Two novel rhenium(i) phosphinine complexes \([\text{Re(CO)}_3\text{Cl(C}_5\text{H}_4\text{ClP)}_2]\) and \([\text{Re(CO)}_2\text{Cl(C}_5\text{H}_4\text{ClP)}_3]\) were synthesized and the relative stabilities of both complexes 1 and 2.

**Introduction**

Heteroarenes of the type \(\text{C}_x\text{H}_y\text{E} (\text{E} = \text{N, P, As, Sb, Bi})\) have found widespread interest and various applications over the years.\(^1\)-\(^4\) Particularly the ambidentate character of pyridines, phosphinines and their derivatives, which enables them to bind metals either via the heteroatom in \(\eta^1\) or the \(\pi\)-system in \(\eta^6\) coordination, helped to establish this versatile class of ligands in organometallic chemistry.\(^3\)-\(^7\) The synthesis of the first phosphinine derivative was described by Märkl in 1966.\(^8\) However, only when Le Floch and Mathey reported more convenient synthetic methodologies, did functionalized phosphinines become more easily accessible.\(^9\)-\(^11\) Various coordination modes of phosphinines and their derivatives to numerous transition metals as well as their application in homogeneous catalysis have been reported since.\(^1\)-\(^4\),\(^12\)-\(^20\) Recently, Mathey et al. and Amouri et al. have described copper and gold complexes featuring phosphinine derivatives with interesting structural motifs and possible catalytic and electronic utilization.\(^21\),\(^22\)

Although potential implementation of phosphinine transition metal complexes in homogeneous catalysis has been discussed in the literature, to the best of our knowledge, electron rich rhenium(i) complexes featuring \(\eta^1\)-coordinated phosphinines have not been reported in more detail, despite the scattered mentioning of such compounds.\(^4\),\(^6\)-\(^23\) The facile synthesis and characterization of two novel rhenium(i) complexes \(\text{cis-}[\text{Re(CO)}_3\text{Cl(}\eta^1\text{-C}_5\text{H}_4\text{ClP)}_2]\) (1) and \(\text{mer-[Re(CO)}_2\text{Cl(}\eta^1\text{-C}_5\text{H}_4\text{ClP)}_3]\) (2) are reported in this work.

**Results and discussion**

Reaction of \([\text{Re(CO)}_3\text{Cl}]\) with 2.5 eq. 2-chlorophosphine in refluxing toluene results in a bright yellow solution, which upon removal of the solvent yields the crude product as a yellow solid. Subsequent crystallization from \(\text{CH}_2\text{Cl}_2/\text{pentane}\) leads to bright yellow crystals of 1 in quantitative yield (based on the Re precursor, Scheme 1).

Complex 1 was characterized by NMR and IR spectroscopy, elemental analysis and single crystal X-ray diffraction. 1 is soluble in chloroform, toluene and benzene, but insoluble in diethyl ether and \(\eta\)-pentane. In solution, only one set of resonances is observed at room temperature in \(\text{H}, \text{C})\) and \(31\text{P}\) spectra of 1. \(31\text{P}\) spectrum shows a highfield shift of the phosphorus signal from 201.9 ppm (free ligand) to a broad signal at 169.4 ppm in 1. \(31\text{P}\) coupling, which could confirm \(\text{cis}\) coordination of the ligands is not observed. A VT-NMR study revealed significant broadening of the signal at elevated temperatures, while a sharp singlet is obtained at lower temperatures.\(^24\) Decoalescence is not
observed. This might be due to a fast dynamic equilibrium, since only one set of phosphinine signals is observed in $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra. The molecular structure of 1 is shown in Fig. 1. The phosphinine ligands are arranged in cis position with trans positioned CO ligands in an overall distorted octahedral geometry. This arrangement explains the chemical equivalency of the two phosphinine rings in solution. Re–P bond lengths of 2.4154(13) and 2.4120(12) Å in compound 1 are similar, yet slightly shorter compared to Re–P bond lengths in the related complex mer-[Re(CO)$_3$Cl(PEt$_3$)$_2$] with 2.430(1) Å. Shorter bond lengths in compound 1 indicate – as previously mentioned – π back-bonding character in electron rich transition metal complexes featuring phosphinine ligands.

The carbonyl vibrations in the IR spectra show a shift from $v_{\text{CO}} = 1983, 2046, 2155$ cm$^{-1}$ in the precursor [Re(CO)$_5$Cl] to $v_{\text{CO}} = 1945, 1992, 2046$ cm$^{-1}$ in complex 1, illustrating the σ-donating character of the phosphinine and the chlorido ligands.$^{25,26}$ The shift to lower wavenumbers in 1 is expected since carbonyls are known to be strong π-acceptors, while phosphinines act both as σ-donors and π-acceptors. The removal of two carbonyls during the formation of 1 additionally influences the remaining carbonyl shifts. In comparison to the related mer-[Re(CO)$_3$Cl(PEt$_3$)$_2$] ($v_{\text{CO}} = 1887, 1940, 2045$ cm$^{-1}$), the phosphinine ligands in 1 exhibit significantly lower σ-donor and higher π-acceptor capabilities than the triethylphosphine ligands.$^{25}$

Further addition of 2-chlorophosphinine to compound 1 and subsequent refluxing in toluene leads to the formation of complex 2 as byproduct in yields up to 15% (based on complex 1; Scheme 2).

Complex 2 was characterized by NMR and IR spectroscopy, elemental analysis and single crystal X-ray diffraction. Solubility of 2 is analogous to 1. Complexes 1 and 2 were separated via crystallization from CH$_2$Cl$_2$/n-pentane with complex 2 crystallizing as dark yellow crystals, similar to 1 in a distorted octahedral geometry (Fig. 2). The three η$^1$-coordinated phosphinines are arranged in a meridional structural motif, resulting in two phosphinines in trans position. This arrangement is to be expected, since 2-chlorophosphinine ligands are relatively bulky and the highest degree of freedom is presented in mer- rather than fac-coordination. In solution, two sets of signals are observed in $^{1}H$, $^{13}C$ and $^{31}P$ spectra of 2. Proximity of two sets of chemically not equivalent phosphorus heteroatoms results in a high multiplicity of resonances. The $^{31}P$ spectrum of compound 2 shows a less pronounced highfield shift of the phosphorus signals of the axial phosphinine (173.1 ppm) and of the two equatorial phosphinines (173.3 ppm), compared to the free 2-chlorophosphinine ligand (201.9 ppm) and to compound 1 (169.4 ppm). Both observed signals are broad, comparable to the situation observed for complex 1. The signal at 173.3 ppm corresponds to a pseudo doublet with a $^{3}J_{P-P}$ coupling constant of 190 Hz for the trans standing phosphinines. Cis coupling was not observed for

---

**Scheme 2** Synthesis of complex 2.

---

**Fig. 1** ORTEP style drawing of 1. Thermal ellipsoids are given at a 50% probability level. Selected bond lengths (Å) and angles (deg): Re1–P1, 2.4154(13); Re1–P2, 2.4120(12); Re1–Cl1, 2.4932(11); Re1–C1, 1.922(5); Re1–C2, 1.964(5); Re1–C3, 1.962(6); P1–Re1–P2, 89.66(4); C1–Re1–P1, 10.72(4); Cl1–Re1–P2, 85.42(4); P1–Re1–C3, 89.32; P2–Re1–C2, 89.74(14).

---

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.
either phosphinite ligand due to the broadness of the signals. The observed NMR data correspond well to the coordination geometry determined by single crystal X-ray diffraction.

Rhenium–phosphorus bond length Re–P1 of complex 2 differs considerably from the trans-positioned Re–P2 and Re–P3 bond lengths. The Re–P1 bond length with 2.4258(10) Å is similar, but slightly longer than the Re–P bond distances in complex 1. The trans-arranged phosphinites in compound 2, however, show shorter bond distances for Re–P2 (2.3584(13) Å) and Re–P3 (2.3508(15) Å) than previously reported bond distances. Absence of a trans-positioned carbonyl ligand, which appears to be a stronger π-acceptor than phosphinite, possibly influences the bond distances due to relatively stronger π-backbonding for both phosphinites. These findings suggest strong σ-donor as well as π-acceptor character of the phosphinite ligands, which also has been noted before for other systems.27–29

The carbonyl vibrations in the IR spectra show a strong shift from \(v_{CO} = 1983, 2046, 2155 \text{ cm}^{-1}\) of the precursor [Re(CO)_5Cl] to \(v_{CO} = 1924, 1965 \text{ cm}^{-1}\) of complex 2, illustrating again the pronounced σ-donating character of the phosphinite and the chlorido ligand.25,26 The shift from \(v_{CO} = 1945, 1992, 2046 \text{ cm}^{-1}\) of 1 to \(v_{CO} = 1924, 1965 \text{ cm}^{-1}\) of 2 further supports the more pronounced σ-donating character of phosphinite ligands compared to carbonyls, resulting in increased back-bonding of the metal center to the remaining carbonyl ligands. In comparison to the related mer-Re(CO)_5Cl[P(OEt_3)]_3 (\(v_{CO} = 1969, 1980 \text{ cm}^{-1}\)), the phosphinite ligands in 2 exhibit slightly higher σ-donor and lower π-acceptor abilities than the triethylphosphate ligands.30 However, compared to mer-Re(CO)_5Cl[PPh(OEt_3)]_3 (\(v_{CO} = 1873, 1985 \text{ cm}^{-1}\)), the phosphinite ligands in 2 exhibit slightly lower σ-donor and higher π-acceptor capabilities than the phosphinite ligands.30 This difference indicates that phosphinite ligands generally show π-backbonding character, with phosphinite ligands having a slightly more pronounced effect than phosphinite ligands.

DFT calculations

In order to gain more detailed information on complex 1 and 2 and π-acceptor properties of the 2-chlorophosphinite ligands, gas phase DFT calculations were carried out on a B3LYP/6-31G** theory level. Detailed calculated bond lengths and angles can be found in the ESI† and correspond well to data obtained from the crystal structures. Calculated IR shifts correspond well to observed shifts.

In Fig. 3 calculated frontier orbitals of complex 1 are depicted. HOMO (Highest Occupied Molecular Orbital) as well as HOMO–1 of complex 1 are located mainly at the Re atoms, the carbonyl and chlorido ligands (Fig. 3, bottom). As mentioned before, complex 1 has a distorted octahedral geometry. The hardly overlapping HOMO and HOMO–1 are perpendicular to each other and have similar energy levels, HOMO – 6.46 eV and HOMO–1 – 6.47 eV, respectively. The calculated energy gap of the gas phase supports the experimental findings that both orbitals are degenerate in solution (the molecule has not been restricted to a certain point group).31 LUMO (Lowest Unoccupied Molecular Orbital) and LUMO+1, on the other hand, are each located at one phosphinite ligand (Fig. 3, top). The LUMO at – 2.48 eV and LUMO+1 at – 2.45 eV are perpendicular to each other with very minor overlap. The energy gap of \(\Delta E = 0.03 \text{ eV}\) in the gas phase calculation implies a nearly degenerate character of both. Complex 1 has
a calculated HOMO–LUMO gap of \( \Delta E = 3.98 \text{ eV} \), suggesting high kinetic stability.

Calculated frontier orbitals of complex 2 are depicted in Fig. 4. The HOMO of complex 2 (at \(-6.06 \text{ eV}\)) is located mainly at the Re atom, the carbonyl and chlorido ligands (Fig. 4, bottom). HOMO–1 (at \(-6.13 \text{ eV}\)) on the other hand, is 0.07 eV lower than the HOMO and is located not only on the Re atom, the carbonyl and chlorido ligands, but also partly on the phosphinine rings. The difference was to be expected, since the phosphinine ligands are chemically not equivalent, which is also evident from NMR spectra and single crystal X-ray diffraction. LUMO at \(-2.24 \text{ eV}\) and LUMO+1 at \(-2.18 \text{ eV}\) are located mainly at the phosphinine ligands (Fig. 4, top). The energy gap between the LUMOs of \( \Delta E = 0.05 \text{ eV} \) is slightly smaller than the gap between the HOMOs of \( \Delta E = 0.07 \text{ eV} \). The higher energy difference in complex 2 between HOMO and HOMO–1 as well as LUMO and LUMO+1 originates from both differently shaped orbitals and location on different complex fragments, corresponding well with the solution-NMR spectra. The HOMO–LUMO gap of complex 2 (\( \Delta E = 3.82 \text{ eV} \)) is slightly smaller than the gap in complex 1 (\( \Delta E = 3.98 \text{ eV} \)), indicating slightly higher kinetic stability of 1.

Natural bond order analysis is used to qualitatively estimate the character of the coordinative bonds and the resulting \( \pi \)-effects.\(^{12-38} \) The relevant compositions of the orbitals are listed in Tables S1–S3† for the precursor [Re(CO)\(_5\)Cl], 1 and 2, respectively. The results show that in the precursor the strongest \( \pi \) back-bonding contribution of rhenium of 33% is directed toward the carbonyl ligand \( \text{trans} \) to chloride. This is to be expected, since chlorido ligands are effectively \( \sigma \)-donor ligands. It has to be noted, however, that even the Re–Cl bond shows \( \pi \) back-bonding character of 25% according to the calculations. The chemically equivalent four Re–C bonds in the plane show a calculated \( \pi \) back-bonding character of rhenium to carbon of 30% each. In 1 the highest contribution of rhenium of 33% is again directed to the carbonyl \( \text{trans} \) to chloride. However, the carbonyl ligands \( \text{trans} \) to the phosphinine ligands show a rather similar \( \pi \) back-bonding interaction at just below 33%. The Re–Cl bond has a calculated \( \pi \) back-bonding character of 23% in 1 and a rather high \( \pi \) back-bonding character of 28% for the Re–P bonds, indicating a stronger \( \pi \)-acceptor character of phosphinines compared to chloride, but a weaker \( \pi \)-acceptor character compared to carbonyl. Accordingly the strongest \( \pi \) back-bonding of 34% is calculated for the carbonyl \( \text{trans} \) to the chlorido ligand in complex 2. The Re–P bond \( \text{trans} \) to carbonyl shows a slightly better back-bonding of 29% compared to complex 1. However, the \( \pi \) back-bonding character of the Re–P bonds \( \text{trans} \) to each other is calculated to be 32% comparable to carbonyl ligands, confirming the \( \pi \)-acceptor character of phosphinines. The rhenium contribution to the Re–Cl \( \pi \) back-bonding is 23% in 2. In case of rhenium, chloride and phosphor s, p and d orbitals are involved in the bond, in case of carbon only s and p orbitals contribute to the bond. The general trend of increased metal-to-ligand back-bonding is due to the step-wise removal of carbonyl ligands and addition of the \( \sigma \)-donor phosphinine, resulting in an overall higher electron density at the rhenium center.

Theoretical investigations on the two different coordination modes of complex 1 also support the higher thermodynamic stability of the \( \text{cis} \) configuration with a lower ground state free energy \( \Delta G \) (12.9 kJ mol\(^{-1}\)) compared to the \( \text{trans} \) configuration. In case of complex 2 the \( \text{meridional} \) configuration has a lower ground state free energy \( \Delta G \) (33.1 kJ mol\(^{-1}\)) compared to the \( \text{facial} \) configuration, which can be explained with steric hindrance of the bulky phosphorus heterocycles.

**Conclusions**

Reaction of [Re(CO)\(_5\)Cl] with 2-chlorophosphinine in refluxing toluene leads to complex 1. Subsequent addition of free ligand 2-chlorophosphinine to 1 and repeated refluxing in toluene leads to formation of complex 2. To the best of our knowledge, complexes 1 and 2 are so far the first rhenium(1) phosphinine complexes with \( \eta^1 \)-coordination. A combined analysis of NMR and IR spectroscopic data and single crystal X-ray data reveals both \( \sigma \)-donor and \( \pi \)-acceptor properties of the phosphinine ligand. The shape and energetic position of the highest
occupied and lowest unoccupied molecular orbitals of 1 and 2 gives information on relative stabilities. NBO analysis was carried out to better understand the π back-bonding situation in 1 and 2.

Experimental

General comments

All reactions were performed under an atmosphere of dry argon in oven-dried glassware using standard Schlenk technique. All solvents were purified and dried by standard methods. Commercially available reagents were used without further purification. [Dichloromethyl]dichlorophosphine oxide,39,40 (dichloromethyl)dichlorophosphine sulfide,41 [dichloromethyl]dichlorophosphine41,42 and 2-chlorophosphinines43–46 were synthesized according to literature procedures. NMR spectra were obtained using Bruker AV360 and Bruker AV500 spectrometers. Signals were referenced to residual solvent signals. 31P spectra are proton decoupled for clarity reasons. Elemental analyses were performed in the microanalytical laboratory of Technische Universität München.

DFT calculations

All calculations were performed with GAUSSIAN-09 47 using the density functional/Hartree–Fock hybrid model Becke3LYP44–46 and the split valence double-ζ (DZ) basis set 6-31+G**. 47–50 Re atoms were described with a Stuttgart 1997 ECP with a DZ description of the valence electrons.49 No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. XYZ coordinates for all calculated compounds can be found in the ESL.†

Synthesis of cis-[Re(CO)3Cl(η1-C5H4CIP)] (1)

2-Chlorophosphine (91.0 mg, 0.69 mmol, 2.50 eq.) was added to a suspension of [Re(CO)3Cl] (100 mg, 0.28 mmol, 1.00 eq.) in 3 mL toluene in a Schlenk tube. The mixture was heated to reflux for 4 h. After some time the mixture turned yellow and the precursor dissolved gradually. After 4 h the solution was allowed to cool down to rt and toluene was removed in vacuo, crystallization from CH2Cl2/pentane afforded 1 as yellow crystals in addition to dark yellow crystals of 2. (Yield 27.8 mg, 15%) 1H NMR (CDCl3): δ = 8.85 (dd, 1JH6-p = 20.4 Hz, 1JH6-H15 = 10.2 Hz, 1JH6-H2 = 1H), 8.57 (qd, 1JH6-H15 = 10.1 Hz, 1JH6-H4 = 1.3 Hz, 2H), 7.97 (q, 1JH6-H15 = 7.9 Hz, 2H), 7.84 (m, 4H), 7.37 (t, 1JH6-H4 = 8.2 Hz, 1H), 7.31 (dt, 1JH6-H15 = 7.4 Hz, 1JH6-H4 = 3.5 Hz, 2H), 13C NMR (CDCl3): δ = 189.33 (dd, 1JPC-C = 75 Hz, 1JPC-P = 11 Hz, CO), 186.19 (m, CO), 156.21 (dt, 1JPC-C = 26.2 Hz, 1JPC-C = 2.7 Hz, Clar), 154.69 (td, 1JPC-C = 18.3 Hz, JPC-P = 3.1 Hz, Clar), 145.73 (m, Clar), 138.39 (m, Clar), 136.21 (t, JPC-C = 7.6 Hz, Clar), 135.8 (d, 1JPC-C = 16.9 Hz, Clar), 128.74 (t, JPC-C = 24.3 Hz, Clar), 127.7 (d, JPC-C = 12.7 Hz, Clar). 31P NMR (CDCl3): δ = 173.1 (ps, 1P), 173.3 (pd, 1JPC-P = 190 Hz, 2P). IR (ATR) ν [cm−1]: 1655, 1628, 1292, 1265, 1182, 1138, 1130, 939, 910, 872, 864, 814, 731, 715, 669, 602, 582. UV/vis (CH2Cl2): λmax [nm] (ε × 103 [L mol−1 cm−1]) = 394 (8.3), 335 (12.7). Anal. calc. for C12H12Cl2O2P3Re (669.22): C, 30.51; H, 1.78. Found: C, 30.27; H, 1.71.

Notes and references


Communication

21 Y. Mao, K. M. H. Lim, Y. Li, R. Ganguly and F. Mathey, Organometallics, 2013, 32, 3562.
24 See ES1 for VT-NMR spectra.