Chemistry of the Carbido- and Nitrido-decaruthenium Cluster Anions $[Ru_{10}H(C)(CO)_{24}]^-$, $[Ru_{10}C(CO)_{24}]^{2-}$ and $[Ru_{10}N(CO)_{24}]^-$ †

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The thermolysis of $[Ru_3(CO)_{12}]$ **1** in the presence of 1,3,5-trimethylbenzene yielded, in addition to hexaruthenium carbido products, the tetracapped octahedral carbido cluster anion $[Ru_{10}H(C)(CO)_{24}]^-$ **2** which has been fully characterised as its $[N(PPh_3)_2]^+$ salt. Deprotonation of **2** yielded the dianion $[Ru_{10}C(CO)_{24}]^{2-}$ **3** which has been similarly characterised. The isostructural decaruthenium nitrido anion $[Ru_{10}N(CO)_{24}]^-$ **4** may be synthesised by condensation of the required stoichiometric quantities of $[Ru_3(CO)_{12}]$ with the preformed nitrides $[Ru_5N(CO)_{14}]^-$ or $[Ru_6N(CO)_{16}]^-$ under thermolysis in bis(2-methoxyethyl) ether (diglyme), or alternatively directly from $[Ru_3(CO)_{12}]$ by reaction with $\frac{1}{3}$ equivalent of $[N(PPh_3)_2][N_3]$ under the same conditions. The anion **4** as its $[N(PPh_3)_2]^+$ salt forms crystals isomorphous to those of **2**, and conclusive evidence for its containing an interstitial nitride was therefore obtained by observation of its ^{14}N NMR resonance at δ 30 [$\delta(^{14}N, MeNO_2) = 0$]. Reaction of **3** with 1 atm CO in solution leads to rapid degradation to $[Ru_6C(CO)_{16}]^{2-}$ and $[Ru_3(CO)_{12}]$ whilst under the same conditions **4** yields $[Ru_5N(CO)_{14}]^-$ and $[Ru_3(CO)_{12}]$.

Until relatively recently the chemistry of high-nuclearity carbonyl clusters of the iron sub-group was dominated by osmium. The decaosmium clusters $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_{10}H_4(CO)_{24}]^{2-}$ have received a great deal of attention which has greatly added to the understanding of structure and reactivity in high-nuclearity systems. Although osmium and ruthenium form a number of isostructural cluster carbonyl species at a variety of nuclearities, the different balance of M–M and M–CO bond strengths for the two metals leads to many cluster species with geometries/stoichiometries which are unique to either metal and, in addition, synthetic routes to clusters of the two metals often differ widely. The existence of an osmium cluster does not therefore guarantee the existence of, or a synthetic route to, its ruthenium analogue and *vice versa*. This has become increasingly evident with the recent synthesis of a number of high-nuclearity ruthenium hydrido carbonyl clusters which have no analogues in osmium chemistry.[1] The isolation of the decaruthenium clusters $[Ru_{10}C(CO)_{24}]^{2-}$ **3** and $[Ru_{10}N(CO)_{24}]^-$ **4** with the tetracapped octahedral metal framework, isostructural to $[Os_{10}C(CO)_{24}]^{2-}$, is therefore significant, indicating an extra stability for this structure possibly associated with it being a fragment of a cubic close-packed array of metal atoms and with the stabilisation of the metal framework by inclusion of interstitial atoms.

We have previously communicated the syntheses, structures and spectroscopy of $[Ru_{10}H(C)(CO)_{24}]^-$ **2**,[2,3] $[Ru_{10}C(CO)_{24}]^{2-}$ **3**[2,3] and $[Ru_{10}N(CO)_{24}]^-$ **4**,[4] and alternative syntheses of **2** and **3** have also been reported by other workers.[5,6] In addition, a detailed NMR study of ligand fluxionality in **2**, and a comparison of this with its osmium analogue, has been reported.[7] This paper is concerned with presenting a systematic view of the chemistry of these decaruthenium clusters.

Results and Discussion

Carbido Anions $[Ru_{10}H(C)(CO)_{24}]^-$ **2** *and* $[Ru_{10}C(CO)_{24}]^{2-}$ **3**.—Our initial synthesis of the decaruthenium carbido species **2** and **3** resulted from an investigation into the mechanism of carbide formation in hexaruthenium systems.[3,8] The thermolysis of $[Ru_3(CO)_{12}]$ **1** in the presence of mesitylene (1,3,5-trimethylbenzene) at temperatures ranging from 100 to 165 °C provides a mixture of soluble products from which the carbido-hexaruthenium cluster $[Ru_6C(CO)_{14}(\eta\text{-}C_6H_3Me_3)]$ **5**, and two non-carbido hexaruthenium species containing μ_4-η^2-carbonyl ligands, the bis edge-bridged tetrahedral $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta\text{-}C_6H_3Me_3)]$ **6** and the equatorial–axial edge-bridged trigonal bipyramidal $[Ru_6H(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu\text{-}\sigma\text{:}\eta^6\text{-}C_6H_3Me_2CH_2)]$ **7**, may be separated by chromatography on silica. The cluster **6** was shown to be the intermediate to the carbide **5** in this reaction since its thermolysis in mesitylene solution or in the solid state provides both **5** and **7** along with CO_2, a reaction which is suggested to proceed *via* a bimolecular C–O bond cleavage mechanism according to the stoichiometry given in equation (1).[9] In addition to the hydrocarbon soluble products, extended thermolysis of the system provides a large quantity of a black microcrystalline material which may be solubilised as the olive green $[N(PPh_3)_2]^+$ salt of $[Ru_{10}H(C)(CO)_{24}]^-$ **2** by dissolution in an acetone–methanol solution of $[N(PPh_3)_2]Cl$. Subsequent filtration followed by slow removal of the acetone under a stream of nitrogen provides the salt as a black, air-stable, microcrystalline substance in 35% yield. Alternatively, if the solution is heated to reflux in the presence of an excess of

$$2\underset{\mathbf{6}}{[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta\text{-}C_6H_3Me_3)]} \longrightarrow \underset{\mathbf{5}}{[Ru_6C(CO)_{14}(\eta\text{-}C_6H_3Me_3)]} + CO_2 + \underset{\mathbf{7}}{[Ru_6H(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu\text{-}\sigma\text{:}\eta^6\text{-}C_6H_3Me_2CH_2)]} \quad (1)$$

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

Non-SI unit employed: atm = 101 325 Pa.

$[N(PPh_3)_2]Cl$ a gradual colour change to bright green occurs and subsequent crystallisation provides the $[N(PPh_3)_2]^+$ salt of $[Ru_{10}C(CO)_{24}]^{2-}$ **3** as a microcrystalline material in similar yield. A quantitative deprotonation of **2** to **3** may also be achieved in CH_2Cl_2 with the base dbu (1,8-diazabicyclo[5.4.0]undec-7-ene), a process which may be reversed with HCl gas, although all other acid–solvent combinations investigated resulted in decomposition.

Although the frequencies of the IR bands attributable to ν_{CO} in the solution (CH_2Cl_2) spectra of the two compounds correspond to those expected for a mono- and di-anion respectively, with those for **2** occurring at higher frequencies than in **3**, the number of bands observed, two for the hydrido monoanion **2** and three for the dianion **3**, is counter to the anticipated symmetries of the two clusters (Table 1). In contrast, for the corresponding osmium systems the dianion $[Os_{10}C(CO)_{24}]^{2-}$ of T_d symmetry has two symmetrical ν_{CO} bands very similar in appearance to those of **2**,[10] whilst the spectrum of the hydrido monoanion $[Os_{10}H(C)(CO)_{24}]^-$ similarly has two bands but with distinct shoulders present indicating the lower symmetry of this system.[11] Since a cluster $[M_{10}C(CO)_{24}]^{2-}$ of T_d symmetry has four IR-active ν_{CO} modes, it would appear that there is coincidence of IR absorptions, and that this, rather than perturbations in the cluster symmetry, governs the number of bands observed in the spectra.

In order to record the IR spectra of **2** and **3** in the ν(Ru–carbide) region (800–600 cm^{-1}), $[NMe_4]^+$ salts were prepared by metathesis with $[NMe_4]Cl$ instead of $[N(PPh_3)_2]Cl$ in the preparation. Such vibrational modes of clusters containing interstitial atoms have been shown to give rise to absorptions of unexpectedly high intensity which, to a good approximation, reflect the symmetry of the co-ordination environment of the atom.[12,13] Infrared spectra of these salts in CsI discs at 293 K and low temperatures were recorded. The spectra of the $[NMe_4]^+$ salt of the dianion **3** are somewhat similar to those obtained for its osmium analogue $[Os_{10}C(CO)_{24}]^{2-}$.[13] A single slightly asymmetric band at 728 cm^{-1} is obtained at room temperature which is split at 105 K to give two bands at 729 and 736 cm^{-1}. This low-temperature splitting of 7 cm^{-1} is slightly larger than that observed for the osmium cluster in which it was considered to reflect slight deviations from octahedral symmetry at the interstitial site, a similar explanation may be offered in the ruthenium case. For the hydrido monoanion **2** the spectrum of the $[NMe_4]^+$ salt displays two completely symmetric ν(Ru–carbide) bands at 736 and 721 cm^{-1} of medium and strong intensities respectively consistent with overall C_{3v} symmetry for the cluster which would be expected to give rise to an A and a degenerate E mode. However, on cooling to 120 K significant shifts in the band frequencies to 744 and 729 cm^{-1} occur and, more significantly, a distinct shoulder at 725 cm^{-1} develops on the low-frequency side of the strong band. Since the combined width of this shoulder and its parent strong band is significantly greater than the width of the original band, this shoulder may unequivocally be assigned as a new band and not simply a result of the higher resolution achieved at low temperature. As such, the three-band low-temperature spectrum reflects the lifting of the degeneracy of the E mode (in C_{3v} symmetry) by reduction of the symmetry of the system to C_{2v} or lower. These observations, in association with solid-state ^1H NMR studies of the $[N(PPh_3)_2]^+$ salt, were originally interpreted as indicating an expulsion of the hydride from an interstitial tetrahedral site to a static location on the cluster surface.[14] However, given the recent realisation that the evidence for interstitial tetrahedral location of hydrides in decanuclear osmium clusters (and by inference now also their ruthenium analogues) is probably misleading (see later), we now favour an explanation consistent with the ^{13}C NMR results discussed below.[7]

Both mass and ^1H NMR spectroscopies of the $[N(PPh_3)_2]^+$ salts of **2** and **3** are consistent with their formulations as $[Ru_{10}H(C)(CO)_{24}]^-$ and $[Ru_{10}C(CO)_{24}]^{2-}$ respectively (Table 1), whilst their variable-temperature ^{13}C NMR spectra obtained from ^{13}C-enriched analogues indicate global carbonyl fluxionality in addition to both localised and global fluxionality (under different temperature regimes) for the hydride in **2**. The spectra of **2** under the low-temperature regime are consistent with C_{3v} symmetry, whilst at intermediate temperatures T_d symmetry is indicated and at higher temperatures global fluxionality of both H and CO ligands provides a single signal. These spectroscopic studies have been detailed elsewhere,[2,3,7] and the data for the low temperature limiting spectra are reproduced in Table 1. Significantly, the coalescence temperatures associated with the carbonyl-exchange processes in the two clusters indicate that the activation energy for the process in the monoanionic system **2** is approximately twice that in the dianion **3**. A likely explanation for this disparity lies in the involvement of a bridging carbonyl geometry along the exchange process pathway. Since such a geometry is more efficient at accommodating charge it will be favoured by an increased charge on the cluster. Consequently the barrier to exchange of a carbonyl ligand between two adjacent metals *via* a bridge formation/opening process will be lowered by such an increase in overall charge on the system. It is interesting to note the magnitude of this effect in this system; an effective increase of the charge at each metal by 0.1 e has the effect of approximately halving the activation barrier. Similar explanations have been used to account for carbonyl-exchange activation energy changes in high-nuclearity rhodium systems.[15]

Single-crystal X-ray crystallographic determination of the

Table 1 Spectroscopic data for clusters **2**, **3** and **4** as their $[N(PPh_3)_2]^+$ salts

	IR/cm^{-1} [a]			NMR (δ)[c]		
	CH_2Cl_2	CsI disc, 293 K	M^+ [b]	^1H	^{13}C [d]	^{14}N [e]
$[Ru_{10}H(C)(CO)_{24}]^-$ **2**	2053vs, 2009s	736m, 721s	1694	−13.5s	374.5 (carbide), 211.3 (1), 209.5 (1), 206.7 (2), 189.9 (3), 188.1 (1)	—
$[Ru_{10}C(CO)_{24}]^{2-}$ **3**	2027vs, 2000m, 1983s	728	1693	—	362.0 (carbide), 213.7 (1), 192.7 (1)	—
$[Ru_{10}N(CO)_{24}]^-$ **4**	2052vs, 2007s, 1960vw(sh)	682 (^{15}N, 658)	1696	—	210.0 (1), 189.4 (1)	30 ($w_{\frac{1}{2}}$ = 21 Hz) −70 ($w_{\frac{1}{2}}$ = 54 Hz)

[a] ν(Ru–carbide/nitride); as the $[NMe_4]^+$ salt. [b] Negative ion FAB. [c] In CD_2Cl_2. [d] Low-temperature limit; relative intensity in parentheses. [e] Reference $MeNO_2$ (δ = 0).

structure of **2**, and the results of a partial X-ray structure determination of the dianion **3**, both as their $[N(PPh_3)_2]^+$ salts, show that both anions possess tetracapped octahedral metal-core geometries of tetrahedral symmetry isostructural with their osmium analogues. Fig. 1 shows the structure of the anion **2**. Final positional parameters are given in Table 2 and selected intramolecular distances and angles are given in Table 3. The structure of the dianion **3** obtained from the partial X-ray structure analysis of its $[N(PPh_3)_2]^+$ salt is illustrated in Fig. 2. The structures of the two salts are isomorphous with those of their osmium analogues.[10,11] Additionally, the structure of the cluster **2** is indistinguishable from that of **3** with the surfaces of both clusters being covered with close-packed terminally co-ordinated carbonyl ligands. In the earlier structure determination of $[Os_{10}H(C)(CO)_{24}]^-$, as its $[AsPh_4]^+$ and $[PPh_3Me]^+$ salts, similar close packing of carbonyl ligands associated with a slight but crystallographically significant expansion of one of the tetrahedral caps was interpreted as indicating the accommodation of the hydride ligand in an interstitial tetrahedral site. For the structure of **2**, the relatively high estimated standard deviations, resulting from pseudo symmetry and the consequent small number of data, do not allow distinction of the four caps

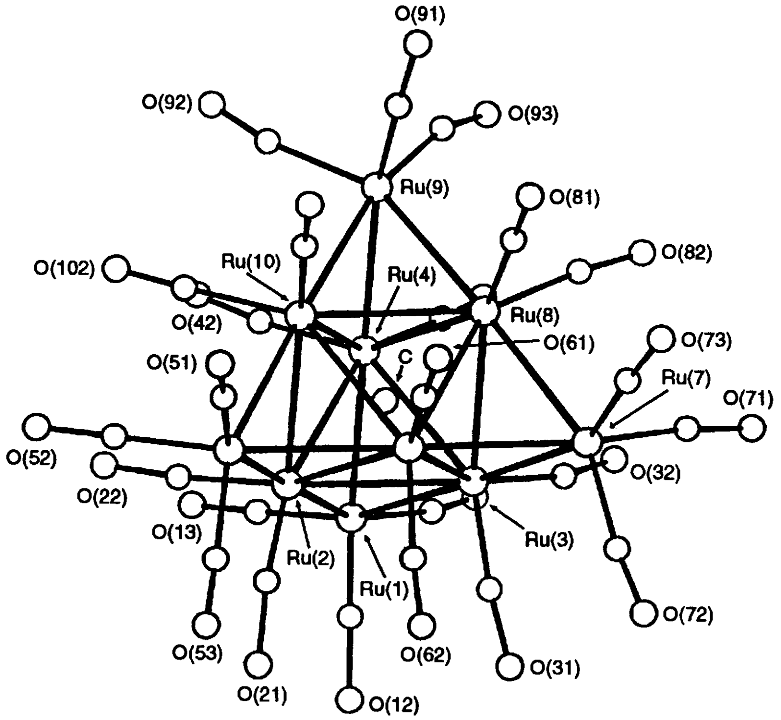


Fig. 1 Structure of $[Ru_{10}H(C)(CO)_{24}]^-$ **2**

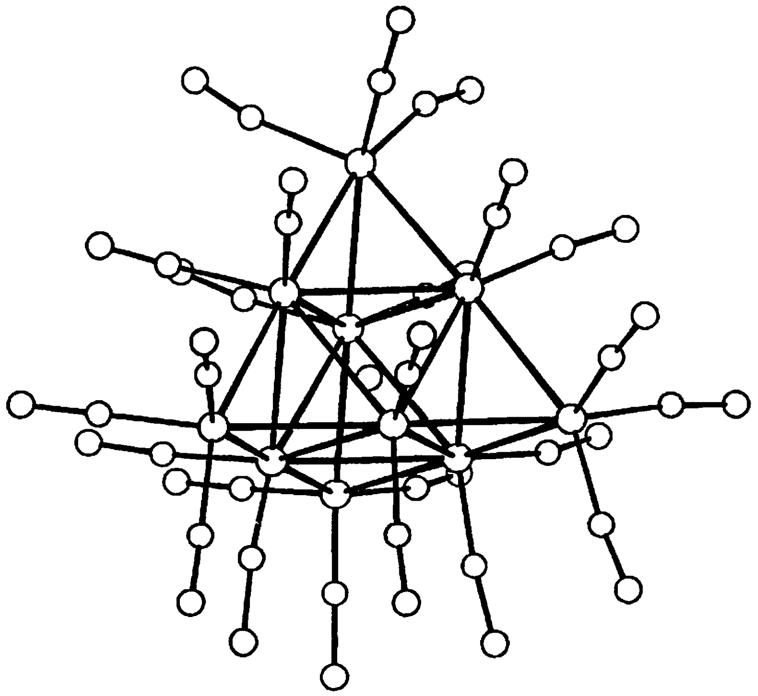


Fig. 2 Structure of $[Ru_{10}C(CO)_{24}]^{2-}$ **3**

Table 2 Fractional atomic coordinates for $[N(PPh_3)_2]^+$ salts of $[Ru_{10}H(C)(CO)_{24}]^-$ **2** (E = carbide) and $[Ru_{10}N(CO)_{24}]^-$ **4** (E = nitride)

	2			**4**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.3165(2)	0.0144(2)	0.1346(1)	0.3167(3)	0.0133(2)	0.1349(1)
Ru(2)	0.1094(2)	0.0092(2)	0.1675(1)	0.1103(3)	0.0077(2)	0.1672(1)
Ru(3)	0.3006(2)	−0.0770(2)	0.1982(1)	0.3025(3)	−0.0786(2)	0.1983(1)
Ru(4)	0.3007(2)	0.0825(2)	0.2047(1)	0.3027(3)	0.0806(2)	0.2050(1)
Ru(5)	−0.0948(2)	0.0012(2)	0.2025(1)	−0.0940(3)	−0.0003(2)	0.2022(1)
Ru(6)	0.0881(2)	−0.0830(2)	0.2325(1)	0.0895(3)	−0.0850(2)	0.2319(1)
Ru(7)	0.2766(3)	−0.1640(2)	0.2626(1)	0.2769(3)	−0.1658(2)	0.2622(1)
Ru(8)	0.2782(2)	−0.0086(2)	0.2709(1)	0.2792(3)	−0.0106(2)	0.2707(1)
Ru(9)	0.2798(3)	0.1478(2)	0.2758(1)	0.2797(3)	0.1455(2)	0.2756(1)
Ru(10)	0.0892(2)	0.0767(2)	0.2397(1)	0.0905(3)	0.0746(2)	0.2395(1)
E	0.1952(22)	0.0006(22)	0.2170(7)	0.1950(23)	−0.0037(18)	0.2169(7)
C(11)	0.4795(38)	0.0077(33)	0.1322(10)	0.4688(39)	0.0110(27)	0.1326(11)
O(11)	0.5750(28)	0.0143(22)	0.1321(8)	0.5728(28)	0.0115(19)	0.1322(8)
C(12)	0.2873(52)	−0.0454(32)	0.1033(16)	0.2900(56)	−0.0522(32)	0.0983(16)
O(12)	0.2717(31)	−0.0925(20)	0.0748(10)	0.2697(39)	−0.0980(24)	0.0734(12)
C(13)	0.2999(38)	0.0912(25)	0.1042(11)	0.2989(48)	0.0906(29)	0.1041(14)
O(13)	0.2854(28)	0.1436(19)	0.0850(8)	0.2847(35)	0.1442(22)	0.0840(10)
C(21)	0.0469(43)	−0.0476(25)	0.1377(13)	0.0453(53)	−0.0531(30)	0.1353(15)
O(21)	−0.0012(25)	−0.0987(16)	0.1124(8)	−0.0014(32)	−0.0985(20)	0.1114(9)
C(22)	0.0609(35)	0.0892(23)	0.1393(10)	0.0620(40)	0.0878(23)	0.1397(11)
O(22)	0.0236(26)	0.1431(17)	0.1229(8)	0.0250(30)	0.1407(18)	0.1211(8)
C(31)	0.2759(39)	−0.1569(26)	0.1692(12)	0.2767(48)	−0.1596(30)	0.1707(14)
O(31)	0.2636(26)	−0.2168(17)	0.1504(8)	0.2662(32)	−0.2173(19)	0.1506(9)
C(32)	0.4595(33)	−0.0927(20)	0.2010(9)	0.4513(43)	−0.0863(23)	0.2009(11)
O(32)	0.5587(23)	−0.0926(14)	0.2053(6)	0.5580(30)	−0.0954(16)	0.2034(8)
C(41)	0.4649(34)	0.0926(21)	0.2121(9)	0.4592(47)	0.0928(26)	0.2092(12)
O(41)	0.5609(27)	0.1035(16)	0.2132(7)	0.5608(37)	0.1021(20)	0.2125(10)
C(42)	0.2714(31)	0.1746(20)	0.1814(9)	0.2778(41)	0.1743(25)	0.1810(12)
O(42)	0.2529(20)	0.2358(13)	0.1714(6)	0.2580(26)	0.2352(16)	0.1713(8)
C(51)	−0.1997(26)	−0.0040(24)	0.2424(8)	−0.2002(38)	−0.0013(28)	0.2403(12)
O(51)	−0.2536(20)	−0.0049(18)	0.2656(6)	−0.2507(28)	−0.0047(20)	0.2659(9)
C(52)	−0.1730(32)	0.0775(21)	0.1797(9)	−0.1761(40)	0.0773(24)	0.1778(11)
O(52)	−0.2265(23)	0.1297(14)	0.1653(7)	−0.2265(28)	0.1284(17)	0.1653(8)
C(53)	−0.1712(33)	−0.0713(21)	0.1737(10)	−0.1689(45)	−0.0704(26)	0.1746(13)
O(53)	−0.2243(25)	−0.1162(15)	0.1561(7)	−0.2237(33)	−0.1176(19)	0.1558(9)
C(61)	0.0139(31)	−0.0973(19)	0.2738(9)	0.0234(39)	−0.1034(23)	0.2754(11)
O(61)	−0.0380(22)	−0.1092(13)	0.3049(6)	−0.0375(27)	−0.1072(16)	0.3039(8)
C(62)	0.0274(37)	−0.1665(24)	0.2063(11)	0.0335(46)	−0.1690(28)	0.2074(13)
O(62)	−0.0030(23)	−0.2181(14)	0.1904(7)	−0.0062(27)	−0.2213(17)	0.1903(8)
C(71)	0.4299(33)	−0.1861(20)	0.2728(9)	0.4232(42)	−0.1863(23)	0.2717(11)
O(71)	0.5255(23)	−0.2047(14)	0.2784(7)	0.5230(29)	−0.2042(16)	0.2766(8)
C(72)	0.2362(30)	−0.2576(18)	0.2433(9)	0.2411(38)	−0.2599(22)	0.2435(11)
O(72)	0.2189(22)	−0.3205(14)	0.2333(6)	0.2166(27)	−0.3202(16)	0.2326(8)
C(73)	0.2331(29)	−0.1829(19)	0.3108(9)	0.2326(37)	−0.1871(22)	0.3115(11)
O(73)	0.2169(24)	−0.1962(14)	0.3428(7)	0.2078(29)	−0.1978(17)	0.3437(9)
C(81)	0.2286(27)	−0.0141(20)	0.3198(9)	0.2363(38)	−0.0133(26)	0.3203(13)
O(81)	0.1998(20)	−0.0175(14)	0.3491(6)	0.2054(25)	−0.0198(16)	0.3493(8)
C(82)	0.4329(31)	−0.0125(23)	0.2893(9)	0.4318(39)	−0.0164(23)	0.2870(11)
O(82)	0.5275(23)	−0.0217(15)	0.2993(6)	0.5300(29)	−0.0194(17)	0.2997(8)
C(91)	0.2426(35)	0.1557(22)	0.3232(12)	0.2422(47)	0.1581(27)	0.3231(15)
O(91)	0.2322(27)	0.1691(17)	0.3544(9)	0.2298(36)	0.1650(21)	0.3555(11)
C(92)	0.2404(34)	0.2482(20)	0.2602(10)	0.2376(44)	0.2444(26)	0.2621(13)
O(92)	0.2246(23)	0.3099(14)	0.2548(6)	0.2222(29)	0.3054(17)	0.2539(8)
C(93)	0.4293(35)	0.1673(21)	0.2880(10)	0.4258(49)	0.1610(25)	0.2882(13)
O(93)	0.5251(26)	0.1803(15)	0.2937(7)	0.5219(36)	0.1769(19)	0.2913(9)
C(101)	0.0145(29)	0.0807(19)	0.2836(9)	0.0137(40)	0.0832(23)	0.2877(12)
O(101)	−0.0362(23)	0.0794(15)	0.3125(7)	−0.0331(31)	0.0815(18)	0.3133(9)
C(102)	0.0301(29)	0.1678(18)	0.2179(9)	0.0305(39)	0.1646(23)	0.2186(11)
O(102)	−0.0087(21)	0.2218(13)	0.2072(6)	−0.0092(27)	0.2210(16)	0.2093(8)
P(1)	0.3534(10)	−0.2657(6)	0.4732(3)	0.3535(12)	−0.2664(6)	0.4729(3)
P(2)	0.1651(9)	−0.1558(6)	0.4899(2)	0.1646(11)	−0.1571(6)	0.4902(3)
N	0.2576(27)	−0.2241(16)	0.4867(7)	0.2542(31)	−0.2231(16)	0.4868(7)
C(111)	0.3246(19)	−0.3583(20)	0.4633(6)	0.3244(27)	−0.3613(24)	0.4650(8)
C(112)	0.3955(19)	−0.4153(20)	0.4784(6)	0.3957(27)	−0.4180(24)	0.4802(8)
C(113)	0.3727(19)	−0.4900(20)	0.4686(6)	0.3755(27)	−0.4925(24)	0.4696(8)
C(114)	0.2792(19)	−0.5077(20)	0.4439(6)	0.2841(27)	−0.5103(24)	0.4437(8)
C(115)	0.2084(19)	−0.4508(20)	0.4288(6)	0.2129(27)	−0.4535(24)	0.4284(8)
C(116)	0.2311(19)	−0.3761(20)	0.4385(6)	0.2330(27)	−0.3790(24)	0.4390(8)
C(121)	0.4092(19)	−0.2265(12)	0.4308(5)	0.4081(24)	−0.2288(15)	0.4304(6)
C(122)	0.4319(19)	−0.1498(12)	0.4286(5)	0.4336(24)	−0.1523(15)	0.4297(6)
C(123)	0.4849(19)	−0.1213(12)	0.3976(5)	0.4862(24)	−0.1219(15)	0.3992(6)
C(124)	0.5152(19)	−0.1694(12)	0.3688(5)	0.5133(24)	−0.1679(15)	0.3692(6)

Table 2 (*continued*)

	2			4		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(125)	0.4924(19)	−0.2461(12)	0.3711(5)	0.4878(24)	−0.2443(15)	0.3698(6)
C(126)	0.4395(19)	−0.2747(12)	0.4021(5)	0.4352(24)	−0.2748(15)	0.4004(6)
C(131)	0.4697(20)	−0.2677(13)	0.5062(8)	0.4723(22)	−0.2672(15)	0.5071(9)
C(132)	0.4463(20)	−0.2646(13)	0.5443(8)	0.4447(22)	−0.2649(15)	0.5448(9)
C(133)	0.5351(20)	−0.2687(13)	0.5725(8)	0.5308(22)	−0.2687(15)	0.5741(9)
C(134)	0.6472(20)	−0.2758(13)	0.5626(8)	0.6445(22)	−0.2747(15)	0.5657(9)
C(135)	0.6705(20)	−0.2789(13)	0.5245(8)	0.6720(22)	−0.2770(15)	0.5280(9)
C(136)	0.5817(20)	−0.2748(13)	0.4963(8)	0.5859(22)	−0.2732(15)	0.4987(9)
C(211)	0.2306(17)	−0.0653(13)	0.4843(5)	0.2289(24)	−0.0654(16)	0.4845(7)
C(212)	0.2045(17)	−0.0220(13)	0.4520(5)	0.2084(24)	−0.0227(16)	0.4516(7)
C(213)	0.2587(17)	0.0468(13)	0.4476(5)	0.2678(24)	0.0441(16)	0.4473(7)
C(214)	0.3389(17)	0.0723(13)	0.4756(5)	0.3476(24)	0.0684(16)	0.4759(7)
C(215)	0.3650(17)	0.0290(13)	0.5079(5)	0.3680(24)	0.0257(16)	0.5088(7)
C(216)	0.3108(17)	−0.0398(13)	0.5123(5)	0.3087(24)	−0.0411(16)	0.5131(7)
C(221)	0.0496(21)	−0.1616(11)	0.4563(5)	0.0491(28)	−0.1624(13)	0.4559(6)
C(222)	−0.0598(21)	−0.1479(11)	0.4675(5)	−0.0601(28)	−0.1485(13)	0.4672(6)
C(223)	−0.1529(21)	−0.1509(11)	0.4408(5)	−0.1539(28)	−0.1515(13)	0.4406(6)
C(224)	−0.1365(21)	−0.1676(11)	0.4030(5)	−0.1384(28)	−0.1685(13)	0.4027(6)
C(225)	−0.0270(21)	−0.1813(11)	0.3919(5)	−0.0292(28)	−0.1825(13)	0.3915(6)
C(226)	0.0660(21)	−0.1782(11)	0.4186(5)	0.0646(28)	−0.1794(13)	0.4181(6)
C(231)	0.1091(22)	−0.1561(12)	0.5343(8)	0.1132(26)	−0.1566(13)	0.5350(9)
C(232)	0.0998(22)	−0.2242(12)	0.5534(8)	0.1047(26)	−0.2246(13)	0.5541(9)
C(233)	0.0548(22)	−0.2258(12)	0.5889(8)	0.0582(26)	−0.2265(13)	0.5893(9)
C(234)	0.0191(22)	−0.1593(12)	0.6052(8)	0.0201(26)	−0.1603(13)	0.6053(9)
C(235)	0.0284(22)	−0.0913(12)	0.5861(8)	0.0286(26)	−0.0923(13)	0.5861(9)
C(236)	0.0734(22)	−0.0897(12)	0.5507(8)	0.0751(26)	−0.0905(13)	0.5509(9)
Cl(1)	0.2586(10)	0.0044(9)	0.6299(3)	0.2562(13)	0.0073(9)	0.6303(4)
Cl(2)	0.0463(14)	−0.1017(8)	0.6177(4)	0.4275(17)	−0.0998(10)	0.6176(5)
C(1)	0.3040(36)	−0.0841(23)	0.6449(10)	0.3031(45)	−0.0855(27)	0.6413(13)

on the grounds of interatomic distances. However, occupation of one of the tetrahedral sites by the hydride was initially considered to be consistent with the observed close packing of the carbonyls and the C_{3v} symmetry indicated by the low-temperature limiting ^{13}C NMR spectrum. However, a more recent neutron diffraction structure determination of the dianion $[Os_{10}H_4(CO)_{24}]^{2-}$, similarly a tetracapped octahedral structure in which structural criteria were originally interpreted in terms of four-fold occupation of interstitial sites, located the four hydrides on the surface of the cluster in bridging and triply bridging geometries.[16] Given these results, it is no longer essential to assume interstitial co-ordination of the hydride in **2** in order to explain the C_{3v} symmetry structure observed in solution. The static co-ordination of the hydride over one face of the central octahedron, also generating a structure of C_{3v} symmetry, has been discounted in the case of the osmium analogue $[Os_{10}H(C)(CO)_{24}]^-$ on the grounds of the number of ^{187}Os satellites observed in its ^1H NMR spectrum.[7,17] In the absence of a suitable spin $\frac{1}{2}$ nucleus of ruthenium, we follow this precedent and interpret the low-temperature limiting ^{13}C NMR spectrum as concealing some residual motion of the hydride which results in its equal association with the three edges/faces of one of the tetrahedral caps. Consistent with this, a recent determination of the crystal structure of **2** as its salt with the binuclear $[Ru_2H(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)]^+$ cation allowed indirect location of the hydride on one of the cap edges based upon a significant lengthening of one Ru–Ru distance and displacement of the carbonyl ligands around this edge.[6]

The $[Ru_2H(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)]^+$ salt of **2** resulted from an alternative synthesis of the anion involving the chlorobenzene thermolysis of $[Ru_3H(\mu\text{-}NC_5H_4)(CO)_{10}]$ which provides the salt **2a** in 66% yield.[6] This synthesis closely mimics the original synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ which involved the solid-state vacuum pyrolysis of $[Os_3(CO)_{11}(NC_5H_5)]$. In our hands, similar vacuum pyrolysis of the triruthenium precursor provides the carbido hexaruthenium dianion $[Ru_6C(CO)_{16}]^{2-}$ and the dicarbido decaruthenium dianion $[Ru_{10}(C)_2(CO)_{24}]^{2-}$.[18] A further synthesis of the carbido-decaruthenium system involving redox condensation of $[Ru_6C(CO)_{16}]^{2-}$ with $[Ru_3(CO)_{12}]$ in bis(2-methoxyethyl) ether (diglyme) has also been reported.[5] This provides the dianion **3** in 81% yield and is probably the most direct route to the carbido decaruthenium system given the ready availability of the hexaruthenium dianion.

Nitrido Anion $[Ru_{10}N(CO)_{24}]^-$ **4**.—Given the existence of the nitrido analogues of the carbides $[Ru_5C(CO)_{14}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ we undertook to investigate the possibility of the synthesis of the nitrido analogue of **3**, $[Ru_{10}N(CO)_{24}]^-$ **4**. The nitrido hexaruthenium anion $[Ru_6N(CO)_{16}]^-$ may be synthesised in good yield by treatment of $[Ru_3(CO)_{12}]$ with 0.5 equivalents of $[N(PPh_3)_2][N_3]$ in tetrahydrofuran (thf) under reflux.[19] The nitride has been shown to be derived from an isocyanate (NCO) ligand co-ordinated to triruthenium intermediates in this reaction. In view of this reaction, and the reaction of $[Ru_6N(CO)_{16}]^-$ with $[Ru_3(CO)_{12}]$ in diglyme to provide high yields of $[Ru_{10}C(CO)_{24}]^{2-}$ **3**, we anticipated that treatment of $[Ru_3(CO)_{12}]$ with 0.3 equivalents of $[N(PPh_3)_2][N_3]$ under reflux in diglyme would provide the desired cluster **4**. Such a reaction does indeed provide a green solution from which moderate yields of its $[N(PPh_3)_2]^+$ salt may be isolated, but this proved unsatisfactory because significant quantities of the carbido dianion **3** and in particular the carbido hydride anion **2**, from which **4** is inseparable by chromatography, were also produced. Deprotonation of **2** with dbu allowed the separation of the nitride from the carbides, however, in anticipation of the crystallographic indistinguishability of **2** and **4**, the synthesis remained unsatisfactory since there always remained a weak hydride signal attributable to **2** in the ^1H NMR spectrum. Since only intermediates containing both CO and NCO ligands are observed in the reaction between $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2][N_3]$,[19] and thermal treatment of $[Ru_3(CO)_{12}]$ alone does not yield decanuclear carbides, the formation of both carbide and nitride products in this reaction presumably reflects a similarity in the ease of cleavage of N–C (NCO) and C–O (CO) bonds in intermediates containing both ligands. In order to avoid these contamination problems, the build up of the nitrido decaruthenium cluster from the preformed nitride $[Ru_6N(CO)_{16}]^-$ by redox condensation with $[Ru_3(CO)_{12}]$, in a reaction entirely analogous to the high-yield synthesis of **3**, was attempted. Such a reaction was indeed found to give **4** as its $[N(PPh_3)_2]^+$ salt in high yield uncontaminated with carbide impurities. The reactions involved in the synthesis of **4** are summarised in Scheme 1. Interestingly, the osmium analogue of **4** has yet to be reported.

Single-crystal X-ray structure analysis of the $[N(PPh_3)_2]^+$ salt of **4** established its tetracapped octahedral geometry and showed it to be almost indistinguishable from the formally isoelectronic $[Ru_{10}H(C)(CO)_{24}]^-$ **2**. Additionally, the two salts were shown to be isomorphous. Accordingly, initial evidence that **4** was the nitride was based upon the nature of the synthetic route. Consistent with this assumption refinement of the interstitial atom as carbon led to an improbably low value for its thermal parameter. Fig. 3 shows the structure of the anion **4**. Final positional parameters are given in Table 2 and selected intramolecular distances and angles are given in Table 3 for ease of comparison with those of the isostructural monohydride **2**.

In order to obtain unequivocal evidence of the identity of the interstitial atom, the ^{14}N NMR spectrum of the $[N(PPh_3)_2]^+$ salt of **4** was recorded (Fig. 4). The spectrum consists of a singlet at δ 30 [$\delta(^{14}N, MeNO_2) = 0$] attributable to the nitride, and a second singlet at δ −70 due to the nitrogen of the counter ion. The low-frequency shift of the interstitial nitride resonance relative to that in $[Ru_6N(CO)_{16}]^-$ (δ 180),[19] follows a similar trend to that observed in the ^{13}C NMR chemical shifts of the carbides in $[Ru_{10}C(CO)_{24}]^{2-}$ **3** (δ 362) and $[Ru_6C(CO)_{16}]^{2-}$ (δ 461).[20] The relatively narrow line width of the nitride resonance ($w_{\frac{1}{2}}$ = 21 Hz) compared to that of the iminium nitrogen

Table 3 Selected bond distances (Å) and angles (°) for $[N(PPh_3)_2]^+$ salts of $[Ru_{10}H(C)(CO)_{24}]^-$ **2** and $[Ru_{10}N(CO)_{24}]^-$ **4**

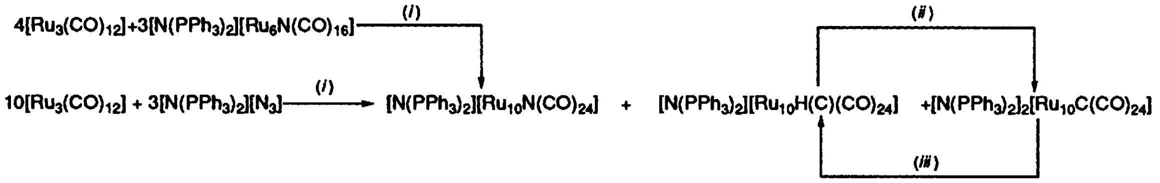
	2	**4**		**2**	**4**
Metal–metal					
Ru(1)–Ru(2)	2.778(4)	2.761(5)	Ru(4)–Ru(8)	2.874(4)	2.864(5)
Ru(1)–Ru(3)	2.795(4)	2.790(5)	Ru(4)–Ru(9)	2.794(4)	2.780(5)
Ru(1)–Ru(4)	2.780(4)	2.767(5)	Ru(4)–Ru(10)	2.859(4)	2.861(5)
Ru(2)–Ru(3)	2.875(4)	2.884(5)	Ru(5)–Ru(6)	2.774(4)	2.774(5)
Ru(2)–Ru(4)	2.845(4)	2.854(5)	Ru(5)–Ru(10)	2.799(4)	2.791(5)
Ru(2)–Ru(5)	2.785(4)	2.789(5)	Ru(6)–Ru(7)	2.793(4)	2.778(5)
Ru(2)–Ru(6)	2.850(4)	2.849(5)	Ru(6)–Ru(8)	2.860(4)	2.855(5)
Ru(2)–Ru(10)	2.847(4)	2.845(4)	Ru(6)–Ru(10)	2.855(4)	2.856(5)
Ru(3)–Ru(4)	2.850(4)	2.846(5)	Ru(7)–Ru(8)	2.782(4)	2.781(5)
Ru(3)–Ru(6)	2.859(4)	2.855(5)	Ru(8)–Ru(9)	2.789(4)	2.787(5)
Ru(3)–Ru(7)	2.783(4)	2.773(5)	Ru(8)–Ru(10)	2.852(4)	2.842(5)
Ru(3)–Ru(8)	2.873(4)	2.862(5)	Ru(9)–Ru(10)	2.804(4)	2.783(5)
Metal–E, E = C **2** or N **4**					
Ru(6)–E	2.05(3)	2.00(3)	Ru(4)–E	1.98(3)	2.03(3)
Ru(2)–E	1.963(23)	1.966(25)	Ru(8)–E	2.087(23)	2.079(24)
Ru(3)–E	2.00(3)	1.98(3)	Ru(10)–E	2.05(3)	2.06(3)
Mean M–C and C–O (carbonyl) distances					
Ru–C(vertex)	1.82(6)	1.82(6)	C–O(vertex)	1.17(7)	1.18(7)
Ru–C(edge)	1.84(4)	1.83(5)	C–O(edge)	1.19(5)	1.20(7)
Counter-ion and solvent distances					
P(1)–N	1.46(3)	1.51(4)	P(2)–C(211)	1.803(24)	1.82(3)
P(1)–C(111)	1.72(4)	1.74(4)	P(2)–C(221)	1.744(23)	1.75(3)
P(1)–C(121)	1.818(22)	1.81(3)	P(2)–C(231)	1.75(3)	1.73(3)
P(1)–C(131)	1.74(3)	1.78(3)	Cl(1)–C(1)	1.74(4)	1.78(5)
P(2)–N	1.64(3)	1.59(3)	Cl(2)–C(1)	1.82(4)	1.76(6)
Metal–metal–metal					
Ru(3)–Ru(1)–Ru(2)	62.1(1)	62.6(1)	Ru(4)–Ru(3)–Ru(2)	59.6(1)	59.7(1)
Ru(4)–Ru(1)–Ru(2)	61.6(1)	62.2(1)	Ru(6)–Ru(3)–Ru(1)	118.3(1)	117.7(2)
Ru(4)–Ru(1)–Ru(3)	61.5(1)	61.6(1)	Ru(6)–Ru(3)–Ru(2)	59.6(1)	59.5(1)
Ru(3)–Ru(2)–Ru(1)	59.2(1)	59.2(1)	Ru(6)–Ru(3)–Ru(4)	89.9(1)	90.0(1)
Ru(4)–Ru(2)–Ru(1)	59.2(1)	59.0(1)	Ru(7)–Ru(3)–Ru(1)	177.4(2)	176.7(2)
Ru(4)–Ru(2)–Ru(3)	59.8(1)	59.5(1)	Ru(7)–Ru(3)–Ru(2)	118.9(1)	118.6(2)
Ru(5)–Ru(2)–Ru(1)	178.1(1)	177.8(2)	Ru(7)–Ru(3)–Ru(4)	119.2(1)	119.4(2)
Ru(5)–Ru(2)–Ru(3)	118.9(1)	118.7(2)	Ru(7)–Ru(3)–Ru(6)	59.3(1)	59.1(1)
Ru(5)–Ru(2)–Ru(4)	119.9(1)	119.6(1)	Ru(8)–Ru(3)–Ru(1)	119.3(1)	119.0(2)
Ru(6)–Ru(2)–Ru(1)	119.2(1)	118.9(2)	Ru(8)–Ru(3)–Ru(2)	89.6(1)	89.4(1)
Ru(6)–Ru(2)–Ru(3)	59.9(1)	59.7(1)	Ru(8)–Ru(3)–Ru(4)	60.3(1)	60.2(1)
Ru(6)–Ru(2)–Ru(4)	90.2(1)	90.0(1)	Ru(8)–Ru(3)–Ru(6)	59.9(1)	59.9(1)
Ru(6)–Ru(2)–Ru(5)	59.0(1)	58.9(1)	Ru(8)–Ru(3)–Ru(7)	58.9(1)	59.1(1)
Ru(10)–Ru(2)–Ru(1)	119.6(1)	119.3(2)	Ru(2)–Ru(4)–Ru(1)	59.2(1)	58.8(1)
Ru(10)–Ru(2)–Ru(3)	90.0(1)	89.7(1)	Ru(3)–Ru(4)–Ru(1)	59.5(1)	59.6(1)
Ru(10)–Ru(2)–Ru(4)	60.3(1)	60.3(1)	Ru(3)–Ru(4)–Ru(2)	60.6(1)	60.8(1)
Ru(10)–Ru(2)–Ru(5)	59.6(1)	59.4(1)	Ru(8)–Ru(4)–Ru(1)	119.8(1)	119.7(2)
Ru(10)–Ru(2)–Ru(6)	60.2(1)	60.2(1)	Ru(8)–Ru(4)–Ru(2)	90.1(1)	90.0(1)
Ru(2)–Ru(3)–Ru(1)	58.6(1)	58.2(1)	Ru(8)–Ru(4)–Ru(3)	60.3(1)	60.2(1)
Ru(4)–Ru(3)–Ru(1)	59.0(1)	58.8(1)	Ru(9)–Ru(4)–Ru(1)	178.3(2)	177.6(2)

Table 3 (*continued*)

	2	**4**		**2**	**4**
Metal–metal–metal					
Ru(9)–Ru(4)–Ru(2)	119.3(1)	118.8(2)	Ru(6)–Ru(8)–Ru(4)	89.4(1)	89.7(1)
Ru(9)–Ru(4)–Ru(3)	119.2(1)	119.3(2)	Ru(7)–Ru(8)–Ru(3)	58.9(1)	58.9(1)
Ru(9)–Ru(4)–Ru(8)	58.9(1)	59.2(1)	Ru(7)–Ru(8)–Ru(4)	118.4(1)	118.5(1)
Ru(10)–Ru(4)–Ru(1)	119.0(1)	118.5(2)	Ru(7)–Ru(8)–Ru(6)	59.3(1)	59.1(1)
Ru(10)–Ru(4)–Ru(2)	59.9(1)	59.7(1)	Ru(9)–Ru(8)–Ru(3)	118.5(1)	118.5(1)
Ru(10)–Ru(4)–Ru(3)	90.2(1)	90.2(1)	Ru(9)–Ru(8)–Ru(4)	59.1(1)	58.9(1)
Ru(10)–Ru(4)–Ru(8)	59.7(1)	59.5(1)	Ru(9)–Ru(8)–Ru(6)	119.6(1)	119.4(2)
Ru(10)–Ru(4)–Ru(9)	59.5(1)	59.1(1)	Ru(9)–Ru(8)–Ru(7)	177.5(1)	177.3(2)
Ru(6)–Ru(5)–Ru(2)	61.7(1)	61.6(1)	Ru(10)–Ru(8)–Ru(3)	89.9(1)	90.2(1)
Ru(10)–Ru(5)–Ru(2)	61.3(1)	61.3(1)	Ru(10)–Ru(8)–Ru(4)	59.9(1)	60.2(1)
Ru(10)–Ru(5)–Ru(6)	61.6(1)	61.8(1)	Ru(10)–Ru(8)–Ru(6)	60.0(1)	60.2(1)
Ru(3)–Ru(6)–Ru(2)	60.5(1)	60.7(1)	Ru(10)–Ru(8)–Ru(7)	119.3(1)	119.2(2)
Ru(5)–Ru(6)–Ru(2)	59.3(1)	59.5(1)	Ru(10)–Ru(8)–Ru(9)	59.6(1)	59.2(1)
Ru(5)—Ru(6)–Ru(3)	119.8(1)	120.2(2)	Ru(8)–Ru(9)–Ru(4)	62.0(1)	61.9(1)
Ru(7)–Ru(6)–Ru(2)	119.4(1)	119.7(2)	Ru(10)–Ru(9)–Ru(4)	61.4(1)	61.9(1)
Ru(7)–Ru(6)–Ru(3)	59.0(1)	59.0(1)	Ru(10)–Ru(9)–Ru(8)	61.3(1)	61.4(1)
Ru(7)–Ru(6)–Ru(5)	178.3(2)	178.3(2)	Ru(4)–Ru(10)–Ru(2)	59.8(1)	60.0(1)
Ru(8)–Ru(6)–Ru(2)	90.3(1)	90.3(1)	Ru(5)–Ru(10)–Ru(2)	59.1(1)	59.3(1)
Ru(8)–Ru(6)–Ru(3)	60.3(1)	60.2(1)	Ru(5)–Ru(10)–Ru(4)	118.9(1)	119.3(1)
Ru(8)–Ru(6)–Ru(5)	119.5(1)	119.1(2)	Ru(6)–Ru(10)–Ru(2)	60.0(1)	60.0(1)
Ru(8)–Ru(6)–Ru(7)	58.9(1)	59.2(1)	Ru(6)–Ru(10)–Ru(4)	89.8(1)	89.7(1)
Ru(10)–Ru(6)–Ru(2)	59.9(1)	59.8(1)	Ru(6)–Ru(10)–Ru(5)	58.8(1)	58.8(1)
Ru(10)–Ru(6)–Ru(3)	90.1(1)	90.1(1)	Ru(8)–Ru(10)–Ru(2)	90.6(1)	90.6(1)
Ru(10)–Ru(6)–Ru(5)	59.6(1)	59.4(1)	Ru(8)–Ru(10)–Ru(4)	60.4(1)	60.3(1)
Ru(10)–Ru(6)–Ru(7)	118.8(1)	118.9(2)	Ru(8)–Ru(10)–Ru(5)	118.9(1)	119.0(1)
Ru(10)–Ru(6)–Ru(8)	59.9(1)	59.7(1)	Ru(8)–Ru(10)–Ru(6)	60.2(1)	60.1(1)
Ru(6)–Ru(7)–Ru(3)	61.7(1)	61.9(1)	Ru(9)–Ru(10)–Ru(2)	118.9(1)	119.0(2)
Ru(8)–Ru(7)–Ru(3)	62.2(1)	62.0(1)	Ru(9)–Ru(10)–Ru(4)	59.1(1)	59.0(1)
Ru(8)–Ru(7)–Ru(6)	61.7(1)	61.8(1)	Ru(9)–Ru(10)–Ru(5)	177.5(1)	177.9(2)
Ru(4)–Ru(8)–Ru(3)	59.4(1)	59.6(1)	Ru(9)–Ru(10)–Ru(6)	119.2(1)	119.5(2)
Ru(6)–Ru(8)–Ru(3)	59.8(1)	59.9(1)	Ru(9)–Ru(10)–Ru(8)	59.1(1)	59.4(1)
C(carbonyl)–metal–metal					
C(11)–Ru(1)–Ru(2)	157(1)	158(1)	C(41)–Ru(4)–Ru(10)	147(1)	150(1)
C(11)–Ru(1)–Ru(3)	97(1)	98(1)	C(42)–Ru(4)–Ru(1)	91(1)	90(1)
C(11)–Ru(1)–Ru(4)	101(1)	100(1)	C(42)–Ru(4)–Ru(2)	95(1)	96(1)
C(12)–Ru(1)–Ru(2)	97(2)	100(2)	C(42)–Ru(4)–Ru(3)	148(1)	148(1)
C(12)–Ru(1)–Ru(3)	99(2)	101(2)	C(42)–Ru(4)–Ru(8)	147(1)	148(1)
C(12)–Ru(1)–Ru(4)	155(2)	158(2)	C(42)–Ru(4)–Ru(9)	90(1)	91(1)
C(13)–Ru(1)–Ru(2)	103(1)	102(2)	C(42)–Ru(4)–Ru(10)	95(1)	96(1)
C(13)–Ru(1)–Ru(3)	161(1)	161(2)	C(51)–Ru(5)–Ru(2)	159.8(9)	161(1)
C(13)–Ru(1)–Ru(4)	101(1)	102(2)	C(51)–Ru(5)–Ru(6)	102(1)	105(1)
C(21)–Ru(2)–Ru(1)	97(2)	97(2)	C(51)–Ru(5)–Ru(10)	101(1)	101(1)
C(21)–Ru(2)–Ru(3)	103(2)	102(2)	C(52)–Ru(5)–Ru(2)	101(1)	101(1)
C(21)–Ru(2)–Ru(4)	155(2)	154(2)	C(52)–Ru(5)–Ru(6)	160(1)	160(1)
C(21)–Ru(2)–Ru(5)	84(2)	84(2)	C(52)–Ru(5)–Ru(10)	102(1)	103(1)
C(21)–Ru(2)–Ru(6)	96(2)	96(2)	C(53)–Ru(5)–Ru(2)	101(1)	101(2)
C(21)–Ru(2)–Ru(10)	142(2)	143(2)	C(53)–Ru(5)–Ru(6)	100(1)	99(2)
C(22)–Ru(2)–Ru(1)	90(1)	90(1)	C(53)–Ru(5)–Ru(10)	158(1)	158(2)
C(22)–Ru(2)–Ru(3)	147(1)	147(1)	C(61)–Ru(6)–Ru(2)	145(1)	149(1)
C(22)–Ru(2)–Ru(4)	96(1)	96(1)	C(61)–Ru(6)–Ru(3)	148(1)	144(1)
C(22)–Ru(2)–Ru(5)	92(1)	92(1)	C(61)–Ru(6)–Ru(5)	89(1)	93(1)
C(22)–Ru(2)–Ru(6)	149(1)	149(1)	C(61)–Ru(6)–Ru(7)	92(1)	88(1)
C(22)–Ru(2)–Ru(10)	97(1)	96(1)	C(61)–Ru(6)–Ru(8)	95(1)	93(1)
C(31)–Ru(3)–Ru(1)	91(1)	93(2)	C(61)–Ru(6)–Ru(10)	94(1)	96(1)
C(31)–Ru(3)–Ru(2)	97(1)	97(2)	C(62)–Ru(6)–Ru(2)	96(1)	98(1)
C(31)–Ru(3)–Ru(4)	148(1)	150(2)	C(62)–Ru(6)–Ru(3)	98(1)	97(2)
C(31)–Ru(3)–Ru(6)	96(1)	94(2)	C(62)–Ru(6)–Ru(5)	89(1)	91(2)
C(31)–Ru(3)–Ru(7)	90(1)	88(2)	C(62)–Ru(6)–Ru(7)	92(1)	90(2)
C(31)–Ru(3)–Ru(8)	147(1)	145(2)	C(62)–Ru(6)–Ru(8)	150(1)	148(2)
C(32)–Ru(3)–Ru(1)	90(1)	88(1)	C(62)–Ru(6)–Ru(10)	147(1)	149(1)
C(32)–Ru(3)–Ru(2)	148(1)	144(1)	C(71)–Ru(7)–Ru(3)	97(1)	96(1)
C(32)–Ru(3)–Ru(4)	98(1)	95(1)	C(71)–Ru(7)–Ru(6)	157(1)	156(1)
C(32)–Ru(3)–Ru(6)	150(1)	152(1)	C(71)–Ru(7)–Ru(8)	101(1)	101(1)
C(32)–Ru(3)–Ru(7)	92(1)	95(1)	C(72)–Ru(7)–Ru(3)	104(1)	105(1)
C(32)–Ru(3)–Ru(8)	100(1)	99(1)	C(72)–Ru(7)–Ru(6)	98(1)	100(1)
C(41)–Ru(4)–Ru(1)	92(1)	90(1)	C(72)–Ru(7)–Ru(8)	159(1)	161(1)
C(41)–Ru(4)–Ru(2)	149(1)	147(1)	C(73)–Ru(7)–Ru(3)	155(1)	156(1)
C(41)–Ru(4)–Ru(3)	96(1)	97(1)	C(73)–Ru(7)–Ru(6)	100(1)	101(1)
C(41)–Ru(4)–Ru(8)	95(1)	99(1)	C(73)–Ru(7)–Ru(8)	95(1)	96(1)
C(41)–Ru(4)–Ru(9)	89(1)	92(1)	C(81)–Ru(8)–Ru(3)	149(1)	152(1)

Table 3 (*continued*)

	2	4		2	4
C(carbonyl)–metal–metal					
C(81)–Ru(8)–Ru(4)	147(1)	146(1)	C(92)–Ru(9)–Ru(10)	97(1)	97(1)
C(81)–Ru(8)–Ru(6)	97(1)	100(1)	C(93)–Ru(9)–Ru(4)	99(1)	98(2)
C(81)–Ru(8)–Ru(7)	93(1)	94(1)	C(93)–Ru(9)–Ru(8)	102(1)	100(1)
C(81)–Ru(8)–Ru(9)	90(1)	88(1)	C(93)–Ru(9)–Ru(10)	158(1)	156(1)
C(81)–Ru(8)–Ru(10)	96(1)	97(1)	C(101)–Ru(10)–Ru(2)	148(1)	151(1)
C(82)–Ru(8)–Ru(3)	98(1)	96(1)	C(101)–Ru(10)–Ru(4)	148(1)	146(1)
C(82)–Ru(8)–Ru(4)	99(1)	98(1)	C(101)–Ru(10)–Ru(5)	91(1)	93(1)
C(82)–Ru(8)–Ru(6)	148(1)	146(1)	C(101)–Ru(10)–Ru(6)	97(1)	99(1)
C(82)–Ru(8)–Ru(7)	90(1)	89(1)	C(101)–Ru(10)–Ru(8)	96(1)	96(1)
C(82)–Ru(8)–Ru(9)	91(1)	92(1)	C(101)–Ru(10)–Ru(9)	91(1)	88(1)
C(82)–Ru(8)–Ru(10)	149(1)	150(1)	C(102)–Ru(10)–Ru(2)	93(1)	93(1)
C(91)–Ru(9)–Ru(4)	158(1)	161(2)	C(102)–Ru(10)–Ru(4)	96(1)	97(1)
C(91)–Ru(9)–Ru(8)	98(1)	101(2)	C(102)–Ru(10)–Ru(5)	88(1)	88(1)
C(91)–Ru(9)–Ru(10)	103(1)	104(2)	C(102)–Ru(10)–Ru(6)	144(1)	144(1)
C(92)–Ru(9)–Ru(4)	99(1)	102(1)	C(102)–Ru(10)–Ru(8)	150(1)	150(1)
C(92)–Ru(9)–Ru(8)	156(1)	157(1)	C(102)–Ru(10)–Ru(9)	93(1)	93(1)
Selected mean angles					
C(carbonyl)–M–C(carbonyl)	95(2)	94(2)	C(phenyl)–P–N	113(2)	113(2)
O–C–M	175(5)	175(6)	C(phenyl)–P–C(phenyl)	106(1)	106(1)
Counter ion and solvent angles					
P(2)–N–P(1)	159(2)	159(2)	Cl(2)–C(1)–Cl(1)	103(2)	107(3)



Scheme 1 Synthesis of $[Ru_{10}N(CO)_{24}]^-$ 4: (*i*) diglyme, 162 °C, 3 h (the decaruthenium clusters were obtained in variable proportions from this reaction. The origin of the hydride ligand is unknown, but is assumed to be derived from traces of water in the solvent); (*ii*) dbu, 20 °C, CH_2Cl_2; (*iii*) HCl gas, 20 °C, CH_2Cl_2, 5 min

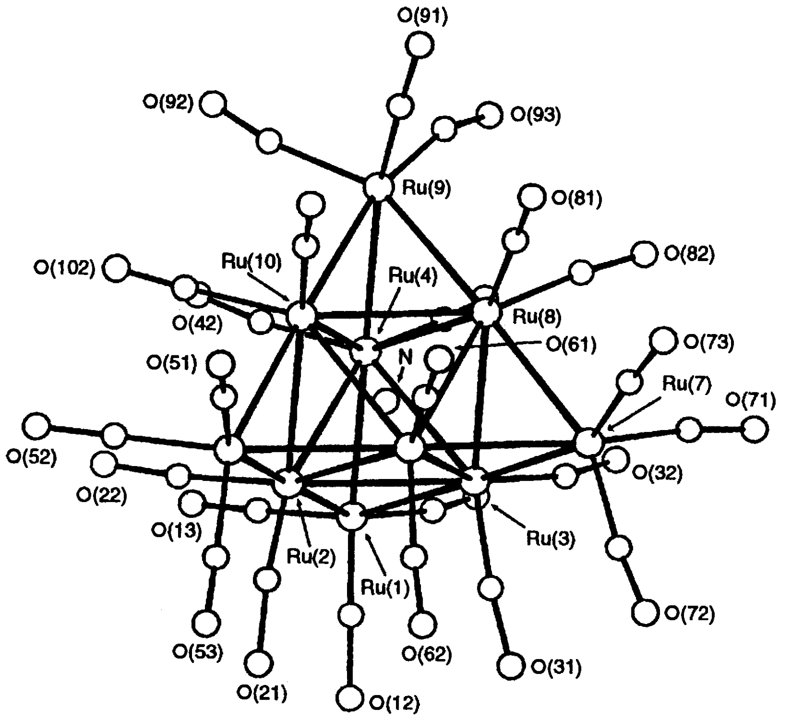


Fig. 3 Structure of $[Ru_{10}N(CO)_{24}]^-$ 4

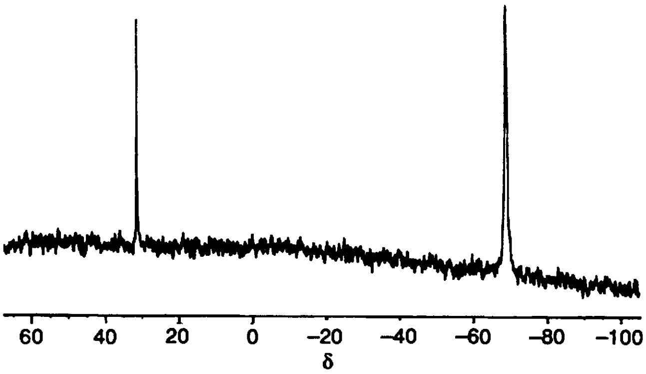


Fig. 4 The 28.90 MHz ^{14}N NMR spectrum of $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$ in CD_2Cl_2 solution at 293 K

resonance of the counter ion ($w_{\frac{1}{2}}$ = 54 Hz), is a reflection of the highly symmetric environment of the quadrupolar ^{14}N nucleus ($I = 1$) in the octahedral interstitial site of the cluster in comparison to the linear co-ordination environment of nitrogen in $[N(PPh_3)_2]^+$. The absence of any observed splitting of the resonance of the $[N(PPh_3)_2]^+$ nitrogen due to $^1J(^{14}N-^{31}P)$ coupling may also be attributed to the highly asymmetric environment of the nitrogen in this system causing the line width to encompass the coupling constant.

As is the case for the carbide $[Ru_{10}C(CO)_{24}]^{2-}$ **3**, the IR spectrum of $[Ru_{10}N(CO)_{24}]^-$ **4** in CH_2Cl_2 solution exhibits three bands in the ν_{CO} region (Table 1). These bands are in the frequency range where those of $[Ru_{10}H(C)(CO)_{24}]^-$ **2** are observed, thus illustrating the monoanionic nature of this cluster species. The shape and relative intensity of the bands are also reminiscent of the two symmetrical bands observed in the spectrum of **2** with the lowest frequency band being only a very weak shoulder. Fig. 5 illustrates the spectra of **2**, **3** and **4** for comparison. This difference between the spectra of the two necessarily isostructural and isosymmetric clusters **3** and **4** suggests that it is the difference in charge between the two which is influencing the appearance of the spectra, and that vibrational modes are being differentially affected by this change in charge.

In order further to establish conclusively the identity of the interstitial atom in **4**, its ^{15}N-labelled analogue was prepared as the $[NMe_4]^+$ salt by condensation of $[NMe_4][Ru_6{}^{15}N(CO)_{16}]$ with $[Ru_3(CO)_{12}]$. Infrared spectra of this salt in a CsI disc at 293 K displayed a single strong absorption at 658 cm^{-1} attributable to vibration of the ^{15}N nitride within the central octahedral cavity of the cluster. The frequency of this band compares with that at 682 cm^{-1} for the unlabelled material, thus demonstrating a shift very close to that expected for replacement of ^{14}N by ^{15}N; assuming infinite mass for the metal-cluster core a frequency of 659 cm^{-1} is predicted for the ^{15}N cluster. By analogy with the carbide [ν(Ru–^{12}C) 728 cm^{-1}], the occurrence of a single band suggests an environment for the nitride closely approximating to octahedral.

The room-temperature ^{13}C NMR spectrum consists of two resonances of equal intensity at δ 210.0 and 189.4 which may be assigned to the 12 $Ru(CO)_2$ carbonyls at the apices of the central octahedron and the 12 $Ru(CO)_3$ carbonyls at the apices of the tetrahedral structure respectively. This assignment is based upon the pattern established for other tetracapped octahedral ruthenium and osmium clusters for which the resonances of the $M(CO)_2$ carbonyls have been shown to occur at higher frequencies than those of the $M(CO)_3$ carbonyls.[7] Although coalescence of the two signals could not be observed in a variable-temperature study due to decomposition of the cluster below the coalescence temperature, it is clear that the activation barrier associated with carbonyl exchange in this species is comparable with that observed for the formally isoelectronic monoanion $[Ru_{10}H(C)(CO)_{24}]^-$ **2**, thus further supporting the proposition that the overall charge on the cluster system strongly influences the ease of carbonyl exchange.

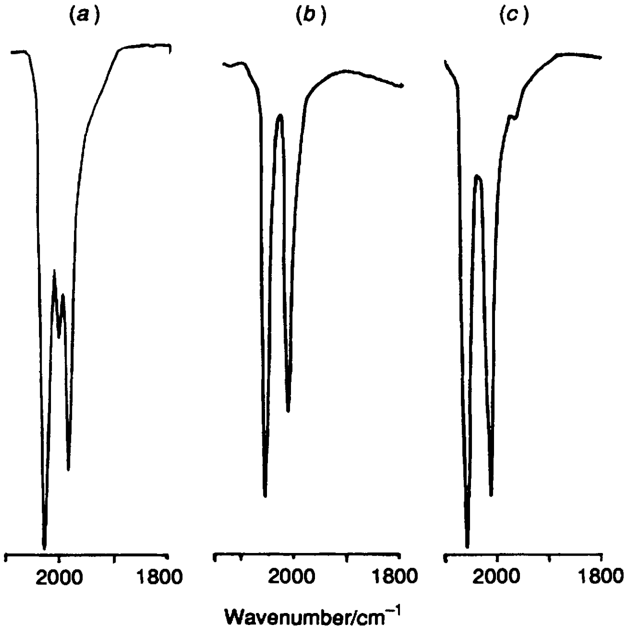


Fig. 5 Solution (CH_2Cl_2) IR spectra of **3** (*a*), **2** (*b*) and **4** (*c*) as their $[N(PPh_3)_2]^+$ salts in the ν(CO) region

$$\underset{\mathbf{3}}{[Ru_{10}C(CO)_{24}]^{2-}} \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} 1.33[Ru_3(CO)_{12}] + [Ru_6C(CO)_{16}]^{2-}$$

$$\underset{\mathbf{2}}{[Ru_{10}H(C)(CO)_{24}]^-} \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} 1.33[Ru_3(CO)_{12}] + [Ru_6H(C)(CO)_{16}]^-$$

$$\underset{\mathbf{4}}{[Ru_{10}N(CO)_{24}]^-} \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} 1.67[Ru_3(CO)_{12}] + [Ru_5N(CO)_{14}]^-$$

Scheme 2 Reversible build up and degradation of decaruthenium clusters: (*i*) CO gas, 20 °C, CH_2Cl_2, 5 min; (*ii*) diglyme, 162 °C, 3 h

Degradation Reactions with Carbon Monoxide.—The facile nature of the syntheses of the decaruthenium systems $[Ru_{10}E(CO)_{24}]^{n-}$ (E = C, n = 2; E = N, n = 1) by condensation of ruthenium carbonyl fragments with the appropriate hexanuclear precursors led us to speculate upon the possible reversibility of these reactions. Such reversible cluster build up/degradation is not without precedent with the hexaruthenium nitride $[Ru_6N(CO)_{16}]^-$ being quantitatively converted to the pentanuclear system $[Ru_5N(CO)_{14}]^-$ and $[Ru_3(CO)_{12}]$ by CO at room temperature and pressure.[19] The reaction is readily reversed in thf at reflux. Analogously, we find that reaction of the $[N(PPh_3)_2]^+$ salt $[Ru_{10}C(CO)_{24}]^{2-}$ **3** with CO in CH_2Cl_2 at room temperature and pressure proceeds quantitatively to yield $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ and $[Ru_3(CO)_{12}]$ within 5 min according to Scheme 2.[21] Unsurprisingly, removal of the solvent and thermolysis of the residue in diglyme under reflux provides **3**, thus illustrating the reversibility of the transformation. In a similar fashion, $[N(PPh_3)_2][Ru_{10}HC(CO)_{24}]$ **2** provides $[N(PPh_3)_2][Ru_6HC(CO)_{16}]$ and $[Ru_3(CO)_{12}]$ on treatment with CO. Similar CO treatment of the nitride $[Ru_{10}N(CO)_{24}]^-$ **4** provides $[Ru_5N(CO)_{14}]^-$ and $[Ru_3(CO)_{12}]$, a reaction which is equally reversible (Scheme 2). The further degradation of the nitride to the pentanuclear system is unsurprising in view of the conversion of the Ru_6N cluster to this species under similar conditions as noted above. This disparity has been attributed to the preference of nitrogen for lower co-ordination numbers relative to carbon in cluster systems reflecting the smaller size of nitrogen and the consequent increasing difficulty of effective bonding to each of the metals as the nuclearity is increased. The result is therefore that, as an interstitial atom, nitrogen is less effective at stabilising a large array of metals than carbon.[19] In this context it is also relevant that the hexaruthenium carbide $[Ru_6C(CO)_{17}]$ is converted to $[Ru_5C(CO)_{15}]$ only under forcing conditions (90 atm, 100 °C).[22] These degradation reactions are in contrast to the stability of the carbidodecaosmium species $[Os_{10}C(CO)_{24}]^{2-}$ which resists degradation by CO even under extreme conditions.[23] This difference may presumably be attributed to a higher ratio of D-(M–M) : D(M–CO) for osmium than for ruthenium (D = bond energy).

Experimental

General Procedures.—The compounds $[N(PPh_3)_2]Cl$,[24] $[N(PPh_3)_2][N_3]$,[25] $[Ru_3(CO)_{12}]$,[26] ^{13}C-enriched (*ca.* 60%) $[Ru_3(CO)_{12}]$[27] and $[N(PPh_3)_2][Ru_6N(CO)_{16}]$[19] were prepared by published procedures. The complex $[NMe_4][Ru_6{}^{15}N(CO)_{16}]$ was prepared using $[NMe_4][^{15}N_3]$ obtained by metathesis of $K^{15}N_3$ with $[NMe_4]Cl$. Tetrahydrofuran, diethyl ether and bis(2-methoxyethyl) ether (diglyme) were distilled from sodium–benzophenone under nitrogen immediately prior to use. Dichloromethane and hexane were distilled from calcium hydride under nitrogen. Acetone and methanol were reagent grade and used as received. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (dbu) was obtained from Aldrich and used as received. All reactions were carried out under an atmosphere of nitrogen. Infrared and NMR spectra were run on Perkin-Elmer FT1710 and Bruker AM400 spectrometers respectively. Low-temperature IR spectra were obtained using an evacuable apparatus supplied by Specac. Negative-ion fast atom bombardment mass spectra were obtained on an AEI/Kratos MS50 instrument. The ^{13}C NMR spectra were obtained from CD_2Cl_2 solutions at 100.62 MHz and tris(acetylacetonato)chromium(III) was routinely added as a shiftless relaxation agent. The ^{14}N NMR spectra were obtained from *ca.* 30 mg of $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$ in CD_2Cl_2 (0.5 cm^3) containing $MeNO_2$ as an internal reference [$\delta(MeNO_2) = 0$]. For the spectrum shown in Fig. 4 the solvent was CD_2Cl_2 alone. The spectroscopic data for the new compounds are summarised in Table 1.

Syntheses.—$[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$. *Method* 1. A suspension of $[Ru_3(CO)_{12}]$ (1 g, 1.56 mmol) in mesitylene (100 cm^3) was heated to reflux for 6 h during which time the solution became dark brown and a large amount of a fine black material was deposited. The hot solution was filtered and the solid collected dissolved in a solution of $[N(PPh_3)_2]Cl$ (0.3 g, 0.52 mmol) in acetone–methanol (1 : 1) (50 cm^3). After stirring for 1 h the olive green solution was filtered to remove insoluble material and the acetone was slowly removed under a stream of nitrogen to provide the salt as a black microcrystalline material (366 mg, 35%).

Method 2. Hydrogen chloride gas was bubbled through a solution of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ (100 mg, 0.036 mmol) in CH_2Cl_2 (20 cm^3) for 5 min. During this time the bright green solution became olive green. Addition of methanol followed by slow removal of the CH_2Cl_2 under a stream of nitrogen provided the salt as above (76 mg, 95%).

$[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$. *Method* 1. The black material obtained from the mesitylene thermolysis of $[Ru_3(CO)_{12}]$ (1 g) as above was dissolved in acetone–methanol (1 : 1) (50 cm^3) containing $[N(PPh_3)_2]Cl$ (600 mg, 1.05 mmol). This solution was heated to reflux for 1 h during which time it changed from olive green to bright green. Slow removal of the acetone under a stream of nitrogen provided the salt as a black microcrystalline material (455 mg, 35%).

Method 2. To a solution of $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$ (100 mg, 0.045 mmol) in CH_2Cl_2 (20 cm^3) was added $[N(PPh_3)_2]Cl$ (30 mg, 0.052 mmol) followed by an excess of dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) (1 drop). The solution was stirred at room temperature for 1 h during which time it changed from olive green to bright green. Addition of methanol (20 cm^3) followed by slow removal of the CH_2Cl_2 under a stream of nitrogen provided the salt as above (120 mg, 97%).

$[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$. *Method* 1. To a suspension of $[Ru_3(CO)_{12}]$ (1 g, 1.56 mmol) in diglyme (50 cm^3) was added $[N(PPh_3)_2][N_3]$ (275 mg, 0.47 mmol) and the mixture was heated to reflux for 3 h. To the resulting green solution was added silica (10 g) followed by ether (200 cm^3). The silica-adsorbed salts were filtered off and washed with ether (2 × 10 cm^3) and the silica then extracted with acetone (3 × 10 cm^3). To the green acetone solution was added methanol (20 cm^3) and the acetone slowly removed under a stream of nitrogen. The resulting black microcrystalline material (420 mg) was found to be a mixture of the $[N(PPh_3)_2]^+$ salts of the carbides **2** and **3** and the nitride **4**. Thin-layer chromatographic (TLC) separation on silica (CH_2Cl_2–hexane, 1 : 1) of this mixture was unsuccessful at separating **2** and **4**, however, addition of dbu and $[N(PPh_3)_2]Cl$ to a solution of the mixture in CH_2Cl_2 prior to separation resulted in the separation of two bright green bands of the $[N(PPh_3)_2]^+$ salts of $[Ru_{10}C(CO)_{24}]^{3-}$ **3** and $[Ru_{10}N(CO)_{24}]^-$ **4**. However, ^1H NMR spectra of the latter derived in this way always contained a weak signal at δ −13.5 due to residual $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$.

Method 2. To a solution of $[N(PPh_3)_2][Ru_6N(CO)_{16}]$ (500 mg, 0.31 mmol) in diglyme (50 cm^3) was added $[Ru_3(CO)_{12}]$ (265 mg, 0.42 mmol) and the mixture was heated to reflux for 3 h. To the resulting green solution was added silica (10 g) followed by ether (200 cm^3). The silica-adsorbed salts were filtered off and washed with ether (2 × 10 cm^3) and the silica was then extracted with acetone (3 × 10 cm^3). To the green acetone solution was added methanol (20 cm^3) and the acetone was slowly removed under a stream of nitrogen. The resulting black microcrystalline material (480 mg, 69%) was found to be $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$ uncontaminated with carbide impurities.

Reactions.—$[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ *and* $[N(PPh_3)_2][Ru_{10}HC(CO)_{24}]$ *with* CO. Carbon monoxide was bubbled through a solution of the $[N(PPh_3)_2]^+$ salt of **3** (50 mg, 0.018 mmol) in CH_2Cl_2 (20 cm^3). Over a period of 5 min the solution first became brown and then orange. Concentration of the solution followed by separation by TLC on silica (CH_2Cl_2) yielded two orange products which were identified as $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ from their IR and mass spectra. In a separate experiment, the orange solution was reduced to dryness and the residue dissolved in diglyme (20 cm^3). Heating of this solution to reflux for 3 h resulted in a green solution whose IR spectrum was identical to that of a solution of **3** in the same solvent. In a similar experiment **2** was subjected to CO which led to an orange solution within 5 min, TLC separation of which (CH_2Cl_2–hexane, 1 : 1) gave two bands which were identified as $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2][Ru_6H(C)(CO)_{16}]$ from their IR spectra.

$[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$ *with* CO. Carbon monoxide was bubbled through a solution of the $[N(PPh_3)_2]^+$ salt of **4** (50 mg, 0.022 mmol) in CH_2Cl_2 (20 cm^3). Over a period of 5 min the solution first became brown and then orange. Concentration of the solution followed by separation by TLC on silica (CH_2Cl_2–hexane, 1 : 1) yielded two orange products which were identified as $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2][Ru_5N(CO)_{14}]$ from their IR and mass spectra. In a separate experiment, removal of CH_2Cl_2 from the solution followed by thermolysis of the residue in diglyme (10 cm^3) led to the reformation of **4**.

Crystal Data and Structure Solution and Refinement.—*Crystal data for* $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$. $C_{61}H_{31}NO_{24}P_2Ru_{10}\cdot CH_2Cl_2$, M = 2319.49, monoclinic, space group $P2_1/c$, a = 11.777(2), b = 17.805(4), c = 35.365(5) Å, β = 94.03(1)°, U = 7397.33 Å^3, D_c = 2.08 g cm^{-3}, Z = 4, μ(Mo-Kα)

= 20.0 cm^{-1}, $F(000)$ = 4432. Crystal dimensions 0.10 × 0.38 × 0.32 mm.

Crystal data for $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$. $C_{60}H_{30}N_2O_{24}P_2Ru_{10}\cdot CH_2Cl_2$, M = 2319.87, monoclinic, space group $P2_1/c$, a = 11.763(2), b = 17.817(4), c = 35.330(5) Å, β = 94.33(1)°, U = 7383.38 Å^3, D_c = 2.09 g cm^{-3}, Z = 4, μ(Mo-Kα) = 19.72 cm^{-1}, $F(000)$ = 4432. Crystal dimensions 0.20 × 0.25 × 0.19 mm.

Data collection. Data were collected in the range θ 3–25° for both $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$ and $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$, with a scan width of 0.80° for the former and 0.90° for the latter, using the technique described previously.[28] Equivalent reflections were merged to give 3555 unique data for $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$ and 2300 for $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$ with $I/\sigma(I) > 3.0$. For both structures absorption corrections were applied to the data after initial refinement with isotropic thermal parameters for all atoms.[29]

Structure solution and refinement.[30] The coordinates of all ten metal atoms in the anion **2** were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The hydride ligand was not located and not included in structure factor calculations. The coordinates of the ten metal atoms from the above hydride $[Ru_{10}H(C)(CO)_{24}]^-$ **2** were used as a 'partial structure' in the solution of $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The interstitial nitrido atom (the first to have been located in a decanuclear cluster) refined satisfactorily giving a final isotropic thermal parameter of 0.0283 Å^2. In view of the very close similarity of the unit-cell dimensions and the atomic parameters to those of the corresponding salt of the monohydrido carbido cluster dianion **2**, the possibility that this species had been isolated in the synthesis was carefully considered. Repetition of the refinement of the structure with the central atom assigned as a carbon atom instead of nitrogen resulted in a very low thermal parameter of 0.0001 Å^2. Conclusive proof of the presence of an interstitial N atom was later obtained from ^{14}N NMR spectroscopy.

For both structures, the carbon atoms of the phenyl rings in the counter ion were constrained to idealised hexagonal geometry (C–C 1.395 Å) with the attached H atoms in calculated sites (C–H 1.08 Å) with fixed isotropic thermal parameters of 0.08 Å^2.

Refinement of both structures was very difficult as four of the ruthenium atoms of the metal core [Ru(1), Ru(2), Ru(5) and Ru(8)] lie close to y = 0, with the remaining metals occurring in pairs lying almost equally either side of this plane. Effectively both clusters have near-mirror symmetry about the plane y = 0.0 and this causes correlations between 'pseudo symmetry'-related atomic parameters on either side of this plane. The correlations were prevented by refining these atoms in alternate cycles of blocked full-matrix refinement. For both structures, the ten ruthenium atoms and the two phosphorus atoms were assigned anisotropic thermal parameters in the final cycles of blocked full-matrix refinement (the nitrogen atom of the counter ion was also assigned anisotropic thermal parameters in **4**), which converged at R = 0.0725 and R' = 0.0650 for $[N(PPh_3)_2][Ru_{10}H(C)(CO)_{24}]$ and R = 0.0613 and R' = 0.0582 for $[N(PPh_3)_2][Ru_{10}N(CO)_{24}]$, with weights of $w = 1/\sigma^2F_o$ assigned to the individual reflections. Although the problems with refinement due to pseudo symmetry in both crystal structures has resulted in relatively high estimated standard deviations, the principal features of both structures are nevertheless well established.

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

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