PX_3-induced migratory insertion reactions of half-sandwich-type carbenerhodium(I) complexes†

Ulrich Herber,[a] Rita Guerrero Sanchez,[b] Olaf Gevert,[a] Matthias Laubender[a] and Helmut Werner*[a]

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: helmut.werner@mail.uni-wuerzburg.de*

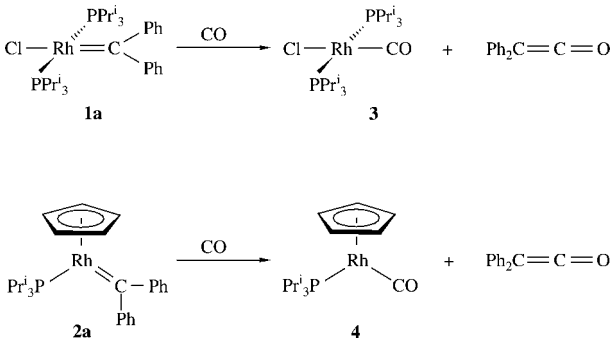
[b] *Grupo de Química Organometálica, Departamento de Chímica Inorgánica, Facultad de Química, Universidad de Murcia, E-30071 Murcia, Spain*

Received (in Strasbourg, France) 23rd October 2000, Accepted 15th November 2000
First published as an Advance Article on the web 15th February 2001

The carbenerhodium(I) complexes *trans*-[RhCl(=CPh_2)$(L)_2$] (L = PPr^i_3, **1a**; $SbPr^i_3$, **1b**) react with PF_3 by cleavage of the rhodium–carbene bond to give the corresponding PF_3 derivatives *trans*-[RhCl(PF_3)$(L)_2$] **5a**,**b**, in good yield. In contrast, treatment of the half-sandwich-type compound [(η^5-C_5H_5)Rh(=CPh_2)(PPr^i_3)], **2a**, with both PF_3 and $P(OPh)_3$ leads to the migratory insertion of the CPh_2 unit into one of the cyclopentadienyl C–H bonds to form the ring-substituted products [{η^5-$C_5H_4(CHPh_2)$}Rh(PX_3)(PPr^i_3)] (X = F, **6a**; OPh, **6b**). The molecular structures of **6a** and **6b** have been determined by X-ray crystallography. The reaction of the stibine complex [(η^5-C_5H_5)Rh(=CPh_2)($SbPr^i_3$)], **2b**, with PF_3 proceeds by ligand displacement to afford the new carbenerhodium(I) compound [(η^5-C_5H_5)Rh(=CPh_2)(PF_3)], **7**. The mechanism of the migratory insertion reaction is discussed.

Recently, we reported that square-planar as well as half-sandwich-type diphenylcarbenerhodium(I) complexes, *trans*-[RhCl(=CPh_2)$(PPr^i_3)_2$], **1a**, and [(η^5-C_5H_5)Rh(=CPh_2)(PPr^i_3)], **2a**, upon treatment with CO easily undergo C–C coupling reactions (Scheme 1).[1] Instead of displacing a phosphine ligand, carbon monoxide induces cleavage of the rhodium–carbene bond and affords, besides *trans*-[RhCl(CO)$(PPr^i_3)_2$], **3**, and [(η^5-C_5H_5)Rh(CO)(PPr^i_3)], **4**, exclusively diphenylketene. By taking the related σ-donor/π-acceptor capabilities of CO and PF_3 into consideration,[2] we became interested to find out how the same starting materials **1a** and **2a** would behave toward PF_3. Although a great number of phosphorus ylides $R_3PCR'_2$ with R′ = aryl are known,[3] to the best of our knowledge a corresponding trifluoro derivative $F_3PCR'_2$ has not been described in the literature as yet.

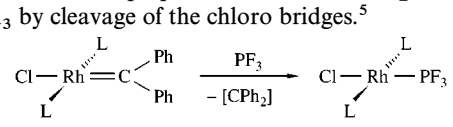
We report in this paper that, not unexpectedly, a coupling of the diphenylcarbene ligand of either **1a** or **2a** with PF_3 does not take place. However, the surprising and most noteworthy result is that the half-sandwich-type complex **2a** reacts under mild conditions with both PF_3 and $P(OPh)_3$ by migratory insertion of the CPh_2 unit into one of the cyclopentadienyl C–H bonds to form a ring-substituted product. Some preliminary observations have already been communicated.[4]



Scheme 1

Results and discussion

Treatment of the square-planar bis(phosphine) complex **1a**, which is easily accessible from **1b** and PPr^i_3 by ligand exchange,[1a,b] with PF_3 in benzene at room temperature leads to displacement of the carbene by PF_3. After recrystallization from acetone, compound **5a** is isolated as a yellow solid in 68% yield. The reaction of the bis(stibine) counterpart **1b** with PF_3 proceeds analogously and gives compound **5b** (Scheme 2). In this case, no free $SbPr^i_3$ can be detected spectroscopically in the reaction mixture, which means that PF_3 behaves completely differently towards **1b** compared with PPr^i_3 and other trialkyl- or triarylphosphines. The latter react with **1b** by substitution of the stibine ligands to afford *trans*-[RhCl(=CPh_2)$(PR_3)_2$]. The ^{31}P NMR spectrum of **5a** exhibits two well-separated resonances at δ 111.9 and 46.8, which due to ^{31}P–^{103}Rh, ^{31}P–^{31}P and ^{31}P–^{19}F couplings appear as doublets of doublets of quartets. In the ^{31}P NMR spectrum of **5b**, a doublet of quartets at δ 120.2 is observed. With regard to the rhodium-free by-products, a GC/MS analysis of the solution revealed that the CPh_2 moiety is mainly transformed into tetraphenylethene. Small amounts of substituted arenes can also be detected. We note that an analog of **5a** with two triphenyl- instead of two triisopropylphosphine ligands is known; it has been prepared from the dimer $[RhCl(PF_3)_2]_2$ and PPh_3 by cleavage of the chloro bridges.[5]

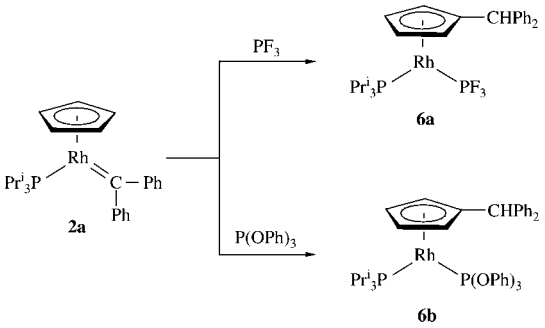


	L
1a, **5a**	PPr^i_3
1b, **5b**	$SbPr^i_3$

Scheme 2

† Dedicated to Professor E.-G. Jäger on the occasion of his 65th birthday.

 DOI: 10.1039/b008601k



Scheme 3

The cyclopentadienyl complex **2a** also reacts with PF_3 at room temperature. Passing a stream of carefully dried phosphorus trifluoride through a solution of **2a** in benzene leads to a smooth change of color from blue to orange and affords, after chromatographic workup and recrystallization from pentane, compound **6a** (being analytically a 1 : 1 adduct of **2a** and PF_3) as an orange air- and moisture-sensitive solid in 72% yield (Scheme 3). The most typical spectroscopic features of **6a** are the signals for the C*H*Ph_2 proton at δ 4.79 in the ^{1}H NMR and the two resonances for the phosphorus nuclei of the PF_3 and PPr^i_3 ligands at δ 119.4 and 79.0 in the ^{31}P NMR spectrum. Both ^{31}P NMR signals show a strong ^{31}P–^{103}Rh coupling of, respectively, 446.3 and 221.0 Hz.

The migratory insertion of the CPh_2 unit into one of the C–H bonds of the ring can be induced not only by PF_3 but also by $P(OPh)_3$. The phosphite, however, is less reactive than PF_3 and therefore the reaction of **2a** with a four-fold excess of $P(OPh)_3$ in toluene at room temperature takes several days. After removal of the solvent and recrystallization of the residue from ether–pentane orange crystals of the insertion product **6b** are obtained; they are considerably more thermally stable than the PF_3 analog **6a**. In agreement with the proposed structure, the ^{1}H NMR spectrum of **6b** displays two signals for the pairwise equivalent C_5H_4 protons at δ 4.69 and 4.47 and the ^{13}C NMR spectrum equally shows two resonances at δ 86.5 and 84.5 for the respective ring carbon atoms. The two resonances in the ^{31}P NMR spectrum of **6b** at δ 132.4 and 75.3 reveal a smaller ^{31}P–^{31}P coupling (64.4 Hz) than those of **6a** (77.6 Hz).

The reaction of the triisopropylstibine complex **2b** with PF_3 follows a different pathway than that of the PPr^i_3 counterpart **2a**. Instead of the carbene, the stibine ligand is displaced and following chromatographic workup the C_5H_5Rh compound **7** is isolated as a deep red microcrystalline solid in 72% yield (see Scheme 4). In this case, PF_3 behaves analogously to CO toward **2b** as the starting material. In contrast, triphenylphosphite does not react with **2b** by ligand substitution. While no reaction takes place using equimolar amounts of **2b** and $P(OPh)_3$ (toluene, room temperature, 2 days), with a four-fold excess of the phosphite a mixture of products is formed, which could not be separated by either fractional crystallization or column chromatography. Since as discussed below the half-sandwich-type complexes $[(\eta^5\text{-}C_5H_5)M(L)_2]$ with M = Co, Rh and Ir prefer to react with Lewis bases by an associative mechanism, it is conceivable that the low reactivity of $P(OPh)_3$ toward **2b** is due to the larger size of the phosphite compared with PF_3.

The results of the single-crystal X-ray diffraction studies of **6a** and **6b** are shown in Fig. 1 and 2. In both compounds, the

Scheme 4

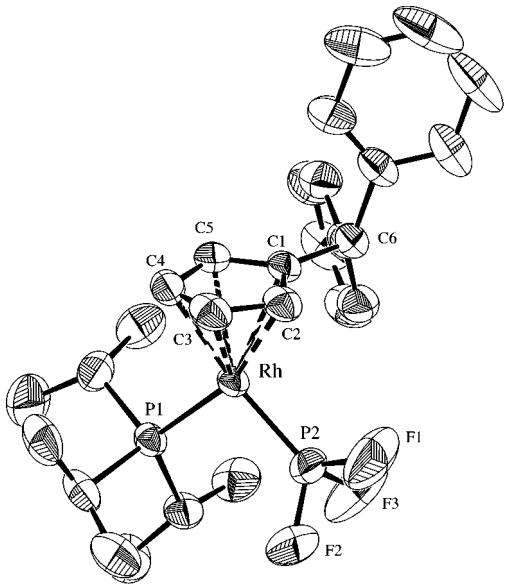


Fig. 1 An ORTEP plot of compound **6a**. The ellipsoids are drawn at the 50% probability level.

rhodium has a somewhat distorted trigonal coordination sphere if the midpoint of the substituted cyclopentadienyl ring is taken as one coordination site. The Rh–PF_3 as well as the Rh–$P(OPh)_3$ bonds are significantly shorter than the Rh-PPr^i_3 distance (see Table 1), which confirms the distinct difference in the π-acceptor strength of PF_3 and $P(OPh)_3$ on one side and of PPr^i_3 on the other. The $CHPh_2$ moiety in **6a** and **6b** is pointing away from the bulky triisopropylphosphine ligand, which probably reduces the steric repulsion between the two units. The distance between rhodium and the substituted ring carbon atom C1 is somewhat larger in the triphenylphosphite complex **6b** than in **6a**, which could also be due to steric requirements.

Regarding the mechanism of formation of **6a** and **6b**, two routes are conceivable. Since it is known, mainly due to the

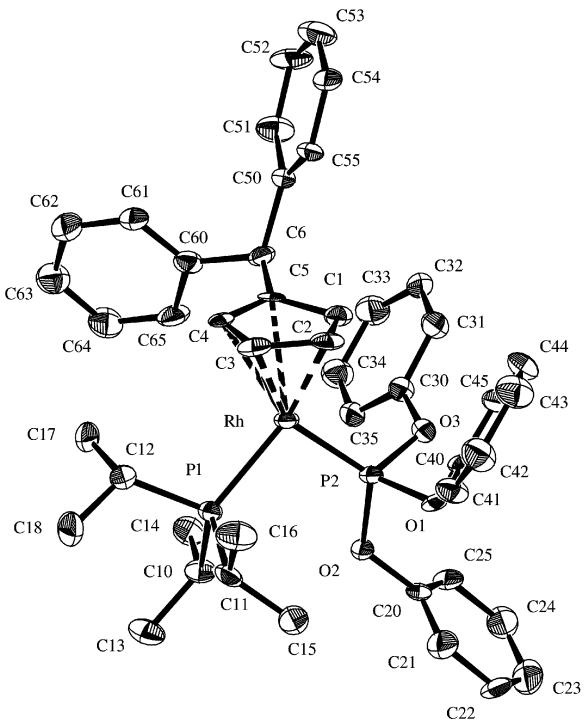


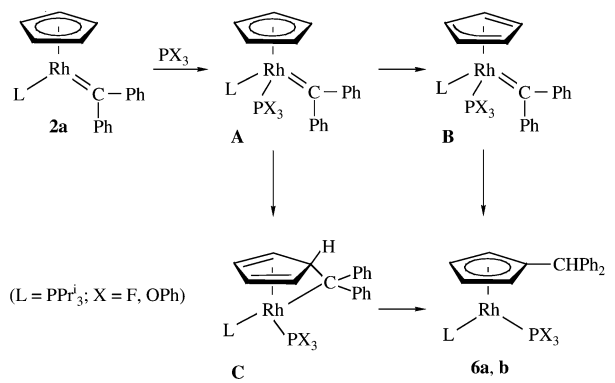
Fig. 2 An ORTEP plot of compound **6b**. The ellipsoids are drawn at the 50% probability level.

Table 1 Selected bond lenghts (Å) and angles (°) for complexes **6a** and **6b**

	6a	6b
Rh–P1	2.275(3)	2.263(2)
Rh–P2	2.082(4)	2.120(2)
Rh–C1	2.307(5)	2.356(7)
Rh–C2	2.220(5)	2.206(8)
Rh–C3	2.294(6)	2.298(8)
Rh–C4	2.258(3)	2.304(7)
Rh–C5	2.304(6)	2.330(7)
C1–C2	1.434(6)	1.45(1)
C2–C3	1.410(6)	1.43(1)
C3–C4	1.385(7)	1.41(1)
C4–C5	1.438(6)	1.43(1)
C5–C1	1.398(5)	1.40(1)
C1–C6	1.518(5)	1.51(1)
P1–Rh–P2	97.0(1)	98.54(8)
C2–C1–C5	106.2(3)	105.3(7)
C5–C1–C6	128.6(4)	129.3(7)
C2–C1–C6	125.1(3)	125.3(7)

work of Basolo and his group,[6] that ligand displacement reactions of cyclopentadienylrhodium(I) complexes $[(\eta^5\text{-}C_5H_5)Rh(L)_2]$ with Lewis bases L′ follow second-order kinetics, we assume that from **2a** and PX_3 a labile 1 : 1 adduct **A** is initially formed (Scheme 5). This 20-electron intermediate could afford, *via* ring slippage, a second intermediate **B** (with an 18-electron configuration at the metal) in which the cyclopentadienyl unit would be η^3- coordinated. Alternatively, the carbene ligand of intermediate **A** could attack the five-membered ring to give the diene alkyl compound **C**, which by subsequent hydrogen transfer to the CPh_2 carbon and breaking of the Rh–C σ-bond affords **6a,b**. The final insertion product could also be generated from **B** *via* migration of the carbene to the uncoordinated C–C double bond or from **B** *via* **C** by insertion of the carbene into an η^3-allylic Rh–C bond. A similar rearrangement probably does occur during formation of the substituted indenylrhodium(I) complexes $[\{\eta^5\text{-}C_9H_6(CHPh_2)\}Rh(CO)(L)]$ (L = $SbPr^i_3$, PPr^i_3, PPh_3, PPr^iPh_2, PPr^i_2Ph), which were prepared from $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(L)]$ and CO.[7] It should be mentioned that the starting material **2a** reacts not only with PF_3 and $P(OPh)_3$ but also with various Brönsted acids HX (X = Cl, Br, I, CF_3CO_2) by formal oxidative addition to yield the ring-substituted hydridorhodium(III) complexes $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhHX(PPr^i_3)]$.[4,8] In this case, a labelling experiment using $[(\eta^5\text{-}C_5D_5)Rh(=CPh_2)(PPr^i_3)]$ and HCl as the substrates suggests that the migratory insertion of the carbene occurs *via* a η^4-cyclopentadienerhodium(I) species as an intermediate.

In conclusion, the present investigations have shown that the half-sandwich-type compound **2a** behaves completely differently toward CO and PX_3 (X = F, OPh). While carbon monoxide reacts with **2a** to give the substitution product **4** and diphenylketene, treatment of **2a** with PX_3 leads to a migratory insertion of the carbene ligand into one of the ring C–H bonds to produce **6a,b**. This process has, to the best of our knowledge and apart from our own work,[4,7,9] no precedence.[10] The closest analogy to the formation of $C_5H_4CHPh_2$ from C_5H_5 and CPh_2 that we are aware of goes back to the work of Guth and Kirmse, which illustrates that arylcarbenes, generated from the corresponding diazo compounds, undergo an intramolecular insertion into the *ortho* C–H bond of a connected phenyl ring.[11]



Scheme 5

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1a,b**,[1b] **2a,b**[1c] and PF_3[12] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; vt, virtual triplet; br, broadened signal; coupling constants *N* and *J* in Hz.

Syntheses

***trans*-[RhCl(PF$_3$)(PPr$^i_3$)$_2$], 5a.** A slow stream of PF_3 was passed through a solution of **1a** (95 mg, 0.15 mmol) in benzene (20 cm^3) for 20 min at room temperature. A change of color from green to yellow occurred. After the reaction mixture had been stirred for 20 min, the solvent was removed *in vacuo* and the oily residue was recrystallized from acetone (5 cm^3) at −60 °C. A yellow solid was formed, which was separated from the mother liquor and dried *in vacuo*: yield 56 mg (68%); mp 112 °C (decomp.) Anal. found: C, 39.13; H, 8.21%. $C_{18}H_{42}ClF_3P_3Rh$ requires: C, 39.54; H, 7.74%. NMR (C_6D_6): δ_H (400 MHz) 2.69 (6 H, m, PC*H*CH$_3$), 1.25 [36 H, dvt, *N* 13.9, *J*(H,H) 6.6, PCHC*H*$_3$]; δ_C (100.6 MHz) 24.0 (vt, *N* 10.5, PCHCH$_3$), 19.0 (s, PCHCH$_3$); δ_P (162.0 MHz) 111.9 [ddq, *J*(F,P) 1267.9, *J*(Rh,P) 390.4, *J*(P,P) 52.2, PF_3], 46.8 [ddq, *J*(Rh,P) 111.9, *J*(P,P) 52.2, *J*(F,P) 6.4, PPr^i_3].

***trans*-[RhCl(PF$_3$)(SbPr$^i_3$)$_2$], 5b.** This compound was prepared as described for **5a** from **1b** (100 mg, 0.12 mmol) and PF_3 in benzene (20 cm^3). Yellow solid: yield 59 mg (68%); mp 88 °C (decomp.) Anal. found: C, 29.53; H, 5.79%. $C_{18}H_{42}ClF_3PRhSb_2$ requires: C, 29.68; H, 5.81%. NMR (C_6D_6): δ_H (200 MHz) 2.37 [6 H, sept, *J*(H,H) 7.3, SbC*H*CH$_3$], 1.38 [36 H, d, *J*(H,H) 7.3, SbCHC*H*$_3$]; δ_P (81.0 MHz) 120.2 [dq, *J*(F,P) 1256.5, *J*(Rh,P) 356.2].

[{η^5-C$_5$H$_4$(CHPh$_2$)}Rh(PF$_3$)(PPr$^i_3$)], 6a. A slow stream of PF_3 was passed through a solution of **2a** (100 mg, 0.20 mmol) in benzene (20 cm^3) at room temperature for 20 min. A change of color from blue to red occurred. After the solution was stirred for 20 min at room temperature, the solvent was removed and the oily residue was dissolved in pentane (2 cm^3). The solution was chromatographed on Al_2O_3. With pentane, an orange–red fraction was eluted, which was evaporated to dryness *in vacuo*. Recrystallization of the residue from acetone (1 cm^3) at −78 °C led to the precipitation of orange crystals, which were separated from the mother liquor, washed with a small amount of pentane at −30 °C and dried: yield 48 mg (41%); mp 42 °C (decomp.) Anal. found: C, 55.49; H, 6.35%. $C_{27}H_{36}F_3P_2Rh$ requires: C, 55.68; H, 6.23%. NMR (C_6D_6): δ_H (200 MHz) 7.26 (4 H, m, *ortho*-H of C_6H_5), 7.02 (8 H, m, *meta*- and *para*-H of C_6H_5), 5.09 [4 H, m, C_5H_4], 4.79 (1 H, m, C*H*Ph$_2$), 1.20 [3 H, dsept, *J*(P,H) 13.3, *J*(H,H) 7.1, PC*H*CH$_3$], 0.82 [18 H, dd, *J*(P,H) 13.7, *J*(H,H) 7.1, PCHC*H*$_3$]; δ_P (81.0 MHz) 119.4 [ddq, *J*(F,P) 849.3, *J*(Rh,P)

446.3, J(P,P) 77.6, PF_3], 79.0 [dd, J(Rh,P) 221.0, J(P,P) 77.6, PPr^i_3].

[{η⁵-C_5H_4(CHPh$_2$)}Rh{P(OPh)$_3$}(PPr^i_3)], 6b. A solution of **2a** (150 mg, 0.30 mmol) in toluene (10 cm^3) was treated with $P(OPh)_3$ (316 μl, 1.20 mmol) and stirred for 3 days at room temperature. A change of color from deep blue to orange occurred. The solvent was removed *in vacuo* and the oily residue was washed three times with 5 cm^3 portions of pentane. The remaining solid was recrystallized from ether–pentane (1 : 10, 3 cm^3) at 5 °C. Orange crystals were formed, which were separated from the mother liquor and dried; yield 128 mg (53%); mp 89 °C (decomp.) Anal. found: C, 67.59; H, 6.14%. $C_{45}H_{51}O_3P_2Rh$ requires: C, 67.16; H, 6.39%. NMR (C_6D_6): δ_H (400 MHz) 7.46–6.78 (15 H, m, C_6H_5 and OC_6H_5), 4.69, 4.47 (4 H, both s, C_5H_4), 4.24 (1 H, s, C*H*Ph$_2$), 2.10 [3 H, dsept, J(P,H) 14.4, J(H,H) 7.3, PC*H*CH_3], 1.11 [18 H, dd, J(P,H) 13.4, J(H,H) 7.3, PCHCH_3]; δ_C(100.6 MHz) 153.2 [d, J(P,C) 7.1, *ipso*-C of OC_6H_5], 145.9 (s, *ipso*-C of C_6H_5), 129.8, 128.2, 125.8, 124.5, 123.8, 122.3 (all s, OC_6H_5 and C_6H_5), 86.5, 84.5 (both s, C_5H_4), 49.6 (s, *C*HPh$_2$), 28.1 [d, J(P,C) 20.3, P*C*HCH_3], 20.0 (s, PCH*C*H_3); δ_P(162 MHz) 132.4 [dd, J(Rh,P) 388.3, J(P,P) 64.4, P(OPh)$_3$], 75.3 [dd, J(Rh,P) 191.6, J(P,P) 64.4, PPr^i_3].

[(η⁵-C_5H_5)Rh(=CPh$_2$)(PF_3)], 7. A slow stream of PF_3 was passed through a solution of **2b** (59 mg, 0.10 mmol) in benzene (20 cm^3) at room temperature for 20 min. A change of color from blue to red occurred. After the solution was stirred for 20 min at room temperature, it was worked up as described for **6a**. Recrystallization from acetone (1 cm^3) at −78 °C led to the formation of deep red crystals. Yield 30 mg (72%); mp 46 °C (decomp.) Anal. found: C, 51.02; H, 3.64%. $C_{18}H_{15}F_3PRh$ requires: C, 51.21; H, 3.58%. NMR (C_6D_6): δ_H (200 MHz) 7.30 (4 H, m, *ortho*-H of C_6H_5), 7.02 (6 H, m, *meta*- and *para*-H of C_6H_5), 4.88 [5 H, d, J(Rh,H) 1.8, C_5H_5]; δ_P (81.0 MHz) 117.1 [dq, J(F,P) 1334.9, J(Rh,P) 488.2].

X-Ray crystallography

Single crystals of **6a** were grown from pentane (8 °C); crystal size 0.55 × 0.30 × 0.25 mm; monoclinic, space group $C2/c$ (no. 15); a = 34.48(9), b = 8.96(2), c = 17.67(3) Å, β = 96.85(2)°, U = 5427(3) Å^3, d_{calc} = 1.426 g cm^{-3}; max. 2Θ = 48° [Mo-Kα λ = 0.71073 Å, graphite monochromator, ω/Θ scan, Zr filter with factor 16.4, T = 293(2) K]; 4548 reflections scanned, 4162 unique [R(int) = 0.0136], 3736 observed [$I > 2\sigma(I)$], Lorentz polarization and empirical absorption corrections (ψ scans, min. transmission 80.0%); direct methods (SHELXS-86),[13] 408 parameters, reflect/parameter ratio 10.2; R_1 = 0.0364, wR_2 = 0.0972; residual electron density 1.058/ −0.425 e Å^{-3}. Ref. code PULRIX, Cambridge Structural Database System, 2000. Single crystals of **6b** were grown from acetone (−20 °C); crystal size 0.12 × 0.10 × 0.08 mm; triclinic, space group $P\bar{1}$ (no. 2); a = 10.170(3), b = 11.177(2), c = 17.401(3) Å, α = 85.68(1), β = 106.85(1), γ = 88.03(2)°, U = 1963.5(7) Å^3, d_{calcd} = 1.361 g cm^{-3}; max. 2Θ = 48° [Mo-Kα, λ = 0.710 73 Å, graphite monochromator, ω/Θ scan, Zr filter with factor 16.4, T = 173(2) K]; 6553 reflections scanned, 6159 unique [R(int) = 0.0467], 4323 observed [$I > 2\sigma(I)$], Lorentz polarization and empirical absorption corrections (ψ scans, min. transmission 64.12%); direct methods (SHELXS-86),[13] 469 parameters, reflect/parameter ratio 13.13; R_1 = 0.0730, wR_2 = 0.1943; residual electron density 1.074/ −1.273 e Å^{-3}.

CCDC reference number 440/244. See http://www.rsc.org/suppdata/nj/b0/b008601k/ for crystallographic files in .cif format

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie and BASF AG. We also thank Mrs R. Schedl and Mr C. P. Kneis (DTA and elemental analyses) and Mrs M.-L. Schäfer and Dr W. Buchner (NMR spectra).

References

1 (*a*) P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, 1993, **105**, 1498; P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1480; (*b*) H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert and J. Wolf, *Chem. Eur. J.*, 1997, **3**, 1375; (*c*) H. Werner, P. Schwab, E. Bleuel, N. Mahr, B. Windmüller and J. Wolf, *Chem. Eur. J.*, 2000, **6**, 4461.
2 (*a*) T. Kruck, *Angew. Chem.*, 1967, **79**, 27; T. Kruck, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 53; (*b*) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 364; (*c*) T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1755.
3 (*a*) G. M. Kosolapoff and L. Maier, *Organophosphorus Compounds*, Wiley–Interscience, New York, 1972, vol. 3; (*b*) H. Schmidbaur, *Adv. Organomet. Chem.*, 1976, **14**, 205.
4 U. Herber, E. Bleuel, O. Gevert, M. Laubender and H. Werner, *Organometallics*, 1998, **17**, 10.
5 (*a*) T. Kruck, N. Derner and W. Lang, *Z. Naturforsch., B*, 1966, **21**, 1020; (*b*) D. A. Clement, J. F. Nixon and M. D. Sexton, *J. Chem. Soc., Chem. Commun.*, 1969, 1509; (*c*) M. A. Bennett and D. J. Patmore, *J. Chem. Soc., Chem. Commun.*, 1969, 1510.
6 (*a*) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, 1966, **88**, 1657; (*b*) F. Basolo, *Inorg. Chim. Acta*, 1985, **100**, 33.
7 E. Bleuel, O. Gevert, M. Laubender and H. Werner, *Organometallics*, 2000, **19**, 3109.
8 E. Bleuel, P. Schwab, M. Laubender and H. Werner, *J. Chem. Soc., Dalton Trans.*, 2001, 266.
9 E. Bleuel and H. Werner, *C. R. Acad. Sci. Ser. IIc: Chim.*, 1999, 341.
10 K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert and K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983.
11 M. Guth and W. Kirmse, *Acta Chem. Scand.*, 1992, **46**, 606.
12 R. J. Clark and H. Belefant, *Inorg. Synth.*, 1989, **26**, 12.
13 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.