Facial vs. Meridional Coordination Modes in Re^I Tricarbonyl Complexes with a Carbodiphosphorane-based Tridentate Ligand

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The reactivity of the novel cationic ligand precursor [(dppm)$_2$CH](PF$_6$) (**1**) with a weakly coordinating anion and [ReBr(CO)$_5$] is reported. The initial coordination results in the formation of the facially coordinated dicationic complex *fac*-[({dppm}$_2$CH)Re(CO)$_3$]X$_2$ (***fac*-2**, X = Br, PF$_6$). The facial coordination mode is retained in *fac*-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (***fac*-3**) upon deprotonation of the central cationic donor group.

Quantum chemical investigations indicate that for both complexes, **2** and **3**, the meridional coordination mode is thermodynamically favored. In line with these findings, the isomerization of the facially coordinated complex ***fac*-3** to the meridionally coordinated complex *mer*-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (***mer*-3**) is observed under irradiation with UV-light.

Introduction

Carbodiphosphoranes (CDPs) with the general composition (R$_3$P)$_2$C can be interpreted as ligand-stabilized carbon(0) compounds with two electron lone pairs mainly located at the central carbon atom.[1–4] This description of the bonding situation is underlined by their ability to act as σ- and π-donor ligands[5–8] as well as μ$_2$-bridging ligands in transition metal complexes[9,10] and between main group element Lewis acids.[11] In this context, CDPs were shown to be strong electron donating ligands,[12,13] which are suited to stabilize transition metal ions over a wide range formal oxidation states.[14,15] Due to their binding properties, CDP-based ligands were predicted to be superb substitutes for carbenes in Grubbs-II type metathesis catalysts and thus should lead to an increased catalytic activity.[16]

The incorporation of CDPs and related groups in pincer-type ligands led to the development of highly active catalysts for cross coupling reactions,[17,18] hydroamination and -arylation reactions.[19–21] Moreover, the two terminal binding sites of the pincer platform, often tertiary phosphines, enable the stabilization of lower oxidation states that result in electron rich transition metal complexes.[12,14,30–32,22–29]

One of the first CDP transition metal complexes was the rhenium(VII) complex [({Ph$_3$P}$_2$C)ReO$_3$]$^+$ reported by Sundermeyer and co-workers.[15] In their study, the authors clearly demonstrated that CDPs are capable of stabilizing transition metal centers in high oxidation states. Within comparison to other carbon-based ligands, such as carbenes, CDPs with their ability to act as double-donor ligands appear to be more related to Schrock-type carbenes. However, in many cases CDP-based ligands act as almost pure σ-donating ligands that are capable of stabilizing transition metal centers in lower oxidation states. In the current study, we use the stabilizing effect of pincer-type ligands to complement the range of accessible rhenium oxidation states with CDP-based ligands and report the synthesis of a series of rhenium(I) triscarbonyl complexes with a CDP-based donor group. Our study shows that facial and meridional binding of the employed tridentate ligand leads to rhenium(I) complexes of very similar stability.

Results and Discussion

In our previous attempts to synthesize CDP-based pincer-type complexes with different transition metals, we frequently encountered problems with respect to poor selectivity of the reactions, when [(dppm)$_2$CH]Cl was used as a pre-ligand (dppm = 1,1'-bis(diphenylphosphino)methane). To circumvent these problems, the pre-ligand **1** with the weaker coordinating PF$_6^-$ counter ion was synthesized and used in this study. As the cationic pre-ligand remains identical in **1**, the spectroscopic data of **1** is almost identical to [(dppm)$_2$CH]Cl and only the additional resonances due to the PF$_6$-counter ion are observed in ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra. The central carbon atom in **1** gives rise to a triplet of triplets resonance with a similar chemical shift in the ^{13}C{^{1}H} NMR spectrum ($\delta_C = -3.0$ ppm, $^1J_{PC} = 123.4$ Hz, $^3J_{PC} = 7.8$ Hz) like the corresponding pre-ligand with a chloride counter ion ($\delta_C = -3.3$ ppm, $^1J_{PC} = 124.2$ Hz, $^3J_{PC} = 8.0$ Hz).[27]

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The reaction of [(dppm)$_2$CH](PF$_6$) (**1**) with one equivalent of [ReBr(CO)$_5$] in THF at 65 °C afforded the dicationic complex *fac*-[({dppm}CH)Re(CO)$_3$]X$_2$ (*fac*-**2**, X=Br, PF$_6$) with a facially coordinated tridentate ligand (Scheme 1). Complex *fac*-**2** gives rise to two multiplet resonances at −0.2 and 42.6 ppm in addition to the septet resonance at −144.1 ppm for the PF$_6$ counter ion in the ^{31}P{^{1}H} NMR spectrum. The triplet resonance at 3.95 ppm ($^2J_{PH}$=17.9 Hz) in the ^{1}H NMR spectrum, corresponding to the hydrogen atom of the coordinated protonated CDP unit, is low field shifted relative to **1**, however this shift is smaller with respect to related complexes.[12,14,27] The ^{13}C{^{1}H} NMR resonance at −5.0 ppm associated with the central carbon atom is only slightly shifted in comparison to the pre-ligand in **1**. The connectivity in *fac*-**2** was confirmed by single crystal X-ray diffraction analysis. The molecular structure is depicted in Figure 1. Despite several attempts under varying conditions, only single crystals of poor quality could be obtained. However, the principal connectivity in *fac*-**2** can be confirmed with confidence. Notably, the purification (48.3% total yield) by recrystallisation gave a pure fraction of *fac*-**2** with two PF$_6^-$ counter ion, respectively. This was further confirmed by elemental analysis.
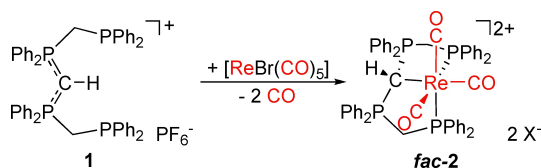
In comparison to other pincer-type ligands, the protonated CDP-moiety in the cation **1**, [(dppm)$_2$CH]$^+$, exhibits an unusual variety of reactivity patterns. For instance, for a central donor group R$_2$EH, with E being the ligating atom, three different reaction pathways can be distinguished upon binding to a metal fragment: (i) R$_2$EH is a rather weak donor ligand and the central donor group remains uncoordinated, (ii) it replaces an ancillary ligand at the central metal atom and gets coordinated or (iii) E−H-oxidative addition takes place. For most central donor groups, only one preferred pathway can be observed and, in some cases, a second one is observed as well. However, the observation of all three pathways for one donor group is rather uncommon. The cation [(dppm)$_2$CH]$^+$ is one of such exception: it reacts with iridium(I) precursors via a C−H-oxidative addition to give a hydride and a CDP-based pincer ligand, respectively (iii).[12,30] The thermal reaction of the cation [(dppm)$_2$CH]$^+$ with [Cr(CO)$_6$] leads to coordination of both terminal phosphine groups and the central protonated CDP-moiety remains uncoordinated (i).[31] In the current case, as well as with [RhCl(CO)$_2$]$_2$, coordination of the central CDP group along with the two terminal phosphine donors can be observed (ii).[14]

The corresponding CDP-based rhenium(I) complex **3** can be obtained when the reaction of [(dppm)$_2$CH](PF$_6$) (**1**) with one equivalent of [ReBr(CO)$_5$] is conducted in the presence of 1.2 equivalents of a base such as 1,4-diazabicyclo[2.2.2]octane (DABCO, Scheme 2). It should be noted that only the *fac*-isomer *fac*-**3** is formed under these conditions. The ^{31}P{^{1}H} NMR spectrum of *fac*-**3** gives rise to two multiplet resonances at 1.4 and 24.3 ppm accompanied by the characteristic septet for the PF$_6^-$ counter ion. Interestingly, the resonance of the rhenium-bound central carbon atom in the ^{13}C{^{1}H} NMR spectrum
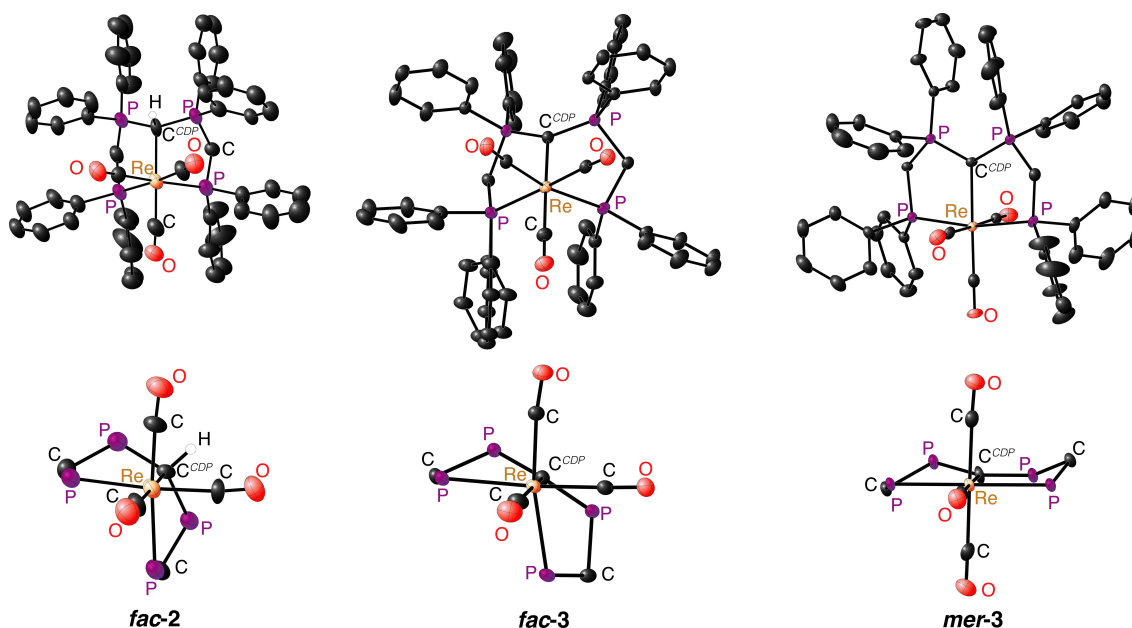

Scheme 1. Complexation of [ReBr(CO)$_5$] by the protonated CDP **1** (X=Br, PF$_6$).
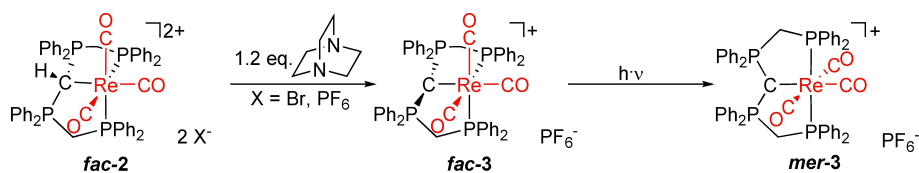

Figure 1. Molecular structures of the cations in in *fac*-**2** (left), *fac*-**3** (middle) and *mer*-**3** (right) in the solid state (ellipsoids are drawn at 30% probability level). The principal connectivity with the arrangement of the tridentate CDP-based ligand are shown at the bottom for all three complexes.

Scheme 2. Deprotonation of *fac*-2 and the fac/mer-isomerization of the resulting complex *fac*-3 under UV-light irradiation.

remains with −5.7 ppm almost unchanged in comparison to the protonated analogue *fac*-2. The IR spectrum of *fac*-3 shows three bands at 2010, 1933 and 1893 cm^{-1} assigned to C−O-stretching vibrations, which are shifted by 22 cm^{-1} to 51 cm^{-1} to lower wave numbers in comparison to *fac*-2. The molecular structure in the solid state, obtained from a single crystal X-ray diffraction study, shows an octahedral rhenium complex with a facially coordinated PC^{CDP}P-type ligand. Upon deprotonation the Re−C^{CDP} bond length in *fac*-3 (2.289 Å) shortens with respect to the protonated complex *fac*-2 (2.348 Å). The trigonal planar environment of the central carbon atom of the CDP-moiety is evident from the sum of angles around this atom, which was found to be 358.66°. Although the CDP-moiety remains planar, a facial coordination mode seems to be facilely adopted for this ligand. However, the P−C−P angle of the CDP-group is increased to 130.87°.

Irradiation of *fac*-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (*fac*-3) in methylene chloride with UV light (150 W mercury-vapor discharge lamp) leads to the clean formation of the corresponding *mer*-isomer *mer*-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (*mer*-3, Scheme 2). The reaction was monitored via ^{31}P{^{1}H} NMR spectroscopy. Complete conversion was achieved after 12 hours reaction time. In contrast, heating a THF solution of *fac*-3 to 60 °C in a closed vessel did not result in any isomerization. Two triplet resonances at 10.7 and 30.0 ppm are observed in the ^{31}P{^{1}H} NMR spectrum for the coordinated pincer ligand. The resonance of the central carbon atom of the CDP group is significantly shifted to lower frequencies and was detected at −19.9 ppm in the ^{13}C{^{1}H} NMR spectrum of *mer*-3. The molecular structure of *mer*-3 was investigated by single crystal X-Ray diffraction and the obtained structure supported the formation of the *mer*-isomer with a Re−C^{CDP} bond distance of 2.282 Å (Figure 1). Heating of *mer*-3 in 1,2-difluorobenzene for an extended period of time (16 h) to 120 °C (oil bath temperature) did not lead to

any reaction, providing further evidence for *mer*-3 being the thermodynamically more stable complex with respect to *fac*-3. For an unconstrained system (e.g. with only monodentate ligands) a *fac*-arrangement would be expected to be thermodynamically more stable, due to the strong *trans*-influence of the carbonyl ligands. This might be outweighed in the current case by a constrained flexibility of the tridentate ligand and by steric factors that disfavor a *cis*-arrangement of the terminal PPh$_2$-groups.

A comparison of distances and angles of the molecular structures in the solid state can provide insights with regard to the differences in bonding of the CDP-moiety in *fac*-2, *fac*-3 and *mer*-3 (Table 1). The protonated CDP-moiety (in *fac*-2) is a cationic ligand that solely acts as σ-donor. A shortening of the Re−C^{CDP} bond of 0.059–0.066 Å is observed upon removal of the proton from the CDP-moiety, which might reflect the stronger σ-donor and the π-donor ability of the neutral CDP-ligand as well as a reduced Coulomb repulsion between the central donor group and the cationic rhenium fragment relative to the protonated CDP-ligand.[13] The lone pair generated by removal of the proton from the protonated CDP may be stabilized to a significant extent by π-back bonding to the neighboring phosphine groups, which is indicated by shorter P−C^{CDP} bond distances (Δ > 0.1 Å). In comparison to the C^{CDP}−P bond distances in the previously reported complex [({Ph$_3$P}$_2$C)ReO$_3$]$^+$ (1.764–1.777 Å)[15] these bond distances in *fac*-3 and *mer*-3 are significantly shorter (1.676–1.704 Å), indicating a stronger delocalization of the CDP lone pair by π-back-bonding to the phosphine groups (negative hyper conjugation) in the reported rhenium(I) complexes. In turn, these findings reflect a significantly reduced π-donor component of the CDP moiety in the reported rhenium(I) complexes.

The preference for a facial coordination mode of a tridentate ligand with a rather rigid and trigonal planar central

Table 1. Selected structural and spectroscopic features of *fac-2*, *fac-3* and *mer-3*.

	fac-2	fac-3	mer-3
Re−C^{CDP}/Å	2.348	2.289	2.282
P−C^{CDP}/Å	1.806/1.817	1.676/1.686	1.701/1.704
P−C^{CDP}−P/°	120.50	130.87	122.46
Σα(C^{CDP})/°	339.92[a]	358.66	359.63
plane angle PC^{CDP}P/LLL (L=CO, PR$_3$)/°		38.03	9.86
δ$_C$(C^{CDP})/ppm [b]	−5.0	−5.7	−19.9
$\tilde{v}_{CO}$/cm^{-1} [c]	2032, 1971, 1944	2010, 1933, 1893	2053, 1942, 1868

[a] Sum of angles around C^{CDP} without consideration of the hydrogen atom. [b] Chemical shift in the ^{13}C{^{1}H} NMR spectrum. [c] Detected by IR spectroscopy.

donor group was unexpected. The main structural difference between **fac-3** and **mer-3** is a widening of the P–C^{CDP}–P angle in **fac-3** by more than 10° in combination with a shortening of the P–C^{CDP} bond, which is in line with an increased π-back donation to the neighboring phosphine groups. It becomes evident that the CDP-plane (P–C^{CDP}–P) in **fac-3** is tilted by 38.03° vs. the central molecular plane of the octahedron defined by the phosphorous atoms of the terminal PPh$_2$-groups and the carbon atom of the carbonyl ligand. This can reduce the potential overlap with rhenium centered orbitals for π-donation, which results in an increased π-back bonding to the phosphine groups. Despite the retained planarity of the CDP-moiety in **fac-3**, the tilting of this donor group seems to be necessary for the realization of the facial coordination mode. A pronounced difference between the facial and meridional coordination mode is observed for the ^{13}C chemical shift of the central CDP-group, which indicates a more electron rich carbon atom of the CDP-moiety for the *mer*-isomer. Both isomers give rise to three bands between 1850 and 2060 cm^{-1} in the IR spectrum for C–O-stretching vibrations, which show a typical pattern for each isomer.

Quantum chemical investigations using density functional theory (DFT) were performed to gain further insights into the stability of the different isomers (B97-D3, def2-TZVP). Both isomers were found to be energetic minima in case of complex **3**, with the mer-isomer **mer-3** being more stable by 11.9 kJ/mol relative to **fac-3**. These findings are in line with the experimental observation that **fac-3** is the kinetic product of the deprotonation of **fac-2**, in which the facial arrangement of the starting material is retained. Notably, the mer-isomer of the protonated **mer-2** was calculated to be more stable than **fac-2** by 7.9 kJ/mol, but the irradiation of the reaction mixture after complexation with **1** does not result in the formation of the *mer*-isomer. The proton affinity of **mer-3** is with 849.1 kJ/mol comparable to those calculated for iridium complexes, but is significantly lower than typical values for amido-based pincer complexes.[33]

Inspection of the molecular orbitals revealed the presence of π-symmetric orbitals between the CDP-ligand and the central rhenium atom in **fac-3** and **mer-3**, supporting the presence of a weak π-donation from the CDP-based ligand. Notably, for the protonated complexes **fac-2** and **mer-2** such molecular orbitals are not observed. Partial charges were calculated using natural population analysis (NPA), which indicate that mainly the partial charge of the CDP carbon atom is changing ($\Delta q = -0.16/-0.18e$) upon deprotonation, while all other partial charges remain almost unchanged. Moreover, the NPA suggest the corresponding *mer*-isomers to be more electron rich at the central rhenium atom with respect to their corresponding *fac*-isomers.

Conclusions

In this manuscript, we demonstrated that the cationic (pre-)ligand [(dppm)$_2$CH]$^+$ in **1** exhibits an unexpected flexibility in its coordination to a rhenium(I) triscarbonyl fragment as chelating

ligand (*fac* vs. *mer*), which is unusual for a central donor group containing a ligating carbon atom in a trigonal planar environment. DFT calculations in our study show that the difference in the calculated Gibbs free energy for both isomers, *fac* and *mer*, is marginal. Moreover, it is demonstrated that the pincer platform can be used to combine CDP-based ligands with rhenium complexes in low oxidation states.

Experimental Section

Materials and Methods All experiments were carried out under an atmosphere of purified argon or nitrogen in the MBraun glove boxes LABmaster 130 and UNIlab or using standard Schlenk techniques. THF and diethyl ether were dried over Na/K alloy, *n*-hexane was dried over LiAlH$_4$, dichloromethane and acetonitrile were dried over CaH$_2$. After drying, solvents were stored over appropriate molecular sieves under argon atmosphere. Deuterated solvents were degassed with freeze-pump-thaw cycles and stored over appropriate molecular sieves under argon atmosphere.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using an Agilent Technologies 400 MHz V NMRs or 500 MHz DD2 spectrometer at 300 K. ^{1}H and ^{13}C {^{1}H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. The resonance of the residual protons in the deuterated solvent was used as internal standard for ^{1}H NMR spectra. The solvent peak of the deuterated solvent was used as internal standard for ^{13}C NMR spectra. ^{31}P NMR chemical shifts are reported in ppm downfield from H$_3$PO$_4$ and referenced to an external 85% solution of phosphoric acid in D$_2$O. The following abbreviations are used for the description of NMR data: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet). FT-IR spectra were recorded by attenuated total reflection of the solid samples on a Bruker Tensor IF37 spectrometer. The intensity of the absorption band is indicated as w (weak), m (medium), s (strong), vs (very strong) and br (broad).

Bis(diphenylphosphino)methane (dppm) was synthesized following the procedure published by K. Sommer.[34] [(dppm)$_2$CH]Cl was synthesized according to the previously published procedure.[35] [ReBr(CO)$_5$] was prepared according to the established literature procedure.[36]

Synthesis of [{dppm}$_2$CH](PF$_6$) (1) 5.00 g [(dppm)$_2$CH]Cl (6.12 mmol) was dissolved in 50 ml CHCl$_3$ and shaken vigorously in a separatory funnel with 25 ml of aqueous, semi-concentrated HPF$_6$. After separation of the aqueous phase, this step was repeated. The organic phase was then washed twice with 75 ml H$_2$O. A ^{31}P{^{1}H} NMR spectrum of the organic phase showed a mixture of mono- and di-protonated ligand precursor. The organic phase was then treated with 25 ml of aqueous ammonia in a separatory funnel two times. The organic phase was subsequently washed twice with 75 ml H$_2$O and finally with 75 ml brine. After separation, the organic phase was dried over MgSO$_4$, filtered and all volatiles removed in vacuo. 4.79 g of **1** (4.43 mmol, 72.3%) were isolated as an off-white powder. The presence of chloride impurities was tested via extraction with water and subsequent treatment of the aqueous phase with AgNO$_3$. No formation of a precipitate was observed. Anal. Calcd for C$_{51}$H$_{45}$F$_6$P$_5$: C 66.10%, H 4.89%; Found: C 66.17%; H, 4.64%. ^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ = 1.65 (br, {Ph$_2$P-CH$_2$-PPh$_2$}$_2$C*H*), 2.99 (d, $^1J_{PH}$ = 12.3 Hz, {Ph$_2$P-C*H*$_2$-PPh$_2$}$_2$CH), 7.21–7.32 (m superimposed, phenyl-*H*), 7.45 (m, phenyl-*H*) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 300 K): δ = −144.1 (sept, $^1J_{FP}$ = 712.8 Hz, *P*F$_6$), −30.7 (dt, J_{PP} = 72.0 Hz, J_{PP} = 14.1 Hz, {Ph$_2$*P*-CH$_2$-PPh$_2$}$_2$CH), 19.1 (dt, J_{PP} = 72.2 Hz, J_{PP} = 14.1 Hz, {Ph$_2$P-CH$_2$-*P*Ph$_2$}$_2$CH) ppm. ^{19}F NMR (376 MHz, CDCl$_3$, 300 K): δ = −73.01 (d, $^1J_{PF}$ = 713.2 Hz, P*F*$_6$) ppm. ^{13}C{^{1}H} NMR

(101 MHz, CDCl$_3$, 300 K): δ = −3.0 (tt, $^1J_{PC}$ = 123.4 Hz, $^3J_{PC}$ = 7.8 Hz, {Ph$_2$P-CH$_2$-PPh$_2$}$_2$CH), 28.1 (m, {Ph$_2$P-CH$_2$-PPh$_2$}$_2$CH), 125.9 (m, phenyl-C), 126.9 phenyl-C), 129.0 (d, J_{PC} = 7.8 Hz, phenyl-C), 129.4 (dd, J_{PC} = 6.0 Hz, phenyl-C), 129.7 (s, phenyl-C), 132.3 (dd, J_{PC} = 6.2 Hz, J_{PC} = 3.9 Hz, phenyl-C), 133.0 (d, J_{PC} = 21.4 Hz, phenyl-C), 133.2 (t, J_{PC} = 1.4 Hz, phenyl-C), 136.3 (dt, J_{PC} = 12.8 Hz, J_{PC} = 3.9 Hz, phenyl-C) ppm.

Synthesis of fac-[({dppm}$_2$CH)Re(CO)$_3$](PF$_6$)$_2$ (fac-2) A 25 mL Schlenk tube equipped with a magnetic stirring bar and teflon valve was charged with 50 mg [Re(CO)$_5$Br] (0.123 mmol) and 111 mg of [(dppm)$_2$CH]PF$_6$ (**1**, 0.120 mmol, 0.98 eq.). Subsequent addition of 6 mL THF gave rise to a clear colorless solution. The mixture was heated in the closed vessel at 65 °C. After 22 h, the reaction mixture was cooled down to ambient temperature and all volatiles were removed *in vacuo*. Subsequently, the colorless residue was dissolved in a minimum of CH$_2$Cl$_2$ (ca. 10 mL). A remaining (minor) colorless solid was filtered off via a syringe filter (PTFE, 0.2 µm porosity). The clear filtrate was layered with Et$_2$O (ca 5 mL) and allowed to crystallize at ambient temperature. After 2 h, first crystals started to form. After 48 h, the mother liquor was decanted from the formed large colorless crystals and the solid was washed with Et$_2$O. Drying at high vacuum gave 78 mg fac-[({dppm}$_2$CH)Re(CO)$_3$](PF$_6$)$_2$, **fac-2** (0.058 mmol, 48.3% yield) as a colorless powder. Anal. Calcd for C$_{54}$H$_{45}$F$_{12}$O$_3$P$_6$Re: C 48.33%, H 3.38%; Found: C 47.94%; H, 3.37%. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 300 K): δ = 3.95 (t, 1H, $^2J_{PH}$ = 17.9 Hz, {R$_3$P}$_2$CH-Re), 4.72 (m, 2H, P-CHH–P), 6.29 (td, 2H, $^2J_{PH}$ = 24.4 Hz, $^2J_{PH}$ = 7.3 Hz, P-CHH-P), 6.96 (m, 4H, phenyl-H), P-CHH–P), 7.03–7.13 (m, 6H, phenyl-H), 7.18–7.38 (m, 12H, phenyl-H), 7.43 (t, 2H, J_{HH} = 7.6 Hz, phenyl-H), 7.48–7.61 (m, 8H, phenyl-H), 7.70 (br dd, 4H, J = 11.4 Hz, J = 7.8 Hz, phenyl-H), 8.11 (br, 4H, phenyl-H) ppm. ^{19}F NMR (162 MHz, CD$_2$Cl$_2$, 300 K): δ = −71.76 (d, $^1J_{PF}$ = 711.8 Hz, PF$_6$) ppm. ^{31}P{^{1}H} NMR (376 MHz, CD$_2$Cl$_2$, 300 K): δ = −144.1 (sept, $^1J_{FP}$ = 712.2 Hz, PF$_6$), −0.2 (m, P-CH-P), 42.6 (m, P-Re-P) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 300 K): δ = −5.0 (t, $^1J_{PC}$ = 32.8 Hz, P-C^{CDP}-P), 26.9 (m, P-CH$_2$-P),118.7 (d, J_{PC} = 8.8 Hz, phenyl-C), 119.6 (d, J_{PC} = 9.2 Hz, phenyl-C), 119.9 (d, J_{PC} = 5.0 Hz, phenyl-C), 119.9 (d, J_{PC} = 5.0 Hz, phenyl-C), 120.6 (d, J_{PC} = 7.2 Hz, phenyl-C), 129.5 (s, phenyl-C), 129.6 (s, phenyl-C), 129.7 (d, J_{PC} = 2.3 Hz, phenyl-C), 129.7 (s, phenyl-C), 129.8 (d, J_{PC} = 6.5 Hz, phenyl-C), 130.1 (d, J_{PC} = 13.0 Hz, phenyl-C), 131.0 (s, phenyl-C), 131.3 (d, J_{PC} = 11.8 Hz, phenyl-C), 131.3 (s superimposed, phenyl-C), 132.0 (br, phenyl-C), 132.3 (d, J_{PC} = 10.3 Hz, phenyl-C), 132.6 (d, J_{PC} = 11.4 Hz, phenyl-C), 132.6 (s superimposed, phenyl-C), 134.4 (d, J_{PC} = 2.7 Hz, phenyl-C), 134.6 (d, J_{PC} = 11.8 Hz, phenyl-C), 134.8 (d, J_{PC} = 2.7 Hz, phenyl-C), 189.7 (m, Re-CO) ppm. IR (ATR): ν/cm^{-1} = 3683 (w), 3577 (w), 3057 (w), 2963 (w), 2784 (w), 2708 (w), 2032 (m, ν$_{CO}$), 1971 (s, ν$_{CO}$), 1944 (s, ν$_{CO}$), 1614 (w), 1588 (w), 1486 (w), 1436 (s), 1385 (w), 1340 (w), 1316 (w), 1271 (w), 1161 (m), 1098 (s), 1026 (w), 1000 (m), 832 (vs), 781 (s), 769 (s), 733 (vs), 683 (vs), 644 (m), 606 (s), 592 (vs), 555 (vs), 514 (vs), 500 (vs), 477 (s), 465 (s), 441 (s), 409 (s), 374 (s), 353 (s), 301 (m).

Synthesis of fac-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (fac-3) A 25 mL Schlenk tube equipped with a magnetic stirring bar and teflon valve was charged with [ReBr(CO)$_5$] (50 mg, 0.123 mmol) and 111 mg (0.120 mmol, 0.98 equiv.) of [(dppm)$_2$CH]PF$_6$ (**1**). Subsequent addition of 6 mL THF and 16 mg 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.143 mmol, 1.16 equiv.) gave rise to a clear slightly yellowish solution. The mixture was heated in the closed vessel at 65 °C. After 40 h the reaction mixture was cooled down. A yellowish solution with minor colorless solid was obtained. All solids were filtered off via a syringe filter (glas filter, 2 µm porosity). The filtrate was layered with Et$_2$O. After 24 h, large yellow crystals were formed accompanied by a minor colorless powder. The crystals were decanted from the mother liquor and washed with Et$_2$O and a minimum amount of cold THF, which removed most of the colorless substance. The

yellow crystals were dried at high vacuum to give 75 mg of the product fac-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$), **fac-3** (0.063 mmol, 51% yield based on [ReBr(CO)$_5$]). Anal. Calcd for C$_{54}$H$_{44}$F$_6$O$_3$P$_5$Re: C 54.23%, H 3.71%; Found: C 54.14%; H, 3.63%. ^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ = 3.70-3.77 (m, 2H, P-CHH-P), 3.90–4.00 (m, 2H, P-CHH-P), 7.02 (t, 4H, J_{HH} = 7.5 Hz, phenyl-H), 7.06 (dd, 4H, J_{HH} = 11.9 Hz, J_{HH} = 6.7 Hz, phenyl-H), 7.13 (t, 4H, J_{HH} = 7.2 Hz, phenyl-H), 7.24 (t, 6H, J_{HH} = 8.7 Hz, phenyl-H), 7.26–7.32 (m, 2H, phenyl-H), 7.35–7.45 (m, 6H, phenyl-H), 7.49-7.62 (m, 10H, phenyl-H), 7.84 (dd, 4H, J_{HH} = 13.1 Hz, J_{HH} = 7.2 Hz, phenyl-H) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$, 300 K): δ = −144.4 (sept, $^1J_{FP}$ = 710.9 Hz, PF$_6$), 1.4 (m, P-Re-P), 24.3 (m, P-Re-P) ppm. ^{19}F NMR (376 MHz, CD$_2$Cl$_2$, 300 K): δ = −72.97 (d, $^1J_{PF}$ = 711.2 Hz, PF$_6$) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 300 K): δ = −5.7 (t, $^1J_{PC}$ = 93.4 Hz, P-C^{CDP}-P), 36.1–37.3 (m, P-CH$_2$-P), 128.3 (s, phenyl-C), 129.3 (t, J_{PC} = 6.1 Hz, phenyl-C), 129.4–192.6 (superimposed, phenyl-C), 131.1 (t, J_{PC} = 5.4 Hz, phenyl-C), 131.4 (t, J_{PC} = 54.3 Hz, phenyl-C), 132.5 (t, J_{PC} = 4.9 Hz, phenyl-C), 132.5-132.6 (superimposed, phenyl-C), 132.6 (s, phenyl-C), 132.7 (s, phenyl-C), 133.0 (t, J_{PC} = 5.9 Hz, phenyl-C), 133.2 (d, J_{PC} = 4.9 Hz, phenyl-C), 133.4 (s, phenyl-C), 133.4 (br, phenyl-C), 133.6 (superimposed, phenyl-C), 133.7 (t, J_{PC} = 2.4 Hz, phenyl-C), 133.7-133.9 (superimposed, phenyl-C), 134.0 (t, J_{PC} = 2.4 Hz, phenyl-C), 134.1 (s, phenyl-C), 149.1 (d, J_{PC} = 63.1 Hz, phenyl-C), 191.9 (dd, $^2J_{PC}$ = 63.8 Hz, $^2J_{PC}$ = 14.4 Hz, Re-CO), 192.8 (t, $^2J_{PC}$ = 8.8 Hz, Re-CO) ppm. IR (ATR): ν/cm^{-1} = 2010 (s, ν$_{CO}$), 1933 (s, ν$_{CO}$), 1893 (s, ν$_{CO}$),1483 (w), 1435 (s), 1176 (m), 1139 (m), 1097 (m), 999 (w), 828 (s), 809 (s), 778 (m), 764 (m), 732 (s), 711 (m), 687 (s), 613 (m), 593 (m), 556 (s), 532 (m), 519 (s), 499 (s), 478 (m), 468 (m), 444 (m), 427 (m), 405 (m).

Synthesis of mer-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$) (mer-3) A 5 mm NMR tube equipped with a teflon valve was charged with fac-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$), **fac-3** (44 mg, 0.037 mmol) dissolved in 0.7 mL CH$_2$Cl$_2$. The solution was exposed to UV light from a 150 W mercury-vapor discharge lamp and the reaction was occasionally monitored by ^{31}P{^{1}H} NMR spectroscopy. After 12 h of irradiation, quantitative conversion was concluded on the basis of the ^{31}P{^{1}H} NMR spectrum of the reaction mixture. The tube was opened and the solution was decanted into a 20 mL glass vial. All volatiles were slowly evaporated in a stream of argon to give 35 mg of the desired product, mer-[({dppm}$_2$C)Re(CO)$_3$](PF$_6$), **mer-3**, as a microcrystalline compound (0.029 mmol, 79% yield). Anal. Calcd for C$_{54}$H$_{44}$F$_6$O$_3$P$_5$Re: C 54.23%, H 3.71%; Found: C 53.83%; H, 3.46%. ^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ = 4.33 (m, 4H, P-CH$_2$-P), 7.20 (t, 8H, J_{HH} = 7.6 Hz, phenyl-H), 7.25–7.32 (m, 8H, phenyl-H), 7.33–7.41 (m, 16H, phenyl-H), 7.48-7.55 (m, 8H, phenyl-H) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$, 300 K): δ = −144.4 (sept, $^1J_{FP}$ = 711.0 Hz, PF$_6$), 10.7 (t, J_{PP} = 37.6 Hz, P-Re-P), 30.0 (t, J_{PP} = 37.8 Hz, P-Re-P) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 300 K): δ = −19.9 (t, $^1J_{PC}$ = 81.2 Hz, P-C^{CDP}-P), 43.9-45.4 (m, P-CH$_2$-P), 129.1 (t, J_{PC} = 5.8 Hz, phenyl-C), 129.3 (t, J_{PC} = 5.3 Hz, phenyl-C), 131.2 (s, phenyl-C), 131.6 (t, J_{PC} = 6.5 Hz, phenyl-C), 132.7 (s, phenyl-C), 133.1 (t, J_{PC} = 5.1 Hz, phenyl-C), 134.5 (d, J_{PC} = 10.7 Hz, phenyl-C), 135.5 (t, J_{PC} = 24.4 Hz, phenyl-C), 191.7 (t, $^2J_{PC}$ = 8.8 Hz, Re-CO), 191.9 (t, $^2J_{PC}$ = 6.5 Hz, Re-CO) ppm. IR (ATR): ν/cm^{-1} = 2053 (w, ν$_{CO}$), 1942 (s, ν$_{CO}$), 1868 (s, ν$_{CO}$),1588 (w), 1483 (w), 1435 (s), 1366 (w), 1311 (w), 1160 (m), 1148 (m), 1098 (s), 1127 (w), 999 (m), 877 (w), 832 (vs), 769 (s), 736 (vs), 690 (vs), 620 (m), 614 (s), 583 (m), 556 (vs), 522 (s), 506 (s), 481 (s), 465 (s), 434 (m), 416 (m).

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

[1] G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597–614.

[2] R. Tonner, G. Frenking, *Chem. A Eur. J.* **2008**, *14*, 3260–3272.

[3] R. Tonner, G. Frenking, *Chem. A Eur. J.* **2008**, *14*, 3273–3289.

[4] R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem. Int. Ed.* **2006**, *45*, 8038–8042; *Angew. Chem.* **2006**, *118*, 8206–8211.

[5] M. A. Celik, G. Frenking, B. Neumüller, W. Petz, *ChemPlusChem* **2013**, *78*, 1024–1032.

[6] W. Petz, G. Frenking, in *Top. Organomet. Chem. 30* (Eds.: R. Chauvin, Y. Canac), **2010**, pp. 49–92.

[7] W. Su, S. Pan, X. Sun, S. Wang, L. Zhao, G. Frenking, C. Zhu, *Nat. Commun.* **2018**, *9*, 4997.

[8] L. Zhao, C. Chai, W. Petz, G. Frenking, *Molecules* **2020**, *25*, 4943.

[9] K. Flosdorf, D. Jiang, L. Zhao, B. Neumüller, G. Frenking, I. Kuzu, *Eur. J. Inorg. Chem.* **2019**, *2019*, 4546–4554.

[10] W. Petz, G. Frenking, in *Top. Organomet. Chem. 30* (Eds.: R. Chauvin, Y. Canac), **2010**, pp. 49–92.

[11] W. Petz, *Coord. Chem. Rev.* **2015**, *291*, 1–27.

[12] L. Maser, C. Schneider, L. Vondung, L. Alig, R. Langer, *J. Am. Chem. Soc.* **2019**, *141*, 7596–7604.

[13] L. Vondung, P. Jerabek, R. Langer, *Chem. A Eur. J.* **2019**, *25*, 3068–3076.

[14] W. Xu, L. Maser, L. Alig, R. Langer, *Polyhedron* **2021**, *196*, 115018.

[15] J. Sundermeyer, K. Weber, K. Peters, *Organometallics* **1994**, *13*, 2560–2562.

[16] R. Tonner, G. Frenking, *Chem. Commun.* **2008**, *1*, 1584–1586.

[17] R. Ambre, H. Yang, W. C. Chen, G. P. A. Yap, T. Jurca, T. G. Ong, *Eur. J. Inorg. Chem.* **2019**, *2019*, 3511–3517.

[18] Y. C. Hsu, V. C. C. Wang, K. C. Au-Yeung, C. Y. Tsai, C. C. Chang, B. C. Lin, Y. T. Chan, C. P. Hsu, G. P. A. Yap, T. Jurca, et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 4622–4626; *Angew. Chem.* **2018**, *130*, 4712–4716.

[19] A. El-Hellani, C. Bour, V. Gandon, *Adv. Synth. Catal.* **2011**, *353*, 1865–1870.

[20] C. C. Roberts, D. M. Matías, M. J. Goldfogel, S. J. Meek, *J. Am. Chem. Soc.* **2015**, *137*, 6488–6491.

[21] M. J. Goldfogel, C. C. Roberts, S. J. Meek, *J. Am. Chem. Soc.* **2014**, *136*, 6227–6230.

[22] C. Reitsamer, W. Schuhe, H. Kopacka, K. Wurst, P. Peringer, *Organometallics* **2009**, *28*, 6617–6620.

[23] G. J. Partl, F. Nussbaumer, I. Schlapp-Hackl, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Acta Crystallogr. Sect. E* **2018**, *74*, 846–852.

[24] I. Schlapp-Hackl, B. Pauer, C. Falschlunger, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Acta Crystallogr. Sect. E* **2018**, *74*, 1643–1647.

[25] B. Pauer, G. J. Partl, S. Oberparleiter, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Acta Crystallogr. Sect. E* **2019**, *75*, 179–184.

[26] I. Schlapp-Hackl, C. Falschlunger, K. Zauner, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Acta Crystallogr. Sect. E* **2019**, *75*, 12–20.

[27] C. Reitsamer, S. Stallinger, W. Schuh, H. Kopacka, K. Wurst, D. Obendorf, P. Peringer, *Dalton Trans.* **2012**, *41*, 3503–3514.

[28] S. Stallinger, C. Reitsamer, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Chem. Commun.* **2007**, *012*, 510–512.

[29] C. Reitsamer, I. Hackl, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *J. Organomet. Chem.* **2017**, *830*, 150–154.

[30] Y. Li, L. Maser, L. Alig, Z. Ke, R. Langer, *Dalton Trans.* **2021**, *50*, 954–959.

[31] L. Maser, P. Korzeniowski, R. Langer, *Can. J. Chem.* **2020**, DOI 10.1139/cjc-2020–0351.

[32] L. Maser, J. Herritsch, R. Langer, *Dalton Trans.* **2018**, *47*, 10544–10552.

[33] L. Maser, C. Schneider, L. Alig, R. Langer, *Inorganics* **2019**, *7*, 61.

[34] K. Sommer, *Z. Anorg. Allg. Chem.* **1970**, *376*, 37–43.

[35] C. Reitsamer, S. Stallinger, W. Schuh, H. Kopacka, K. Wurst, D. Obendorf, P. Peringer, *Dalton Trans.* **2012**, *41*, 3503.

[36] S. P. Schmidt, W. C. Trogler, F. Basolo, M. A. Urbancic, J. R. Shapley, *Inorg. Synth.* **1990**, *28*, 160–165.