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Synthesis, characterization and structure of rhodium(I) carbonyl complexes with *O*,*P*-chelating 1′-(diphenylphosphino)ferrocenecarboxylate or *P*-monodentate 1′-(diphenylphosphino)ferrocenecarboxylic acid

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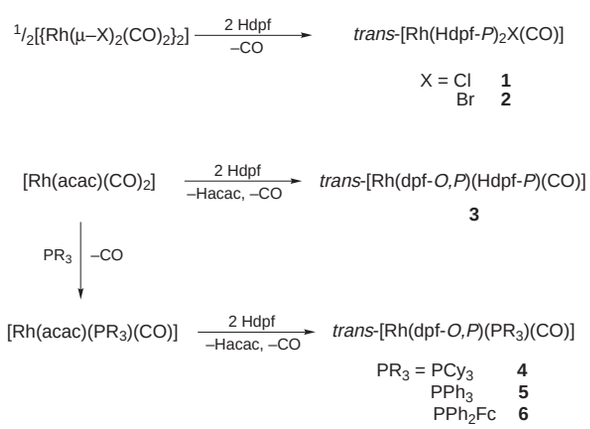
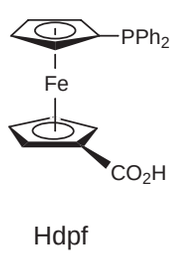
The reaction of 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf) with [{Rh(μ-X)$(CO)_2$}$_2$] (X = Cl or Br) afforded rhodium(I) complexes *trans*-[Rh(Hdpf-*P*)$_2$X(CO)] containing the ligand as the *P*-bonded phosphine. On the other hand, pentane-2,4-dionato rhodium(I) complexes reacted with Hdpf by an acid–base reaction yielding novel *O*,*P*-chelated rhodium(I) complexes and pentane-2,4-dione (Hacac). The compound [Rh(acac)$(CO)_2$] reacted with 2 equivalents of Hdpf to give *trans*-[Rh(dpf-*O*,*P*)(Hdpf-*P*)(CO)] which exhibits proton exchange between the two forms of the ligand. Likewise, related complexes [Rh(acac)(PR_3)(CO)], where PR_3 = PCy_3, PPh_3 or PPh_2Fc (Cy = cyclohexyl, Fc = ferrocenyl), afforded the corresponding complexes *trans*-[Rh(dpf-*O*,*P*)-(PR_3)(CO)]. The formation of the *O*,*P* chelates is regioselective and might be considered as a rather unusual displacement of pentane-2,4-dionate by the phosphinocarboxylate dpf$^-$ with concurrent proton exchange. All the compounds were characterized by ^{1}H, ^{13}C, ^{31}P and IR spectroscopies and by FAB mass spectrometry. The crystal structure determination of *trans*-[Rh(dpf-*O*,*P*)(PCy_3)(CO)] confirmed the presence of an unprecedented heteroannular *O*,*P*-chelating ferrocene ligand.

Hybrid ligands that possess simultaneously hard and soft donor groups according to the Pearson's hard/soft acid/base (HSAB) concept are known to co-ordinate transition metals in a variety of manners. The bond between the hard donor atom and a soft metal may readily be cleaved to produce a free co-ordination site while the ligand remains bonded to the metal centre by its soft donor group. For this reason, the complexes of catalytically active metals such as Rh^I, Pt^{II} and Pd^{II} with hybrid phosphines have been widely used as catalysts.[1] In addition, the catalytic properties of hybrid ligands may be finely tuned by changing stereoelectronic properties of substituents and/or the backbone of the ligand. Furthermore, hybrid ligands may bear substituents suitable for attachment of the ligand to a solid support. The use of redox active (ferrocene-based) ligands enables one to assemble redox active groups at the surface.[2]

Recently, we reported the synthesis of the organometallic carboxyphosphine 1′-(diphenylphosphino)ferrocenecarboxylic acid [Fe(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4CO_2H$)] (Hdpf)[3] and of its complexes with Pd^{II} and Pt^{II}[4] in which the ligand behaves as the *P*-donor, the unco-ordinated carboxyl group being involved in hydrogen bonding of various types. In order to force the *O*,*P*-chelation of this ligand, we have studied its reactivity towards pentane-2,4-dionato complexes of Rh^I in analogy to the reaction of a simpler ligand, (diphenylphosphino)acetic acid, which forms *O*,*P*-chelated (diphenylphosphino)acetato complexes.[5,6] Transition-metal complexes containing chelating ferrocene ligands appear to be limited almost exclusively to *P*,*P*-donors such as 1,1′-bis(diphenylphosphino)ferrocene or *N*,*P* ligands of the 1-(dialkylamino)methyl-2-phosphinoferrocene family with much less attention being paid to ferrocene-based *O*,*P*-donors in general. In this paper we report syntheses and spectral characterization of rhodium(I) complexes containing the *O*,*P*-chelating dpf$^-$, [Rh(dpf-*O*,*P*)L(CO)], where L = Hdpf-*P*, PCy_3, PPh_3 or PPh_2Fc (Cy = cyclohexyl, Fc = ferrocenyl) and of the analogous complexes *trans*-[Rh(Hdpf-*P*)$_2$-X(CO)] (X = Cl or Br) containing Hdpf as the *P*-bonded phosphine. The crystal structure of *trans*-[Rh(dpf-*O*,*P*)(PCy_3)(CO)] as representative of heteroannular *O*,*P* chelation of the ferrocene ligand is also presented.



Scheme 1 Hacac = pentane-2,4-dione.



Hdpf

Results and discussion

Rhodium(I) complexes with Hdpf as the *P*-bonded phosphine

The complexes *trans*-[Rh(Hdpf-*P*)$_2$X(CO)], where X = Cl **1** or Br **2**, were synthesized by cleavage of the halogeno bridges in the [{Rh(μ-X)$(CO)_2$}$_2$] dimers with a stoichiometric amount of Hdpf in benzene (Scheme 1). They were characterized by elemental analyses, FAB mass spectrometry and ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopies. The ^{31}P NMR spectra of **1** and **2** exhibit one doublet shifted downfield in comparison to the free Hdpf. Coupling constants ^1J(RhP) 126 Hz for both complexes

evidence the *trans* configuration of the phosphine ligands.[7] In the ^{13}C NMR spectra, the signals of the phosphinylated cyclopentadienyl ring and those of the phenyl rings (*o*-, *m*-*C*H) appear as apparent triplets of AA′X spin systems (A = P, X = C) typical for *trans*-bis(phosphine) complexes with large *J*(PP) values.[8] On the contrary, the signal of the terminal carbonyl group was observed as a regular doublet of triplets at δ_C 186.9 (186.3) with ^1J(RhC) 74 (76) and ^2J(PC) 16 (16) Hz for **1** and **2**, respectively. These values are close to those reported for other mononuclear rhodium(I) carbonyl complexes.[9] Fourier-transform IR spectra of **1** and **2** exhibit bands of terminal carbonyl groups at 1957 cm^{-1} as well as $\nu_{C=O}$ stretching frequencies of the protonated carboxyl groups at 1674 cm^{-1}. The latter values indicate that the carboxyl groups are involved in hydrogen bonding (*cf.* 1696–1703 cm^{-1} for Hdpf). In the positive-ion FAB mass spectra measured in *m*-nitrobenzyl alcohol matrix the molecular ions, ions $[M - CO]^+$ and ions due to elimination of the halogen atom $[M - X]^+$, *m*/*z* 959, are observed. As the latter are isobaric with $[\mathbf{3} + H]^+$, further ions in the mass spectra of **1** and **2** are the same as those originating from **3** under the same conditions: *m*/*z* $[(Hdpf)Rh(dpf)]^+$, 849 $[959 - C_6H_6O_2]^+$, 821 $[849 - CO]^+$, 545 $[(Hdpf)Rh(CO)]^+$ and 414 $[Hdpf]^+$.

Complexes with *O*,*P*-chelating 1′-(diphenylphosphino)ferrocenecarboxylate

The pentane-2,4-dionato complex $[Rh(acac)(CO)_2]$ reacts with different phosphine and phosphite ligands by substitution of either one or two CO molecules to give complexes $[Rh(acac)L_n(CO)_{2-n}]$ ($n = 1$ or 2), the course of the reaction (*n*) depending on the stereoelectronic properties of the ligand applied.[10] On the other hand, (diphenylphosphino)acetic acid replaces pentane-2,4-dione and one CO molecule yielding $[Rh(Ph_2PCH_2CO_2\text{-}O,P)(Ph_2PCH_2CO_2H\text{-}P)(CO)]$. Similarly, the reaction of $[Rh(acac)(CO)_2]$ with 2 equivalents of 1′-(diphenylphosphino)ferrocenecarboxylic acid in hot toluene afforded cinnamon orange *trans*-[Rh(dpf-*O*,*P*)(Hdpf-*P*)(CO)] **3** (see Scheme 1). In the IR spectrum of **3** the carbonyl stretching frequency $\nu_{C=O}$ appears at 1962 cm^{-1}. The bands at 1703 and 1551 cm^{-1} were assigned to protonated and chelating carboxyl groups respectively. Unexpectedly, ^1H, ^{13}C and ^{31}P NMR spectra of this mixed Hdpf–dpf complex display only one set of ligand resonances indicating the equivalence of both phosphine ligands due to the proton exchange which is fast on the NMR timescale at 294 K. Its ^{31}P NMR spectrum exhibits one doublet at δ_P 20.2 (co-ordination shift, Δ_P 37.8 ppm), *i.e.* roughly halfway between that observed for Hdpf-*P* (δ_P 22.2) and other dpf-*O*,*P* (δ_P *ca.* 18.6) complexes. The phosphine ligands occupy *trans* positions in the square-planar environment around Rh^I as deduced from the ^1J(RhP) coupling constant. Similarly to **1** and **2**, the ^{13}C NMR spectra show apparent triplets due to AA′X spin systems, whereas the signal of the terminal carbonyl group is observed as a normal doublet of triplets with δ_C 189.8, ^1J(RhC) 75 and ^2J(PC) 17 Hz.

In $[^2H_6]$dimethyl sulfoxide solution the signals in the NMR spectra of complex **3** are significantly broader, most likely as the result of a lowered rate of the chemical exchange (Scheme 2) on introduction of the good hydrogen-bond acceptor. The ^{31}P and ^1H NMR spectra of the mixtures with $[Rh(acac)(CO)_2]$:Hdpf ratios of 1:1, 1:2 and 1:3 in $CDCl_3$ demonstrated that the formation of **3** is fast and proceeds with the displacement of pentane-2,4-dione even at 1:1 molar ratio where 0.5 equivalent of the parent rhodium(I) complex remains. Addition of the second equivalent of Hdpf completes the reaction and the third equivalent remains unconsumed. No further ^1H NMR signals were observed down to δ_H −30 in this system.

In order to eliminate the factor of proton exchange, we synthesized analogous complexes containing other monodentate phosphines in the place of undissociated Hdpf. The complexes

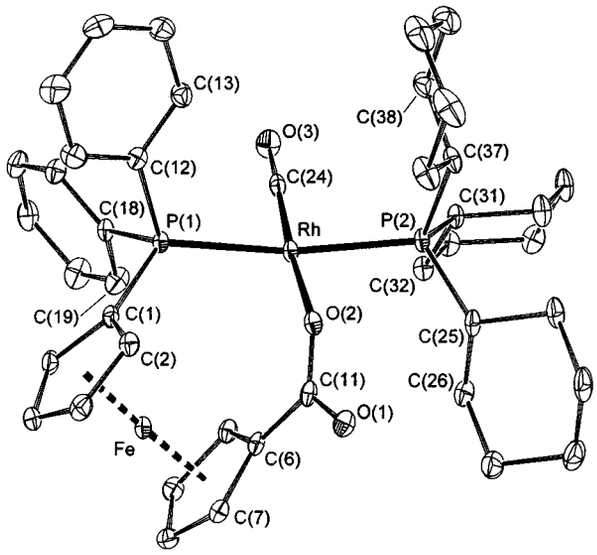
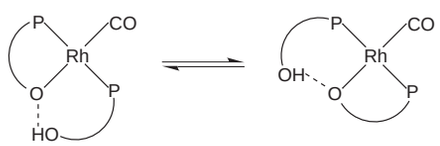


Fig. 1 Molecular structure of *trans*-[Rh(dpf-*O*,*P*)(CO)(PCy_3)] **4**. Thermal ellipsoids are shown at the 30% probability level. The hydrogen atoms were omitted for clarity.



Scheme 2

[Rh(dpf-*O*,*P*)L(CO)], where L = PCy_3 **4**, PPh_3 **5** or PPh_2Fc **6**, were all prepared in a similar manner, *i.e.* by mixing solutions of Hdpf and the corresponding pentane-2,4-dionato complex [Rh(acac)L(CO)] in hot butan-2-one followed by cooling. The IR spectra of **4**–**6** exhibit a strong band for terminal carbonyl between 1961 and 1965 cm^{-1} and the carboxylate band in the range 1567–1606 cm^{-1}. The ^1H, ^{13}C and ^{31}P NMR data are consistent with the proposed structures. The degeneracy of the A′AX spin system (to give A_2X; A = P, X = C) observed in the case of **3** due to the proton exchange is removed and the ^{31}P NMR signals of **4**–**6** appear as double doublets of ABM systems (A, B = P; M = Rh). The coupling constants $^2J(PP) \approx 325$–353 Hz and $^1J(RhP) \approx 128$–134 Hz imply that the phosphines are mutually *trans*. Similarly, the signals of the phosphinylated cyclopentadienyl and phenyl rings in the ^{13}C NMR spectra appear as simple doublets (or dd) located in the usual range. In ^1H NMR spectra the resonances associated with the cyclopentadienyl hydrogen atoms of **3**–**6** are observed as ill resolved apparent multiplets of AA′BB′X and AA′BB′ spin systems (A, B = H, X = P) for phosphinylated and carboxylated cyclopentadienyls, respectively.

The FAB MS spectra of complexes **3**–**6** in a *m*-nitrobenzyl alcohol matrix display protonated molecular ions $[M + H]^+$, ions due to loss of carbon monoxide, *i.e.* $[M - CO]^+$ for **3** and $[M - CO + H]^+$ for **4**–**6**. Another common feature is the presence of peaks due to free (Hdpf for all compounds, $FcPPh_2$) or protonated phosphines (Cy_3PH^+ and Ph_3PH^+) and species at *m*/*z* 545, $[(Hdpf)Rh(CO)]^+$. Ions at *m*/*z* 849 due to loss of the carboxylated cyclopentadienyl ring were observed for **3**, while the spectra of complexes **4**–**6** display ions $[M - 72]^+$ reflecting most likely the simultaneous loss of CO and CO_2.

Crystal structure of complex 4

Complex **4** crystallizes in space group $P\bar{1}$ with one discrete molecule in the asymmetric unit. The structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The four donor atoms form a square-planar environment around Rh^I. The perpendicular distance of Rh from the ligand

Table 1 Selected bond lengths (Å), angles (°) and dihedral angles of least-squares planes[a] (°) with estimated standard deviations in parentheses for complex **4**

Rh–P(1)	2.335(1)	C(06)–C(11)	1.498(4)
Rh–P(2)	2.342(1)	P(1)–C(01)	1.804(3)
Rh–O(2)	2.071(2)	P(1)–C(12)	1.820(3)
Rh–C(24)	1.793(3)	P(1)–C(18)	1.835(3)
O(3)–C(24)	1.153(4)	P(2)–C(31)	1.850(3)
O(1)–C(11)	1.232(4)	P(2)–C(25)	1.850(3)
O(2)–C(11)	1.273(4)	P(2)–C(37)	1.855(3)
C–C (Fc)[b]	1.425(7)	C–C (Ph)[b]	1.382(9)
C–C (Cy)[b]	1.53(1)		
C(24)–Rh–O(2)	175.8(1)	O(1)–C(11)–O(1)	123.6(3)
C(24)–Rh–P(1)	87.4(1)	C(01)–P(1)–C(12)	103.48(1)
O(2)–Rh–P(1)	95.99(6)	C(01)–P(1)–C(18)	102.45(1)
C(24)–Rh–P(2)	89.8(1)	C(12)–P(1)–C(18)	103.47(1)
O(2)–Rh–P(2)	86.48(6)	C(31)–P(2)–C(25)	110.9(2)
P(1)–Rh–P(2)	170.60(3)	C(31)–P(2)–C(37)	104.5(2)
O(3)–C(24)–Rh	179.2(3)	C(25)–P(2)–C(37)	104.8(2)
Cp1 *vs.* Cp2	4.8(3)	RhL *vs.* CO_2	60.9(3)
Cp1 *vs.* Ph1	77.6(1)	Cp2 *vs.* CO_2	25.9(4)
Cp1 *vs.* Ph2	73.8(1)	Ph1 *vs.* Ph2	87.3(1)

[a] The planes are defined as follows: Cp1, C(1)–C(5), phosphinylated cyclopentadienyl ring; Cp2, C(6)–C(10), carboxylated cyclopentadienyl ring; Ph1, C(12)–C(17); Ph2, C(18)–C(23); CO_2, C(11), O(1), O(2); RhL, P(1), P(2), O(2), C(24). [b] Mean value.

plane is 0.111(1) Å (*cf.* mean deviation of the plane defining atoms of 0.07 Å) and the sum of the bond angles around Rh is 360°. A slight opening of the O–Rh–P angle to 95.99(6)° reflects the steric requirements of the chelating ligand. The Rh–P distances 2.335(1) and 2.342(1) Å are in keeping with those found in 1,1′-bis(diphenylphosphino)ferrocene complexes [Rh(dppf-*P*,*P*′)(η^4-nbd)][11] and [Rh(dppf-*P*,*P*′)$(MeCN)_2$][12] of 2.335(2), 2.317(2) and 2.247(1), 2.232(1) Å, respectively. The dpf^- anion is further bonded through its deprotonated hydroxy oxygen atom thus completing the chelation. The geometry around the oxygen donor of the ligand is typical for a covalently bonded carboxylate: Rh–O 2.071(2), C=O 1.232(4) and C–O 1.273(4) Å, O–C=O 123.6(3)° with the dihedral angle subtended by the carboxyl group and the co-ordination polyhedron defined by atoms P(1), O(2), P(2) and C(24) of 60.9(3)°. The bond lengths resemble that reported for the cationic η^1-acetato complex *cis*-[NBu^n_4][$Rh(O_2CMe)_2(CO)_2$][13] and analogous chelates *trans*-[$Pd(Ph_2PCH_2CO_2$-*O*,*P*$)_2$][14] and *trans*-[$Rh(Ph_2PCH_2CO_2$-*O*,*P*$)(Ph_2PCH_2CO_2H$-*P*$)(CO)$].[5] The arrangement of the Rh–C≡O moiety is nearly linear with no unexceptional features when compared to *trans*-$[Rh(PR_3)_2Cl(CO)]$ complexes[15] [Rh–C 1.793(3), C≡O 1.153(4) Å, Rh–C≡O 179.2(3)°].

With respect to the solid-state structure of unco-ordinated Hdpf, the ferrocene moiety exhibits no significant deformation of its bond lengths and angles on chelate formation. The iron–centroid distance is 1.614(2) Å for both cyclopentadienyls (Cp). The Cp rings are slightly tilted at the dihedral angle of 4.8(3)° and adopt an eclipsed conformation with *syn*-arranged substituents: the torsion angle P(1)–Cp1–Cp2–C(11) is −60.0(1)°. In contrast to the free ferrocene ligand, the carboxyl group is rotated towards its parent Cp plane by 25.9(4)° as required by the *O*,*P* chelation. A similar *syn*-eclipsed conformation was observed in another complex of a chelating ferrocene derivative, [Rh{(η^5-$C_5H_4PPh_2$)Fe[η^5-C_5H_4(2-C_5H_4N)]-*N*,*P*}-(η^4-cod)].[16] For the cases of dppf chelates mentioned above, however, the Cp rings are *syn*-staggered, most likely due to the absence of a 'spacer' between one of the two donor atoms directly bonded to the ferrocene framework.

The cyclohexyl rings of the PCy_3 ligand are bonded to phosphorus in equatorial positions and adopt an almost exact chair conformation with ring puckering coordinates[17] $Q = 0.577(4)$, 0.582(4) and 0.566(5) Å and $\theta = 0.0(4)$, 178.1(4) and 1.9(5)° for the rings involving C(25), C(31) and C(37), respectively. The P–C bonds of both phosphine ligands are almost perfectly eclipsed when looking along the P(1)···P(2) line.

As the result of fixing the positions of the substituents on the Cp rings by co-ordination, the dpf ligand exhibits conformational chirality. The R_{Fc} enantiomer chosen arbitrarily for the refinement is related to its enantiomeric counterpart through the crystallographic symmetry centre to form the racemic crystal. There are no significant intermolecular contacts below the sum of van der Waals radii between the molecules in the crystal.

Conclusion

The results described here exemplify the ability of 1′-(diphenylphosphino)ferrocenecarboxylic acid to displace pentane-2,4-dionato ligand in its rhodium(I) complexes [Rh(acac)(CO)L] (L = CO or PR_3) with concomitant proton transfer, affording *O*,*P*-chelated complexes in good yields. In accordance with the *trans* effect, only one regioisomer is formed in which the *P*-donors are mutually *trans*. The mechanism of the *O*,*P*-chelate formation might involve oxidative addition (with Rh^{III}–H intermediates) or substitution with η^1-pentane-2,4-dione as an intermediate. The reaction is relatively fast and no direct evidence of an intermediate was obtained. However, such intermediates could hardly be expected to be stable towards subsequent chelation. According to recent calorimetric data,[18] the formation of [Rh(acac)(PR_3)(CO)] from [Rh(acac)-$(CO)_2$] is rapid and quantitative and the reaction enthalpy depends upon stereoelectronic properties of the incoming phosphine. Therefore, substitution of one of the carbonyl ligands by Hdpf may represent the first step of the formation of complex **3**.

Experimental

General comments

All manipulations were carried out in an argon atmosphere. The solvents were purified and dried by refluxing and distillation from potassium (benzene, toluene, diethyl ether) or standing over K_2CO_3 followed by distillation (butan-2-one). Light petroleum (fraction with bp 40–60 °C) and methanol were used as received.

Infrared spectra were recorded in Nujol mulls between KBr plates on an FT IR Mattson Genesis instrument, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra on a Varian UNITY Inova 400 spectrometer. Chemical shifts (δ) are in ppm. Standards: internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given as absolute values. The assignment of the signals was based on ^{13}C APT (attached proton test), COSY-45 and ^{13}C HMQC (heteronuclear multiple quantum correlation) experiments. The multiplets are labelled as usual with 'a' indicating an apparent multiplet of a second-order spin system. Positive ion FAB mass spectra in a *m*-nitrobenzyl alcohol matrix were measured on a VG-7070E spectrometer (xenon fast atoms; 8 kV, 2 mA; accelerating voltage 6 kV). The spectra were interpreted by comparison of measured and simulated isotopic patterns. The mass of selected fragment ions given here corresponds to the isotopomer containing ^{79}Br, ^{35}Cl, ^{56}Fe and ^{103}Rh.

The compounds [Rh(acac)$(CO)_2$],[19] [Rh(acac)(PR_3)(CO)][6] (R = Cy or Ph), [{Rh(μ-X)$(CO)_2$}$_2$] (X = Cl[20] or Br[21]) and Hdpf[3] were prepared by literature procedures.

Preparations

***trans*-[Rh(Hdpf-*P*)$_2$Cl(CO)] 1.** Following the general procedure,[22] a solution of Hdpf (83.0 mg, 0.20 mmol) in hot benzene (4 cm^3) was added to a solution of [{Rh(μ-Cl)$(CO)_2$}$_2$] (19.4 mg, 0.050 mmol) in the same solvent (2 cm^3). The

resulting clear orange solution was left to stand at room temperature overnight. The precipitate formed was filtered off, washed with benzene (5 cm^3) and light petroleum (3 × 5 cm^3), and dried under reduced pressure to yield complex **1** as an orange solid. Yield 96.5 mg, 96% (Found: C, 56.55; H, 4.03. $C_{47}H_{38}ClFe_2O_5P_2Rh$ requires C, 56.75; H, 3.85%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1957s, 1674s, 1299m, 1164m, 1097m, 1033m, 836m, 750m, 696m, 682m, 575m, 695s, 510s, 506s and 471m. NMR [$(CD_3)_2SO$, 298 K]: ^1H, δ 4.47 (2 H, br s, C_5H_4C CH), 4.51 (2 H, br at, C_5H_4P CH), 4.64 (2 H, at, C_5H_4C CH), 4.82 (2 H, at, C_5H_4C CH), 7.46–7.52 [6 H, m, $P(C_6H_5)_2$], 7.58–7.66 [4 H, m, $P(C_6H_5)_2$] and 12.38 (1 H, s, CO_2H); ^{13}C-{^1H}, δ 71.2 (s, C_5H_4C CH), 73.1 (s, C_5H_4C C_{ipso}), 73.4 (at, C_5H_4C CH), 73.7 (at, C_5H_4P CH), 74.9 (at, C_5H_4P CH), 75.5 (at, C_5H_4P C_{ipso}), 128.1 [at, $P(C_6H_5)_2$ CH_m], 130.2 [at, $P(C_6H_5)_2$ CH_p], 133.3 [at, $P(C_6H_5)_2$ CH_o], 133.7 [at, $P(C_6H_5)_2$ C_{ipso}], 171.3 (s, C=O) and 186.9 [dt, J(RhC) 74, J(PC) 16 Hz, C≡O]; ^{31}P-{^1H}, δ 22.2 [d, J(RhP) 126 Hz, Hdpf]. FAB^+: m/z 994, M^+; 959, $[M - Cl]^+$; 930, [(Hdpf)Rh(dpf)]$^+$; 849, [959 − $C_6H_6O_2$ (*i.e.* $C_5H_4CO_2$-H + H)]$^+$; 821, [849 − CO]$^+$; 545, [(Hdpf)Rh(CO)]$^+$; and 414, [Hdpf]$^+$.

***trans*-[Rh(Hdpf-*P*)$_2$Br(CO)] 2.** The reaction of [{Rh(μ-Br)(CO)$_2$}$_2$] (23.5 mg, 0.050 mmol) and Hdpf (83.0 mg, 0.20 mmol) was carried out using the same procedure as for **1**. A similar work-up gave **2** as an orange solid. Yield 100.7 mg, 97% (Found: C, 54.68; H, 3.92. $C_{47}H_{38}BrFe_2O_5P_2Rh$ requires C, 54.32; H, 3.69%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1957s, 1674s, 1297m, 1161m, 1096m, 1032m, 837m, 732m, 694m, 567m, 512s, 504s and 470m. NMR [$(CD_3)_2SO$, 298 K]: ^1H, δ 4.50 (2 H, br s, C_5H_4C CH), 4.52 (2 H, br at, C_5H_4P CH), 4.60 (2 H, at, C_5H_4C CH), 4.82 (2 H, at, C_5H_4C CH), 7.46–7.51 [6 H, m, $P(C_6H_5)_2$], 7.59–7.66 [4 H, m, $P(C_6H_5)_2$] and 12.40 (1 H, s, CO_2H); ^{13}C-{^1H}, δ 71.3 (s, C_5H_4C CH), 73.1 (s, C_5H_4C C_{ipso}), 73.3 (at, C_5H_4C CH), 73.6 (at, C_5H_4P CH), 75.1 (at, C_5H_4P CH), 75.8 (at, C_5H_4P C_{ipso}), 128.0 [at, $P(C_6H_5)_2$ CH_m], 130.2 [at, $P(C_6H_5)_2$ CH_p], 133.3 [at, $P(C_6H_5)_2$ CH_o], 134.2 [at, $P(C_6H_5)_2$ C_{ipso}], 171.3 (s, C=O) and 186.3 [dt, J(RhC) 76, J(PC) 16 Hz, C≡O]; ^{31}P-{^1H}, δ 22.2 [d, J(RhP) 126 Hz, Hdpf]. FAB^+: m/z 1038, M^+; 1010, $[M - CO]^+$; 959, $[M - Br]^+$; 930, [(Hdpf)-Rh(dpf)]$^+$; 849, [959 − $C_6H_6O_2$ (*i.e.* $C_5H_4CO_2H$ + H)]$^+$; 821, [849 − CO]$^+$; 545, [(Hdpf)Rh(CO)]$^+$; and 414, [Hdpf]$^+$.

[Rh(acac)(PPh$_2$Fc)(CO)]. A slurry of [Rh(acac)(CO)$_2$] (258 mg, 1.00 mmol) and $FcPPh_2$ (408 mg, 1.10 mmol) in diethyl ether (20 cm^3) was heated to boiling until a clear orange solution resulted (CO evolution). Methanol (15 cm^3) was added and the volume was reduced to *ca.* 10 cm^3 *in vacuo*. The resulting precipitate was filtered off, washed with a little methanol and dried in air to give the complex as an orange microcrystalline solid. Yield 524 mg, 87% (Found: C, 56.06; H, 4.36. $C_{28}H_{26}FeO_3PRh$ requires C, 56.03; H, 4.37%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1960s, 1574s, 1567s, 1524s, 1275m, 1164m, 1097m, 1040m, 821m, 748m, 745m, 696s, 524m, 497s and 469m. NMR ($CDCl_3$, 294 K): ^1H, δ 1.62 (3 H, s, CH_3), 2.11 (3 H, s, CH_3), 4.23 (5 H, s, C_5H_5), 4.39 (2 H, aq, C_5H_4), 4.45 (2 H, m, C_5H_4), 7.31–7.43 [6 H, m, $P(C_6H_5)_2$] and 7.61–7.69 [4 H, m, $P(C_6H_5)_2$]; ^{13}C-{^1H}, δ 26.6 (s, CH_3), 27.6 [d, J(PC) 6, CH_3], 70.0 (s, C_5H_5), 71.0 [d, J(PC) 8, C_5H_4 CH], 74.2 [d, J(PC) 11, C_5H_4 CH], 75.1 [d, J(PC) 60, C_5H_4P C_{ipso}], 100.7 [d, J(PC) 2, =CH−], 127.6 [d, J(PC) 11, $P(C_6H_5)_2$ CH_m], 129.9 [d, J(PC) 2, $P(C_6H_5)_2$ CH_p], 133.9 [d, J(PC) 112, $P(C_6H_5)_2$ CH_o], 134.6 [d, J(PC) 52, $P(C_6H_5)_2$ C_{ipso}], 185.2 (s, C=O), 187.5 (s, C=O) and 189.8 [dd, J(RhC) 76, J(PC) 25 Hz, C≡O]; ^{31}P-{^1H}, δ 42.5 [d, J(RhP) 176 Hz, $FcPPh_2$]. FAB^+: m/z 600, M^+; 572, $[M - CO]^+$; 501, $[M - acac]^+$; and 370, $[FcPPh_2]^+$.

***trans*-[Rh(dpf-*O*,*P*)(Hdpf-*P*)(CO)] 3.** Complex [Rh(acac)(CO)$_2$] (51.6 mg, 0.20 mmol) and Hdpf (166 mg, 0.40 mmol) were suspended in toluene (10 cm^3). A vigorous gas evolution (CO) was observed instantly. The mixture was heated to boiling and the resulting clear orange solution was cooled to room temperature and left to stand at 0 °C overnight. Filtration, washing with diethyl ether (3 × 5 cm^3) and light petroleum (3 × 5 cm^3), and drying *in vacuo* afforded **3** as a cinnamon orange powder. Yield 179 mg, 93% (Found: C, 58.80; H, 3.98. $C_{47}H_{37}Fe_2O_5P_2Rh$ requires C, 58.90; H, 3.89%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1962s, 1703s, 1551s, 1348m, 1255m, 1164m, 1097m, 1030m, 834m, 695s and 503s. NMR ($CDCl_3$, 294 K): ^1H, δ 4.42 (2 H, br s, C_5H_4C CH), 4.50 (4 H, m, C_5H_4P CH), 4.99 (2 H, at, C_5H_4C CH), 7.33–7.42 [6 H, m, $P(C_6H_5)_2$] and 7.65–7.75 [4 H, m, $P(C_6H_5)_2$]; ^{13}C-{^1H}, δ 72.3 (s, C_5H_4C CH), 72.5 (s, C_5H_4C CH), 72.9 (at, C_5H_4P C_{ipso}), 73.2 (at, C_5H_4P CH), 74.9 (at, C_5H_4P CH), 76.5 (s, C_5H_4C C_{ipso}), 128.4 [at, $P(C_6H_5)_2$ CH_m], 130.4 [at, $P(C_6H_5)_2$ CH_p], 133.2 [at, $P(C_6H_5)_2$ C_{ipso}], 133.7 [at, $P(C_6H_5)_2$ CH_o], 175.2 (s, C=O) and 189.8 [dt, J(RhC) 75, J(PC) 17 Hz, C≡O]; ^{31}P-{^1H}, δ 20.2 [d, J(RhP) 132 Hz, Hdpf and dpf]. FAB^+: m/z 959, $[M + H]^+$; 930, $[M - CO]^+$; 849, $[M - C_6H_5O_2]^+$; 821, $[M - C_6H_5O_2 - CO]^+$; 545, [(Hdpf)-Rh(CO)]$^+$; and 414, [Hdpf]$^+$.

***trans*-[Rh(dpf-*O*,*P*)(PCy$_3$)(CO)] 4.** The complex [Rh(acac)(PCy$_3$)(CO)] (256 mg, 0.50 mmol) was dissolved in boiling butan-2-one (5 cm^3) and a solution of Hdpf (217 mg, 0.52 mmol) in the same solvent (2 cm^3) was added. The mixture was refluxed for 10 min, cooled to room temperature and left to stand at 0 °C overnight. Filtration, washing with cold butan-2-one (2 cm^3) and drying in air afforded **4** as a bright yellow crystalline solid. Yield 368 mg, 89% (Found: C, 60.91; H, 6.29. $C_{42}H_{51}FeO_3P_2Rh$ requires C, 61.18; H, 6.23%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1961s, 1602s, 1582m, 1567m, 1321s, 1177m, 1164m, 1095m, 1031m, 849m, 813m, 782m, 755m, 693m, 591m, 509s and 469m. NMR ($CDCl_3$, 294 K): ^1H, δ 1.20–2.32 [33 H, m, $P(C_6H_{11})_3$], 4.06 (2 H, aq, C_5H_4P CH), 4.28 (2 H, at, C_5H_4C CH), 4.43 (2 H, at, C_5H_4P CH), 5.37 (2 H, at, C_5H_4C CH), 7.36–7.44 [6 H, m, $P(C_6H_5)_2$] and 7.69–7.78 [4 H, m, $P(C_6H_5)_2$]; ^{13}C-{^1H}, δ 26.6 (s, $C_6H_{11}P$ γ-CH_2), 27.6 [d, J(PC) 11 Hz, $C_6H_{11}P$ α-CH_2], 30.2 (s, $C_6H_{11}P$ β-CH_2), 33.6 [d, J(PC) 11, $C_6H_{11}P$ CH], 70.9 (s, C_5H_4C CH), 71.8 [d, J(PC) 5 Hz, C_5H_4P CH), 72.7 [dd, J(PC) 10 and 2, C_5H_4P C_{ipso}], 74.0 (s, C_5H_4C CH), 75.8 [d, J(PC) 10, C_5H_4P CH), 78.7 (s, C_5H_4C C_{ipso}), 128.2 [d, J(PC) 10, $P(C_6H_5)_2$ CH_m], 130.2 [d, J(PC) 2, $P(C_6H_5)_2$ CH_p], 133.2 [d, J(PC) 12, $P(C_6H_5)_2$ CH_o], 133.7 [d, J(PC) 42, $P(C_6H_5)_2$ C_{ipso}], 174.7 (s, C=O) and 190.5 [dt, J(RhC) 72, J(PC) 17 Hz, C≡O]; ^{31}P-{^1H}, δ 18.4 [dd, J(RhP) 128, J(PP) 325, dpf] and 41.8 [dd, J(RhP) 127, J(PP) 325 Hz, PCy_3]. FAB^+: m/z 825, $[M + H]^+$; 797, $[M - CO + H]^+$; 752, $[M - CO - CO_2]^+$; 545, [(Hdpf)-Rh(CO)]$^+$; and 281, $[PCy_3H]^+$.

***trans*-[Rh(dpf-*O*,*P*)(PPh$_3$)(CO)] 5.** The complex [Rh(acac)(PPh$_3$)(CO)] (246 mg, 0.50 mmol) and Hdpf (217 mg, 0.52 mmol) were treated in a similar fashion as for **4** to give **5** as an orange solid. Yield 251 mg, 62% (Found: C, 62.12; H, 4.27. $C_{42}H_{33}FeO_3P_2Rh$ requires C, 62.56; H, 4.12%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1965s, 1606m, 1583m, 1326m, 1164m, 1096m, 1027m, 743m, 694s and 510s. NMR ($CDCl_3$, 294 K): ^1H, δ 4.15 (2 H, at, C_5H_4C CH), 4.35 (2 H, aq, C_5H_4P CH), 4.47 (2 H, at, C_5H_4P CH), 4.83 (2 H, at, C_5H_4C CH), 7.30–7.44 [15 H, m, $P(C_6H_5)_2$ and $P(C_6H_5)_3$], 7.63–7.78 [10 H, m, $P(C_6H_5)_2$ and $P(C_6H_5)_3$]; ^{13}C-{^1H}, δ 70.5 (s, C_5H_4C CH), 71.0 [d, J(PC) 48, C_5H_4P C_{ipso}], 71.9 [d, J(PC) 7, C_5H_4P CH], 72.3 (s, C_5H_4C CH), 74.6 [d, J(PC) 10, C_5H_4P CH], 80.7 (s, C_5H_4C C_{ipso}), 128.3 [d, J(PC) 10, $P(C_6H_5)_2$ CH_m], 128.5 [d, J(PC) 10, $P(C_6H_5)_3$ CH_m], 130.3 [d, J(PC) 2, $P(C_6H_5)_2$ CH_p], 130.5 [d, J(PC) 2, $P(C_6H_5)_3$ CH_p], 131.4 [dd, J(PC) 42 and 2, $P(C_6H_5)_3$ C_{ipso}], 133.9 [d, J(PC) 44, $P(C_6H_5)_2$ C_{ipso}], 133.9 [d, J(PC) 13, $P(C_6H_5)_2$ CH_o], 134.4 [d, J(PC) 12, $P(C_6H_5)_3$ CH_o], 175.1 (s, C=O) and 189.9 [dt, J(RhC) 71, J(PC) 18 Hz, C≡O]; ^{31}P-{^1H}, δ 18.8 [dd, J(RhP) 134, J(PP) 344, dpf] and 28.1 [dd, J(RhP) 131, J(PP) 344 Hz, PPh_3]. FAB^+: m/z 807, $[M + H]^+$; 779, $[M - CO + H]^+$; 734, $[M - CO -$

$CO_2]^+$; 545, $[(Hdpf)Rh(CO)]^+$; 414, $[Hdpf]^+$; and 263, $[PPh_3H]^+$.

***trans*-[Rh(dpf-*O*,*P*)(PPh_2Fc)(CO)] 6.** Starting from [Rh(acac)(PPh_2Fc)(CO)] (301 mg, 0.50 mmol) and Hdpf (217 mg, 0.52 mmol), the same procedure as for complex **4** afforded **6** as an orange microcrystalline solid. Yield 193 mg, 42% (Found: C, 60.51; H, 4.15. $C_{46}H_{37}Fe_2O_3P_2Rh$ requires C, 60.43; H, 4.08%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1961s, 1603m, 1583m, 1324m, 1164m, 1096m, 1028m, 744m, 694s, 586m and 497s. NMR ($CDCl_3$, 294 K): ^1H, δ 4.12 (2 H, at, C_5H_4C CH), 4.31 (2 H, aq, C_5H_4P CH, $FcPPh_2$ or dpf), 4.39 (5 H, s, C_5H_5 $FcPPh_2$), 4.41 (2 H, m, C_5H_4P CH, $FcPPh_2$ or dpf), 4.46 (4 H, m, C_5H_4P CH, $FcPPh_2$ or dpf), 4.83 (2 H, at, C_5H_4C CH), 7.31–7.43 [12 H, m, $P(C_6H_5)_2$, $FcPPh_2$ or dpf] and 7.64–7.81 [8 H, m, $P(C_6H_5)_2$, $FcPPh_2$ or dpf]; ^{13}C-{^1H}, δ 70.1 (s, C_5H_5 $FcPPh_2$), 70.5 (s, C_5H_4C CH), 71.0 [dd, J(PC) 47, unresolved J, C_5H_4P C_{ipso}, $FcPPh_2$ or dpf], 71.5 [d, J(PC) 7, C_5H_4P CH, $FcPPh_2$ or dpf], 71.9 [d, J(PC) 6, C_5H_4P CH, $FcPPh_2$ or dpf], 72.6 (s, C_5H_4C CH), 73.1 [dd, J(PC) 47, J 5, C_5H_4P C_{ipso}, $FcPPh_2$ or dpf], 74.2 [d, J(PC) 11, C_5H_4P CH, $FcPPh_2$ or dpf], 74.7 [d, J(PC) 10, C_5H_4P CH, $FcPPh_2$ or dpf], 80.4 (s, C_5H_4C C_{ipso}), 128.1 [d, J(PC) 10, $P(C_6H_5)_2$ CH_m, $FcPPh_2$ or dpf], 128.3 [d, J(PC) 10, $P(C_6H_5)_2$ CH_m, $FcPPh_2$ or dpf], 130.1 [d, J(PC) 2, $P(C_6H_5)_2$ CH_p, $FcPPh_2$ or dpf], 130.3 [d, J(PC) 2, $P(C_6H_5)_2$ CH_p, $FcPPh_2$ or dpf], 133.2 [dd, J(PC) 44, J 2, $P(C_6H_5)_2$ C_{ipso}, $FcPPh_2$ or dpf], 133.8 [d, J(PC) 8, $P(C_6H_5)_2$ CH_o, $FcPPh_2$ or dpf], 133.9 [d, J(PC) 8, $P(C_6H_5)_2$ CH_o, $FcPPh_2$ or dpf], 134.0 [dd, J(PC) *ca.* 40, J 2, $P(C_6H_5)_2$ C_{ipso}, $FcPPh_2$ or dpf], 175.2 (s, C=O) and 190.3 [dt, J(RhC) 72, J(PC) 18 Hz, C≡O]; ^{31}P-{^1H}, δ 18.7 [dd, J(RhP) 133, J(PP) 353, dpf] and 24.0 [dd, J(RhP) 132, J(PP) 353 Hz, PPh_3]. FAB^+: m/z 915, $[M + H]^+$; 887, $[M - CO + H]^+$; 894, $[M - C_5H_5]^+$; 842, $[M - CO - CO_2]^+$; 545, $[(Hdpf)Rh(CO)]^+$; and 370, $[PPh_2Fc]^+$.

X-Ray crystallography

Crystal data and intensity collection parameters. $C_{42}H_{51}FeO_3P_2Rh$, $M = 824.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.901(1)$, $b = 12.875(5)$, $c = 15.427(2)$ Å, $\alpha = 96.69(1)$, $\beta = 101.28(1)$, $\gamma = 94.46(1)°$, $U = 1905.2(8)$ Å^3 (by least squares from 25 automatically centered diffractions with $24 \leqslant 2\theta \leqslant 28°$), $T = 150.0(1)$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 1.437$ g cm^{-3}, $F(000) = 856$, μ(Mo-Kα) = 0.94 mm^{-1}, yellow prism grown by a slow cooling of a hot butan-2-one solution, dimensions $0.1 \times 0.2 \times 0.4$ mm, Enraf-Nonius CAD4 four circle diffractometer, θ–2θ scan, data collection range $-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 14$, $-17 \leqslant l \leqslant 17$ ($2\theta_{max} = 48°$), variation of three periodically measured standard diffractions 4.7%; 5963 unique diffractions were measured ($R_\sigma = 0.018$) and used in all calculations. The data were corrected for Lorentz-polarization effects.

Structure solution and refinement. The structure was solved by direct methods (SIR 92, ref. 23) and refined by full-matrix least squares on F^2 (SHELXL 97, ref. 24). Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$, $w_1 = 0.0702$ and $w_2 = 2.4986$ was applied. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and then freely isotropically refined. Final $R = 0.035$ and $R' = 0.097$ for 5377 observed diffractions [$I > 2\sigma(I)$] and $R = 0.039$ and $R' = 0.101$ (all data); 646 parameters, largest Δ/σ 0.001, goodness of fit 1.027, extremes on the residual electron density map +1.69 and −0.79 e Å^{-3}.

CCDC reference number 186/1077.

See http://www.rsc.org/suppdata/dt/1998/2807/ for crystallographic files in .cif format.

Acknowledgements

We thank Mr. M. Polášek for FAB MS measurements and Professor J. Podlaha for useful discussion and comments. Financial support from the Grant Agency of Charles University (grant No. 209/96/B) and Czech Republic (No. 203/97/0242) is gratefully acknowledged.

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Received 19*th May* 1998; *Paper* 8/03743D