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Template synthesis of a macrocycle with a mixed NHC/phosphine donor set

Verena Blase, Tania Pape, F. Ekkehardt Hahn*

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

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ABSTRACT

Reaction of *cis*-[ReCl(NHC)(CO)$_4$] *cis*-[**1**] (NHC = NH,NH-substituted saturated cyclic diaminocarbene) with diphosphine (2-F–C$_6$H$_4$)$_2$P–CH$_2$CH$_2$–P(C$_6$H$_4$-2-F)$_2$ **2** yields complex *fac*-[Re(NHC)(**2**)(CO)$_3$]Cl *fac*-[**3**]Cl. Deprotonation of the NH,NH-NHC ligand in *fac*-[**3**]Cl with KO*t*Bu leads to an intramolecular nucleophilic aromatic substitution of one fluorine atom from each –P(C$_6$H$_4$-2-F) group by the NHC ring nitrogen atoms with formation of complex *fac*-[**4**]Cl bearing a *facially* coordinated [11]ane-P$_2$C^{NHC} ligand. Reaction of *cis*-[MnBr(NHC)(CO)$_4$] *cis*-[**5**] (NHC = NH,NH-substituted saturated cyclic diaminocarbene) with diphosphine **2** yields complex [MnBr(NHC)(**2**)(CO)$_2$] [**6**] without substitution of the bromo ligand and with the phosphine donors from the bidentate diphosphine occupying one *cis* and one *trans* position to the NHC donor.

1. Introduction

Metal complexes bearing macrocyclic ligands have attracted attention for many years [1]. Compared to complexes with acyclic ligands, those with macrocyclic derivatives featuring otherwise an identical donor set normally exhibit a higher stability due to the macrocyclic effect [2]. This enhanced stability and robustness often allows the use of complexes with macrocyclic ligands as catalysts for selected transformations [3].

A large number of complexes used in homogeneous catalysis contain phosphine [4] or N-heterocyclic carbene (NHC) ligands [5]. While many complexes bearing macrocyclic ligands with nitrogen donor atoms are known [6], cyclic polyphosphine [7] or cyclic poly-NHC ligands [8] are less common and macrocyclic ligands containing both NHC and phosphine donor groups have only recently been developed and are still quite rare [9]. This situation is most likely caused by the synthetic problems encountered during the ligand synthesis.

Triphosphine macrocycles have been generated in a purely organic approach using high dilution methods [7a,b]. This synthesis allows only few variations in the linkers between the phosphorus atoms and the P$_3$-macrocycles are always obtained as a mixture of all possible diastereomers, whereas only the all-*syn* isomer can coordinate to a metal center in a *facial* orientation. Alternatively, a metal template controlled synthesis leads stereoselectively to the all-*syn* isomer which, however, remains coordinated to the metal center after its formation [7d–o]. Originally, the metal template controlled macrocyclization reaction was carried out via a radical induced intramolecular hydrophosphination of allylphosphines coordinated to a {M(CO)$_3$} template center [7c,d]. Further development of this approach using the versatile {CpFe}$^+$ template allowed the coupling of allyl [7e–h] or vinylphosphines via hydrophosphinations [7i,j] and an example for a coordinated [12]ane-P$_3$ macrocycle is depicted as **A** in Fig. 1. Apart from the more robustly coordinating 9-membered P$_3$-ring system [7i,j], this template methods gives access to a range of functionalized 9-, 10-, and 11-and 12-membered P$_3$-macrocycles [7].

Besides the radical induced intramolecular hydrophosphination an alternative metal template approach utilizing the nucleophilic attack of coordinated phosphides at coordinated *o*-fluorophenyl diphosphines has also been developed [7o]. This method provides a versatile and facile route to template controlled P–C bond formation. In principle, this fluoride displacement should also be feasible with nitrogen (amido) nucleophiles.

Complexes bearing macrocyclic poly-NHC ligands like **B** (Fig. 1) are also accessible by a template synthesis [8a] or by metalation of cyclic polyimidazolium salts. The latter reaction can lead to mononuclear [8b], dinuclear [8b,c] or even polynuclear complexes [8c,d].

Only template syntheses have so far given access to macrocyclic ligands with a mixed phosphine/NHC donor set. We have described the synthesis of rhenium(I) and manganese(I) complexes of type **C** (Fig. 1) bearing the [11]ane-P$_2$C^{NHC} ligand [9a]. A similar synthetic strategy can be employed for the generation of the [11]ane-P$_2$C^{NHC}

* Corresponding author. Tel.: +49 251 8333111; fax: +49 251 8333108.
E-mail address: fehahn@uni-muenster.de (F.E. Hahn).

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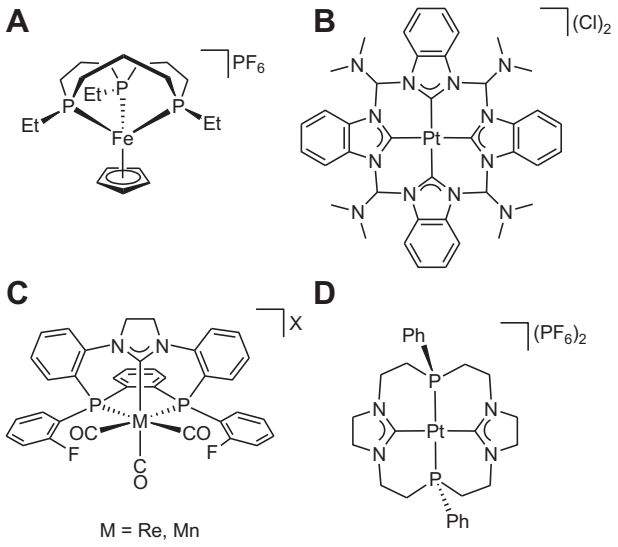


Fig. 1. Complexes bearing macrocyclic ligands with phosphine and/or NHC donors.

ligand at ruthenium(II) [9b] and iron(II) [9c] metal centers. In addition, platinum(II) complex **D** with a tetradentate [16]ane-$P_2C^{NHC}_2$ has been obtained in a template controlled reaction [9d] (Fig. 1).

We became interested in the template synthesis of [11]ane-P_2C^{NHC} macrocycles featuring an aliphatic spacer between the phosphorus atoms instead of the aromatic one in complexes of type **C**. It was expected that macrocycles featuring alkylphosphine donor groups are more basic than the [11]ane-P_2C^{NHC} macrocycle in complex **C** which contains two triphenylphosphine donors. Here we present the synthesis of a novel [11]ane-P_2C^{NHC} macrocycle at the rhenium(I) template with an aliphatic spacer between the phosphine donors. In addition, we describe our unsuccessful efforts to generate an [11]ane-P_2C^{NHC} macrocycle with the aliphatic spacer between the phosphine donors at the manganese(I) template.

2. Results and discussion

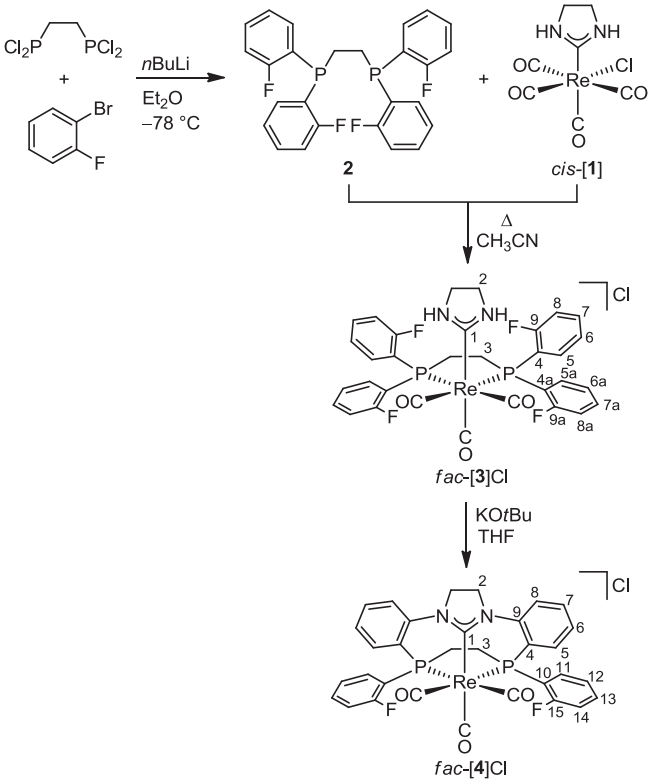
The macrocycle [11]ane-P_2C^{NHC} of complex *fac*-[**4**]Cl (Scheme 1) has been generated at the Re^{I} template by linkage of the NH,NH-NHC ligand to an ethylene bridged diphosphine, all of which were coordinated in *facial* geometry in complex *fac*-[**3**]Cl. Complex *fac*-[**3**]Cl was synthesized from the known diphosphine **2** [10] and complex *cis*-[**1**] bearing an NH,NH-substituted NHC ligand.

We have slightly modified the published procedure for the synthesis of diphosphine **2** to obtain the ligand in an improved yield of 80% (Scheme 1). Several methods for the generation of complexes bearing NH,NH- or NH,O-substituted NHC ligands by template controlled cyclization of β-functionalized isocyanide ligands have been reported [11] and saturated NH,NH-NHC ligands are accessible by the cyclization reaction of 2-aminoethyl isocyanide at suitable metal templates [11f,g]. For this study, however, precursor complex *cis*-[**1**] was prepared according to the method described by Liu et al. from [Re(Cl)(CO)$_5$] and an amino-phosphinimine leading to a phosphinimine substituted isocyanide ligand which upon hydrolysis of the phosphinimine function reacted via cyclization to give complex *cis*-[**1**] [12]. Complex *fac*-[**3**]Cl was finally obtained by heating of diphosphine **2** and complex *cis*-[**1**] in acetonitrile for three days.

The diphosphine ligand in *fac*-[**3**]Cl coordinated to the Re^{I} center via substitution of one CO and the chloro ligand from *cis*-[**1**]. The $^{13}C\{^1H\}$ NMR spectrum of *fac*-[**3**]Cl exhibits the resonance for the carbene carbon atom at $\delta = 186.6$ ppm as a triplet due to coupling with the two *cis*-phosphorus atoms ($^2J_{CP} = 9.6$ Hz). Two resonances for the carbonyl carbon atoms were observed at $\delta = 190.8$ ppm (*cis* to NHC) and $\delta = 189.5$ ppm (*trans* to NHC). Only one resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 19.4$ ppm for the two chemically equivalent phosphorus atoms. Coordination of the diphosphine to the metal center prevents inversion of the configuration at the phosphorus atoms leading to chemically non-equivalent phenyl groups. Consequently, two slightly different resonances were found in the $^{19}F\{^1H\}$ NMR spectrum at $\delta = -100.9$ ppm and $\delta = -101.1$ ppm.

Single crystals of *fac*-[**3**]Cl·0.5CH_2Cl_2 suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated solution of complex *fac*-[**3**]Cl in dichloromethane. The structure analysis confirms the expected *facial* arrangement of the ligands in a distorted octahedral complex (Fig. 2). The asymmetric unit contains two essentially identical molecules of *fac*-[**3**]Cl and one molecule of dichloromethane.

Bond lengths and angles in the cation *fac*-[**3**]$^+$ fall in the range observed previously for related Re^{I} NHC/diphosphine complexes [9a,13]. Compared to the related complex with the 1,2-phenylene bridged diphosphine ligand, which served as starting material for the synthesis of complex **C** (Fig. 1), (Re—P 2.428(2) Å and 2.420(2) Å) [9a] the Re—P bond distances in cation *fac*-[**3**]$^+$ are slightly enlarged (range Re—P 2.4443(12) Å to 2.4516(13) Å). The bond angles P—Re—P measure 82.08(4)° and 82.70(4)° and thus exhibit the largest deviation from octahedral geometry. These angle are slightly larger than the P—Re—P angle in the analogous complex bearing the 1,2-phenylene bridged diphosphine ligand (80.11(5)°) [9a]. This slight angle expansion is apparently caused by the slightly larger bite of the ethylene bridged diphosphine in comparison to the 1,2-phenylene bridged derivative. The plane of the carbene



Scheme 1. Synthesis of the macrocyclic [11]ane-P_2C^{NHC} ligand at the rhenium(I) template (the numbering refers to the assignment of the NMR resonances in the Experimental section).

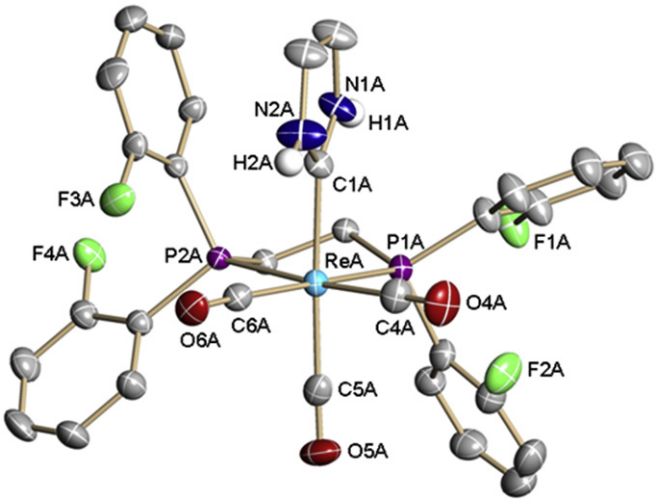


Fig. 2. Molecular structure of *fac*-[**3**]$^+$ in *fac*-[**3**]Cl·0.5CH_2Cl_2 (50% probability ellipsoids). Hydrogen atoms, except for the N–H hydrogen atoms, have been omitted. Selected bond lengths (Å) and angles (deg) for molecule A [molecule B]: Re–P1 2.4443(12) [2.4516(13)], Re–P2 2.4450(12) [2.4500(14)], Re–C1 2.188(5) [2.204(5)], Re–C4 1.965(6) [1.929(6)], Re–C5 1.961(6) [1.962(6)], Re–C6 1.954(5) [1.958(6)]; P1–Re–P2 82.08(4) [82.70(4)], P1–Re–C1 92.06(13) [89.04(13)], P1–Re–C4 96.2(2) [93.0(2)], P1–Re–C5 86.43(15) [88.9(2)], P1–Re–C6 172.6(2) [177.3(2)], P2–Re–C1 88.47(13) [93.29(13)], P2–Re–C4 175.9(2) [174.8(2)], P2–Re–C5 93.2(2) [86.7(2)], P2–Re–C6 90.99(15) [95.0(2)], C1–Re–C4 87.9(2) [89.6(2)], C1–Re–C5 177.6(2) [178.0(2)], C1–Re–C6 90.4(2) [89.8(2)], C4–Re–C5 90.4(2) [90.3(2)], C4–Re–C6 90.8(2) [89.4(2)], C5–Re–C6 91.4(2) [92.3(2)].

ligand is oriented in a fashion which allows for a minimal interaction with the substituents of the coordinated diphosphine ligand.

The final step in the macrocycle synthesis is the linkage of the dicarbene ligand to the phenyl groups of the coordinated diphosphine. Stirring of *fac*-[**3**]Cl together with KO*t*Bu in THF for five days causes deprotonation of the N–H functions followed by nucleophilic attack of the ring nitrogen atoms at the fluorine substituted carbon atoms of the phenyl groups. This nucleophilic aromatic substitution reaction leads to formation of *fac*-[**4**]Cl (Scheme 1).

The absence of the N–H signal in the ^{1}H NMR spectrum of *fac*-[**4**]Cl and the observation of only one resonance in the ^{19}F{^{1}H} NMR spectrum indicate the formation of the [11]ane-P_2C^{NHC} macrocycle. The ^{13}C{^{1}H} NMR spectrum exhibits the resonance of the carbene carbon atom at δ = 190.9 ppm as a triplet ($^2J_{CP}$ = 3.0 Hz). Arylation of the nitrogen atoms of the NHC ligand leads only to a slight downfield shift of the C_{NHC} resonance compared to *fac*-[**3**]Cl ($\delta(C_{NHC})$ = 186.6 ppm). Contrary to complex *fac*-[**3**]Cl, the NHC ligand in *fac*-[**4**]Cl cannot rotate about the Re–C_{NHC} bond and consequently the protons of the imidazolidin-2-ylidene ligand become diastereotopic giving rise to two multiplets at δ = 4.84–4.79 ppm and δ = 4.47–4.43 ppm in the ^{1}H NMR spectrum.

Crystals of *fac*-[**4**]Cl·CH_2Cl_2·0.5H_2O were obtained by diffusion of diethyl ether into a saturated solution of [**4**]Cl in dichloromethane. An X-ray diffraction study with these crystals confirmed the formation of the P_2C^{NHC} macrocycle in *fac*-[**4**]Cl (Fig. 3). The asymmetric unit contains one molecule of *fac*-[**4**]Cl together with one disordered molecule of CH_2Cl_2 and 0.5 molecules of H_2O. Upon formation of the macrocycle in *fac*-[**4**]$^+$ the Re–C_{NHC} and Re–P bond distances become significantly shorter than the equivalent bonds in *fac*-[**3**]$^+$, while the Re–CO bond distances remain essentially unchanged. Due to the steric constraints introduced by the formation of the macrocycle, all bond angles involving the rhenium atom and atoms from the macrocycle are now smaller than 90°. While the P–Re–P angles in *fac*-[**3**]$^+$ (82.08(4)° and 82.70(4)°) and *fac*-[**4**]$^+$ (82.44(5)°) assume almost identical values in both cations,

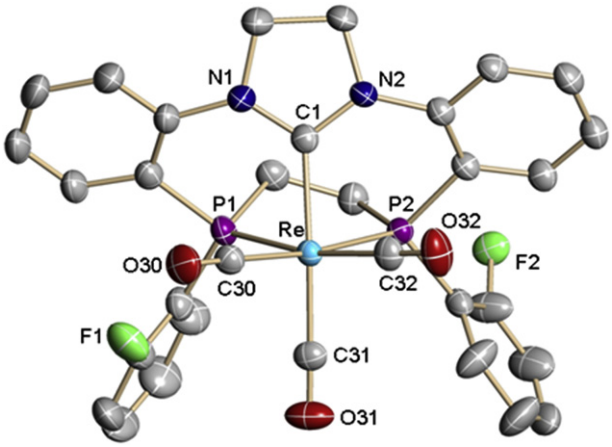


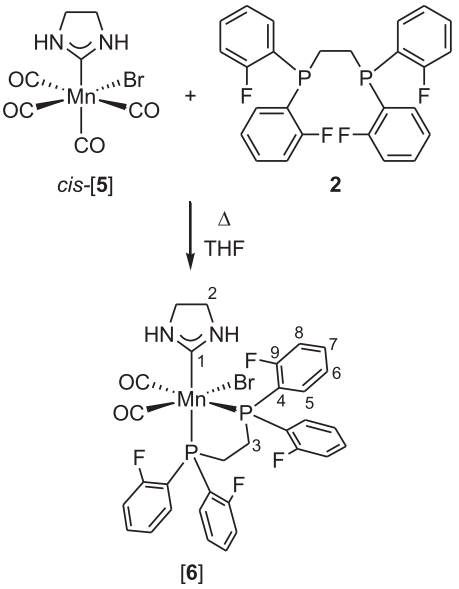
Fig. 3. Molecular structure of *fac*-[**4**]$^+$ in *fac*-[**4**]Cl·CH_2Cl_2·0.5H_2O (50% probability ellipsoids). Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Re–P1 2.3880(14), Re–P2 2.3968(12), Re–C1 2.157(5), Re–C30 1.970(6), Re–C31 1.952(6), Re–C32 1.962(6); P1–Re–P2 82.44(5), P1–Re–C1 77.84(15), P1–Re–C30 93.3(2), P1–Re–C31 95.3(2), P1–C1–C32 168.6(2), P2–Re–C1 81.09(14), P2–Re–C30 172.9(2), P2–Re–C31 94.7(2), P2–Re–C32 90.3(2), C1–Re–C30 92.4(2), C1–Re–C31 172.3(2), C1–Re–C32 92.4(2), C30–Re–C31 91.4(2), C30–Re–C32 93.0(2), C31–Re–C32 94.0(3).

the C_{NHC}–Re–P angles in *fac*-[**4**]$^+$ (77.84(15)° and 81.09(14)°) are significantly smaller than the equivalent angles in *fac*-[**3**]$^+$ (range 88.47(13)° to 93.29(13)°). For the macrocycle formation the NHC ligand in *fac*-[**3**]$^+$ must rotate by about 90° about the Re–C_{NHC} bond. In addition, the two phenyl groups linked to the NHC ligand must rotate about the P–C_{phenyl} bonds. After macrocycle formation, the plane of the NHC ligand adopts an almost coplanar arrangement with the two phenyl groups it is linked to.

To assess the general applicability of the synthesis protocol described above, we tried to generate the [11]ane-P_2C^{NHC} using diphosphine **2** at a Mn^I center. Manganese complexes bearing NHC ligands are less common and most of these complexes bear unsaturated imidazolin-2-ylidene ligands [14]. Complex *cis*-[**5**] bearing a saturated NH,NH-substituted NHC ligand was synthesized from [$MnBr(CO)_5$] and 2-(triphenylphosphinimine)ethylamine as previously described [9a]. Surprisingly, heating the diphosphine **2** and complex *cis*-[**5**] in THF for two days did not yield the expected Mn^I complex with a *facial* arrangement of the ligands as was previously observed for the reaction of the 1,2-phenylene bridged diphosphine ligand and complex *cis*-[**5**] [9a]. Instead, complex [**6**] was obtained (Scheme 2) featuring a *meridional* arrangement of the diphosphine and the NHC ligands. In contrast to the reaction of rhenium(I) complex *cis*-[**1**] with **2**, the halogenato ligand in *cis*-[**5**] was not substituted by the diphosphine ligand **2** leading to the neutral Mn^I complex [**6**].

Complex [**6**] was characterized by ^{31}P{^{1}H} NMR spectroscopy showing two resonances for the two chemically different phosphorus atoms at δ = 72.2 ppm and δ = 58.9 ppm. The ^{19}F NMR spectrum features four resonances for the four chemically different Ar–F atoms and the ^{13}C{^{1}H} NMR spectrum shows the resonance for the C_{NHC} atom at δ = 227.9 ppm in addition to four sets of resonances for the phenyl substituents.

Composition and coordination geometry of complex [**6**] have been confirmed by an X-ray diffraction analysis carried out with crystals of [**6**]·CH_2Cl_2·H_2O which were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of [**6**]. The structure analysis (Fig. 4) confirms that the phosphine donors are located in *trans* (P1) and *cis* (P2) positions relative to the NHC in a slightly distorted octahedral complex. The asymmetric unit



Scheme 2. Reaction of *cis*-[**5**] with **2** yielding manganese(I) complex [**6**] (the numbering refers to the assignment of the NMR resonances in the Experimental section).

contains one molecule each of [**6**], CH_2Cl_2 and water, the water molecule being disordered.

The Mn–C_{NHC} bond length (2.013(4) Å) is shorter than previously reported values for Mn^I complexes bearing saturated [9] or unsaturated [14] NHC ligands. It falls in the range described for Mn^{IV} or Mn^{III} NHC complexes [15]. The short Mn^I–C_{NHC} bond may be attributed to the unusual position of the NHC ligand *trans* to one of the phosphine donors. In previous studies with NHC/PPh_3 complexes of palladium(II) and platinum(II), it has been noticed that the NHC ligand normally avoids the *trans* position to the PPh_3 ligand and that the *cis*-[M(NHC)(PPh_3)L_2] complexes are the thermodynamically most stable reaction products [16]. The Mn–P distances differ significantly in lengths with the shorter distance observed for the phosphine donor located in *trans* position to the NHC ligand. Owing to the generally shorter M–P distances in the Mn^I complex [**6**] compared to the Re^I complexes *fac*-[**3**]Cl and *fac*-[**4**]Cl the bite angle of the diphosphine increases to 85.68(4)°.

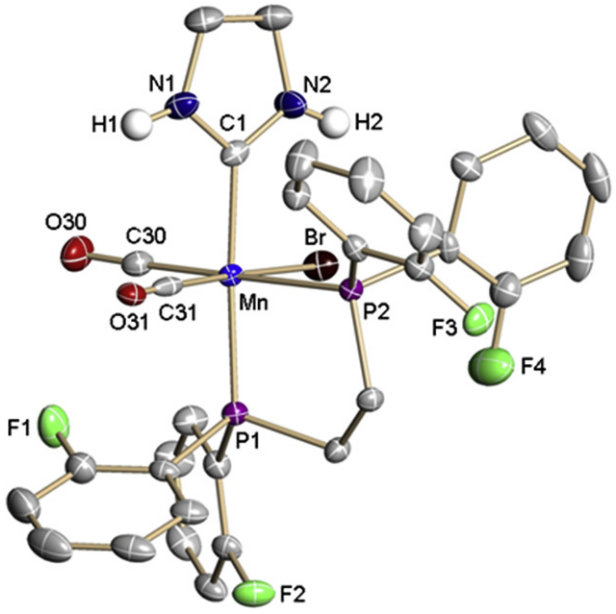


Fig. 4. Molecular structure of [**6**] in [**6**]Cl·CH_2Cl_2·H_2O (50% probability ellipsoids). Hydrogen atoms, except for the N–H atom, have been omitted. Selected bond lengths (Å) and angles (deg): Mn–Br 2.5639(8), Mn–P1 2.2812(12), Mn–P2 2.3287(12), Mn–C1 2.013(4), Mn–C30 1.807(5), Mn–C31 1.833(7); Br–Mn–P1 88.13(4), Br–Mn–P2 87.32(4), Br–Mn–C1 88.91(13), Br–Mn–C30 92.6(2), Br–Mn–C31 177.72(14), P1–Mn–P2 85.68(4), P1–Mn–C1 176.21(14), P1–Mn–C30 94.70(14), P1–Mn–C31 89.65(14), P2–Mn–C1 91.82(13), P2–Mn–C30 179.60(15), P2–Mn–C31 92.01(14), C1–Mn–C30 87.8(2), C1–Mn–C31 93.3(2), C30–Mn–C31 88.1(2).

3. Conclusions

We present the synthesis of a new macrocyclic [11]ane-P_2C^{NHC} ligand obtained in a template synthesis from an NH,NH-NHC ligand and the ethylene bridged diphosphine (2-F–C_6H_4)$_2$P–CH_2CH_2–P(C_6H_4-2-F)$_2$ **2** coordinated *facially* to the Re^I template center. Attempts to extend this synthesis to Mn^I as template metal were unsuccessful as the NH,NH-NHC and the diphosphine ligands could not be coordinated in the required *facial* geometry but instead the Mn^I complex with the *meridional* arrangement of these ligands was formed. The reasons for the formation of complex [**6**]Cl are not obvious at this time. We can only conclude that even a slight modification in the spacer of the diphosphine from phenylene to ethylene can cause a significant change in the coordination mode of the diphosphine.

4. Experimental section

4.1. General methods

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove-box techniques. Solvents were dried by standard methods under argon and were freshly distilled prior to use. ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were measured on a Bruker AVANCE I 400 or a Bruker AVANCE III 400 spectrometer. Chemical shifts (δ) are expressed in ppm using the residual protonated solvent signal as internal standard. Coupling constants are expressed in Hertz. Mass spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific) or a MicroTof (Bruker Daltonics) spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer. The preparation of *cis*-[ReCl(CO)$_4$(NHC)] *cis*-[**1**] [9a] and *cis*-[MnBr(CO)$_4$(NHC)] *cis*-[**5**] [9a] was carried out as described. Consistent microanalytical data were difficult to obtain due to the presence of fluorine in all complexes. ESI HRMS data and ^1H, $^{13}C\{^1H\}$, ^{19}F, and ^{31}P NMR spectroscopic data for all complexes are provided instead.

4.2. Synthesis of diphosphine **2**

The published procedure for the synthesis of **2** [10] has been modified leading to a higher yield. The reaction has to be carried out at −78 °C. All reactants have to be cooled to this temperature prior to use. A solution of *o*-bromofluorobenzene (1.3 mL, 11.9 mmol) in diethyl ether (15 mL) was added dropwise to a solution of *n*-buthyllithium (1.6 M in hexane, 7.1 mL, 11.4 mmol) in diethyl ether (30 mL). Caution: this reaction can lead to a higly reactive benzyne at reaction temperatures above −78 °C [17]. After stirring for 30 min a solution of 1,2-bis(dichlorophosphino)ethane (0.4 mL, 2.7 mmol) in diethyl ether (15 mL) was added dropwise over a period of 2 h. The reaction mixture was stirred for 4 h at −78 °C and then for 12 h at ambient temperature. A saturated aqueous ammonium chloride solution (100 mL) was added and the mixture was extracted with diethyl ether (3 × 60 mL). The combined organic phases were dried over magnesium sulfate and

the solvent was removed *in vacuo*. The residue was recrystallized from methanol giving compound **2** as a colorless solid. Yield: 1.01 g (2.1 mmol, 81%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.37–7.31 (m, 4H, Ar–H), 7.26–7.21 (m, 4H, Ar–H), 7.11–7.08 (m, 4H, Ar–H), 7.03–6.99 (m, 4H, Ar–H), 2.28 (t, $^{3}J_{HP}$ = 4.8 Hz, 4H, H-1). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 164.6 (dd, $^{1}J_{CF}$ = 246.0 Hz, $^{2}J_{CP}$ = 11.1 Hz, C-7), 133.6, 131.2 (m, C-3, C5), 124.4 (m, C4), 123.4 (m, C-2), 115.5 (d, $^{2}J_{CF}$ = 23.9 Hz, C-6), 21.2 (m, C-1). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ −32.9 (m). ^{19}F{^{1}H} NMR (376.4 MHz, $CDCl_3$): δ −103.9 (m). HRMS (ESI, positive ions) *m*/*z* (%): 493.0876 (100) [**2** + Na]$^{+}$ (calcd for [**2** + Na]$^{+}$ 493.0869), 471.1055 (8) [**2** + H]$^{+}$ (calcd for [**2** + H]$^{+}$ 471.1049).

4.3. Synthesis of fac-[3]Cl

A solution of *cis*-[**1**] (100.0 mg, 0.25 mmol) and diphosphine **2** (151.0 mg, 0.32 mmol) in acetonitrile (10 mL) was heated under reflux for 3 d. After cooling to ambient temperature the solution was concentrated and diethyl ether (25 mL) was added. The precipitate which formed upon addition of the diethyl ether was isolated by filtration, washed with diethyl ether (20 mL) and dried *in vacuo* giving complex *fac*-[**3**]Cl as a colorless solid. Yield: 48 mg (0.06 mmol, 23% of the solvent free compound). ^{1}H NMR (400 MHz, DMSO-d_6, for assignment of the resonances see Scheme 1): δ 7.76–7.69 (m, 2H, H-5a), 7.61–7.56 (m, 8H, H-5, H-7, H-7a, NH), 7.40–7.33 (m, 4H, H-6, H-6a), 7.30–7.20 (m, 4H, H-8, H-8a), 3.69–3.61 (m, 2H, H-3), 3.12–3.04 (m, 2H, H-3), 2.86 (s, 4H, H-2). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, for assignment of the resonances see Scheme 1): δ 190.8 (d, $^{2}J_{CP\text{-}trans}$ = 53.4 Hz, $CO_{cis\text{-}C1}$), 189.5 (t, $^{2}J_{CP\text{-}cis}$ = 6.6 Hz, $CO_{trans\text{-}C1}$), 186.6 (t, $^{2}J_{CP}$ = 9.6 Hz, C-1), 163.0 (d, $^{1}J_{CF}$ = 247.5 Hz, C-9), 162.5 (d, $^{1}J_{CF}$ = 247.9 Hz, C-9a), 134.3 (C-5, C-7, C-7a), 132.4 (dd, $^{2}J_{CP}$ = 9.1 Hz, $^{3}J_{CF}$ = 1.6 Hz, C-5a), 125.0 (dd, $^{3}J_{CP}$ = 9.9 Hz, $^{4}J_{CF}$ = 2.1 Hz, C-6a), 124.5 (dd, $^{3}J_{CP}$ = 9.9 Hz, $^{4}J_{CF}$ = 2.3 Hz, C-6), 119.9 (dd, $^{1}J_{CP}$ = 48.9 Hz, $^{2}J_{CF}$ = 16.9 Hz, C-4a), 117.0 (dd, $^{1}J_{CP}$ = 44.4 Hz, $^{2}J_{CF}$ = 17.6 Hz, C-4), 116.6 (d, $^{2}J_{CF}$ = 23.7 Hz, C-8a), 116.0 (d, $^{2}J_{CF}$ = 22.2 Hz, C-8), 44.1 (C-2), 26.5 (dd, $^{1}J_{CP}$ = 33.5 Hz, $^{2}J_{CP}$ = 9.6 Hz, C-3). ^{31}P{^{1}H} NMR (162.0 MHz, DMSO-d_6): δ (ppm) = 19.4. ^{19}F{^{1}H} NMR (376.4 MHz, DMSO-d_6): δ −101.1 (C9–F), −100.9 (C9a–F). IR (KBr): ν (cm^{-1}): 2036 (s, CO), 1971 (s, CO), 1923 (s, CO), the NH vibration could not be identified. HRMS (ESI, positive ions) *m*/*z* (%): 811.09001 (100) [**3**]$^{+}$ (calcd for [**3**]$^{+}$ 811.09083).

4.4. Synthesis of fac-[4]Cl

Complex *fac*-[**3**]Cl (20.0 mg, 0.024 mmol) was suspended in THF (10 mL) and KO*t*Bu (6.0 mg, 0.047 mmol) was added. The colorless solution was stirred for 5 d at ambient temperature during which time the solution turned yellow. The solvent was removed *in vacuo* and the remaining residue was dissolved in dichloromethane. After filtration the solution was concentrated and diethyl ether (20 mL) was added. A precipitate formed which was isolated by filtration and dried *in vacuo*. Complex *fac*-[**4**]Cl was isolated as a pale yellow solid. Yield: 15.0 mg (0.019 mmol, 79%). ^{1}H NMR (400.1 MHz, CD_2Cl_2, for assignment of the resonances see Scheme 1): δ 7.69–7.52 (m, 8H, H-7, H-8, H-11, H-13), 7.42–7.38 (m, 2H, H-12), 7.32–7.27 (m, 2H, H-14), 7.20–7.17 (m, 2H, H-6), 6.91–6.86 (m, 2H, H-5), 4.84–4.79 (m, 2H, H-2), 4.47–4.43 (m, 2H, H-2), 3.20 (m, 2H, H-3), 2.99 (m, 2H, H-3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, for assignment of the resonances see Scheme 1): δ 193.7 (br, $CO_{trans\text{-}C1}$), 190.9 (t, $^{2}J_{CP}$ = 3.0 Hz, C-1), 190.1 (d, $^{2}J_{CP\text{-}trans}$ = 48.8 Hz, $CO_{cis\text{-}C1}$), 164.3 (d, $^{1}J_{CF}$ = 251.0 Hz, C-15), 145.7 (d, $^{2}J_{CP}$ = 11.6 Hz, C-9), 135.8 (C-11, C-13), 133.6 (d, $^{4}J_{CP}$ = 2.1 Hz, C-7), 131.2 (d, $^{2}J_{CP}$ = 2.6 Hz, C-5), 126.7 (d, $^{3}J_{CP}$ = 7.9 Hz, C-6), 126.3 (dd, $^{3}J_{CP}$ = 10.0 Hz, $^{4}J_{CF}$ = 3.2 Hz, C-12), 124.0 (d, $^{3}J_{CP}$ = 6.9 Hz, C-8), 123.3 (d, $^{1}J_{CP}$ = 49.2 Hz, C-4), 117.5 (dd, $^{2}J_{CF}$ = 23.0 Hz, $^{3}J_{CP}$ = 3.8 Hz, C-14), 114.2 (br, C-10), 52.5 (C-2), 29.4 (br, C-3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 15.8 (br). ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −97.1. IR (KBr): ν (cm^{-1}): 2033 (s, CO), 1944 (s, CO), 1871 (m, CO). HRMS (ESI, positive ions) *m*/*z* (%): 771.07854 (100) [**4**]$^{+}$ (calcd for [**4**]$^{+}$ 771.07822).

4.5. Synthesis of [6]

A solution of *cis*-[**5**] (110.0 mg, 0.35 mmol) and diphosphine **2** (180.0 mg, 0.38 mmol) in THF (3 mL) was heated under reflux for 2 d. After cooling to ambient temperature diethyl ether (10 mL) was added. A precipitate formed which was isolated by filtration, washed with diethyl ether (20 mL) and dried *in vacuo*. Yield: 149 mg (0.20 mmol, 59%) of an orange solid. ^{1}H NMR (400.1 MHz, CD_2Cl_2, for assignment of the resonances see Scheme 2): δ 8.18 (br, 1H, Ar–H), 7.91 (br, 1H, Ar–H), 7.66 (br, 1H, Ar–H), 7.35–6.93 (m, 13H, Ar–H), 6.81 (s, br, 2H, NH), 3.63 (s, 4H, H-2), 2.80–3.33 (m, 4H, H-3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, for assignment of the resonances see Scheme 2): δ 228.8 (CO), 227.9 (d, $^{2}J_{CP\text{-}trans}$ = 17.6 Hz, C-1), 226.2 (CO), 164.1 (d, $^{1}J_{CF}$ = 246.8 Hz, C-9), 163.6 (d, $^{1}J_{CF}$ = 246.6 Hz, C-9), 163.4 (d, $^{1}J_{CF}$ = 247.3 Hz, C-9), 163.4 (d, $^{1}J_{CF}$ = 247.3 Hz, C-9), 136.7 (dd, $^{2}J_{CP}$ = 12.7 Hz, $^{3}J_{CF}$ = 4.1 Hz, C-5), 135.7 (dd, $^{2}J_{CP}$ = 15.8 Hz, $^{3}J_{CF}$ = 2.8 Hz, C-5), 135.2 (dd, $^{2}J_{CP}$ = 7.8 Hz, $^{3}J_{CF}$ = 4.8 Hz, C-5), 133.0 (d, $^{3}J_{CF}$ = 9.7 Hz, C-7), 132.9 (C-5), 132.4 (d, $^{3}J_{CF}$ = 8.3 Hz, C-7), 132.3 (d, $^{3}J_{CF}$ = 8.6 Hz, C-7), 132.0 (d, $^{3}J_{CF}$ = 8.1 Hz, C-7), 124.2 (d, $^{3}J_{CP}$ = 10.9 Hz, C-6), 124.2 (d, $^{3}J_{CP}$ = 9.8 Hz, C-6), 123.7 (dd, $^{3}J_{CP}$ = 10.6 Hz, $^{4}J_{CF}$ = 1.9 Hz, C-6), 123.2 (dd, $^{3}J_{CP}$ = 8.2 Hz, $^{4}J_{CF}$ = 2.8 Hz, C-6), 116.5–115.4 (m, 4× C-8), 45.9 (C-2), 27.6 (m, C-3), 26.2 (m, C-3). The resonance for the C-4 atoms was not detected. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 72.2, 58.9. ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ −100.0, −101.1, −101.6, −102.0. IR (KBr): ν (cm^{-1}): 3397 (m, NH), 2027 (m, CO), 1940 (s, CO), 1850 (s, CO). HRMS (ESI, positive ions) *m*/*z* (%): 651.07807 (100) [**6**–Br]$^{+}$ (calcd for [**6**–Br]$^{+}$ 651.07806).

4.6. Crystal structure determinations

X-ray diffraction data for all compounds were collected for all at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) for *fac*-[**3**]Cl·0.5CH_2Cl_2 and *fac*-[**4**]Cl·CH_2Cl_2·0.5H_2O or Cu-Kα radiation (λ = 1.54178 Å) for [**6**]Cl·CH_2Cl_2·H_2O. Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97 [18] package using direct methods and were refined with SHELXL-97 [18] against all $|F^2|$ using first isotropic and later anisotropic thermal parameters. Hydrogen atoms were added to the structure models in calculated positions (for exceptions see description of the individual molecular structures).

4.6.1. Crystal data for fac-[3]Cl·0.5CH_2Cl_2

$C_{32.5}H_{27}N_2Cl_2F_4O_3P_2Re$, M = 888.60, triclinic, $P\bar{1}$, a = 12.3472(6), b = 14.8272(7), c = 19.5326(9) Å, α = 91.1340(10), β = 90.8400(10), γ = 111.7320(10)°, V = 3320.2(3) Å^3, Z = 4, D_{calc} = 1.778 g cm^{-3}, μ = 3.977 mm^{-1}, 39258 measured intensities (3.0° ≤ 2θ ≤ 60.0°), 19234 independent (R_{int} = 0.0312) diffractions data, refinement of 838 parameters, R = 0.0453, wR = 0.1106 for 14874 observed intensities ($I \geq 2\sigma(I)$). The asymmetric unit contains two formula units.

4.6.2. Crystal data for fac-[4]Cl·CH_2Cl_2·0.5H_2O

$C_{33}H_{27}N_2Cl_3F_2O_{3.5}P_2Re$, M = 900.06, monoclinic, $C2/c$, a = 30.1945(11), b = 12.3444(4), c = 20.7168(7) Å, β = 104.1940(10)°, V = 7486.1(4) Å^3, Z = 8, D_{calc} = 1.597 g cm^{-3}, μ = 3.591 mm^{-1}, 43287 measured intensities (2.8° ≤ 2θ ≤ 60.0°),

10903 independent (R_{int} = 0.0319) diffraction data, refinement of 457 parameters, R = 0.0444, wR = 0.1392 for 8797 observed intensities ($I \geq 2\sigma(I)$). The asymmetric unit contains one formula unit. The CH_2Cl_2 molecule is disordered. Non-hydrogen atoms of solvent molecules were refined with isotropic thermal parameters, no hydrogen atoms of solvent molecules were added to the structure model.

*4.6.3. Crystal data for [**6**]·CH_2Cl_2·H_2O*

$C_{32}H_{30}N_2BrCl_2F_4MnO_3P_2$, M = 834.27, triclinic, $P\bar{1}$, a = 11.2319(4), b = 12.1710(4), c = 13.3111(4) Å, α = 85.396(2), β = 87.881(2), γ = 78.617(2)°, V = 1777.71(10) Å^3, Z = 2, D_{calc} = 1.559 g cm^{-3}, μ = 7.064 mm^{-1}, 10041 measured intensities (6.7° ≤ 2θ ≤ 143°), 5942 independent (R_{int} = 0.0484) diffraction data, refinement of 427 parameters, R = 0.0599, wR = 0.1835 for 5206 observed intensities ($I \geq 2\sigma(I)$). The asymmetric unit contains one formula unit. The H_2O molecule is disordered. The water molecule is disordered. Positional parameters of the water oxygen atom were refined with isotropic thermal parameters. No hydrogen atoms for the water molecule were added to the structure model.

Appendix A. Supplementary material

CCDC-829156 (*fac*-[**3**]Cl·0.5CH_2Cl_2), CCDC-829157 (*fac*-[**4**]Cl·CH_2Cl_2·0.5H_2O), and CCDC-829158 ([**6**]·CH_2Cl_2·H_2O) contain the supplementary crystallographic data for this paper. These date can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data/request/cif.

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