Six-Coordinate Ruthenium(II) Complexes Containing Unsymmetrical 1,2-Bis(phosphanyl)ethanes and 1-Arsanyl-2-phosphanylethanes as Ligands

Guido Fries,[a] Kerstin Ilg,[a] Matthias Pfeiffer,[a] Dietmar Stalke,[a] and Helmut Werner*[a]

Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

Keywords: Acetylacetonato complexes / Allyl complexes / Ruthenium / Chelates / Phosphorus / Arsenic

The bis(η^3-2-methallyl)ruthenium(II) complexes [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$Ph_2PCH_2CH_2PR_2$)] [R = *i*Pr (**2**), Cy (**3**)] were prepared from the cycloocta-1,5-diene derivative [Ru(η^3-2-MeC_3H_4)$_2$(η^4-C_8H_{12})] (**1**) and the unsymmetrical 1,2-bis(phosphanyl)ethanes $Ph_2PCH_2CH_2PR_2$. The As,P analogue [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$Ph_2PCH_2CH_2AstBu_2$)] (**4**) was obtained by the same route. The reaction of **2** with hexafluoroacetylacetone afforded the chelate compound [Ru(κ^2-[F_6]-acac)$_2$(κ^2-*i*$Pr_2PCH_2CH_2PPh_2$)], whereas treatment of **2** and **3** with pentachlorophenol gave the related, more labile complexes [Ru(κ^2-*O*,*Cl*-OC_6Cl_5)$_2$(κ^2-$R_2PCH_2CH_2PPh_2$)] [R = *i*Pr (**6**), Cy (**7**)]. Preparation of the parent bis(acac) compound [Ru(κ^2-acac)$_2$(κ^2-*i*$Pr_2PCH_2CH_2PPh_2$)] (**8**), which could not be obtained from **2** and acacH, was achieved by ligand exchange of **6** and acetylacetone. The molecular structures of **2** and **6** were determined by X-ray crystallography.

Introduction

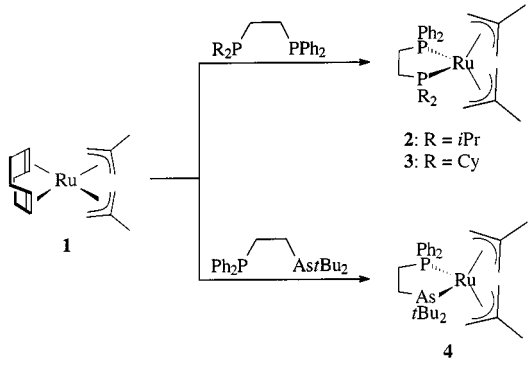
By attempting to modify the donor/acceptor properties of bidentate ligands with P, As, and Sb as donor atoms, we recently described two new synthetic methodologies for unsymmetrical bis(phosphanyl)methanes and 1,2-bis(phosphanyl)ethanes as well as for their As,P analogues.[1,2] While the methane derivatives $R_2PCH_2ER'_2$ were prepared from the stannylated phosphanes $R_2PCH_2SnR''_3$ by metalation with MeLi or PhLi in the presence of tetramethylethylenediamine followed by treatment with R'_2PCl or R'_2AsCl,[1] the corresponding disubstituted ethanes $R_2PCH_2CH_2ER'_2$ were obtained in a one-pot reaction from the cyclic sulfate $C_2H_4O_2SO_2$ by stepwise addition of R'_2ELi and R_2PLi, respectively. The latter method is also suitable for the preparation of *chiral* bidentate P,P donors of the general composition $R_2PCH_2CH(Me)PPh_2$ and $R_2PCH_2CH_2CH(Me)PPh_2$ where the substituent R is a bulky alkyl or cycloalkyl group such as *i*Pr, *t*Bu, or C_6H_{11}.[2,3]

In the initial phase of these studies, we tested the coordination properties of the new ligands toward rhodium(I) and isolated a series of square-planar and half-sandwich-type complexes including [Rh(η^4-C_8H_{12})(κ^2-*R*-$Ph_2PCH(Me)CH_2PCy_2$)]PF_6[3] and [(η^6-C_6H_5R)Rh(κ^2-$Cy_2PCH_2Pi Pr_2$)]PF_6 (R = H, Me).[1] In this paper we report the synthesis of a series of ruthenium(II) compounds with both $Ph_2PCH_2CH_2PR_2$ and $Ph_2PCH_2CH_2AstBu_2$ as chelating ligands and η^3-2-methallyl, pentachlorphenolate, and acetylacetonates as ancillary bidentate units. Some preliminary results of this work have already been communicated.[2]

[a] Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Results and Discussion

The preparation of the chelate complexes **2** and **3** (Scheme 1) followed the route which was used by Holle, Jolly, and Kuhnigk to obtain the related bis(η^3-allyl)ruthenium(II) compounds with $iPr_2P(CH_2)_nPiPr_2$ (n = 1, 2, and 3) as ligands.[4] The reaction proceeds in hexane under reflux conditions and affords the products as yellow solids in about 70% isolated yield. Compounds **2** and **3** are only slightly air-sensitive and, apart from pentane and ether, readily soluble in most common organic solvents. The ^{31}P NMR spectra of both **2** and **3** display two sharp doublets for the nonequivalent phosphorus nuclei with ^{31}P-^{31}P coupling constants of 8.5 and 7.6 Hz, respectively. Due to the presence of the unsymmetrical 1.2-bis(phosphanyl)ethane ligand, the ^1H NMR spectra of **2** and **3** are rather complex, thus making an exact assignment of the signals for the CH_2 allyl protons difficult.



Scheme 1

The molecular structure of compound **2**, of which single crystals were obtained from a saturated solution in hexane, was determined by X-ray crystallography. The molecular

  1434–1948/00/1212–2597 $ 17.50+.50/0

diagram (Figure 1) reveals that the coordination geometry around the metal center can be described as a distorted tetrahedron with the two phosphorus atoms P1 and P2 and the two central carbon atoms C40 and C50 of the allylic moieties at the corners of the tetrahedron. The bond lengths Ru−C40 and Ru−C50 are somewhat shorter than those from the ruthenium center to the terminal carbon atoms of the 2-methallyl ligands. This results in dihedral angles of 37.7(1)° and 34.9(1)° between the planes [C40,C41,C42] and [C50,C51,C52] of the π-allyl units and the plane of the five-membered chelate ring [Ru,P1,C2,C1,P2]. The distances Ru−P1 and Ru−P2 differ only slightly to those in similar phosphaneruthenium(II) complexes[5−7] while the bite angle P1−Ru−P2 of 85.32(3)° is nearly identical to that in $[Ru(\eta^3\text{-}2\text{-}MeC_3H_4)_2(\kappa^2\text{-}Cy_2PCH_2CH_2PCy_2)]$ [85.03(4)°].[5]

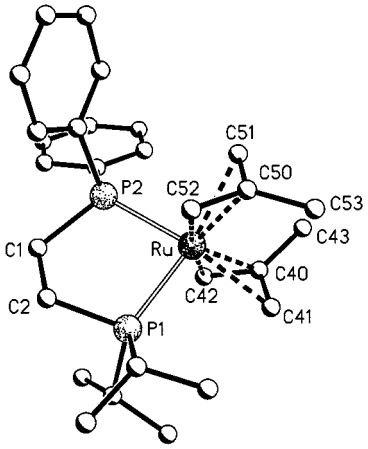
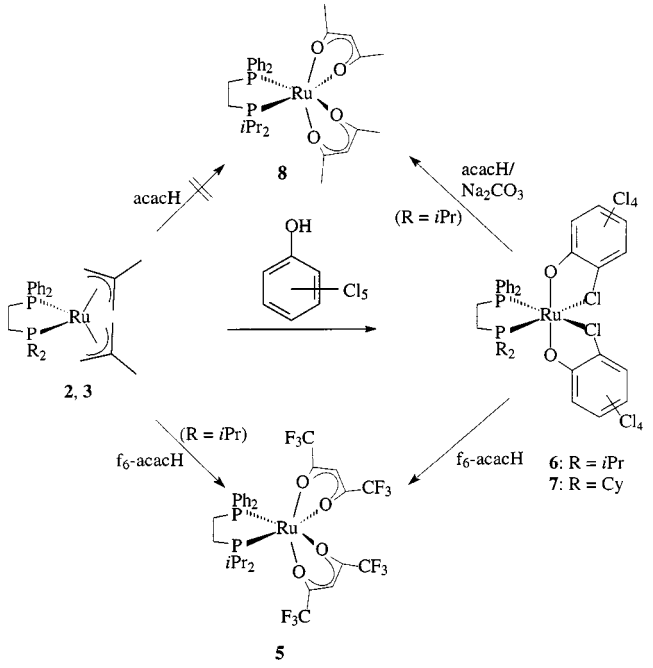


Figure 1. Molecular structure of compound **2**; selected bond lengths [Å] and angles [°]: Ru−P1 2.3278(9), Ru−P2 2.2981(8), Ru−C40 2.178(3), Ru−C41 2.237(4), Ru−C42 2.232(4), Ru−C50 2.181(3), Ru−C51 2.247(3), Ru−C52 2.230(4), P1−C2 1.854(3), P2−C1 1.851(3); P1−Ru−P2 85.32(3), C1−P2−Ru 110.07(11), C2−P1−Ru 107.03(11), C1−C2−P1 111.9(2), C2−C1−P2 110.1(2), C41−C40−C42 116.4(3), C51−C50−C52 117.9(3)

In contrast to $iPr_2PCH_2AstBu_2$, which does not react with the starting material **1** by substitution of the cyclooctadiene ligand,[3] the reaction of the ethane derivative $Ph_2PCH_2CH_2AstBu_2$ with **1** affords the chelate complex **4** (see Scheme 1) as a yellow solid in 51% isolated yield. While the ^{31}P NMR spectrum of **4** displays, in agreement with the proposed structure, a single resonance at δ = 79.4, the ^1H NMR spectrum is very complex and shows several overlapping signals between δ = 2.95 and 0.51, which originate from the allyl, the *tert*-butyl and the CH_2 protons of the coordinated As,P donor unit. In the ^{13}C NMR spectrum of **4**, the CH_2 carbon atoms of the 2-methallyl units give rise to four doublets at δ = 39.6, 36.9, 36.3, and 33.4, thus confirming the presence of an additional unsymmetrical bidentate ligand.

Similarly to the starting material **1**, the substituted compounds **2** and **3** are also quite reactive towards Brönsted acids. However, in contrast to **1** which reacts cleanly with CF_3CO_2H to give $[Ru(\eta^4\text{-}C_8H_{12})(\mu\text{-}O_2CCF_3)_2]_2$,[8] treatment of **2** or **3** with trifluoroacetic acid leads to a mixture of products which could not be separated by conventional techniques.

The reaction of **2** with two equivalents of hexafluoracetylacetone affords, by protonation of both 2-methallyl ligands (and elimination of isobutene), the chelate complex **5** (Scheme 2) as a red air-stable solid in almost quantitative yield. Due to the coordination of the unsymmetrical 1,2-bis(phosphanyl)ethane, the two [F_6]acac units are nonequivalent and therefore the ^{13}C NMR as well as the ^{19}F NMR spectrum of **5** display four resonances for the carbon and fluorine nuclei of the CF_3 groups. The appearance of four quadruplets for the CF_3CO and of two singlets for the $COCHCO$ carbon atoms equally illustrates the stereochemical nonequivalence of the [F_6]acac ligands.



Scheme 2

In contrast to the hexafluoro derivative [F_6]acacH, the parent compound acacH does not react, even in refluxing toluene, with the starting material **2**. The lower acidity of acetylacetone (pK_a = 9.0) compared to the hexafluoro analogue (pK_a = 5.3)[9] presumably causes the difference in the reactivity of the two diketones toward the η^3-2-methallylruthenium(II) complex **2**.

However, the bis(acac) compound **8** is accessible in a stepwise route via the intermediate bis(pentachlorophenolato) complex **6**. Both **6** and **7** are obtained in excellent yield as orange, moderately air-sensitive solids upon treatment of **2** and **3** with two equivalents of C_6Cl_5OH in toluene at room temperature. With regard to the spectroscopic data of **6** and **7**, the interesting feature is that the ^{13}C NMR spectra (in [D_8]toluene) display at both 295 K and 188 K only one signal for the *ortho*- and one signal for the *meta*-carbon atoms of the OC_6Cl_5 units. This observation indicates that a fluxional process takes place in solution, which involves (on the NMR time scale) rapid coordination/decoordination of the chlorine atoms in *ortho* position of the six-membered rings to the metal center. There is good reason to believe that the stability of the chelating bonding mode (via

oxygen and chlorine) of the pentachlorophenolato ligands to the ruthenium center depends significantly on the coordination sphere since the tris(chelate) complexes [Ru(κ^2-OC_6Cl_5)$_2$(κ^2-$Ph_2PCH_2PR_2$)] (R = *i*Pr, Cy) are fluxional at 295 K but rigid at 188 K,[10] while the hydrido compound [RuH(κ^2-OC_6Cl_5)(CO)(P*i*Pr$_3$)$_2$] is nonfluxional on the NMR timescale even at room temperature.[11]

The X-ray crystal structure analysis of **6** (Figure 2) confirms the existence of weak Ru−Cl interactions comparable to those between transition metals and other C−Cl bonds.[12] The Ru−Cl distances of 2.498(1) Å and 2.524(1) Å are significantly longer than in *trans*-[RuCl$_2$(κ^2-$Ph_2PCH_2CH_2PPh_2$)$_2$] [2.4325(12) Å][13] and *trans*-[RuCl$_2$(κ^2-$Ph_2PCH_2PPh_2$)$_2$] [2.426(1) Å,[14] where "normal" covalent Ru−Cl bonds are present. The coordination geometry around the metal center in **6** is a distorted octahedron with a bite angle P1−Ru−P2 of 84.32(5)° that is almost identical to that in compound **2**. The bond angles Ru−O1−C1 [120.6(3)°] and Ru−O2−C7 [119.3(3)°] are considerably smaller than in the hydrido complex *trans*-[RuH(OC_6H_4-4-Me)(κ^2-$Me_2PCH_2CH_2PMe_2$)$_2$] [137.58(16)°][15] where no additional interaction between the C−H units of the phenolato ligand and the metal exists.

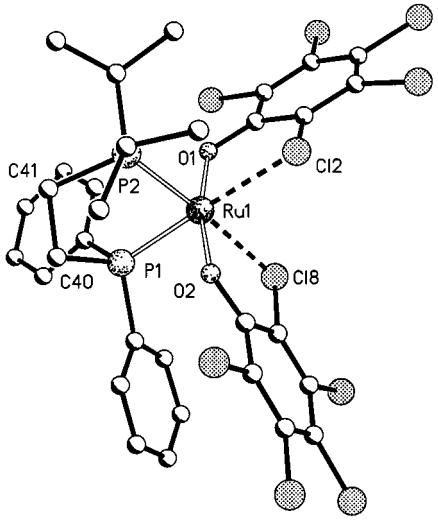


Figure 2. Molecular structure of compound **6**; the THF molecule is omitted for clarity; selected bond lengths [Å] and angles [°]: Ru−P1 2.2341(13), Ru−P2 2.2578(13), Ru−O1 2.088(3), Ru−O2 2.078(3), Ru−Cl2 2.5240(13), Ru−Cl8 2.4978(13); P1−Ru−P2 84.32(5), P1−Ru−O1 99.45(9), P1−Ru−O2 89.24(9), P1−Ru−Cl2 176.70(4), P1−Ru−Cl8 94.03(5), P2−Ru−O1 94.51(9), P2−Ru−O2 93.00(8), P2−Ru−Cl2 98.90(5), P2−Ru−Cl8 174.32(4), O1−Ru−O2 169.03(11), O1−Ru−Cl2 79.60(9), O1−Ru−Cl8 91.12(9), O2−Ru−Cl2 91.34(9), O2−Ru−Cl8 81.53(8), Cl2−Ru−Cl8 82.85(4)

In contrast to **2**, compound **6** reacts with acetylacetone in the presence of Na_2CO_3 to afford the bis(acac) complex **8** as a yellow air-stable solid in 89% isolated yield. Moreover, the bis(pentachlorophenolato) derivative **6** affords the bis([F$_6$]acac) complex **5** almost instantaneously upon treatment with [F$_6$]acacH in toluene. This pattern of reactivity indicates that **6** (and equally **7**) could be considered as a masked 14-electron species in which the additional interaction between the chlorine atoms in *ortho* position of the OC_6Cl_5 units and the metal center prevents a subsequent oligomerization or decomposition process. We note that quite recently Baratta et al. reported another example of a ruthenium(II) complex with a formal 14-electron configuration; in this case two strong agostic RuHC interactions relieve part of the electronic unsaturation at the metal center.[16]

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting material **1**[17] as well as the ligands $Ph_2PCH_2CH_2PR_2$ (R = *i*Pr, Cy) and $Ph_2PCH_2CH_2AstBu_2$[2,3] were prepared as described in the literature. − IR: Perkin−Elmer 1320. − NMR: Bruker AC 200 and AMX 400. − Melting points determined by DTA.

1. Preparation of [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$Ph_2PCH_2CH_2P$*i*Pr_2)] (2): A suspension of **1** (261 mg, 0.8 mmol) in hexane (8 mL) was treated with $Ph_2PCH_2CH_2P$*i*Pr_2 (252 mg, 0.8 mmol) and heated at reflux for 12 h. After cooling to room temperature, the solvent was evaporated in vacuo, the residue was washed with pentane (10 mL) and dried. A yellow microcrystalline solid was obtained; yield 308 mg (72%); m.p. 114 °C. − ^{1}H NMR (400 MHz, C_6D_6): δ = 7.96 (m, 2 H, C_6H_5), 7.30 (m, 4 H, C_6H_5), 7.00 (m, 4 H, C_6H_5), 2.93 (br m, 1 H, one H of PCH_2), 2.48, 2.25 (both s, 3 H each, CH_3 of 2-MeC_3H_4), 2.42−2.15 (br m, 5 H, PCH_2 and CH_2 of 2-MeC_3H_4), 2.10 [sept, 2 H, *J*(PH) = 1.7 Hz, PC*H*CH$_3$], 1.73−1.52 (br m, 4 H, CH_2 of 2-MeC_3H_4), 1.47 [dd, 3 H, *J*(PH) = 14.2, *J*(HH) = 7.2 Hz, PCHC*H*$_3$], 1.24 [dd, 3 H, *J*(PH) = 11.3, *J*(HH) = 7.2 Hz, PCHC*H*$_3$], 1.13 [dd, 1 H, *J*(PH) = 15.1, *J*(HH) = 4.8 Hz, one H of 2-MeC_3H_4], 0.92 [dd, 3 H, *J*(PH) = 9.4, *J*(HH) = 7.3 Hz, PCHC*H*$_3$], 0.89 [dd, 3 H, *J*(PH) = 9.6, *J*(HH) = 7.3 Hz, PCHC*H*$_3$], 0.50 [d, 1 H, *J*(PH) = 13.5 Hz, one H of 2-MeC_3H_4]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 140.5 [d, *J*(PC) = 40.5 Hz, *ipso*-C of C_6H_5], 138.9 [d, *J*(PC) = 21.0 Hz, *ipso*-C of C_6H_5], 133.8 [d, *J*(PC) = 10.5 Hz, *ortho*-C of C_6H_5], 131.3 [d, *J*(PC) = 6.7 Hz, *ortho*-C of C_6H_5], 129.2 [d, *J*(PC) = 1.9 Hz, *para*-C of C_6H_5], 126.9 (s, *para*-C of C_6H_5), 126.7 [d, *J*(PC) = 8.6 Hz, *meta*-C of C_6H_5], 126.3 [d, *J*(PC) = 7.6 Hz, *meta*-C of C_6H_5], 95.2 (s, *C*CH$_3$ of 2-MeC_3H_4), 94.2 [d, *J*(PC) = 1.9 Hz, *C*CH$_3$ of 2-MeC_3H_4], 41.6 [dd, *J*(P^{1}C) = 19.1, *J*(P^{2}C) = 1.9 Hz, CH_2 of 2-MeC_3H_4], 38.0, 36.8 (both m, CH_2 of 2-MeC_3H_4), 34.2, 34.0 [both d, *J*(PC) = 1.9 Hz, C*C*H$_3$ of 2-MeC_3H_4], 32.7 [dd, *J*(P^{1}C) = 25.3, *J*(P^{2}C) = 18.1 Hz, PCH_2], 31.1 [dd, *J*(P^{1}C) = *J*(P^{2}C) = 21.9 Hz, PCH_2], 26.8 [d, *J*(PC) = 28.6 Hz, P*C*HCH$_3$], 26.6 [d, *J*(PC) = 18.6 Hz, P*C*HCH$_3$], 21.2 [d, *J*(PC) = 4.8 Hz, PCH*C*H$_3$], 20.7, 19.8 (both s, PCH*C*H$_3$), 19.6 [d, *J*(PC) = 2.9 Hz, PCH*C*H$_3$]. − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 81.4 [d, *J*(PP) = 8.5 Hz, *i*Pr$_2$P], 73.9 [d, *J*(PP) = 8.5 Hz, Ph_2P]. − $C_{28}H_{42}P_2Ru$ (541.4): calcd. C 62.09, H 7.82; found C 61.81, H 8.07.

2. Preparation of [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$Ph_2PCH_2CH_2PCy_2$)] (3): Analogous to the procedure described for **2**, using **1** (152 mg, 0.5 mmol) and $Ph_2PCH_2CH_2PCy_2$ (189 mg, 0.5 mmol) as starting materials. Yellow microcrystalline solid; yield 308 mg (70%); m.p. 108 °C. − ^{1}H NMR (200 MHz, C_6D_6): δ = 7.76−6.66 (br m, 10 H, C_6H_5), 3.25−0.43 (br m, 40 H, PCH_2, CH_2 and CH_3 of 2-MeC_3H_4 and C_6H_{11}). − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 134.8 [d, *J*(PC) = 13.2 Hz, *ipso*-C of C_6H_5], 134.6 [d, *J*(PC) = 9.0 Hz, *ipso*-C of C_6H_5], 133.7 [d, *J*(PC) = 14.2 Hz, *ortho*-C of C_6H_5], 131.4 [d, *J*(PC) = 8.3 Hz, *ortho*-C of C_6H_5], 129.5, 128.1 [both d, *J*(PC) = 1.9 Hz, *para*-C of C_6H_5], 128.3 [d, *J*(PC) = 7.5 Hz, *meta*-C of C_6H_5], 127.7 [d, *J*(PC) = 8.5 Hz, *meta*-C of C_6H_5], 95.4, 94.6 (both

s, *C*CH$_3$ of 2-MeC$_3$H$_4$), 43.0 [dd, *J*(P^{1}C) = 10.3, *J*(P^{2}C) = 6.1 Hz, CH of C$_6$H$_{11}$], 39.4 [d, *J*(PC) = 3.4 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 38.8 [d, *J*(PC) = 4.2 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 38.6 [d, *J*(PC) = 5.1 Hz, CH of C$_6$H$_{11}$], 36.1, 36.0 [both d, *J*(PC) = 4.0 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 33.1 [dd, *J*(P^{1}C) = 24.7, *J*(P^{2}C) = 16.9 Hz, PCH$_2$], 31.1 [dd, *J*(P^{1}C) = 22.7, *J*(P^{2}C) = 18.9 Hz, PCH$_2$], 30.4, 30.2 (both s, CH$_2$ of C$_6$H$_{11}$), 30.6 [d, *J*(PC) = 4.0 Hz, CH$_2$ of C$_6$H$_{11}$], 29.3 [d, *J*(PC) = 3.1 Hz, CH$_2$ of C$_6$H$_{11}$], 28.5 [d, *J*(PC) = 12.2 Hz, CH$_2$ of C$_6$H$_{11}$], 27.6 [d, *J*(PC) = 9.2 Hz, CH$_2$ of C$_6$H$_{11}$], 27.5 [d, *J*(PC) = 7.3 Hz, CH$_2$ of C$_6$H$_{11}$], 27.1 [d, *J*(PC) = 10.1 Hz, CH$_2$ of C$_6$H$_{11}$], 26.8, 26.7 (both s, CH$_2$ of C$_6$H$_{11}$), 26.6, 25.9 (both s, C*C*H$_3$ of 2-MeC$_3$H$_4$). – ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ = 81.5 [d, *J*(PP) = 7.6 Hz, Cy$_2$P], 66.6 [d, *J*(PP) = 7.6 Hz, Ph$_2$P]. – C$_{34}$H$_{50}$P$_2$Ru (621.8): calcd. C 65.68, H 8.11; found C 65.57, H 7.82.

3. Preparation of [Ru(η^3-2-MeC$_3$H$_4$)$_2$(κ^2-Ph$_2$PCH$_2$CH$_2$As*t*Bu$_2$)] (4): Analogous to the procedure described for **2**, using **1** (281 mg, 0.9 mmol) and Ph$_2$PCH$_2$CH$_2$As*t*Bu$_2$ (355 mg, 0.88 mmol) as starting materials. Yellow microcrystalline solid; yield 275 mg (51%); m.p. 99 °C. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.89 (m, 2 H, C$_6$H$_5$), 7.22–7.09 (br m, 4 H, C$_6$H$_5$), 6.87 (m, 4 H, C$_6$H$_5$), 2.95–0.51 (br m, 36 H, CH$_2$ and CH$_3$ of 2-MeC$_3$H$_4$, PCH$_2$, and AsCCH$_3$). – ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 140.4 [d, *J*(PC) = 37.2 Hz, *ipso*-C of C$_6$H$_5$], 139.3 [d, *J*(PC) = 22.9 Hz, *ipso*-C of C$_6$H$_5$], 134.1 [d, *J*(PC) = 11.4 Hz, *ortho*-C of C$_6$H$_5$], 131.7 [d, *J*(PC) = 6.7 Hz, *ortho*-C of C$_6$H$_5$], 129.2 [d, *J*(PC) = 1.9 Hz, *para*-C of C$_6$H$_5$], 126.9 (s, *para*-C of C$_6$H$_5$), 126.5 [d, *J*(PC) = 9.5 Hz, *meta*-C of C$_6$H$_5$], 126.3 [d, *J*(PC) = 6.7 Hz, *meta*-C of C$_6$H$_5$], 95.0, 91.2 (both s, *C*CH$_3$ of 2-MeC$_3$H$_4$), 39.6, 36.3 [both d, *J*(PC) = 2.9 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 39.1, 39.0 (both s, As*C*CH$_3$), 36.9 [d, *J*(PC) = 4.8 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 33.4 [d, *J*(PC) = 2.3 Hz, CH$_2$ of 2-MeC$_3$H$_4$], 32.8 [d, *J*(PC) = 24.8 Hz, PCH$_2$], 32.2, 31.5 (both s, AsC*C*H$_3$), 25.9, 25.7 (both s, C*C*H$_3$ of 2-MeC$_3$H$_4$), 21.6 [d, *J*(PC) = 20.2 Hz, AsCH$_2$]. – ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 79.4 (s). – C$_{30}$H$_{46}$AsPRu (613.7): calcd. C 58.72, H 7.56; found C 58.37, H 7.06.

4. Preparation of [Ru(κ^2-[F$_6$]acac)$_2$(κ^2-Ph$_2$PCH$_2$CH$_2$P*i*Pr$_2$)] (5): a) A solution of **2** (104 mg, 0.2 mmol) in toluene (5 mL) was treated at –78 °C with hexafluoroacetylacetone (88 μL, 0.4 mmol), which led to a rapid change of color from yellow to dark red. After warming to room temperature and stirring the solution for 20 min, the solvent was evaporated in vacuo and the residue was dissolved in pentane (2 mL). The solution was chromatographed on Al$_2$O$_3$ (basic, activity grade I, height of column 10 cm). With pentane a red fraction was eluted, from which a dark red microcrystalline solid was obtained upon removal of the solvent; yield 147 mg (92%). – b) A solution of **6** (164 mg, 0.2 mmol) in toluene (5 mL) was treated with hexafluoroacetylacetone (71 μL, 0.4 mmol), which led to a rapid change of color from orange to dark red. The solvent was evaporated in vacuo, the residue was washed with pentane (5 mL, –20 °C) and dried. Orange microcrystalline solid; yield 133 mg (93%); m.p. 148 °C. – IR (CH$_2$Cl$_2$): ν([F$_6$]acac) = 1611, 1522 cm^{-1}. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.97 (m, 2 H, C$_6$H$_5$), 7.63 (m, 3 H, C$_6$H$_5$), 7.46–7.34 (br m, 3 H, C$_6$H$_5$), 7.18 (m, 2 H, C$_6$H$_5$), 6.37, 5.67 (both s, 1 H each, CH of acac-f$_6$), 3.40–2.76 (br m, 2 H, PCH$_2$), 2.64–2.52 (br m, 1 H, PC*H*CH$_3$), 2.48–2.34 (br m, 2 H, PCH$_2$), 2.28–2.12 (br m, 1 H, PC*H*CH$_3$), 1.49 [dd, 3 H, *J*(PH) = 9.4, *J*(HH) = 7.0 Hz, PCHC*H*$_3$], 1.45 [dd, 3 H, *J*(PH) = 10.4, *J*(HH) = 7.2 Hz, PCHC*H*$_3$], 1.18 [dd, 3 H, *J*(PH) = 14.1, *J*(HH) = 7.0 Hz, PCHC*H*$_3$], 1.07 [dd, 3 H, *J*(PH) = 14.2, *J*(HH) = 7.2 Hz, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 175.1, 174.0, 172.1, 171.3 [all q, *J*(FC) = 34.3 Hz, CO of acac-f$_6$], 134.9 [d, *J*(PC) = 42.9 Hz, *ipso*-C of C$_6$H$_5$], 133.3 [d, *J*(PC) = 10.5 Hz, *ortho*-C of C$_6$H$_5$], 132.0 [d, *J*(PC) = 43.9 Hz, *ipso*-C of C$_6$H$_5$], 130.6 [d, *J*(PC) = 9.5 Hz, *ortho*-C of C$_6$H$_5$], 129.2 [d, *J*(PC) = 2.9 Hz, *para*-C of C$_6$H$_5$], 128.3 [d, *J*(PC) = 9.5 Hz, *meta*-C of C$_6$H$_5$], 118.5, 117.7, 116.3, 116.1 [all q, *J*(FC) = 284.2 Hz, CF$_3$], 91.2, 89.9 (both s, CH of acac-f$_6$), 27.8 [dd, *J*(P^{1}C) = 34.3, *J*(P^{2}C) = 8.6 Hz, PCH$_2$], 25.3 [d, *J*(PC) = 22.9 Hz, PC*H*CH$_3$], 25.0 [d, *J*(PC) = 23.8 Hz, PC*H*CH$_3$], 23.9 [dd, *J*(P^{1}C) = 38.6, *J*(P^{2}C) = 12.4 Hz, PCH$_2$], 18.3, 18.3, 18.2, 18.0 (all s, PCH*C*H$_3$). – ^{19}F NMR (376.5 MHz, CDCl$_3$): δ = –75.7, –75.4, –74.6, –74.2 (all s). – ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 90.4 [d, *J*(PP) = 25.4 Hz, *i*Pr$_2$P], 79.1 [d, *J*(PP) = 25.4 Hz, Ph$_2$P]. – C$_{30}$H$_{30}$F$_{12}$O$_4$P$_2$Ru (845.6): calcd. C 42.61, H 3.58; found C 42.30 H 3.22.

5. Preparation of [Ru(κ^2-*O*,*Cl*-OC$_6$Cl$_5$)$_2$(κ^2-Ph$_2$PCH$_2$CH$_2$P*i*Pr$_2$)] (6): A solution of **2** (135 mg, 0.3 mmol) in toluene (5 mL) was treated at –30 °C with a solution of pentachlorophenol (133 mg, 0.5 mmol) in toluene (5 mL). After warming to room temperature and stirring for 10 min, the solvent was evaporated in vacuo. The residue was washed with pentane (5 mL) and dried. An orange microcrystalline solid was obtained; yield 221 mg (92%); m.p. 165 °C. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.09 (m, 2 H, C$_6$H$_5$), 7.19 (m, 3 H, C$_6$H$_5$), 6.87 (m, 2 H, C$_6$H$_5$), 6.69 (m, 3 H, C$_6$H$_5$), 2.17–1.96 (br m, 2 H, PCH$_2$), 1.72 (m, 1 H, PC*H*CH$_3$), 1.60–1.49 (br m, 2 H, PCH$_2$), 1.43–1.29 (br m, 1 H, PC*H*CH$_3$), 1.21 [dd, 3 H, *J*(PH) = 14.1, *J*(HH) = 7.0 Hz, PCHC*H*$_3$], 1.15 [dd, 3 H, *J*(PH) = 13.9, *J*(HH) = 7.7 Hz, PCHC*H*$_3$], 0.60 [dd, 3 H, *J*(PH) = 11.4, *J*(HH) = 7.0 Hz, PCHC*H*$_3$], 0.56 [dd, 3 H, *J*(PH) = 11.7, *J*(HH) = 7.0 Hz, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 163.6, 162.7 (both s, *ipso*-C of C$_6$Cl$_5$), 134.6 [d, *J*(PC) = 10.5 Hz, *ortho*-C of C$_6$H$_5$], 133.8 [d, *J*(PC) = 47.7 Hz, *ipso*-C of C$_6$H$_5$], 132.6 [d, *J*(PC) = 45.8 Hz, *ipso*-C of C$_6$H$_5$], 131.7 [d, *J*(PC) = 8.6 Hz, *ortho*-C of C$_6$H$_5$], 131.3, 129.4 [both d, *J*(PC) = 1.9 Hz, *para*-C of C$_6$H$_5$], 128.6 [d, *J*(PC) = 10.5 Hz, *meta*-C of C$_6$H$_5$], 127.5 [d, *J*(PC) = 9.5 Hz, *meta*-C of C$_6$H$_5$], 125.7, 125.4, 118.0, 117.8, 116.4, 115.6 (all s, C$_6$Cl$_5$), 28.1 [dd, *J*(P^{1}C) = 36.2, *J*(P^{2}C) = 7.2 Hz, PCH$_2$], 26.7, 26.2 [both d, *J*(PC) = 24.8 Hz, PC*H*CH$_3$], 20.9 [dd, *J*(P^{1}C) = 30.0, *J*(P^{2}C) = 11.0 Hz, PCH$_2$], 19.3, 18.5, 18.1, 18.0 (all s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 99.2 [d, *J*(PP) = 28.8 Hz, *i*Pr$_2$P], 84.8 [d, *J*(PP) = 28.8 Hz, Ph$_2$P]. – C$_{32}$H$_{28}$Cl$_{10}$O$_2$P$_2$Ru (962.2): calcd. C 39.95 H 2.91; found C 40.04 H 3.22.

6. Preparation of [Ru(κ^2-*O*,*Cl*-OC$_6$Cl$_5$)$_2$(κ^2-Ph$_2$PCH$_2$CH$_2$PCy$_2$)] (7): Analogous to the procedure described for **6**, using **3** (246 mg, 0.5 mmol) and pentachlorophenol (245 mg, 1.0 mmol) as starting materials. Orange microcrystalline solid; yield 221 mg (92%); m.p. 208 °C. – ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 8.10–6.60 (br m, 10 H, C$_6$H$_5$), 2.32–0.38 (br m, 26 H, PCH$_2$ and C$_6$H$_{11}$). – ^{13}C NMR (50.3 MHz, C$_6$D$_6$): δ = 162.6, 162.5 (both s; *ipso*-C of C$_6$Cl$_5$), 135.1 [d, *J*(PC) = 43.2 Hz, *ipso*-C of C$_6$H$_5$], 134.8 [d, *J*(PC) = 39.8 Hz, *ipso*-C of C$_6$H$_5$], 133.8 [d, *J*(PC) = 14.1 Hz, *ortho*-C of C$_6$H$_5$], 131.3 [d, *J*(PC) = 8.0 Hz, *ortho*-C of C$_6$H$_5$], 129.9, 128.0 [both d, *J*(PC) = 1.9 Hz, *para*-C of C$_6$H$_5$], 128.4, 127.3 [both d, *J*(PC) = 7.1 Hz, *meta*-C of C$_6$H$_5$], 125.6, 125.4, 118.7, 118.0, 116.7, 116.1 (all s, C$_6$Cl$_5$), 43.3 [dd, *J*(P^{1}C) = 12.1, *J*(P^{2}C) = 5.8 Hz, CH of C$_6$H$_{11}$], 38.4 [d, *J*(PC) = 6.1 Hz, CH of C$_6$H$_{11}$], 32.5 [dd, *J*(P^{1}C) = 24.2, *J*(P^{2}C) = 16.7 Hz, PCH$_2$], 31.0 [dd, *J*(P^{1}C) = 22.5, *J*(P^{2}C) = 18.9 Hz, PCH$_2$], 30.8, 30.0, 26.5, 26.4 (all s, CH$_2$ of C$_6$H$_{11}$), 30.4, 29.9 [both d, *J*(PC) = 4.3 Hz, CH$_2$ of C$_6$H$_{11}$], 29.0 [d, *J*(PC) = 9.7 Hz, CH$_2$ of C$_6$H$_{11}$], 26.9 [d, *J*(PC) = 9.4 Hz, CH$_2$ of C$_6$H$_{11}$], 26.8 [d, *J*(PC) = 6.9 Hz, CH$_2$ of C$_6$H$_{11}$], 26.7 [d, *J*(PC) = 10.6 Hz, CH$_2$ of C$_6$H$_{11}$]. – ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ = 91.3 [d, *J*(PP) = 28.7 Hz, Cy$_2$P], 85.4 [d, *J*(PP) = 28.7 Hz, Ph$_2$P]. – C$_{38}$H$_{36}$Cl$_{10}$O$_2$P$_2$Ru (1042): calcd. C 43.78 H 3.48; found C 44.08 H 3.45.

7. Preparation of [Ru(κ²-acac)₂(κ²-Ph₂PCH₂CH₂P*i*Pr₂)] (8): A solution of **6** (189 mg, 0.2 mmol) in toluene (8 mL) was treated with acetylacetone (55 mg, 0.6 mmol) and Na_2CO_3 (69 mg, 0.7 mmol) and then heated for 1 h at 65 °C. After cooling to room temperature, the solvent was evaporated in vacuo. The residue was dissolved in pentane (5 mL), the solution filtered and the filtrate was brought to dryness in vacuo. A yellow microcrystalline solid was obtained; yield 112 mg (89%); m.p. 157 °C. – IR (CH_2Cl_2): ν(acac) = 1580, 1518 cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.88–7.76 (br m, 2 H, C_6H_5), 7.30–6.95 (br m, 8 H, C_6H_5), 5.14, 4.55 (both s, 1 H each, CH of acac), 2.62–2.50, 2.24–2.12 (both br m, 2H each, PCH_2), 1.99–1.83 (br m, 2 H, PC*H*CH_3), 1.86, 1.68, 1.62, 1.20 (all s, 3H each, CH_3 of acac), 1.24–1.18 (br m, 6 H, PCHC*H*$_3$), 0.86–0.76 (br m, 6 H, PCHC*H*$_3$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 184.7, 183.9, 183.3, 182.7 (all s, CO of acac), 138.6 [d, *J*(PC) = 37.6 Hz, *ipso*-C of C_6H_5], 136.3 [d, *J*(PC) = 36.6 Hz, *ipso*-C of C_6H_5], 134.0, 131.1 [both d, *J*(PC) = 8.1 Hz, C_6H_5], 129.1, 127.7, 127.3 (all s, C_6H_5), 127.2 [d, *J*(PC) = 8.4 Hz, C_6H_5], 97.1, 96.6 (both s, CH of acac), 27.9 [dd, $J(P^1C)$ = 34.8, $J(P^2C)$ = 8.6 Hz, PCH_2], 27.8, 27.6, 27.3, 27.1 (all s, CH_3 of acac), 25.2 [d, *J*(PC) = 18.9 Hz, P*C*HCH$_3$], 25.0 [d, *J*(PC) = 23.8 Hz, P*C*HCH$_3$], 22.9 [dd, $J(P^1C)$ = 29.6, $J(P^2C)$ = 10.4 Hz, PCH_2], 18.4, 18.3, 18.2, 18.0 (all s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 91.2 [d, *J*(PP) = 23.4 Hz, *i*Pr_2P], 82.5 [d, *J*(PP) = 23.4 Hz, Ph_2P]. – $C_{30}H_{42}O_4P_2Ru$ (629.7): calcd. C 57.22 H 6.73; found C 56.89 H 7.03.

X-ray Structure Determination of Compounds 2 and 6:[18] Single crystals of **2** were grown from hexane at 25 °C and those of **6** from THF at 25 °C. Crystal data collection parameters for these structures are presented in Table 1. The data were collected with an Enraf–Nonius CAD4 diffractometer using monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for both structures [Ψ scans; T_{min} = 0.90, T_{max} = 1.00 (**2**); T_{min} = 0.59, T_{max} = 0.80 (**6**)]. The structures were solved by Patterson methods with SHELXS-97.[19] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-97.[20] The positions of all hydrogen atoms were calculated according to ideal geometry and refined by employing the riding method, except for H41a, H41b, H42a, H42b, H51a, H51b, H52a, and H52b of **2**, which were found in a differential Fourier synthesis and refined without restraints.

Table 1. Crystal data for complexes **2** and **6**

	2	**6** · C_4H_8O
Empirical formula	$C_{27}H_{42}P_2Ru$	$C_{36}H_{36}Cl_{10}O_3P_2Ru$
M	541.38	1034.16
Crystal system	monoclinic	triclinic
Space group	*C*2/*c* (no. 15)	*P*$\bar{1}$ (no. 2)
a [Å]	22.795(2)	12.381(4)
b [Å]	10.982(1)	13.088(2)
c [Å]	23.162(3)	14.374(4)
α [°]	–	66.69(2)
β [°]	112.856(5)	80.19(2)
γ [°]	–	71.57(2)
V [Å³]	5342.8(10)	2027.7(7)
Z	8	2
D_c [g cm^{-3}]	1.314	1.695
Temperature [K]	193(2)	193(2)
μ [mm^{-1}]	0.718	1.162
No. reflections measured	4814	7185
No. unique reflections (R_{int})	4682 (0.0241)	5269 (0.0245)
$R1$[a]	0.034	0.035
$wR2$[b]	0.072	0.083

[a] $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o > 2\sigma(F_o)$]. – [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie. We are grateful to the latter in particular for a Ph.D. scholarship (to K. I.). We also thank Dr. W. Buchner and Mrs. M.-L. Schäfer for NMR measurements, Mrs. R. Schedl and Mr. C. P. Kneis for elemental analysis and DTA measurements. Generous support by the BASF AG and the Degussa-Hüls AG is also gratefully acknowledged.

[1] J. Wolf, M. Manger, U. Schmidt, G. Fries, D. Barth, B. Weberndörfer, D. A. Vice, W. D. Jones, H. Werner, *J. Chem. Soc., Dalton. Trans.* **1999**, 1867–1875.
[2] G. Fries, J. Wolf, M. Pfeiffer, D. Stalke, H. Werner, *Angew. Chem.* **2000**, *112*, 575–578; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 564–566.
[3] G. Fries, Dissertation, Universität Würzburg, **2000**.
[4] S. Holle, P. W. Jolly, J. Kuhnigk, *J. Organomet. Chem.* **1997**, *543*, 255–258.
[5] C. Six, B. Gabor, H. Görls, R. Mynott, P. Philipps, W. Leitner, *Organometallics* **1999**, *18*, 3316–3326.
[6] J. P. Genet, X. Pfister, V. Ratovelomanana-Vidal, C. Pinel, J. A. Laffitte, S. Malort, M. C. Cano de Andrade, *Tetrahedron*: *Asymm.* **1994**, *5*, 665–674.
[7] H. Werner, T. Braun, T. Daniel, O. Gevert, M. Schulz, *J. Organomet. Chem.* **1997**, *541*, 127–141.
[8] B. Heiser, E. A. Broger, Y. Crameri, *Tetrahedron*: *Asymmetry* **1991**, *2*, 51–62.
[9] J. R. Jones, S. P. Patel, *J. Am. Chem. Soc.* **1974**, *96*, 574–575.
[10] H. Werner, G. Fries, B. Weberndörfer, *J. Organomet. Chem.*, in press.
[11] M. A. Tena, O. Nürnberg, H. Werner, *Chem. Ber.* **1993**, *126*, 1597–1602.
[12] [12a] M. F. Richardson, G. Wulfsberg, R. Marlow, S. Zaghonni, D. McCorkle, K. Shadid, J. Gagliardi, Jr., B. Farris, *Inorg. Chem.* **1993**, *32*, 1913–1919. – [12b] W. Beck, K. Schloter, *Z. Naturforsch., B* **1978**, *33*, 1214–1222. – [12c] R. J. Kulawiec, R. H. Crabtree, *Coord. Chem. Rev.* **1990**, *99*, 89–115.
[13] C.-W. Chang, P.-C. Ting, Y.-C. Lin, G.-H. Lee, Y. Wang, *J. Organomet. Chem.* **1998**, *553*, 417–425.
[14] A. R. Chakravarty, F. A. Cotton, W. Schwotzer, *Inorg. Chim. Acta* **1984**, *84*, 179–185.
[15] M. J. Burn, M. G. Fickes, F. J. Hollander, R. G. Bergman, *Organometallics* **1995**, *14*, 137–150.
[16] W. Baratta, E. Herdtweck, P. Rigo, *Angew. Chem.* **1999**, *111*, 1733–1735; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1629–1631.
[17] M. O. Albers, E. Singleton, Y. E. Yates, *Inorg. Synth.* **1989**, *26*, 253–254.
[18] Crystallograhic data (excluding structure factors) for the structures of **2** and **6** have been deposited with the Cambridge Crystallograhic Data Centre as supplementary publication no. CCDC-143547 (**2**) and -133284 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[20] G. M. Sheldrick, *Program for crystal structure refinement*, Universität Göttingen, **1996**.

Received April 17, 2000
[I00149]