m, 2H, Ar−H11), 6.56 (s, 2H, NH), 3.21 ppm (s, 4H, H2). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN, assignment of signals see Scheme 4): δ = 191.0 (dd, $^2J_{C,P\text{-}trans}$ = 50.4 Hz, $^2J_{C,P\text{-}cis}$ = 8.2 Hz, $CO_{cis\text{-}C1}$), 190.0 (m, br, $CO_{trans\text{-}C1}$), 189.8 (t, $^2J_{C,P}$ = 9.8 Hz, C1), 164.5 (d, $^1J_{C,F}$ = 249 Hz, C13), 163.4 (dd, $^1J_{C,F}$ = 247 Hz, $^2J_{CP}$ = 4.9 Hz, C7), 139.2 (dd, $^1J_{C,P}$ = 48.5 Hz, $^2J_{C,P}$ = 33.4 Hz, C3), 136.8 (dd, $^2J_{C,P}$ = 14.0 Hz, $^3J_{C,P}$ = 2.5 Hz, C4), 136.8 (m, C17), 136.6 (dd, $^3J_{C,F}$ = 9.5 Hz, $^4J_{C,P}$ = 2.0 Hz, C15), 134.9 (dd, $^3J_{C,F}$ = 8.5 Hz, $^4J_{C,P}$ = 1.6 Hz, C9), 134.8 (dd, $^3J_{C,P}$ = 6.2 Hz, $^4J_{C,P}$ = 2.2 Hz, C5), 133.0 (m, C11), 126.5 (dd, $^3J_{C,P}$ = 11.2 Hz, $^4J_{C,F}$ = 3.0 Hz, C16), 125.6 (dd, $^3J_{C,P}$ = 8.3 Hz, $^4J_{C,F}$ = 3.0 Hz, C10), 122.2 (ddd, $^1J_{C,P}$ = 53 Hz, $^2J_{C,F}$ = 17 Hz, $^4J_{C,P}$ = 2.0 Hz, C6), 118.2 (dd, $^2J_{C,F}$ = 23.8 Hz, $^3J_{C,P}$ = 3.4 Hz, C14), 117.3 (ddd, $^1J_{C,P}$ = 45 Hz, $^2J_{C,F}$ = 16.4 Hz, $^4J_{C,P}$ = 2.8 Hz, C12), 117.0 (dd, $^2J_{C,F}$ = 23.0 Hz, $^3J_{C,P}$ = 3.7 Hz, C8), 45.9 ppm (C2). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_3CN): δ = 21.8 ppm (d, $^3J_{P,F}$ = 14.7 Hz). ^{19}F NMR (376.5 MHz, CD_3CN): δ = −97.6, −100.3 ppm. IR (KBr): ν = 3460 (w, NH), 2043 (s, CO), 1971 (s, CO), 1949 (s, CO). MS (ES, positive ions): *m/e* (%): 859.0893 (100) (calcd $[H_2\text{-}\mathbf{6}]^+$ 859.0909).

Synthesis of $[H_2\text{-}\mathbf{6}][\mathbf{9}]$. A solution of [**5**] (165 mg, 0.41 mmol) and **2** (275 mg, 0.53 mmol) in tetrahydrofuran (5 mL) was heated under reflux for 2 h. After cooling to ambient temperature the mixture was concentrated and diethyl ether (20 mL) was added. Compound $[H_2\text{-}\mathbf{6}][\mathbf{9}]$ was subsequently isolated by filtration. Yield: 240 mg (0.19 mmol, 92%). Notice the spectroscopic data of $[H_2\text{-}\mathbf{6}]^+$ are identical in both salts $[H_2\text{-}\mathbf{6}]Cl$ reported above and $[H_2\text{-}\mathbf{6}][\mathbf{9}]$. Reported here are only the data for the two isomers (*fac* and *mer,cis*) of the anion $[\mathbf{9}]^-$. The assignment was based on the observed intensities. Isomer I (abundance 40%): ^1H (400.1 MHz, CD_3CN): δ = 7.20 (s, 2H, NH), 3.60 ppm (s, 4H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN): δ = 203.6 (NCN), 196.6 (CO), 196.0 (CO), 192.1 (CO), 45.8 ppm (NCH_2CH_2N). Isomer II (abundance 60%): ^1H (400.1 MHz, CD_3CN): δ = 7.06 (s, 2H, NH), 3.56 ppm (s, 4H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN): δ = 208.6 (NCN), 200.0 (CO), 196.2 (CO), 45.8 ppm (NCH_2CH_2N). IR (KBr): ν = 3378 (w, br, NH), 2004 (s, CO), 1895 (s, CO), 1849 cm^{-1} (s, CO). MS (MALDI, negative ions): *m/e* (%): 411 (100) (calcd $[\mathbf{9}]^-$ 410.9303).

Synthesis of [8]Cl. A suspension of $[H_2\text{-}\mathbf{6}]Cl$ (280 mg, 0.31 mmol) in THF (5 mL) was treated dropwise with a solution of KO*t*Bu (12.5 mL of a 0.05 *M* solution, 0.62 mmol). A clear solution was obtained after the addition. This solution was stirred at ambient temperature for 5 d. During this period a solid had formed which was isolated by filtration and dissolved in dichloromethane. Insoluble solids were separated by filtration. Complex [**8**]Cl was obtained as a pale yellow solid after removal of the solvent. Yield: 240 mg (0.28 mmol, 91%). ^1H (400.1 MHz, CD_3CN, assignment of the signals see Scheme 4): δ = 7.83 (m, 2H, Ar−H5), 7.81 (m, 2H, Ar−H4), 7.69 (m, 2H, Ar−H17), 7.66 (m, 2H, Ar−H9), 7.63 (m, 2H, Ar−H14), 7.39 (m, 2H, Ar−H16), 7.38 (m, 2H, Ar−H15), 7.37 (m, 2H, Ar−H8), 7.25 (t, 2H, Ar−H10), 6.97 (m, 2H, Ar−H11), 4.61 (m, 2H, N−C*H*H−C*H*H−N), 3.15 ppm (m, 2H, N-CH*H*-CH*H*-N). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN, assignment of the signals see Scheme 4): δ = 193.4 (br, $CO_{trans\text{-}C1}$), 192.3 (t, $^2J_{C,P}$ = 13.8 Hz, C1), 191.1 (m, $^2J_{C,P\text{-}trans}$ = 46.0 Hz, $CO_{cis\text{-}C1}$), 164.4 (dd, $^1J_{C,F}$ = 249 Hz, $^2J_{C,P}$ = 5.0 Hz, C7), 145.8 (d, $^2J_{C,P}$ = 11.8 Hz, C13), 139.9 (m, Ar−C3), 136.6 (d, $^3J_{C,F}$ = 9.2 Hz, C9), 136.2 (m, C4), 134.7 (d, $^2J_{C,P}$ = 1.6 Hz, C17), 134.6 (m, C5), 134.3 (m, C11) 131.2 (d, $^4J_{C,P}$ = 1.6 Hz, C15), 127.4 (d, $^3J_{C,P}$ = 8.3 Hz, C16), 126.8 (m, C10), 125.6 (d, $^3J_{C,P}$ = 6.3 Hz, C14), 123.8 (dd, $^1J_{C,P}$ = 56.4 Hz, $^4J_{C,F}$ = 4.9 Hz, C12), 117.8 (dd, $^2J_{C,F}$ = 21.9 Hz, $^3J_{C,P}$ = 4.2 Hz, C8), 115.1 (dd, $^1J_{C,P}$ = 54.6 Hz, $^2J_{C,F}$ = 17.7 Hz, C6), 52.4 ppm (C2). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_3CN): δ = 15.8 ppm (d, $^3J_{P,F}$ = 16.6 Hz). ^{19}F NMR (376.5 MHz, CD_3CN): δ = −97.4 ppm (m). IR (KBr): ν = 2031 (s, CO), 1963 (s, CO), 1937 cm^{-1} (s, CO). MS (ES, positive ions): *m/e* (%): 819.0770 (100) (calcd $[\mathbf{8}]^+$ 819.0784).

Synthesis of [10]. Complex [**10**] was isolated from a reaction of $[H_2\text{-}\mathbf{6}]Cl$ with KO*t*Bu as described for the synthesis of [**8**]Cl. After one day a solid had formed which was isolated by filtration. The solid contained both compounds [**8**]Cl and [**10**]. This solid was dissolved in dichloromethane and the solvent was slowly evaporated. From this solution block shaped crystals of [**8**]Cl and prisms of [**10**] crystallized. Attempts to separate the two compounds led invariably to the conversion of [**10**] into [**8**]Cl.

Synthesis of [11]. A mixture of [**8**]Cl (340 mg, 0.40 mmol) and $Me_3NO{\cdot}2H_2O$ (46 mg, 0.42 mmol) in dichloromethane (10 mL) was stirred for 24 h. The precipitate formed was separated by filtration and washed with ethanol (10 mL). After drying *in vacuo* complex [**11**] was obtained as a bright yellow solid. Yield: 245 mg (0.30 mmol, 75%). The poor solubility of [**11**] in common organic solvents prevented its ^1H and ^{13}C NMR spectroscopic characterization. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 30.9 (s, Cl *trans* to carbene), 27.9 and 25.5 ppm (m, Cl *cis* to carbene). IR (KBr): ν = 1941 (s, CO), 1878 cm^{-1} (s, CO). MS (MALDI, positive ions): *m/e* (%): 826 (100) (calcd $[\mathbf{11}]^+$ 826.0520), 770 (57) (calcd $[\mathbf{11} - 2CO]^+$ 770.0621).

Synthesis of [12]. Complex [**12**] was prepared as described for [**5**][14,16b] from $[MnBr(CO)_5]$ (550 mg, 2.0 mmol) and $H_2NCH_2CH_2N{=}PPh_3$ (640 mg, 2.0 mmol) in THF (20 mL) and was obtained as a yellow solid. Yield: 65%. ^1H (400.1 MHz, $CDCl_3$): δ = 6.95 (s, br, 2H, NH), 3.80 ppm (s, 4H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 219.7 (NCN), 212.6 (CO), 212.1 (CO), 210.8 (CO), 45.7 ppm (NCH_2CH_2N). IR (KBr): ν = 3451 (w, NH), 3388 (m, NH), 3363 (m, NH), 2092 (m, CO), 1993 (s, CO), 1949 (s, br, CO), 1935 cm^{-1} (s, br, CO).

Synthesis of [H_2-13]Br. A solution of [**12**] (120 mg, 0.38 mmol) and ligand **2** (250 mg, 0.48 mmol) in tetrahydrofuran (5 mL) was heated under reflux for 6 h. A yellow precipitate formed during this period which was isolated by filtration, washed with diethyl ether (5 mL) and dried *in vacuo*. Yield: 120 mg (0.15 mmol, 39%). ^{1}H (400.1 MHz, CD_3CN, assignment of signals see Scheme 7): δ = 8.09 (s, br, 2H, Ar−H4), 7.97 (s, br, 2H, Ar−H5), 7.70 (s, br, 2H, Ar−H15), 7.43 (s, br, 6H, Ar−H9, Ar−H16, Ar−H17), 7.29 (s, br, 2H, Ar−H14), 7.08 (m, br, 4H, Ar−H8, Ar−H10), 6.94 (s, br, 2H, NH), 6.80 (s, br, 2H, Ar−H11), 3.37 ppm (s, br, 4H, H2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3CN, assignment of signals see Scheme 7): δ = 219.1 ($CO_{cis\text{-}C1}$), 215.9 ($CO_{trans\text{-}C1}$), 210.5 (t, $^2J_{C,P}$ = 19.3 Hz, C1), 164.5 (d, $^1J_{C,F}$ = 250 Hz, C13), 163.4 (d, $^1J_{C,F}$ = 245 Hz, C7), 138.7 (t, $^1J_{C,P}$ = 39.7 Hz, $^2J_{C,P}$ = 39.7 Hz, C3), 136.5 (m, C4, C15, C17), 135.1 (C5), 134.7 (d, $^3J_{C,F}$ = 8.6 Hz, C9), 132.7 (C11), 126.6 (C16), 125.6 (C10), 123.2 (m, C6), 118.4 (d, $^2J_{C,F}$ = 24.2 Hz, C14), 117.7 (dd, $^1J_{C,P}$ = 41.5 Hz, $^2J_{C,F}$ = 15.3 Hz, C12), 116.1 (d, $^2J_{C,F}$ = 22.4 Hz, C8), 46.3 ppm (C2). ^{31}P{^{1}H} NMR (162.0 MHz, CD_3CN): δ = 70.3 ppm. ^{19}F NMR (376.5 MHz, CD_3CN): δ = −97.3, −100.6 ppm. IR (KBr): ν = 3455 (w, NH), 2041 (s, CO), 1979 (s, CO), 1966 cm^{-1} (s, CO). MS (MALDI, positive ions): *m/e* (%): 727 (100%) (calcd [H_2-**13**]$^+$ 727.0735).

Synthesis of [14]Br. A suspension of [H_2-**13**]Br (110 mg, 0.14 mmol) in THF (5 mL) was treated dropwise with a solution of KO*t*Bu (5.9 mL of a 0.05 *M* solution, 0.29 mmol). A clear solution was obtained after completion of the addition. This solution was stirred at ambient temperature for 3 d. The solid formed during this time was isolated by filtration and dissolved in dichloromethane. Remaining solids were separated by filtration. Compound [**14**]Br was obtained as an orange-red solid after removal of the solvent. Yield: 65 mg (0.085 mmol, 62%). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, assignment of signals see Scheme 7): δ = 216.6 (br, $CO_{cis\text{-}C1}$), 215.2 (br, $CO_{trans\text{-}C1}$), 212.4 (br, $^2J_{C,P\text{-}trans}$, C1), 163.3 (d, $^1J_{C,F}$ = 251 Hz, C7), 143.9 (br, Ar−C13), 139.7 (t, $^1J_{C,P}$ = 44 Hz, $^2J_{C,P}$ = 44 Hz, Ar−C3), 135.2 (d, $^3J_{C,F}$ = 8.3 Hz, Ar−C9), 134.1 (Ar−C17), 133.5 (br, Ar−C4), 133.2 (br, Ar−C5), 132.4 (Ar−C11), 129.4 (Ar−C15), 126.1 (Ar−C14), 125.6 (Ar−C16), 124.4 (br, Ar−C10), 120.5 (m, Ar−C12), 116.8 (d, $^2J_{C,F}$ = 22 Hz, Ar−C8), 115.2 (m, Ar−C6), 52.6 ppm (br, C2). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 73.4 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −95.1 ppm. IR (KBr): ν = 2030 (s, CO), 1953 (s, CO), 1895 cm^{-1} (s, CO). MS (MALDI, positive ions): *m/e* (%): 687 (100%) (calcd [**14**]$^+$ 687.0611).

Synthesis of [15]. A mixture of [**14**]Br (155 mg, 0.20 mmol) and $Me_3NO\cdot 2H_2O$ (23 mg, 0.21 mmol) in dichloromethane (5 mL) was stirred for 24 h. The precipitate formed was separated by filtration and washed with ethanol (10 mL). After drying *in vacuo* complex [**15**] was obtained as a bright red solid. Yield: 96 mg (0.13 mmol, 65%). The poor solubility of [**15**] in common organic solvents prevented its ^{1}H and ^{13}C NMR spectroscopic characterization. ^{31}P{^{1}H} NMR (162.0 MHz, CH_2Cl_2/D_2O): δ = 109.1 (m), 106.6 (m), 83.0 ppm (s). IR (KBr): ν = 1947 (s, CO), 1891 cm^{-1} (s, CO). MS (MALDI, positive ions): *m/e* (%): 684 (100%) (calcd [**15** - 2CO]$^+$ 683.9932).

X-Ray Crystallography. X-ray diffraction data were collected with CuKα ([**10**]) or MoKα (all other compounds). All raw data were corrected for absorption. The structure solutions were found with SHELXS[26] and the refinement was carried out with SHELXL[27] using anisotropic thermal parameters for all non-hydrogen atoms. Positional parameters for hydrogen atom were added to the structure models on calculated positions and were not refined.

[3] $C_{34}H_{20}F_4O_4P_2W$, M = 814.29, colorless crystal, 0.25 × 0.20 × 0.15 mm, T = 150(2) K, orthorhombic, space group *P*nma, Z = 4, a = 16.893(3), b = 21.358(4), c = 8.073(2) Å, V = 2912.9(10) Å^3, ρ_{calc} = 1.857 g·cm^{-3}, μ = 4.142 mm^{-1}, ω- and ϕ-scans, 5715 measured intensities (5.9° ≤ 2θ ≤ 53.0°), λ = 0.71073 Å, semiempirical absorption correction (0.417 ≤ T ≤ 0.541), 3099 independent (R_{int} = 0.0212) and 2830 observed intensities ($I \geq 2\sigma(I)$), refinement of 221 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0208, wR = 0.0450, R_{all} = 0.0247, wR_{all} = 0.0463. The asymmetric unit contains 1/2 molecule of the complex.

[5]. $C_7H_6N_2ClO_4Re$, M = 403.79, colorless crystal, 0.20 × 0.15 × 0.08 mm, T = 150(2) K, monoclinic, space group $P2_1/c$, Z = 4, a = 8.852(2), b = 10.297(2), c = 12.389(3) Å, β = 107.84(3)°, V = 1075.0(4) Å^3, ρ_{calc} = 2.495 g·cm^{-3}, μ = 11.547 mm^{-1}, ω- and ϕ-scans, 3540 measured intensities (6.4° ≤ 2θ ≤ 54.0°), λ = 0.71073 Å, semiempirical absorption correction (0.245 ≤ T ≤ 0.411), 2315 independent (R_{int} = 0.0249) and 2070 observed intensities ($I \geq 2\sigma(I)$), refinement of 136 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0264, wR = 0.0596, R_{all} = 0.0312, wR_{all} = 0.0619. The asymmetric unit contains one molecule of the complex.

[H_2-6]Cl·3THF. $C_{48}H_{50}N_2ClF_4O_6P_2Re$, M = 1110.49, colorless crystal, 0.50 × 0.30 × 0.30 mm, T = 150(2) K, triclinic, space group *P*-1, Z = 2, a = 11.201(5), b = 11.800(5), c = 20.504(5) Å, α = 92.239(5), β = 100.058(5), γ = 117.123(5)°, V = 2353(2) Å^3, ρ_{calc} = 1.567 g·cm^{-3}, μ = 2.773 mm^{-1}, ω- and ϕ-scans, 16641 measured intensities (6.0° ≤ 2θ ≤ 52.0°), λ = 0.71073 Å, semiempirical absorption correction (0.3378 ≤ T ≤ 0.4901), 9177 independent (R_{int} = 0.0307) and 8650 observed intensities ($I \geq 2\sigma(I)$), refinement of 551 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0415, wR = 0.0987, R_{all} = 0.0448, wR_{all} = 0.1005. The asymmetric unit contains one molecule [H_2-**6**]Cl·3THF and three molecules of THF, two of which are disordered.

[H_2-6]*fac*-[9]·CH_2Cl_2. $C_{43}H_{34}N_4Cl_4F_4O_6P_2Re_2$, M = 1354.88, colorless crystal, 0.18 × 0.15 × 0.10 mm, T = 150(2) K, triclinic, space group *P*-1, Z = 2, a = 11.465(2), b = 11.577(2), c = 18.720(4) Å, α = 91.16(3), β = 103.05(3), γ = 104.05(3)°, V = 2340.7(8) Å^3, ρ_{calc} = 1.922 g·cm^{-3}, μ = 5.531 mm^{-1}, ω- and ϕ-scans, 16690 measured intensities (5.8° ≤ 2θ ≤ 52.0°), λ = 0.71073 Å, semiempirical absorption correction (0.548 ≤ T ≤ 0.762), 9094 independent (R_{int} = 0.0277) and 7813 observed intensities ($I \geq 2\sigma(I)$), refinement of 592 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0308, wR = 0.0625, R_{all} = 0.0393, wR_{all} = 0.0658. The asymmetric unit contains one formula unit of [H_2-**6**]*fac*-[**9**] and one molecule of CH_2Cl_2. Atom Cl1 and the CO ligand in *trans* position to Cl1 of the anion *fac*-[**9**]$^-$ are disordered.

[8]Cl·3H_2O. $C_{36}H_{30}N_2ClF_2O_6P_2Re$, M = 908.21, light yellow crystal, 0.30 × 0.20 × 0.10 mm, T = 150(2) K, triclinic, space group *P*-1, Z = 2, a = 9.030(5), b = 10.898(5), c = 19.929(5) Å, α = 75.388(5), β = 82.356(5), γ = 68.013(5)°, V = 1758.1(13) Å^3, ρ_{calc} = 1.716 g·cm^{-3}, μ = 3.862 mm^{-1}, ω- and ϕ-scans, 11366 measured intensities (6.3° ≤ 2θ ≤ 54.0°), λ = 0.71073 Å, semiempirical absorption correction (0.4046 ≤ T ≤ 0.7097), 7586 independent (R_{int} = 0.0269) and 6915 observed intensities ($I \geq 2\sigma(I)$), refinement of 451 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0308, wR = 0.0660, R_{all} = 0.0368, wR_{all} = 0.0690. The asymmetric unit contains one formula unit of [H_2-**6**]Cl and three water molecules.

[10]. $C_{36}H_{24}N_2F_3O_3P_2Re$, M = 837.71, yellow crystal, 0.18 × 0.08 × 0.05 mm, T = 153(2) K, monoclinic, space group $P2_1/c$, Z = 4, a = 9.8118(4), b = 19.1632(6), c = 17.1424(7) Å, β = 93.836(3)°, V = 3216.0(2) Å^3, ρ_{calc} = 1.730 g·cm^{-3}, μ = 8.826 mm^{-1}, ω- and ϕ-scans, 17912 measured intensities (6.9° ≤ 2θ ≤ 130.0°), λ = 1.54178 Å, semiempirical absorption correction (0.2995 ≤ T ≤ 0.6666), 5439 independent (R_{int} = 0.0596) and 3763 observed intensities ($I \geq 2\sigma(I)$), refinement of 424 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0359, wR = 0.0671, R_{all} = 0.0567, wR_{all} = 0.0702. The asymmetric unit contains one molecule of [**10**]Cl.

[11]·0.25H_2O·CH_2Cl_2. $C_{36}H_{26.5}N_2Cl_3F_2O_{2.25}P_2Re$, M = 915.58, orange crystal, 0.09 × 0.05 × 0.03 mm, T = 153(2) K, triclinic,

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(27) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Germany, 1997.

space group *P*-1, $Z = 2$, $a = 9.9913(12)$, $b = 10.8606(14)$, $c = 18.072(2)$ Å, $\alpha = 96.301(3)$, $\beta = 101.241(2)$, $\gamma = 114.690(2)°$, $V = 1706.9(4)$ Å^3, $\rho_{calc} = 1.781$ g·cm^{-3}, $\mu = 3.937$ mm^{-1}, ω- and ϕ-scans, 19743 measured intensities ($2.4° \leq 2\theta \leq 60.1°$), $\lambda = 0.71073$ Å, semiempirical absorption correction ($0.7183 \leq T \leq 0.8910$), 9780 independent ($R_{int} = 0.0417$) and 8471 observed intensities ($I \geq 2\sigma(I)$), refinement of 452 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0415$, $wR = 0.0858$, $R_{all} = 0.0518$, $wR_{all} = 0.0895$. The asymmetric unit contains one molecule of [**11**], one molecule of CH_2Cl_2 and 0.25 molecules of water.

[12]. $C_7H_6N_2BrMnO_4$, $M = 316.99$, yellow crystal, $0.25 \times 0.22 \times 0.22$ mm, $T = 150(2)$ K, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 12.506(3)$, $b = 13.456(3)$, $c = 12.976(3)$ Å, $\beta = 91.53(3)°$, $V = 2182.9(8)$ Å^3, $\rho_{calc} = 1.929$ g·cm^{-3}, $\mu = 4.865$ mm^{-1}, ω- and ϕ-scans, 9229 measured intensities ($6.1° \leq 2\theta \leq 54.0°$), $\lambda = 0.71073$ Å, semiempirical absorption correction ($0.280 \leq T \leq 0.355$), 4749 independent ($R_{int} = 0.0284$) and 4014 observed intensities ($I \geq 2\sigma(I)$), refinement of 271 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0282$, $wR = 0.0511$, $R_{all} = 0.0387$, $wR_{all} = 0.0541$. The asymmetric unit contains two independent molecules of [**12**].

[14]Br·CH_2Cl_2. $C_{37}H_{26}N_2BrCl_2F_2MnO_3P_2$, $M = 852.29$, orange crystal, $0.12 \times 0.09 \times 0.05$ mm, $T = 153(2)$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.493(3)$, $b = 11.902(2)$, $c = 18.845(3)$ Å, $\beta = 105.589(4)°$, $V = 3563.1(10)$ Å^3, $\rho_{calc} = 1.589$ g·cm^{-3}, $\mu = 1.782$ mm^{-1}, ω- and ϕ-scans, 40549 measured intensities ($2.6° \leq 2\theta \leq 60.1°$), $\lambda = 0.71073$ Å, semiempirical absorption correction ($0.8146 \leq T \leq 0.9162$), 10395 independent ($R_{int} = 0.0467$) and 7651 observed intensities ($I \geq 2\sigma(I)$), refinement of 451 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0449$, $wR = 0.1054$, $R_{all} = 0.0684$, $wR_{all} = 0.1155$. The asymmetric unit contains one formula unit of [**14**]Br and one molecule of CH_2Cl_2.

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Supporting Information Available: X-ray crystallographic files for [**3**], [**5**], [H_2-**6**]Cl·3THF, [H_2-**6**]*fac*-[**9**]·CH_2Cl_2, [**8**]Cl·$3H_2O$, [**10**], [**11**]·$0.25H_2O$·CH_2Cl_2, [**12**], and [**14**]Br·CH_2Cl_2 (nine CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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