Mononuclear Ruthenium and Hetero-Tetranuclear Ruthenium-Silver Complexes Containing the Unsymmetrical Bidentate Ligands $R_2P(CH_2)_nER'_2$ (n = 1, 2; E = P, As) as Chelating or Bridging Units

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Dedicated to Professor Gerhard Roewer on the occasion of his 60th birthday

Keywords: Arene complexes / Heteronuclear complexes / Ruthenium / Silver / Unsymmetrical chelating ligands

The chelate complexes [(*p*-cym)RuCl(κ²-$Ph_2PCH_2CH_2As$*t*Bu_2)]PF_6 (**3**), [(arene)RuCl(κ²-$Ph_2PCH_2CH_2PR_2$)]PF_6 (**4**, **7**, **8**) and [(*p*-cym)RuCl(κ²-*i*Pr_2PCH_2As*t*Bu_2)]PF_6 (**11**) were prepared either from [(arene)RuCl(NCMe)$_2$]PF_6 (**1**, **5**) or from [(arene)$RuCl_2$]$_2$ (**2**, **6**), in the presence of NH_4PF_6 or $AgPF_6$. The stepwise reaction of [(*p*-cym)$RuCl_2$]$_2$ (**2**) with Ph_2P-CH_2CH_2P*t*Bu_2 and $AgPF_6$ gave the hetero-tetranuclear compound [{(*p*-cym)RuAg(μ-Cl)$_2$(μ-P^1_{Ru},P^2_{Ag}-$Ph_2P^1CH_2CH_2P^2$-*t*Bu_2)}$_2$]$(PF_6)_2$ (**9**), the structure of which was determined by an X-ray crystal structure analysis. The bidentate As,O donor $Ph_2P(O)CH_2CH_2As$*t*Bu_2 also reacted with **2**, in the presence of $AgPF_6$, to afford the chelate complex [(*p*-cym)RuCl-{κ²(*As*,*O*)-$Ph_2P(O)CH_2CH_2As$*t*Bu_2}]PF_6 (**10**), which was also characterized crystallographically.

Introduction

In the search for new, possibly hemilabile, bidentate ligands, we recently described a simple and fairly general one-pot synthesis for unsymmetrical 1,2-bis(phosphanyl)-ethanes and 1-arsanyl-2-phosphanylethanes with and without a stereogenic center.[1] In an initial attempt, we tested the coordination properties of one of the new ligands, $Ph_2PCH_2CH_2P$*i*Pr_2, towards ruthenium(II) and prepared a series of octahedral complexes including [Ru{κ²(*O*,*Cl*)-OC_6Cl_5}$_2$($Ph_2PCH_2CH_2P$*i*Pr_2)] in which the pentachlorophenolate anions behave as chelating ligands.[1,2] In the last decade the chemistry of (arene)ruthenium(II) complexes has attracted a great deal of attention[3] and so we became interested in finding out whether the compounds $Ph_2PCH_2CH_2PR_2$ and $Ph_2PCH_2CH_2AsR_2$, even with bulky substituents R such as *tert*-butyl or cyclohexyl, could also bind to an [(arene)RuCl]$^+$ fragment in a chelating fashion. The present paper reports the preparation of several complexes of the general type [(arene)RuCl(L−L′)]PF_6, and describes the isolation and structural characterization of a novel dicationic tetranuclear Ru_2Ag_2 compound in which two $Ph_2PCH_2CH_2P$*t*Bu_2 ligands bridge the Ru^{II} and Ag^{I} metal centers.

Results and Discussion

The preparation of the chelate complexes **3**, **4** and **7**, **8** (see Scheme 1) can be achieved by two different routes, using either the cationic bis(acetonitrile)ruthenium(II) compounds **1** and **5**[4] or the well-known (arene)ruthenium dichloride dimers **2** and **6** as the starting materials. While **1** and **5** react quite smoothly with the new unsymmetrical 1,2-bis(phosphanyl)- or 1-arsanyl-2-phosphanylethanes in acetonitrile at room temperature to give the half-sandwich-type complexes **3**, **4** and **7**, **8**, respectively, the dimers **2** and **6** are somewhat less reactive and only in the presence of NH_4PF_6 or $AgPF_6$, in dichloromethane as solvent, do they afford the products in good yields.

Compounds **3**, **4** and **7**, **8** are orange, air-stable solids that are soluble in polar solvents such as CH_2Cl_2, THF, methanol, or acetone, and which have been characterized both by elemental analysis and conductivity measurements. Compared to the free ligands $Ph_2PCH_2CH_2PR_2$ and $Ph_2PCH_2CH_2As$*t*Bu_2, the resonances in the ^{31}P-NMR spectra of **3**, **4**, **7**, and **8** are shifted to significantly lower fields, the difference in the chemical shifts being 50−90 ppm.

The unusual tetranuclear complex **9** (Scheme 2) is obtained if the reaction of **2** with $Ph_2PCH_2CH_2P$*t*Bu_2 is carried out in the presence of $AgPF_6$ instead of NH_4PF_6. In contrast to **4**, which also contains $Ph_2PCH_2CH_2P$*t*Bu_2 as a ligand, the ^{31}P-NMR spectrum of **9** displays, besides the signal for the PF_6^- anion, a doublet at δ = 28.0 and two doublet of doublets at δ = 68.0 and 67.9, which arise from the coupling of the ^{31}P nuclei of the P*t*Bu_2 unit with the silver isotopes ^{107}Ag and ^{109}Ag, respectively. The resulting coupling constants $J(^{31}P^{107}Ag)$ = 643.0 Hz and $J(^{31}P^{109}Ag)$ = 743.3 Hz are considerably larger than in a variety of (phosphane)silver(I) complexes.[5] Similar $J(^{31}P^{107}Ag)$ and $J(^{31}P^{109}Ag)$ values (657.5 and 758.8 Hz) have recently been observed for the tris(pyrazolyl)borato compound [{HB[3,5-$(CF_3)_2$pz]$_3$}Ag(PPh_3)] where the coordination number of Ag^{I} is four.[6]

The result of the X-ray crystal structure analysis of the cation of **9** is shown in Figure 1. The coordination sphere around the two ruthenium centers in the centrosymmetric dimer corresponds to that of a half-sandwich-type molecule

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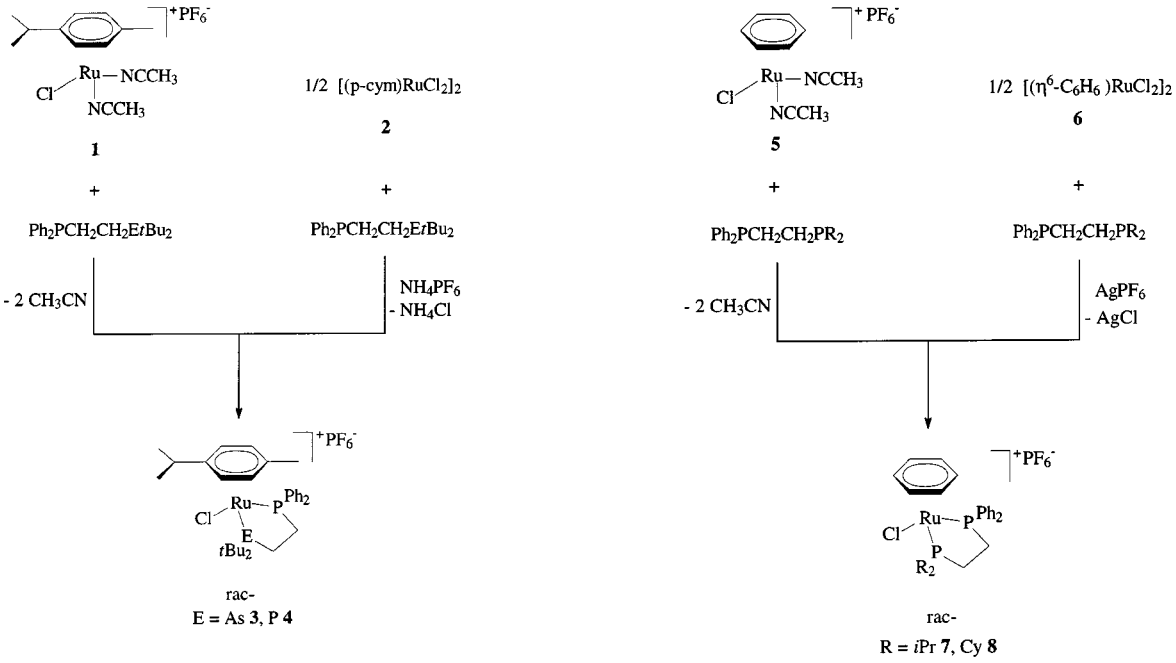
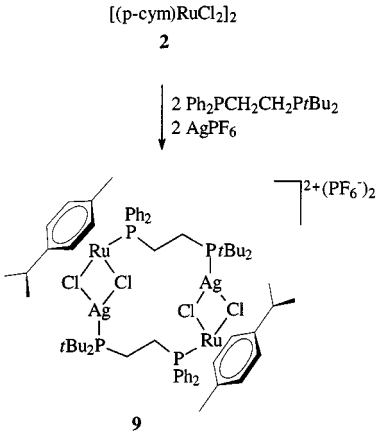


Scheme 1



Scheme 2

with the tridentate *p*-cymene, the phosphorus atom of the PPh_2 unit and the two chlorine atoms Cl1 and Cl2 occupying the six coordination sites. The geometry around the two silver centers is distorted trigonal-planar, one angle (Cl1−Ag2−P2A) being nearly 120° while the two others (Cl2−Ag2−P2A and Cl1−Ag2−Cl2) deviate significantly from the value expected for an sp^2-hybridized metal atom. The distance Ag2−P2A of 2.3592(1) Å is somewhat shorter than in the anionic species $[Cl(C_6Cl_5)_2Pt(\mu\text{-}Cl)Ag(PPh_3)]^-$ [2.395(2) Å][7] and in the neutral compounds $[(PPh_3)_2Ag(\mu\text{-}Cl)_2OsCl_2(\mu\text{-}Cl)_2Ag(PPh_3)_2]$ [2.452(3) and 2.455(3) Å][8] and $[(PPh_3)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]$ (2.43−2.47 Å).[9] The most remarkable feature, however, is the short bond length Ag2−Cl2 [2.4707(18) Å], which is not only much shorter than the distance Ag2−Cl1 [2.7261(19) Å] but also differs from the Ag−Cl bond lengths found in other chloride-bridged silver-metal complexes.[7,8,9] In contrast to the distances Ag2−Cl1 and Ag2−Cl2, the bond lengths Ru1−Cl1 and Ru1−Cl2 are almost identical [2.4234(17) and 2.4432(18) Å] and only slightly longer than those in the mononuclear compounds $[(arene)RuCl_2(L)]$.[10] We note that quite recently a tetranuclear Ru_2Ag_2 complex has been reported in which an $Ag(\mu\text{-}iPr_2PCH_2CH_2PiPr_2)Ag$ fragment is linked to two phenylethynyl ligands, each of which is σ-bonded to one ruthenium center.[11]

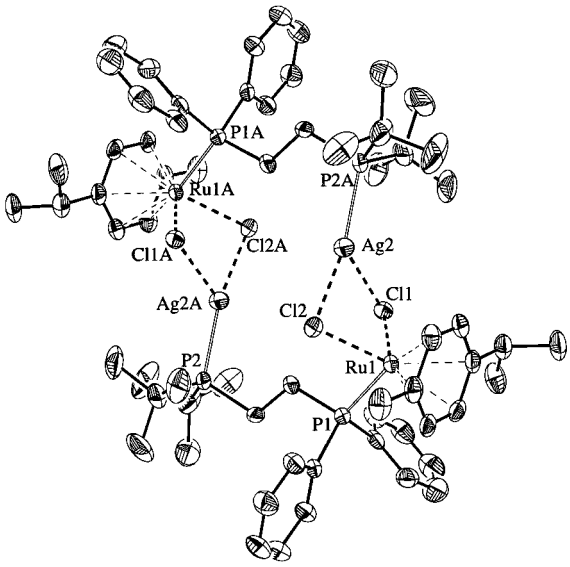


Figure 1. Molecular structure (ORTEP plot) of **9**; the PF_6^- ions are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru1−P1 2.3608(17), Ru1−Cl1 2.4234(17), Ru1−Cl2 2.4432(18), Ag2−Cl1 2.7261, Ag2−Cl2 2.4707(18), Ag2−P2A 2.3592(19); P1−Ru1−Cl1 84.50(6), P1−Ru1−Cl2 88.28(6), Cl1−Ru1−Cl2 87.31(6), Ru1−Cl1−Ag2 82.70(5), Ru1−Cl2−Ag2 87.88(6), Cl1−Ag2−P2A 121.69(6), Cl2−Ag2−P2A 157.48(6), Cl1−Ag2−Cl2 80.39(5)

The observation that not only the 1,2-bis(phosphanyl)-ethanes $Ph_2PCH_2CH_2PR_2$ (R = *i*Pr, *t*Bu, Cy) but also the As,P counterpart $Ph_2PCH_2CH_2AstBu_2$ is easily oxidized to

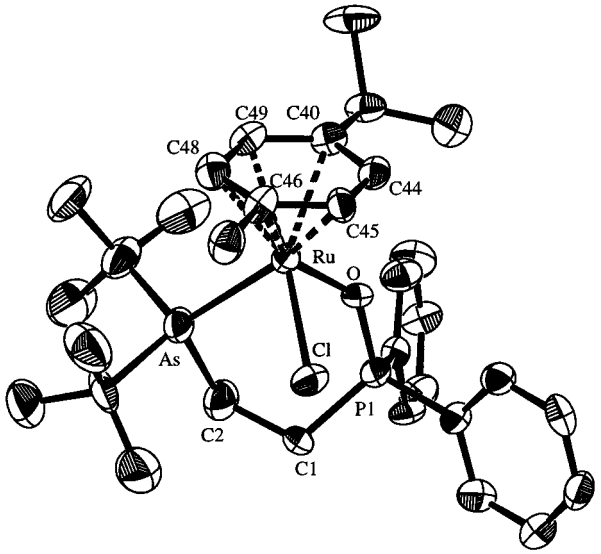
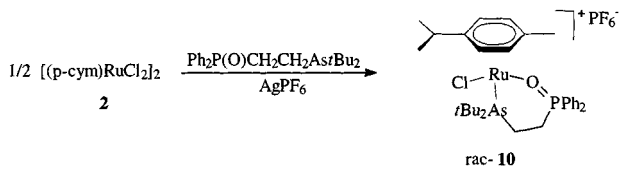


Figure 2. Molecular structure (ORTEP plot) of **10**; the PF_6^- ion is omitted for clarity; selected bond lengths [Å] and angles [°]: Ru−As 2.5490(11), Ru−O 2.141(5), Ru−Cl 2.386(2), P1−O 1.510(5), Ru−C40 2.215(7), Ru−C44 2.201(8), Ru−C45 2.198(8), Ru−C46 2.212(7), Ru−C48 2.171(8), Ru−C49 2.176(7); As−Ru−O 83.49(13), As−Ru−Cl 87.67(6), Cl−Ru−O 88.19(14), Ru−O−P1 135.7(3), Ru−As−C2 111.7(2), As−C2−C1 116.2(6), P1−C1−C2 110.0(6), O−P1−C1 113.9(3)

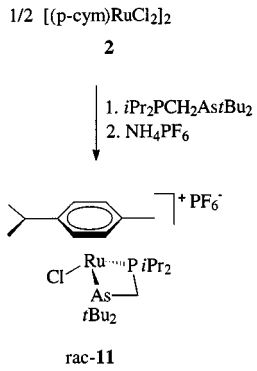
the corresponding oxide $Ph_2P(O)CH_2CH_2AstBu_2$, prompted us to use this molecule as a ligand in (arene)ruthenium(II) chemistry. Treating a solution of the oxide $Ph_2P(O)CH_2CH_2AstBu_2$, generated in situ from the precursor $Ph_2PCH_2CH_2AstBu_2$ and molecular oxygen, with a solution of **2** in CH_2Cl_2, in the presence of one equivalent of $AgPF_6$, leads to the formation of the PF_6 salt of the cationic complex **10** (Scheme 3) in which the oxophosphorane forms a six-membered chelate ring with the metal center. The dark-red solid is air-stable and readily soluble in THF, nitromethane and methanol. The resonance in the ^{31}P-NMR spectrum of **10** appears at $\delta = 53.8$ and is shifted by ca. 17 ppm upfield compared to the corresponding signal for **3**. In the latter compound the nonoxidized ligand $Ph_2PCH_2CH_2AstBu_2$ is coordinated to the ruthenium center rather than $Ph_2P(O)CH_2CH_2AstBu_2$.

The molecular structure of the cation of **10** is shown in Figure 2. The single crystals, which were grown from a solution in methanol, contained only one enantiomer of the cationic (arene)ruthenium complex in which, owing to the calculated structural parameter x of −0.025(15), the asymmetric metal center possesses the (*R*) configuration.[12] In analogy to the situation in **9**, the coordination geometry around the ruthenium center is pseudo-octahedral with the arsenic, the oxygen and the chlorine atoms bonded opposite to the tridentate *p*-cymene ligand. The distance Ru−Cl [2.386(2) Å] is ca. 0.05 Å shorter than the two Ru−Cl bond lengths in **9** but quite similar to the Ru−Cl distances found in other cationic (arene)(chloro)ruthenium(II) complexes.[13] The Ru−As bond length [2.5490(11) Å] is slightly longer than the average Ru−As distance in the neutral compounds *trans*-$[RuI_2(AsMe_2Ph)_4]$ [2.458−2.504 Å][14] and $[RuCl_2(CO)_2(AsPh_3)_2]$ [2.4927(6) Å, 2.4855(6) Å],[15] where six monodentate ligands are bonded to the ruthenium(II) ion. The distances Ru−O and P1−O are nearly the same as in the related cations $[(p\text{-cym})RuCl\{\kappa^2(P,O)\text{-}Ph_2P(O)CH_2PPh_2\}]^+$ and $[(p\text{-cym})RuCl\{\kappa^2(P,O)\text{-}Ph_2P(O)CH(CH_3)PPh_2\}]^+$, which were quite recently prepared by Faller et al. and structurally characterized as the SbF_6^- salts.[16]



Scheme 3

To compare the ligand behavior of 1-arsanyl-2-phosphanylethanes and (arsanyl)(phosphanyl)methanes, the reaction of the starting material **2** with $iPr_2PCH_2AstBu_2$ was also carried out. After heating the two substrates in ethanol, the cationic complex $[(p\text{-cym})RuCl\{\kappa^2\text{-}iPr_2PCH_2AstBu_2\}]^+$ with chloride as the counterion was formed, which upon salt metathesis with NH_4PF_6 gave **11** in 80% yield (Scheme 4). Similarly to **3**, compound **11** is a yellow air-stable solid that is soluble in polar solvents and, in nitromethane, shows the conductivity of a 1:1 electrolyte. The chemical shift of the singlet resonance in the ^{31}P-NMR spectrum of **11** indicates a chelate coordination of the unsymmetrical bidentate As,P ligand to the ruthenium center.[17] In agreement with the structural proposal, the ^{1}H-NMR spectrum of **11** displays two signals at $\delta = 3.41$ and 3.22 for the CH_2 protons of the $AsCH_2P$ unit and, due to P−H and H−H couplings, these are split into doublets of doublets.



Scheme 4

Conclusions

The work presented in this paper has shown that 1,2-bis(phosphanyl)ethanes as well as 1-arsanyl-2-phosphanylethanes, regardless of the bulk of the PR_2 or AsR_2 units, prefer to coordinate to a cationic $[(arene)RuCl]^+$ fragment in a chelating fashion. Only in the presence of silver(I) as an additional metal center was a heteronuclear Ru_2Ag_2 complex isolated and, in this case, the unsymmetrical bidentate ligand $Ph_2PCH_2CH_2PtBu_2$ binds in a bridging mode. Although four-membered chelate rings are generally less favored than five-membered rings, the methane derivat-

ive iPr$_2$PCH$_2$AstBu$_2$, like Ph$_2$PCH$_2$CH$_2$AstBu$_2$, generates a chelate complex with [(*p*-cym)RuCl]$^+$ as a building block.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1**, **5**,[4] **2** and **6**[18] as well as the ligands iPr$_2$PCH$_2$AstBu$_2$,[19] Ph$_2$PCH$_2$CH$_2$AstBu$_2$ and Ph$_2$PCH$_2$CH$_2$PR$_2$ (R = iPr, tBu, Cy)[1,2] were prepared as described in the literature. − NMR: Bruker AC 200 and AMX 400. − Conductivity measurements (in nitromethane): Schott conductometer CG 851. − Melting points determined by DTA.

1. Preparation of [(*p*-cym)RuCl(κ^2-Ph$_2$PCH$_2$CH$_2$AstBu$_2$)]PF$_6$ (3): (a) A solution of 120 mg (0.2 mmol) of **1** in 3 mL of CH$_3$CN was treated dropwise with a solution of 97 mg (0.2 mmol) of Ph$_2$PCH$_2$CH$_2$AstBu$_2$ in 3 mL of CH$_3$CN at room temperature. A change of color from yellow to orange occurred. The solution was concentrated to dryness in vacuo, the residue was washed with 5 mL of pentane and dried. An orange microcrystalline solid was obtained; yield 128 mg (65%). − (b) A suspension of 133 mg (0.2 mmol) of **2** in 5 mL of CH$_2$Cl$_2$ was treated with 177 mg (0.4 mmol) of Ph$_2$PCH$_2$CH$_2$AstBu$_2$ and stirred for 2 h at room temperature. A solution of 72 mg (0.4 mmol) of NH$_4$PF$_6$ in 3 mL of CH$_2$Cl$_2$ was added and the resulting reaction mixture was stirred for 2 h and then filtered. The filtrate was concentrated to dryness in vacuo, the residue was washed with 10 mL of ether and dried. An orange microcrystalline solid was obtained; yield 216 mg (60%); m.p. 145 °C (dec.). − Conductivity Λ = 74.3 cm^{2}Ω^{-1}mol^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.65−7.30 (m, 10 H, C$_6$H$_5$), 6.50 [d, 1 H, J(HH) = 5.8 Hz, 1 × H of C$_6$H$_4$], 6.37, 5.85 [both d, 1 H each, J(HH) = 6.2 Hz, 2 × H of C$_6$H$_4$], 5.64 [d, 1 H, J(HH) = 5.8 Hz, 1 × H of C$_6$H$_4$], 3.28−3.23 (br m, 1 H, 1 × H of PCH$_2$CH$_2$As), 2.76 [sept, 1 H, J(HH) = 7.0 Hz, CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$], 2.50−2.43, 2.31−2.22, 1.91−1.82 (each br m, 3 H, 3 × H of PCH$_2$CH$_2$As), 1.52, 1.36 (both s, 9 H each, AsCCH$_3$), 1.35, 1.30 [both d, 3 H each, J(HH) = 7.0 Hz, CH$_3$C$_6$H$_4$CH(C*H*$_3$)$_2$], 1.04 [s, 3 H, C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$]. − ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 135.5 [d, J(PC) = 42.9 Hz, *ipso*-C of C$_6$H$_5$], 134.0 [d, J(PC) = 8.6 Hz, C$_6$H$_5$], 133.1 [d, J(PC) = 58.2 Hz, *ipso*-C of C$_6$H$_5$], 131.8 [d, J(PC) = 8.6 Hz, C$_6$H$_5$], 131.6 [d, J(PC) = 5.7 Hz, C$_6$H$_5$], 131.6 (s, C$_6$H$_5$), 129.6 [d, J(PC) = 9.5 Hz, C$_6$H$_5$], 129.0 [d, J(PC) = 10.5 Hz, C$_6$H$_5$], 126.1 [d, J(PC) = 5.7 Hz, C$_6$H$_4$], 98.4, 92.3, 89.7, 89.0 (all s, C$_6$H$_4$), 86.2 [d, J(PC) = 8.6 Hz, C$_6$H$_4$], 46.7, 42.0 (both s, As*C*CH$_3$), 32.0 (s, AsC*C*H$_3$), 30.6 [s, CH$_3$C$_6$H$_4$*C*H(CH$_3$)$_2$], 30.1 (s, As*C*CH$_3$), 29.8 [d, J(PC) = 35.3 Hz, P*C*H$_2$CH$_2$As], 22.8, 20.8 [both s, CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$], 19.3 [d, J(PC) = 8.6 Hz, PCH$_2$*C*H$_2$As], 15.3 [s, *C*H$_3$C$_6$H$_4$CH(CH$_3$)$_2$]. − ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 71.1 (s, Ph$_2$P), −144.3 [sept, J(FP) = 710.6 Hz, PF$_6^-$]. − C$_{32}$H$_{46}$AsClF$_6$P$_2$Ru (818.1): calcd. C 46.98, H 5.67; found C 46.43, H 5.15.

2. Preparation of [(*p*-cym)RuCl(κ^2-Ph$_2$PCH$_2$CH$_2$PtBu$_2$)]PF$_6$ (4): (a) In an analogous way to that described for **3** [method (a)] using 174 mg (0.4 mmol) of **1** and 127 mg (0.4 mmol) of Ph$_2$PCH$_2$CH$_2$PtBu$_2$ as starting materials. Yield 203 mg (75%). − (b) In an analogous way to that described for **3** [method (b)] using 162 mg (0.3 mmol) of **2**, 191 mg (0.5 mmol) of Ph$_2$PCH$_2$CH$_2$PtBu$_2$ and 86 mg (0.5 mmol) of NH$_4$PF$_6$ as starting materials. Orange microcrystalline solid; yield 287 mg (70%); m.p. 152 °C (dec.). − Conductivity Λ = 61.8 cm^{2}Ω^{-1}mol^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.68−7.35 (m, 10 H, C$_6$H$_5$), 6.45, 6.18, 5.95, 5.46 [all d, 1 H each, J(HH) = 6.2 Hz, C$_6$H$_4$], 3.31−3.19 (br m, 2 H, PC*H*$_2$CH$_2$P), 2.81−2.77 (br m, 1 H, PC*H*CH$_3$), 2.60−2.42 (br m, 3 H, PCH$_2$C*H*$_2$P and PC*H*CH$_3$), 2.20 [s, 3 H, C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$], 1.60−1.10 [m, 24 H, CH$_3$C$_6$H$_4$CH(C*H*$_3$)$_2$ and PCCH$_3$]. − ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 136.0 [d, J(PC) = 11.4 Hz, C$_6$H$_5$], 132.8 (m, C$_6$H$_5$), 131.0 [d, J(PC) = 2.9 Hz, C$_6$H$_5$], 129.8 [d, J(PC) = 41.0 Hz, C$_6$H$_5$], 128.8, 128.3 [both d, J(PC) = 10.5 Hz, C$_6$H$_5$], 125.8, 102.9 (both s, C$_6$H$_4$), 93.0 [d, J(PC) = 3.8 Hz, C$_6$H$_4$], 92.2 [d, J(PC) = 2.9 Hz, C$_6$H$_4$], 91.9, 90.3 [both d, J(PC) = 6.7 Hz, C$_6$H$_4$], 36.8 [dd, J(P^{1}C) = 25.7, J(P^{2}C) = 14.3 Hz, P*C*H$_2$CH$_2$P], 35.2 [dd, J(P^{1}C) = 31.9, J(P^{2}C) = 10.0 Hz, PCH$_2$*C*H$_2$P], 31.3 [s, CH$_3$C$_6$H$_4$*C*H(CH$_3$)$_2$], 28.5 [d, J(PC) = 25.7 Hz, P*C*CH$_3$], 27.7 [d, J(PC) = 20.0 Hz, P*C*CH$_3$], 22.4 [s, *C*H$_3$C$_6$H$_4$CH(CH$_3$)$_2$], 21.7 [d, J(PC) = 2.9 Hz, PC*C*H$_3$], 20.9 [s, CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$], 20.7 [d, J(PC) = 3.9 Hz, PC*C*H$_3$], 20.2 [s, CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$]. − ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 85.2 [d, J(PP) = 33.1 Hz, tBu$_2$P], 78.3 [d, J(PP) = 33.1 Hz, Ph$_2$P], −144.9 [sept, J(FP) = 709.5 Hz, PF$_6^-$]. − C$_{32}$H$_{46}$ClF$_6$P$_3$Ru (774.2): calcd. C 49.65, H 5.99; found C 49.64, H 5.76.

3. Preparation of [(η^6-C$_6$H$_6$)RuCl(κ^2-Ph$_2$PCH$_2$CH$_2$PiPr$_2$)]PF$_6$ (7): (a) In an analogous way to that described for **3** [method (a)], by using 163 mg (0.4 mmol) of **5** and 129 mg (0.4 mmol) of Ph$_2$PCH$_2$CH$_2$PiPr$_2$ as starting materials. Yield 207 mg (77%). − (b) A suspension of 273 mg (0.6 mmol) of **6** in 8 mL of CH$_3$CN was treated with 361 mg (1.1 mmol) of Ph$_2$PCH$_2$CH$_2$PiPr$_2$ and 258 mg (1.1 mmol) of AgPF$_6$ and stirred for 2 h at 60 °C. Upon cooling to room temperature, the solvent was removed in vacuo and the residue was extracted with 10 mL of CH$_2$Cl$_2$. The extract was then concentrated to dryness in vacuo, the residue was washed with 10 mL of ether and dried. An orange microcrystalline solid was obtained; yield 570 mg (75%); m.p. 148 °C (dec.). − Conductivity Λ = 69.8 cm^{2}Ω^{-1}mol^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.78−7.12 (m, 10 H, C$_6$H$_5$), 5.86 (s, 6 H, C$_6$H$_6$), 2.70−1.83 (br m, 6 H, PCH$_2$CH$_2$P and PC*H*CH$_3$), 1.37 [dd, 6 H, J(PH) = 15.8, J(HH) = 7.9 Hz, PCHC*H*$_3$], 1.28 [dd, 3 H, J(PH) = 15.1, J(HH) = 7.2 Hz, PCHC*H*$_3$], 1.22 [dd, 3 H, J(PH) = 14.4, J(HH) = 7.0 Hz, PCHC*H*$_3$]. − ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 135.5 [d, J(PC) = 47.8 Hz, *ipso*-C of C$_6$H$_5$], 133.9, 133.3 [both d, J(PC) = 9.2 Hz, C$_6$H$_5$], 131.6, 129.9 [both d, J(PC) = 10.2 Hz, C$_6$H$_5$], 129.2, 129.1 [both d, J(PC) = 11.1 Hz, C$_6$H$_5$], 93.4 [d, J(PC) = 2.0 Hz, C$_6$H$_6$], 31.6 [d, J(PC) = 24.4 Hz, P*C*HCH$_3$], 26.6 [d, J(PC) = 26.4 Hz, P*C*HCH$_3$], 26.6 [dd, J(P^{1}C) = 35.6, J(P^{2}C) = 8.1 Hz, P*C*H$_2$CH$_2$P], 21.3 [dd, J(P^{1}C) = 30.0, J(P^{2}C) = 10.7 Hz, PCH$_2$*C*H$_2$P], 20.6 (s, PCH*C*H$_3$), 19.7 [d, J(PC) = 2.0 Hz, PCH*C*H$_3$], 19.4 (s, PCH*C*H$_3$), 18.8 [d, J(PC) = 3.0 Hz, PCH*C*H$_3$]. − ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 86.9 [d, J(PP) = 32.7 Hz, iPr$_2$P], 70.0 [d, J(PP) = 32.7 Hz, Ph$_2$P], −144.3 [sept, J(FP) = 710.6 Hz, PF$_6^-$]. − C$_{26}$H$_{34}$ClF$_6$P$_3$Ru (690.0): calcd. C 45.26, H 4.97; found C 44.98, H 5.06.

4. Preparation of [(η^6-C$_6$H$_6$)RuCl(κ^2-Ph$_2$PCH$_2$CH$_2$PCy$_2$)]PF$_6$ (8): (a) In an analogous way to that described for **3** [method (a)], by using 120 mg (0.3 mmol) of **5** and 119 mg (0.3 mmol) of Ph$_2$PCH$_2$CH$_2$PCy$_2$ as starting materials. Yield 270 mg (78%). − (b) In an analogous way to that described for **7** [method (b)], by using 225 mg (0.5 mmol) of **6**, 370 mg (0.9 mmol) of Ph$_2$PCH$_2$CH$_2$PCy$_2$ and 227 mg (0.9 mmol) of AgPF$_6$ as starting materials. Orange microcrystalline solid; yield 520 mg (75%); m.p. 131 °C (dec.). − Conductivity Λ = 71.6 cm^{2}Ω^{-1}mol^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.72−7.18 (m, 10 H, C$_6$H$_5$), 5.92 (s, 6 H, C$_6$H$_6$), 2.84−2.72 (m, 2 H, PC*H*$_2$CH$_2$P), 2.42−2.23 (m, 2 H, PCH$_2$C*H*$_2$P), 2.20−1.15 (br m, 22 H, CH and CH$_2$ of C$_6$H$_{11}$). − ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 135.5 [d, J(PC) = 48.6 Hz, *ipso*-C of C$_6$H$_5$], 133.8, [d, J(PC) = 9.5 Hz, C$_6$H$_5$], 132.0, 131.9 [both d,

J(PC) = 2.9 Hz, C_6H_5], 131.7 [d, *J*(PC) = 9.5 Hz, C_6H_5], 130.4 [d, *J*(PC) = 54.3 Hz, *ipso*-C of C_6H_5], 129.9 [d, *J*(PC) = 9.5 Hz, C_6H_5], 129.1 [d, *J*(PC) = 10.5 Hz, C_6H_5], 93.3 (s, C_6H_6), 42.9 [d, *J*(PC) = 21.9 Hz, CH of C_6H_{11}], 37.1 [d, *J*(PC) = 25.7 Hz, CH of C_6H_{11}], 30.7, 30.0, 29.9, 29.8 (all s, CH_2 of C_6H_{11}), 29.4 [d, *J*(PC) = 4.8 Hz, CH_2 of C_6H_{11}], 28.1 [d, *J*(PC) = 13.4 Hz, CH_2 of C_6H_{11}], 27.4 [d, *J*(PC) = 9.5 Hz, CH_2 of C_6H_{11}], 27.7, 27.1 [both d, *J*(PC) = 10.5 Hz, CH_2 of C_6H_{11}], 26.6 [dd, $J(P^1C)$ = 35.3, $J(P^2C)$ = 6.7 Hz, P*C*$H_2$$CH_2$P], 26.2 [d, *J*(PC) = 10.5 Hz, CH_2 of C_6H_{11}], 20.3 [dd, $J(P^1C)$ = 30.5, $J(P^2C)$ = 10.5 Hz, PCH_2*C*H_2P]. – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 79.2 [d, *J*(PP) = 30.5 Hz, Cy_2P], 70.2 [d, *J*(PP) = 30.5 Hz, Ph_2P], −142.1 [sept, *J*(FP) = 710.6 Hz, PF_6^-]. – $C_{32}H_{42}ClF_6P_3Ru$ (770.1): calcd. C 49.91, H 5.50; found C 49.46, H 5.86.

5. Preparation of [(*p*-cym)RuAg(μ-Cl)$_2$(μ-P^1_{Ru},P^2_{Ag}-Ph$_2$P^{1}CH$_2$-CH$_2$P^2*t*Bu$_2$)]$_2$(PF$_6$)$_2$ (9): A solution of 245 mg (0.4 mmol) of **1** and 286 mg (0.8 mmol) of $Ph_2PCH_2CH_2Pt$Bu$_2$ in 5 mL of CH_2Cl_2 was stirred for 1 h and then treated dropwise with a solution of 198 mg (0.8 mmol) of $AgPF_6$ in 3 mL of CH_2Cl_2. After 1 h of stirring at room temperature, the resulting reaction mixture was filtered. The filtrate was concentrated to dryness in vacuo, the residue was washed with 10 mL of pentane and dried. A red microcrystalline solid was obtained; yield 701 mg (95%); m.p. 204 °C (dec.). – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.78 (m, 4 H, C_6H_5), 7.58 (m, 6 H, C_6H_5), 5.44, 5.25 [both d, 4 H, *J*(HH) = 5.0 Hz, C_6H_4], 2.63−2.52 (m, 2 H, PC$H_2$$CH_2$P), 2.22 [sept, 1 H, *J*(HH) = 7.0 Hz, $CH_3C_6H_4CH(CH_3)_2$], 1.33−1.19 (br m, 2 H, PCH_2CH_2P), 1.04 [s, 3 H, C$H_3C_6H_4CH(CH_3)_2$], 0.98 [d, 18 H, *J*(PH) = 15.0 Hz, PCCH_3], 0.77 [d, 3 H, *J*(HH) = 6.8 Hz, $CH_3C_6H_4CH(CH_3)_2$], 0.73 [d, 3 H, *J*(HH) = 7.0 Hz, $CH_3C_6H_4CH(CH_3)_2$]. – ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 132.9 [d, *J*(PC) = 9.5 Hz, C_6H_5], 132.5 [d, *J*(PC) = 3.5 Hz, C_6H_5], 129.7 [d, *J*(PC) = 44.8 Hz, *ipso*-C of C_6H_5], 129.7 [d, *J*(PC) = 9.5 Hz, C_6H_5], 108.8, 95.6 [both s, C_6H_4], 91.4 [d, *J*(PC) = 3.8 Hz, C_6H_4], 86.4 [d, *J*(PC) = 4.8 Hz, C_6H_4], 34.2 [dd, $J(P^1C)$ = 11.0, $J(P^2C)$ = 5.2 Hz, P*C*CH_3], 31.0 [s, $CH_3C_6H_4CH(CH_3)_2$], 29.4 [d, *J*(PC) = 6.7 Hz, PC*C*H_3], 25.4 [dd, $J(P^1C)$ = 21.5, $J(P^2C)$ = 15.7 Hz, P*C*$H_2$$CH_2$P], 21.2, 17.8 [both s, $CH_3C_6H_4CH(CH_3)_2$ and $CH_3C_6H_4CH(CH_3)_2$], 13.9 (m, PCH_2*C*H_2P). – ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 68.0 [dd, $^1J(^{109}AgP)$ = 743.3 Hz, *J*(PP) = 39.2 Hz, *t*Bu$_2$P], 67.9 [dd, $^1J(^{107}AgP)$ = 643.0 Hz, *J*(PP) = 39.2 Hz, *t*Bu$_2$P], 28.0 [d, *J*(PP) = 39.2 Hz, Ph_2P], −144.3 [sept, *J*(FP) = 710.8 Hz, PF_6^-]. – $C_{64}H_{92}Ag_2Cl_4F_{12}P_6Ru_2$ (1835): calcd. C 41.89, H 5.05, Ag 11.76; found C 41.87, H 5.33, Ag 11.63.

6. Preparation of [(*p*-cym)RuCl{κ^2(As,O)-Ph$_2$P(O)CH$_2$CH$_2$-As*t*Bu$_2$}]PF$_6$ (10): A solution of 214 mg (0.5 mmol) of $Ph_2PCH_2CH_2Ast$Bu$_2$ in 10 mL of CH_2Cl_2 was treated with oxygen for ca. 10 min at room temperature and then added to a solution of 165 mg (0.3 mmol) of **1** in 4 mL of CH_2Cl_2. After 1 h of stirring, a solution of 132 mg (0.5 mmol) of $AgPF_6$ in 3 mL of CH_2Cl_2 was added dropwise. The resulting reaction mixture was stirred for 20 min and then filtered. The filtrate was concentrated to dryness in vacuo, the residue was washed twice with 4 mL of cold methanol and dried. A dark-red microcrystalline solid was obtained; yield 199 mg (45%); m.p. 131 °C (dec.). – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.75−7.26 (m, 10 H, C_6H_5), 6.53 [d, 1 H, *J*(HH) = 5.8 Hz, 1 × H of C_6H_4], 6.39, 5.89 [both d, 1 H each, *J*(HH) = 6.4 Hz, 2 × H of C_6H_4], 5.62 [d, 1 H, *J*(HH) = 6.1 Hz, 1 × H of C_6H_4], 3.30−3.20 (br m, 1 H, 1 × H of PC$H_2$$CH_2$As), 2.74 [sept, 1 H, *J*(HH) = 7.1 Hz, $CH_3C_6H_4CH(CH_3)_2$], 2.52−2.46, 2.35−2.21, 1.89−1.82 (all br m, 3 H, PC$H_2$$CH_2$As), 1.51, 1.34 (both s, 9 H each, AsCCH_3), 1.33, 1.30 [both d, 3 H each, *J*(HH) = 7.1 Hz, $CH_3C_6H_4CH(CH_3)_2$], 1.10 [s, 3 H, C$H_3C_6H_4CH(CH_3)_2$]. – ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 142.5 [d, *J*(PC) = 43.9 Hz, *ipso*-C of C_6H_5], 135.0 [d, *J*(PC) = 8.4 Hz, C_6H_5], 134.3 [d, *J*(PC) = 52.2 Hz, *ipso*-C of C_6H_5], 132.8 [d, *J*(PC) = 8.4 Hz, C_6H_5], 131.6 [d, *J*(PC) = 5.8 Hz, C_6H_5], 131.5 (s, C_6H_5), 129.4 [d, *J*(PC) = 9.5 Hz, C_6H_5], 129.0 [d, *J*(PC) = 10.5 Hz, C_6H_5], 125.8 [d, *J*(PC) = 4.7 Hz, C_6H_4], 97.4, 92.6, 89.9, 89.1 (all s, C_6H_4), 87.2 [d, *J*(PC) = 8.7 Hz, C_6H_4], 46.5, 42.3 (both s, As*C*CH_3), 32.3 (s, AsC*C*H_3), 30.4 [s, $CH_3C_6H_4CH(CH_3)_2$], 31.8 [d, *J*(PC) = 30.3 Hz, P*C*$H_2$$CH_2$As], 30.1 (s, AsC*C*$H_3$), 22.5, 21.3 [both s, $CH_3C_6H_4CH(CH_3)_2$], 20.3 [d, *J*(PC) = 6.6 Hz, PCH_2*C*H_2As], 14.8 [s, *C*$H_3C_6H_4CH(CH_3)_2$]. – ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 53.8 [s, Ph_2P(O)], −144.2 [sept, *J*(FP) = 710.8, PF_6^-]. – $C_{32}H_{46}AsClF_6OP_2Ru$ (834.1): calcd. C 46.08, H 5.56; found C 45.56, H 5.15.

7. Preparation of [(*p*-cym)RuCl(κ^2-*i*Pr$_2$PCH$_2$As*t*Bu$_2$)]PF$_6$ (11): A solution of 32 mg (0.1 mmol) of **2** in 5 mL of ethanol was treated with a solution of 67 mg (0.2 mmol) of *i*Pr$_2$PCH$_2$As*t*Bu$_2$ in 5 mL of ethanol and the mixture stirred under reflux for 24 h. Upon cooling to room temperature, 17 mg (0.1 mmol) of NH_4PF_6 was added to the reaction mixture. After 10 min of stirring, the solvent was removed in vacuo, the residue was washed three times with 10 mL of pentane and dried. A yellow solid was obtained; yield 75 mg (80%); m.p. 86 °C. – Conductivity Λ = 70.2 $cm^2\Omega^{-1}mol^{-1}$. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.34 [d, 1 H, *J*(HH) = 5.3 Hz, 1 × H of C_6H_4], 6.14 [d, 1 H, *J*(HH) = 5.8 Hz, 1 × H of C_6H_4], 6.08 [d, 1 H, *J*(HH) = 5.9 Hz, 1 × H of C_6H_4], 5.28 [d, 1 H, *J*(HH) = 5.3 Hz, 1 × H of C_6H_4], 3.41 [dd, 1 H, *J*(PH) = 15.0, *J*(HH) = 9.9 Hz, 1 × H of PCH_2As], 3.22 [dd, 1 H, *J*(PH) = 14.8, *J*(HH) = 9.9 Hz, 1 × H of PCH_2As], 2.57, 2.65, 2.77 [all m, 1 H each, PC*H*CH_3 and $CH_3C_6H_4C$*H*$(CH_3)_2$], 2.19 [s, 3 H, C$H_3C_6H_4CH(CH_3)_2$], 1.56 [dd, 3 H, *J*(PH) = 16.1, *J*(HH) = 7.3 Hz, PCHCH_3], 1.46, 1.40 (both s, 9 H each, AsCCH_3), 1.32 [dd, 3 H, *J*(PH) = 11.4, *J*(HH) = 7.2 Hz, PCHCH_3], 1.29 [dd, 3 H, *J*(PH) = 10.8, *J*(HH) = 6.9 Hz, PCHCH_3], 1.27 [dd, 3 H, *J*(PH) = 9.7, *J*(HH) = 7.3 Hz, PCHCH_3], 1.25 [d, 3 H, *J*(HH) = 7.1 Hz, $CH_3C_6H_4CHCH_3$], 1.19 [d, 3 H, *J*(HH) = 7.0 Hz, $CH_3C_6H_5CHCH_3$]. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 124.0 [d, *J*(PC) = 5.7 Hz, C_6H_4], 95.4, 88.3, 88.1 (all s, C_6H_4), 84.4 [d, *J*(PC) = 7.6 Hz, C_6H_4], 82.9 (s, C_6H_4), 45.6 [d, *J*(PC) = 6.7 Hz, As*C*CH_3], 39.4 (s, As*C*CH_3), 31.8 (s, AsC*C*H_3), 31.7 [d, *J*(PC) = 19.0 Hz, PCH_2As], 29.4 [s, $CH_3C_6H_4C$*H*$(CH_3)_2$], 28.4 (s, AsC*C*H_3), 27.0, 27.2 [both d, *J*(PC) = 17.9 Hz, P*C*HCH_3], 22.4 [s, $CH_3C_6H_4CH(CH_3)_2$], 18.8, 19.0, 19.8, (all s, PCH*C*H_3), 17.5 [d, *J*(PC) = 2.9 Hz, PCH*C*H_3], 17.3 [s, *C*$H_3C_6H_4CH(CH_3)_2$]. – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.3 (s, P*i*Pr$_2$), −142.1 [sept, *J*(FP) = 710.6 Hz, PF_6^-]. – $C_{25}H_{48}AsClF_6P_2Ru$ (736.0): calcd. C 40.80, H 6.57; found C 40.53, H 6.29.

X-ray Structure Determination of Compounds 9 and 10:[20] Single crystals of **9** were grown from acetone/methanol at 25 °C and those of **10** from methanol 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 (**9**) and with a Stoe IPDS diffractometer using monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (**10**) with SHELXS-97.[21] All structures were refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[22] The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by employing the riding method. For **10** the Flack parameter was refined to a value of −0.025(15)[12] and the extinction coefficient was refined to 0.00116(10).

Table 1. Crystal data for complexes **9** and **10**

	9	**10**
Formula	$C_{64}H_{92}Ag_2Cl_4F_{12}P_6Ru_2$	$C_{32}H_{46}AsClF_6OP_2Ru$
M	1834.9	834.1
Crystal system	triclinic	orthorhombic
Space group	*P*($\bar{1}$) (no. 2)	*Pna*2 (1) (no.33)
a [Å]	10.383(4)	19.770(4)
b [Å]	14.144(5)	12.180(2)
c [Å]	15.424(6)	14.510(3)
α [°]	95.67(2)	90
β [°]	108.36(2)	90
γ [°]	103.54(2)	90
V [Å^3]	2053.3(14)	3494(1)
Temperature [K]	193(2)	173(2)
Z	2	4
D_c [g cm^{-3}]	1.560	1.586
μ [mm^{-1}]	1.146	1.614
No. reflections measured	8514	18919
No. unique reflections (R_{int})	7202 (0.0352)	6072 (0.0882)
$R1$[a]	0.0810	0.0408
$wR2$[b]	0.1270	0.0774

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o > 2\,\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. – [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0452\,P)^2 + 7.7438P]$ (**9**), $[\sigma^2(F_o^2) + (0.0111P)^2 + 0.0000P]$ (**10**), where $P = (F_o^2 + 2F_c^2)/3$; for all data reflections, respectively.

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[1] G. Fries, J. Wolf, M. Pfeiffer, D. Stalke, H. Werner, *Angew. Chem.* **2000**, *112*, 575–577; *Angew. Chem. Int. Ed.* **2000**, *39*, 564–566.

[2] G. Fries, Dissertation, Universität Würzburg, **2000**.

[3] [3a]H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.* **1989**, *29*, 163–247. – [3b]M. A. Bennett, in: *Comprehensive Organometallic Chemistry*, vol. 7 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1995**, chapter 9. – [3c]R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102.

[4] [4a]D. E. Fogg, B. R. James, *J. Organomet. Chem*. **1993**, *462*, C21–C23. – [4b]F. B. McCormick, D. D. Cox, W. B. Gleason, *Organometallics* **1993**, *12*, 610–612.

[5] R. J. Lancashire, in: *Comprehensive Coordination Chemistry*, vol. 5 (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, New York, **1987**, p. 800.

[6] H. V. Rasika Dias, W. Jin, H.-J. Kim, H.-L. Lu, *Inorg. Chem.* **1996**, *35*, 2317–2328.

[7] R. Uson, J. Fornies, M. Tomas, I. Ara, J. M. Casas, *Polyhedron* **1992**, *11*, 1783–1787.

[8] P. D. Robinson, C. C. Hinckley, M. Matusz, P. A. Kibala, *Polyhedron* **1987**, *6*, 1695–1698.

[9] P. Braunstein, D. G. Kelly, Y. Dusausoy, D. Bayeul, M. Lanfranchi, M. Tiripicchio, *Inorg. Chem.* **1994**, *33*, 233–242.

[10] [10a] M. R. J. Elsegood, D. A. Tocher, *Polyhedron* **1995**, *14*, 3147–3156. – [10b] P. D. Smith, A. H. Wright, *J. Organomet. Chem.* **1998**, *559*, 141–147. – [10c] S. Serron, S. P. Nolan, Y. A. Abramov, L. Brammer, J. L. Petersen, *Organometallics* **1998**, *17*, 104–110. – [10d] D. K. Gupta, A. N. Sahay, D. S. Pandey, N. K. Jha, P. Sharma, G. Espinosa, A. Cabrera, M. C. Puerta, P. Valerga, *J. Organomet. Chem*. **1998**, *568*, 13–20.

[11] I. de los Rios, M. J. Tenorio, M. C. Puerta, P. Valerga, *Organometallics* **1998**, *17*, 3356–3363.

[12] [12a] S. Freitag, R. Herbst-Irmer, L. Lameyer, D. Stalke, *Organometallics* **1996**, *15*, 2839–2841. – [12b] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881. – [12c] G. Bernadinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, *41*, 500.

[13] [13a] G. Henig, M. Schulz, H. Werner, *Chem. Commun.* **1997**, 2349–2350. – [13b] J. Bank, P. Steinert, B. Windmüller, W. Wolfsberger, H. Werner, *J. Chem. Soc., Dalton Trans.* **1996**, 1153–1159. – [13c] I. de los Rios, M. J. Tenorio, M. A. J. Tenorio, M. C. Puerta, P. Valerga, *J. Organomet. Chem.* **1996**, *525*, 57–64. – [13d] I. S. Thorburn, S. J. Rettig, B. R. James, *J. Organomet. Chem.* **1985**, *296*, 103–114.

[14] N. J. Holmes, W. Levason, M. Webster, *J. Chem. Soc., Dalton Trans.* **1997**, 4223–4229.

[15] A. A. Batista, J. Zukerman-Schpector, O. M. Porcu, S. L. Queiroz, M. P. Araujo, G. Oliva, D. H. F. Souza, *Polyhedron* **1994**, *13*, 689–693.

[16] J. W. Faller, B. P. Patel, M. A. Albrizzio, M. Curtis, *Organometallics* **1999**, *18*, 3096–3104.

[17] H. Werner, M. Manger, U. Schmidt, M. Laubender, B. Weberndörfer, *Organometallics* **1998**, *17*, 2619–2627.

[18] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

[19] 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.

[20] Crystallographic data (excluding structure factors) for the structures of **9** and **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140027 (**9**) and -140028 (**10**). 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).

[21] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[22] G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, **1996**.

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