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A series of mononuclear ruthenium(II) complexes with sterically demanding bis(phosphino)methanes and arsino(phosphino)methanes as ligands

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Dedicated to Professor Martin Bennett, a good friend and creative scientist, on the occasion of his 65th birthday.

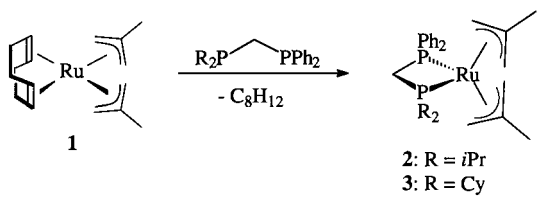
Abstract

The bis(η^3-2-methylallyl)ruthenium(II) complexes [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$R_2PCH_2PPh_2$)] (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 bis(phosphino)methanes $R_2PCH_2PPh_2$ (R = *i*Pr, Cy). Treatment of **2** with benzoic acid and with acetic acid in the presence of $iPr_2PCH_2PPh_2$ led, after proton-assisted cleavage of the allyl–metal bond, to the formation of the bis(carboxylato)ruthenium(II) compounds **4** and **5a**/**5b**, respectively. Similarly, the bis(trifluoroacetate) [Ru(η^1-O_2CCF_3)$_2$(κ^2-$iPr_2PCH_2PiPr_2$)$_2$] (**7**) was prepared and the molecular structure determined by X-ray crystallography. The reaction of **2** and **3** with hexafluoroacetone afforded the chelate complexes [Ru(η^2-acac-f_6)$_2$(κ^2-$R_2PCH_2PPh_2$)] (R = *i*Pr **8**, Cy **9**) which were also accessible from [Ru(η^2-OC_6Cl_5)$_2$(κ^2-$R_2PCH_2PPh_2$)] (R = *i*Pr **10**, Cy **11**) by treatment with Hacac-f_6. The preparation of the non-fluorinated bis(acac) compound [Ru(η^2-acac)$_2$(κ^2-$iPr_2PCH_2PPh_2$)] (**12**), which could not be obtained from **2** and Hacac, was achieved by ligand exchange from **10** and acetylacetone in the presence of Na_2CO_3. The reaction of **10** with CO and CN*t*Bu gave by partial opening of the chelate rings the substitution products [Ru(OC_6Cl_5)$_2$(CO)(κ^2-$iPr_2PCH_2PPh_2$)] (**13**) and [Ru(OC_6Cl_5)$_2$(CN*t*Bu)$_3$(κ^1-$Ph_2PCH_2PiPr_2$)] (**14**), the latter containing the unsymmetrical bis(phosphino)methane as a monodentate ligand. With the dimer [RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)]$_2$ (**15**) as the starting material, the mononuclear ruthenium(IV) complexes [RuCl(η^3:η^3-$C_{10}H_{16}$)(κ^2-$iPr_2PCH_2PiPr_2$)]BF_4 (**16**) and [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(κ-*P*-$iPr_2PCH_2AstBu_2$)] (**17**) were prepared.

Keywords: Ruthenium; η^3-Allyl complexes; Bis(phosphino)methane complexes; Carboxylato complexes; Pentachlorophenolato complexes

1. Introduction

Following our interest in the use of new, possibly hemilabile, bidentate ligands as part of d^6 and d^8 metal complexes [1], we recently described the preparation of new symmetrical and unsymmetrical bis(phosphino)methanes and arsino(phosphino)methanes with bulky substituents R and R′ at the donor centers [2,3]. The search for these ligands was initiated by the fact that apart from the well-known compounds $Ph_2PCH_2PPh_2$ (dppm) and $Me_2PCH_2PMe_2$ (dmpm) related, in particular unsymmetrical, derivatives of the general composition $R_2PCH_2PR'_2$ were almost unknown [4]. After we prepared at the beginning of these studies a variety of rhodium(I) complexes with $iPr_2PCH_2PPh_2$, $iPr_2PCH_2PCy_2$ [2] and $iPr_2PCH_2AsR_2$ (R = *i*Pr, *t*Bu) [3] as ligands, we mainly report in this paper the synthesis of a series of ruthenium(II) compounds with either one or two bis(phosphino)methanes linked to the metal center. Some preliminary results of this work have already been communicated [5].



Scheme 1.

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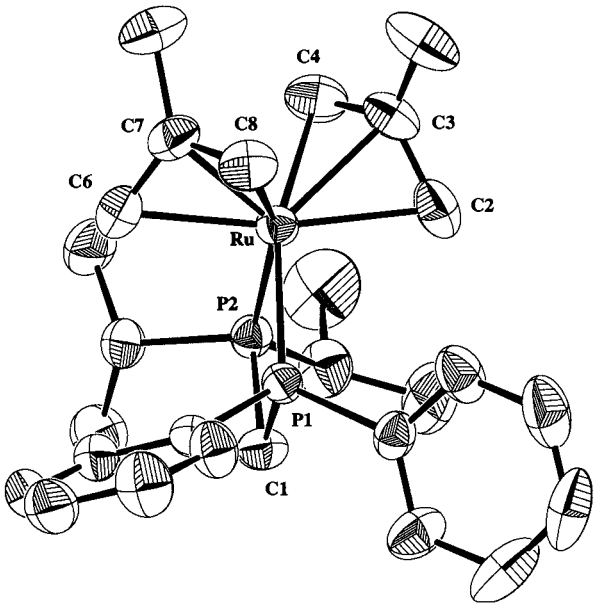


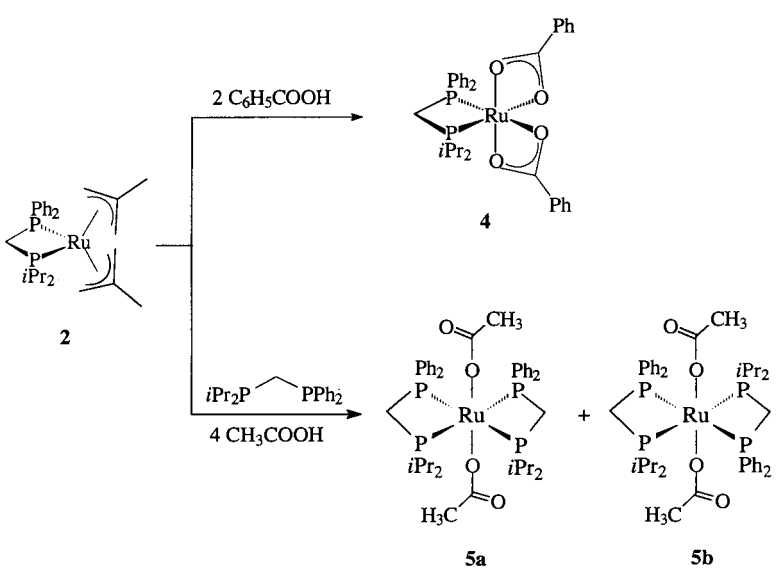
Fig. 1. Molecular structure (ORTEP diagram) of compound **2**. Selected bond lengths (Å) and bond angles (°): Ru–P1 2.286(2), Ru–P2 2.345(2), Ru–C2 2.237(2), Ru–C3 2.185(2), Ru–C4 2.238(2), Ru–C6 2.227(2), Ru–C7 2.172(2), Ru–C8 2.232(2), P1–C1 1.842(4), P2–C1 1.848(4); P1–Ru–P2 72.06(7), Ru–P1–C1 97.5(1), Ru–P2–C1 95.3(1), P1–C1–P2 95.2(2), C2–C3–C4 117.5(4), C6–C7–C8 118.7(4).

2. Results and discussion

Applying the methodology, recently developed by Holle et al. [6] and Leitner and coworkers [7], we prepared the bis(η^3-2-methylallyl)ruthenium(II) complexes **2** and **3** (Scheme 1) from the cycloocta-1.5-diene derivative **1** as the starting material. The reaction proceeds in hexane under reflux conditions and gives the products as yellow solids in 75–82% yield. Compounds **2** and **3** are practically air-stable, readily soluble in benzene and dichloromethane, and moderately soluble in pentane and ether. The ^{31}P-NMR spectra of **2** and **3** display two doublets for the non-equivalent phosphorus nuclei with $^{31}P-^{31}P$ coupling constants of 31.7 and 30.5 Hz. In contrast to iPr$_2$PCH$_2$PPh$_2$ and Cy$_2$PCH$_2$PPh$_2$, the starting material **1** does not react with iPr$_2$PCH$_2$AstBu$_2$ and is recovered unchanged after heating the reaction mixture in hexane for 6 h under reflux.

The molecular structure of compound **2**, of which single crystals were obtained from ether at 0°C, was determined by X-ray crystallography. The ORTEP plot (Fig. 1) reveals that the coordination geometry can be regarded as pseudo-tetrahedral with the two phosphorus atoms P1 and P2 and the two central carbon atoms C3 and C7 of the allylic units at the corners of the tetrahedron. The bond lengths Ru–C3 and Ru–C7 are significantly shorter than those from ruthenium to the terminal carbon atoms of the 2-MeC$_3$H$_4$ ligands. This results in dihedral angles of 40.66(24) and 39.08(38)° between the planes of the π-allylic systems, [C2,C3,C4] and [C6,C7,C8], and the plane of the four-membered chelate ring [Ru,P1,C1,P2]. The carbon atoms C3 and C7 are bent away from the metal center, analogously as found in [Ru(η^3-C$_3$H$_5$)$_2$(PPh$_3$)$_2$] [8]. The distances Ru–P1 and Ru–P2 differ only slightly to those in other phosphineruthenium(II) complexes [8,9] while the bite angle P1–Ru–P2 of 72.06(7)° is almost the same as in some compounds with Ru(dppm) as the molecular unit [10].

Likewise to the cycloocta-1.5-diene complex **1**, which upon treatment with CF$_3$CO$_2$H affords the dinuclear product [Ru(μ-O$_2$CCF$_3$)$_2$(η^4-C$_8$H$_{12}$)]$_2$ [11], the analogous compound **2** is also quite reactive towards



Scheme 2.

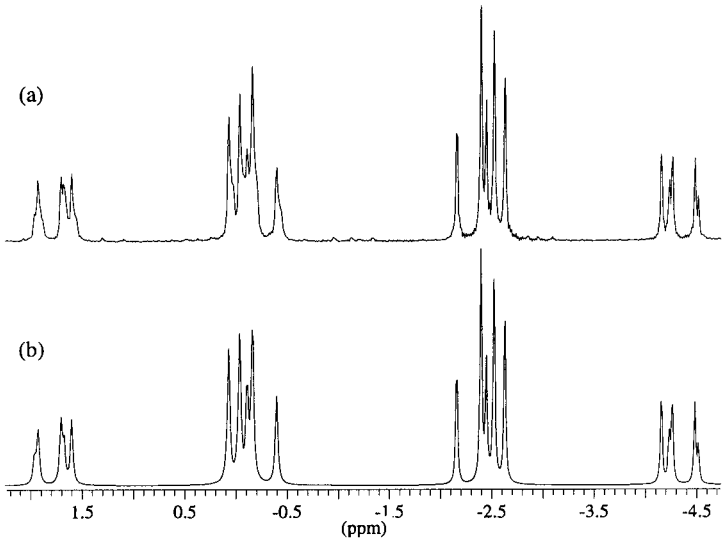


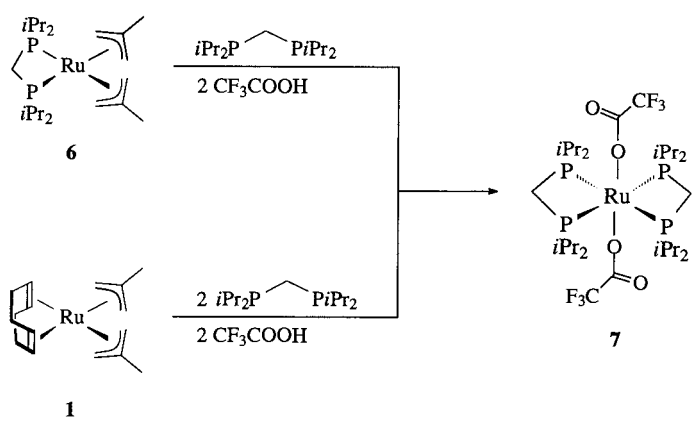
Fig. 2. Comparision of the measured (a) and the simulated (b) ^{31}P-NMR spectrum (AA′BB′ spin system) of compound **5a**.

carboxylic acids. With benzoic acid, the mononuclear complex **4** (Scheme 2) is formed in which both benzoate anions are coordinated as bidentate ligands to the metal center. The IR spectrum of **4** displays two ν(OCO) bands at 1493 and 1415 cm^{-1}, the positions of which are typical for a chelating bonding mode of the $PhCO_2^-$ units [12].

The reactions of **2** with CH_3CO_2H and CF_3CO_2H led, either at -78°C or at room temperature, to a mixture of products which could not be separated by fractional crystallization or chromatographic techniques. If, however, the bis(η^3-2-methylallyl) compound **2** is treated with acetic acid in ether in the presence of an equimolar amount of iPr$_2$PCH$_2$PPh$_2$, a yellow, only slightly air-sensitive solid can be isolated in 72% yield. The ^{31}P-NMR spectrum of the product indicates that two stereoisomers, **5a** and **5b**, in the ratio of approximately 85:15 are formed. For the major isomer **5a**, in which the two PPh$_2$ and the two PiPr$_2$ units are *cis* to each other, four signals appear which are part of an AA′BB′ spin system. From the simulation (see Fig. 2), four ^{31}P–^{31}P coupling constants of 301.6 ($J_{P1,P3} = J_{P2,P4}$), -37.0 ($J_{P1,P4} = J_{P2,P3}$), -23.6 and -23.3 Hz have been determined, of which the last two represent either a P1,P2 or a P3,P4 coupling. These values are in good agreement with data reported by Baker and Field for the six-coordinate ruthenium(II) complex *trans*-[RuCl$_2$(PMe$_2$Ph)$_2$(κ^2-Ph$_2$PCH$_2$PPh$_2$)] [13]. The minor, centro-symmetrical isomer **5b** shows two doublets of doublets with ^{31}P–^{31}P coupling constants of 30.3 and 28.6 Hz, respectively. The IR spectrum of **5a**/**5b**, in which two OCO stretching frequencies at 1583 and 1389 cm^{-1} appear, supports the assumption that the two acetate ligands are linked in a monodentate fashion to the metal center.

Treatment of the bis(η^3-2-methylallyl)ruthenium(II) compound **6**, containing the symmetrical chelating ligand iPr$_2$PCH$_2$PiPr$_2$, with CF_3CO_2H in the presence of an equimolar amount of bis(diisopropylphosphino)methane, leads to the formation of the octahedral complex **7**. An alternative preparative pathway to compound **7**, which is structurally related to the isomeric bis(acetato) derivatives **5a**/**5b**, consists in the reaction of **1** with two equivalents of both CF_3CO_2H and iPr$_2$PCH$_2$PiPr$_2$ (Scheme 3). In either way, the isolated yield of **7** is about 80%. The ^{31}P-NMR spectrum of **7** displays one singlet resonance at δ -2.3, while the IR spectrum shows two bands at 1683 and 1456 cm^{-1} for the symmetrical and antisymmetrical ν(OCO) stretching frequencies.

The result of the X-ray crystal structure analysis of **7** is illustrated in Fig. 3. The coordination sphere around the metal center corresponds to a perfect octahedron with P–Ru–P and O–Ru–O bond angles of 180°. The trifluoroacetate ligands are *trans* disposed, the planes



Scheme 3.

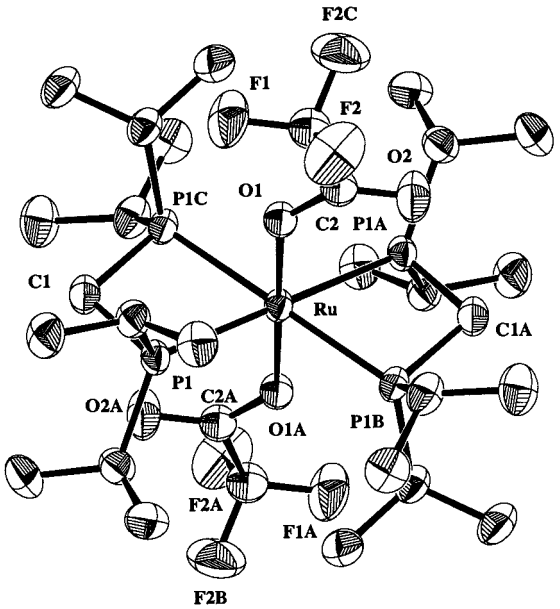


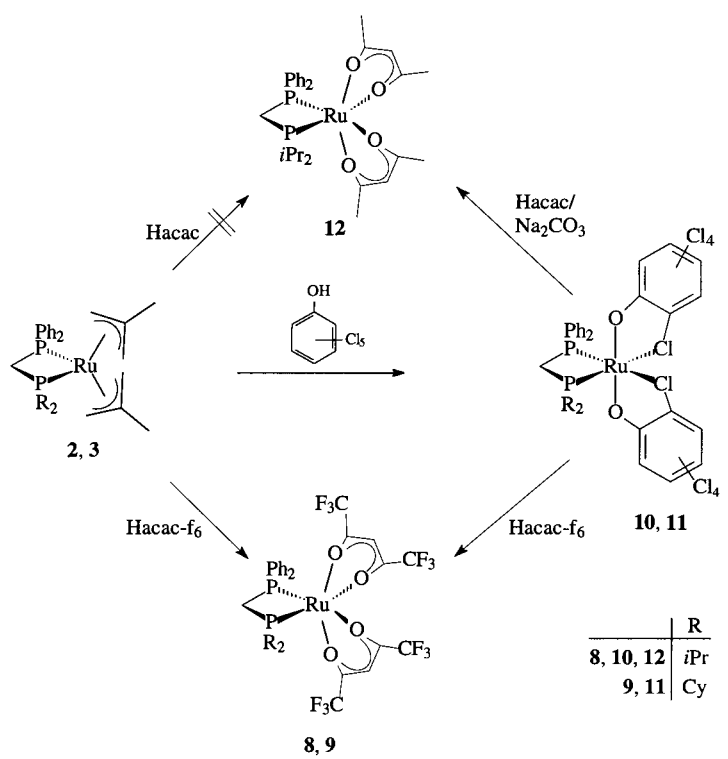
Fig. 3. Molecular structure (ORTEP diagram) of compound **7**. Selected bond lengths (Å) and bond angles (°): Ru–P1 2.3938(8), Ru–O1 2.121(3), O1–C2 1.260(6), O2–C2 1.213(6); P1–Ru–P1C 71.14(4), P1–Ru–P1B 108.86(4), P1–Ru–P1A 180.0, O1–Ru–O1A 180.0.

containing the atoms O1,C2,O2 and O1A,C2A,O2A are perpendicular to the basal plane with the metal and the phosphorus atoms. The four Ru–P distances of 2.3938(8) Å are similar to those in $[Ru(\eta^1\text{-}O_2CCF_3)_2(BIPHOS)_2]$ [14] and in the cationic complex $[Ru(\eta^2\text{-}O_2CCH_3)(\kappa^2\text{-}Ph_2PCH_2PPh_2)_2]^+$ [10c] where instead of $PiPr_2$ two less bulky PPh_2 groups are present.

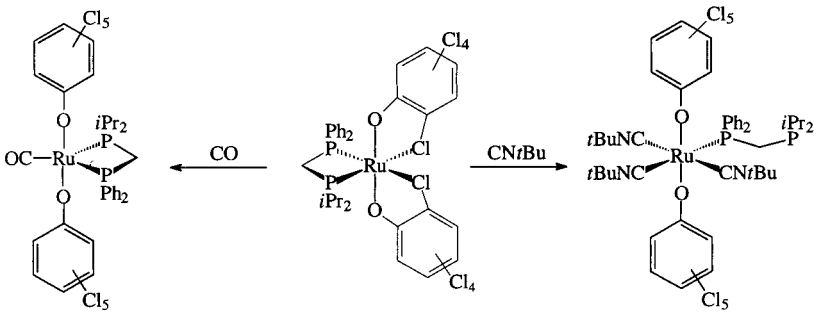
The 2-methylallyl ligands in compounds **2** and **3** can also be substituted by the anion of hexafluoroacetylacetone. Treatment of **2** or **3** with Hacac-f_6 in benzene or toluene yields the chelate complexes **8** and **9** (Scheme 4) as red air-stable solids in almost quantitative yield. Due to the coordination of the unsymmetrical bis(phosphino)methane, the two acac-f_6 units are non-equivalent and therefore both the ^{13}C- and ^{19}F-NMR spectra of **8** and **9** display four resonances for the carbon and fluor nuclei of the CF_3 groups in the rather narrow ranges of δ 118.4 to 117.1 (^{13}C) and -75.7 to -74.4 (^{19}F), respectively.

In contrast to Hacac-f_6, the non-fluorinated counterpart Hacac does not react, even in refluxing toluene, with either **2** or **3**. We assume that the lower acidity of acetylacetone ($pK_s = 9.0$) compared to the hexafluoro analogue ($pK_s = 5.3$) [15] explains the difference in the reactivity of the two diketones toward the bis(η^3-2-methylallyl)ruthenium(II) complexes.

However, the wanted bis(acac) derivative **12** can be prepared indirectly via the bis(pentachlorophenolato)metal compound **10** as an intermediate. Both **10** and **11** are obtained upon treatment of **2** or **3** with C_6Cl_5OH in toluene at room temperature as yellow solids in 98 and 95% yield. With regard to the spectroscopic data of **10** and **11**, the interesting feature is that in the ^{13}C-NMR spectra at 300 K instead of ten only



Scheme 4.



Scheme 5.

six signals for the ^{13}C nuclei of the C–Cl moieties appear. The most reasonable explanation for this observation is that under these conditions the two complexes exhibit a fluxional behavior which involves (on the NMR time scale) a rapid coordination–decoordination of the *ortho*-chlorine atoms of the six-membered rings to the metal center and thus leads to an equivalence of the carbons atoms in *ortho* and *meta* positions of each of the two OC_6Cl_5 units. The ^{13}C-NMR spectrum of **10** displays at 188 K, apart from the two signals for the *ipso*-C atoms, the expected ten resonances for the *ortho*, *meta* and *para* carbon atoms of the C_6Cl_5 rings, indicating that at this temperature a rigid structure for the molecule can be assumed. It seems that the stability of the chelating bonding mode (via oxygen and chlorine) of pentachlorophenolate ligands to ruthenium depends considerably on the coordination sphere since the hydrido compound $[RuH(\eta^2\text{-}OC_6Cl_5)(CO)(PiPr_3)_2]$ is non-fluxional on the NMR time scale at room temperature [16] while the complex $[Ru(\eta^2\text{-}OC_6Cl_5)_2(\kappa^2\text{-}iPr_2PCH_2CH_2PPh_2)]$ reveals a dynamic behavior resulting in an equivalence of the *ortho*-disposed C–Cl units even at 188 K [17].

Due to the lability of the $Ru\text{–}OC_6Cl_5$ linkages, compound **10** does not only react quite smoothly with Hacac-f_6 to give **8** but also, in the presence of Na_2CO_3, with acetylacetone to afford the bis(acac) complex **12** (see Scheme 4). The isolated yield of **12** was 96%. Without Na_2CO_3, no reaction occurs. The bidentate coordination mode of the acac ligands in **12** is indicated by the appearance of two strong IR bands at 1575 and 1512 cm^{-1}, that is in a very similar position as in various other $M(\eta^2\text{-acac})$ derivatives [18].

A partial cleavage of the $Ru(\eta^2\text{-}OC_6Cl_5)$ chelates takes place upon treatment of **10** with carbon monoxide and *tert*-butylisocyanide (Scheme 5). Passing a stream of CO through a solution of **10** in benzene leads to a change of color from orange–red to yellow and after removal of the solvent affords the slightly air-sensitive complex **13** in 85% isolated yield. Since the IR spectrum of **13** displays only one intense ν(CO) band at 1971 cm^{-1} and the ^{13}C-NMR spectrum only one resonance in the typical region for M–CO carbon atoms, there is no doubt that a monocarbonyl compound is obtained. The ^{31}P-NMR spectrum of **13** shows at room temperature two broad signals at δ 28.5 and 6.5, which upon cooling to 245 K split into two sharp doublets at δ 28.5 and 13.9 and two rather broad doublets at δ 43.2 and 9.2, respectively. Further lowering of the temperature to 217 K results in a sharpening of the latter two signals which now appear as sharp doublets with a $^{31}P\text{–}^{31}P$ coupling constant of 68.7 Hz. At 325 K, the ^{31}P-NMR spectrum of **13** is quite simple and shows two doublets at δ 35.4 and 11.6 with $J(PP) = 71.3$ Hz. We assume that the strong temperature-dependence of the ^{31}P-NMR spectrum of **13** is due to a dynamic process which at room temperature and above involves a fast cleavage and reformation of one Ru–Cl bond. Under these conditions, there is probably an equilibrium between the five-coordinate species, depicted in Scheme 5, and two six-coordinate isomers (with one η^1- and one $\eta^2\text{-}OC_6Cl_5$ units), in one of which the CO ligand is *trans* to the $PiPr_2$ and in the other *trans* to the PPh_2 moiety. At 217 K, this process is extremely slow (on the NMR time scale) and thus the two frozen isomers can be observed. A similar situation exists in the case of the corresponding monocarbonylruthenium(II) complex $[RuCl_2(CO)(\kappa\text{-}P\text{-}iPr_2PCH_2CO_2Me)(\kappa^2\text{-}P,O\text{-}iPr_2PCH_2CO_2Me)]$ where at elevated temperatures an exchange between the monodentate and the bidentate phosphinocarboxylate ligands occurs [1g].

In contrast to CO, the starting material **10** reacts with CN*t*Bu to give the tris(isocyanide)ruthenium(II) compound **14** in 87% yield. The unexpected addition of three isocyanide ligands to the metal center is not only supported by the elemental analysis but even more by the appearance of two signals for the $CNCCH_3$ protons in the ^1H-NMR spectrum at δ 1.21 and 1.01 in the relative ratio of 2:1 (or 18:9, respectively). The ^{13}C-NMR spectrum of **14** leaves no doubt that the two OC_6Cl_5 units are identical. Although on the basis of the spectroscopic data it can not conclusively be decided

whether the P*i*Pr$_2$ or the PPh$_2$ fragment of the bis(phosphino)methane ligand is linked to ruthenium, the smooth reaction of **14** with oxygen indicates that the more bulky P*i*Pr$_2$ moiety is not involved in coordination. After leaving the solution of **14** (in C_6D_6) in air, in the ^{31}P-NMR spectrum instead of the signal at δ 3.6 (J(PP) = 69.1 Hz) a new doublet resonance at δ 40.9 (J(PP) = 11.1 Hz) is observed which we tentatively assign to a P(O)*i*Pr$_2$ unit. It should be mentioned that both the ^{1}H- and ^{13}C-NMR spectra of **14** are not temperature-dependent which means that in solution no dynamic process takes place.

For comparison, we have not only studied the reactivity of the bis(η^3-allyl) complex **1** but also that of the chain-like octadienediyl compound **15** toward *i*Pr$_2$PCH$_2$PPh$_2$. In the presence of $AgBF_4$, a clean reaction occurs which, after separation of AgCl and evaporation of the solvent, affords the ionic complex **16** (Scheme 6) in 82% yield. Apart from the elemental analysis, the conductivity measurement confirms that a 1:1 electrolyte has been formed. The ^{31}P-NMR spectrum of **16** displays two doublet resonances at δ −14.2 and −20.0 with a ^{31}P–^{31}P coupling of 48.3 Hz.

The reaction of **15** with the sterically demanding arsino(phosphino)methane *i*Pr$_2$PCH$_2$As*t*Bu$_2$ results in the cleavage of the chlorine bridges and the formation of the mononuclear complex **17**. The ^{31}P-NMR spectrum of the orange, practically air-stable species displays a singlet at δ 25.0, the position of which indicates that the P*i*Pr$_2$ unit is coordinated to ruthenium. Attempts to generate a cationic complex, structurally related to **16**, by treatment of **17** with $NaBPh_4$ failed.

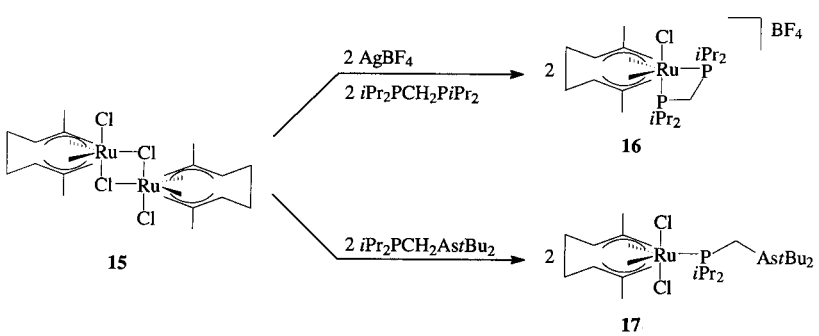
In summary, we have shown that the new unsymmetrical bis(phosphino)methanes R$_2$PCH$_2$PPh$_2$, containing two bulky substituents such as cyclohexyl or isopropyl at one of the donor centers, prefer to coordinate to ruthenium(II) in a chelating fashion. The anionic ligands which complete the coordination sphere could be either η^3-allyl, carboxylates, fluorinated or unfluorinated acetylacetonates, and — quite remarkably — also pentachlorophenolate. The symmetrical bis(phosphino)methane derivative *i*Pr$_2$PCH$_2$P*i*Pr$_2$ even forms a chelate bond with the [RuCl(η^3:η^3-$C_{10}H_{16}$)]$^+$ fragment thus generating a cationic ruthenium(IV) complex with the coordination number seven at the metal center.

3. Experimental

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1** [19], **6** [6], **15** [20] as well as the ligands *i*Pr$_2$PCH$_2$P*i*Pr$_2$, R$_2$PCH$_2$PPh$_2$ (R = *i*Pr, Cy) [2] and *i*Pr$_2$PCH$_2$As*t*Bu$_2$ [2] were prepared according to published methods. IR: Perkin–Elmer 1320. NMR: Bruker AC 200 and AMX 400. Mass spectra: Finnigan 90 MAT and 8200 MAT. Melting and decomposition points were determined by DTA.

3.1. Preparation of [Ru(η^3-2-MeC$_3$H$_4$)$_2$(κ^2-*i*Pr$_2$PCH$_2$PPh$_2$)] (2)

A suspension of 228 mg (0.71 mmol) of **1** in 10 ml of hexane was treated with a solution of 226 mg (0.71 mmol) of *i*Pr$_2$PCH$_2$PPh$_2$ in 10 ml of hexane and heated under reflux for 12 h. After cooling to r.t., the solvent was evaporated in vacuo, the remaining yellow solid was washed with 10 ml of pentane and dried. Yield 281 mg (75%), m.p. 147°C. Anal. Found: C, 61.02; H, 7.70. Calc. for $C_{27}H_{40}P_2Ru$: C, 61.46; H, 7.64%. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.90 (m, 2H, C_6H_5), 7.40, 7.22 (both m, 3H each, C_6H_5), 7.01 (m, 2H, C_6H_5), 4.15 (m, 1H, one H of P^{1}CH$_2$P^2), 3.83 [ddd, J(P^{1}H) = 14.8, J(P^{2}H) = 9.6, J(HH) = 7.6 Hz, 1H, one H of P^{1}CH$_2$P^2), 2.60 (m, 2H, C_3H_4), 2.29, 2.02 (both m, 1H each, PC*H*CH$_3$), 1.92, 1.79 (both s, 3H each, C_3H_4C*H*$_3$), 1.70 (d, J(PH) = 12.4 Hz, 1H, one H of C_3H_4), 1.58 (dd, J(P^{1}H) = 13.8, J(P^{2}H) = 5.0 Hz, 1H, one H of C_3H_4), 1.42 (dd, J(PH) = 15.2, J(HH) = 7.6 Hz, 3H, PCHC*H*$_3$), 1.32 (dd, J(PH) = 13.2, J(HH) = 7.2 Hz, 3H, PCHC*H*$_3$), 1.08 (dd, J(PH) = J(HH) = 2.4 Hz, 1H, one H of C_3H_4), 1.02 (m, 1H, one H of C_3H_4), 1.00 (dd, J(PH) = 10.8, J(HH) = 7.2 Hz, 3H, PCHC*H*$_3$), 0.86



Scheme 6.

(dd, J(PH) = 13.4, J(HH) = 7.6 Hz, 3H, PCHCH_3), 0.53 (dd, $J(P^1H)$ = 15.2, $J(P^2H)$ = 4.8 Hz, 1H, one H of C_3H_4), 0.48 (d, J(PH) = 14.4 Hz, 1H, one H of C_3H_4). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): δ 140.8 (dd, $J(P^1C)$ = 30.0, $J(P^2C)$ = 3.5 Hz, *ipso*-C of C_6H_5), 135.3 (dd, $J(P^1C)$ = 14.1, $J(P^2C)$ = 11.1 Hz, *ipso*-C of C_6H_5), 133.6 (d, J(PC) = 14.1, *ortho*-C of C_6H_5), 131.2 (d, J(PC) = 8.0 Hz, *ortho*-C of C_6H_5), 129.4 (d, J(PC) = 2.0 Hz, *para*-C of C_6H_5), 128.2 (d, J(PC) = 7.1 Hz, *meta*-C of C_6H_5), 128.1 (d, J(PC) = 2.0 Hz, *para*-C of C_6H_5), 128.0 (d, J(PC) = 9.0 Hz, *meta*-C of C_6H_5), 95.5, 94.9 (both s, CCH$_3$ of C_4H_7), 41.8, 41.6 (both d, J(PC) = 15.3 Hz, CH_2 of C_4H_7), 38.8, 38.6 (both d, J(PC) = 3.8 Hz, CH_2 of C_4H_7), 35.5 (dd, $J(P^1C)$ = 16.1, $J(P^2C)$ = 3.3 Hz, $P^1CH_2P^2$), 32.4 (d, J(PC) = 18.2 Hz, PCHCH$_3$), 27.3 (d, J(PC) = 7.5 Hz, PCHCH$_3$), 25.8, 25.6 (both s, CCH$_3$ of C_4H_7), 20.4 (d, J(PC) = 5.6 Hz, PCHCH$_3$), 20.0 (s, PCHCH$_3$), 19.7 (d, J(PC) = 2.1 Hz, PCHCH$_3$), 19.4 (d, J(PC) = 2.9 Hz, PCHCH$_3$). ^{31}P-NMR (162.0 MHz, CD_2Cl_2): δ 14.4 (d, J(PP) = 31.7 Hz, PiPr$_2$), 12.7 (d, J(PP) = 31.7 Hz, PPh_2).

3.2. Preparation of [Ru(η^3-2-MeC_3H_4)$_2$(κ^2-$Cy_2PCH_2PPh_2$)] (3)

This was carried out analogously as described for **2**, using 112 mg (0.35 mmol) of **1** and 128 mg (0.35 mmol) of $Cy_2PCH_2PPh_2$ as starting materials; time for reflux was 4 h. Yellow solid; yield 174 mg (82%), m.p. 101°C. Anal. Found: C, 65.43; H, 7.56. Calc. for $C_{33}H_{48}P_2Ru$: C, 65.22; H, 7.96%. ^{1}H-NMR (400 MHz, C_6D_6): δ 8.08 (m, 2H, C_6H_5), 7.27–6.94 (m, 8H, C_6H_5), 4.04, 3.66 (both m, 1H each, $P^1CH_2P^2$), 3.22, 3.01, 2.54 (all br m, 1H each, CH_2 of C_3H_4), 2.35, 2.19 (both s, 3H each, $C_3H_4CH_3$), 2.19–0.90 (m, 27H, CH_2 of C_3H_4 and C_6H_{11}). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 135.6 (dd, $J(P^1C)$ = 14.2, $J(P^2C)$ = 9.1 Hz, *ipso*-C of C_6H_5), 133.8 (d, J(PC) = 14.2 Hz, *ortho*-C of C_6H_5), 131.2 (d, J(PC) = 8.1 Hz, *ortho*-C of C_6H_5), 129.3 (d, J(PC) = 2.0 Hz, *para*-C of C_6H_5), 128.3 (d, J(PC) = 7.6 Hz, *meta*-C of C_6H_5), 128.0 (d, J(PC) = 1.7 Hz, *para*-C of C_6H_5), 127.9 (d, J(PC) = 9.5 Hz, *meta*-C of C_6H_5), 95.7, 95.6 (both s, CCH$_3$ of C_4H_7), 44.0 (dd, $J(P^1C)$ = 10.2, $J(P^2C)$ = 6.1 Hz, CH of C_6H_{11}), 40.0 (dd, $J(P^1C)$ = 17.5, $J(P^2C)$ = 14.2 Hz, $P^1CH_2P^2$), 39.1 (d, J(PC) = 3.0 Hz, CH_2 of C_4H_7), 38.9 (d, J(PC) = 4.1 Hz, CH_2 of C_4H_7), 38.2 (d, J(PC) = 5.1 Hz, CH of C_6H_{11}), 36.2, 36.0 (both d, J(PC) = 4.1 Hz, CH_2 of C_4H_7), 30.7 (s, CH_2 of C_6H_{11}), 30.6 (d, J(PC) = 4.1 Hz, CH_2 of C_6H_{11}), 30.2 (s, CH_2 of C_6H_{11}), 29.5 (d, J(PC) = 3.1 Hz, CH_2 of C_6H_{11}), 28.2 (d, J(PC) = 12.2 Hz, CH_2 of C_6H_{11}), 27.8 (d, J(PC) = 9.2 Hz, CH_2 of C_6H_{11}), 27.6 (d, J(PC) = 7.1 Hz, CH_2 of C_6H_{11}), 27.3 (d, J(PC) = 10.2 Hz, CH_2 of C_6H_{11}), 26.8, 26.5 (both s, CH_2 of C_6H_{11}), 26.8, 26.1 (both s, CCH$_3$ of C_4H_7). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 14.7 (d, J(PP) = 30.5 Hz, Cy_2P), 6.0 (d, J(PP) = 30.5 Hz, Ph_2P).

3.3. Preparation of [Ru(η^2-O_2CPh)$_2$(κ^2-$iPr_2PCH_2PPh_2$)] (4)

A solution of 83 mg (0.16 mmol) of **2** in 10 ml of ether was treated at −78°C with a solution of 39 mg (0.32 mmol) of benzoic acid in 5 ml of ether. After warming to r.t., the solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 5 ml of pentane and dried. Yield 62 mg (60%). IR (C_6H_6): $\nu(OCO_{asym})$ 1493, $\nu(OCO_{sym})$ 1415 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ 8.39–6.81 (m, 20H, C_6H_5), 4.30, 3.78 (both m, 1H each, $P^1CH_2P^2$), 2.28 (m, 2H, PCHCH$_3$), 1.44 (dd, J(PH) = 15.7, J(HH) = 7.2 Hz, 3H, PCHCH_3), 1.23 (dd, J(PH) = 15.8, J(HH) = 7.0 Hz, 3H, PCHCH_3), 1.19 (dd, J(PH) = 14.7, J(HH) = 7.0 Hz, 3H, PCHCH_3), 1.11 (dd, J(PH) = 13.4, J(HH) = 7.2 Hz, 3H, PCHCH_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 180.6, 178.0 (both s, OCO), 137.2 (d, J(PC) = 2.8 Hz, C_6H_5), 136.7 (d, J(PC) = 4.6 Hz, C_6H_5), 136.4 (d, J(PC) = 3.8 Hz, C_6H_5), 136.1 (s, C_6H_5), 135.7 (d, J(PC) = 36.2 Hz, *ipso*-C of C_6H_5), 133.5, 132.1 (both d, J(PC) = 10.5 Hz, C_6H_5), 130.4 (s, C_6H_5), 130.0 (d, J(PC) = 6.7 Hz, C_6H_5), 129.9 (d, J(PC) = 9.5 Hz, C_6H_5), 129.4, 128.9, (both s, C_6H_5), 128.7 (d, J(PC) = 10.5 Hz, C_6H_5), 128.2 (d, J(PC) = 23.8 Hz, *ipso*-C of C_6H_5), 127.8 (d, J(PC) = 13.4 Hz, C_6H_5), 42.7 (dd, $J(P^1C)$ = 21.0, $J(P^2C)$ = 14.3 Hz, $P^1CH_2P^2$), 26.4 (d, J(PC) = 19.0 Hz, PCHCH$_3$), 24.9 (s, PCHCH$_3$), 20.1, 19.7 (both s, PCHCH$_3$), 19.2, 18.1 (both d, J(PC) = 2.7 Hz, PCHCH$_3$). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 36.3 (d, J(PP) = 89.1 Hz, PiPr$_2$), 20.8 (d, J(PP) = 89.1 Hz, PPh_2).

3.4. Preparation of [Ru(η^1-O_2CCH_3)$_2$(κ^2-$iPr_2PCH_2PPh_2$)$_2$] (5a,b)

A solution of 148 mg (0.28 mmol) of **2** and 89 mg (0.28 mmol) of $iPr_2PCH_2PPh_2$ in 5 ml of ether was treated at −78°C with 32 μl (0.56 mmol) of acetic acid. After warming to r.t., the solution was stirred for 10 min which led to a change of color from yellow to orange. The solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 5 ml of pentane and dried. Yield 172 mg (72%), m.p. 152°C. Anal. Found: C, 58.77; H, 7.24. Calc. for $C_{42}H_{58}O_4P_4Ru$: C, 59.22; H, 6.86%. IR (CH_2Cl_2): $\nu(OCO_{asym})$ 1583, $\nu(OCO_{sym})$ 1389 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.20–7.00 (m, 20H, C_6H_5), 4.99 (m, 4H, $P^1CH_2P^2$), 2.70 (m, 4H, PCHCH$_3$), 1.36–1.10 (m, 24H, PCHCH_3). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): δ 179.2, 178.5 (both s, OC(O)CH$_3$), 137.0, 132.5, 128.2 (all br m, C_6H_5), 46.0 (br m, $P^1CH_2P^2$), 26.3 (d, J(PC) = 7.8 Hz, PCHCH$_3$), 24.7 (s, OC(O)CH$_3$), 19.5–18.4 (br m, PCHCH$_3$). ^{31}P-NMR (162.0 MHz, CD_2Cl_2): δ 6.0 (dd, J(PP) = 30.3, J(PP′) = 28.6 Hz, PiPr$_2$), 1.9–4.5 (br m), −5.3 (dd, J(PP) = 30.3 Hz, J(PP′) = 28.6 Hz, PPh_2).

3.5. Preparation of $[Ru(\eta^1\text{-}O_2CCF_3)_2(\kappa^2\text{-}iPr_2PCH_2PiPr_2)_2]$ (7)

(a) A solution of 102 mg (0.35 mmol) of **1** and 174 mg (0.70 mmol) of $iPr_2PCH_2PiPr_2$ in 6 ml of ether was treated with 54 μl (0.70 mmol) of CF_3CO_2H at r.t. After the solution was heated under reflux for 6 h, it was cooled to r.t. and the solvent was evaporated in vacuo. The remaining yellow microcrystalline solid was washed with 3 ml of pentane and dried; yield 224 mg (78%).

(b) A solution of 138 mg (0.30 mmol) of **6** and 75 mg (0.30 mmol) of $iPr_2PCH_2PiPr_2$ in 5 ml of ether was treated at −78°C with 48 μl (0.60 mmol) of CF_3CO_2H. After the solution was warmed to r.t., it was stirred for 10 min and then worked up as described for a); yield 203 mg (82%), m.p. 145°C. Anal. Found: C, 43.41; H, 7.02. Calc. for $C_{30}H_{60}F_6O_4P_4Ru$: C, 43.74; H, 7.34%. IR (CH_2Cl_2): $\nu(OCO_{asym})$ 1683, $\nu(OCO_{sym})$ 1456 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 4.43 (m, 4H, PCH_2P), 2.34 (s, 8H, $PCHCH_3$), 1.39–1.15 (m, 48H, $PCHCH_3$). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): δ 164.9 (br m, CO_2), 113.5 (q, J(FC) = 292.7 Hz, CF_3), 40.5 (m, PCH_2P), 27.4 (d, J(PC) = 4.4 Hz, $PCHCH_3$), 19.7, 18.3 (both s, $PCHCH_3$).^{19}F-NMR (376.5 MHz, CD_2Cl_2): δ −75.5 (s). ^{31}P-NMR (162.0 MHz, CD_2Cl_2): δ −2.3 (s).

3.6. Preparation of $[Ru(\eta^2\text{-}acac\text{-}f_6)_2(\kappa^2\text{-}iPr_2PCH_2PPh_2)]$ (8)

(a) A solution of 132 mg (0.25 mmol) of **2** in 8 ml of benzene was treated dropwise with 71 μl (0.50 mmol) of hexafluoroacetylacetone, which led to a rapid change of color from yellow to dark red. After stirring for 20 min, the solvent was evaporated in vacuo and the residue was dissolved in 5 ml of pentane. The solution was filtered and the filtrate was brought to dryness in vacuo to give a dark red solid; yield 201 mg (97%).

(b) A solution of 125 mg (0.13 mmol) of **10** in 5 ml of toluene was treated with 37 μl (0.26 mmol) of hexafluoroacetylacetone. After stirring for 5 min at r.t., the solution was worked up as described for a). Yield 99 mg (92%), m.p. 91°C. Anal. Found: C, 42.34; H, 3.24. Calc. for $C_{29}H_{28}F_{12}O_4P_2Ru$: C, 41.89; H, 3.39%. IR (CH_2Cl_2): ν(acac-f_6) 1733, 1608 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 7.74 (m, 2H, C_6H_5), 7.02 (m, 8H, C_6H_5), 6.45, 6.06 (both s, 1H each, CH of acac-f_6), 3.82–3.49 (br m, 2H, $P^1CH_2P^2$), 2.22, 1.64 (both br m, 1H each, $PCHCH_3$), 1.17 (dd, J(PH) = 16.4, J(HH) = 7.3 Hz, 3H, $PCHCH_3$), 0.99 (dd, J(PH) = 14.6, J(HH) = 7.3 Hz, 3H, $PCHCH_3$), 0.64 (dd, J(PH) = 15.8, J(HH) = 6.9 Hz, 3H, $PCHCH_3$), 0.54 (dd, J(PH) = 16.1, J(HH) = 6.9 Hz, 3H, $PCHCH_3$). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 175.5, 174.8, 172.7, 172.6 (all q, J(FC) = 34 Hz, CO of acac-f_6), 133.9 (d, J(PC) = 3.7 Hz, C_6H_5), 133.0 (d, J(PC) = 11.1 Hz, C_6H_5), 131.6 (d, J(PC) = 40.7 Hz, *ipso*-C of C_6H_5), 131.1 (d, J(PC) = 1.9 Hz, C_6H_5), 130.5 (d, J(PC) = 11.1 Hz, C_6H_5), 130.1, 128.8 (both d, J(PC) = 2.8 Hz, C_6H_5), 128.6 (d, J(PC) = 3.7 Hz, C_6H_5), 118.4, 118.2 (both q, J(FC) = 284.8 Hz, CF_3), 117.2, 117.1 (both q, J(FC) = 283.8 Hz, CF_3), 91.5, 90.8 (both s, CH of acac-f_6), 42.2 (dd, $J(P^1C)$ = 23.1, $J(P^2C)$ = 17.6 Hz, $P^1CH_2P^2$), 25.4 (dd, $J(P^1C)$ = 17.1, $J(P^2C)$ = 3.7 Hz, $PCHCH_3$), 24.1 (d, J(PC) = 19.4 Hz, $PCHCH_3$), 18.6 (d, J(PC) = 2.7 Hz, $PCHCH_3$), 18.3 (d, J(PC) = 1.9 Hz, $PCHCH_3$), 18.0 (s, $PCHCH_3$), 17.5 (d, J(PC) = 1.8 Hz, $PCHCH_3$). ^{19}F-NMR (188.3 MHz, C_6D_6): δ −75.7, −75.5, −74.7, −74.6, (all s). ^{31}P-NMR (81.0 MHz, C_6D_6): δ 34.5 (d, J(PP) = 80.1 Hz, $PiPr_2$), 15.2 (d, J(PP) = 80.1 Hz, PPh_2).

3.7. Preparation of $[Ru(\eta^2\text{-}acac\text{-}f_6)_2(\kappa^2\text{-}Cy_2PCH_2PPh_2)]$ (9)

A solution of 259 mg (0.43 mmol) of **3** in 5 ml of toluene was treated dropwise at −78°C with 122 μl (0.87 mmol) of hexafluoroacetylacetone. A rapid change of color from yellow to dark red occurred. After the reaction mixture was warmed to r.t., it was stirred for 10 min, and than the solvent was evaporated in vacuo. The residue was dissolved in 2 ml of ether and the solution was chromatographed on Al_2O_3 (basic, activity grade I, height of column 12 cm). With 1:1 ether–pentane a dark red fraction was eluted which after removal of the solvent gave a dark red solid. Yield 327 mg (97%), m.p. 142°C. Anal. Found: C, 52.34; H 4.48. Calc. for $C_{35}H_{36}F_{12}O_4P_2Ru$: C, 52.70; H, 4.55%. IR (CH_2Cl_2): ν(acac-f_6) 1623, 1501 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.65 (m, 2H, C_6H_5), 7.42–7.06 (br m, 8H, C_6H_5), 6.07, 5.71 (both s, 1H each, CH of acac-f_6), 4.18–3.95 (br m, 2H, $P^1CH_2P^2$), 2.09–0.85 (br m, 22H, C_6H_{11}). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 174.8, 174.2, 171.9, 171.8 (all q, J(FC) = 34 Hz, CO of acac-f_6), 133.2 (dd, $J(P^1C)$ = 38.1, $J(P^2C)$ = 13.5 Hz, *ipso*-C of C_6H_5), 132.8 (d, J(PC) = 11.2 Hz, *ortho*-C of C_6H_5), 131.6 (d, J(PC) = 38.7 Hz, *ipso*-C of C_6H_5), 130.6 (d, J(PC) = 3.0 Hz, *para*-C of C_6H_5), 130.4 (d, J(PC) = 11.2 Hz, *ortho*-C of C_6H_5), 129.8 (d, J(PC) = 2.0 Hz, *para*-C of C_6H_5), 128.5, 128.4 (both d, J(PC) = 10.2 Hz, *meta*-C of C_6H_5), 117.7, 117.6, 117.5, 117.4 (all q, J(FC) = 284.5 Hz, CF_3), 90.9, 90.3 (both s, CH of acac-f_6), 40.3 (dd, $J(P^1C)$ = 22.9, $J(P^2C)$ = 17.8 Hz, $P^1CH_2P^2$), 35.6 (dd, $J(P^1C)$ = 16.8, $J(P^2C)$ = 2.5 Hz, CH of C_6H_{11}), 35.1 (d, J(PC) = 17.3 Hz, CH of C_6H_{11}), 28.8, 28.5, 28.4, 27.2, 26.0, 25.6 (all s, CH_2 of C_6H_{11}), 28.3, 27.4, 26.8, 26.7 (all d, J(PC) = 3.1 Hz, CH_2 of C_6H_{11}), ^{19}F-NMR (376.5 MHz, $CDCl_3$): δ −75.7, −75.5, −74.6, −74.4, (all s). ^{31}P-NMR (162.0 MHz, $CDCl_3$): δ 25.2 (d, J(PP) = 76.3 Hz, Cy_2P), 15.9 (d, J(PP) = 76.3 Hz, Ph_2P).

3.8. Preparation of $[Ru(\eta^2\text{-}OC_6Cl_5)_2(\kappa^2\text{-}iPr_2PCH_2PPh_2)]$ (**10**)

A solution of 112 mg (0.21 mmol) of **2** and 112 mg (0.42 mmol) of pentachlorophenol in 10 ml of toluene was stirred for 30 min at r.t. The solvent was evaporated in vacuo, the residue was washed with 10 ml of ethanol and 10 ml of pentane (0°C) and dried. Yellow solid; yield 195 mg (98%), m.p. 224°C. Anal. Found: C, 39.58; H, 2.77. Calc. for $C_{31}H_{26}Cl_{10}O_2P_2Ru$: C, 39.27; H, 2.76%. ^{1}H-NMR (400 MHz, CD_2Cl_2, 188 K): δ 8.12 (m, 2H, C_6H_5), 7.46 (m, 3H, C_6H_5), 7.19–6.91 (m, 5H, C_6H_5), 4.16, 3.36 (both m, 1H each, $P^1CH_2P^2$), 2.74, 2.24 (both m, 1H each, PC*H*CH_3), 1.41, 0.68 (both br m, 6H each, PCHC*H*$_3$). ^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ 8.22 (m, 2H, C_6H_5), 7.28 (m, 3H, C_6H_5), 7.10 (m, 2H, C_6H_5), 6.85 (m, 3H, C_6H_5), 3.85, 3.53 (both m, 1H each, $P^1CH_2P^2$), 2.64, 1.78 (both m, 1H each, PC*H*CH_3), 1.43 (dd, J(PH) = 16.8, J(HH) = 7.3 Hz, 3H, PCHC*H*$_3$), 1.19 (dd, J(PH) = 15.1, J(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), 0.64 (dd, J(PH) = 11.7, J(HH) = 6.9 Hz, 3H, PCHC*H*$_3$), 0.60 (dd, J(PH) = 12.0, J(HH) = 7.5 Hz, 3H, PCHC*H*$_3$). ^{13}C-NMR (100.6 MHz, CD_2Cl_2, 188 K): δ 161.9, 161.3 (both s, *ipso*-C of C_6Cl_5), 137.2, 131.0 (both s, C_6H_5), 134.4 (br d, J(PC) = 12.3 Hz, C_6H_5), 130.4 (d, J(PC) = 8.5 Hz, C_6H_5), 129.9, 128.8, 128.1 (all s, C_6H_5), 129.5 (d, J(PC) = 12.3 Hz, C_6H_5), 127.5, 127.3, 126.7, 124.4, 123.8, 123.5, 117.0, 116.5, 113.5, 113.2 (all s, C_6Cl_5), 44.4 (m, $P^1CH_2P^2$), 26.6 (d, J(PC) = 20.0 Hz, P*C*HCH$_3$), 25.1 (d, J(PC) = 19.1 Hz, P*C*HCH$_3$), 18.5, 17.3, 16.9, 16.5 (all s, PCH*C*H$_3$). ^{13}C-NMR (100.6 MHz, C_6D_6, 300 K): δ 163.8, 163.0 (both s, *ipso*-C of C_6Cl_5), 134.4 (d, J(PC) = 11.4 Hz, *ortho*-C of C_6H_5), 132.5 (d, J(PC) = 48.0 Hz, *ipso*-C of C_6H_5), 131.7 (d, J(PC) = 53.0 Hz, *ipso*-C of C_6H_5), 131.5 (d, J(PC) = 2.9 Hz, *para*-C of C_6H_5), 130.8 (d, J(PC) = 10.5 Hz, *ortho*-C of C_6H_5), 129.6 (d, J(PC) = 2.9 Hz, *para*-C of C_6H_5), 128.6 (d, J(PC) = 11.4 Hz, *meta*-C of C_6H_5), 128.0 (d, J(PC) = 10.5 Hz, *meta*-C of C_6H_5), 125.6, 125.4, 118.4, 118.0, 116.4, 115.9 (all s, C_6Cl_5), 43.3 (dd, J(PC) = 22.9, J(PC) = 19.1 Hz, $P^1CH_2P^2$), 27.2, 25.1 (both d, J(PC) = 20.0 Hz, P*C*HCH$_3$), 19.5, 18.1, 17.9, 17.8 (all s, PCH*C*H$_3$). ^{31}P-NMR (162.0 MHz, C_6D_6, 300 K): δ 37.2 (d, J(PP) = 98.5 Hz, P*i*Pr$_2$), 15.4 (d, J(PP) = 98.5 Hz, PPh$_2$).

3.9. Preparation of $[Ru(\eta^2\text{-}OC_6Cl_5)_2(\kappa^2\text{-}Cy_2PCH_2PPh_2)]$ (**11**)

This was carried out analogously as described for **10**, using 135 mg (0.22 mmol) of **3** and 112 mg (0.44 mmol) of pentachlorophenol as starting material. Yellow solid; yield 195 mg (95%), m.p. 216°C. Anal. Found: C, 43.02; H, 2.93. Calc. for $C_{37}H_{34}Cl_{10}O_2P_2Ru$: C, 43.22; H, 3.33%. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.76–6.66 (br m, 10H, C_6H_5), 3.25–0.43 (br m, 24H, $P^1CH_2P^2$ and C_6H_{11}). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 162.8, 162.6 (both s, *ipso*-C of C_6Cl_5), 134.2 (dd, $J(P^1C) = 12.2$, $J(P^2C) = 7.0$ Hz, *ipso*-C of C_6H_5), 133.9 (d, J(PC) = 14.2 Hz, C_6H_5), 131.4 (d, J(PC) = 8.0 Hz, C_6H_5), 129.9, 128.1 (both d, J(PC) = 1.9 Hz, C_6H_5), 128.6 (d, J(PC) = 7.3 Hz, C_6H_5), 127.6 (d, J(PC) = 7.5 Hz, C_6H_5), 125.7, 125.4, 118.6, 118.0, 116.9, 116.2 (all s, C_6Cl_5), 43.9 (dd, $J(P^1C) = 12.2$, $J(P^2C) = 6.0$ Hz, CH of C_6H_{11}), 40.2 (dd, $J(P^1C) = 17.8$, $J(P^2C) = 14.4$ Hz, $P^1CH_2P^2$), 38.1 (d, J(PC) = 6.1 Hz, CH of C_6H_{11}), 30.8, 30.2 (both s, CH_2 of C_6H_{11}), 30.5 (d, J(PC) = 4.3 Hz, CH_2 of C_6H_{11}), 29.8 (d, J(PC) = 4.1 Hz, CH_2 of C_6H_{11}), 29.2 (d, J(PC) = 10.0 Hz, CH_2 of C_6H_{11}), 27.9 (d, J(PC) = 9.3 Hz, CH_2 of C_6H_{11}), 27.2 (d, J(PC) = 6.9 Hz, CH_2 of C_6H_{11}), 27.0 (d, J(PC) = 10.6 Hz, CH_2 of C_6H_{11}), 26.7, 26.4 (both s, CH_2 of C_6H_{11}). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 25.8 (d, J(PP) = 79.4 Hz, Cy_2P), 15.4 (d, J(PP) = 79.4 Hz, Ph_2P).

3.10. Preparation of $[Ru(\eta^2\text{-}acac)_2(\kappa^2\text{-}iPr_2PCH_2PPh_2)]$ (**12**)

A solution of 227 mg (0.24 mmol) of **10** in 10 ml of toluene was treated with 48 mg (0.48 mmol) of acetylacetone and 69 mg (0.65 mmol) of Na_2CO_3 and then heated for 1 h at 65°C. After cooling to r.t., the solvent was evaporated in vacuo. The residue was dissolved in 5 ml of pentane, the solution was filtered and the filtrate was brought to dryness in vacuo. Yellow solid; yield 139 mg (96%), m.p. 152°C. Anal. Found: C, 56.02; H, 6.86. Calc. for $C_{29}H_{40}O_4P_2Ru$: C, 56.58; H, 6.55%. IR (CH_2Cl_2): ν(acac) 1575, 1512 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.85 (m, 2H, C_6H_5), 7.28 (m, 8H, C_6H_5), 5.29, 4.98 (both s, 1H each, CH of acac), 4.14–3.78 (m, 2H, $P^1CH_2P^2$), 2.42–1.91 (m, 2H, PC*H*CH_3), 1.90, 1.89, 1.82, 1.45 (all s, 3H each, CH_3 of acac), 1.24 (dd, J(PH) = 10.6, J(HH) = 7.7 Hz, 3H, PCHC*H*$_3$), 1.22 (dd, J(PH) = 13.0, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$), 0.99 (dd, J(PH) = 14.4, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$), 0.84 (dd, J(PH) = 14.8, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$). ^{31}P-NMR (81.0 MHz, $CDCl_3$): δ 34.9 (d, J(PP) = 78.8 Hz, P*i*Pr$_2$), 17.0 (d, J(PP) = 78.8 Hz, PPh$_2$).

3.11. Preparation of $[Ru(OC_6Cl_5)_2(CO)(\kappa^2\text{-}iPr_2PCH_2PPh_2)]$ (**13**)

A slow stream of CO was passed through a solution of 100 mg (0.11 mmol) of **10** in 5 ml of benzene at r.t. Stirring the solution for 1 h led to a change of color from orange–red to yellow. The solvent was evaporated in vacuo, the residue was washed with 5 ml of pentane and dried. Yellow solid; yield 91 mg (85%), m.p. 158°C. Anal. Found: C, 39.67; H, 2.89. Calc. for $C_{32}H_{26}Cl_{10}O_3P_2Ru$: C, 39.38; H, 2.68%. IR (CH_2Cl_2):

ν(CO) 1971 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6, 295 K): δ 7.85 (br s, 2H, C_6H_5), 7.65 (m, 2H, C_6H_5), 6.98 (m, 6H, C_6H_5), 3.69, 2.98 (both m, 1H each, $P^1CH_2P^2$), 2.55 (br s, 1H, PC*H*CH_3), 1.64 (m, 1H, PC*H*CH_3), 0.98 (m, 3H, PCHC*H*$_3$), 0.84 (dd, J(PH) = 17.6, J(HH) = 7.3 Hz, 3H, PCHC*H*$_3$), 0.79 (dd, J(PH) = 17.3, J(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), 0.70 (dd, J(PH) = 15.5, J(HH) = 6.7 Hz, 3H, PCHC*H*$_3$). ^{1}H-NMR (200 MHz, toluene-d_8, 325 K): δ 7.76, 7.62 (both m, 2H each, C_6H_5), 7.00 (m, 6H, C_6H_5), 3.80, 3.11 (both ddd, $J(P^1H)$ = 15.5, $J(P^2H)$ = 10.5, J(HH) = 10.0 Hz, 1H each, $P^1CH_2P^2$), 2.70, 1.79 (both m, 1H each, PC*H*CH_3), 1.08 (dd, J(PH) = 17.9, J(HH) = 7.3 Hz, 3H, PCHC*H*$_3$), 0.98 (dd, J(PH) = 16.5, J(HH) = 6.2 Hz, 3H, PCHC*H*$_3$), 0.90 (dd, J(PH) = 17.3, J(HH) = 6.2 Hz, 3H, PCHC*H*$_3$), 0.85 (dd, J(PH) = 12.2, J(HH) = 6.9 Hz, 3H, PCHC*H*$_3$). ^{13}C-NMR (100.6 MHz, C_6D_6, 295 K): δ 201.7 (dd, $J(P^1C)$ = 18.3, $J(P^2C)$ = 15.3 Hz, CO), 161.6, (s, *ipso*-C of C_6Cl_5), 132.7 (br d, J(PC) = 11.2 Hz, *ortho*-C of C_6H_5), 132.0 (d, J(PC) = 3.0 Hz, *para*-C of C_6H_5), 131.9 (d, J(PC) = 11.2 Hz, *ortho*-C of C_6H_5), 131.7 (d, J(PC) = 2.0 Hz, *para*-C of C_6H_5), 130.3 (br s, *ipso*-C of C_6H_5), 129.3, 128.8 (both d, J(PC) = 11.2 Hz, *meta*-C of C_6H_5), 128.1, 127.9, 117.1 (all s, C_6Cl_5), 41.3 (dd, $J(P^1C)$ = 28.5, $J(P^2C)$ = 20.3 Hz, $P^1CH_2P^2$), 28.2 (d, J(PC) = 4.1 Hz, P*C*HCH$_3$), 28.0 (d, J(PC) = 3.1 Hz, P*C*HCH$_3$), 25.4, 25.2 (both s, P*C*H*C*H$_3$), 19.3 (d, J(PC) = 4.1 Hz, PCH*C*H$_3$), 18.3 (s, PCH*C*H$_3$). ^{31}P-NMR (162.0 MHz, C_6D_6, 295 K): δ 28.5 (br s, P*i*Pr$_2$), 6.5 (br d, J(PP) = 69.5 Hz, PPh_2). ^{31}P-NMR (81.0 MHz, toluene-d_8, 325 K): δ 35.4 (d, J(PP) = 71.3 Hz, P*i*Pr$_2$), 11.6 (d, J(PP) = 71.3 Hz, PPh_2). ^{31}P-NMR (81.0 MHz, toluene-d_8, 245 K): δ 43.2 (br s, P*i*Pr$_2$), 28.4 (d, J(PP) = 77.5 Hz, P*i*Pr$_2$), 13.9 (d, J(PP) = 77.5 Hz, PPh_2), 9.2 (br s, PPh_2). ^{31}P-NMR (81.0 MHz, toluene-d_8, 217 K): δ 43.2 (d, J(PP) = 68.7 Hz, P*i*Pr$_2$), 28.4 (d, J(PP) = 75.0 Hz, P*i*Pr$_2$), 13.8 (d, J(PP) = 75.0 Hz, PPh_2), 9.5 (d, J(PP) = 68.7 Hz, PPh_2).

3.12. Preparation of *[Ru(OC$_6$Cl$_5$)$_2$(CNtBu)$_3$(κ^1-Ph$_2$PCH$_2$PiPr$_2$)]* (**14**)

A solution of 110 mg (0.12 mmol) of **10** in 5 ml of toluene was treated with an excess (ca. 0.50 mmol) of CN*t*Bu. After stirring for 1 h, the solvent was evaporated in vacuo, the residue was washed with 5 ml of pentane and dried. Yellow solid; yield 122 mg (87%), m.p. 135°C. Anal. Found: C, 46.14; H, 4.23; N, 3.55. Calc. for $C_{46}H_{53}Cl_{10}N_3O_3P_2Ru$: C, 45.53; H, 4.40, N, 3.46%. IR (CH_2Cl_2): ν(CN) 2161, 2136 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.75, 7.08 (both m, 4H each, C_6H_5), 6.99 (m, 2H, C_6H_5), 3.64 (dd, $J(P^1H)$ = 6.7, $J(P^2H)$ = 3.2 Hz, 2H, $P^1CH_2P^2$), 3.12 (m, 2H, PC*H*CH_3), 1.50 (dd, J(PH) = 14.1, J(HH) = 7.0 Hz, 12H, PCHC*H*$_3$), 1.21 (s, 18H, CNCC*H*$_3$), 1.01 (s, 9H, CNCC*H*$_3$). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 167.1 (d, J(PC) = 1.9 Hz, *ipso*-C of C_6Cl_5), 150.5 (d, J(PC) = 14.2 Hz, *C*NCCH$_3$), 140.9 (dd, $J(P^1C)$ = 17.1, $J(P^2C)$ = 3.8 Hz, *C*NCCH$_3$), 133.6, 133.4, 129.3, 129.0 (all s, C_6H_5), 130.4, 127.9 (both s, C_6Cl_5), 128.8 (d, J(PC) = 7.6 Hz, C_6H_5), 116.9 (s, OC_6Cl_5), 56.6 (s, CN*C*CH$_3$), 30.2, 30.1 (both s, CNC*C*H$_3$), 24.8 (dd, $J(P^1C)$ = 19.6, $J(P^2C)$ = 6.2 Hz, P*C*HCH$_3$), 19.7 (dd, $J(P^1C)$ = 35.3, $J(P^2C)$ = 11.4 Hz, $P^1CH_2P^2$), 18.0 (d, J(PC) = 1.9 Hz, PCH*C*H$_3$), 17.9 (d, J(PC) = 6.6 Hz, PCH*C*H$_3$). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 3.6 (d, J(PP) = 69.1 Hz, P*i*Pr$_2$), −19.6 (d, J(PP) = 69.1 Hz, PPh_2).

3.13. Preparation of *[RuCl(η^3:η^3-C$_{10}$H$_{16}$)(κ^2-iPr$_2$PCH$_2$PiPr$_2$)]BF$_4$* (**16**)

A suspension of 100 mg (0.16 mmol) of **15** in 10 ml of acetone was treated with a solution of 63 mg (0.32 mmol) of $AgBF_4$ in 3 ml of acetone and stirred for 20 min at r.t. The reaction mixture was filtered and to the filtrate 79.5 mg (0.32 mmol) of *i*Pr$_2$PCH$_2$P*i*Pr$_2$ was added. After stirring the solution for 20 min, the solvent was evaporated in vacuo, the residue was washed with 2 ml of pentane and dried. Orange solid; yield 160 mg (82%), m.p. 178°C (dec.). Conductivity: Λ 75.4 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 44.97; H, 7.34. Calc. for $C_{23}H_{46}BClF_4P_2Ru$: C, 45.44; H, 7.63%. ^{1}H-NMR (200 MHz, CD_2Cl_2): δ 4.59, 4.45 (both m, 1H each, H_1 and H_9), 3.92 (d, J(PH) = 3.7 Hz, 1H, H_2 or H_{10}), 3.66 (m, 2H, H_3 and H_8), 3.32 (m, 1H, H_2 or H_{10}), 3.17–2.63 (m, 6H, PC*H*CH$_3$ and PCH$_2$P), 2.56–2.43 (m, 4H, H_{4-7}), 2.11 (s, 6H, CH_3 of $C_{10}H_{16}$), 1.80–1.02 (m, 24H, PCHC*H*$_3$). ^{13}C-NMR (50.3 MHz, CD_2Cl_2): δ 108.4 (s, C_2 and C_7), 86.1 (s, C_3 and C_6), 66.1, 63.0 (both s, C_1 and C_8), 38.4, 29.5 (both s, C_4 and C_5), 35.5 (d, J(PC) = 16.6 Hz, P*C*HCH$_3$), 34.3 (dd, J(PC) = 15.7 and 4.6 Hz, P*C*HCH$_3$), 32.1 (t, J(PC) = 24.0 Hz, PCH$_2$P), 30.8 (s, PCH*C*H$_3$), 28.8 (dd, J(PC) = 13.9 and 6.5 Hz, P*C*HCH$_3$), 27.7 (d, J(PC) = 12.0 Hz, P*C*HCH$_3$), 21.7, 21.6, 21.3, 20.8, 20.3, 20.1, 19.9, 19.8, 19.6, 19.4, 18.8, 18.7 (PCH*C*H$_3$ and CH_3 of $C_{10}H_{16}$). ^{31}P-NMR (81.0 MHz, CD_2Cl_2): δ −14.2, −20.0 (both d, J(PP) = 48.3 Hz). For assignment of protons and carbon atoms see Fig. 4.

3.14. Preparation of *[RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)(κ-P-iPr$_2$PCH$_2$AstBu$_2$)]* (**17**)

A solution of 154 mg (0.25 mmol) of **15** in 10 ml of CH_2Cl_2 was treated at −78°C with a solution of 164 mg (0.51 mmol) of *i*Pr$_2$PCH$_2$As*t*Bu$_2$ in 5 ml of CH_2Cl_2. After stirring for 10 min, the solution was warmed to r.t. and then the solvent was evaporated. The residue was washed with 5 ml of pentane and dried. Pale red solid; yield 304 mg (97%), m.p. 92°C. Anal. Found: C,

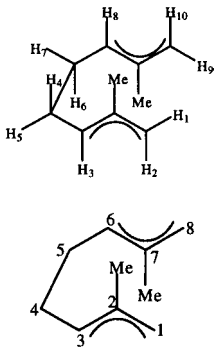


Fig. 4. Assignment of protons and carbon atoms of the octadienediyl ligand of compounds **16** and **17**.

47.53; H, 7.67. Calc. for $C_{25}H_{50}AsCl_2PRu$: C, 47.77; H, 8.02%. ^{1}H-NMR (400 MHz, C_6D_6): δ 5.30 (m, 2H, H_1 and H_9), 4.77 (d, $J(PH) = 7.6$ Hz, 2H, H_3 and H_8), 3.59 (d, $J(PH) = 2.8$ Hz, 2H, H_2 and H_{10}), 3.12 (m, 2H, H_5 and H_7), 2.67 (m, 2H, PC*H*CH_3), 2.56, 2.29 (both dd, $J(PH) = 14.5$, $J(HH) = 6.8$ Hz, 1H each, PCH_2As), 2.20 (s, 6H, CH_3 of $C_{10}H_{16}$), 2.13 (m, 2H, H_4 and H_6), 1.64 (dd, $J(PH) = 14.4$, $J(HH) = 7.2$ Hz, 3H, PCHC*H*$_3$), 1.53 (dd, $J(PH) = 11.6$, $J(HH) = 6.8$ Hz, 3H, PCHC*H*$_3$), 1.52 (dd, $J(PH) = 14.2$, $J(HH) = 7.2$ Hz, 3H, PCHC*H*$_3$), 1.41 (dd, $J(PH) = 14.2$, $J(HH) = 7.2$ Hz, 3H, PCHC*H*$_3$), 1.18, 1.17 (both s, 9H each, AsCC*H*$_3$). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 124.2 (s, C_2 and C_7), 108.3 (s, C_3 and C_6), 62.9 (d, $J(PC) = 5.0$ Hz, C_1 and C_8), 36.4 (s, C_4 and C_5), 36.3 (d, $J(PC) = 3.0$ Hz, As*C*CH$_3$), 34.4 (d, $J(PC) = 1.7$ Hz, As*C*CH$_3$), 30.6 (d, $J(PC) = 18.7$ Hz, P*C*HCH$_3$), 30.4, 30.2 (both s, AsC*C*H$_3$), 29.3 (d, $J(PC) = 20.6$ Hz, P*C*HCH$_3$), 21.0 (s, CH_3 of $C_{10}H_{16}$), 19.9 (d, $J(PC) = 7.2$ Hz, PCH*C*H$_3$), 19.5, 19.0, 18.4 (all s, PCH*C*H$_3$), 12.7 (d, $J(PC) = 13.1$ Hz, PCH_2As). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 25.0 (s). For assignment of protons and carbon atoms see Fig. 4.

3.15. Crystal structure analysis of **2**

Single crystals were grown from ether. Crystal data (from 25 reflections with $7 < \theta < 25°$): triclinic, space group $P\bar{1}$ (no. 2), $a = 8.861(7)$, $b = 9.796(9)$, $c = 15.12(1)$ Å, $\alpha = 80.47(6)$, $\beta = 81.81(6)$, $\gamma = 85.58(6)°$, $V = 1279(2)$ Å^3; $Z = 2$, $D_{calc} = 1.370$ g cm^{-3}, $\mu = 0.741$ mm^{-1}. Crystal size $0.2 \times 0.2 \times 0.1$ mm. Enraf–Nonius CAD4 diffractometer, Mo–K_α radiation (0.71073 Å), graphite monochromator, $T = 293(2)$ K, ω–θ scan, max. $2\theta = 50°$; 5534 reflections scanned, 5163 reflections independent, 5163 included in dataset; intensity data corrected for Lorentz and polarization effects, empirical absorption correction applied (Ψ-scans, minimum transmission 91.91%). The structure was solved by direct methods (SHELXS-86); atomic coordinates were refined by full-matrix least-squares against F_o^2 (307 parameters, SHELXL-93). The positions of H1a, H1b, H2a, H2b, H4a, H4b, H6a, H6b, H8a and H8b were found in a final difference Fourier synthesis and were refined isotropically with fixed distance (C–H 0.93 Å). The positions of all other hydrogen atoms were calculated according to ideal geometry. $R_1 = 0.0397$, $wR_2 = 0.0920$ for 4497 observed reflections [$I > 2\sigma(I)$], $R_1 = 0.0479$, $wR_2 = 0.0986$ for all 5163 data reflections; reflex to parameter ratio 16.8; residual electron density $+0.816/-1.067$ e Å^{-3}.

3.16. Crystal structure analysis of **7**

Single crystals were grown from toluene. Crystal data (from 5000 reflections with $2° < \theta < 26°$): monoclinic, space group $I2/m$ (no. 12), $a = 10.441(2)$, $b = 14.452(3)$, $c = 16.380(3)$ Å, $\beta = 108.27(2)°$, $V = 2347.1(7)$ Å^3; $Z = 2$, $D_{calc} = 1.296$ g cm^{-3}, $\mu = 0.522$ mm^{-1}. Crystal size $0.2 \times 0.2 \times 0.2$ mm^3. Stoe IPDS diffractometer, Mo–K_α radiation (0.71073 Å), graphite monochromator, $T = 173(2)$ K, Φ-scan, max. $2\theta = 52°$; 15 607 reflections scanned, 2397 reflections independent, 2396 included in the dataset; intensity data corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86); atomic coordinates were refined by full-matrix least-squares against F_o^2 (129 parameters, SHELXL-93). The asymmetric unit contains only one-fourth of **7** with the ruthenium atom on the centre of symmetry. The complete molecule is generated by applying the symmetry operations #1: $-x, -y, -z$; #2: $-x, y, -z$ and #3: $x, -y, z$. The positions of the hydrogen atoms were calculated according to ideal geometry. The asymmetric unit contains one-fourth of a solvent molecule (toluene) which was refined isotropically with restraints. The highest peak of the final Fourier synthesis is located near to this solvent molecule. $R_1 = 0.0448$, $wR_2 = 0.1190$ for 1872 observed reflections [$I > 2\sigma(I)$], $R_1 = 0.0607$, $wR_2 = 0.1273$ for all 2396 data reflections; reflex to parameter ratio 18.6; residual electron density $+1.108/-0.974$ e Å^{-3}.

4. Supplementary material

Detailed crystallographic data (excluding structure factors) for the structure of **2** and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 141732 (**2**) and 141733 (**7**). Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@chemcrys.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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