Protonation of *cyclo*-Platinumdirhodium Complexes. *X*-Ray Crystal Structure of $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$ †

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The cluster compounds $[PtRh_2(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2]$ (L = L′ = CO; L = CO, L′ = PPh$_3$; L–L′ = cyclo-C_8H_{12}) react with HBF$_4$ in diethyl ether to give the salts $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2][BF_4]$ which exhibit in solution novel dynamic behaviour, as revealed by n.m.r. studies. The structure of $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$ has been established by *X*-ray diffraction on a single crystal that was orthorhombic, space group *Pbca*, *Z* = 8 in a unit cell of dimensions *a* = 21.503(12), *b* = 23.728(8), and *c* = 15.896(5) Å. The structure was refined to *R* 0.048 (*R*′ 0.050) for 4 901 independent reflections ($2\theta \leqslant 55°$, Mo-K_α *X*-radiation) collected at room temperature. The cation consists of a Pt(H)(CO)(PPh$_3$) unit bonded to the dirhodium fragment $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ such that co-ordination about the Pt atom is essentially planar. The two rhodium–platinum bonds [2.805(1) and 2.705(1) Å] differ by 0.1 Å, and evidence is presented that the hydrido-ligand bridges the longer bond, *cis* to the PPh$_3$ ligand. The two carbonyl groups which bridge the rhodium–rhodium bond show much weaker interaction with the Pt atom [Pt–C 2.75(1) Å (mean)] than in the neutral precursor. Relationships between the platinumdirhodium cations, platinum–olefin complexes, and protonated cyclopropanes are discussed.

We have recently shown [1] that the complexes $[Rh_2(\mu\text{-}CR^1R^2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ ($R^1 = R^2$ = H or CF$_3$; R^1 = H, R^2 = CO$_2$Et or CH=CH$_2$) and $[PtRh_2(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2]$ [L = L′ = CO; L = CO, L′ = PPh$_3$; L–L′ = cyclo-octa-1,5-diene(cod)] can be obtained in high yield by addition of CRR′ and PtLL′ groups, respectively, to the formally unsaturated dirhodium compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.[2] This study was stimulated by a proposal [3] that the bridged alkylidene complex $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ [4] and the anion $[Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$ (ref. 5) can be regarded as arising from interaction of the filled a_1 and empty $2b_2$ orbitals of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ with the σ and π orbitals of the isolobal moieties CH$_2$ and $Rh(CO)_2^-$, respectively.

Complexes containing the core structure $\overline{M(\mu\text{-}CR_2)M}$ (M = Co or Rh) have many interesting properties.[6,7] For example, the Rh(η-C$_5$Me$_5$) species protonate immediately on attempted chromatography with such weakly acidic supports as silica or alumina.[8] Theoretical studies on $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ indicate that the metal–metal bond and the ligated carbene–carbon atom are especially electron rich,[9] and it has been shown [10] that protonation occurs initially on the metal–metal bond. Moreover, treatment of the dirhodium complex with $^2H^+$ results in exchange with the μ-CH$_2$ proton, most probably *via* tautomerism between μ-CH$_3$ and μ-hydrido–μ-carbene species, although the methyl-containing intermediates could not be isolated, nor were they observed spectroscopically.[10] The cation $[Rh_2(\mu\text{-}H)(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]^+$ (or its μ-^{2}H analogue), in the absence of co-ordinating anions such as halide, decomposes with release of H$_2$ and CH$_4$ to afford the carbyne complex cation $[Rh_3(\mu_3\text{-}CH)(CO)_2(\eta\text{-}C_5H_5)_3]^+$. However, protonation of the neutral dirhodium compound with HX (X = Cl or Br) gives stable terminally bound methylrhodium compounds $[Rh_2(X)(Me)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.

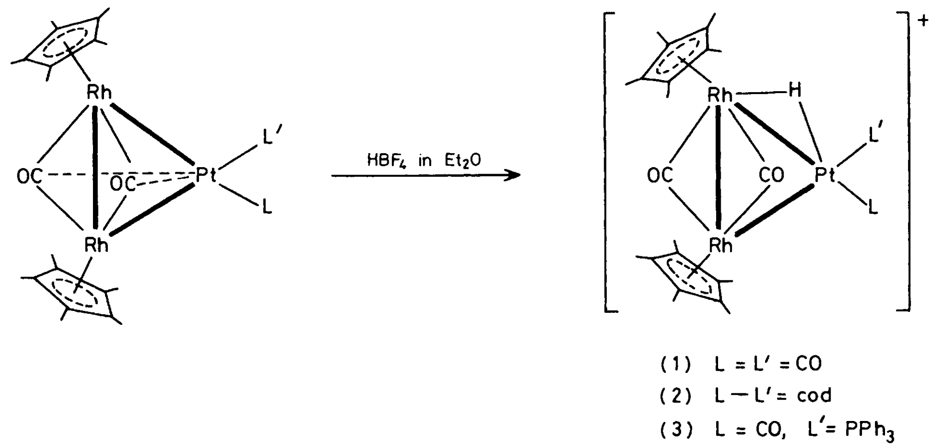
Protonation of metal–metal bonds is often observed with dimetal compounds, and occurs, for example, with $[Re_2(CO)_5(\eta\text{-}C_5H_5)_2]$,[11] $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$,[12] and $[Pt_2\{\mu\text{-}(\eta^1\text{-}CF_3C_2CF_3)\}(cod)_2]$.[13] A recent study [14] of the protonation of the triruthenium anion $[Ru_3H(CO)_{11}]^-$ has shown that although the initial product has the proton bonded to the oxygen of a carbonyl group, the thermodynamically stable product is formed by migration of the proton to the metal–metal bond.[14] Hence the presence of both electron rich metal–metal bonds and potentially nucleophilic semi-triply bridging CO ligands in the compounds $[PtRh_2(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2]$ make these species an interesting subject for protonation studies, especially in the context of current interest in proton-induced reduction of CO.[15] A preliminary account of our work has been given.[16]

RESULTS AND DISCUSSION

Addition of HBF$_4$ in diethyl ether to the complexes $[PtRh_2(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2]$ afforded quantitatively salts $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2][BF_4]$ (1, L = L′ = CO; 2, L–L′ = cod; 3, L = CO and L′ = PPh$_3$) (Scheme), characterised by analyses and spectroscopic data (Experimental section). The ^{1}H n.m.r. spectra indicated that protonation had occurred on a Pt–Rh edge of the *triangulo*-cations, and there was no evidence for CO-protonated isomers. Variable-temperature n.m.r. measurements indicated that in solution (1)—(3) underwent dynamic behaviour, as discussed below, but to ascertain the ground-state structure of these trimetal species an *X*-ray diffraction study was carried out on (3) for which a suitable crystal was available.

The molecular structure is shown in Figure 1, together with the atom-numbering scheme, and the results are summarized in Tables 1 and 2. As found for the neutral

† 2,3;2,3-Di-μ-carbonyl-1-carbonyl-1,2-μ-hydrido-2,3-bis(η-pentamethylcyclopentadienyl)-1-triphenylphosphine-*triangulo*-platinumdirhodium(2 *Pt–Rh*)(*Rh–Rh*) tetrafluoroborate.



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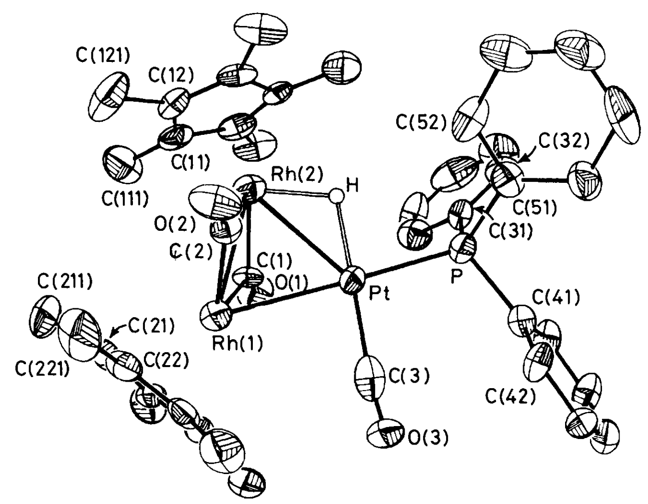

FIGURE 1 Molecular structure of $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]^+$ (3) showing the crystallographic numbering

precursor,[1] the three metal atoms and the centroids of the C_5Me_5 rings form a plane which is perpendicular to the η-C_5Me_5 ring planes. This plane also forms a dihedral angle of 9° with the plane defined by Pt, P, C(3), and O(3). Although the hydrido-ligand was not located unequivocally from electron-density difference maps, it must bridge the Pt–Rh(2) vector on the basis of this edge [2.805(1) Å] being 0.1 Å longer than Pt–Rh(1) [2.705(1) Å], the widened Rh(2)–Pt–P angle {117.4(1)° compared with 105.7(1)° in $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [1]}, and calculation [17] of a minimum potential-energy site in this position, *trans* to the carbonyl [H–Pt–C(3) 178.6(4)°]. The metal–metal bonds Rh(1)–Rh(2) [2.667(2) Å], Pt–Rh(2), and Pt–Rh(1) are all longer (0.02, 0.11, and 0.09 Å, respectively) than in the neutral precursor. Moreover, the bonds from platinum to C(3), P, C(1), and C(2) are also longer (Table 2) than those in $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [1] of 1.83(2), 2.285(4), 2.56(2), and 2.48(2) Å, respectively.

The two CO groups which bridge the Rh(1)–Rh(2) edge lean slightly towards the platinum atom. Thus the dihedral angles between the plane defined by the metals with the planes defined by Rh(1),Rh(2),C(1) and Rh(1),Rh(2),C(2) are 85° and 86°, respectively, compared with the smaller angles of 81° and 78°, respectively, in the neutral complex.

The reduced interaction of platinum with the bridging carbonyls in the protonated complex, evident from the diffraction data, is also reflected in the ^{13}C n.m.r. spectrum, which shows much smaller ^{195}Pt–^{13}C coupling of 49 Hz, compared with 125 Hz in the neutral complex.

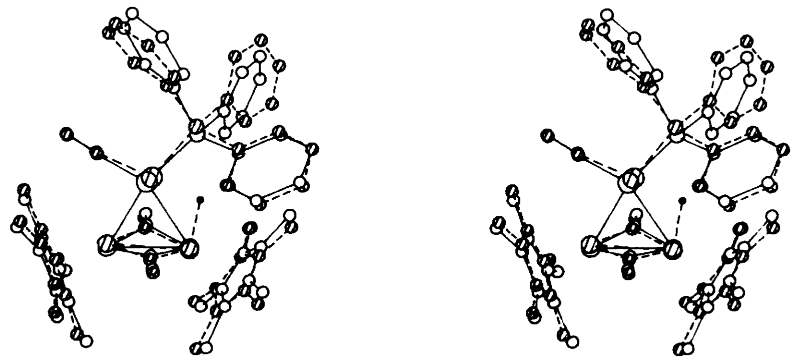

FIGURE 2 Molecular structure of $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ (open circles) superimposed on the molecular structure of $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]^+$ (shaded circles)

The ^{13}C n.m.r. spectrum also shows reduced coupling of Rh to the bridging carbonyls [*J*(RhC) 39 Hz compared with 44 Hz], consistent with the slightly longer Rh–CO distance in the protonated compound (3) [2.009 Å (mean) compared with 2.001 (mean) Å]. Moreover, Rh(2) has slightly longer bonds to the bridging carbonyls than Rh(1), indicating partial localization of charge on Rh(2). The hydride ligand, as mentioned above, widens the Rh(2)–Pt–P angle by 12°, and this is accompanied by contraction of the angles P–Pt–C(3) and C(3)–Pt–Rh(1) by 2° and 8°, respectively, compared with the corresponding angles in $[\mathrm{PtRh_2}(\mu\text{-CO})_2(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-C_5Me_5})_2]$. The widened angle Rh(2)–Pt–P results in the C_5Me_5 ring on Rh(1) being brought closer to the terminal CO ligand, and steric repulsion between these two groups probably is responsible for the bending of the carbonyl group [Pt–C(3)–O(3) 174(1)°], and the abnormally large deviation of the C(23)–C(23′) and C(24)–C(24′) vectors from the ring plane [8° (mean)]. In Figure 2 the neutral complex is shown stereographically superimposed on the cation; from this the minor differences in geometry can be readily appreciated.

TABLE 1

Atomic positional parameters (fractional co-ordinates) for $[\mathrm{PtRh_2}(\mu\text{-H})(\mu\text{-CO})_2(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-C_5Me_5})_2][\mathrm{BF_4}]$ (3), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.229 31(2)	0.107 70(2)	0.147 59(3)
Rh(1)	0.232 66(4)	0.192 15(3)	0.261 82(5)
Rh(2)	0.120 75(4)	0.156 07(4)	0.213 55(5)
P	0.218 41(14)	0.027 73(12)	0.067 5(2)
C(1)	0.180 5(5)	0.128 7(5)	0.303 2(7)
O(1)	0.179 2(5)	0.094 8(4)	0.357 0(6)
C(2)	0.180 5(6)	0.214 6(5)	0.165 0(7)
O(2)	0.177 5(5)	0.248 1(4)	0.111 2(6)
C(3)	0.320 2(8)	0.110 7(6)	0.154 4(9)
O(3)	0.370 5(5)	0.108 5(6)	0.154 1(7)
C(11)	0.040 4(6)	0.180 0(6)	0.292 8(8)
C(12)	0.040 4(6)	0.214 1(5)	0.214 0(8)
C(13)	0.032 4(5)	0.179 1(6)	0.147 4(8)
C(14)	0.027 8(5)	0.120 2(5)	0.179 3(8)
C(15)	0.030 2(5)	0.123 0(6)	0.268 1(8)
C(11′)	0.041 7(8)	0.201 3(8)	0.376 6(10)
C(12′)	0.043 9(7)	0.275 9(6)	0.213 8(12)
C(13′)	0.028 8(7)	0.197 8(7)	0.056 7(9)
C(14′)	0.013 3(7)	0.072 3(7)	0.126 9(11)
C(15′)	0.022 9(7)	0.074 0(7)	0.325 8(9)
C(21)	0.244 2(6)	0.260 3(5)	0.358 2(8)
C(22)	0.274 3(6)	0.278 0(5)	0.281 1(8)
C(23)	0.321 6(6)	0.240 4(5)	0.263 9(8)
C(24)	0.323 4(6)	0.198 3(5)	0.328 7(8)
C(25)	0.276 8(5)	0.211 9(5)	0.387 8(8)
C(21′)	0.195 4(7)	0.291 2(7)	0.404 4(10)
C(22′)	0.259 8(8)	0.330 7(5)	0.232 0(11)
C(23′)	0.368 8(7)	0.246 4(7)	0.193 4(10)
C(24′)	0.372 9(6)	0.154 9(7)	0.343 5(9)
C(25′)	0.267 9(8)	0.180 8(6)	0.469 0(8)
C(31)	0.163 7(6)	−0.021 2(5)	0.117 6(8)
C(32)	0.129 1(6)	−0.058 9(6)	0.074 3(10)
C(33)	0.088 0(8)	−0.095 2(7)	0.113 1(12)
C(34)	0.083 0(8)	−0.093 6(7)	0.198 5(14)
C(35)	0.118 2(8)	−0.056 5(6)	0.245 4(10)
C(36)	0.157 3(7)	−0.020 6(6)	0.204 3(9)
C(41)	0.291 8(6)	−0.011 2(6)	0.056 6(8)
C(42)	0.341 5(6)	0.017 2(6)	0.017 0(8)
C(43)	0.398 4(6)	−0.010 3(7)	0.013 3(10)
C(44)	0.406 0(7)	−0.064 3(7)	0.046 7(9)
C(45)	0.358 1(8)	−0.090 0(7)	0.083 4(10)
C(46)	0.300 4(7)	−0.064 2(6)	0.088 1(8)
C(51)	0.186 8(6)	0.035 5(5)	−0.037 0(8)
C(52)	0.137 4(7)	0.070 5(6)	−0.049 9(10)
C(53)	0.106 2(8)	0.072 6(7)	−0.126 2(9)
C(54)	0.126 1(8)	0.045 3(8)	−0.191 0(10)
C(55)	0.177 7(10)	0.010 7(8)	−0.184 6(10)
C(56)	0.209 1(7)	0.003 7(7)	−0.105 6(8)
B	0.400 5(10)	0.332 9(10)	0.441 4(13)
F(1)	0.441 8(7)	0.369 2(7)	0.465 1(13)
F(2)	0.404 6(8)	0.287 9(8)	0.489 2(12)
F(3)	0.341 4(6)	0.351 7(7)	0.441 4(13)
F(4)	0.412 4(7)	0.312 2(8)	0.367 6(9)

The ^{1}H n.m.r. spectra of compounds (1)—(3) were recorded from −50 °C to 25 °C. The limiting low temperature spectrum for each complex has two signals for the inequivalent C_5Me_5 groups, and a resonance for the hydrido-ligand appearing as a doublet [*J*(RhH) 29.4, 25, and 23 Hz for (1), (2), and (3), respectively], with platinum satellites [*J*(PtH) 365, 576, and 426 Hz, respectively]. Evidently, in the limiting spectra the hydride couples only with one rhodium nucleus. The values of the coupling constants are in the ranges normally found for hydrido-ligands bridging to rhodium [10,12,18] or to platinum.[19] Variable-temperature ^{1}H n.m.r. spectra for complex (1) in the hydride region are shown in Figure 3. Similar patterns were observed in the spectra of (2) and

TABLE 2

Selected bond lengths (Å) and angles (°) for $[\mathrm{PtRh_2}(\mu\text{-H})(\mu\text{-CO})_2(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-C_5Me_5})_2][\mathrm{BF_4}]$ (3), with estimated standard deviations in parentheses

(*a*) Distances

Pt–Rh(1)	2.705(1)	Rh(1)–C(21)	2.241(12)
Pt–Rh(2)	2.805(1)	Rh(1)–C(22)	2.247(11)
Rh(1)–Rh(2)	2.667(2)	Rh(1)–C(23)	2.230(11)
Pt–C(1)	2.733(1)	Rh(1)–C(24)	2.227(11)
Rh(1)–C(1)	1.989(11)	Rh(1)–C(25)	2.265(12)
Rh(2)–C(1)	2.026(11)	Rh(2)–C(11)	2.212(12)
C(1)–O(1)	1.174(14)	Rh(2)–C(12)	2.210(11)
Pt–C(2)	2.760(11)	Rh(2)–C(13)	2.240(11)
Rh(1)–C(2)	1.977(11)	Rh(2)–C(14)	2.240(11)
Rh(2)–C(2)	2.044(11)	Rh(2)–C(15)	2.271(11)
C(2)–O(2)	1.169(14)	C(21)–C(21′)	1.47(2)
Pt–P	2.297(3)	C(22)–C(22′)	1.51(2)
P–C(31)	1.836(12)	C(23)–C(23′)	1.52(2)
P–C(41)	1.836(13)	C(24)–C(24′)	1.50(2)
P–C(51)	1.803(12)	C(25)–C(25′)	1.50(2)
Pt–C(3)	1.96(2)	C(11)–C(11′)	1.43(2)
C(3)–O(3)	1.08(2)	C(12)–C(12′)	1.47(2)
C–C *	1.43	C(13)–C(13′)	1.51(2)
C–C (Ph)	1.37	C(14)–C(14′)	1.44(2)
Pt–H	1.750(1)	C(15)–C(15′)	1.49(2)
Rh(2)–H	1.747(1)		

(*b*) Angles

Rh(1)–Pt–Rh(2)	57.9(1)	Rh(1)–Pt–C(3)	84.8(4)
Pt–Rh(1)–Rh(2)	62.9(1)	Rh(2)–Pt–C(3)	142.6(4)
Pt–Rh(2)–Rh(1)	59.2(1)	C(3)–Pt–P	99.4(4)
Pt–C(1)–Rh(1)	67.8(3)	Pt–C(3)–O(3)	174.0(12)
Pt–C(1)–Rh(2)	70.4(3)	Pt–P–C(31)	110.3(4)
Rh(1)–C(1)–Rh(2)	83.2(4)	Pt–P–C(41)	112.4(4)
Pt–C(1)–O(1)	122.9(8)	Pt–P–C(51)	117.7(4)
Rh(1)–C(1)–O(1)	140.6(9)	C(31)–P–C(41)	105.8(5)
Rh(2)–C(1)–O(1)	135.8(9)	C(41)–P–C(51)	106.7(5)
Pt–C(2)–Rh(1)	67.3(3)	C(51)–P–C(31)	102.9(6)
Pt–C(2)–Rh(2)	69.6(3)	P–C(31)–C(32)	123.3(10)
Rh(1)–C(2)–Rh(2)	83.1(4)	P–C(41)–C(42)	116.9(9)
Pt–C(2)–O(2)	124.9(8)	P–C(51)–C(52)	119.5(10)
Rh(1)–C(2)–O(2)	141.7(9)	C–C–C *	108.0
Rh(2)–C(2)–O(2)	134.7(9)	C–C–C (Ph)	120.0
Rh(2)–H–Pt	106.6(1)		

* In cyclopentadienyl ring.

(3), with the latter showing additional coupling due to phosphorus [J(PH) 13 Hz]. The magnitude of this coupling constant is consistent with the hydride being *cis* to the phosphine.[19] In the room-temperature spectra of (1)—(3) the two most important features are a high-field triplet due to coupling of the hydrido-ligand resonance with two ^{103}Rh nuclei [J(RhH) halved to 14.7, 12.5, and 11.5 Hz for (1), (2), and (3), respectively], and the observation of only one signal for the two η-C_5Me_5 ligands, even though the X-ray diffraction study on (3) shows they are non-equivalent. The platinum–hydride coupling remains unchanged over the entire temperature range studied. These studies are consistent with rapid two-site exchange involving movement of the hydride from one Pt–Rh vector to the other, in such a way that the hydride remains bonded to platinum throughout. The ^{31}P n.m.r. spectrum of (3) provides additional information regarding the dynamic process. At −50 °C the ^{31}P-{^{1}H} signal is a doublet due to the coupling with the ***trans*** rhodium [J(RhP) 6 Hz] with strong coupling to platinum (3 260 Hz), although the latter value is significantly smaller than is found for the neutral precursor (4 004 Hz). On warming to room temperature the ^{31}P-{^{1}H} resonance changes to a triplet. Since the J(PtH) and J(PH) couplings do not change between the limiting spectra observed at −50 °C and the spectra measured at 25 °C, while the J(RhH) and J(RhP) couplings are halved over this range, the dynamic process must involve rotation of the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ fragment about an axis through Pt and the midpoint of the Rh=Rh unit, while the Pt(H)-(CO)(PPh_3) moiety retains its integrity at all times.[16] Such a rotation does not occur for the neutral precursor. Moreover, comparison of the X-ray data for (3) with those for [$PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2$] [1] suggests that for the former species rotation in the manner described is facilitated by movement of the PPh_3 group away from the η-C_5Me_5 rings, by the increased length of the Rh–Pt bonds, and consequently the reduced interaction of the platinum atom with the bridging carbonyl groups. The n.m.r. spectra of (2) indicate entirely analogous dynamic behaviour, showing that the hydride ligand maintains its position relative to the Pt(cod) moiety during rotation, since at room temperature two resonances are observed for the CH protons and carbons in the ^{1}H and ^{13}C n.m.r. spectra respectively, whereas the η-C_5Me_5 and bridging carbonyl groups are made equivalent.

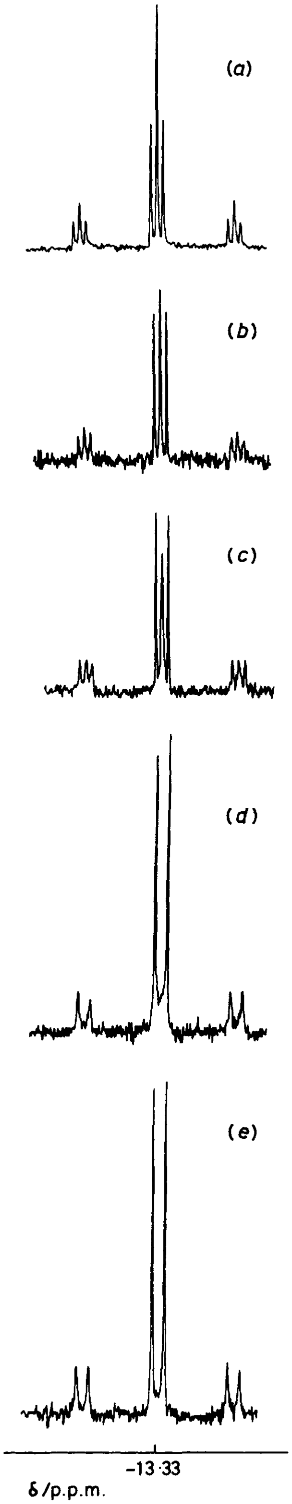

FIGURE 3 Proton n.m.r. spectra for the μ-H ligand in [$PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2$][$BF_4$] (1) at (*a*) 25, (*b*) −10, (*c*) −20, (*d*) −40, and (*e*) −45 °C

From the ^{1}H spectra and the coalescence temperatures of the η-C_5Me_5 signals, the activation energies ($\Delta G_{T_c}^‡$) for the dynamic process are estimated as 49.3, 56.0, and 58.1 kJ mol^{-1} for (1), (2), and (3) respectively. Similar values are found for the rotation of alkenes in alkene–platinum compounds.[20] The relative magnitudes of the energies might be determined by the bulk or mass of the ligands on platinum, although electronic effects are probably an important factor.

There is an analogy between the structures of the cations of compounds (1)—(3) and the recently reported cation [$Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\eta\text{-}C_5H_5)_2$]$^+$ in which the bridging methyl group exhibits a C ··· H ··· Fe interaction.[21] The group CH_3^+ is isolobal with the platinum moieties $PtH(CO)_2^+$, $PtH(\eta\text{-}C_8H_{12})^+$, and $PtH(CO)(PPh_3)^+$. Moreover, it is particularly interesting that the cations of compounds (1)—(3) may be compared in the context of isolobal relationships [3] with the favoured edge-protonated structure of protonated cyclopropane.[22]

EXPERIMENTAL

The instrumentation used and techniques employed were as previously described.[1] Hydrogen-1, ^{31}P-{^{1}H}, and ^{13}C-{^{1}H} n.m.r. spectra were measured at 200, 40.48, and 25.15 MHz, respectively. Chemical shifts are positive to high frequency of the reference, $SiMe_4$ for ^{13}C and ^{1}H and H_3PO_4 (85%, external) for ^{31}P, and coupling constants are in Hz. Infrared bands were measured in Nujol, unless otherwise stated. The diethyl ether–HBF_4 reagent was commercially available (Aldrich Chemical Co. Ltd), and the platinum-dirhodium compounds employed were prepared as reported earlier.[1]

Synthesis of the Salts $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2][BF_4]$ (1)—(3).—Solutions of the red-brown complexes $[PtRh_2(\mu\text{-}CO)_2(L)(L')(\eta\text{-}C_5Me_5)_2]$ (0.5 mmol) in diethyl ether (10 cm^3) were treated dropwise with a slight excess of HBF_4–diethyl ether until the supernatant solution was colourless. The precipitated salts were formed quantitatively, and isolated by washing with diethyl ether and drying *in vacuo*.

(*a*) $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2][BF_4]$ (1), red *crystals* (Found: C, 33.7; H, 4.1. $C_{24}H_{31}BF_4O_4PtRh_2$ requires C, 33.1; H, 3.6%), $\nu_{max.}$(CO) 2 048vs, 2 010vs, 1 806m, and 1 740s cm^{-1}; $\nu_{max.}$(CO) (CH_2Cl_2) 2 060vs, 2 026vs, and 1 767s cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, 25 °C), δ 1.89 (s, 30 H, C_5Me_5) and −13.17 [t, 1 H, μ-H, *J*(RhH) 14.7, *J*(PtH) 367]; ^{1}H (CD_2Cl_2, −50 °C), δ 1.83 (s, 15 H, C_5Me_5), 1.77 (s, 15 H, C_5Me_5), and −13.33 [d, 1 H, μ-H, *J*(RhH) 29.4, *J*(PtH) 365].

(*b*) $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(\eta\text{-}C_8H_{12})(\eta\text{-}C_5Me_5)_2][BF_4]$ (2), yellow-brown *crystals* (Found: C, 39.0; H, 5.0. $C_{30}H_{43}BF_4O_2PtRh_2$ requires C, 39.0; H, 4.7%), $\nu_{max.}$(CO) 1 805m and 1 755vs cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, 25 °C), δ 5.44 [s, 2 H, CH, *J*(PtH) 58], 5.39 [s, 2 H, CH, *J*(PtH) 78], 2.1 (m, br, 8 H, CH_2), 1.86 (s, 30 H, C_5Me_5), and −14.40 [t, 1 H, μ-H, *J*(RhH) 12.5, *J*(PtH) 582]; ^{1}H ($CDCl_3$, −50 °C), δ 5.47 (s, 2 H, CH), 5.38 (s, 2 H, CH), 2.1 (m,br, 8 H, CH_2), 1.95 (s, 15 H, C_5Me_5), 1.80 (s, 15 H, C_5Me_5), and −14.26 [d, 1 H, μ-H, *J*(RhH) 25, *J*(PtH) 576]; ^{13}C-{^{1}H} ($CDCl_3$, 25 °C), δ 234.4 [t, CO, *J*(RhC) 39], 104.9 (C_5Me_5), 98.0 [CH, *J*(PtC) 84], 95.5 [CH, *J*(PtC) 120], 31.3 (CH_2), 30.6 (CH_2), and 9.2 p.p.m. ($C_5\mathit{Me}_5$).

(*c*) $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$ (3), red *crystals* [Found: C, 44.4; H, 4.7; *M* (f.d. mass spectrum) 1 018. $C_{41}H_{46}BF_4O_3PPtRh_2$ requires C, 44.5; H, 4.2%; *M* 1 018], $\nu_{max.}$(CO) 2 065s, 1 773vs, and 1 769vs cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, 25 °C), δ 7.6—7.1 (m, 15 H, Ph), 1.76 (s, 30 H, C_5Me_5), and −11.83 [d of t, 1 H, μ-H, *J*(PH) 13, *J*(RhH) 11.5, *J*(PtH) 426]; ^{1}H ($CDCl_3$, −50 °C), δ 7.6—7.1 (m, 15 H, Ph), 1.94 (s, 15 H, C_5Me_5), 1.61 (s, 15 H, C_5Me_5), and −11.81 [d of d, 1 H, μ-H, *J*(PH) 13, *J*(RhH) 23, *J*(PtH) 426]; ^{1}H-{^{31}P} ($CDCl_3$, 25 °C), δ 7.6—7.1 (m, 15 H, Ph), 1.76 (s, 30 H, C_5Me_5), and −11.8 [t, 1 H, μ-H, *J*(RhH) 11.5, *J*(PtH) 426]; ^{13}C-{^{1}H} ($CDCl_3$, 25 °C), δ 235.5 [t, μ-CO, *J*(RhC) 39, *J*(PtC) 49], 187.5 (br, PtCO), 134.9—129.0 (Ph), 105.5 [d, C_5Me_5, *J*(RhC) 5], and 9.0 p.p.m. ($C_5\mathit{Me}_5$); ^{31}P-{^{1}H} ($CDCl_3$, 25 °C), δ 11.1 p.p.m. [t, *J*(RhP) 3, *J*(PtP) 3 266]; ^{31}P-{^{1}H} ($CDCl_3$, −50 °C) δ 11.1 p.p.m. [d, *J*(RhP) 6, *J*(PtP) 3 266].

Crystal Structure Determination of Complex (3).—A suitable crystal of dimensions *ca.* 0.30 × 0.30 × 0.13 mm was mounted under nitrogen in a Lindemann capillary. Intensities were collected at 293 K on a Nicolet *P3m* four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 55°$. Of the total 7 201 independent reflections measured, only 4 901 had $I \geqslant 3.0\sigma(I)$ and these, corrected for Lorentz, polarisation, and *X*-ray absorption effects, were used in the solution and refinement of the structure. The intensities of two check reflections which were measured every 48 reflections showed no significant decay.

Crystal data. $C_{41}H_{46}BF_4O_3PPtRh_2$, $M = 1\,105.1$, Orthorhombic, $a = 21.503(12)$, $b = 23.728(8)$, $c = 15.896(5)$ Å, $U = 8\,111(6)$ Å^3, D_m not measured, $Z = 8$, $D_c = 1.81$ g cm^{-3}, $F(000) = 4\,320$, space group *Pbca* (no. 61), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 43.6 cm^{-1}.

The structure was solved by location of the Pt and Rh atoms from a Patterson synthesis, and all other non-hydrogen atoms by successive electron-density difference syntheses. In the cascade refinement by least squares, all these atoms were allowed anisotropic thermal motion and rigid geometry was not used. Hydrogen atoms were incorporated at calculated positions; all except the hydride were included in riding mode with C–H = 0.96 Å, while the hydride itself was located from potential-energy calculations [17] and kept fixed at that location. Chemically equivalent hydrogen atoms were given a common isotropic thermal parameter. Refinement converged at *R* 0.048 (*R'* 0.050). Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the standard deviation based on counting statistics only; a satisfactory weight analysis was obtained. On the final electron-density difference map the only significant features were maxima *ca.* 1.7 and minima *ca.* −1.5 e Å^{-3} in the neighbourhood of the metal atoms. Scattering factors, and corrections for anomalous dispersion, were taken from ref. 23. All computations were carried out within the laboratory on an 'Eclipse' Data General minicomputer, with the 'SHELXTL' system of programs.[24] Observed and calculated structure factors, hydrogen atom co-ordinates, all thermal parameters, a complete set of bond lengths and angles, and the equations of least-squares planes from which interplanar angles have been calculated are in Supplementary Publication No. SUP 23285 (29 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

REFERENCES

[1] N. M. Boag, M. Green, R. M. Mills, G. N. Pain F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1980, 1171; M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, preceding paper.

[2] A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.

[3] A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29.

[4] W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 334; W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *J. Organomet. Chem.*, 1977, **140**, 73.

[5] W. D. Jones, M. A. White, and R. E. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 6770.

[6] W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; W. A. Herrmann, J. M. Huggins, B. Reiter, and C. Bauer, *J. Organomet. Chem.*, 1981, **214**, C19.

[7] K. H. Theopold and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 2489.

[8] A. D. Clauss, P. A. Dimas, and J. R. Shapley, *J. Organomet. Chem.*, 1980, **201**, C31.

[9] P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 554.

[10] W. A. Herrmann, J. Plank, E. Guggolz, and M. L. Ziegler, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 651; W. A. Herrmann, J. Plank, M. L. Ziegler, and B. Balbach, *J. Am. Chem. Soc.*, 1980, **102**, 5906; W. A. Herrmann, J. Plank, D. Riedel, M. L. Ziegler, K. Weidenhammer, E. Guggolz, and B. Balbach, *ibid.*, 1981, **103**, 63.

[11] L. N. Lewis and K. G. Caulton, *J. Am. Chem. Soc.*, 1981, **20**, 1139.

[12] W. A. Herrmann, J. Plank, and D. Riedel, *J. Organomet. Chem.*, 1980, **190**, C47.

[13] N. M. Boag, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1980, 128.

[14] J. B. Keister, *J. Organomet. Chem.*, 1980, **190**, C36.

[15] K. Whitmire, D. F. Shriver, and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1980, 780 and refs. therein.

[16] M. Green, J. A. K. Howard, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 869.

[17] A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

[18] J. Plank, D. Riedel, and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 937.

[19] L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134, 1274.

[20] N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1337 and refs. therein.

[21] G. M. Dawkins, M. Green, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 41.

[22] D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 1972, **9**, 179.

[23] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[24] G. M. Sheldrick, SHELXTL, a system of crystallographic programs, University of Cambridge, 1976.