Reactions of Metal Carbonyl Cluster Complexes with Multidentate Phosphine Ligands; the Preparation and Thermolysis of Bis(dimethylphosphino)methane Derivatives of $[Ru_3(CO)_{12}]$, and the *X*-Ray Crystal Structure of $[Ru_3(CO)_9(H)(Me_2PCHPMe_2)]$†

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The complexes $[Ru_3(CO)_{10}(dmpm)]$ and $[Ru_3(CO)_8(dmpm)_2]$ [dmpm = bis(dimethylphosphino)-methane] have been prepared by the direct reaction between $[Ru_3(CO)_{12}]$ and dmpm. Both derivatives undergo thermolysis reactions in refluxing benzene in which the methylene group of a dmpm ligand is metallated to yield $[Ru_3(CO)_9(H)(Me_2PCHPMe_2)]$ and $[Ru_3(CO)_7(H)(Me_2PCHPMe_2)(dmpm)]$ respectively. The crystal structure of the former derivative has been determined.

The co-ordination of multidentate ligands to metal cluster complexes has been shown to increase the stability of the metal atom framework of the cluster, and thus provide a means of preventing cluster fragmentation during catalytic reactions.[1–10] Recent studies on the use of tris(diphenylphosphino)methane and bis(diphenylphosphino)methane (dppm), however, have shown that cluster carbonyl derivatives of these stabilising ligands readily undergo thermolysis reactions in which *ortho*-metallation of a phenyl ring and P–Ph bond cleavage are predominant reaction pathways. For example, the thermolysis of $[Ru_3(CO)_{10}(dppm)]$ in refluxing benzene leads to the formation of $[Ru_3(CO)_9\{PhPCH_2P(Ph)C_6H_4\}]$ (**1**),[4] and $[Ru_3(CO)_8(dppm)_2]$ undergoes both P–Ph and P–CH_2 bond cleavage to give the capped phosphinidene complex $[Ru_3(CO)_7(\mu_3\text{-}PPh)(\mu\text{-}CHPPh_2)(dppm)]$ (**2**).[9] Thus, while the nuclearity of the cluster is preserved, the creation of a vacant co-ordination site on these clusters by loss of a carbonyl ligand on heating leads to attack on the co-ordinated phosphine ligand. With this in mind, we have investigated the thermolysis reactions of the analogous complexes containing the ligand bis(dimethylphosphino)methane (dmpm), in order to determine whether this ligand would lead to a greater thermal stability of the metal cluster.

Results and Discussion

Treatment of a thf solution of $[Ru_3(CO)_{12}]$ with one equivalent of dmpm leads to the formation of $[Ru_3(CO)_{10}(dmpm)]$ in good yield. The i.r., ^1H and ^{31}P n.m.r. spectroscopic data of this complex (Table 1) are consistent with a structure analogous to that found for $[Ru_3(CO)_{10}(dppm)]$,[10] in which the bidentate phosphine ligand bridges one Ru–Ru bond, the phosphine groups occupying equatorial co-ordination sites. Treatment of a benzene solution of $[Ru_3(CO)_{10}(dmpm)]$ with one equivalent of dmpm gives the complex $[Ru_3(CO)_8(dmpm)_2]$. Again, the spectroscopic data for this complex (Table 1) are in agreement with a structure in which the two dmpm ligands bridge different Ru–Ru bonds with the phosphine groups all occupying equatorial co-ordination sites, as found in the analogous complex $[Ru_3(CO)_8(dppm)_2]$.[11]

The thermolysis of $[Ru_3(CO)_{10}(dmpm)]$ in refluxing benzene proceeds smoothly to give a high yield of an orange-red product which has been characterised both spectroscopically (Table 1) and by an *X*-ray crystal structure determination as the metallated derivative $[Ru_3(CO)_9(H)(Me_2PCHPMe_2)]$ (**3**). Under similar reaction conditions, $[Ru_3(CO)_8(dmpm)_2]$ is converted at a faster rate to the metallated complex $[Ru_3(CO)_7(H)(Me_2PCHPMe_2)(dmpm)]$ (**4**). For both complexes (**3**) and (**4**) the site of metallation is characterised as being at the methylene group of the dmpm ligand by the ^1H n.m.r. spectra (Table 1) which show a high-field shift of the remaining methylene hydrogen [to δ 1.40 in (**3**) and to δ 1.49 in (**4**)]. Such shifts have previously been observed in the analogous complex $[Fe_2(CO)_6(H)(Ph_2PCHPPh_2)]$.[12] The presence of the hydride ligands in complexes (**3**) and (**4**) is established by the high-field resonances at δ −17.41 and −16.21, respectively, in the ^1H n.m.r. spectra. Since a full structural characterisation of (**3**) could not be obtained from the spectroscopic data, the structure of this complex was determined by *X*-ray diffraction methods.

The structure of complex (**3**) is shown in the Figure. Selected bond lengths and angles are given in Table 2, atom co-ordinates in Table 3. In complex (**3**), the diphosphine ligand bridges a Ru–Ru edge and the methylene carbon atom is co-ordinated to the remaining Ru atom. This metallation of the methylene carbon atom requires that the diphosphine occupies axial co-ordination sites. The hydride ligand, located directly from the electron-density map, bridges the same metal–metal edge as the diphosphine ligand, as expected from the ^1H n.m.r. spectrum of this complex. The small size of the metallated diphosphine ligands leads to considerable distortions in both the metal–ligand and metal–metal framework. Thus, although the two phosphorus atoms P(1) and P(2) are essentially perpendicular to the Ru(2)–Ru(3) edge [P(1)–Ru(2)–Ru(3) 89.3, P(2)–Ru(3)–Ru(2) 88.5°], they are pulled over towards Ru(1) [P(1)–Ru(2)–Ru(1) 70.0, P(2)–Ru(3)–Ru(1) 70.7°] by the requirements of the Ru(1)–C(10) bond. This distortion also causes an opposite swing in the two axial carbonyls *trans* to P(1) and P(2) [Ru(1)–Ru(2)–C(5) 100.7, Ru(1)–Ru(3)–C(7) 100.3°]. Also, the metal triangle is significantly distorted so that Ru(1) is drawn in towards the Ru(2)–Ru(3) edge, presumably again due to the requirements of the Ru(1)–C(10) bond. This distortion is demonstrated by the large bond angle at Ru(1) [Ru(2)–Ru(1)–Ru(3) 66.9°] while the corresponding angles at Ru(2) and Ru(3)

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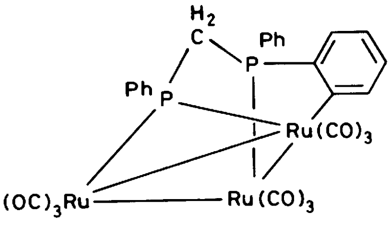
† μ_3-[Bis(dimethylphosphino)methyl-*P*(Ru^1)*P′*(Ru^2)*C*(Ru^3)]-1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2-μ-hydrido-*triangulo*-triruthenium.

Supplementary data available (No. SUP 56655, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc, Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

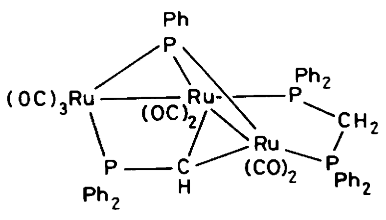
Table 1. Spectroscopic data for $[Ru_3(CO)_{10}(dmpm)]$, $[Ru_3(CO)_8(dmpm)_2]$, and complexes (**3**) and (**4**)

Complex	I.r.[a] (ν_{CO}/cm^{-1})	^1H N.m.r.[b] (δ/p.p.m.)	^{31}P N.m.r.[c] (δ/p.p.m.)
$[Ru_3(CO)_{10}(dmpm)]$	2 078m, 2 015 (sh), 2 004vs, 1 991vs, 1 949m	3.09 [t, CH_2, *J*(PH) 10.7], 1.5—1.7 (m, PCH_3)	−13.1 (s)
$[Ru_3(CO)_8(dmpm)_2]$	2 029m, 1 949vs, 1 923(sh), 1 878w	2.83 [t, CH_2, *J*(PH) 9.8], 1.4—1.7 (m, PCH_3)	AA′BB′ spectrum centred at −8.7
(**3**)	2 077s, 2 044s, 2 017vs, 1 995w, 1 979m, 1 938w	−17.41 [td, Ru–H, ^2J(PH) 13.4, ^4J(HH) 3.9], 1.40 [td, CH, ^2J(PH) 7.8, ^4J(HH) 3.9], 1.5—1.9 (m, PCH_3)	−14.1 (s)
(**4**)	2 012m, 1 975vs, 1 967vs, 1 920s	−16.21 [qnt, Ru-H, ^2J(PH) 12.3], 1.49 (m, CH), 2.92 (m, CH_2), 3.27 (m, CH_2), 1.3—1.8 (m, PCH_3)	−7.7 (m)

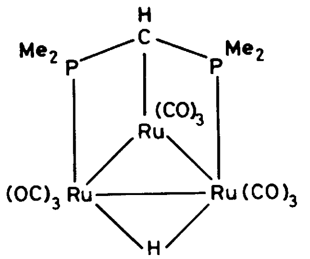
[a] CH_2Cl_2 Solvent. [b] CD_2Cl_2 Solvent; m = multiplet, s = singlet, d = doublet, t = triplet, qnt = quintet; coupling constants in Hz. [c] CD_2Cl_2 Solvent, chemical shifts with respect to 85% H_3PO_4.



(**1**)



(**2**)



(**3**)

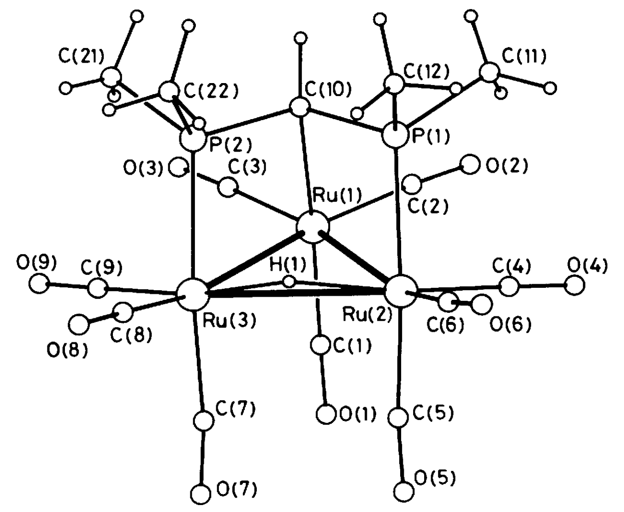


Figure. Molecular structure of $[\overline{Ru_3(CO)_9(H)(Me_2PCHPMe_2)}]$ (**3**)

are significantly more acute [Ru(1)–Ru(2)–Ru(3) 56.4, Ru(1)–Ru(3)–Ru(2) 56.6°].

It is noteworthy that the distortions imposed by the requirements of the metallated diphosphine ligand cause both P(1) and P(2) to come reasonably close to Ru(1) [Ru(1) ··· P(1) 2.985(1), Ru(1) ··· P(2) 3.003(1) Å]. It may be that the electron imbalance of the molecule [Ru(1) is electron deficient while Ru(2) and Ru(3) are electron rich] is partly corrected by some interaction of Ru(1) with P(1) and P(2), in a similar manner to that commonly observed in complexes containing semi-bridging carbonyl ligands. All the Ru–C–O angles in complex (**3**) are approximately linear (173—179°).

The ^{31}P n.m.r. spectroscopic data for complex (**4**) (Table 1) suggest that the four phosphorus atoms are in similar chemical environments, which leads us to suggest that all the phosphine groups are co-ordinated at axial sites, and are bridging the same Ru–Ru edge of the Ru_3 triangle. Other arrangements of the two bidentate ligands would lead to ^{31}P n.m.r. chemical shift differences either due to axial–equatorial site inequivalance, or due to co-ordination of two phosphine groups to a single Ru atom. The ^1H n.m.r. data for complex (**4**) (Table 1) show that only one dmpm ligand has metallated at the central methylene carbon atom (giving a CH resonance at δ 1.49 p.p.m.), while the second dmpm ligand remains intact. We therefore propose the structure shown for complex (**4**).*

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* The structure of complex (**4**) has been confirmed by a preliminary *X*-ray crystal structure analysis. However, disorder problems have precluded a satisfactory refinement of the structure.

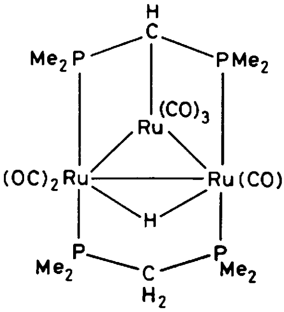
Table 2. Selected bond lengths (Å) and angles (°) for $[Ru_3(CO)_9(H)(Me_2PCHPMe_2)]$ (**3**)

Ru(1)–Ru(2)	2.812(1)	Ru(1)–C(1)	1.910(5)	Ru(1)···P(1)	2.985(1)	Ru(2)–C(6)	1.923(6)
Ru(1)–Ru(3)	2.804(1)	Ru(1)–C(2)	1.896(5)	Ru(1)···P(2)	3.003(1)	Ru(3)–C(7)	1.940(5)
Ru(2)–Ru(3)	3.097(1)	Ru(1)–C(3)	1.885(5)	Ru(2)–H(1)	1.816(55)	Ru(3)–C(8)	1.935(5)
Ru(1)–C(10)	2.266(4)	Ru(2)–C(4)	1.880(6)	Ru(3)–H(1)	1.850(60)	Ru(3)–C(9)	1.878(5)
Ru(2)–P(1)	2.351(1)	Ru(2)–C(5)	1.939(5)	P(1)–C(10)	1.767(5)	P(2)–C(10)	1.778(5)
Ru(3)–P(2)	2.348(1)						

Ru(2)–Ru(1)–Ru(3)	66.9(1)	Ru(1)–Ru(2)–P(1)	70.0(1)	Ru(2)–Ru(3)–P(2)	88.5(1)	Ru(2)–C(3)–O(3)	175.4(4)
Ru(1)–Ru(2)–Ru(3)	56.4(1)	Ru(3)–Ru(2)–P(1)	89.3(1)	Ru(1)–Ru(3)–C(7)	100.3(1)	Ru(2)–C(4)–O(4)	178.6(5)
Ru(1)–Ru(3)–Ru(2)	56.6(1)	Ru(1)–Ru(2)–C(5)	100.7(2)	Ru(2)–Ru(3)–C(7)	87.8(1)	Ru(2)–C(5)–O(5)	174.1(5)
Ru(2)–Ru(1)–C(10)	79.5(1)	Ru(3)–Ru(2)–C(5)	86.4(2)	P(2)–Ru(3)–C(7)	170.8(1)	Ru(2)–C(6)–O(6)	175.4(5)
Ru(3)–Ru(1)–C(10)	79.8(1)	P(1)–Ru(2)–C(4)	90.0(2)	P(2)–Ru(3)–C(8)	95.7(1)	Ru(3)–C(7)–O(7)	172.9(4)
C(10)–Ru(1)–C(1)	164.1(2)	P(1)–Ru(2)–C(5)	170.6(2)	P(2)–Ru(3)–C(9)	88.9(1)	Ru(3)–C(8)–O(8)	177.0(5)
C(10)–Ru(1)–C(2)	97.0(2)	P(1)–Ru(2)–C(6)	94.3(2)	Ru(1)–C(1)–O(1)	178.2(4)	Ru(3)–C(9)–O(9)	178.9(4)
C(10)–Ru(1)–C(3)	96.0(2)			Ru(1)–C(2)–O(2)	174.1(5)	P(1)–C(10)–P(2)	116.0(2)
Ru(1)–Ru(3)–P(2)	70.7(1)						

Table 3. Fractional atomic co-ordinates with standard deviations in parentheses for $[Ru_3(CO)_9(H)(Me_2PCHPMe_2)]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.139 1(0)	0.234 2(0)	−0.062 1(0)	C(9)	0.115 8(4)	0.350 8(3)	0.202 1(4)
Ru(2)	0.335 0(0)	0.173 8(0)	0.008 7(0)	O(9)	0.043 0(3)	0.380 7(2)	0.221 8(4)
Ru(3)	0.236 8(0)	0.303 7(0)	0.170 5(0)	H(1)	0.352 3(43)	0.262 3(35)	0.119 7(52)
P(1)	0.330 3(1)	0.273 8(1)	−0.158 0(1)	C(10)	0.226 8(3)	0.338 2(3)	−0.141 2(4)
P(2)	0.238 7(1)	0.400 9(1)	0.001 5(1)	H(101)	0.198 6(38)	0.371 6(33)	−0.228 6(46)
C(1)	0.097 1(4)	0.145 6(3)	0.040 6(4)	C(11)	0.307 0(5)	0.237 7(4)	−0.326 3(6)
O(1)	0.070 2(3)	0.092 1(3)	0.099 1(4)	H(111)	0.261 1(35)	0.206 0(28)	−0.334 4(39)
C(2)	0.099 4(4)	0.177 5(3)	−0.221 6(5)	H(112)	0.305 9(49)	0.286 2(42)	−0.371 2(62)
O(2)	0.069 3(3)	0.140 0(3)	−0.312 6(4)	H(113)	0.361 3(47)	0.194 6(38)	−0.340 0(54)
C(3)	0.017 8(4)	0.294 0(3)	−0.076 0(4)	C(12)	0.445 3(5)	0.333 0(4)	−0.161 9(7)
O(3)	−0.059 1(3)	0.325 2(3)	−0.084 2(4)	H(121)	0.477 7(38)	0.351 1(31)	−0.083 4(48)
C(4)	0.301 6(5)	0.088 8(4)	−0.115 6(5)	H(122)	0.417 7(51)	0.380 7(43)	−0.233 3(62)
O(4)	0.281 5(4)	0.036 2(3)	−0.188 8(4)	H(123)	0.480 4(61)	0.287 9(50)	−0.194 7(71)
C(5)	0.315 3(4)	0.092 7(3)	0.141 1(5)	C(21)	0.136 9(4)	0.476 4(4)	−0.030 0(5)
O(5)	0.308 0(4)	0.040 6(3)	0.212 8(4)	H(211)	0.081 1(38)	0.449 1(31)	−0.035 7(42)
C(6)	0.478 3(4)	0.165 0(4)	0.037 2(5)	H(212)	0.143 1(58)	0.494 7(50)	−0.117 1(73)
O(6)	0.562 8(3)	0.157 9(4)	0.045 7(5)	H(213)	0.154 7(53)	0.508 1(46)	0.036 4(63)
C(7)	0.220 0(4)	0.213 5(3)	0.290 4(4)	C(22)	0.344 7(4)	0.472 5(4)	0.020 5(6)
O(7)	0.206 7(3)	0.167 0(2)	0.368 1(4)	H(221)	0.405 1(41)	0.446 4(34)	0.049 2(47)
C(8)	0.327 2(4)	0.365 9(3)	0.298 1(5)	H(222)	0.331 8(41)	0.507 5(37)	0.094 0(53)
O(8)	0.376 4(4)	0.402 2(3)	0.375 2(4)	H(223)	0.348 1(43)	0.499 6(37)	−0.066 5(52)



(**4**)

Further studies are in progress to determine whether thermal activation of these dmpm derivatives in the presence of other reactive substrates can lead to further differences in the chemistry in comparison to that observed for the dppm derivatives.

Experimental

Reactions were carried out under a dry oxygen-free atmosphere. All solvents were dried and degassed before use. Infrared spectra were recorded for CH_2Cl_2 solutions in 0.5-mm NaCl cells on a Perkin-Elmer 681 spectrometer. The n.m.r. measurements were made with Bruker WM250 or JEOL 90Q instruments using CD_2Cl_2 solutions. The complex $[Ru_3(CO)_{12}]$ was prepared by a published procedure,[13] and dmpm was used as received from Strem Chemicals. Microanalyses were carried out by Elemental Microanalysis Ltd. (Devon).

Preparation of $[Ru_3(CO)_{10}(dmpm)]$.—The ligand dmpm (0.196 g, 1.44 mmol) in tetrahydrofuran (thf) (20 cm^3) was added dropwise over 30 min to a warmed (45 °C) and stirred solution of $[Ru_3(CO)_{12}]$ (0.915 g, 1.43 mmol) in thf (60 cm^3). Stirring was continued for a further 30 min and the resultant red solution was evaporated to dryness *in vacuo*. The red solid was recrystallised from cold acetone–ethanol to give red crystals of $[Ru_3(CO)_{10}(dmpm)]$ (0.792 g, 77%) (Found: C, 25.3; H, 2.15; P, 8.00. $C_{15}H_{14}O_{10}P_2Ru_3$ requires C, 25.05; H, 1.95; P, 8.60%).

Preparation of $[Ru_3(CO)_8(dmpm)_2]$.—The ligand dmpm (0.139 g, 1.02 mmol) in benzene (20 cm^3) was added dropwise over 30 min, with stirring, to a heated (60 °C) solution of $[Ru_3(CO)_{10}(dmpm)]$ (0.689 g, 0.958 mmol) in benzene (40 cm^3). Infrared monitoring showed the reaction to be complete after a further 1 h at 60 °C. The resultant deep red solution was evaporated to dryness *in vacuo*. Recrystallisation of the resultant red solid from CH_2Cl_2–heptane gave orange crystals of $[Ru_3(CO)_8(dmpm)_2]$ (0.498 g, 65%) (Found: C, 27.1; H, 3.50; P, 15.65. $C_{18}H_{28}O_8P_4Ru_3$ requires C, 27.05; H, 3.55; P, 15.50%).

Thermolysis of $[Ru_3(CO)_{10}(dmpm)]$.—$[Ru_3(CO)_{10}(dmpm)]$ (0.250 g) in benzene (40 cm^3) was heated under reflux for 50 h. The resulting red solution was distilled to dryness *in vacuo*. The red solid thus obtained was recrystallised from cold acetone–ethanol to give orange crystals of $[Ru_3(CO)_9(H)(Me_2PCH\text{-}PMe_2)]$ (3) (0.196 g, 82%) (Found: C, 24.45; H, 2.05; P, 9.30. $C_{14}H_{14}O_9P_2Ru_3$ requires C, 24.3; H, 2.05; P, 8.95%).

Thermolysis of $[Ru_3(CO)_8(dmpm)_2]$.—$[Ru_3(CO)_8(dmpm)_2]$ (0.320 g) in benzene (40 cm^3) was heated under reflux for 5 h. The resulting deep red solution was evaporated to dryness *in vacuo*, to give a red solid. This solid was recrystallised from cold acetone–ethanol to give red needle-shaped crystals of $[Ru_3(CO)_7(H)(Me_2PCHPMe_2)(dmpm)]$ (4) (0.264 g, 86%) (Found: C, 26.9: H, 3.75; P, 16.15. $C_{17}H_{28}O_7P_4Ru_3$ requires C, 26.45; H, 3.65; P, 16.05%).

Crystal Structure Determination of $[Ru_3(CO)_9(H)(Me_2PCH\text{-}PMe_2)]$ (3).—Orange crystals of the complex (3) were grown from acetone–ethanol. The crystal chosen for study had dimensions *ca.* 0.25 × 0.3 × 0.5 mm. Intensity data were recorded on a Nonius CAD4 diffractometer, and were corrected for absorption empirically (transmission factors 1.000—0.613).

Crystal data. $C_{14}H_{14}O_9P_2Ru_3$, $M = 691$, monoclinic, $a = 13.549(1)$, $b = 15.909(2)$, $c = 10.432(2)$ Å, $\beta = 98.944(12)°$, $U = 2\,221$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $D_m = 2.23$ g cm^{-3}, $Z = 4$, $D_c = 2.07$ g cm^{-3}, μ(Mo-K_α) = 21.6 cm^{-1}.

For the structure solution and refinement, 3 281 independent reflections ($1.5 \leqslant \theta \leqslant 25.0$) with $F_o > 4\sigma(F_o)$ were used. The structure was solved by Patterson and Fourier methods (using the program SHELX[14]) and was refined by least-squares methods, with anisotropic thermal parameters for ruthenium, phosphorus, and carbonyl carbon and oxygen atoms. The methyl hydrogen atoms were included at calculated positions (C–H 1.080 Å). A peak of 0.8 e Å^{-3} appeared at 1.85 Å from Ru(2) and Ru(3) and was assumed to be the hydride, H(1). The highest peaks in the final electron-density difference map were 0.7 e Å^{-3} from the Ru atoms, and 0.5 e Å^{-3} elsewhere. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,15(F_o{}^2)]$ gave satisfactory agreement analyses. Final R and R' values were 0.029 and 0.037 $\{R = \Sigma|F_o - F_c|/\Sigma(F_o),\ R' = [\Sigma(F_o - F_c)^2w/\Sigma F_o{}^2w]^{\frac{1}{2}}\}$.

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