The Triruthenium Cluster Anion $[Ru_3H(CO)_{11}]^-$: † Preparation, Structure, and Fluxionality

By **Brian F. G. Johnson, Jack Lewis,* Paul R. Raithby,** and **Georg Süss,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The cluster anion $[Ru_3H(CO)_{11}]^-$ has been prepared in high yields by the reaction of $[Ru_3(CO)_{12}]$ with $Na[BH_4]$ in tetrahydrofuran. The anion is isolated as the tetraethylammonium and the bis(triphenylphosphine)iminium salts. The salt $[N(PPh_3)_2][Ru_3H(CO)_{11}]$ crystallizes in the monoclinic space group $P2_1/c$, with the cell dimensions a = 16.355(5), b = 17.057(4), c = 17.715(5) Å, β = 106.29(2)°, and Z = 4. The structure has been solved by a combination of multisolution sign-expansion and Fourier-difference methods, and refined to R 0.053 for 4 341 observed intensities. The three ruthenium atoms define an isosceles triangle, the shortest edge of which is symmetrically bridged by a carbonyl group and a hydride ligand. A variable-temperature ^{13}C n.m.r. study of $[NEt_4][Ru_3H(CO)_{11}]$ reveals the anion to be fluxional in solution; the spectra are indicative of several dynamic processes occurring over the range −116 to 32 °C which are distinctly different from those proposed for the iron analogue $[Fe_3H(CO)_{11}]^-$.

THE anion $[Fe_3H(CO)_{11}]^-$ has been known for more than 20 years[1] and has been extensively studied;[2-5] however, there has been only a brief report of the formation of the ruthenium analogue $[Ru_3H(CO)_{11}]^-$, and the salt $[NEt_4][Ru_3H(CO)_{11}]$ was not isolated in a pure form and was ill characterized.[6] In this paper we report a method of preparation giving high yields of $[Ru_3H(CO)_{11}]^-$, a single-crystal X-ray analysis of the bis(triphenylphosphine)iminium salt, and an investigation of the fluxional properties of the anion.

RESULTS AND DISCUSSION

Preparation and Characterization.—Dodecacarbonyltriruthenium, $[Ru_3(CO)_{12}]$, reacts in tetrahydrofuran (thf) with sodium tetrahydroborate, $Na[BH_4]$, at room temperature within 20 min to yield almost quantitatively the hydrido-anion $[Ru_3H(CO)_{11}]^-$. This anionic cluster can be isolated preferably as the tetraethylammonium salt $[NEt_4][Ru_3H(CO)_{11}]$ which crystallizes from methanol. The reaction solution also contains a very small amount of an ionic product which seems to be identical with a compound previously described as $[Ru_6(CO)_{18}]^{2-}$.[7]

$$[Ru_3(CO)_{12}] + Na[BH_4] \xrightarrow[25^{\circ}C]{thf} Na[Ru_3H(CO)_{11}] + CO + 0.5B_2H_6$$

The recently reported[8] formation of a series of neutral ruthenium clusters in very low yields as products of the reaction of $[Ru_3(CO)_{12}]$ and $Na[BH_4]$ in refluxing thf can be considered as the decomposition of the air-sensitive salt $Na[Ru_3H(CO)_{11}]$ under the reaction conditions.

The salt $[NEt_4][Ru_3H(CO)_{11}]$ is obtained as deep red crystals which are slightly air-sensitive and decompose under nitrogen rather indistinctly over the range 325—330 °C. The i.r. and ^1H Fourier-transform n.m.r. spectroscopic data are presented in Tables 1 and 2, respectively [data for the initially formed sodium salt and for the bis(triphenylphosphine)iminium salt also being included]. The i.r. spectrum has only one broad carbonyl band at significantly lower wavenumber than the other four absorptions in the carbonyl region, indicative of a CO bridge besides terminal carbonyl groups. The single high-field resonance in the ^1H n.m.r. spectrum can be ascribed to a bridging hydride.

A comparison of the i.r. spectra of $[NEt_4][Ru_3H(CO)_{11}]$ with those of the corresponding sodium and bis(triphenylphosphine)iminium salts shows that there is a remarkable dependence of the position of the carbonyl-bridge frequency upon the nature of the counter ion and the solvent. Similar observations have been reported for $[Fe_3H(CO)_{11}]^-$,[5] and these have been attributed to interactions between the carbonyl bridge of the cluster anion and the cation in solution, depending on the polarity of the solvent.

X-Ray Structural Analysis.—In the solid state, the overall molecular geometry of the $[Ru_3H(CO)_{11}]^-$ anion (Figure 1) is the same as that reported for $[Fe_3H(CO)_{11}]^-$.[3] The three ruthenium atoms define an isosceles triangle

TABLE 1

Carbonyl stretching frequencies of $[Ru_3H(CO)_{11}]^-$ salts

Cation	Solvent	ν(CO) terminal (cm⁻¹)	ν(CO) bridge (cm⁻¹)
$[NEt_4]^+$	CH_3CN	2 075vw, 2 018vs, 1 985s, 1 945m	1 702w
	CH_2Cl_2	2 073vw, 2 014vs, 1 984s, 1 950m	1 691w
$[Na]^+$	CH_3CN	2 075vw, 2 016vs, 1 985s, 1 950m	1 706w
	CH_2Cl_2	2 077vw, 2 017vs, 1 986s, 1 954m	1 646w
$[N(PPh_3)_2]^+$	CH_3CN	2 073vw, 2 015vs, 1 985s, 1 954m	1 713w
	CH_2Cl_2	2 073vw, 2 014vs, 1 985s, 1 952m	1 698w

TABLE 2

^1H F.T. n.m.r. data of $[Ru_3H(CO)_{11}]^-$ salts

Cation	Solvent	^1H resonances (p.p.m.)
$[NEt_4]^+$	CD_3CN	δ(CH_2) 3.14(Q); δ(CH_3) 1.35(T); δ(Ru_2H) −12.76(S)
$[Na]^+$	CD_3CN	δ(Ru_2H) −13.93(S)
$[N(PPh_3)_2]^+$	CD_3CN	δ(C_6H_5) 7.51(M); δ(Ru_2H) −12.62(S)

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† 1,2-μ-Carbonyl-1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-hydrido-*triangulo*-triruthenate(1−).

the shorter edge of which is bridged by a carbonyl group and a hydride. These two ligands lie on opposite sides of the metal triangle, and the Ru(1)Ru(2)H(1) and the Ru(1)Ru(2)C(1)O(1) planes, respectively, make angles of 69.1 and 104.4° with the Ru_3 plane. Atoms Ru(1) and Ru(2) are each co-ordinated to three terminal carbonyl groups, while Ru(3) has four. The molecule has $C_s(m)$ pseudo-symmetry, which is obeyed exactly to within the estimated standard deviations. An approximate mirror plane passes through Ru(3), C(10), O(10), C(11), O(11), C(1), O(1), and H(1), and bisects the Ru(1)–Ru(2) vector. Some interatomic distances and bond angles are given in Tables 3 and 4, respectively.

The two longer Ru–Ru distances are *ca.* 0.01 Å shorter than the mean distance of 2.854 Å in $[Ru_3(CO)_{12}]$.[9] The dibridged metal–metal distance is reduced by a further 0.029 Å. There is substantial evidence that the presence of an unsupported μ_2-hydride causes the metal–metal distance to lengthen, while a μ_2-hydride supported by another bridging ligand may result in a lengthening or shortening effect depending on the nature of the other ligand.[10] A comparison with the bridged (mean 2.801 Å) and unbridged (mean 2.828 Å) Ru–Ru distances in $[Ru_3H(CO)_{10}(CNMe_2)]$,[10] where the ligand polyhedron is similar, shows a reduction of 0.027 Å in the dibridged metal–metal length. So both a μ_2-CO and a μ_2-$CNMe_2$ ligand have a similar bond-shortening effect which more than counterbalances the lengthening effect of the μ_2-hydride.

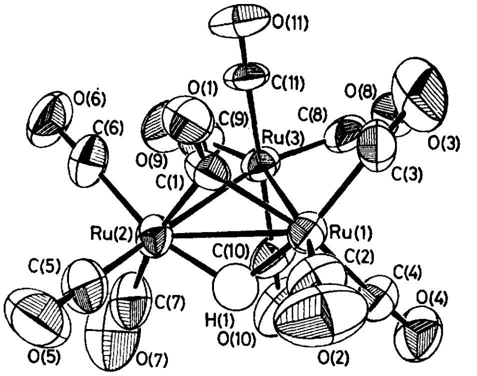


FIGURE 1 The $[Ru_3H(CO)_{11}]^-$ anion. The thermal ellipsoids enclose 50% electron probability

TABLE 3

Bond lengths (Å)

Ru(2)–Ru(1)	2.815(2)	C(1)–Ru(1)	2.073(10)
Ru(3)–Ru(1)	2.845(3)	C(2)–Ru(1)	1.898(15)
Ru(3)–Ru(2)	2.843(2)	C(3)–Ru(1)	1.891(12)
H(1)–Ru(1)	1.720(90)	C(4)–Ru(1)	1.951(13)
H(1)–Ru(2)	1.655(99)	C(1)–Ru(2)	2.066(10)
O(1)–C(1)	1.180(12)	C(5)–Ru(2)	1.867(14)
O(2)–C(2)	1.143(20)	C(6)–Ru(2)	1.909(18)
O(3)–C(3)	1.137(16)	C(7)–Ru(2)	1.972(10)
O(4)–C(4)	1.138(16)	C(8)–Ru(3)	1.919(13)
O(5)–C(5)	1.155(17)	C(9)–Ru(3)	1.902(15)
O(6)–C(6)	1.127(19)	C(10)–Ru(3)	1.919(14)
O(7)–C(7)	1.133(13)	C(11)–Ru(3)	1.946(11)
O(8)–C(8)	1.147(17)	O(10)–C(10)	1.140(17)
O(9)–C(9)	1.160(19)	O(11)–C(11)	1.126(15)
P(1)–N(1)	1.574(8)	P(2)–N(1)	1.584(7)
C(101)–P(1)	1.797(7)	C(201)–P(2)	1.796(7)
C(111)–P(1)	1.802(6)	C(211)–P(2)	1.795(8)
C(121)–P(1)	1.789(8)	C(221)–P(2)	1.803(6)

TABLE 4

Bond angles (°)

Ru(3)–Ru(1)–Ru(2)	60.3(1)	C(1)–Ru(1)–Ru(2)	47.0(3)
Ru(3)–Ru(2)–Ru(1)	60.4(1)	C(1)–Ru(1)–Ru(3)	78.7(3)
Ru(2)–Ru(3)–Ru(1)	59.3(1)	C(2)–Ru(1)–Ru(2)	108.0(4)
C(2)–Ru(1)–C(1)	88.7(5)	C(2)–Ru(1)–Ru(3)	166.8(4)
C(3)–Ru(1)–C(1)	94.8(5)	C(3)–Ru(1)–Ru(2)	132.5(4)
C(3)–Ru(1)–C(2)	95.6(6)	C(3)–Ru(1)–Ru(3)	89.4(4)
C(4)–Ru(1)–C(1)	166.9(4)	C(4)–Ru(1)–Ru(2)	119.8(3)
C(4)–Ru(1)–C(2)	97.3(6)	C(4)–Ru(1)–Ru(3)	94.3(5)
C(4)–Ru(1)–C(3)	96.2(5)	C(1)–Ru(2)–Ru(1)	47.3(3)
C(5)–Ru(2)–C(1)	87.6(5)	C(1)–Ru(2)–Ru(3)	78.8(3)
C(6)–Ru(2)–C(1)	93.9(5)	C(5)–Ru(2)–Ru(1)	106.9(4)
C(6)–Ru(2)–C(5)	95.9(6)	C(5)–Ru(2)–Ru(3)	165.7(4)
C(7)–Ru(2)–C(1)	164.7(4)	C(6)–Ru(2)–Ru(1)	132.1(4)
C(7)–Ru(2)–C(5)	100.4(5)	C(6)–Ru(2)–Ru(3)	89.5(4)
C(7)–Ru(2)–C(6)	98.2(5)	C(7)–Ru(2)–Ru(1)	117.5(3)
C(9)–Ru(3)–C(8)	104.8(6)	C(7)–Ru(2)–Ru(3)	91.9(3)
C(10)–Ru(3)–C(8)	95.4(6)	C(8)–Ru(3)–Ru(1)	96.4(5)
C(10)–Ru(3)–C(9)	94.3(6)	C(8)–Ru(3)–Ru(2)	155.7(5)
C(11)–Ru(3)–C(8)	93.1(5)	C(9)–Ru(3)–Ru(1)	158.7(4)
C(11)–Ru(3)–C(9)	91.2(5)	C(9)–Ru(3)–Ru(2)	99.5(4)
C(11)–Ru(3)–C(10)	168.4(6)	C(10)–Ru(3)–Ru(1)	82.4(4)
H(1)–Ru(1)–C(1)	75.9(30)	C(10)–Ru(3)–Ru(2)	83.3(4)
H(1)–Ru(1)–C(2)	97.7(38)	C(11)–Ru(3)–Ru(1)	88.8(4)
H(1)–Ru(1)–C(3)	163.5(41)	C(11)–Ru(3)–Ru(2)	85.7(3)
H(1)–Ru(1)–C(4)	91.7(30)	H(1)–Ru(1)–Ru(2)	32.8(36)
H(1)–Ru(2)–C(1)	77.4(30)	H(1)–Ru(1)–Ru(3)	75.6(39)
H(1)–Ru(2)–C(5)	96.4(37)	H(1)–Ru(2)–Ru(1)	34.2(38)
H(1)–Ru(2)–C(6)	164.6(38)	H(1)–Ru(2)–Ru(3)	76.4(38)
H(1)–Ru(2)–C(7)	88.6(30)	Ru(2)–C(1)–Ru(1)	85.7(8)
Ru(2)–H(1)–Ru(1)	113.0(62)	O(1)–C(1)–Ru(1)	136.3(8)
O(2)–C(2)–Ru(1)	177.1(13)	O(1)–C(1)–Ru(2)	137.7(8)
O(4)–C(4)–Ru(1)	173.1(11)	O(3)–C(3)–Ru(1)	178.2(12)
O(6)–C(6)–Ru(2)	178.7(13)	O(5)–C(5)–Ru(2)	176.8(11)
O(8)–C(8)–Ru(3)	178.7(11)	O(7)–C(7)–Ru(2)	176.2(9)
O(9)–C(9)–Ru(3)	177.9(12)	O(10)–C(10)–Ru(3)	178.1(14)
O(11)–C(11)–Ru(3)	177.3(12)	P(2)–N(1)–P(1)	139.7(6)
C(201)–P(1)–N(1)	106.2(8)	C(101)–P(1)–N(1)	109.0(4)
C(211)–P(2)–N(1)	115.1(8)	C(111)–P(1)–N(1)	108.5(3)
C(211)–P(2)–C(201)	106.7(3)	C(111)–P(1)–C(101)	107.8(3)
C(221)–P(2)–N(1)	112.0(3)	C(121)–P(1)–N(1)	114.4(4)
C(221)–P(2)–C(201)	107.5(3)	C(121)–P(1)–C(101)	108.5(3)
C(221)–P(2)–C(211)	109.0(3)	C(121)–P(1)–C(111)	108.5(4)
C(202)–C(201)–P(2)	119.6(4)	C(102)–C(101)–P(1)	122.1(6)
C(206)–C(201)–P(2)	120.4(5)	C(106)–C(101)–P(1)	117.7(4)
C(212)–C(211)–P(2)	121.6(4)	C(112)–C(111)–P(1)	119.6(4)
C(216)–C(211)–P(2)	118.3(6)	C(116)–C(111)–P(1)	120.2(4)
C(222)–C(221)–P(2)	122.1(5)	C(122)–C(121)–P(1)	120.6(4)
C(226)–C(221)–P(2)	117.8(5)	C(126)–C(121)–P(1)	119.1(6)

The ten carbonyls may be divided into four groups. There are four equatorial carbonyls, one associated with each of Ru(1) and Ru(2), and two with Ru(3). There are two truly axial carbonyls bonded to Ru(3), while the four remaining ligands are best considered as lying *trans* to either the hydride or the bridging carbonyl. Although some of the bond-length differences are not statistically significant, the trend is the same as in $[Ru_3(CO)_{12}]$.[9] The axial Ru–C(carbonyl) bonds (mean 1.933 Å) are longer than the equatorial (mean 1.897 Å); the Ru–C–O angles are approximately linear [range 177.1(13)—178.7(11)°]. This result is in agreement with the accepted model for metal–carbonyl bonding, the longer axial lengths being due to the competition for d_π electron density between mutually *trans* carbonyl groups. The Ru(1)–C(4) and Ru(2)–C(7) distances, those *trans* to the

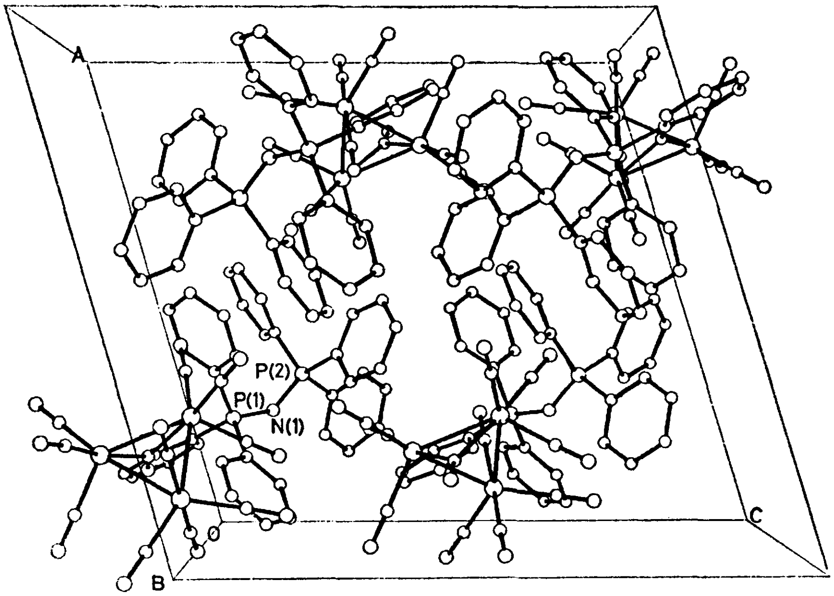


FIGURE 2 The unit-cell contents viewed down the *b* axis. Hydrogen atoms have been omitted for clarity

bridging carbonyl, average 1.962 Å while the metal–carbon distances in the carbonyls *trans* to the bridging hydride [Ru(1)–C(3) and Ru(2)–C(6)] average 1.900 Å. This suggests that the bridging carbonyl exerts a much stronger *trans*-lengthening influence than the hydride. The angles at the carbon atoms of the carbonyls *trans* to the hydride are linear (mean 178.5°), but those *trans* to the bridging carbonyl are slightly bent (mean 174.7°). This is presumably due to the short contacts between the C(4) and C(7) atoms and the hydride H(1) (2.639 and 2.544 Å, respectively).

The bridging carbonyl group is symmetrical (mean Ru–C 2.070 Å), which is consistent with equivalent electronic environments at the two ruthenium atoms. The Ru–C distances are slightly shorter than the range of bond lengths [2.073(5)—2.219(6) Å] found in [$Ru_3(CO)_{10}(C_4H_4N_2)$].[11] The C(1)–O(1) distance is 0.02 Å longer than any of the terminal carbonyl C–O distances (mean 1.141 Å), and significantly longer than the value of 1.154 Å for the bridging ligands in the 1,2-diazine complex.[11] This may indicate a localization of anionic charge on O(1), but the whole range of C–O distances [1.126(15)—1.180(12) Å] is only *ca.* 3.2σ. This proposal of localization of charge is in agreement with the observation that methylation of the anion with [OMe_3][BF_4] occurs at the oxygen atom of the bridging carbonyl.[12]

The hydride also bridges the Ru(1)–Ru(2) vector symmetrically to within estimated standard deviations. The mean Ru–H distance of 1.69 Å and Ru–H–Ru angle of 113(6)° are in good agreement with the range of values found in a number of μ_2-bridged triruthenium clusters.[13] The H(1)Ru(1)Ru(2)C(3)C(6) system is approximately planar, the H–Ru–C angles average 164°, and this causes the extensions of the Ru–C(carbonyl) bonds *trans* to the hydride to intersect near the centre of the Ru–H–Ru triangle. Thus the Ru–H–Ru bonds are best considered as ' closed ',[14] and appreciable metal–metal bonding is present.

The dimensions of the cation are similar to those found in a number of other cluster compounds also containing the [$N(PPh_3)_2$]$^+$ ion.[15] The cation is included in Figure

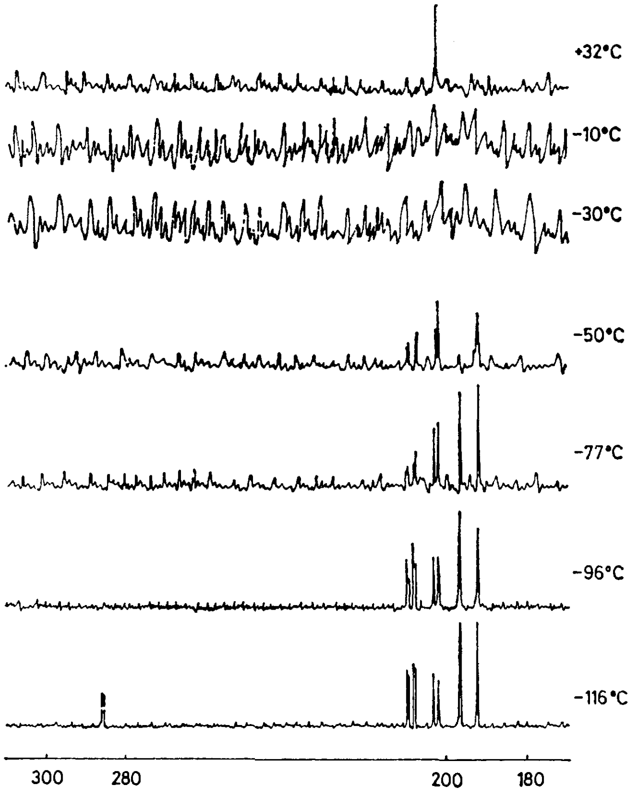


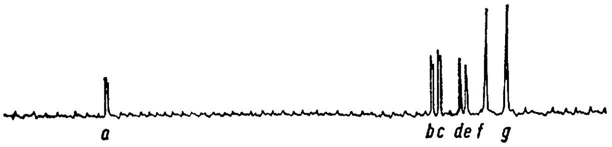
FIGURE 3 Variable-temperature ^{13}C n.m.r. spectra of [$Ru_3H(CO)_{11}$]$^-$

2, a diagram of the unit-cell contents. Cations and anions are separated by normal van der Waals distances, with the shortest intermolecular contact of 2.209 Å between H(204) and O(1′), where O(1′) is generated from O(1) by the transformation $1 - x, \bar{y}, 1 - z$.

Study of Fluxionality.—The fluxional properties of the $[Ru_3H(CO)_{11}]^-$ anion have been studied by variable-temperature ^{13}C n.m.r. spectroscopy. The low-temperature limiting spectrum, reflecting the rigid structure of the molecule corresponding to the structure in the solid state, was obtained at −116 °C. Upon increasing the temperature, subsequent dynamic processes occurred until at 32 °C a single signal indicated complete scrambling of the carbonyl groups (Figure 3).

A comparison of the spectra of $[Ru_3H(CO)_{11}]^-$ with the ^{13}C n.m.r. spectra reported [5] for $[Fe_3H(CO)_{11}]^-$ indicates two major differences. For the iron complex, proton coupling is only observed at the low-temperature limit, and on increasing the temperature the signal corresponding to the CO bridge coalesces with one of the unique terminal carbonyl signals, accompanied by a broadening of all carbon resonances. In contrast, the spectra of the ruthenium anion, over the range −116 to −50 °C, show coalescence between the CO bridge signal and subsequently the signals of equivalent terminal carbonyl groups, whereas the signals of the unique terminal CO ligands are not affected. The remaining signals are not broadened and the ^1H–^{13}C coupling is maintained (Figure 4).

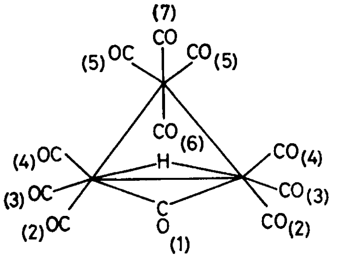
On the grounds of chemical shift, proton coupling, and intensity, the signals (*a*), (*b*), and (*c*) can be assigned unambiguously to carbonyl groups (1), (2), and (3), respectively (Figure 5). The further assignment of (*d*) and (*e*) to (6) and (7), and (*f*) and (*g*) to (4) and (5), is not unequivocal with respect to the sequence given here.



Signal	δ(SiMe$_4$)	Relative intensity	$J(^1H-^{13}C)$/Hz
(*a*)	286.2	1	5.2
(*b*)	209.2	2	7.5
(*c*)	207.6	2	3.8
(*d*)	202.3	1	
(*e*)	201.7	1	
(*f*)	196.7	2	
(*g*)	192.2	2	

FIGURE 4 Limiting ^{13}C n.m.r. spectrum of $[Ru_3H(CO)_{11}]^-$ at −116 °C

On the basis of this assignment a possible interpretation of the variable-temperature measurements, over the range −116 to −50 °C, comprises dynamic exchange processes of bridging and terminal carbonyl groups, whereby the hydride remains unchanged in the bridging position. The first observed coalescence of (*a*) with (*b*) and (*c*) suggests an exchange mechanism between the bridging carbonyl (1) and the terminal groups (2) and (3). The disappearance of signal (*f*) at −50 °C is consistent with the assumption that the sterically hindered carbonyl ligands (4) become involved in a terminal–bridge exchange process at this temperature. The maintenance of the ^1H–^{13}C coupling and the fact that the signals of the carbonyl groups (6) and (7) are not concerned with the first dynamic process exclude a fluxional mechanism involving opening and migration of the hydride bridge as proposed for $[Fe_3H(CO)_{11}]^-$.[5]



Signal	Carbon atom
(*a*)	(1)
(*b*)	(2)
(*c*)	(3)
(*d*)	(6) or (7)
(*e*)	(7) or (6)
(*f*)	(4) or (5)
(*g*)	(5) or (4)

FIGURE 5 Assignments for spectrum of $[Ru_3H(CO)_{11}]^-$

Upon further warming the spectrum collapses totally, and at 32 °C a single carbon resonance is observed at δ 202.2 indicating that complete scrambling of the carbonyl groups occurs in $[Ru_3H(CO)_{11}]^-$.

EXPERIMENTAL

All operations were carried out with rigorous exclusion of air by using Schlenk techniques. The solutions were distilled over drying agents such as sodium–potassium alloy or calcium hydride, and saturated with purified nitrogen.

Preparations.—$[NEt_4][Ru_3H(CO)_{11}]$. A solution of $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and $Na[BH_4]$ (100 mg, 2.5 mmol) in tetrahydrofuran (50 cm^3) was stirred for 20 min; the solution turned dark red, due to the formation of $Na[Ru_3H(CO)_{11}]$. The reaction mixture was filtered through filter floc, and the filtrate evaporated to dryness. The residue was dissolved in methanol (20 cm^3), and after addition of $[NEt_4]Br$ (125 mg, 0.6 mmol) in methanol (5 cm^3) the solution was concentrated to 10 cm^3. The product was allowed to crystallize at room temperature for 6 h, then the solution was cooled to −78 °C. After 15 h the crystalline precipitate, which is analytically pure $[NEt_4][Ru_3H(CO)_{11}]$, was isolated, washed three times with methanol (2 cm^3) at −78 °C, and dried under high vacuum (yield 280 mg, 76%) (Found: C, 31.0; H, 3.00; N, 2.00. Calc. for $C_{19}H_{21}NO_{11}Ru_3$: C, 30.75; H, 2.85; N, 1.90%).

$[N(PPh_3)_2][Ru_3H(CO)_{11}]$. The thf solution of $Na[Ru_3H(CO)_{11}]$ was prepared from $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and $Na[BH_4]$ (100 mg, 2.5 mmol) as described above. After filtration through filter floc the solvent was drawn off, and the residue dissolved in methanol (20 cm^3). Then

$[N(PPh_3)_2]Cl$ (350 mg, 0.6 mmol) in methanol (5 cm^3) was added, and the solution concentrated to 10 cm^3. After 15 h the solution was filtered, and the precipitate, which is presumably $[N(PPh_3)_2]_2[Ru_6(CO)_{18}]$, discarded. The filtrate, which contains the pure $[N(PPh_3)_2][Ru_3H(CO)_{11}]$, was evaporated to dryness. The remaining product was washed three times with water (30 cm^3) and dried under high vacuum (yield 410 mg, 71%) (Found: C, 49.2; H, 2.75; N, 1.35; P, 5.65. Calc. for $C_{47}H_{31}NO_{11}P_2Ru_3$: C, 49.05; H, 2.70; N, 1.20; P, 5.60%).

X-*Ray Structural Analysis*.—Red-brown platelets of $[N(PPh_3)_2][Ru_3H(CO)_{11}]$ were obtained by recrystallization from methanol. The crystals, which were slightly air-sensitive, were mounted in 0.5-mm Lindemann tubes under nitrogen. 7 680 Intensities were measured on a Syntex $P2_1$ four-circle diffractometer, using Mo-K_α radiation and a crystal of dimensions *ca.* 0.638 × 0.413 × 0.113 mm. Cell constants were derived from angular measurements of 15 strong reflections ($20 < 2\theta < 30°$). Data were collected in the range $3.0 < 2\theta \leqslant 55.0°$, using a 96-step θ—2θ scan procedure; the scan rate was determined from a preliminary 2-s peak count and varied from 0.033 3 to 0.488 3° s^{-1} according to the peak intensity; reflections with intensities of $\leqslant 14$ counts s^{-1} were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

A semiempirical absorption correction based on a pseudo-ellipsoid model and 424 azimuthal scan data from 12 independent reflections was applied. Transmission factors ranged from 1.054 to 0.602 for the full data set. Lorentz polarization corrections were also applied, and equivalent reflections averaged to give 4 355 unique observed intensities $[I > 1.5\sigma(I)]$.

Crystal Data.—$C_{47}H_{31}NO_{11}P_2Ru_3$, $M = 1\,150.9$, Monoclinic, $a = 16.355(5)$, $b = 17.057(4)$, $c = 17.715(5)$ Å, $\beta = 106.29(2)°$, $U = 4\,743.5$ Å^3, $D_c = 1.611$ g cm^{-3}, $Z = 4$, $F(000) = 2\,279.94$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 10.16 cm^{-1}, space group $P2_1/c$ from systematic absences.

The three ruthenium atom positions were located by multisolution Σ_2 sign expansion, and all the remaining non-hydrogen atoms from a subsequent electron-difference synthesis. The structure was refined by blocked full-matrix least squares. The Ru, C, and O atoms of the anion were assigned anisotropic thermal parameters as were the P atoms of the cation; the N atom and C atoms of the cation were assigned individual isotropic temperature factors. The phenyl rings, including hydrogen atoms having a common isotropic temperature factor, were refined as rigid groups with idealized geometry (C–C 1.395, C–H, 1.08 Å; C–C–C 120.0, C–C–H 120.0°). The R factor at this stage was 0.053, and a difference map computed using the full data set revealed at its highest peak (0.75 e Å^{-3}) the position of the hydride atom. This atom was assigned an isotropic temperature factor and included in further cycles of refinement. Fourteen low-angle reflections, which were considered to suffer from secondary extinction, were zero weighted, and a weighting scheme of the form $w = 0.379\,1/[\sigma^2(F) + 0.000\,5|F|^2]$ introduced. The converged residuals for the remaining 4 341 reflections were R 0.053 and R' 0.051 $(= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|)$. A final difference synthesis revealed no regions of significant electron density.

TABLE 5

Atom co-ordinates (× 10^4)

	x/a	y/b	z/c
Ru(1)	7 998(1)	2 853(1)	5 841(1)
Ru(2)	7 325(1)	2 440(1)	4 249(1)
Ru(3)	8 746(1)	3 470(1)	4 698(1)
C(1)	8 096(8)	1 853(5)	5 207(6)
O(1)	8 395(6)	1 222(4)	5 351(4)
C(2)	7 435(10)	2 245(7)	6 441(7)
O(2)	7 112(8)	1 851(6)	6 794(6)
C(3)	9 097(9)	2 753(6)	6 552(7)
O(3)	9 752(7)	2 707(6)	6 992(5)
C(4)	7 749(11)	3 881(7)	6 206(7)
O(4)	7 665(10)	4 465(5)	6 488(7)
C(5)	6 504(10)	1 668(6)	4 208(8)
O(5)	6 025(8)	1 170(5)	4 207(8)
C(6)	7 822(10)	1 949(7)	3 516(7)
O(6)	8 103(9)	1 650(6)	3 078(6)
C(7)	6 633(8)	3 231(6)	3 538(7)
O(7)	6 222(7)	3 654(5)	3 099(5)
C(8)	9 629(11)	4 054(6)	5 420(8)
O(8)	10 150(8)	4 416(6)	5 846(7)
C(9)	8 898(10)	3 677(6)	3 692(8)
O(9)	9 017(8)	3 811(6)	3 089(6)
C(10)	7 882(10)	4 254(7)	4 604(8)
O(10)	7 379(8)	4 733(5)	4 536(6)
C(11)	9 440(8)	2 527(6)	4 808(7)
O(11)	9 854(7)	1 993(5)	4 848(6)
H(1)	7 163(72)	2 929(46)	5 001(54)
N(1)	2 530(5)	2 431(4)	1 760(4)
P(1)	2 410(2)	3 022(1)	1 055(1)
C(101)	1 675(8)	3 776(3)	1 145(4)
C(102)	1 624(4)	4 492(3)	755(4)
C(103)	1 000(4)	5 036(3)	795(4)
C(104)	427(8)	4 862(3)	1 225(4)
C(105)	478(4)	4 146(3)	1 615(4)
C(106)	1 102(4)	3 602(3)	1 575(4)
C(111)	1 946(5)	2 501(3)	151(4)
C(112)	1 669(5)	2 917(3)	−553(4)
C(113)	1 249(5)	2 526(3)	−1 245(4)
C(114)	1 107(5)	1 721(3)	−1 233(4)
C(115)	1 385(5)	1 305(3)	−529(4)
C(116)	1 804(5)	1 696(3)	163(4)
C(121)	3 374(5)	3 478(3)	992(8)
C(122)	3 831(5)	3 168(3)	504(4)
C(123)	4 627(5)	3 475(3)	525(4)
C(124)	4 967(5)	4 091(3)	1 033(4)
C(125)	4 511(5)	4 401(3)	1 521(4)
C(126)	3 714(5)	4 095(3)	1 500(4)
P(2)	3 267(2)	2 065(1)	2 451(1)
C(201)	2 786(4)	1 289(4)	2 862(3)
C(202)	1 942(4)	1 080(8)	2 504(3)
C(203)	1 561(8)	482(4)	2 824(3)
C(204)	2 025(4)	93(4)	3 502(3)
C(205)	2 870(4)	302(4)	3 860(3)
C(206)	3 250(4)	900(4)	3 540(3)
C(211)	4 129(5)	1 636(3)	2 153(4)
C(212)	4 836(5)	2 075(3)	2 117(4)
C(213)	5 474(5)	1 731(3)	1 845(4)
C(214)	5 404(5)	948(3)	1 609(8)
C(215)	4 697(5)	509(3)	1 645(4)
C(216)	4 059(5)	853(3)	1 917(4)
C(221)	3 693(4)	2 766(3)	3 223(4)
C(222)	4 519(4)	2 707(3)	3 722(4)
C(223)	4 806(4)	3 242(3)	4 334(4)
C(224)	4 268(4)	3 838(3)	4 447(4)
C(225)	3 442(4)	3 897(3)	3 949(4)
C(226)	3 154(4)	3 361(3)	3 337(4)

Complex neutral-atom scattering factors[16] were employed. Table 5 lists the final atomic co-ordinates, while details of phenyl hydrogen-atom co-ordinates, thermal parameters, molecular planes, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22544 (31 pp.).* All computing was carried out on the IBM 370/165 computer at the University of Cambridge using ' SHELX 76 '.[17] Figure 1 was drawn

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

using the ORTEP[18] plotting program, and Figure 2 with the PLUTO program written by Dr. W. D. S. Motherwell.

Variable-temperature ^{13}C *N.M.R. Study*.—The measurements were performed with a Varian XL-100-15 spectrometer using solutions of $[NEt_4][Ru_3H(CO)_{11}]$. The anion was *ca.* 30% ^{13}C-enriched. For the range −116 to −77 °C, a mixture of CD_2Cl_2 and $CHCl_2F$ (1 : 3) was used as solvent, for the range −50 to 32 °C CD_2Cl_2 was used. Tris(acetylacetonato)chromium(III) was added as a relaxation agent only for the range −50 to 32 °C. The chemical shifts were measured relative to the CD_2Cl_2 signal and related to the standard $SiMe_4$ using the conversion $\delta(SiMe_4) = \delta(CD_2Cl_2) + 53.9$.

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