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Preliminary communication

THE REACTION OF $Ru_3(CO)_{12}$ WITH $HC(PPh_2)_3$. CHARACTERISATION OF $Ru_3(CO)_9[HC(PPh_2)_3]$, AND CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)] \cdot CHCl_3$

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Summary

Reaction of $Ru_3(CO)_{12}$ with $HC(PPh_2)_3$ leads to a variety of products, two of which have been characterised. One is the symmetrically capped product $Ru_3(CO)_9[HC(PPh_2)_3]$, which was characterised spectroscopically. The second product was characterised crystallographically as $Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)] \cdot CHCl_3$.

Transition metal cluster complexes have attracted a great deal of attention in recent years, especially with respect to their potential as homogeneous catalysts [1]. The interest derives mainly from the idea that adjacent metal centres offer the possibility for cooperative reactivity leading to new, more active, or more selective catalysts. However, such clusters often undergo metal—metal bond rupture under catalytic reaction conditions, so that fragmentation and/or aggregation to metal particles occurs [2]. Recent reports have indicated that the use of tridentate phosphine ligands, capable of coordinating to three different metal centres in a cluster complex, and thus holding those centres together, renders the cluster more resistant to fragmentation than the parent compounds [3—5]. Thus, for example, it has been claimed that $Ru_3(CO)_9$-$[MeSi(PBu_2)_3]$ is more resistant to dissociation into monomeric species than $Ru_3(CO)_{12}$ when treated with a mixture of hydrogen and carbon monoxide at high (100 bar) pressure and temperature (300°C) [3]. Also, $Co_4(CO)_9[HC(PPh_2)_3]$ and $Rh_4(CO)_9[HC(PPh_2)_3]$ undergo no change in toluene at 100°C under CO (30 bar) [5] whereas under such conditions the parent carbonyls, $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$, are unstable [6].

We have also investigated the reactions of transition metal cluster com-

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pounds with the tridentate ligand $HC(PPh_2)_3$. We wish to report here the results we have obtained using $Ru_3(CO)_{12}$.

Treatment of a tetrahydrofuran solution of $Ru_3(CO)_{12}$ with an equimolar quantity of $HC(PPh_2)_3$ gives rise to the formation of at least eight products, none of which appears to be particularly favoured, the yield of each product being less than 10%. Three of these products, separated by chromatography, contain bridging CO ligands (infrared analysis), one of which we identified spectroscopically as the symmetrically capped product, $Ru_3(CO)_9[HC(PPh_2)_3]$ (I) (Fig. 1), analogous to the previously reported $Ru_3(CO)_9[MeSi(PBu_2)_3]$ [3,4]. The spectroscopic data are given in Table 1.

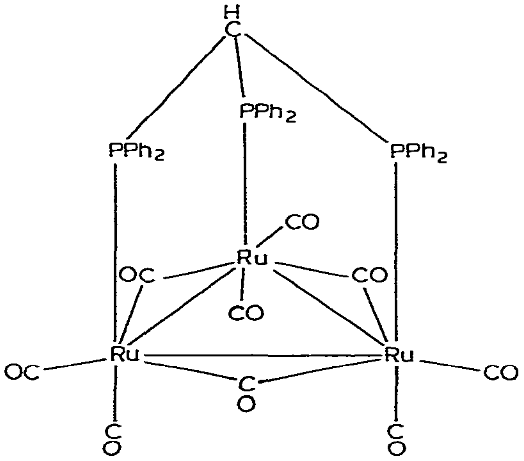

Fig. 1. $Ru_3(CO)_9[HC(PPh_2)_3]$ (I).

TABLE 1

INFRARED AND ^{31}P NMR DATA

Compound	Infrared (ν(CO), cm^{-1}) (CH_2Cl_2 solution)	$^{31}P\{^1H\}$ NMR δ(rel. H_3PO_4)
$Ru_3(CO)_9[MeSi(PBu_2)_3]$	2035s, 1985s, 1948w, 1925s, 1842m, 1800s	Not reported [4
$HC(PPh_2)_3$		−9.4s
$Ru_3(CO)_9[HC(PPh_2)_3]$ (I)	2045vs, 1991s, 1953w, 1930s, 1845w, 1792s	+47.55
$Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)]$ (II)	2072vw(sh), 2052vs, 2002s, 1960w(sh), 1941s, 1850w(sh), 1807s	[a]

[a] Insufficient pure product isolated to obtain ^{31}P NMR spectrum.

The ^{31}P NMR spectrum of I shows that all three phosphorus atoms are equivalent, while the infrared spectrum is very similar to that of $Ru_3(CO)_9[MeSi(PBu_2)_3]$ [4]. The formation of I has been mentioned in a footnote [5], but no spectroscopic data have been reported. The low yield of I has been suggested to be due to the fact that triangular clusters generally substitute at an equatorial site, whereas I derives from axial substitution. We agree that this contributes to the low yield, but another factor appears to be that reactions other than the simple substitution of CO ligands take place. This is exemplified by our characterisation of a second product containing bridging CO ligands.

We obtained brown/red crystals from chloroform/heptane solution, suitable for X-ray analysis, of a second product containing bridging CO ligands. The molecular structure of this complex is $Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)]$ (II), in which the ligand has undergone a reaction of which the end result is an *ortho*-substitution of a phenyl ring of one phosphine moiety by the phosphorus atom of a second phosphine moiety, together with the loss of benzene. The spectroscopic data for II are given in Table 1.

Crystals of the chloroform solvate of II are orthorhombic, $Ru_3(CO)_9(C_{31}H_{25}P_3)\cdot CHCl_3$, mol. wt. 1164.5, *a* 17.296(3), *b* 14.804(5), *c* 16.938(5) Å, *U* 4337 Å^3, D_{meas} 1.8 × 10^3 kg m^{-3}, $Z = 4$, D_{calc} 1.72 × 10^3 kg m^{-3}, space group *Pnma* (from systematic absences and structure solution), Mo-K_α radiation, λ 0.7107 Å, μ 14.1 cm^{-1}. Diffraction data were recorded on a Nonius CAD4 diffractometer. The structure was solved by Patterson and Fourier methods. The molecule of II, and the molecule of $CHCl_3$ of crystallisation each have symmetry *m*. Least squares refinement of positional and anisotropic thermal parameters, treating each phenyl ring as a rigid group and using the atomic scattering factors from reference 8 lead to an agreement factor *R* 6.4% for 2291 unique reflections with $F_0 > 2.5\sigma(F_0)$.

The structure is shown in Fig. 2 and selected bond lengths and angles given in Table 2.

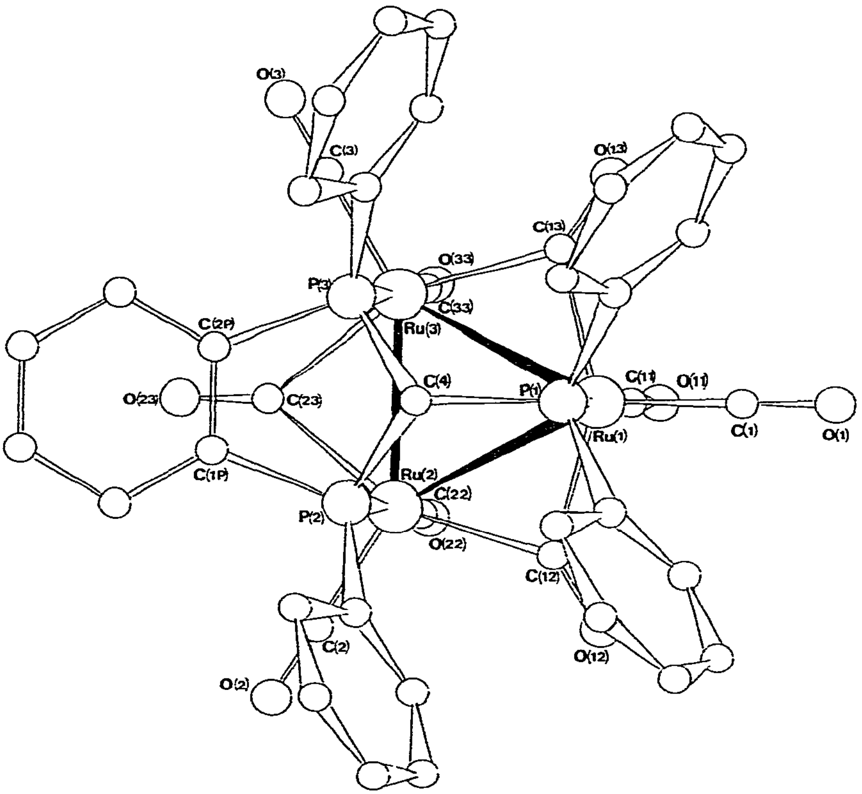

Fig. 2. Molecular structure of $Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)]$ (II) drawn by the program PLUTO [9]. Hydrogen atoms have been omitted. The molecule has a plane of symmetry through Ru(1) and C(4), and bisecting Ru(2)—Ru(3).

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (degrees) FOR $Ru_3(CO)_9[HC(PPh_2)(PhPC_6H_4PPh)]$ (II)

Ru(1)—Ru(2)	2.903(1)	Ru(2)—Ru(1)—Ru(3)	59.4(1)
Ru(2)—Ru(3)	2.878(1)	P(2)—Ru(2)—Ru(1)	91.8(1)
Ru(1)—P(1)	2.406(4)	P(1)—Ru(1)—Ru(2)	91.3(1)
Ru(2)—P(2)	2.364(2)	P(1)—Ru(1)—C(11)	176.8(4)
P(1)—C(4)	1.819(14)	P(1)—Ru(1)—C(1)	89.8(4)
P(2)—C(4)	1.873(10)	P(1)—Ru(1)—C(12)	91.5(2)
P(1)—C(1P)	1.819(10)	P(2)—Ru(2)—C(22)	174.8(3)
Ru(1)—C(1)	1.848(14)	P(2)—Ru(2)—C(2)	86.4(3)
Ru(1)—C(11)	1.870(14)	P(2)—Ru(2)—C(12)	94.0(2)
Ru(1)—C(12)	2.148(9)	P(2)—Ru(2)—C(23)	89.2(4)
Ru(2)—C(12)	2.107(9)	P(1)—C(4)—P(2)	110.6(5)
Ru(2)—C(2)	1.863(10)	P(2)—C(4)—P(3)	96.1(7)
Ru(2)—C(22)	1.930(9)	Ru(1)—C(12)—Ru(2)	86.1(3)
Ru(2)—C(23)	2.155(10)		

The essential features of II are a triangular array of Ru atoms capped by a tridentate phosphine ligand in which two P atoms are equivalent and the third P atom, P(1), unique. P(1) has undergone no change from the parent ligand, $HC(PPh_2)_3$. P(2) and P(3), in addition to being linked by C(4), are linked via C(1P) and C(2P), to form an *ortho*-disubstituted benzene ring. This has been achieved by the overall loss of benzene from the parent ligand.

The *ortho*-disubstituted benzene introduces some distortion from threefold symmetry in the ligand: the angles at C(4) are different (P(2)—C(4)—P(3) 96.1°, P(1)—C(4)—P(2) 110.6°), as are the distances Ru(1)—P(1) and Ru(2)—P(2) (2.406(4) and 2.364(2) Å). In turn, the distances Ru(1)—Ru(2) and Ru(2)—Ru(in the complex are different (2.903(1) and 2.878(1) Å) and there is slight asymmetry (only possibly significant) in the bridging carbonyl groups that do not lie across the mirror plane (Ru(1)—C(13)2.148(9), Ru(3)—C(13), 2.107(9)).

The ^{31}P NMR spectra of three of the other products from this reaction also show the presence of two equivalent and one unique phosphine group, all with terminal CO ligands only. We are currently investigating the structures of these products which may give an indication of the mechanism by which II is formed.

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