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Bimetallic complexes
V. [1] Synthesis and reactions of $C_5H_4PPh_2$-bridged zirconium-rhenium complexes

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Abstract

Bimetallic Zr–Re complexes with bridging $C_5H_4PPh_2$ ligands (henceforth abbreviated as Cp′) are accessible from the mononuclear zirconocene dichloride Cp'_2ZrCl_2 (**1**) and reactive rhenium complexes. The attempted synthesis of a cationic complex from **1** and $[Re(CO)_3(NCMe)_3]BF_4$ resulted in the formation of the zirconium-free compound $[ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)]$ (**2**). **2** is apparently formed by cleavage of the Cp′–Zr bonds followed by intramolecular Diels–Alder addition. The compound was fully characterized including an X-ray crystal structure determination of the $CDCl_3$ solvate (triclinic, space group $P\bar{1}$ (No. 2), $a = 945.1(5)$ pm, $b = 1113.9(6)$ pm, $c = 1888.5(10)$ pm, $\alpha = 92.36(3)°$, $\beta = 89.98(3)°$, $\gamma = 113.49(2)°$, $V = 1.821(2) \times 10^9$ pm^3, $Z = 2$). **1** and the highly reactive 'salt' $[Re(CO)_5FBF_3]$ give the mono-bridged ionic complex $[Cp'Cl_2Zr(\mu\text{-}Cp')Re(CO)_5]BF_4$ (**3**). The doubly Cp′-bridged complex $[Cp'_2Cl_2ZrReCl(CO)_3]$ (**4**) may be obtained from **1** and either $[Re(CO)_5Cl]$ or, more cleanly, $[Re_2(\mu\text{-}Cl)_2(CO)_6(THF)_2]$. Reaction of **4** with a stoichiometric amount of $LiAlH_4$ gives the bridging hydride complex $[Cp'_2ClZr(\mu\text{-}H)ReH(CO)_3]$ (**5**). From **5** and NaSMe the analogous methyl thiolate complex **6** was obtained in an NMR tube experiment. Reduction of **4** using sodium amalgam produces the dark blue-green complex $[Cp'_2ClZr\text{-}Re(CO)_3]$ (**7**) which contains a direct Zr–Re bond. Addition of HCl across this polar metal–metal bond gives two isomeric hydrides $[Cp'_2Cl_2ZrReH(CO)_3]$ (**8a**, **b**) in a 1:1 ratio and with *fac* and *mer* coordination geometries around rhenium, respectively. © 1998 Elsevier Science S.A.

Keywords: Bimetallic complexes; Hydride; Metal–metal bonds; Rhenium; Zirconium

1. Introduction

In our previous work on $C_5H_4PPh_2$-bridged binuclear complexes [1–3] we have described several attempts to construct reactive species which would rapidly add and transform small, polar substrate molecules. The various approaches included (a) ligand addition to M–(μ-Cl)–M′-bridged complexes (M = Ti, Zr; M′ = Mo, W) [2], (b) coupling of zirconium-bound methyl groups with tungsten-bound nitrile ligands [3], and (c) addition and insertion reactions of binuclear zirconium(II) cyclohexyne complexes [1]. It was hoped that an extension of this work to include binuclear zirconium–rhenium complexes might open up further opportunities to discover new types of reactions: (a) Cationic compounds isoelectronic to the known zirconium–tungsten complexes [2] should readily undergo nucleophilic addition at either the rhenium atom itself or at a rhenium-bound carbonyl group; (b) Zr(IV)–Re(I) complexes should be readily reducible to metal–metal bonded Zr(III)–Re(0) compounds which in turn might be expected to undergo 1,2-addition reactions.

2. Results and discussion

At room temperature, tris(acetonitrile)tricarbonylrhenium-tetrafluoroborate [4] did not react with bis(diphenyl-phosphinocyclopentadienyl)zirconium dichloride (**1**) [5]. Upon prolonged heating to 80°C a

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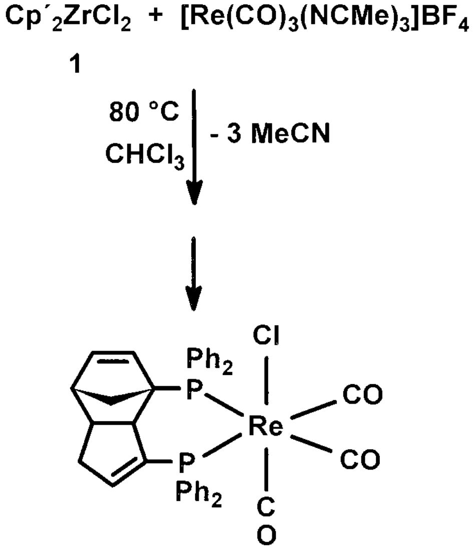
[1] For Part III, see Ref. [1].

slow reaction could be observed, the only isolable product, however, was the mononuclear complex **2** which obviously resulted from Zr–Cp′ bond cleavage followed by Diels–Alder dimerization of the two cyclopentadienyl groups (Eq. (1)). Similar observations were made when (norbornadiene)tetracarbonylrhenium [6] or (mesitylene)tricarbonylrhenium salts [7] were used instead.



2

(1)

Compound **2** is an off-white crystalline compound which is readily soluble in all common organic solvents except aliphatic hydrocarbons. Its ^{1}H-NMR spectrum is very similar to those of the analogous $M(CO)_4$ (M = Cr, Mo) complexes [8,9]. The two phosphorus nuclei are nonequivalent and give two widely separated doublet resonances in the ^{31}P-NMR spectrum. Unambiguous proof of the identity of **2** came from a X-ray structure determination of the $CDCl_3$ solvate (Fig. 1).

The coordination geometry of the Re atom is almost perfectly octahedral. The Re–Cl and Re–P distances are within the normal range, the Re–C(1) bond *trans* to the Cl ligand is, as expected, distinctly shorter than Re–C(2) and Re–C(3), *trans* to P (Table 1). The P(1)–Re–P(2) angle is only slightly larger than the P–Mo–P angle in the analogous molybdenum complex (89.4°) [8], and even the tricyclic C_{10} skeletons of the two compounds are almost superimposable.

2 may well arise from the decomposition of a binuclear Zr–Re complex which, unexpectedly, was too unstable to survive the relatively harsh reaction conditions. Thus, a more reactive source of coordinatively unsaturated rhenium carbonyl cations had to be sought. Indeed, the weakly coordinated 'salt' $[Re(CO)_5FBF_3]$ which is readily obtained in situ from $[Re(CO)_5CH_3]$ and HBF_4 [10–12], upon reaction with **1** gave the mono-bridged binuclear complex **3** (Eq. (2)) in quantitative yield.

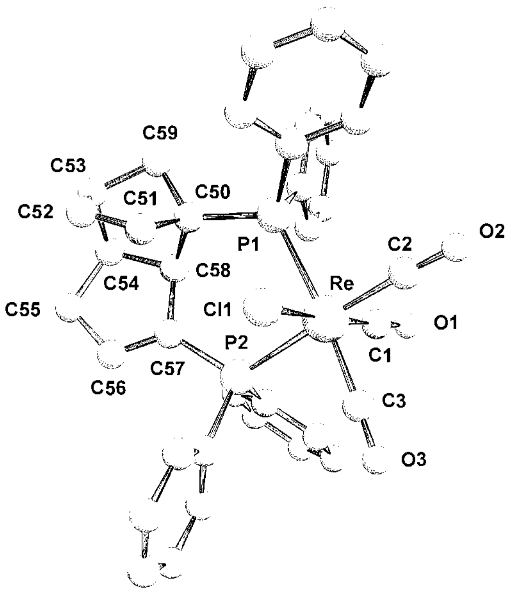
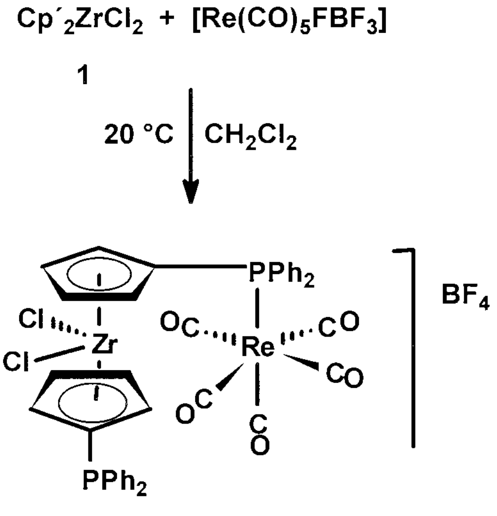


Fig. 1. Molecular structure and partial atomic numbering scheme for $[ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)]$ (**2**).



3

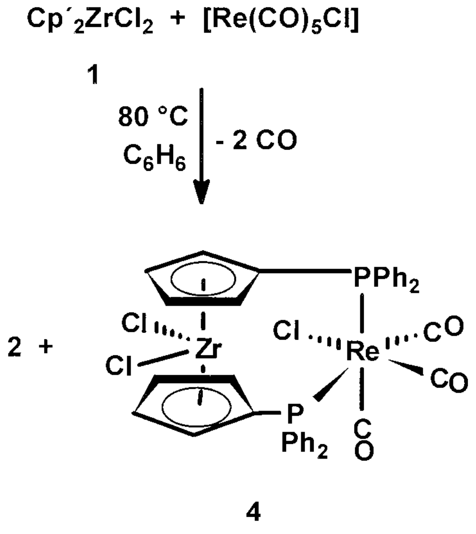
(2)

3 is a colourless crystalline compound which is soluble only in polar organic solvents. Its infrared spectrum in the ν(CO) region exhibits the typical pattern of a cationic $Re(CO)_5$ complex. The ^{31}P-NMR spectrum of **3** consists of two singlets, one with a chemical shift close to that of **1** and the other one slightly downfield at -5.0 ppm which is typical of a Re-bound PPh_2R ligand (Table 2).

Table 1
Selected bond distances (pm) and angles (°) for $[ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)]*CDCl_3$ (**2**$*CDCl_3$)

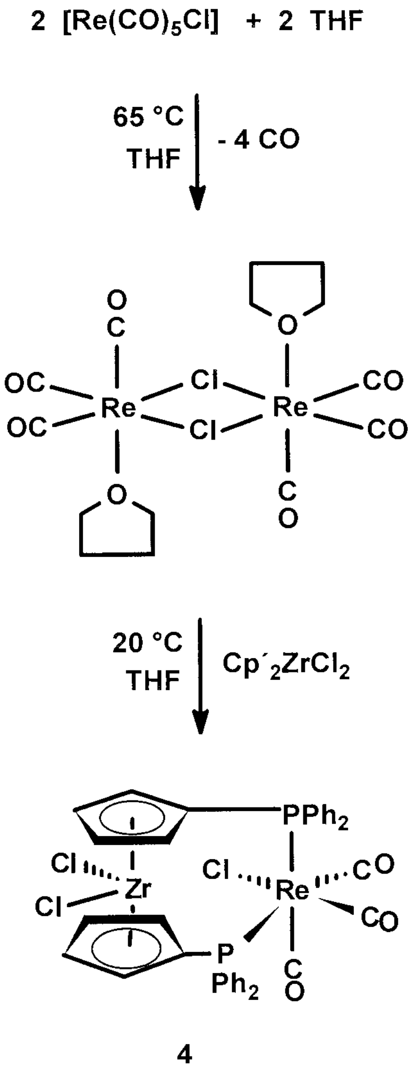
Re–Cl(1)	249.7(2)	Cl(1)–Re–P(1)	85.84(6)
Re–P(1)	248.7(2)	Cl(1)–Re–P(2)	94.10(6)
Re–P(2)	249.6(2)	Cl(1)–Re–C(1)	173.11(12)
Re–C(1)	190.9(4)	Cl(1)–Re–C(2)	88.93(12)
Re–C(2)	193.9(4)	Cl(1)–Re–C(3)	86.82(12)
Re–C(3)	194.5(4)	P(1)–Re–P(2)	91.05(5)
P(1)–C(11)	183.3(4)	P(1)–Re–C(1)	95.91(12)
P(1)–C(21)	182.7(4)	P(1)–Re–C(2)	91.27(12)
P(1)–C(50)	183.9(4)	P(1)–Re–C(3)	172.27(11)
P(2)–C(31)	182.9(4)	P(2)–Re–C(1)	92.48(12)
P(2)–C(41)	182.6(4)	P(2)–Re–C(2)	176.25(12)
P(2)–C(57)	181.0(4)	P(2)–Re–C(3)	86.78(12)
C(1)–O(1)	112.5(5)	C(1)–Re–C(2)	84.4(2)
C(2)–O(2)	114.3(5)	C(1)–Re–C(3)	91.6(2)
C(3)–O(3)	113.3(5)	C(2)–Re–C(3)	91.3(2)

Any attempt to convert **3** into a doubly bridged complex failed. UV irradiation or reaction with Me_3NO gave only intractable product mixtures. A doubly bridged neutral complex, however, was obtained upon refluxing a mixture of **1** and $[Re(CO)_5Cl]$ in benzene (Eq. (3)). The expected compound **4** could be isolated in 62% yield, a major side product being the 'Cp-dimer' complex **2**. **4** is a colourless crystalline compound which is readily soluble in chlorinated hydrocarbons and THF. Its IR spectrum exhibits the typical three-band pattern of *fac*-$[ReXL_2(CO)_3]$ complexes, similar to that of **2**. A singlet in the ^{31}P-NMR spectrum indicates that the two phosphorus nuclei are equivalent.



(3)

Since **4** is thermally labile—upon heating in toluene rapid decomposition to **2** occurs—a milder synthesis was attempted. Thus, $[Re(CO)_5Cl]$ was converted to a binuclear '$[Re(CO)_3Cl]$ equivalent' [13] which reacts with **1** to give **4** in quantitative yield (Eq. (4)).



(4)

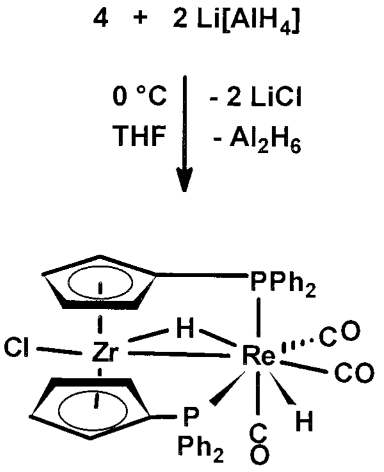
Although **4** seemed to be a fairly stable compound, surprising difficulties were encountered upon attempting substitution reactions. Thus, treatment of **4** with either $LiCH_3$, $Al_2(CH_3)_6$, $NaSCH_3$, or KO*t*–Bu, even under mild conditions, gave mainly the zirconium-free mononuclear complex **2** and none of the desired exchange products. Careful addition of a stoichiometric amount of $LiAlH_4$ in THF, however, produced a small

Table 2
Spectroscopic data of the binuclear Zr–Re complexes **3**–**8**

Number	IR ν(CO)	^{1}H-NMR[a] Cp′	Re–H	^{31}P-NMR PPh$_2$
3	2153 (w)[b] 2043 (s) 1988 (m)	5.50 to 6.50 (m)[c]		$-$12.7 (s)[c] 9.5 (s)
4	2036 (s)[d] 1961 (s) 1916 (s)	6.39 (m)[e] 6.76 (m) 6.84 (m)		$-$1.9 (s)[e]
5	2007 (m)[f] 1931 (vs)	5.42 (m)[g] 5.50 (m) 5.54 (m) 6.45 (m)	$-$4.56 (t)[h] $-$7.16 (t)[h]	6.95 (s)[g]
6		5.35 (m)[g] 5.45 (m) 5.72 (m) 6.39 (m)[i]	$-$6.02 (t)[h] $-$7.70 (t)[k]	7.55 (s)[g]
7	1992 (w)[l] 1912 (s) 1891 (s)	4.26 (m)[g] 4.71 (m) 6.23 (m) 6.35 (m)		10.6 (s)[g]
8a	2014 (m)[m] 1928 (s) 1905 (m)	5.93 (m)[g] 5.99 (m) 6.51 (m) 6.94 (m)	$-$3.98 (t)[n]	11.2 (s)[g]
8b	2031 (m)[m] 1946 (s)	6.21 (m)[g] 6.36 (m) 6.52 (m) 6.56 (m)	$-$5.55 (d)[o]	8.2 (d)[p] 9.0 (d)[p]

[a] Aryl signals in the 6.5–8.0 ppm region are uncharacteristic and have been omitted.
[b] CH_2Cl_2. [c] CD_2Cl_2. [d] $CHCl_3$. [e] $CDCl_3$. [f] Nujol. [g] C_6D_6. [h] ^2J(P–H) = 15 Hz. [i] 2.37 (s, SCH_3), [k] ^2J(P–H) = 17 Hz. [l] C_6H_6. [m] $C_6H_5CH_3$. [n] ^2J(P–H) = 27 Hz. [o] ^2J(P–H) = 25 Hz. [p] ^2J(P–P) = 22 Hz.

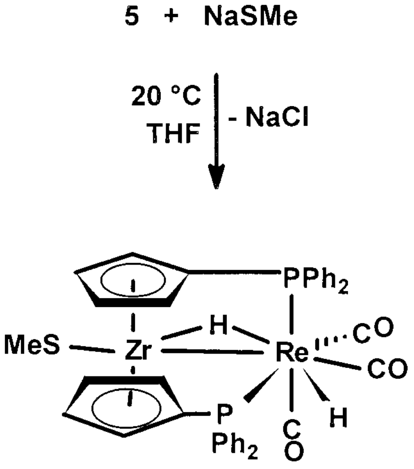
quantity of the dihydride **5** (Eq. (5)) along with some insoluble materials.



5

(5)

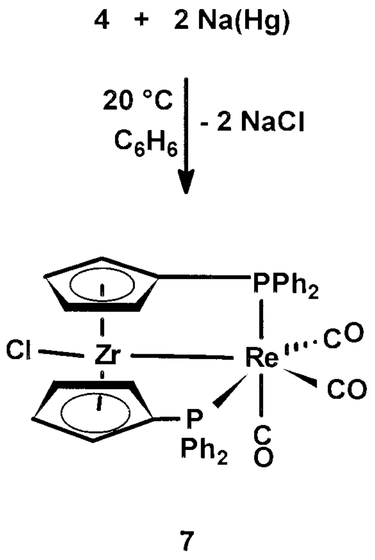
The infrared spectrum of **5** in the ν(CO) region exhibits two bands of unequal intensity but in the same frequency range as other tricarbonyl hydride complexes of rhenium [14]. This indicates that **5** is a neutral tricarbonyl with a geometry distinctly distorted from octahedral. The two equivalent phosphorus nuclei give rise to a singlet in the ^{31}P-NMR spectrum downfield from that of the starting compound **4**. Two hydride triplets are observed in the ^{1}H-NMR spectrum which collapse to singlets upon phosphorus decoupling. At first sight it seems unusual that no coupling is observed between the two nonequivalent hydride ligands. However, it is well-known that in second- and third-row complexes there is a sign change between *cis* and *trans* couplings. The situation is particularly well-documented for phosphine complexes where $^2J(cis)$ is negative and $^2J(trans)$ is positive [15–20]. It is, therefore, not too surprising that at an intermediate H–Re–H angle in a formally seven-coordinate structure ^2J(H–H) should assume a value close to zero. Indeed, similar Zr–Ru complexes with bridging $C_5Me_4PMe_2$, Cl, and H ligands have recently been synthesized which were found to have also very small H–H couplings between bridging and terminal hydrides [21,22].



6

(6)

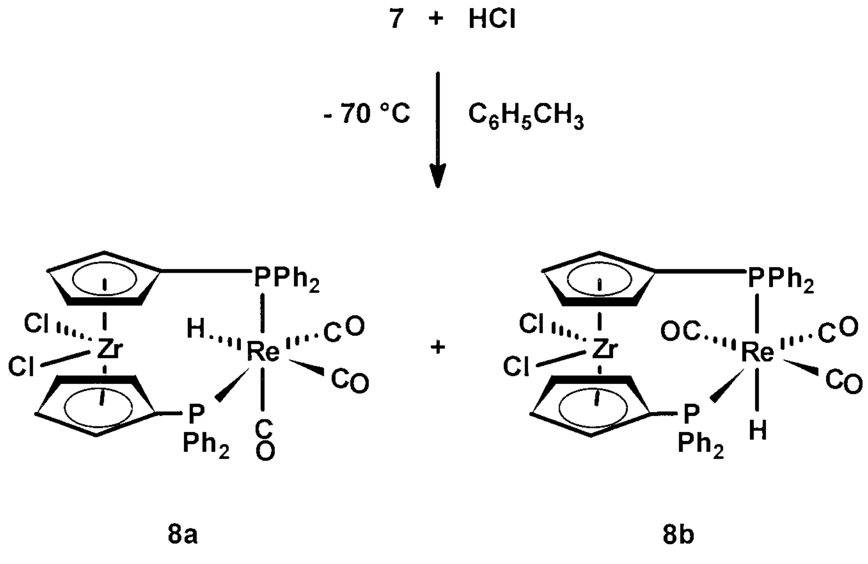
Evidence that in the hydride transfer reaction (Eq. (5)) one chloride ligand is retained at zirconium comes from the following experiment (Eq. (6)). A small quantity of **5** was treated in THF with an excess of NaSMe and the C_6D_6 soluble part examined by ^{1}H- and ^{31}P-NMR. Clean spectra were obtained which exhibited slightly shifted ^{31}P and hydride signals (Table 2). A new singlet at 2.37 ppm in the correct intensity ratio is typical of a Zr-bound SMe group [1–3].



(7)

Careful reduction of **4** using sodium amalgam produces the dark blue-green metal–metal bonded complex **7** (Eq. (7)). It is advisable to monitor the progress of the reaction by IR spectroscopy and separate the solution from excess amalgam as soon as the starting compound **4** is consumed completely. Otherwise, overreduction to a brown intractable mixture occurs. **7** can be isolated in good yield from a benzene solution by freeze-drying. The IR spectrum of **7** exhibits three ν(CO) bonds at distinctly lower frequencies compared to **4**, consistent with a change in the formal oxidation state of the rhenium atom from +I to zero. Furthermore, there is a conspicuous change in relative band intensities which means that two of the three CO ligands form a quite large OC–Re–CO angle. Obviously, the coordination geometry around the rhenium atom is severely distorted from a regular octahedron as a result of the constraints imposed by the zirconium–rhenium bond.

It was hoped that the addition of dihydrogen to **7** would provide a cleaner access to the dihydride complex **5**. However, no reaction occurred at room temp. up to a pressure of 50 bar. At higher temperatures complete decomposition was observed, mainly to the inescapable mononuclear compound **2**. Similarly, attempted nucleophilic substitution reactions with SMe^-, O*t*-Bu^-, ligand additions with isonitriles, alkynes, or 1,2- additions of aldehydes, methyl iodide or iodine resulted in decomposition to untractable materials.



(8)

Gaseous HCl, however, was cleanly added giving a 1:1 mixture of two isomeric monohydride complexes **8a**, **b** (Eq. (8)). In **8a** the two phosphorus nuclei are equivalent (Table 2), and consequently the hydride signal is split into a regular triplet. This isomer certainly has a *fac*-octahedral structure similar to that of *fac*-[ReH(dppe)$(CO)_3$] [23]. Of the five observable ν(CO) absorptions those at 2014, 1928 and 1905 cm^{-1} may be attributed to this isomer. The second isomer **8b** gives only a doublet signal in the hydride region which sharpens to a singlet upon phosphorus decoupling. The $^{31}P\{^1H\}$-NMR spectrum consists of a clean AB system; with off-resonance decoupling (such that the hydride region remains coupled) the signal at 8.2 ppm changes into a doublet of doublets. Thus, it is clear that in **8b** the hydride ligand is coupled to only one of the two phosphorus nuclei. Surprisingly, complexes of the type *mer*-[ReH($R_2P \frown PR_2$)$(CO)_3$] to be compared with **8b** have, to our knowledge, not yet been described. Complexes *mer*-[ReH$(PR_3)_2(CO)_3$] with monodentate phosphines adopt a *trans*-$(PR_3)_2$ geometry [14–18,20]. However, there are a few examples of poly(phosphine)-hydride complexes of rhenium which seemingly have two features in common: (a) $|^2J(\mathrm{P-H})(trans)|$ is distinctly *smaller* than $|^2J(\mathrm{P-H})(cis)|$, and (b) isomers, although often in thermodynamic equilibrium, do not interconvert on the NMR timescale [24–26]. Thus, it is perfectly reasonable to assume a slightly distorted *mer*-octahedral structure for **8b**. This would also explain the remaining ν(CO) bands at 2031 and 1946 cm^{-1} [23], a weak feature at 1815 cm^{-1} may be ascribed to overlapping ν(Re–H) absorptions of both isomers.

3. Conclusions

The assembly of binuclear zirconium–rhenium complexes with bridging $C_5H_4PPh_2$ ligands rests on the use of highly reactive mononuclear rhenium complexes capable of undergoing ligand exchange under mild conditions. A severely limiting factor is the unexpected lability of the Zr-$C_5H_4PPh_2$ linkage. Nevertheless, reduced complexes with Zr–Re and Re–H bonds are accessible under carefully controlled conditions and might pave the way to a further development of this chemistry.

4. Experimental section

All manipulations were carried out in Schlenk-type glassware under an atmosphere of purified nitrogen or argon. Solvents were dried and distilled under nitrogen prior to use. NMR solvents were degassed and stored under nitrogen over molecular sieves. NMR: Bruker AMX 400; chemical shifts are reported in ppm vs. TMS (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). IR: Bruker IFS 25, Perkin–Elmer 283.

The following starting materials were prepared by published procedures: Cp'_2ZrCl_2 (**1**) [5], $[Re(CO)_3(NCMe)_3]BF_4$ [4], $[Re(CO)_4(norbornadiene)]BF_4$ [6], $[Re(CO)_3(mesitylene)]BF_4$ [7], $[Re(CO)_5FBF_3]$ [12], $[Re(CO)_5Cl]$ [27], $[Re(CO)_5Me]$ [12], $[Re_2(\mu\text{-}Cl)_2(THF)_2(CO)_6]$ [13]. All other reagents were used as obtained commercially.

4.1. $[ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)]$ (**2**)

A solution of Cp'_2ZrCl_2 (0.10 g, 0.15 mmol) and $[Re(CO)_3(NCMe)_3]BF_4$ (0.072 g, 0.15 mmol) in $CDCl_3$ (0.5 ml) was heated to 80°C and the reaction monitored by ^{31}P-NMR. Aside from a number of unidentified decomposition products **2** was formed slowly as the main component of the mixture. Solids were separated by centrifugation and **2** was crystallized by addition of hexane. Colorless crystalline powder, m.p. 134°C (dec.). ^{1}H-NMR (400 MHz, CD_2Cl_2): $\delta = 0.79$, 1.89, 1.90, 2.38, 2.92, 2.93, 3.42, 5.52, 6.14 (m, $C_{10}H_{10}$), 7.1–7.9 (m, Ph). ^{31}P-NMR (162 MHz, CD_2Cl_2): $\delta = -10.1$, 2.5 (AB-system, $J(AB) = 28$ Hz). Anal. found: C, 56.38; H, 3.92. $C_{37}H_{30}ClO_3P_2Re$ (806.25) calcd.: C, 55.12; H, 3.75.

4.2. $[Cp'Cl_2Zr(\mu\text{-}Cp')Re(CO)_5]BF_4$ (**3**)

To a solution of $[Re(CO)_5Me]$ (51 mg, 0.15 mmol) in dichloromethane (5.0 ml) an equimolar amount of $HBF_4 * Et_2O$ is added. Within 2 h $[Re(CO)_5FBF_3]$ separates as colorless crystals [12] which are washed with dichloromethane and dried under vacuum. Cp'_2ZrCl_2 (**1**) (100 mg, 0.15 mmol) an dichloromethane (5.0 ml) are added and stirred for 15 min. The product is isolated after filtration by partial evaporation and addition of pentane. Yield 145 mg (93%), colorless microcrystalline powder, m.p. 104°C (dec.). Anal. found: C, 44.36; H, 2.58. $C_{39}H_{28}BCl_2F_4O_5P_2ReZr$ (1073.74) calcd.: C, 43.63; H, 2.63.

4.3. $[Cp'_2ZrCl_2ReCl(CO)_3]$ (**4**)

(a) A suspension of Cp'_2ZrCl_2 (**1**) (0.43 g, 0.65 mmol) and $[Re(CO)_5Cl]$ (0.23 g, 0.65 mmol) in benzene (10 ml) is heated under reflux for 15 min. The solution is filtered and evaporated to 3 ml whereupon **4** separates as an almost colorless crystalline powder. The filtrate contains a mixture of **4** and **2** which can be completely converted to **2** by prolonged heating. Yield 0.39 g (62%), m.p. 115°C (dec.). Anal. found: C, 45.63; H, 3.03. $C_{37}H_{28}Cl_3O_3P_2ReZr$ (966.37) calcd.: C, 45.99; H, 2.92.

(b) $[Re(CO)_5Cl]$ (0.11 g, 0.30 mmol) is refluxed in THF (10 ml) overnight whereby it is completely converted to $[Re_2(\mu\text{-}Cl)_2(CO)_6(THF)_2]$ [13]. Cp'_2ZrCl_2 (**1**) (0.20 g, 0.30 mmol) is added and the mixture is stirred for 30 min at 20°C. **4** is isolated in quantitative yield upon evaporation and addition of pentane.

4.4. $[Cp'_2ClZr(\mu\text{-}H)ReH(CO)_3]$ (**5**)

To a solution of **4** (0.17 g, 0.18 mmol) in THF (3.0 ml) is added, at 0°C, 4.0 ml of a 0.10 M solution of $LiAlH_4$ (0.40 mmol) in the same solvent. After the mixture has been stirred overnight at 20°C it is taken to dryness and the residue extracted with benzene. Upon evaporation 53 mg (33%) of spectroscopically pure **5** remain as colorless crystalline powder.

4.5. $[Cp'_2ClZrRe(CO)_3]$ (**7**)

To sodium amalgam, prepared from 1.0 ml of mercury and 0.20 g of sodium, is added benzene (10 ml) and **4** (0.35 g, 0.36 mmol). The mixture is repeatedly degassed and flushed with argon and stirred vigorously whereupon the solution turns blue-green. As soon as the staring compound **4** is consumed (to be checked by IR) the mixture is filtered over Celite and the product isolated from the filtrate by freeze-drying. Yield 0.20 g (62%), green-black microcrystalline powder, m.p. 63°C (dec.). Anal. found: C, 49.63; H, 3.66. $C_{37}H_{28}ClO_3P_2ReZr$ (895.46) calcd.: C, 49.63; H, 3.15.

4.6. *[$Cp'_2Cl_2ZrReH(CO)_3$] (**8**)*

Gaseous HCl is introduced for a few seconds into a solution of **7** (0.30 g, 0.34 mmol) in toluene (5.0 ml) at −70°C. The mixture, which turns colorless immediately, is evaporated to dryness and the residue recrystallized from toluene/pentane. Yield 0.26 g (83%), colorless microcrystalline powder. Anal. found: C, 47.60; H, 3.79. $C_{37}H_{29}Cl_2O_3P_2ReZr$ (932.92) calcd.: C, 47.69; H, 3.14.

4.7. *X-ray structure determination of [$ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)$] * $CDCl_3$ (**2** * $CDCl_3$)*

Clear colorless crystals of **2** * $CDCl_3$ were obtained from a NMR sample of **2**. 25 centered reflections from a crystal of the size $0.10*0.15*0.50$ mm^3 in the range $10° < \Theta < 13°$ gave a triclinic unit cell of the dimensions listed in Table 3. Data were collected from one half of the reflection sphere in the range $2° < \Theta < 24°$ (Enraf–Nonius CAD diffractometer, Mo K_α radiation, graphite monochromator, filter factor 15.41). An empirical absorption correction based on the intensities of 9 reflections was applied. The structure was solved by the Patterson method in the space group $P\bar{1}$ (No. 2) using the SHELXS86 [28] program package. Hydrogen atoms were included in fixed positions, coupled to their respective carbon atoms. Least squares cycles using the SHELXL93 [29] program package led to the R values given in Table 3. Atomic coordinates are listed in Table 4. Further details of the structure determination may be

Table 3
Crystallographic data for [$ReCl(CO)_3(C_{10}H_{10}(PPh_2)_2)$] * $CDCl_3$ (**2** * $CDCl_3$)

Chemical formula	$C_{37}H_{30}ClO_3P_2Re*CDCl_3$
Formula weight	806.25 + 120.37
Temperature (K)	298
space group	$P\bar{1}$ (No. 2)
a (pm)	945.1(5)
b (pm)	1113.9(6)
c (pm)	1888.5(10)
α (°)	92.36(3)
β (°)	89.98(3)
γ (°)	113.49(2)
V (pm3)	$1.821(2)*10^9$
Z	2
λ (pm)	70.930
ρ_{calc} (g cm^{-1})	1.690
μ (cm^{-1})	4.60
R_1 [$I > 2\sigma(I)$]	0.0211
wR_2 [$I > 2\sigma(I)$]^a	0.0502

[a] $wR_2 = \{[\Sigma w(F_c^2 - F_o^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm^2 $\times 10^{-1}$) for **2** * $CDCl_3$

	X	Y	Z	U_{eq}
Re	1828(1)	2059(1)	8257(1)	33(1)
P(1)	4680(1)	3233(1)	8200(1)	33(1)
P(2)	1865(1)	341(1)	7375(1)	36(1)
O(1)	1819(4)	479(3)	9528(2)	63(1)
O(3)	−1710(3)	758(3)	8105(2)	65(1)
O(2)	1615(4)	3966(3)	9438(2)	82(1)
Cl(1)	1719(1)	3568(1)	7336(1)	57(1)
C(1)	1838(4)	1030(4)	9039(2)	43(1)
C(2)	1723(4)	3303(4)	8982(2)	48(1)
C(3)	−410(5)	1230(4)	8175(2)	45(1)
C(11)	5805(4)	2783(3)	8849(2)	36(1)
C(12)	5378(4)	1477(3)	8999(2)	41(1)
C(13)	6278(5)	1108(4)	9452(2)	49(1)
C(14)	7578(5)	2030(4)	9770(2)	57(1)
C(15)	7993(5)	3327(4)	9630(2)	58(1)
C(16)	7138(4)	3702(4)	9169(2)	48(1)
C(21)	5308(4)	5002(3)	8351(2)	39(1)
C(22)	5855(4)	5897(3)	7827(2)	46(1)
C(23)	6261(5)	7217(4)	7981(2)	57(1)
C(24)	6142(5)	7671(4)	8648(3)	63(1)
C(25)	5579(5)	6794(4)	9179(2)	60(1)
C(26)	5171(5)	5471(4)	9026(2)	49(1)
C(31)	345(4)	−236(4)	6689(2)	44(1)
C(32)	84(5)	676(4)	6286(2)	56(1)
C(33)	−1019(5)	260(5)	5749(2)	66(1)
C(34)	−1873(6)	−1046(6)	5614(2)	71(1)
C(35)	−1631(6)	−1942(5)	6005(3)	74(1)
C(36)	−532(5)	−1558(4)	6552(2)	60(1)
C(41)	1612(4)	−1171(3)	7802(2)	41(1)
C(42)	2530(5)	−1858(4)	7676(2)	54(1)
C(43)	2193(6)	−3046(4)	7976(3)	66(1)
C(44)	928(6)	−3586(4)	8390(3)	72(1)
C(45)	14(5)	−2898(4)	8540(3)	64(1)
C(46)	355(5)	−1710(4)	8247(2)	51(1)
C(50)	5546(4)	2983(3)	7364(2)	38(1)
C(51)	5120(5)	3481(4)	6698(2)	48(1)
C(52)	6150(5)	3527(4)	6214(2)	62(1)
C(53)	7247(5)	3011(4)	6521(2)	59(1)
C(54)	6317(4)	1515(4)	6598(2)	50(1)
C(55)	5322(5)	749(4)	5956(2)	57(1)
C(56)	3704(5)	337(4)	6199(2)	51(1)
C(57)	3600(4)	698(3)	6867(2)	41(1)
C(58)	5156(4)	1476(3)	7192(2)	39(1)
C(59)	7314(4)	3513(4)	7298(2)	51(1)
C(61)	2433(6)	5651(5)	6003(3)	80(1)
Cl(2B)	2065(10)	4308(7)	5425(5)	111(2)
Cl(3B)	4348(8)	6658(10)	6044(6)	132(3)
Cl(4B)	1424(10)	6558(9)	5694(7)	121(2)
Cl(2A)	2372(13)	4364(7)	5457(5)	149(4)
Cl(3A)	4234(8)	6894(9)	6031(5)	134(3)
Cl(4A)	1061(12)	6199(11)	5779(9)	175(5)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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