The Reactions of $[Ru_6C(CO)_{17}]$ with Dissolved and Anchored Phosphines. Crystal and Molecular Structure of $[Ru_6C(CO)_{16}(PPh_2Et)]$†

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Substitution reactions of $[Ru_6C(CO)_{17}]$ (1) have yielded $[Ru_6C(CO)_{17-n}L_n]$ (L = PPh_2Et, $n = 1$ and 2; L = $P(OMe)_3$, n = 1—4). The structure of $[Ru_6C(CO)_{16}(PPh_2Et)]$ (2) was determined by *X*-ray diffraction and used as a basis for interpreting the n.m.r. data of the other complexes. Complex (1) and the two PPh_2Et derivatives all exhibit one ^{13}CO n.m.r. signal at room temperature. Infrared spectral studies indicated that $[Ru_6C(CO)_{16}(PPh_2C_2H_4R)][R = Si(OEt)_x(O{-}Si{\leqslant})_{3-x}]$ is formed when (1) is interacted with phosphinated silica gel under ambient conditions. At 50 °C, a second substitution by a surface phosphine occurs. By 100 °C (*in vacuo*), the cluster integrity is lost and *cis*-$[Ru(CO)_2(O{-}Si{\leqslant})_2(PPh_2C_2H_4R)_2]$ is considered to be the carbonyl-containing species. Complex (2) is monoclinic, space group $P2_1/n$, with a = 18.754(3), b = 17.624(3), c = 22.841(3) Å, β = 91.94(2)°, and Z = 8. The structure was determined using 10 739 observed intensities and refined to R = 0.043. Complex (2) has a similar molecular geometry to that of (1), with one CO group substituted by a PPh_2Et ligand. The phosphine lies asymmetrically over the bridging carbonyl, and renders each molecule enantiomeric.

As part of our programme of synthesising new heterogeneous catalysts with a single metal particle type,[1] we were interested in preparing an anchored second-transition-series metal carbonyl cluster, particularly since the triosmium systems previously prepared have been found to be relatively poor catalysts.[2-4] Derivatives of $[Ru_6C(CO)_{17}]$ (1) had good potential since (1) was reported to undergo a single substitution with PPh_3 under mild conditions.[5] Specific substitutions are virtually essential for the preparation of well characterised anchored clusters. In addition, the central carbon[6] might be expected to give extra stability to the cluster under catalytic conditions; this has been observed in the homogeneous catalytic conversion of synthesis gas catalysed by rhodium clusters.[7] Finally, the carbido-cluster can now be synthesised in moderate yields from $[Ru_3(CO)_{12}]$.[8] The structures of the PPh_3 substitution products had not been investigated. We therefore began our investigation by studying the substitution reactions of PPh_2Et, an analogue of phosphinated silica gel, and $P(OMe)_3$ (a good n.m.r. probe). In the course of this work, a preliminary account of the substitution reactions of $P(OMe)_3$ was published.[9] Our results showed that a specific anchoring reaction was possible and so we also report the synthesis and thermal decomposition of $[Ru_6C(CO)_{16}(PPh_2CH_2CH_2R)]$ $[R = Si(OEt)_x(O{-}Si{\leqslant})_{3-x}]$.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer with a model 3500 Data Station. Hydrogen-1 and ^{13}C n.m.r. spectra were run on a Varian Associates XL-100 and mass spectra on an AEI MS12, using tris(perfluoroheptyl)-*sym*-triazine as reference.

All preparations were carried out under white-spot N_2. Chromatography was on 1-mm silica t.l.c. plates unless otherwise stated. Solvents were all dried prior to use by distillation above CaH_2, and stored over molecular sieves.

$[Ru_6C(CO)_{17}]$ (1).—(*a*) A suspension of $[Ru_3(CO)_{12}]$ (1.5116 g) in di-n-butyl ether (30 cm^3) was heated under reflux for 6 h and the product extracted (as in ref. 5) to give $[Ru_6C(CO)_{17}]$ (0.2885 g, 22%).

(*b*) $[Ru_3(CO)_{12}]$ (0.2500 g) and n-hexane (50 cm^3) were charged into a 100-ml Roth autoclave which was then purged and pressurised (50 bar ‡) with ethylene.[9,10] On stirring the pressure dropped, due to ethylene dissolution, and was adjusted to a final value of 20 bar. This was then heated for 3 h at 150 °C after which time the stirrer was switched off, the autoclave removed from its heater-housing and allowed to cool. Filtration separated crystalline $[Ru_6C(CO)_{17}]$ (0.0926 g) from a brown supernatant solution, believed to contain various co-ordinated ethylene adducts;[11] yield of (1) = 43%. Mass spectrum: M = 1 096 based on Ru_6 = 608.

$[Ru_6C(CO)_{16}(PPh_2Et)]$ (2).—An equimolar quantity of PPh_2Et (0.0088 g, 0.0408 mmol) was added to a solution of $[Ru_6C(CO)_{17}]$ (0.0451 g, 0.0412 mmol) in CH_2Cl_2 (35 cm^3). After an immediate darkening in colour the solution was stirred for several hours until total consumption of the starting material had occurred. Removal of the solvent *in vacuo* and chromatographing the residue, using ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 4, v/v) as eluant, gave $[Ru_6C(CO)_{16}(PPh_2Et)]$ (R_f = 0.63, 0.0450 g) as large acicular crystals; yield = 85% (Found: C, 29.4; H, 1.20. Calc.: C, 29.5; H, 1.15%). I.r. (KBr disc): ν(CO) 2 084m, 2 053(sh), 2 038vs, 2 021s (sh), 2 008vs, 1 997ms, 1 993(sh), 1 984m (sh), 1 979ms, 1 972m, 1 962m, 1 815m cm^{-1}.

A similar mixture of reactants heated under reflux in n-hexane (20 cm^3) for 30 min gave the same result.

$[Ru_6C(CO)_{16}(PPh_3)]$ (3).—A suspension of $[Ru_6C(CO)_{17}]$ (0.0508 g, 0.0464 mmol) and PPh_3 (0.0247 g, 0.0941 mmol) was heated under reflux in n-hexane (20 cm^3) for 3 h. Isolation as above gave $[Ru_6C(CO)_{16}(PPh_3)]$[5] (R_f = 0.67, 0.0433 g); yield = 71%.

$[Ru_6C(CO)_{15}(PPh_2Et)_2]$ (4).—$[Ru_6C(CO)_{17}]$ (0.0452 g, 0.0413 mmol) and PPh_2Et (0.0199 g, 0.0929 mmol) were heated under reflux in n-hexane for 3 h, during which time the solution changed from a deep red to a dark brown. After removing the solvent on a rotary evaporator, the residue was chromatographed with ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 4, v/v) to give a single, broad band characterised as $[Ru_6C(CO)_{15}(PPh_2Et)_2]$ (R_f = 0.49,

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† μ_6-Carbido-μ-carbonyl-pentadecacarbonyl(ethyldiphenylphosphine)-*octahedro*-hexaruthenium.

‡ Throughout this paper: 1 bar ≈ 101 325 N m^{-2}; 1 Torr ≈ (101 325/760) N m^{-2}.

0.0384 g); yield = 64% (Found: C, 37.2; H, 1.90. Calc.: C, 36.0; H, 2.05%).

When a similar mixture was stirred in CH_2Cl_2 for 4 days the same product was obtained.

$[Ru_6C(CO)_{17-x}\{P(OMe)_3\}_x]$ (x = 1, 2, 3, *or* 4).—(*a*) $[Ru_6C(CO)_{17}]$ (0.0280 g, 0.0255 mmol) was dissolved in CH_2Cl_2 (25 cm^3), $P(OMe)_3$ (0.0042 g, 0.0338 mmol) added, and the resulting solution stirred for 2 h at room temperature. The crimson residue, obtained after removing the solvent under reduced pressure, was chromatographed with n-hexane–CH_2Cl_2 (1 : 1 v/v) as eluant to give two distinct bands.

Band (*i*), $[Ru_6C(CO)_{16}\{P(OMe)_3\}]$ (5) (R_f = 0.37, 0.0133 g); yield = 44% (Found: C, 19.6; H, 1.05. Calc.: C, 20.2; H, 0.75%). Mass spectrum: M = 1 192 based on Ru_6 = 608. ^{1}H N.m.r.: δ (p.p.m.) 3.77 [d, J(PH) 12 Hz].

Band (*ii*), $[Ru_6C(CO)_{15}\{P(OMe)_3\}_2]$ (6) (R_f = 0.20, 0.0127 g); yield = 39% (Found: C, 20.4; H, 1.55. Calc.: C, 20.5; H, 1.40%). ^{1}H N.m.r.: δ (p.p.m.) 3.68 [d, J(PH) 12], 3.75 [d, J(PH) 12 Hz], relative intensity *ca.* 1 : 2.

(*b*) $[Ru_6C(CO)_{17}]$ (0.0428 g, 0.0391 mmol) was dissolved in CH_2Cl_2 (25 cm^3), $P(OMe)_3$ (0.014 9 g, 0.12 mmol) added, and the solution stirred for 2 h. The crimson residue obtained was chromatographed, as above, to give two bands. The most mobile band was identified as $[Ru_6C(CO)_{15}\{P(OMe)_3\}_2]$ (0.016 g); yield = 32%. The second, found just above the baseline, was characterised as $[Ru_6C(CO)_{14}\{P(OMe)_3\}_3]$ (7) (0.0285 g); yield = 53% (Found: C, 21.0; H, 1.80. Calc.: C, 20.8; H, 1.95%). ^{1}H N.m.r.: δ (p.p.m.) 3.69 [d, J(PH) 12], 3.78 [d, J(PH) 12 Hz], relative intensity 2 : 1.

(*c*) $[Ru_6C(CO)_{17}]$ (0.0295 g, 0.0269 mmol) was heated under reflux in n-hexane (15 cm^3) with $P(OMe)_3$ (0.0142 g, 0.1142 mmol) for 2 h. After allowing to cool, the solvent was removed *in vacuo* and the brown-purple residue chromatographed, using n-hexane–ethyl acetate (2 : 1, v/v) as eluant, to give a single product identified as $[Ru_6C(CO)_{13}\{P(OMe)_3\}_4]$ (8) (0.0271 g); yield = 68% (Found: C, 21.7; H, 2.15. Calc.: C, 21.1; H, 2.45%). ^{1}H N.m.r.: δ (p.p.m.) 3.69 [d, J(PH) 12], 3.75 [d, J(PH) 12 Hz], relative intensity 1 : 1.

Preparation and Pyrolysis of $[Ru_6C(CO)_{16}(PPh_2CH_2CH_2R)]$ (9).—A quantity of $PPh_2CH_2CH_2R$,[12] prepared from AEROSIL 200, was added to a concentrated solution of $[Ru_6C(CO)_{17}]$ in CH_2Cl_2. The resulting slurry was stirred for 2 h, after which filtration and atmospheric drying gave a red, particulate solid characterised as $[Ru_6C(CO)_{16}(PPh_2CH_2CH_2R)]$. The filtrate was shown to contain only unreacted $[Ru_6C(CO)_{17}]$.

A sample was pressed (10 tonnes) into a self-supporting disc which was then held in the evacuable cell and heated to a predetermined temperature under vacuum (2×10^{-2} Torr). After a specified time the disc was allowed to cool to room temperature prior to being removed, mulled, and studied by i.r. spectroscopy.

Crystal-structure Determination.—Deep red air-stable crystals of $[Ru_6C(CO)_{16}(PPh_2Et)]$ were grown from n-hexane–CH_2Cl_2 solution. Preliminary photographic examination established the monoclinic crystal system, approximate cell dimensions, and the systematic absences. Accurate cell dimensions were obtained by least-squares refinement of the setting angles of 25 carefully centred reflections using a Nonius CAD4 diffractometer. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely indicated the centrosymmetric space group $P2_1/n$.

Crystal data. $C_{31}H_{15}O_{16}PRu_6$, M = 1 280.6, Monoclinic, a = 18.754(3), b = 17.624(3), c = 22.841(3) Å, β = 91.94(2)°, U = 7 545.9 Å^3, D_m (flotation) = 2.28(1) g cm^{-3}, Z = 8, D_c = 2.249, F(000) = 4 864, space group $P2_1/n$, μ(Mo-K_α) = 23.77 cm^{-1}.

Three dimensional X-ray intensities of 13 089 unique reflections were recorded using graphite monochromated Mo-K_α radiation (λ = 0.7107 Å) from two octants of reciprocal space ($3.5 < 2\theta < 60°$) using a ω—2θ scan on a Nonius CAD4 diffractometer. Two standard reflections were monitored and all the intensities were corrected for Lorentz and polarisation factors and the small crystal deterioration. The data were also corrected for absorption (crystal size $0.18_7 \times 0.18_7 \times 0.67_5$ mm, transmission coefficients vary from 0.703 to 0.610) and the removal of reflections with $F_o^2 < 3\sigma(F_o^2)$, where the standard deviation (σ) was estimated from the counting statistics, gave 10 739 observed structure amplitudes which were used in the structure determination.

Structure determination. The Patterson synthesis gave clear indications from the Ru–Ru vectors around the origin for an Ru_6 octahedron and the location of the two similar but crystallographically non-equivalent groups in the structure was established by multisolution sigma two-sign expansion available within the SHELX package.[13] The most favourable E-map consisted of the expected two octahedra. All the other non-hydrogen atoms were located by a sequence of structure factor and electron-density calculations in the normal manner. Full-matrix least-squares refinement [anisotropic Ru and P, isotropic C and O, rigid-body phenyl groups (C–C = 1.395 Å)] was carried out. Hydrogen atoms were included in the calculated positions for the phenyl groups (C–H = 1.08 Å) and were given a common refined isotropic temperature factor. A weighting scheme $w = 1/\sigma^2(F_o)$ was applied and gave a

TABLE 1

Infrared carbonyl stretching frequencies [a]

Complex	ν(CO)/cm^{-1}
(3) $[Ru_6C(CO)_{16}(PPh_3)]$ [b]	2 084m, 2 056vs, 2 045ms, 2 029vs, 2 003m, 1 984m, 1 844w
(2) $[Ru_6C(CO)_{16}(PPh_2Et)]$	2 084m, 2 056s, 2 046s, 2 032vs, 2 020m (sh), 2 003w, 1 985w, 1 845vw
(5) $[Ru_6C(CO)_{16}\{P(OMe)_3\}]$	2 086w, 2 057m, 2 046s, 2 034vs, 2 020m (sh), 1 986w, 1 843vw
(9) $[Ru_6C(CO)_{16}(PPh_2C_2H_4R)]$ [c]	2 083w, 2 055ms, 2 044s, 2 030vs, 2 017 (sh), 1 984w, 1 956vw, 1 840vw
(10) $[Ru_6C(CO)_{15}(PPh_3)_2]$ [d]	2 069w (sh), 2 064w, 2 046s, 2 018s,br, 1 998w, 1 987w, 1 845w,br
(4) $[Ru_6C(CO)_{15}(PPh_2Et)_2]$	2 071w (sh), 2 064m, 2 045vw, 2 028s, 2 018vs, 2 014vs, 1 991w, 1 979w, 1 971w (sh), 1 949vw, 1 857vw, 1 838vw
(6) $[Ru_6C(CO)_{15}\{P(OMe)_3\}_2]$	2 072w, 2 048vw, 2 032s (sh), 2 020vs, 1 878w, 1 864vw, 1 840w
(11) $[Ru_6C(CO)_{15}(PPh_2C_2H_4R)_2]$ [c]	2 065m, 2 045w, 2 028s, 2 019vs, ~1 990 (sh), 1 974w, 1 856vw, 1 835vw
(7) $[Ru_6C(CO)_{14}\{P(OMe)_3\}_3]$	2 060w, 2 010vs, 1 960w, 1 832vw
(8) $[Ru_6C(CO)_{13}\{P(OMe)_3\}_4]$	2 042w, 1 999vs,br, 1 965w, 1 815vw

[a] In cyclohexane unless otherwise stated. [b] In CCl_4. [c] Nujol mull. [d] See ref. 5.

satisfactory variation of $w\Delta F^2$ when analysed in terms of $\sin\theta$ and F_o. Problems with the amount of data and the number of refinable parameters led to the necessity of using a block refinement procedure in which only certain parameters were allowed to refine in each least-squares cycle. Omitting those reflections for which $F_o^2 < 4\sigma(F_o^2)$ and when $2\theta > 50°$ reduced the number of data points by 2 123 to 8 616 which were used in the refinement. The total number of refined parameters is 456, giving a ratio of reflections/parameters of 18.9. The converged R was 0.0431 ($R' = 0.0426$) and a difference electron-density synthesis showed only weak features ($-1.31 <$ electron density < 1.47 e Å^{-3}).

The atomic scattering factors and anomalous dispersion terms for neutral C, O, P, and H atoms were taken from the SHELX package and the corresponding values for ruthenium taken from ref. 14.

TABLE 2

Fractional atomic co-ordinates * ($\times 10^4$) with estimated standard deviations in parentheses

Molecule A

Atom	X/a	Y/b	Z/c
Ru(1A)	4 079(1)	4 430(1)	2 888(1)
Ru(2A)	4 735(1)	5 527(1)	2 077(1)
Ru(3A)	3 201(1)	5 568(1)	2 131(1)
Ru(4A)	3 127(1)	3 967(1)	1 942(1)
Ru(5A)	4 736(1)	3 944(1)	1 826(1)
Ru(6A)	3 832(1)	4 929(1)	1 134(1)
P(1A)	3 412(2)	4 764(2)	3 707(1)
C(01A)	3 971(4)	4 727(4)	2 024(3)
C(02A)	2 437(7)	4 672(7)	3 597(5)
C(03A)	1 979(7)	4 853(7)	4 121(5)
C(11)	3 589(4)	5 655(4)	3 999(3)
C(12)	3 388(4)	5 910(4)	4 598(3)
C(13)	3 536(4)	6 627(4)	4 830(3)
C(14)	3 937(4)	7 144(4)	4 517(3)
C(15)	4 191(4)	6 944(4)	3 971(3)
C(16)	4 043(4)	6 227(4)	3 738(3)
C(21)	3 589(4)	4 103(4)	4 298(3)
C(22)	3 257(4)	3 484(4)	4 413(3)
C(23)	3 411(4)	3 002(4)	4 884(3)
C(24)	3 950(4)	3 189(4)	5 294(3)
C(25)	4 336(4)	3 860(4)	5 233(3)
C(26)	4 182(4)	4 342(4)	4 762(3)
C(1A)	4 873(8)	4 566(8)	3 393(6)
O(1A)	5 356(7)	4 579(7)	3 733(5)
C(2A)	3 995(8)	3 431(8)	3 116(6)
O(2A)	4 022(6)	2 790(6)	3 247(5)
C(3A)	2 660(9)	3 317(9)	2 444(7)
O(3A)	2 355(6)	2 930(7)	2 768(5)
C(4A)	2 774(7)	6 135(8)	2 721(6)
O(4A)	2 502(6)	6 506(6)	3 067(4)
C(5A)	2 762(8)	6 229(8)	1 614(6)
O(5A)	2 463(7)	6 631(8)	1 280(6)
C(6A)	4 288(9)	6 507(9)	2 130(7)
O(6A)	4 206(7)	7 138(7)	2 166(5)
C(7A)	5 419(9)	5 775(9)	1 515(7)
O(7A)	5 836(7)	5 937(7)	1 177(5)
C(8A)	5 451(9)	5 706(9)	2 655(7)
O(8A)	5 910(7)	5 858(7)	2 994(5)
C(9A)	5 422(10)	3 626(10)	2 390(8)
O(9A)	5 885(7)	3 478(7)	2 709(6)
C(10A)	5 454(9)	3 962(9)	1 264(7)
O(10A)	5 922(8)	3 973(8)	941(6)
C(11A)	2 737(9)	3 391(9)	1 315(7)
O(11A)	2 519(7)	3 018(7)	941(6)
C(12A)	4 437(10)	2 976(10)	1 654(7)
O(12A)	4 295(8)	2 368(9)	1 458(6)
C(13A)	4 035(10)	5 838(10)	767(7)
O(13A)	4 143(8)	6 418(8)	550(6)
C(14A)	2 925(10)	4 873(10)	756(7)
O(14A)	2 362(7)	4 864(7)	538(5)
C(15A)	4 236(11)	4 360(12)	557(9)
O(15A)	4 423(8)	3 989(8)	157(7)
C(16A)	2 373(8)	4 788(8)	2 037(6)
O(16A)	1 754(6)	4 833(6)	2 048(4)

TABLE 2 (*continued*)

Molecule B

Atom	X/a	Y/b	Z/c
Ru(1B)	9 091(1)	5 369(1)	2 756(1)
Ru(2B)	8 245(1)	4 108(1)	2 090(1)
Ru(3B)	9 763(1)	4 196(1)	2 023(1)
Ru(4B)	9 729(1)	5 749(1)	1 667(1)
Ru(5B)	8 090(1)	5 665(1)	1 789(1)
Ru(6B)	8 847(1)	4 699(1)	1 038(1)
P(1B)	8 483(1)	5 102(2)	3 619(1)
C(01B)	8 969(4)	4 983(4)	1 922(3)
C(02B)	7 513(6)	5 217(6)	3 515(4)
C(03B)	7 042(7)	5 082(7)	4 051(5)
C(31)	8 658(4)	4 165(3)	3 948(3)
C(32)	8 421(4)	4 040(3)	4 537(3)
C(33)	8 516(4)	3 319(3)	4 779(3)
C(34)	8 900(4)	2 770(3)	4 482(3)
C(35)	9 188(4)	2 942(3)	3 943(3)
C(36)	9 093(4)	3 663(3)	3 701(3)
C(41)	8 687(4)	5 740(4)	4 163(3)
C(42)	8 382(4)	6 483(4)	4 251(3)
C(43)	8 604(4)	7 014(4)	4 671(3)
C(44)	9 180(4)	6 852(4)	5 054(3)
C(45)	9 534(4)	6 159(4)	5 015(3)
C(46)	9 312(4)	5 628(4)	4 594(3)
C(1B)	9 922(8)	5 378(8)	3 242(6)
O(1B)	10 417(7)	5 443(7)	3 545(5)
C(2B)	8 938(8)	6 394(9)	2 892(6)
O(2B)	8 895(6)	7 031(6)	2 981(5)
C(3B)	7 579(8)	6 379(8)	2 222(6)
O(3B)	7 252(7)	6 798(7)	2 483(5)
C(4B)	7 819(8)	3 646(8)	2 739(6)
O(4B)	7 525(6)	3 350(6)	3 102(4)
C(5B)	7 834(8)	3 328(8)	1 657(6)
O(5B)	7 615(7)	2 810(7)	1 387(5)
C(6B)	10 419(8)	4 052(8)	2 661(6)
O(6B)	10 831(7)	3 939(7)	3 030(5)
C(7B)	9 349(9)	3 219(9)	2 107(7)
O(7B)	9 286(7)	2 561(8)	2 152(6)
C(8B)	10 532(8)	3 939(8)	1 534(6)
O(8B)	10 983(6)	3 788(6)	1 237(5)
C(9B)	10 455(9)	6 137(9)	2 171(7)
O(9B)	10 921(7)	6 349(7)	2 458(5)
C(10B)	10 396(9)	5 659(9)	1 070(7)
O(10B)	10 831(7)	5 582(7)	738(5)
C(11B)	7 627(9)	6 033(9)	1 112(7)
O(11B)	7 343(7)	6 276(7)	687(5)
C(12B)	7 990(9)	4 337(10)	690(7)
O(12B)	7 486(7)	4 098(7)	465(5)
C(13B)	9 367(8)	3 961(8)	656(6)
O(13B)	9 663(6)	3 507(7)	389(5)
C(14B)	9 410(10)	6 702(10)	1 421(7)
O(14B)	9 219(7)	7 287(8)	1 234(6)
C(15B)	8 934(9)	5 458(9)	458(7)
O(15B)	8 970(6)	5 917(7)	94(5)
C(16B)	7 378(8)	4 846(8)	1 947(6)
O(16B)	6 754(6)	4 781(6)	1 964(4)

* Carbon atoms of the phenyl groups are labelled C(*ij*) where *i*(1—4) indicates the ring and *j*(1—6) identifies the atoms of a ring. Carbonyl group atoms are labelled C(*n*A), O(*n*A), C(*n*B), and O(*n*B), where *n* runs from 1 to 16 and A and B indicate the appropriate molecule.

In Table 2 are presented the atomic co-ordinates and in Table 3 the values of selected bond lengths and angles are tabulated. Tables of anisotropic and isotropic temperature factors, hydrogen-atom positions, and structure factor listings have been deposited as Supplementary Publication No. SUP 23132 (53 pp).*

Calculations were carried out on an ICL 2970 computer at Southampton University and a CDC 7600 computer at

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 3

Selected bond lengths (Å) and angles (°), for Molecule A only (Molecule B has similar values), with estimated standard deviations in parentheses

(*a*) Heavy-atom distances

Ru(1A)–Ru(2A)	2.972(1)	Ru(3A)–Ru(4A)	2.856(1)
Ru(1A)–Ru(3A)	3.088(1)	Ru(3A)–Ru(6A)	2.834(1)
Ru(1A)–Ru(4A)	2.875(1)	Ru(4A)–Ru(5A)	3.039(1)
Ru(1A)–Ru(5A)	2.890(1)	Ru(4A)–Ru(6A)	2.863(1)
Ru(2A)–Ru(3A)	2.885(1)	Ru(5A)–Ru(6A)	2.865(1)
Ru(2A)–Ru(5A)	2.850(1)	Ru(1A)–P(1A)	2.359(3)
Ru(2A)–Ru(6A)	2.894(1)		

(*b*) Metal–carbide distances

Ru(1A)–C(01A)	2.047(6)	Ru(4A)–C(01A)	2.077(7)
Ru(2A)–C(01A)	2.010(7)	Ru(5A)–C(01A)	2.054(7)
Ru(3A)–C(01A)	2.089(7)	Ru(6A)–C(01A)	2.071(6)

(*c*) Phosphine ligand parameters

P(1A)–C(02A)	1.844(13)	Ru(1A)–P(1A)–C(02A)	114.8(4)
P(1A)–C(11)	1.734(7)	Ru(1A)–P(1A)–C(11)	115.6(3)
P(1A)–C(21)	1.806(7)	Ru(1A)–P(1A)–C(21)	110.0(3)
C(02A)–C(03A)	1.530(17)		

(*d*) Bridging carbonyl group

Ru(3A)–C(16A)	2.079(14)	Ru(3A)–C(16A)–Ru(4A)	87.8(6)
Ru(4A)–C(16A)	2.038(14)	Ru(3A)–C(16A)–O(16A)	133.9(11)
C(16A)–O(16A)	1.165(19)	Ru(4A)–C(16A)–O(16A)	138.3(11)

(*e*) Terminal carbonyl groups

Ru–C	1.924(16)	Maximum
	1.833(18)	Minimum
	1.870(26)	Mean (standard deviation)
Ru–C–O	177.7(14)	Maximum
	162.0(15)	Minimum
C–O	1.162(17)	Mean (standard deviation)

(*f*) Carbonyl group angles

C(6A)–Ru(2A)–C(7A)	98.1(7)
C(6A)–Ru(2A)–C(8A)	96.3(7)
C(7A)–Ru(2A)–C(8A)	87.3(7)
C(9A)–Ru(5A)–C(10A)	89.1(8)
C(9A)–Ru(5A)–C(12A)	93.9(8)
C(10A)–Ru(5A)–C(12A)	95.2(7)
C(1A)–Ru(1A)–C(2A)	91.3(6)
C(1A)–Ru(1A)–P(1A)	84.9(4)
C(2A)–Ru(1A)–P(1A)	87.8(4)
C(13A)–Ru(6A)–C(14A)	91.9(8)
C(13A)–Ru(6A)–C(15A)	92.9(8)
C(14A)–Ru(6A)–C(15A)	91.7(8)
C(4A)–Ru(3A)–C(5A)	86.0(6)
C(4A)–Ru(3A)–C(16A)	95.3(6)
C(5A)–Ru(3A)–C(16A)	92.1(6)
C(3A)–Ru(4A)–C(11A)	87.6(7)
C(3A)–Ru(4A)–C(16A)	91.7(6)
C(11A)–Ru(4A)–C(16A)	102.2(6)

Manchester University using the programs SHELX,[13] ORTEP,[15] and PLUTO.[16]

RESULTS AND DISCUSSION

The complex $[Ru_6C(CO)_{17}]$ (1) evidently undergoes phosphine substitution reactions under mild conditions. The degree of substitution under a particular set of conditions is dependent upon the *P*-donor. Thus, while refluxing (1) in n-hexane with 2 moles of PPh_3 only yielded the mono-substituted product, a disubstituted product was formed with PPh_2Et. Nevertheless, this ligand, which is a close analogue of $PPh_2CH_2CH_2R$, will give a mono-substituted product specifically at room temperature. Trimethyl phosphite is more reactive and gives rise to $[Ru_6C(CO)_{16}\{P(OMe)_3\}]$ and $[Ru_6C(CO)_{15}\{P(OMe)_3\}_2]$ under ambient conditions. In all, the first four phosphite substitution products have been isolated. The ν(CO) i.r. bands of all these substitution products, except (4) and (6), contain one bridging absorption and suggest the basic geometry of (1), with one μ-CO, is maintained in the substitution products. However, the site of substitution could not be established on the basis of this and the n.m.r. data obtained on these systems. So a single-crystal *X*-ray diffraction study of one derivative, $[Ru_6C(CO)_{16}(PPh_2Et)]$ (2) was undertaken. The n.m.r. results are discussed below.

Crystal and Molecular Structure of (2).—The molecular structures of the two crystallographically independent molecules (A and B) are shown in Figure 1. They possess the basic $Ru_6C(CO)_{17}$ structure,[6] with the phosphine on a ruthenium atom sharing a face with the two bridged metal atoms. The geometry of the substituted ruthenium appears to differ in molecules A and B, and a view down the Ru(1A)–C(carbide) bond is shown in Figure 2. The phosphine is placed unsymmetrically over the bridging carbonyl rendering each molecule enantiomeric. Four molecules of each of A and B are in the unit cell (Figure 3) and there are two pairs of mirror images of both molecules. The ORTEP drawings in Figure 1 show two approximate enantiomers.

There are three different ruthenium environments in $[Ru_6C(CO)_{17}]$. It is interesting that the metal atom bearing the substituent in (2) is also that binding the arene ligand in $[Ru_6C(CO)_{14}(C_6H_3Me_3\text{-}1,3,5)]$.[17] In addition, it is also one of the metal types co-ordinating the organic ligands in $[Ru_6C(CO)_{14}(\text{bitropyl})]$ [18] and $[Ru_6C(CO)_{15}(C_6H_{10})]$ (C_6H_{10} = hexa-2,4-diene).[11]

The bond lengths and angles (Table 3) show typical Ru–C and C–O carbonyl distances. Both molecules are similar, so information about one (molecule A) is tabulated here. The mean Ru–C(carbide) distance taken over both molecules is 2.060(26) Å and so is not significantly different from that reported for (1) (2.05 Å),[6] $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$ (2.04 Å),[17] $[Ru_6C(CO)_{14}(\text{bitropyl})]$ (2.06 Å),[18] and $[Ru_6C(CO)_{15}(C_6H_{10})]$ (2.06 Å).[11] A slight lengthening of the mean Ru–Ru bonding distance was observed, but this was also scarcely significant. Means and standard deviations of 2.912(86), 2.907(70), 2.903(60), 2.899(46), and 2.882(38) Å were determined for (2), $[Ru_6C(CO)_{14}(\text{bitropyl})]$, (1), $[Ru_6C(CO)_{15}(C_6H_{10})]$, and $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$ respectively. Perhaps more significant is the variation in the metal–metal bond lengths to the substituted ruthenium atom. In (2), this mean is 2.958(92) Å, as compared with a mean of 2.901(49) Å for the corresponding distances in (1). A contraction of these distances was found in $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$, giving a mean of 2.859(6) Å.

N.M.R. Spectra.—^{13}CO-enriched $[Ru_6C(CO)_{17}]$ was prepared by direct substitution under 90 atom% ^{13}CO in n-hexane at 70 °C for 90 h, with no detectable decomposition. At 31 °C in $CDCl_3$ solution, the ^{13}C n.m.r. spectrum consisted of a sharp singlet at δ 197.1. No change occurred down to −20 °C when sample precipit-

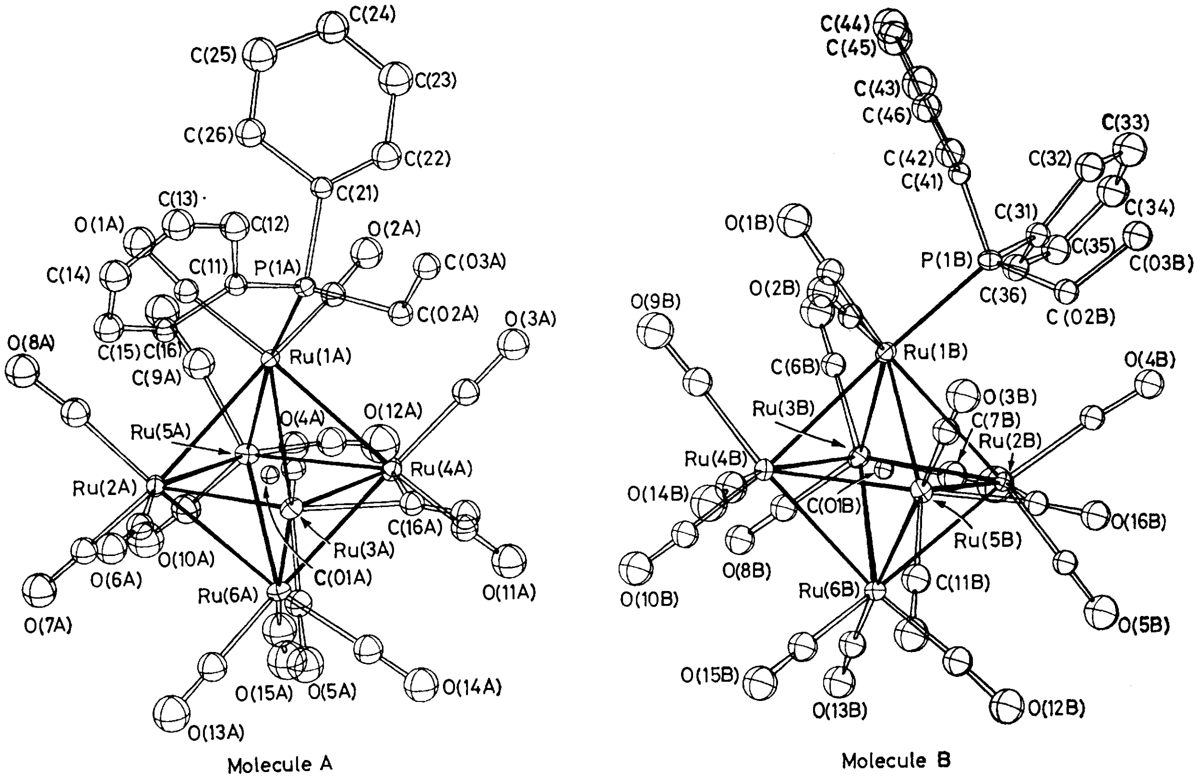


FIGURE 1 Molecular structure of $[Ru_6C(CO)_{16}(PPh_2Et)]$ (molecules A and B). The thermal ellipsoids enclose 20% probability

ation precluded further study. Evidently there is a fast exchange process equivalencing all carbonyl groups.

An enriched sample of $[Ru_6C(CO)_{16}(PPh_2Et)]$ could be studied between −130 and 31 °C in CD_2Cl_2 and CD_2Cl_2–$CHFCl_2$ owing to its higher solubility. Under ambient conditions, the averaged CO resonance was observed at δ 200.5, showing the commonly observed downfield shift with phosphine substitution.[19] The spectra are shown in Figure 4. Broadening occurs below −50 °C and the highest energy process is frozen out at −85 °C to yield three resonances at δ 202.8 (a), 200.9 (b), and 193.7 (c). The peaks appear to result from relative populations of either 7 : 7 : 2 or 8 : 6 : 2. At −100 °C, resonance (b) broadens as a second process is slowed and at −130 °C, the lowest temperature possible, a third process is

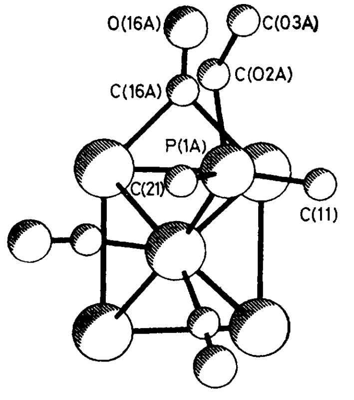


FIGURE 2 View down the Ru(1A)–C(carbide) bond in $[Ru_6C(CO)_{16}(PPh_2Et)]$ (molecule A) excluding 13 carbonyl groups and the phenyl groups for clarity

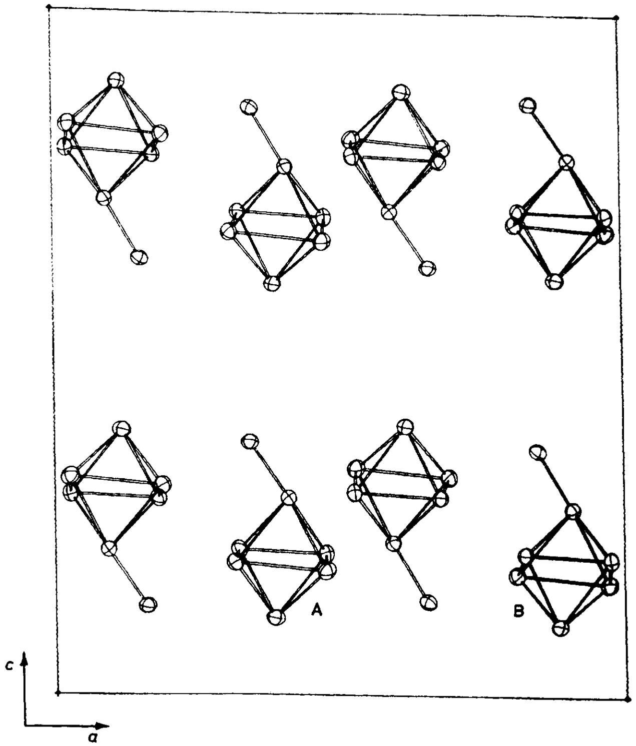


FIGURE 3 View of the unit cell in the positive *b* direction excluding C and O atoms for clarity and showing the molecular packing

slowed and the partially averaged environment (a) also broadens.

While these data are ambiguous, the following explanation is plausible. The two carbons of resonance (c) are bound to the phosphine-substituted ruthenium atoms. Although these two are inequivalent by virtue of the phosphine orientation in the crystal, they are likely to be averaged very readily in solution and so are equivalenced at −130 °C. If one accepts the 8 : 6 : 2 population ratio of the three resonances at −85 °C, then the group of six, resonance (b), are probably the two $Ru(CO)_3$ groups *cis* to the substituted metal atom. Localised rotation at these centres would give one resonance, as observed at −85 °C. This leaves the eight carbonyl groups of the bridge, two $Ru(CO)_2$ moieties, and the last $Ru(CO)_3$ group, *trans* to the substituted metal atom; a localised internuclear exchange process associated with one Ru_3 face is evidently occurring. Above −85 °C, a total scrambling process then equivalences all these partially averaged environments.

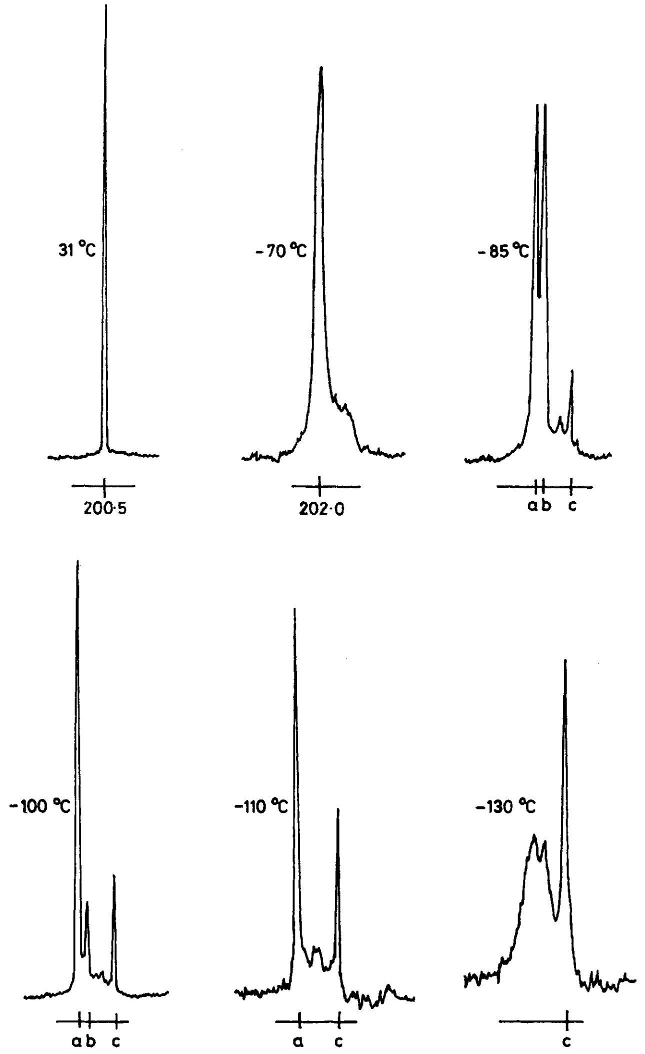
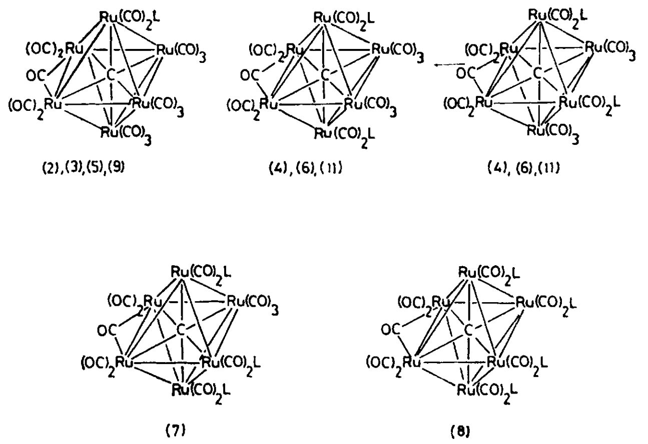


FIGURE 4 Carbon-13 n.m.r. spectra of $[Ru_6C(^*CO)_{16}(PPh_2Et)]$ in CD_2Cl_2–$CHCl_2F$ mixtures: δ (p.p.m.) 202.8 (a), 200.9 (b), 193.7 (c)

The ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample of $[Ru_6C(CO)_{15}(PPh_2Et)_2]$ also exhibits one resonance in the carbonyl region at δ 204.7, again indicating rapid total exchange. Broadening occurred at *ca.* −70 °C, and new resonances emerged at lower temperatures but at the lowest temperature studied (−120 °C) these were still ill defined.

The ^1H n.m.r. spectra of the polysubstituted phosphite complexes all contained more than one methyl doublet and on the basis of the ^{13}C n.m.r. data above it is probable that any inequivalence must arise from the relative phosphite sites on the octahedron; the CO envelope is migrating sufficiently rapidly that in itself it cannot confer any inequivalence. The similarity of the i.r. spectra of the three monosubstituted products (2), (3), and (5) suggests that they are isostructural in solution. However, there are two bridging ν(CO) absorptions observed for solutions of two disubstituted products (4) and (6). Combined with the observations of two ^1H n.m.r. doublets for (6), this suggests that two isomers exist in solution, since substitution of *cis* and *trans* rutheniums will each give one phosphite environment. Observation of a pair of methyl resonances of ratio 2 : 1 and one bridging ν(CO) for the trisubstituted product (7) indicates a *mer* arrangement of the phosphites and finally the two phosphite environments in $[Ru_6C(CO)_{13}\{P(OMe)_3\}_4]$ indicate a *cis* arrangement. A preliminary *X*-ray diffraction study of (8) has shown the phosphites are indeed bonded to separate ruthenium atoms.[10] The probable structures for these complexes are shown in Figure 5. In all cases, the ruthenium atoms involved in the bridging group remain unsubstituted as has been observed in all the *X*-ray diffraction studies discussed above.



(2),(3),(5),(9)

(4),(6),(11)

(4),(6),(11)

(7)

(8)

FIGURE 5 Proposed structures for $[Ru_6C(CO)_{17-n}L_n]$ complexes

$[Ru_6C(CO)_{16}(PPh_2CH_2CH_2R)]$ (9) —Stirring a suspension of $PPh_2CH_2CH_2R$ in a solution of $[Ru_6C(CO)_{17}]$ in CH_2Cl_2 for 2 h at room temperature produced a red solid, (9). The i.r. spectrum of (9) in the range 1 800—

2 200 cm^{-1} is shown in Figure 6. There is close agreement in the terminal region of the spectra of (9) and its isolable model complex (2) and this is further enhanced by computer subtraction of the background spectrum of the phosphinated silica gel. This clarifies the bridging absorption. The tabulated absorption frequencies of (2) and (9) also correlate closely (Table 1); so these two complexes are essentially isostructural at the cluster.

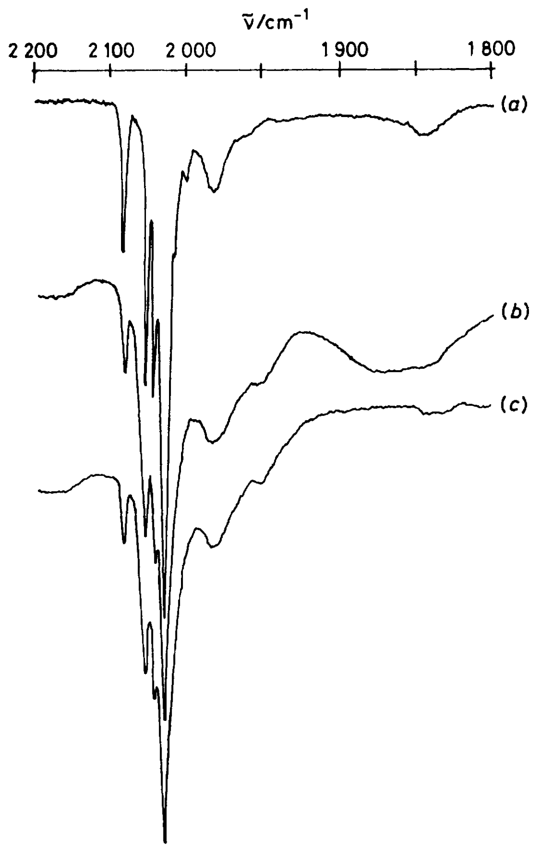


FIGURE 6 Infrared spectral characterisation of $[Ru_6C(CO)_{16}(PPh_2C_2H_4R)]$ (9): (*a*) $[Ru_6C(CO)_{16}(PPh_2Et)]$ (in cyclohexane); (*b*) $[Ru_6C(CO)_{16}(PPh_2C_2H_4R)]$ (Nujol); (*c*) computer-simulated difference spectrum between (*b*) and $PPh_2C_2H_4R$ (Nujol)

Using a more dilute solution of (1), the silica gel had a deeper tan colour and its i.r. spectrum in this region contained additional peaks at 2 064 and 2 028 cm^{-1}. Storage or mild heating of (9) also gave these additional peaks and the results of the thermolysis study are shown in Figure 7. At 50 °C, bands due to a second complex appear and computer subtraction of the absorptions of (9) was made scaling on the 2 084 cm^{-1} peak. The result correlates well with the solution spectrum of $[Ru_6C(CO)_{15}(PPh_2Et)_2]$ and so it is concluded that the second species is a disubstituted anchored product, $[Ru_6C(CO)_{15}(PPh_2CH_2CH_2R)_2]$ (11); complex (11) also appears to exist as two isomers. After heating at 65 °C *in vacuo*, (11) is predominant.

A sequence of thermal decomposition experiments involving heating a self-supported disc of (9) *in vacuo* at various temperatures overnight was performed. While a well defined spectrum due to (9) and/or (11) was observable up to 65 °C, by 80 °C the pattern was broader and three ν(CO) absorptions at 2 053m, 2 011vs, and 1 997(sh) cm^{-1} were observed. At 100 °C, the disc darkened to a deep brown and now exhibited only two broad ν(CO) bands at 2 052 and 1 981 cm^{-1}. Continued heating at 150 °C gave rise to a disc of black lustrous appearance and almost total loss of the carbonyl vibrations. Weak bands were observed at 2 068, 2 048, and 1 972 cm^{-1}. It is noteworthy that pyrolysis of $[Ru_3(CO)_{12-x}(PPh_2CH_2CH_2R)_x]$ ($x = 1$ and 2)[20] to 100 °C gave a similar i.r. spectrum to the pyrolysis product of (9) under similar conditions [ν(CO) 2 058 and 1 984 cm^{-1}] and so the CO environments in these pyrolysed materials are independent of the original supported clusters. The same observation was made for $[Ru_6C(CO)_{17}]$ and $[Ru_3(CO)_{12}]$ directly bonded to γ-alumina.[21]

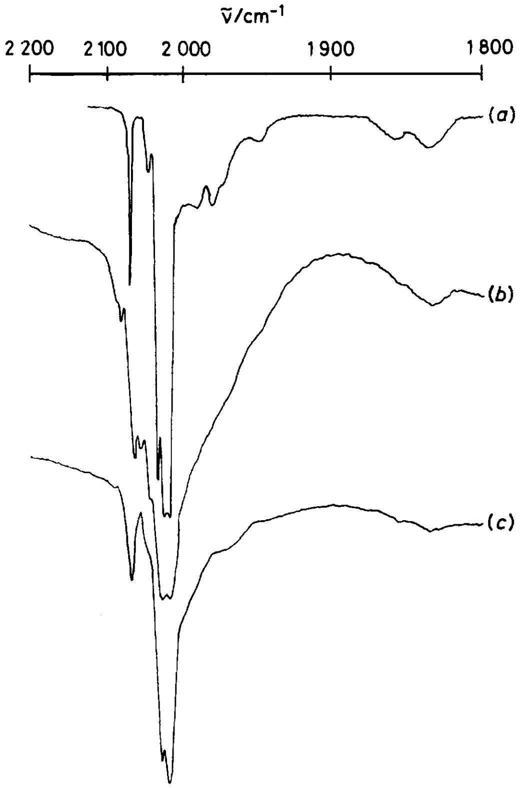


FIGURE 7 Infrared spectral characterisation of $[Ru_6C(CO)_{15}(PPh_2C_2H_4R)_2]$ (11): (*a*) $[Ru_6C(CO)_{15}(PPh_2Et)_2]$ (in cyclohexane); (*b*) complex (9) heated at 50 °C *in vacuo* (Nujol); (*c*) difference spectrum between (*b*) and that of (9), supported absorption subtracted from (*b*) and (*c*)

The frequencies observed at 100 °C differ from those reported for pyrolysis of $[Ru_3(CO)_{12}]$ adsorbed onto unfunctionalised silica gel,[21,22] and so it is probable that the ruthenium atoms are bound to phosphorus under those conditions. Analysis of one sample of (9) indicated a P : Ru ratio of *ca.* 15 : 1.[4] The observed carbonyl stretching frequencies were compared to those reported for several types of chloro–carbonyl–phosphine complexes since the ν(CO) vibrations of $[Rh_2(CO)_4(OSi\leqslant)_2]$ and $[Rh_2(CO)_4Cl_2]$ have very similar frequencies.[4] Structures similar to those of $[\{Ru(CO)_2Cl_2\}_n]$,[23] $[\{Ru(CO)_2(PR_3)Cl_2\}_2]$,[24,25] and $[\{M(CO)_3Cl_2\}_2]$ (M = Ru or Os) [26,27] with planar bridges offer very improbable surface sites due to steric congestion of the axial ligands at the surface; species of the types $[\{M(CO)_x(O\text{-})_2\}_n]$ ($x = 2$ or 3) have been proposed nevertheless.[21,28] The compounds *cis*-$[Ru(CO)_2Cl_2(PPh_2Me)_2]$ [29] [ν(CO) 2 059 and 1 996 cm^{-1}] and $[Ru(CO)_2(PPhBu^t_2)Cl_2]$ [25] [ν(CO) 2 024, 1 988, and 1 949 cm^{-1}] are possible surface analogues and the C–O stretching frequencies of the former agree more closely with the pyrolysis product at 100 °C. This product may tentatively be assigned as having a similar structure to *cis*-$[Ru(CO)_2Cl_2(PPh_2Me)_2]$.

Further heating gives a dark material, which may be aggregated ruthenium or a carbide. The carbonyl groups are largely lost from this sample and those remaining do not give the same i.r. spectra as CO adsorbed on silica supported ruthenium.[30]

The chemistry of these surface-bound clusters (9) is complex, but three features are apparent. First, there is an initial phosphine substitution reaction up to 65 °C which gives a particular species $[Ru_6C(CO)_{15}(PPh_2CH_2CH_2R)_2]$ entirely analogous with the solution chemistry. Secondly, up to 100 °C, the ruthenium clusters break up and are oxidised to Ru^{II}, presumably by surface hydroxyl groups. Finally, up to 150 °C, the CO groups are lost and the metal apparently aggregates.

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