Synthesis, Reactivity and Catalytic Activity of [RuH-(η^1-OCMe$_2$)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$*

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The solvento complex [RuH(η^1-OCMe$_2$)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$ **2**, which is an active catalyst for the exclusive hydrogenation of phenylacetylene to styrene and the hydrosilylation of the same alkyne to *cis*-PhCH=CH(SiEt$_3$), was prepared by reaction of [Ru(H)Cl(OC)$_2$(Pr$^i_3$P)$_2$] **1** with AgBF$_4$ in acetone as solvent. The reactivity of **2** has been investigated. This compound reacts with Lewis bases (L) to give [RuH(CO)$_2$L(PPr$^i_3$)$_2$]BF$_4$ [L = H$_2$O **3**, MeCN **4**, CO **5** or pyrazole (Hpz) **6**]. Complex **5** can be deprotonated by KOH to afford [Ru(OC)$_3$(Pr$^i_3$P)$_2$] **7**, while the reaction of **6** with [{Rh(μ-OMe)(diolefin)}$_2$] [diolefin = tetrafluorobenzobarrelene (tfbb) or cycloocta-1,5-diene, (cod)] led to heterobinuclear compounds of formula [(OC)$_2$(Pr$^i_3$P)$_2$Ru(μ-H)(μ-pz)Rh(diolefin)]BF$_4$ (diolefin = tfbb **10** or cod **11**). The molecular structure of **11** was determined by an X-ray investigation. Compound **11** crystallises in the orthorhombic space group *Fdd*2, with cell dimensions *a* = 28.290(2), *b* = 22.572(1), *c* = 23.126(1) Å and *Z* = 16. The structure was refined to *R* and *R'* values of 0.0232 and 0.0258 for 6297 observed reflections. The cation in **11** can be described as a ruthenium–rhodium heterobinuclear species where the metals are connected through a bidentate pyrazolate group and a bridging hydrido ligand. The metal–metal distance is 3.1323(3) Å. Complex **2** reacts with HCl to give [RuCl$_2$(CO)$_2$(PPr$^i_3$)$_2$] **12**, which can be also prepared by reaction of [RuCl(η^1-OCMe$_2$)(CO)$_2$-(PPr$^i_3$)$_2$]BF$_4$ **13** with NaCl. This compound in the presence of Lewis bases affords [RuCl(CO)$_2$L-(PPr$^i_3$)$_2$]BF$_4$ (L = H$_2$O **14**, MeCN **15**, CO **16** or Hpz **17**). The reactions of **17** with [{Rh(μ-OMe)(diolefin)}$_2$] lead to [(OC)$_2$(Pr$^i_3$P)$_2$Ru(μ-Cl)(μ-pz)Rh(diolefin)]BF$_4$ (diolefin = tfbb **18** or cod **19**). Carbon disulfide, SCNR (R = Me or Ph) and HC≡CCO$_2$Me, undergo insertion reactions into the Ru–H bond of **2** to give the corresponding insertion products, [Ru(η^2-S$_2$CH)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$ **20**, [Ru{η^2-SN(R)CH}(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$ (R = Me **21** or Ph **22**) and [Ru{C[C(O)OMe]=CH$_2$}(CO)$_2$-(PPr$^i_3$)$_2$]BF$_4$ **23**.

Eight years ago, the synthesis of the five-co-ordinate ruthenium(II) complex [Ru(H)Cl(CO)(PPr$^i_3$)$_2$] was reported.[1] At room temperature, it adds Lewis bases (L) that are not bulky [*e.g.* CO and P(OMe)$_3$] to form octahedral compounds of formula [Ru(H)Cl(CO)L(PPr$^i_3$)$_2$].[1] Upon reaction with NaBH$_4$, Na(acac) (Hacac = acetylacetone) and Na(O$_2$CMe) the six-co-ordinate complexes [RuH(η^2-H$_2$BH$_2$)(CO)-(PPr$^i_3$)$_2$],[2] [RuH(η^2-acac)(CO)(PPr$^i_3$)$_2$][1] and [RuH(η^2-O$_2$C-Me)(CO)(PPr$^i_3$)$_2$][1] are formed. Alkynes such as phenylacetylene and acetylene undergo insertion into the Ru–H bond to afford [Ru{(*E*)-CH=CHR}Cl(CO)(PPr$^i_3$)$_2$].[3]

In the presence of KOH or NaBH$_4$, the complex [Ru(H)Cl(CO)(PPr$^i_3$)$_2$] catalyses hydrogen-transfer reactions from propan-2-ol to cyclohexanone, acetophenone,[4] benzylideneacetophenone[5] and phenylacetylene.[6] Whereas in the presence of Et$_3$SiH, phenylacetylene is selectively transformed into *cis*-PhCH=CH(SiEt$_3$).[7]

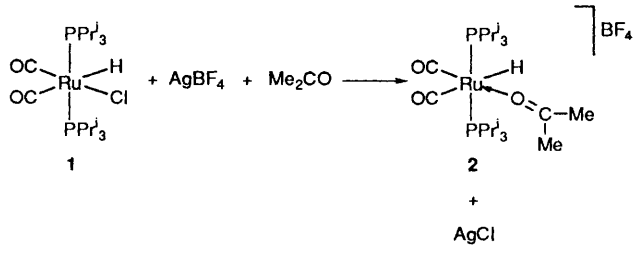
We have now found that the *cis*-dicarbonyl compound [Ru(H)Cl(CO)$_2$(PPr$^i_3$)$_2$] reacts with AgBF$_4$ in acetone to give [RuH(η^1-OCMe$_2$)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$, which is a selective catalyst for the hydrogenation of phenylacetylene to styrene and for the hydrosilylation of phenylacetylene with triethylsilane.

Transition-metal solvento complexes are of great interest because the facile dissociation of the labile solvent molecules can create the vacant co-ordination sites which are required for substrate binding, and its subsequent activation.[8–14] Although acetone complexes have been known for some time,[15–20] *cis*-hydrido acetone derivatives are rare,[21] and as far as we know, ruthenium complexes of this type have not been previously reported.

In this paper, we describe the synthesis, characterisation, reactivity and catalytic activity of the *cis*-hydrido(η^1-acetone) complex, [RuH(η^1-OCMe$_2$)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$. In addition, the X-ray diffraction structure of the heterobimetallic derivative [(OC)$_2$(Pr$^i_3$P)$_2$Ru(μ-H)(μ-pz)Rh(cod)]BF$_4$ (pz = pyrazolate, cod = cycloocta-1,5-diene) is reported.

Results and Discussion

Synthesis and Characterisation of [RuH(η^1-OCMe$_2$)-(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$.—Acetone solutions of complex [Ru(H)Cl-(CO)$_2$(PPr$^i_3$)$_2$] **1** react with AgBF$_4$ to give silver chloride and the solvento complex [RuH(η^1-OCMe$_2$)(CO)$_2$(PPr$^i_3$)$_2$]BF$_4$ **2** according to Scheme 1.



Scheme 1

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Complex **2** was isolated by addition of diethyl ether as a colourless microcrystalline solid in 82% yield, and was fully characterised by elemental analysis, IR and ^1H, ^{31}P-$\{^1H\}$ and ^{13}C-$\{^1H\}$ NMR spectroscopy. Consistently with the mutually *cis* disposition of the two carbonyl ligands, the IR spectrum of **2** shows two ν(CO) bands at 1978 and 1931 cm^{-1} together with the ν(Ru–H) absorption at 2031 cm^{-1}. Furthermore, the spectrum contains the absorption due to BF_4^- with T_d symmetry, and the band corresponding to the carbonyl group of the acetone ligand at 1667 cm^{-1}. This value, which is typical for the η^1-co-ordination mode of the acetone molecule,[22] agrees well with that observed in the IR spectrum of the complex $[Ru\{C(=CHPh)OC(O)Me\}(\eta^1\text{-}OCMe_2)(CO)(PPr^i_3)_2]BF_4$ (1680 cm^{-1}), where a weak Ru–O bond has been observed in the X-ray diffraction analysis [Ru–O 2.205(6) Å].[23] In accordance with the existence of a feeble interaction, both **2** and $[Ru\{C(=CHPh)OC(O)Me\}(\eta^1\text{-}OCMe_2)(CO)(PPr^i_3)_2]BF_4$ dissociate the acetone molecule in solution. The formation of the five-co-ordinate derivative $[RuH(CO)_2(PPr^i_3)_2]BF_4$ and acetone is supported by the IR spectrum in dichloromethane and the ^{13}C-$\{^1H\}$ NMR spectrum in $CDCl_3$ of **2**. The band of the carbonyl group in the IR spectrum appears at 1715 cm^{-1} and the ^{13}C-$\{^1H\}$ NMR spectrum shows the resonance corresponding to the carbon atom of the carbonyl group at δ 207.4.

The most noticeable feature in the ^1H NMR spectrum of **2** in $CDCl_3$, in which the compound is stable, is the hydrido signal, which appears at δ −3.86 as a triplet with a P–H coupling constant of 18.3 Hz. The ^{31}P-$\{^1H\}$ NMR spectrum shows a singlet at δ 64.5.

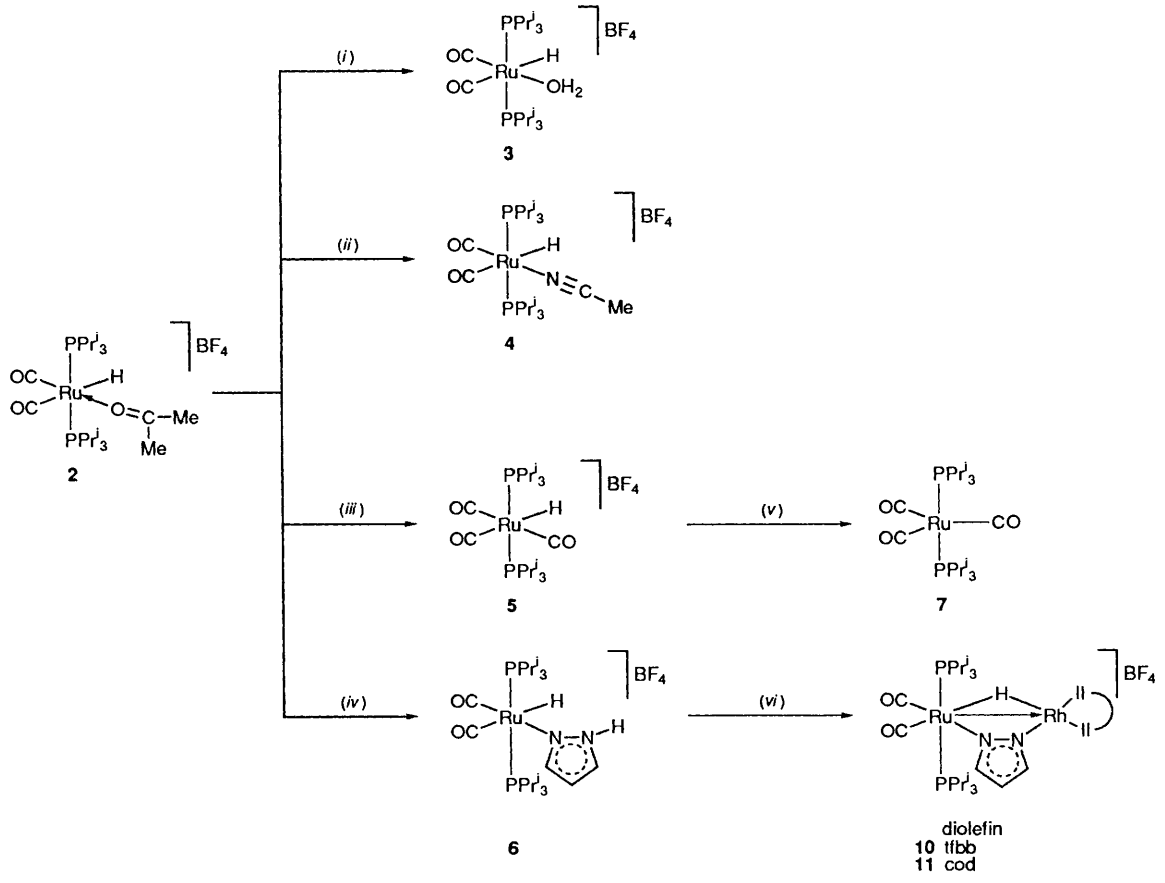
Ligand-substitution Reactions of Complex **2**.—The easy dissociation of the acetone molecule of **2** allows the synthesis of the cationic complexes **3**–**6** by reaction with water, acetonitrile, carbon monoxide and pyrazole (Scheme 2).

These compounds were characterised by elemental analysis, IR, ^1H and ^{31}P-$\{^1H\}$ NMR spectroscopy. In the IR spectrum of **3** in Nujol, the splitting of the asymmetric BF_4^- stretching band (1100–1000 cm^{-1}) suggests that this anion is involved in a network of hydrogen bonds with the co-ordinated water molecule. A similar situation has been established in the complex $[RuH(CO)_2(H_2O)(PPh_3)_2]BF_4$, by X-ray diffraction.[24] The IR spectra of **4**–**6**, in contrast to the IR spectrum of **3**, show the absorption due to the BF_4^- anion in T_d symmetry. Furthermore all of the spectra contain two bands in the terminal carbonyl region, in agreement with the mutually *cis* disposition of these ligands. For **5**, the presence of three carbonyl ligands in a *mer* disposition was inferred from its ^{13}C-$\{^1H\}$ NMR spectrum, which shows two carbonyl signals at δ 200.9 and 198.2 in a 1:2 ratio.

The most noticeable signals in the ^1H NMR spectra of **3**–**5** are the hydrido resonances which appear between δ −4.63 and −7.80 as triplets with P–H coupling constants of about 18 Hz. The ^{31}P-$\{^1H\}$ NMR spectra of these compounds show singlets between δ 59.8 and 61.4 indicating that the two phosphine ligands are equivalent and are mutually *trans* disposed.

The hydrido ligand of **5** has some protic character. Thus, it can be deprotonated by strong bases such as KOH, to give the tricarbonyl compound **7** which can be also prepared by reaction of $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(PPr^i_3)_2]$ with carbon monoxide.[25] The protic character of this hydrido could be related to the presence of three π-acid ligands (CO) co-ordinated to the metallic centre of **5**.

The NMR spectra of **6** show that there must be two isomers, or two conformers of this compound in solution. In the hydrido region of the ^1H NMR spectrum, both species are characterised



Scheme 2 (*i*) $+H_2O$, $-Me_2CO$; (*ii*) +MeCN, $-Me_2CO$; (*iii*) +CO, $-Me_2CO$; (*iv*) +Hpz, $-Me_2CO$; (*v*) KOH, $-H_2O$, $-KBF_4$; (*vi*) $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ (diolefin = tfbb **8** or cod **9**), −MeOH

by triplets at δ −5.06 (major) and −5.31 (minor) with P–H coupling constants of 19.5 and 18.9 Hz respectively. Furthermore, the spectrum contains eight pyrazole signals at δ 11.14 (NH), 8.05, 7.43 and 6.26 (major) and δ 11.90 (NH), 7.97, 7.34 and 6.20 (minor). The $^{31}P-\{^1H\}$ NMR spectrum shows a singlet for each compound at δ 57.6 (major) and 57.0 (minor), indicating that the phosphine ligands are equivalent.

Two isomers are possible for a $[RuH(CO)_2(Hpz)(PPr^i_3)_2]^+$ formulation with equivalent phosphines *cis* disposed to the hydrido ligand: *trans*-carbonyl (**a**) and *cis*-carbonyl (**b**). For isomer **b**, furthermore, the existence of two conformers may be ascribed to hindered rotations around the Ru–N axis (Fig. 1). It is known from previous studies[21c,26] that chemical shifts of the hydrido ligands *trans* to pyrazole ligand appear at higher fields than those mentioned above. So, we assume that the signals observed in the NMR spectra correspond to both conformers of the isomer **b**.

The pyrazole ligand in **6** contains an acidic NH group which is capable of reacting with the methoxy-bridged dimers $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ [diolefin = tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene) (tfbb) **8** or cycloocta-1,5-diene (cod) **9**] to give the heterobinuclear complexes **10** and **11** (Scheme 2). The presence of a bridging hydride ligand in these compounds is substantiated by the ^1H NMR spectra that show in the high-field region a doublet of triplets owing to Rh–H and P–H coupling. In agreement with the structure shown in Scheme 2, the ^1H NMR spectrum of **10** shows three resonances due to the tetrafluorobenzobarrelene diolefin; one aliphatic at δ 5.50 and two olefinic at δ 4.42 and 3.94. Similarly, the ^1H NMR spectrum of **11** contains five resonances due to the cycloocta-1,5-diene diolefin; two of them olefinic at δ 4.67 and 4.41 and three of them aliphatic at δ 2.30, 2.00 and 1.90.

As the rhodium centre in these heterobimetallic compounds is co-ordinatively unsaturated, a dative Ru→Rh bond could be proposed. Related osmium–rhodium[21b] and iridium–rhodium[27] complexes have been recently prepared in our laboratory. In order to ascertain the existence of this ruthenium–rhodium interaction, an X-ray diffraction experiment was carried out on a single crystal of **11**. A view of the molecular geometry of this complex is shown in Fig. 2. Selected bond distances and angles are listed in Table 1.

The molecule is binuclear and consists of a distorted square-planar co-ordination around rhodium and a distorted octahedron around ruthenium connected through a double bridge: a pyrazolate and a hydrido ligand [Rh–H–Ru 126(2)°]. The co-ordination sphere around the rhodium atom is defined by the hydride situated *cis* to a nitrogen atom of the pyrazolate group [N(2)–Rh–H 93(1)°], and the two olefinic bonds [C(6)–C(7) and C(10)–C(11)] of a cyclooctadiene molecule. An ideal plane of the octahedral co-ordination around the ruthenium atom is formed by the carbonylic carbons, C(1) and C(2), mutually *cis* disposed [C(1)–Ru–C(2) 94.8(2)°], the hydrido ligand and the nitrogen atom of the pyrazolate ligand [N(1)–Ru–H 89(1)°]. The triisopropylphosphine ligands occupy opposite positions, P(1)–Ru–P(2) 179.20(3)°.

The most remarkable features of the structure of **11** are, first, the ruthenium–rhodium separation and, secondly, the bond lengths in the Ru–H–Rh sequence. The intramolecular Ru–Rh distance, 3.1323(3) Å, lies close on the upper end of the range of distances [2.879(1)–3.0306(6) Å] observed for the closely related ruthenium–rhodium heterobimetallic compounds, $[(cod)Rh(\mu\text{-}H)(\mu\text{-}L)Ru(dppm)_nL'_{(2-n)}]$ [n = 2, L = Cl; n = 1, L = PR_2, L' = Ph; n = 1, L = $CH(PPh_2)_2$, L' = H; dppm = bis(diphenylphosphino)methane], where a hydrido-bridged metal–metal bond is proposed to exist.[28] The Rh–H bond has a length, 1.68(4) Å, in the range previously found for terminal Rh–H distances (*ca.* 1.62 Å),[29] and compares well with those values reported in the binuclear ruthenium–rhodium complexes referred to above [1.64–1.82(4) Å].[28] However the

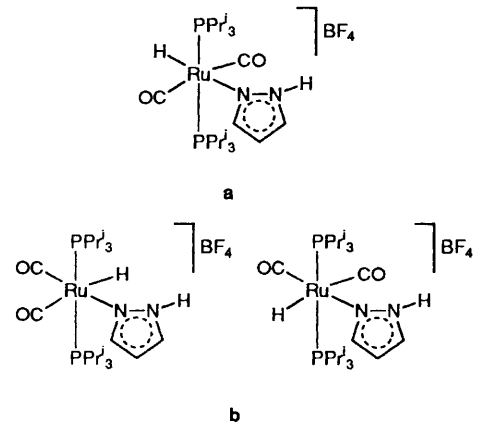


Fig. 1 Possible isomers/conformers for compound **6**

Table 1 Selected bond distances (Å) and angles (°) for the complex $[(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(cod)]BF_4$ **11**

Ru–Rh	3.1323(3)	Rh–C(6)	2.139(4)
Ru–P(1)	2.4666(9)	Rh–C(7)	2.163(4)
Ru–P(2)	2.4645(9)	Rh–C(10)	2.117(4)
Ru–C(1)	1.875(4)	Rh–C(11)	2.125(4)
Ru–C(2)	1.886(4)	Rh–N(2)	2.048(3)
Ru–N(1)	2.103(3)	Rh–H	1.68(4)
Ru–H	1.85(4)	C(6)–C(7)	1.380(6)
C(1)–O(1)	1.147(5)	C(10)–C(11)	1.386(6)
C(2)–O(2)	1.132(5)	N(1)–N(2)	1.356(4)
P(1)–Ru–P(2)	179.20(3)	C(1)–Ru–C(2)	94.8(2)
P(1)–Ru–N(1)	92.61(8)	C(1)–Ru–H	176(1)
P(1)–Ru–C(1)	85.1(1)	G(1)–Rh–G(2)*	86.9(2)
P(1)–Ru–C(2)	91.6(1)	G(1)–Rh–N(2)	176.2(1)
P(1)–Ru–H	91(1)	G(1)–Rh–H	88(1)
P(2)–Ru–N(1)	87.41(8)	G(2)–Rh–N(2)	91.9(2)
P(2)–Ru–C(1)	94.1(1)	G(2)–Rh–H	174(1)
P(2)–Ru–C(2)	88.5(1)	N(2)–Rh–H	93(1)
P(2)–Ru–H	90(1)	Ru–N(1)–N(2)	115.1(2)
N(1)–Ru–C(1)	91.0(2)	Ru–C(1)–O(1)	175.4(4)
N(1)–Ru–C(2)	173.1(1)	Ru–C(2)–O(2)	177.4(4)
N(1)–Ru–H	89(1)	Rh–N(2)–N(1)	115.4(2)
C(2)–Ru–H	85(1)	Ru–H–Rh	126(2)

* G(1) and G(2) represent the midpoints of the C(6)–C(7) and C(10)–C(11) olefinic bonds.

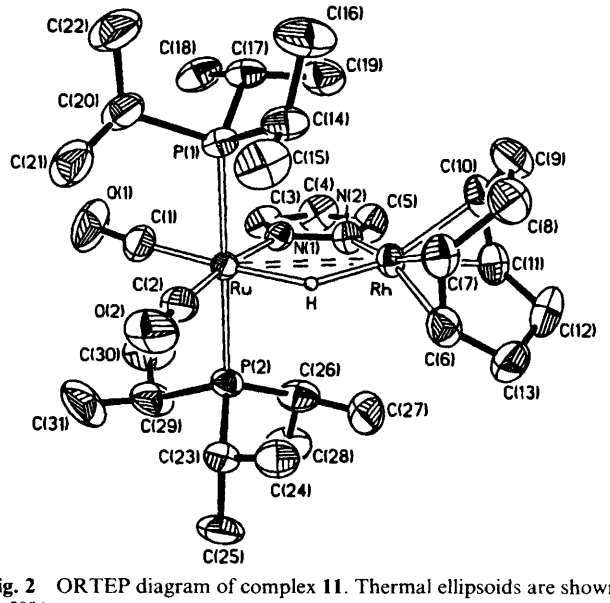


Fig. 2 ORTEP diagram of complex **11**. Thermal ellipsoids are shown at 50%

Ru–H separation is slightly longer, 1.85(4) Å, well over the distances reported for terminal Ru–H bonds, 1.62 Å,[30] and shorter than the distances described in agostic M–(C–H), 1.95(3)–2.10(3) Å.[31] The difference in Rh–H and Ru–H distances (0.17 Å), reflects some kind of asymmetry in the hydride bridge, but should be discussed with great care as the real accuracy of the determination could be lower than the precision obtained.

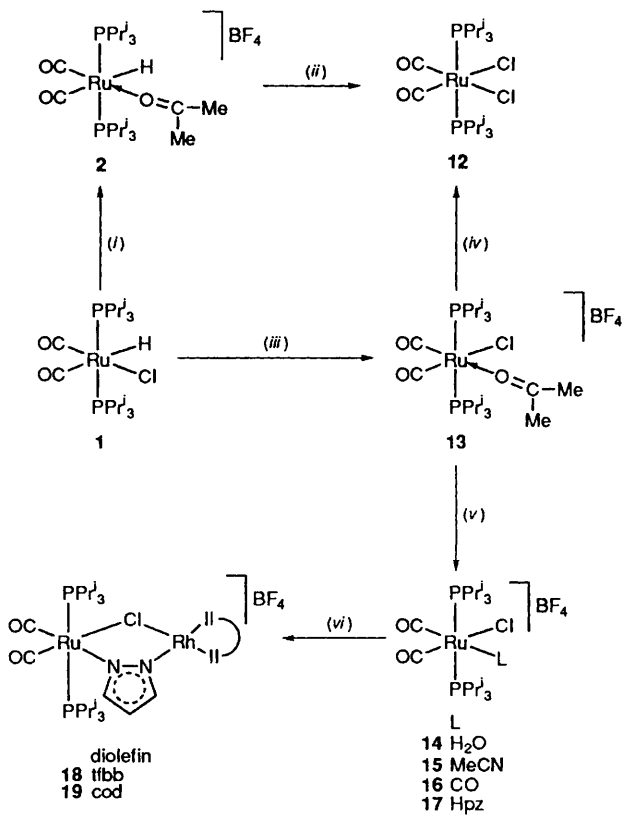
A similar situation to that found in **11**, in terms of Ru–H [1.60(5)–2.05(6) Å] and Ru–Ru [3.105(5)–3.166(1) Å] separations, has been previously observed in the complexes $[(cod)(Hpz)Ru(\mu\text{-}H)(\mu\text{-}pz)_2Ru(cod)L]^{n+}$ (L = H or Cl, n = 0; L = Hpz, n = 1) where, together with a semi-bridging hydrido ligand (when L = H),[32a] a bond sequence M–H–M has been described as a three-centre two-electron bond with some metal–metal interaction.[32] We believe that an analogous situation is present in our complex **11**, in such a way that the proposed Ru–Rh interaction could be responsible for the lack of fluxionality observed.

The metal–nitrogen bond distances involved in the pyrazolate bridge, Ru–N(1) 2.103(3) and Rh–N(2) 2.048(3) Å, compare well with the values previously found in other ruthenium–rhodium heterobinuclear complexes.[33] Both olefinic bond distances are essentially identical, 1.380(6) and 1.386(6) Å, and in agreement with the mean value observed in transition metal–olefin complexes [1.38(5) Å], and do not reflect the asymmetry of the rhodium co-ordination sphere. In that sense the Rh–C olefinic bond distances seem to be more sensitive to this fact showing shorter values for the carbon atoms *trans* to the hydride [mean 2.121(3) Å], than for those opposite to the pyrazolate group [mean 2.151(3) Å]. The Ru–P and the Ru–CO distances are also clearly in the range expected and require no further comment.

Reaction of Complex **2** *with* HCl: *Synthesis of Chloro-Solvento Complexes.*—We have mentioned previously that, in solution, complex **2** dissociates the acetone molecule to give the five-co-ordinate derivative $[RuH(CO)_2(PPr^i_3)_2]BF_4$. Five-co-ordinate hydrido–osmium(II) complexes containing two triisopropylphosphine ligands react with HX molecules (X = halide) to give dihydrogen derivatives.[34] The behaviour of the cation $[RuH(CO)_2(PPr^i_3)_2]^+$ toward HCl is out of keeping with the trend shown by these osmium compounds. Thus, treatment of a dichloromethane solution of **2** with a propan-2-ol solution of HCl in 1:1 molar ratio leads to the dichloro complex $[RuCl_2(CO)_2(PPr^i_3)_2]$ **12**, which was isolated as a white solid in 49% yield. When the reaction was carried out in a 1:2 molar ratio, the same compound was obtained with 79% yield. In agreement with the structure shown in Scheme 3, the IR spectrum of **12** in Nujol shows two ν(CO) bands in the terminal carbonyl region at 2015 and 1983 cm^{-1}, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a singlet at δ 38.5.

The formation of **12** could involve the initial nucleophilic attack of a chloride anion to the metallic centre of $[RuH(CO)_2(PPr^i_3)_2]^+$ to give **1**, which could undergo electrophilic attack of H^+ to afford an unstable dihydrogen derivative $[RuCl(\eta^2\text{-}H_2)(CO)_2(PPr^i_3)_2]^+$. Thus, the loss of the hydrogen molecule from the co-ordination sphere of this cation, and the subsequent co-ordination of a new chloride anion should give **12**. In support of this proposal, we have found that complex **1** reacts with a stoichiometric amount of $HBF_4{\cdot}OEt_2$ in acetone to give molecular hydrogen and $[RuCl(\eta^1\text{-}OCMe_2)(CO)_2(PPr^i_3)_2]BF_4$ **13**, which by reaction with NaCl affords **12** (Scheme 3).

Complex **13** was isolated as a white powder in 72% yield. Consistent with the mutually *cis* disposition of the two carbonyl ligands, the IR spectrum of this powder in Nujol shows two ν(CO) bands at 2090 and 2022 cm^{-1}. Furthermore, the spectrum contains the absorption due to the BF_4^- with T_d symmetry, and the band corresponding to the carbonyl group of the acetone molecule at 1670 cm^{-1}, indicating that this ligand is co-ordinated in η^1 fashion. Similarly to **2**, complex **13** dissociates



Scheme 3 (*i*) $AgBF_4$–Me_2CO, –AgCl; (*ii*) HCl, $-H_2$; (*iii*) HBF_4–Me_2CO, $-H_2$; (*iv*) NaCl, $-NaBF_4$; (*v*) +L, $-Me_2CO$; (*vi*) $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ (diolefin = tfbb **8** or cod **9**), –MeOH

the acetone molecule in solution. The formation of $[RuCl(CO)_2(PPr^i_3)_2]^+$ and acetone is supported by the IR spectrum in dichloromethane solution, and $^{13}C\text{-}\{^1H\}$ NMR in $CDCl_3$ of **13**. The IR spectrum shows the band of the carbonyl group of the acetone at 1715 cm^{-1}, whereas, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum, the resonance of the carbonyl group appears at δ 207.4.

Six-co-ordination for ruthenium can be achieved by addition of water, acetonitrile, carbon monoxide or pyrazole to the metal centre of $[RuCl(CO)_2(PPr^i_3)_2]^+$. Thus, the reactions of **13** with these ligands lead to the six-co-ordinate cationic complexes **14**–**17** (Scheme 3), which were isolated as white solids in good yields (74–82%).

Similarly to the IR spectrum of **3**, the IR spectrum of **14** in Nujol shows splitting of the asymmetric BF_4^- stretching band, suggesting that in this case the anion is also involved in a network of hydrogen bonds with the co-ordinated water molecule. The IR spectra of **15**–**17** show absorptions due to the BF_4^- anion in T_d symmetry. Furthermore, the spectra of **14**–**17** contain two bands in the terminal carbonyl region, in agreement with the structures shown in Scheme 3. For **16**, the presence of three carbonyl ligands in a *mer* fashion is supported by the $^{13}C\text{-}\{^1H\}$ NMR spectrum, which contains two carbonyl resonances at δ 191.5 and 189.0, in a 2:1 ratio. Both signals appear as triplets with P–C coupling constants of 10.7 and 8.3 Hz respectively.

The ^1H NMR spectrum of **17** indicates that there are two conformers of this compound in solution. The major species is characterised by four resonances due to the pyrazole protons at δ 12.38, 8.20, 7.61 and 6.69, whereas the resonances due to the minor species are observed at δ 12.23, 8.43, 8.16 and 6.43. In six-co-ordinate chloro–pyrazole compounds containing these two ligands mutually *cis* disposed, N–H · · · Cl interactions have been previously observed.[35] Since in our case, this interaction can only take place in the conformer with structure **a** (Fig. 3), we assume that this conformer is the major species. In the

^{31}P-$\{^1H\}$ NMR spectrum of **17**, the conformer **a** is characterised by a singlet at δ 37.4 and the conformer **b** by another singlet at δ 37.5.

The ^{31}P-$\{^1H\}$ NMR spectra of **14**–**16** show singlets between δ 41.5 and 47.6, in agreement with the mutually *trans* disposition of the triisopropylphosphine ligands.

The unusual range of ligands, soft (CO) and hard (H_2O), bound by the $[RuH(CO)_2(PPr^i_3)_2]^+$ and $[RuCl(CO)_2(PPr^i_3)_2]^+$ fragments may be due to the combination of a positive charge and two carbonyl ligands that allows hard ligands to bind* and to the presence of two basic phosphine and a hydrido ligand which encourage soft ligand binding. In this way, the ruthenium site seems to be both σ acid and π base in character.

The acidic NH group of the pyrazole ligand of **13** can be easily deprotonated by dimers of the type $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$. The reactions of **13** with **8** and **9** lead to the heterobinuclear complexes **18** and **19** respectively. These compounds were isolated as yellow solids in 74% (**18**) and 83% (**19**) yield. Their IR and ^{31}P-$\{^1H\}$ NMR spectra are in good agreement with the structure proposed in Scheme 3. The most noticeable bands in the IR spectra of both compounds are two ν(CO) absorptions at about 2000 cm^{-1} and a very strong absorption at about 1100 cm^{-1}, which is due to the BF_4^- anion in T_d symmetry. The ^{31}P-$\{^1H\}$ NMR spectra for both compounds show singlets at δ 36.5.

The co-ordination geometry around the rhodium atoms of **18** and **19** is square planar. Two vinylic resonances due to the diolefin therefore are expected in the ^1H NMR spectra of both compounds. However, the spectrum of **18**, as well as the ^1H NMR spectrum of **19**, shows only a single vinylic resonance at room temperature and at −60 °C. This suggests the existence of a rapid exchange process on the NMR time-scale, even at −60 °C, between the pyrazole and the chloro ligands. A similar phenomenon has been previously observed for rhodium and iridium square-planar compounds of type [M(X)L (diolefin)], where L is a nitrogen-donor ligand.[37] The key of this exchange process could be the dissociation of Rh(pz)(diolefin) fragments from the heterobinuclear unit. In this context should be mentioned that previous studies on chloro–pyrazolato heterobridged compounds have shown that the cleavage of the bridge can easily occur.[38] Interestingly, the heterobinuclear complexes **10** and **11** with a hydrido instead of a chloro ligand in the bridge have a rigid structure in solution. This could be a result of the metal–metal interaction in these hydrido-bridged compounds. The Ru–Rh interaction in **10** and **11** could prevent the dissociation of Rh(pz)(diolefin) fragments.

Insertion Reactions into the Ru–H *Bond of Complex* **2**.—Carbon disulfide and heteroallenes (*e.g.* SCNR) behave as electrophiles. Their δ^+ charged central carbon atom can be attacked not only by conventional nucleophiles (*e.g.* OR^-, SR^-, NHR^-, *etc.*) but also by metallic bases to form $M(\eta^2\text{-}CS_2)$ and $M(\eta^2\text{-}C_{heteroallene})$.[39] The stability of these intermediates is mainly determined by the energetics of subsequent reactions. For example, when the metal centre binds a hydrido ligand, the transfer of the hydrido ligand from the metal to the central carbon atom of the heteroallene is observed.[40] In agreement with the π-base character of the fragment $[RuH(CO)_2(PPr^i_3)_2]^+$, complex **2** reacts with CS_2 and SCNR (R = Me or Ph) to give the compounds **20**–**22** (Scheme 4), resulting from the insertion of the unsaturated substrates into the Ru–H bond.

Complex **20** was isolated as a yellow solid in 80% yield. The dithioformato ligand is formulated as bidentate on the basis of its IR spectrum in Nujol, which shows bands at 1225 [ν(HCS)] and 935 cm^{-1} [$\nu(CS_2)_{asym}$], in accordance with those found for

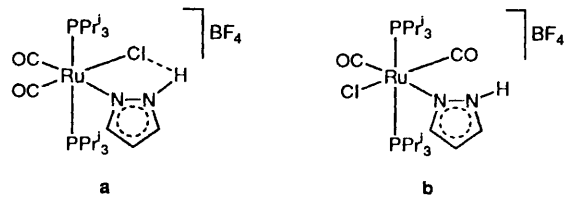


Fig. 3 Conformers of compound **17**

related ruthenium compounds.[41] In addition, the IR spectrum of **20** contains two ν(CO) bands at 2040 and 1985 cm^{-1} and a very strong absorption between 1100 and 1000 cm^{-1}, due to the BF_4^- anion with T_d symmetry. In the ^1H NMR spectrum, the most noticeable signal is a singlet at δ 11.31, which was assigned to the dithioformato proton. The ^{31}P-$\{^1H\}$ NMR shows a singlet at δ 48.0.

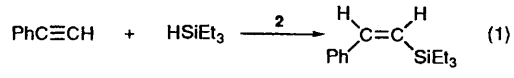
Complexes **21** and **22** were isolated as white solids in 78 and 81% yield, respectively. The IR spectra of these compounds in Nujol show, similarly to the IR spectrum of **20**, two ν(CO) bands in the terminal carbonyl region, and the characteristic absorption of the BF_4^- with T_d symmetry. Furthermore, they contain bands assigned to the thioformamido ligands, co-ordinated in a η^2 fashion,[42] at *ca.* 1520, 1280 and 880 cm^{-1}. The thioformamido protons appear in the ^1H NMR spectrum at δ 8.82 (**21**) and 9.50 (**22**) as singlets. The ^{31}P-$\{^1H\}$ NMR spectra show singlets at δ 42.8 (**21**) and δ 40.7 (**22**).

Methyl propiolate also undergoes reaction with the fragment $[RuH(CO)_2(PPr^i_3)_2]^+$. Thus, treatment of **2** with the alkyne in 1,2-dichloroethane affords the vinyl complex **23** which was isolated as a yellow solid in 72% yield. The proposal that the ester unit co-ordinates to the ruthenium atom *via* the C=O oxygen atom is strongly supported by the IR spectrum, which shows the ν(CO) stretching frequency at 1560 cm^{-1}. Characteristic signals of this complex in the ^1H NMR spectrum are the vinyl protons, which appear at δ 7.19 and 6.33. The ^{31}P-$\{^1H\}$ NMR spectrum shows a singlet at δ 43.9.

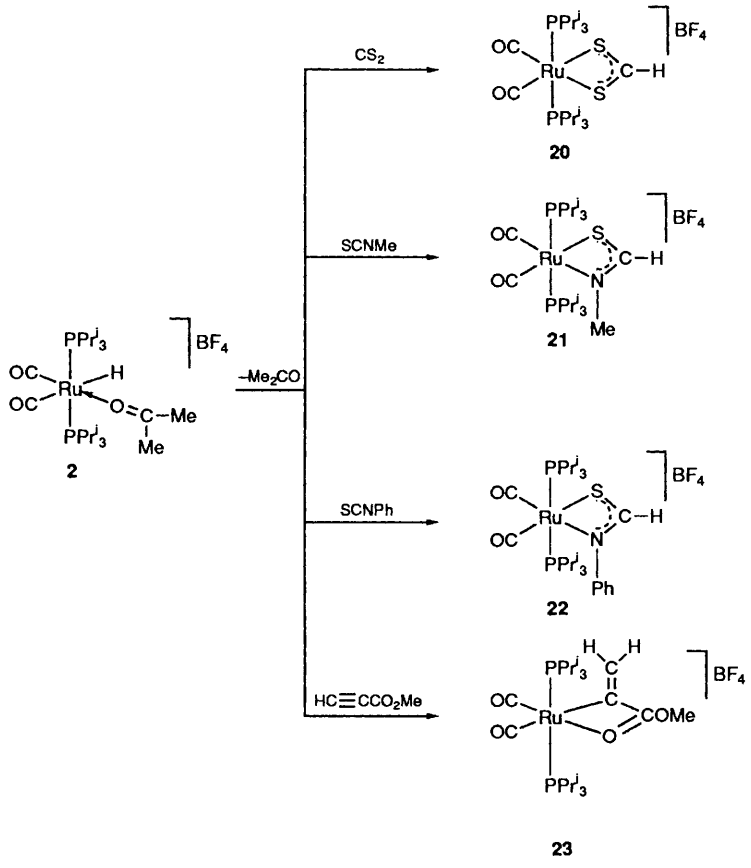
The reactions of terminal alkynes with transition-metal hydride complexes generally result in the formation of vinyl derivatives by an insertion reaction of the alkyne into the M–H bonds.[43] However, when the metal centre is electron rich, H–C(sp) activation can take place.[44] Thus, the reaction with terminal alkynes of the fragment $[OsH_2(CO)(PPr^i_3)_2]$, which inserts CS_2 to give $[OsH(\eta^2\text{-}S_2CH)(CO)(PPr^i_3)_2]$,[45] leads to the hydrido–alkynyl–dihydrogen complex $[OsH(C_2R)(\eta^2\text{-}H_2)(CO)(PPr^i_3)_2]$ (R = Ph or $SiMe_3$).[34b] The fragment $[RuH(CO)_2(PPr^i_3)_2]^+$ seems to be both π base and σ acid in character. Its base character could favour the insertions of CS_2 and SCNR, while its acid character could prevent the formal oxidative addition of the H–C(sp) bond of methyl propiolate encouraging its insertion.

Catalytic Activity of **2**.—1,2-Dichloroethane solutions of **2** efficiently catalyse the hydrogenation of phenylacetylene to styrene. At 30 °C and atmospheric pressure of hydrogen, the selectivity of the reaction towards the olefin is 100% (Fig. 4). Subsequent reduction of styrene to ethylbenzene is not observed.

In 1,2-dichloroethane at 60 °C, and under an atmospheric pressure (*ca.* 10^5 Pa) of argon, complex **2** also catalyses the addition of triethylsilane to phenylacetylene, to give *cis*-PhCH=CH($SiEt_3$) with a selectivity of 100%. Thus, the formation of 0.16 mol dm^{-3} *cis*-PhCH=CH($SiEt_3$) is observed after 1 h 40 min, by treatment of phenylacetylene (0.24 mol dm^{-3}) with triethylsilane (0.24 mol dm^{-3}) in the presence of **2** (2.4×10^{-3} mol dm^{-3}) [equation (1)].



* It has been previously suggested that the positive charge of a complex makes the metal centre a good σ acid, encouraging the co-ordination of hard ligands.[8g] In a *trans* arrangement a more stable complex results when a ligand is soft and the other one is hard.[36]



Scheme 4

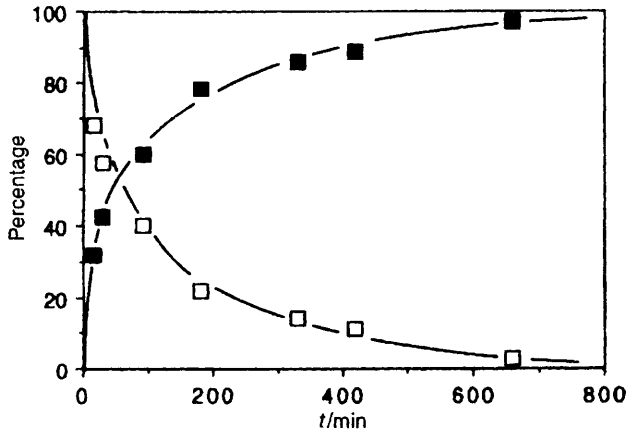


Fig. 4 Hydrogenation of phenylacetylene catalysed by $[Ru(\eta^1\text{-}OCMe_2)(CO)_2(PPr^i{}_3)_2]BF_4$ **2** in 1,2-dichloroethane at 30 °C {H_2 (1 atm), **2** (1.03×10^{-3} mol dm^{-3}), PhC≡CH (0.1 mol dm^{-3})}; (□) phenylacetylene, (■) styrene

The hydrosilylation of terminal alkynes catalysed by transition-metal complexes can give rise to four products,[46] *cis*-$R^1CH{=}CH(SiR^2{}_3)$, *trans*-$R^1CH{=}CH(SiR^2{}_3)$, $R^1(SiR^2{}_3)C{=}CH_2$ and $R^1C{\equiv}CSiR^2{}_3$, and much effort has been expended in developing highly selective catalysts.[47] The formation of the thermodynamically less stable isomers, *cis*-$RCH{=}CH(SiR'_3)$, is interesting because these compounds are a result of the *trans* addition of the silane to the alkyne. Highly selective catalytic formation of *anti*-addition products has been reported in a few cases, where the reactions were carried out in the presence of an excess of alkyne or silane.[46b,47b,f,i] However, as far as we know, selectivities of 100% have been previously obtained only in the presence of the complex $[Ru(H)Cl(CO)(PPr^i{}_3)_2]$.[7]

Conclusion

The chemical properties of the species $[RuH(CO)_2(PPr^i{}_3)_2]^\bullet$ seem to be a result of the combination around the metal centre of: (*i*) a positive charge and two carbonyl ligands which would allow it to act as a σ acid, and (*ii*) one hydrido and two phosphine ligands, which would account for its π-base character.

Experimental

General Considerations.—All reactions were carried out with rigorous exclusion of air by using Schlenk-tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting materials $[Ru(H)Cl(CO)_2(PPr^i{}_3)_2]$[1] and $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ (diolefin = tfbb or cod)[48] were prepared by published methods.

Physical Measurements.—NMR spectra were recorded on Varian 200 XL and UNITY 300 spectrophotometers. Chemical shifts are expressed in ppm upfield from ($SiMe_4$($^{13}C\text{-}\{^1H\}$, ^1H) and 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$). Coupling constants *J* and *N* are given in Hz. Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer as either solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). Carbon, H and N analyses were carried out with a Perkin-Elmer 240C microanalyser. The hydrogenation was followed, at constant pressure of hydrogen, by measuring the hydrogen consumption as a function of time in a gas burette (Afora 516256). Analysis of the products of the catalytic reaction was carried out on a Perkin-Elmer 8500 gas chromatograph with an FFAP (free fatty acid phase) on Chromosorb GHP 80/100 mesh (9.14 × 0.3175 cm)

column at 150 °C. The hydrosilylation reaction was carried out in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was closed by a silicone septum to allow samples to be removed by syringe without opening the system. The reaction was followed by measuring the silane consumption as a function of time using C_6H_{12} as internal standard with a 15% β,β′-oxydipropionitrile on a Chromosorb W HP 80/100-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionisation detector. The analysis of the reaction product was carried out by using a FFAP on Chromosorb GHP 80/100-mesh column at 175 °C.

Preparations.—$[RuH(\eta^1\text{-}OCMe_2)(CO)_2(PPr^i_3)_2]BF_4$ **2**. A solution of **1** (149 mg, 0.29 mmol) in acetone (15 cm^3) was treated with $AgBF_4$ (59.28 mg, 0.30 mmol). After stirring for 30 min in the dark, at room temperature, the suspension was filtered and concentrated to *ca.* 1 cm^3. A white product was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 148 mg (82%) (Found: C, 44.50; H, 8.30. Calc. for $C_{23}H_{49}BF_4O_3P_2Ru$: C, 44.30; H, 7.90%). IR (Nujol, cm^{-1}): ν(RuH), 2031; ν(CO), 1978, 1931; ν(C=O), 1667; ν(BF_4), 1120–1000. IR (CH_2Cl_2, cm^{-1}): ν(CO), 2045, 1975; ν(C=O), 1715. NMR ($CDCl_3$): ^1H (200 MHz), δ 2.40 (m, 6 H, PC*H*CH_3), 2.14 [s, 6 H, (CH_3)$_2$CO], 1.30 [dvt, 36 H, N = 14.3 Hz, J(HH) = 7.2, PCHCH_3] and −3.86 [t, 1 H, J(PH) = 18.3 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 64.5 (s); ^{13}C-{^1H} (75.33 MHz), δ 207.4 [br, (CH_3)$_2$*C*O], 199.7 [t, J(PC) = 6.0, CO], 198.3 [t, J(PC) = 6.9, CO], 30.9 (s, *Me*$_2$CO), 24.4 (vt, N = 11.5 Hz, P*C*HCH$_3$), 19.2 and 18.9 (both s, PCH*C*H$_3$).

$[RuH(H_2O)(CO)_2(PPr^i_3)_2]BF_4$ **3**. A solution of **1** (106.4 mg, 0.21 mmol) in acetone (15 cm^3) was first treated with *ca.* 10 drops of water and then a stoichiometric amount of $AgBF_4$ (47.3 mg, 0.24 mmol) was added. After stirring for 30 min in the dark, at room temperature, the suspension was filtered and concentrated to *ca.* 1 cm^3. A white product was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 98 mg (80%) (Found: C, 41.65; H, 8.20. Calc. for $C_{20}H_{45}BF_4O_3P_2Ru$: C, 41.20; H, 7.75%). IR (Nujol, cm^{-1}): ν(OH), 3395 (br); ν(RuH), 2049; ν(CO), 1970, 1931; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (200 MHz), δ 3.40 (s, 2 H, H_2O), 2.40 (m, 6 H, PC*H*CH_3), 1.35 [dvt, 36 H, N = 14.3, J(HH) = 7.2, PCHCH_3] and −4.63 [t, 1 H, J(PH) = 18.7 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 61.4 (s).

$[RuH(MeCN)(CO)_2(PPr^i_3)_2]BF_4$ **4**. A solution of **1** (99.5 mg, 0.19 mmol) in acetone (15 cm^3) was first treated with MeCN (21 μl, 0.4 mmol) and then with $AgBF_4$ (40 mg, 0.20 mmol). After stirring for 30 min in the dark, at room temperature, the suspension was filtered and concentrated to *ca.* 1 cm^3. A white product was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 86.4 mg (75%) (Found: C, 43.75; H, 8.45; N, 2.30. Calc. for $C_{22}H_{46}BF_4NO_2P_2Ru$: C, 43.55; H, 7.65; N, 2.30%). IR (Nujol, cm^{-1}): ν(C≡N), 2325; ν(RuH), 2040; ν(CO), 1985, 1928; ν(BF_4), 1150–1050. NMR ($CDCl_3$): ^1H (200 MHz), δ 2.43 (s, 3 H, CH_3CN), 2.35 (m, 6 H, PC*H*CH_3), 1.25 [dvt, 36 H, N = 14.4, J(HH) = 7.2, PCHCH_3] and −6.00 [t, 1 H, J(PH) = 18.0 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 59.8 (s).

$[RuH(CO)_3(PPr^i_3)_2]BF_4$ **5**. A stream of CO was bubbled through a solution of **2** (135 mg, 0.22 mmol) in CH_2Cl_2 (15 cm^3). After 30 min the solution was concentrated to *ca.* 1 cm^3. A white product was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 108 mg (83%) (Found: C, 42.65; H, 8.05. Calc. for $C_{21}H_{43}BF_4O_3P_2Ru$: C, 42.50; H, 7.30%). IR (Nujol, cm^{-1}): ν(RuH), 2100; ν(CO), 2040, 2020; ν(BF_4), 1100–1000. IR (CH_2Cl_2, cm^{-1}): ν(RuH), 2095; ν(CO), 2045, 2025. NMR ($CDCl_3$): ^1H (200 MHz), δ 2.40 (m, 6 H, PC*H*CH_3), 1.40 [dvt, 36 H, N = 15.8, J(HH) = 8.4, PCHCH_3] and −7.80 [t, 1 H, J(PH) = 15.6 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 60.5 (s); ^{13}C-{^1H} (75.33 MHz), δ 200.9 [t, J(PC) = 12.6, *C*O], 198.2 [t, J(PC) = 5.8, *C*O], 24.3 [vt, N = 11.3 Hz, P*C*HCH$_3$), 19.1 and 18.9 (both s, PCH*C*H$_3$).

$[RuH(CO)_2(Hpz)(PPr^i_3)_2]BF_4$ **6**. This compound was prepared analogously as described for **4**, starting from **1** (124 mg, 0.24 mmol), $AgBF_4$ (50 mg, 0.25 mmol) and pyrazole (17 mg, 0.25 mmol). A white solid was obtained. Yield 152 mg (78%) (Found: C, 43.15; H, 8.05; N, 4.45. Calc. for $C_{23}H_{47}BF_4N_2O_2P_2Ru$: C, 43.60; H, 7.50; N, 4.40%). IR (Nujol, cm^{-1}): ν(NH), 3265; ν(RuH), 2045; ν(CO), 1983, 1935; ν(BF_4), 1100–1000. NMR ($CDCl_3$): (major isomer); ^1H (200 MHz), δ 11.14 (br, 1 H, N*H*), 8.05, 7.43, 6.26 (all br, 1 H each, $C_3H_3N_2$), 1.8 (m, 6 H, PC*H*CH_3), 1.25 [dvt, 36 H, N = 14.0 Hz, J(HH) = 6.8 Hz, PCHCH_3] and −5.06 [t, 1 H, J(PH) = 19.5 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 57.6 (s); (minor isomer); ^1H, δ 11.90 (br, 1 H, N*H*), 7.97, 7.34, 6.20 (all br, 1 H each, $C_3H_3N_2$), 1.6 (m, 6 H, PC*H*CH_3), 1.25 [dvt, 36 H, N = 14.0 Hz, J(HH) = 6.8, PCHCH_3] and −5.31 [t, 1 H, J(PH) = 18.9 Hz, Ru*H*]; ^{31}P-{^1H} (80.9 MHz), δ 57.0 (s).

$[Ru(CO)_3(PPr^i_3)_2]$ **7**. A solution of **5** (75.2 mg, 0.15 mmol) in MeOH (6 cm^3) was treated with a stoichiometric amount of KOH in MeOH (0.75 cm^3, 0.15 mmol). After stirring for 15 min and cooling to −80 °C a white precipitate was formed. This solid was repeatedly washed with MeOH and dried *in vacuo*. Yield 57 mg (75%) (Found: C, 50.05; H, 9.35. Calc. for $C_{21}H_{42}O_3P_2Ru$: C, 49.90; H, 8.35%). IR (Nujol, cm^{-1}): ν(CO), 1925. NMR (C_6D_6): ^1H (300 MHz), δ 2.20 (m, 6 H, PC*H*CH_3), 1.30 [dvt, 36 H, N = 14.1, J(HH) = 7.1 Hz, PCHCH_3]; ^{31}P-{^1H} (80.9 MHz), δ 72.8 (s), see ref. 25.

$[(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(tfbb)]BF_4$ **10**. A solution of **6** (95 mg, 0.15 mmol) in acetone (10 cm^3) was treated with **8** (40 mg, 0.07 mmol) and stirred under reflux for 24 h. The yellow solution was then filtered off and concentrated to *ca.* 0.5 cm^3. After addition of diethyl ether, a yellow solid was obtained. This solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 127 mg (88%) (Found: C, 43.65; H, 6.25; N, 2.70. Calc. for $C_{31}H_{58}BF_4N_2O_2P_2RhRu$: C, 43.70; H, 5.45; N, 2.90%). IR (Nujol, cm^{-1}): ν(CO), 2030, 1980; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (200 MHz), δ 7.20, 6.76 and 6.21 (all br, each 1 H, $C_3H_3N_2$), 5.50 (br, 2 H, –C*H* of tfbb), 4.42 and 3.94 (both br, each 2 H, =C*H*– of tfbb), 2.57 (m, 6 H, PC*H*CH_3), 1.40 [dvt, 18 H, N = 14.7, J(HH) = 7.3, PCHCH_3], 1.20 [dvt, 18 H, N = 13.1, J(HH) = 6.2, PCHCH_3] and −13.70 [dt, J(PH) = 12.1, J(RhH) = 19.8 Hz, Rh*H*Ru]; ^{31}P-{^1H} (80.9 MHz), δ 51.7 (s).

$[(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(cod)]BF_4$ **11**. This compound was prepared analogously as described for **10**, starting from **6** (67.5 mg, 0.11 mmol) and **9** (31 mg, 0.05 mmol). A yellow solid was obtained. Yield 83.5 mg (90%) (Found: C, 44.45; H, 7.30; N, 3.65. Calc. for $C_{31}H_{58}BF_4N_2O_2P_2RhRu$: C, 44.15; H, 6.95; N, 3.30%). IR (Nujol, cm^{-1}): ν(CO), 2050, 1990; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (200 MHz), δ 7.15 and 6.9 [both d, each 1 H, J(HH) = 1.8, H_B and H_C of pz], 6.18 [t, J(HH) = 1.8, 1 H, H_A of pz], 4.67 and 4.41 (both br, each 2 H, =CH– of cod), 2.6 (m, 6 H, PC*H*CH_3), 2.30, 2.00 and 1.90 (all br, 8 H, –CH_2– of cod), 1.4 [dvt, 18 H, N = 14.7, J(HH) = 7.2, PCHCH_3], 1.1 [dvt, 18 H, N = 13.8, J(HH) = 6.9, PCHCH_3] and −13.3 [dt, J(PH) = 12.3, J(RhH) = 16.5 Hz, Rh*H*Ru]; ^{31}P-{^1H} (80.9 MHz), δ 49.1 (s).

$[RuCl_2(CO)_2(PPr^i_3)_2]$ **12**. A solution of **2** (78.2 mg, 0.12 mmol) in CH_2Cl_2 was treated with a solution of HCl in Pr^{i}OH (60 μl, 0.13 mmol). After stirring for 30 min the solvent was removed and diethyl ether (2 cm^3) was added. The solution was cooled to −25 °C and then colourless crystals formed. Yield 36 mg (49%). The same reaction was also carried out using an excess of HCl: **2** (100 mg, 0.15 mmol) and HCl–Pr^{i}OH (200 μl, 0.4 mmol HCl). Yield 62 mg (72%) (Found: C, 44.05; H, 8.85. Calc. for $C_{20}H_{42}Cl_2O_2P_2Ru$: C, 43.80; H, 7.70%). IR (Nujol, cm^{-1}): ν(CO), 2015, 1983. NMR (C_6D_6): ^1H (300 MHz), δ 2.78 (m, 6 H, PC*H*CH_3) and 1.26 [dvt, 36 H, N = 13.8, J(HH) = 6.8 Hz, PCHCH_3]; ^{31}P-{^1H} (80.9 MHz), δ 38.5 (s).

$[RuCl(\eta^1\text{-}OCMe_2)(CO)_2(PPr^i_3)_2]BF_4$ **13**. A solution of **1** (263.8 mg, 0.51 mmol) in diethyl ether (12 cm^3) was treated with acetone (*ca.* 2 cm^3), and then with an ether solution of HBF_4 (70 μl, 0.5 mmol). After the mixture was stirred for 5 min a white solid precipitated. This solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 366 mg (72%) (Found: C, 41.45; H, 7.75. Calc. for $C_{23}H_{48}BClF_4O_3P_2Ru$: C, 42.00; H, 7.35%). IR (Nujol, cm^{-1}): ν(CO), 2090, 2022; ν(C=O), 1670; ν(BF_4), 1100–1000. IR (CH_2Cl_2, cm^{-1}): ν(CO), 2025, 1995; ν(C=O), 1715. NMR ($CDCl_3$): ^1H (300 MHz), δ 2.8 (m, 6 H, PC*H*CH_3), 2.15 [s, 6 H, (CH_3)$_2$CO], 1.41 [dvt, 36 H, *N* = 14.1, *J*(HH) = 7.4 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 47.6 (s); $^{13}C\text{-}\{^1H\}$ (75.33 MHz), δ 207.4 [br, (CH_3)$_2$*C*O], 199.7 [t, *J*(PC) = 6.0, CO], 198.3 [t, *J*(PC) = 6.9, *C*O], 32.0 [s, (*C*H$_3$)$_2$CO], 23.6 (vt, *N* = 10.5 Hz, P*C*HCH$_3$), 19.9 and 19.2 (both s, PCH*C*H$_3$).

$[RuCl(H_2O)(CO)_2(PPr^i_3)_2]BF_4$ **14**. This compound was prepared analogously as **13** starting from **2** (132 mg, 0.26 mmol), HBF_4·OEt_2 (70 μl, 0.52 mmol) and *ca.* 20 drops of water. A white powder was obtained. Yield 119 mg (74%) (Found: C, 39.50; H, 7.85. Calc. for $C_{20}H_{44}BClF_4O_3P_2Ru$: C, 38.90; H, 7.10%). IR (Nujol, cm^{-1}): ν(O–H), 3450–3300; ν(CO), 2050, 1985; δ(O–H), 1620; ν(BF_4), 1150–950. NMR ($CDCl_3$): ^1H (300 MHz), δ 4.05 (s, 2 H, *H*$_2$O), 2.8 (m, 6 H, PC*H*CH_3) and 1.4 [dvt, 36 H, *N* = 14.2, *J*(HH) = 7.1 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 42.3 (s).

$[RuCl(MeCN)(CO)_2(PPr^i_3)_2]BF_4$ **15**. A solution of **13** (100 mg, 0.15 mmol) in CH_2Cl_2 (10 cm^3) was treated with MeCN (32 μl, 0.6 mmol). The solvent was removed and diethyl ether (5 cm^3) was added. The resulting white solid was washed with diethyl ether and dried *in vacuo*. Yield 76 mg (79%) (Found: C, 40.90; H, 7.4; N, 2.10. Calc. for $C_{20}H_{44}BClF_4NO_2P_2Ru$: C, 41.25; H, 7.10; N, 2.20%). IR (Nujol, cm^{-1}): ν(C≡N), 2310; ν(CO), 2055, 1990; ν(BF_4), 1150–1000. NMR ($CDCl_3$): ^1H (300 MHz), δ 2.80 (m, 6 H, PC*H*CH_3), 2.61 (s, 3 H, C*H*$_3$CN), 1.40 [dvt, 36 H, *N* = 13.5, *J*(HH) = 6.6 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 41.5 (s).

$[RuCl(CO)_3(PPr^i_3)_2]BF_4$ **16**. This compound was prepared analogously as described for **5** starting from **13** (102 mg, 0.15 mmol). A white solid was obtained. Yield 77.2 mg (82%) (Found: C, 40.20; H, 7.15. Calc. for $C_{21}H_{42}BClF_4O_3P_2Ru$: C, 40.15; H, 6.75%). IR (Nujol, cm^{-1}): ν(CO), 2060, 2025. IR (CH_2Cl_2, cm^{-1}): ν(CO), 2065, 2030; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (200 MHz), δ 2.80 (m, 6 H, PC*H*CH_3) and 1.40 [dvt, 36 H, *N* = 15.1, *J*(HH) = 7.8 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 47.6 (s); $^{13}C\text{-}\{^1H\}$ (75.33 MHz), δ 191.5 [t, *J*(PC) = 10.7, *C*O], 189.0 [t, *J*(PC) = 8.3, *C*O], 26.4 (vt, *N* = 11.2 Hz, P*C*HCH$_3$) and 19.6 (s, PCH*C*H$_3$).

$[RuCl(CO)_2(Hpz)(PPr^i_3)_2]BF_4$ **17**. This compound was prepared analogously as described for **6** starting from **13** (148 mg, 0.22 mmol) and pyrazole (13.5 mg, 0.22 mmol). A white solid was obtained. Yield 120.2 mg (80%) (Found: C, 41.60; H, 7.30; N, 4.15. Calc. for $C_{23}H_{46}BClF_4N_2O_2P_2Ru$: C, 41.35; H, 6.95; N, 4.20%). IR (Nujol, cm^{-1}): ν(N–H), 3310, 3150; ν(CO), 2040, 1990; ν(BF_4), 1100–1000. NMR ($CDCl_3$): (major isomer); ^1H, δ 12.38 (br, N*H*), 8.20, 7.61, 6.69, (all br, 1 H each, $C_3H_3N_2$), 2.40 (m, PC*H*CH_3), 1.20 [dvt, *N* = 14.1, *J*(HH) = 7.1 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 37.4 (s); (minor isomer); ^1H, δ 12.23 (br, N*H*), 8.43, 8.16, 6.43 (all br, 1 H each, $C_3H_3N_2$), 2.40 (m, PC*H*CH_3) and 1.20 [dvt, *N* = 14.1, *J*(HH) = 7.1 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 37.5 (s).

$[(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)Rh(tfbb)]BF_4$ **18**. This compound was prepared analogously as described for **10**, starting from **17** (100 mg, 0.15 mmol) and **8** (54 mg, 0.07 mmol) Yield 110.5 mg (74%) (Found: C, 42.60; H, 5.70; N, 2.80. Calc. for $C_{35}H_{51}BClF_8N_2O_2P_2RhRu$: C, 42.20; H, 5.15; N, 2.80%). IR (Nujol, cm^{-1}): ν(CO), 2025, 1994; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.74, 6.71, 6.33 (all br, each 1 H, $C_3H_3N_2$), 5.50 (br, 2 H, –C*H* of tfbb), 3.85 (br, 4 H, =C*H* of tfbb), 2.6 (m, 6 H, PC*H*CH_3), 1.40 [dvt, 18 H, *N* = 14.4, *J*(HH) = 7.3, PCHC*H*$_3$] and 1.20 [dvt, 18 H, *N* = 13.7, *J*(HH) = 6.9 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 36.5 (s).

$[(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)Rh(cod)]BF_4$ **19**. This compound was prepared analogously as described for **10**, starting from **17** (112 mg, 0.17 mmol) and **9** (41 mg, 0.08 mmol). Yield 124 mg (83%) (Found: C, 43.25; H, 6.80; N, 3.05. Calc. for $C_{31}H_{57}BClF_4N_2O_2P_2RhRu$·$0.5C_4H_{10}O$: C, 43.30; H, 6.85; N, 3.05%). IR (Nujol, cm^{-1}): ν(CO), 2050, 1995; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.70 and 6.94 [both d, each 1 H, *J*(HH) = 2 Hz, H_B and H_C of pz], 6.33 [t, *J*(HH) = 2 Hz, 1 H, H_A of pz], 4.25 (m, 4H, –*H*C=C*H*– of cod), 2.60 (m, 6 H, PC*H*CH_3), 2.38, 1.90 (both br, 4 H each –CH_2– of cod), 1.40 [dvt, 18 H, *N* = 14.6, *J*(HH) = 7.5, PCHC*H*$_3$] and 1.20 [dvt, 18 H, *N* = 13.8, *J*(HH) = 6.8 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 36.5 (s).

$[Ru(\eta^2\text{-}S_2CH)(CO)_2(PPr^i_3)_2]BF_4$ **20**. A solution of **2** (112 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) was treated with an excess of CS_2 (16.2 μl, 0.25 mmol) and stirred for 15 min at room temperature. The solution was concentrated to *ca.* 0.5 cm^3 and a yellow solid was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 87.2 mg (80%) (Found: C, 39.70; H, 6.90. Calc. for $C_{21}H_{43}BF_4O_2P_2RuS_2$: C, 39.30; H, 6.75%). IR (Nujol, cm^{-1}): ν(CO), 2040, 1985; ν(HCS), 1225; ν(BF_4), 1100–1000; ν$(CS_2)_{asym}$, 935. NMR ($CDCl_3$): ^1H (300 MHz), δ 11.31 (s, 1 H, C*H*), 2.72 (m, 6 H, PC*H*CH_3) and 1.40 [dvt, 36 H, *N* = 12.6, *J*(HH) = 6.3 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 48.0 (s).

$[Ru\{\eta^2\text{-}SN(Me)CH\}(CO)_2(PPr^i_3)_2]BF_4$ **21**. This compound was prepared analogously as described for **20**, starting from **2** (105 mg, 0.16 mmol) and MeNCS (18.5 mg, 0.24 mmol). A white solid was precipitated. Yield 79.7 mg (78%) (Found: C, 41.50; H, 8.10; N, 2.30. Calc. for $C_{22}H_{46}BF_4NO_2P_2RuS$: C, 41.40; H, 7.25; N, 2.20%). IR (Nujol, cm^{-1}): ν(CO), 2040, 1980; ν(SCN), 1520, 1260, 880; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (300 MHz), δ 8.82 (s, 1 H, C*H*), 3.4 (s, 3 H, C*H*$_3$), 2.60 (m, 6 H, PC*H*CH_3) and 1.42 [dvt, 36 H, *N* = 13.5, *J*(HH) = 6.5 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz, $CDCl_3$), δ 42.8 (s).

$[Ru\{\eta^2\text{-}SN(Ph)CH\}(CO)_2(PPr^i_3)_2]BF_4$ **22**. This compound was prepared analogously as described for **20**, starting from **2** (106 mg, 0.16 mmol) and PhNCS (41 μl, 0.32 mmol). A white solid was precipitated. Yield 91 mg (81%) (Found: C, 45.85; H, 7.25; N, 1.85. Calc. for $C_{27}H_{48}BF_4NO_2P_2RuS$: C, 46.30; H, 6.90; N, 2.00%). IR (Nujol, cm^{-1}): ν(CO), 2040, 1975; ν(SCN), 1580, 1280, 885; ν(BF_4), 1100–1000. NMR ($CDCl_3$): ^1H (300 MHz), δ 9.50 (s, 1 H, C*H*), 7.2–7.4 (5 H, C_6H_5), 2.61 (m, 6 H, PC*H*CH_3) and 1.35 [dvt, 36 H, *N* = 15.2 Hz, *J*(HH) = 8.0 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 40.7 (s).

$[Ru\{C[C(O)OMe]=CH_2\}(CO)_2(PPr^i_3)_2]BF_4$ **23**. A solution of **2** (100 mg, 0.16 mmol) in CH_2Cl_2 (15 cm^3) was treated with 3 equivalents of methyl propiolate (42.9 μl, 0.48 mmol) and stirred for 12 h at room temperature. The solution was concentrated to *ca.* 0.5 cm^3 and a yellowish solid was precipitated by addition of diethyl ether. The solid was repeatedly washed with diethyl ether and dried *in vacuo*. Yield 74.8 mg (72%) (Found: C, 44.75; H, 7.45. Calc. for $C_{24}H_{47}BF_4O_4P_2Ru$: C, 44.40; H, 7.30%). IR (Nujol, cm^{-1}): ν(CO), 2060, 1985; ν(C=O), 1560; ν(BF_4), 1100–1000. IR (CH_2Cl_2, cm^{-1}): ν(CO), 2049, 1984. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.19, 6.33 (both br, 1 H each, H_2C=), 4.02 (s, 3 H, OCH_3), 2.52 (m, 6 H, PC*H*CH_3) and 1.30 [dvt, 36 H, *N* = 14.5, *J*(HH) = 7.1 Hz, PCHC*H*$_3$]; $^{31}P\text{-}\{^1H\}$ (80.9 MHz), δ 43.9 (s).

Hydrogenation of Phenylacetylene.—The catalyst, **2** (5.2 mg, 8.3×10^{-3} mmol), was carried with a solution of PhC≡CH (81.74 mg, 0.80 mmol) in 1,2-dichloroethane (8 cm^3) into a Schlenk manifold. The flask was closed by a silicone septum. The system was evacuated and refilled with hydrogen five times, and the flask was then immersed in a constant-temperature bath at 30 °C. The mixture was vigorously shaken during the run.

Hydrosilylation of Phenylacetylene.—A solution of **2** (4.8×10^{-3} mol dm^{-3}) in 1,2-dichloroethane (4 cm^3) was added to a 1,2-dichloroethane solution (4 cm^3) containing 0.48 mol

dm^{-3} $HSiEt_3$, 0.48 mol dm^{-3} PhC_2H and C_6H_{12}. The flask was then immersed in a bath at 60 °C, and the reaction mixture was magnetically stirred. The product *cis*-PhCH=CH($SiEt_3$) was isolated by column chromatography (Al_2O_3:hexane) and was characterised by ^1H NMR spectroscopy in $CDCl_3$: δ 7.45 [d, PhC*H*=, *J*(HH) = 15.1], 7.36–6.94 (Ph), 5.57 [d, =C*H*($SiEt_3$), *J*(HH) = 15.1], 0.86 [t, $SiCH_2CH_3$, *J*(HH) = 7.6], 0.58 [q, $SiCH_2CH_3$, *J*(HH) = 7.6 Hz].

X-Ray Diffraction Study of [$(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(cod)$]$BF_4$ **11**.—Suitable crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **11** at room temperature. The selected crystal was an orange block of approximate dimensions 0.390 × 0.477 × 0.561 mm. Intensity data were recorded ($3 \leqslant 2\theta \leqslant 50°$) on a Siemens-Stoe AED-2 diffractometer equipped with a highly oriented graphite-crystal monochromator. Cell parameters were determined from 56 accurately centred reflections in the range $22 \leqslant 2\theta \leqslant 40°$. Crystal data and details associated with structure refinement are summarised in Table 2. Three standard reflections were monitored during data collection every 55 min of measuring time; no variation was observed. A total of 8052 reflections were measured (6495 unique, $R_{int} = 0.0154$), of which 6297 were considered observed [$F_o \geqslant 4.0\sigma(F_o)$]. The data were corrected for Lorentz and polarisation effects, and a semiempirical correction, based on azimuthal ψ-scans from seven reflections,[49] was also applied (min. and max. transmission factors 0.705 and 0.637).

The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms of the cation were isotropically and subsequently anisotropically refined. Most of the H atoms were included in calculated positions and refined using a riding model with fixed C–H distance (0.96 Å). At this point, the BF_4^- counter anion was observed to be highly disordered and located in two different spatial regions. In both zones the boron atoms were situated on two-fold axes and consequently a total occupancy of 0.5 was assumed for each group of atoms. The disorder was modelled including three [F(11)–F(17)] and two [F(21)–F(24)] different orientations for each BF_4^- moiety. The hydride position was clearly obtained from the difference Fourier map and subsequently refined as a free isotropic atom. An extinction correction $\{x = 3.4 \times 10^{-5}$, where $F^* = F[1 + 0.002F^2/\sin(2\theta)]^{-\frac{1}{4}}\}$ as also included in the refinement.[50] Scattering factors were taken from ref. 51. All calculations were performed on a μ-VAX 3400 computer with the SHELXTL PLUS package.[50] Final atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 2 Details of the X-ray crystal structure analysis of [$(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(cod)$]$BF_4$ **11**

Molecular formula	$C_{31}H_{58}BF_4N_2O_2P_2RhRu$
M	843.54
Crystal system	Orthorhombic
Space group	*Fdd*2
Crystal colour	Orange
Crystal size/mm	0.390 × 0.477 × 0.561
a/Å	28.290(2)
b/Å	22.572(1)
c/Å	23.126(1)
U/Å^3, *Z*	14 767(1), 16
D_c/g cm^{-3}, *F*(000)	1.518, 6944.0
Radiation	Mo-Kα (λ = 0.710 73 Å)
μ(Mo-Kα)/cm^{-1}	9.8
No. of reflections measured	8052 ($3 \leqslant 2\theta \leqslant 50°$)
No. of unique data used	6297 ($\|F_o\| \geqslant 4.0\sigma\|F_o\|$)
R,[a] R'[b] (observed data)	0.0232, 0.0258

[a] $R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$. [b] $R' = \Sigma w^{\frac{1}{2}}\|\Delta F\|/\Sigma w^{\frac{1}{2}}\|F_o\|$; $w^{-1} = \sigma^2(F) + 0.000\,30F^2$.

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Table 3 Atomic coordinates (× 10^5; × 10^4 for H atom) for [$(OC)_2(Pr^i_3P)_2Ru(\mu\text{-}H)(\mu\text{-}pz)Rh(cod)$]$BF_4$ **11**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	27 289(1)	823(1)	25 000	C(19)	13 217(14)	−3 828(21)	27 846(21)
Rh	23 275(1)	2 268(1)	37 544(1)	C(20)	23 671(15)	−12 385(20)	17 318(21)
H[a]	2 742(12)	−120(17)	32 924(19)	C(21)	28 867(18)	−13 674(24)	16 218(23)
P(1)	22 154(3)	−7 937(4)	23 906(4)	C(22)	20 770(20)	−17 965(24)	16 556(28)
P(2)	32 419(3)	9 594(4)	25 945(4)	C(23)	38 356(13)	7 855(18)	28 899(17)
O(1)	26 429(16)	1 415(18)	11 995(14)	C(24)	38 479(15)	4 445(20)	34 507(18)
O(2)	36 129(10)	−6 655(14)	25 148(18)	C(25)	41 779(15)	13 239(23)	29 344(22)
N(1)	21 488(9)	6 572(12)	25 924(12)	C(26)	29 757(15)	15 760(17)	30 107(20)
N(2)	19 980(10)	7 377(13)	31 434(12)	C(27)	30 042(18)	14 741(19)	36 678(20)
C(1)	26 912(15)	1 346(19)	16 921(18)	C(28)	31 659(20)	22 014(19)	28 738(26)
C(2)	32 767(13)	−3 938(16)	25 002(18)	C(29)	33 941(16)	13 020(22)	18 869(19)
C(3)	18 991(13)	10 214(15)	22 458(16)	C(30)	29 580(21)	15 307(24)	15 619(23)
C(4)	15 803(14)	13 335(17)	25 716(19)	C(31)	36 889(19)	9 152(34)	15 072(22)
C(5)	16 523(14)	11 443(19)	31 362(18)	B(1)[b]	0	50 000	22 813(44)
C(6)	28 084(15)	143(20)	44 373(16)	F(11)[b]	0	50 000	28 507(66)
C(7)	25 291(14)	−4 767(18)	43 399(16)	F(12)[b]	3 472(48)	48 048(78)	19 742(55)
C(8)	21 204(18)	−6 718(21)	47 391(19)	F(13)[b]	−2 152(58)	55 028(78)	20 224(72)
C(9)	16 564(17)	−3 975(22)	45 542(22)	F(14)[b]	4 130(95)	53 156(105)	24 053(131)
C(10)	17 021(15)	1 893(20)	42 558(18)	F(15)[b]	−1 990(45)	46 947(59)	27 805(61)
C(11)	19 738(15)	6 623(19)	44 447(16)	F(16)[b]	1 270(71)	44 556(98)	21 988(97)
C(12)	22 475(18)	6 540(22)	50 100(19)	F(17)[b]	4 542(51)	52 257(74)	19 948(69)
C(13)	27 550(17)	4 592(25)	49 181(19)	B(2)[b]	0	0	23 726(51)
C(14)	22 170(14)	−12 798(18)	30 436(20)	F(21)[b]	3 229(23)	−2 433(30)	19 719(29)
C(15)	26 891(17)	−15 710(23)	31 481(25)	F(22)[b]	−3 652(28)	−5 034(33)	25 363(36)
C(16)	18 130(19)	−17 351(24)	30 916(27)	F(23)[b]	−1 223(44)	−2 692(51)	28 395(55)
C(17)	15 732(12)	−6 573(17)	22 591(17)	F(24)[b]	2 818(26)	−4 018(35)	21 405(36)
C(18)	14 749(16)	−3 176(19)	17 029(20)				

[a] These coordinates correspond to the isotropically refined hydride position. [b] These atoms, involved in disorder, were isotropically refined. The assigned occupancy factors were: for F(11), F(13), F(14) 20%; for F(12), F(21), F(22), F(23), F(24) 50% and, for F(15), F(16), F(17) 30%.

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