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Cluster chemistry

LXXVI. * A new C_2 complex from reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with pyridine. X-Ray structure of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$

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Abstract

The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) and pyridine results in the formation of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (**5**) which has been fully characterised by an X-ray structure determination. The cluster core consists of an Ru_4 butterfly metallated at a wingtip. A C_2 ligand, formed by cleavage of the P–C(*sp*) bond in **1**, is attached to all metal atoms, although one of the carbons has only a weak interaction with the hinge atoms. The overall C_2Ru_5 geometry is a distorted capped trigonal bipyramid, an Ru–C edge of which is bridged by the fifth Ru atom.

Introduction

One of our objectives in developing the chemistry of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) has been to synthesise complexes containing the cluster-bonded C_2 ligand, with a view to determining the reactivity and possible synthetic utility of this species. To date, we have been successful in making three such clusters, namely $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**2**) [2] and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe_2)_2(\mu\text{-}PPh_2)_2(CO)_n$ ($n = 12$ (**3**), 11 (**4**)) [3]. This paper reports the preparation and characterisation of a further example, obtained from the reaction between **1** and pyridine.

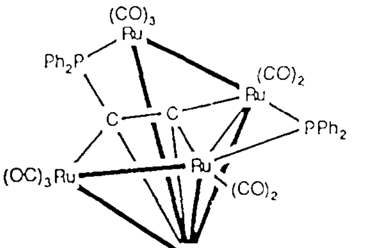
* For Part LXXV see ref. 1.

Results and discussion

The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and pyridine was carried out in benzene at 90 °C for 4 h. Preparative TLC enabled the isolation of black $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (**5**), together with $Ru_4\{\mu_4\text{-}CCH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (**6**) and $Ru_6(\mu\text{-}C_2H)(\mu\text{-}PPh_2)_2(\mu\text{-}NC_5H_4)(\mu\text{-}CO)(CO)_{12}$ (**7**). The latter two complexes will be fully described elsewhere [4]. The molecular structure of **5** was established by an X-ray study and is shown in Fig. 1; Table 1 collects some significant bond parameters.

The metal core consists of a somewhat flattened Ru_4 butterfly (dihedral 32.58(4)°) to one wing-tip of which is attached the fifth Ru atom [Ru(4)–Ru(5) 2.9357(5) Å]. The Ru–Ru bonds range between 2.7184 and 2.9357(5) Å, the extremes being the hinge (shorter) and the Ru(4)–Ru(5) separation. The latter corresponds to an Ru(5) → Ru(4) donor bond, Ru(5) achieving a formal 18-electron count from 2CO, 2py, the μ-PPh_2 ligand (1 e) and C(1) (1 e). The PPh_2-bridged Ru(3)–Ru(4) vector is the same length as the non-bridged Ru(1)–Ru(2) separation; there are no obvious reasons for the differences between these bonds and the Ru(1)–Ru(4) and Ru(2)–Ru(3) bonds.

Two adjacent Ru–Ru vectors are bridged asymmetrically by the PPh_2 groups [Ru(3)–P(1) 2.302(1), Ru(4)–P(1) 2.242(1), Ru(4)–P(2) 2.249(1), Ru(5)–P(2) 2.367(1) Å], while ten CO ligands are attached to the four Ru atoms forming the butterfly; one of these is semi-bridging Ru(1)–Ru(4) [Ru(1)–C(13) 1.909(4), Ru(4)–C(13) 2.672(5) Å, Ru(1)–C(13)–O(13) 163.7(4)°]. The fifth Ru atom is coordinated to



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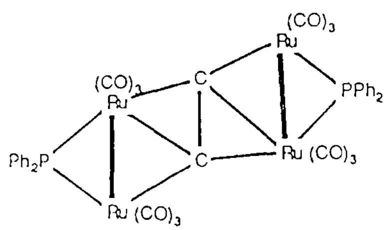

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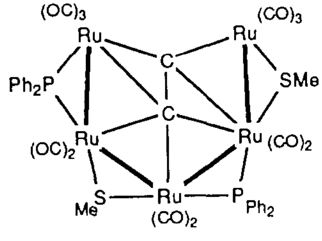

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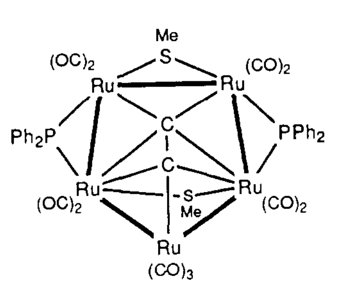

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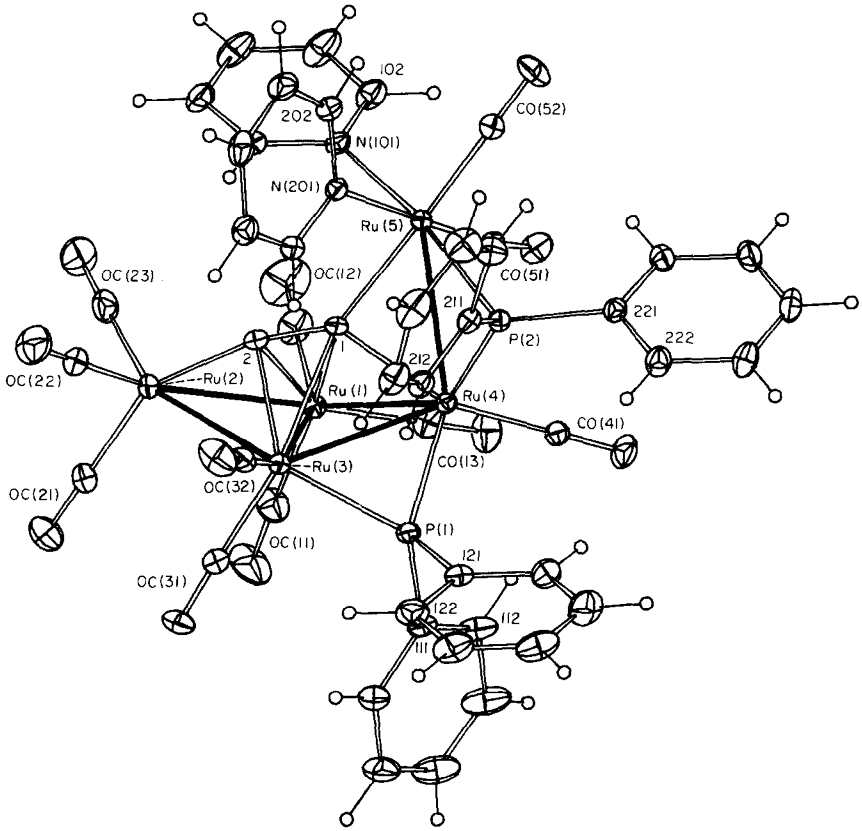

Fig. 1. ORTEP plot of a molecule of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (**5**), showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

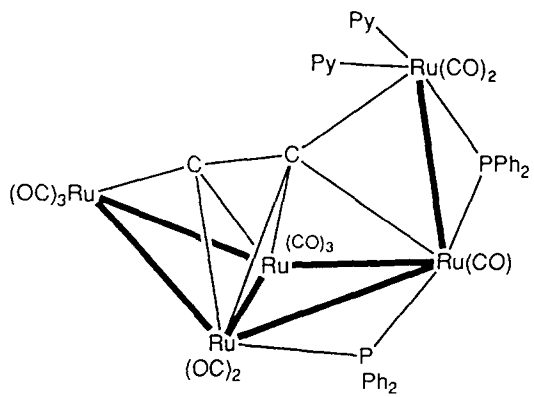

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Table 1

Selected bond distances (Å) and angles (deg) for $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (**5**)

Distances			
Ru(1)–Ru(2)	2.8418(5)	Ru(5)–N(1)	2.211(3)
Ru(1)–Ru(3)	2.7184(6)	Ru(5)–N(2)	2.195(3)
Ru(1)–Ru(4)	2.8859(6)	Ru(1)–C(1)	2.309(4)
Ru(2)–Ru(3)	2.8112(5)	Ru(1)–C(2)	2.210(4)
Ru(3)–Ru(4)	2.8425(5)	Ru(2)–C(2)	1.955(4)
Ru(4)–Ru(5)	2.9357(5)	Ru(3)–C(1)	2.434(3)
Ru(3)–P(1)	2.302(1)	Ru(3)–C(2)	2.165(3)
Ru(4)–P(1)	2.242(1)	Ru(4)–C(1)	2.123(3)
Ru(4)–P(2)	2.249(1)	Ru(5)–C(1)	2.192(4)
Ru(5)–P(2)	2.367(1)	C(1)–C(2)	1.301(5)
Angles			
Ru(1)–Ru(4)–Ru(5)	90.45(1)	Ru(4)–C(1)–Ru(5)	85.7(2)
Ru(3)–Ru(4)–Ru(5)	100.87(1)	Ru(2)–C(2)–C(1)	162.6(3)
Ru(1)–C(2)–Ru(2)	85.8(2)	Ru(4)–C(1)–C(2)	135.5(3)
Ru(2)–C(2)–Ru(3)	85.9(1)	Ru(5)–C(1)–C(2)	138.7(3)

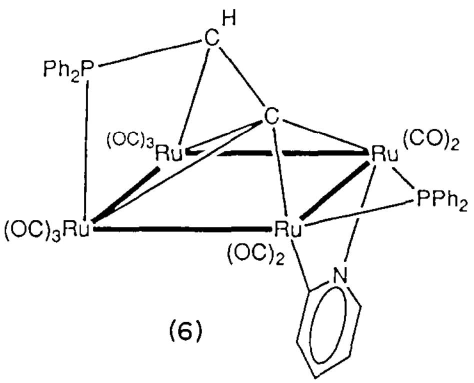
Dihedral angle Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(3)–Ru(4) 32.58(4)°

Ru–CO	range 1.863–1.916(6), av. 1.891 Å
C–O	range 1.125–1.153(8), av. 1.139 Å
P–C(Ph)	range 1.819–1.834(4), av. 1.825 Å
Ru–C–O	range 172.1–179.2(5), av. 177.5°

one CO and to two pyridine molecules [Ru(5)–N(101, 201) 2.211(3), 2.195(3) Å]. The latter distances are longer than those found in most *N*-donor complexes of $Ru_3(CO)_{12}$ [5], although Ru–N bonds of 2.19 Å have been observed in $Ru_3(\mu\text{-}CO)_2(CO)_8(bpy)$ [6] and $Ru_3(\mu\text{-}napy)(\mu\text{-}CO)_3(CO)_7$ [7].

Unlike $Ru_4(\mu_4\text{-}C_2Ph_2)(CO)_{12}$ (**8**), for example, which contains a distorted octahedral C_2Ru_4 polyhedron, the central core in **5** forms a distorted capped trigonal bipyramid (or bicapped tetrahedron), of which a C–Ru edge is bridged by Ru(5). The C_2 ligand is attached to all five Ru atoms, in an asymmetric η^2 mode to the two hinge atoms [Ru(1)–C(1) 2.309(4), Ru(1)–C(2) 2.210(4), Ru(3)–C(1) 2.434(4), Ru(3)–C(2) 2.165(3) Å] and with C(2) being σ-bonded to Ru(2) [Ru(2)–C(2) 1.955(4) Å] and C(1) bridging the Ru(4)–Ru(5) bond [Ru(4)–C(1) 2.123(4), Ru(5)–C(1) 2.192(4) Å]. Simple electron counting requires the C_2 ligand to act as a 6e donor; individual Ru atoms have 18e configurations, except for Ru(1), which has 19 and Ru(2) which has 17. An alternative view takes account of the short Ru(2)–C(2) and long Ru(3)–C(1) interactions, formulating the C_2 unit as a carbene as found in **4**, for example.

A detailed consideration of the interaction of the C_2 unit with the Ru_5 cluster suggests an arrangement such as **A**, similar to that proposed for the C_2Ph ligand in $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$ (**9**) [8], an isomer of **1**, and related to that considered for the amino-alkyne in $Os_3(\mu\text{-}H)_2(\mu_3\text{-}HC_2NEt_2)(CO)_9$ (**10**) [9]. The C(1)–C(2) separation of 1.301(5) Å is consistent with a bond order between two and three; the short Ru(2)–C(2) bond suggests a multiple bond, while C(2) is also relatively close to Ru(1) and Ru(3). In contrast, the C(1)–Ru(1) and C(1)–Ru(3) separations are much larger and this carbon is within normal σ-bonding distance of Ru(4) and Ru(5) [Ru(4)–C(1)–Ru(5) 85.7(1)°]. The C_2 moiety thus forms a dipolar ligand, being electron-rich at C(2) and electron-poor at C(1). A similar polarity has been suggested by EHMO calculations for the C_2 ligand in **4** and is evidenced by the reactivity of this complex [10].



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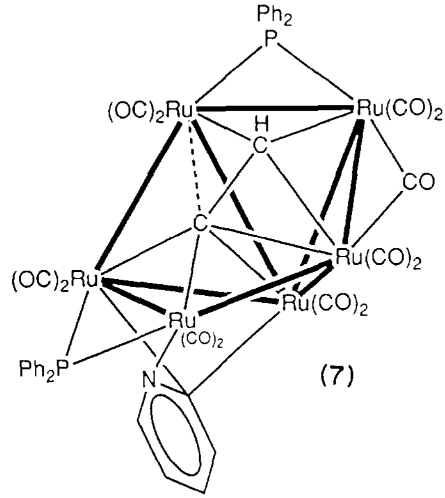

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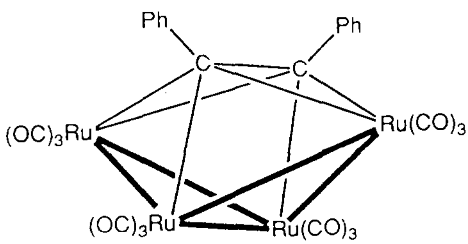

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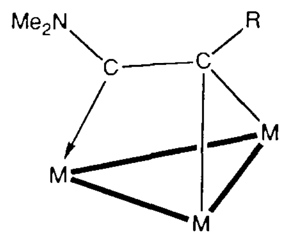

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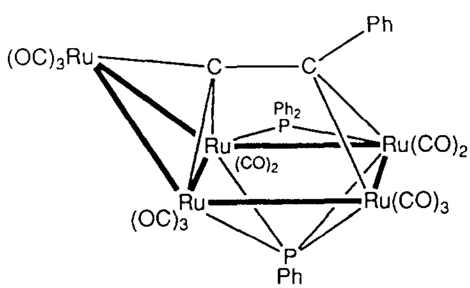

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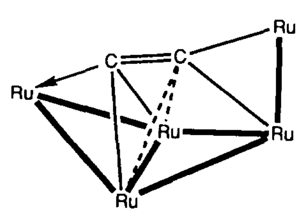

(A)

Table 2

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (**5**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.79480(2)	0.66754(2)	0.60852(3)	0.0336(2)
Ru(2)	0.95664(2)	0.61238(2)	0.75210(3)	0.0387(2)
Ru(3)	0.87461(2)	0.78800(2)	0.80440(3)	0.0302(1)
Ru(4)	0.68285(2)	0.77422(2)	0.72448(2)	0.0264(1)
Ru(5)	0.63354(2)	0.58400(2)	0.80580(2)	0.0268(1)
C(11)	0.8687(3)	0.7306(4)	0.5307(4)	0.063(3)
O(11)	0.9108(3)	0.7680(4)	0.4818(4)	0.109(3)
C(12)	0.7682(4)	0.5349(4)	0.5225(4)	0.066(3)
O(12)	0.7512(4)	0.4588(3)	0.4672(4)	0.128(3)
C(13)	0.6868(3)	0.7107(3)	0.5168(4)	0.049(2)
O(13)	0.6277(2)	0.7233(3)	0.4418(3)	0.067(2)
C(21)	1.0512(3)	0.6621(4)	0.6932(4)	0.058(3)
O(21)	1.1079(3)	0.6927(3)	0.6592(4)	0.095(3)
C(22)	1.0301(3)	0.5996(3)	0.8963(5)	0.058(3)
O(22)	1.0712(3)	0.5923(3)	0.9846(3)	0.089(2)
C(23)	0.9545(3)	0.4752(4)	0.6887(5)	0.061(3)
O(23)	0.9533(3)	0.3923(3)	0.6530(4)	0.096(3)
C(31)	0.9729(3)	0.8525(3)	0.7684(4)	0.048(2)
O(31)	1.0324(2)	0.8952(2)	0.7474(3)	0.068(2)
C(32)	0.9242(3)	0.8214(3)	0.9602(4)	0.045(2)
O(32)	0.9568(2)	0.8400(3)	1.0539(3)	0.077(2)
C(41)	0.5845(3)	0.8336(3)	0.6411(3)	0.037(2)
O(41)	0.5243(2)	0.8695(2)	0.5887(3)	0.062(2)
C(51)	0.5616(3)	0.5936(3)	0.6614(4)	0.038(2)
O(51)	0.5129(2)	0.5888(2)	0.5745(2)	0.056(2)
C(52)	0.5300(3)	0.5268(3)	0.8410(4)	0.044(2)
O(52)	0.4682(2)	0.4924(3)	0.8602(3)	0.081(2)
P(1)	0.78038(7)	0.91516(7)	0.75996(8)	0.0320(4)
C(111)	0.7967(3)	0.9863(3)	0.6488(4)	0.041(2)
C(112)	0.7353(4)	0.9796(3)	0.5462(4)	0.062(3)
C(113)	0.7501(5)	1.0366(4)	0.4651(4)	0.086(3)
C(114)	0.8301(5)	1.0970(5)	0.4859(5)	0.089(4)
C(115)	0.8921(4)	1.1057(4)	0.5865(6)	0.081(4)
C(116)	0.8760(3)	1.0512(4)	0.6707(4)	0.061(3)
C(121)	0.7626(3)	1.0232(3)	0.8537(3)	0.038(2)
C(122)	0.8321(3)	1.0730(3)	0.9399(4)	0.057(2)
C(123)	0.8171(4)	1.1577(4)	1.0049(4)	0.072(3)
C(124)	0.7352(5)	1.1924(4)	0.9862(5)	0.074(3)
C(125)	0.6641(4)	1.1425(4)	0.9014(5)	0.075(3)
C(126)	0.6782(3)	1.0587(3)	0.8348(4)	0.054(2)
P(2)	0.61151(6)	0.75631(7)	0.85678(8)	0.0287(4)
C(211)	0.6563(2)	0.7962(3)	1.0060(3)	0.033(2)
C(212)	0.7341(3)	0.8605(3)	1.0514(3)	0.041(2)
C(213)	0.7694(3)	0.8821(3)	1.1662(4)	0.055(2)
C(214)	0.7279(4)	0.8385(4)	1.2353(4)	0.068(3)
C(215)	0.6484(4)	0.7762(4)	1.1918(4)	0.071(3)
C(216)	0.6122(3)	0.7547(3)	1.0774(4)	0.051(2)
C(221)	0.4962(2)	0.7932(3)	0.8308(3)	0.035(2)
C(222)	0.4836(3)	0.8898(3)	0.8754(4)	0.049(2)
C(223)	0.3982(3)	0.9242(4)	0.8517(4)	0.059(3)
C(224)	0.3246(3)	0.8614(4)	0.7849(4)	0.053(2)

Table 2 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(225)	0.3364(3)	0.7671(4)	0.7399(4)	0.051(2)
C(226)	0.4214(3)	0.7323(3)	0.7616(4)	0.045(2)
C(1)	0.7565(2)	0.6475(3)	0.7713(3)	0.028(2)
C(2)	0.8385(2)	0.6242(3)	0.7791(3)	0.032(2)
N(101)	0.6715(2)	0.4322(2)	0.7519(3)	0.036(2)
C(102)	0.6104(3)	0.3667(3)	0.6756(4)	0.056(2)
C(103)	0.6313(4)	0.2742(4)	0.6344(5)	0.081(3)
C(104)	0.7164(4)	0.2461(4)	0.6720(5)	0.075(3)
C(105)	0.7797(3)	0.3116(3)	0.7522(4)	0.056(2)
C(106)	0.7542(3)	0.4036(3)	0.7898(4)	0.041(2)
N(201)	0.7178(2)	0.5654(2)	0.9729(2)	0.032(1)
C(202)	0.6948(3)	0.4911(3)	1.0291(4)	0.044(2)
C(203)	0.7401(3)	0.4827(4)	1.1381(4)	0.057(3)
C(204)	0.8127(3)	0.5514(4)	1.1932(4)	0.055(2)
C(205)	0.8392(3)	0.6255(3)	1.1360(4)	0.049(2)
C(206)	0.7913(3)	0.6297(3)	1.0275(3)	0.038(2)

The formation of **5** can be followed by addition of two molecules of pyridine to the Ru_5 cluster in **1**, resulting in cleavage of an Ru–Ru bond and displacement of two CO molecules. A concomitant transformation results in cleavage of the P–C(*sp*) bond in **1** to give the second μ-PPh_2 group and the cluster-bound C_2 fragment. The preparation of a cluster such as **5**, in which there are two easily displaceable ligands (py) provides another entry into the chemistry of cluster-bound C_2, which is currently being explored.

Experimental

General reaction conditions [11] and the synthesis of **1** [12] have been described elsewhere.

Reaction of $Ru_5(\mu_5$-$C_2PPh_2)(\mu$-$PPh_2)(CO)_{13}$ with pyridine

A solution of complex **1** (200 mg, 0.158 mmol) in benzene (10 ml) containing pyridine (1 ml) was heated in a Carius tube at 90 °C for 1.25 h. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 4:1). A brown band (R_f 0.25) was recrystallised (CH_2Cl_2/MeOH) to yield black crystals of $Ru_5(\mu_5$-$C_2)(\mu$-$PPh_2)_2(CO)_{11}(py)_2$ (**5**) (71 mg, 33%), m.p. 219–222 °C (dec.). Anal. Found: C, 40.87; H, 2.36; N, 1.98%; $[M-2py]^+$, 1209. $C_{47}H_{30}N_2O_{11}P_2Ru_5$ calc.: C, 41.31; H, 2.21; N, 2.05%; *M*, 1366. R: ν(CO)(CH_2Cl_2) 2051s, 2033sh, 2026s, 1996vs, 1985vs, 1973sh, 1943m, 1913m cm^{-1}. FAB MS (m/z): 1208, $[M-2py]^+$; 1180–900, $[M-2py-nCO]^+$ (n = 1–11). The instability of this complex has so far precluded measurement of a ^{13}C NMR spectrum.

Crystallography

A unique data set was measured at *ca*. 295 K within the limit $2\theta_{max} = 50°$ using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K_α

radiation, λ 0.7107$_3$ Å); 8101 independent reflections were obtained, 6891 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement following gaussian absorption correction, after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values (see Table 2). Conventional residuals R, R' on $|F|$ are 0.025, 0.029, using a statistical weights derivative of $\sigma^2(I) = \sigma^2(I)_{diff} + 0.0004\sigma^4(I_{diff})$. Computation used the XTAL 3.0 program system [13] implemented by S.R. Hall; neutral atom complex scattering factors were employed.

Crystal and refinement data

$Ru_5(C_2)(PPh_2)_2(CO)_{11}(py)_2 \equiv C_{47}H_{30}N_2O_{11}P_2Ru_5$, $M = 1366.1$. Triclinic, space group $P\bar{1}$, $a = 15.427(2)$, $b = 13.1870(8)$, $c = 12.547(3)$ Å, $\alpha = 95.92(1)$, $\beta = 105.69(1)$, $\gamma = 93.635(7)°$, $V = 2433$ Å^3, $Z = 2$, $\rho_c = 1.86$ g cm^{-3}, $F(000) = 1328$. Crystal dimensions: $0.22 \times 0.15 \times 0.27$ mm, $\mu(\text{Mo-}K_\alpha) = 14.8$ cm^{-1}, A^*(min, max) = 1.17, 1.32 (Gaussian).

Acknowledgements

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