'Capped' Tri-ruthenium Carbonyl Cluster: *X*-Ray Crystal Structure of $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$

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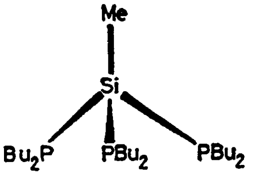
Summary The tridentate tertiary-phosphine ligand $MeSi(PBu_2)_3$ reacts with $Ru_3(CO)_{12}$ in refluxing benzene to give the symmetrical complex $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$, containing three bridging carbonyl ligands and one phosphorus centre co-ordinated to each of the ruthenium atoms as shown by *X*-ray crystallography.

SEVERAL groups[1] have recognized the potential of transition-metal cluster complexes as homogeneous catalysts. Since, however, such compounds frequently undergo cluster rupture reactions under potentially interesting reaction conditions, *e.g.* high carbon monoxide pressure,[2] it is often difficult unambiguously to assign any catalytic activity observed to the presence of the polynuclear species.[1,3]

One approach we have adopted[4] in an attempt to stabilize trimetallic cluster compounds towards dissociation into mono-metallic species is to use a tridentate ligand capable of simultaneously complexing all three metal centres and thus of holding them together. Such a ligand could then be visualised as a 'cap' fitting over the cluster's head and protecting it.

Molecular models suggested that (**1**), prepared in 70% yield as a viscous, colourless, air-sensitive oil by reaction of Bu_2PLi with $MeSiCl_3$ in diethyl ether at −80 °C,[4,5] would be a suitable 'cap' for $Ru_3(CO)_{12}$.



(**1**)

Addition of (**1**) to $Ru_3(CO)_{12}$ in refluxing benzene gave a yellow-brown air-stable complex (**2**), $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$, recovered in 16% yield.‡ Crystallization from methanol–acetone yielded yellow, diamond-shaped prisms, the molecular structure of which was determined by single crystal *X*-ray analysis.

Crystal data. From precession photographs and θ, θ measurements the following data were obtained: space group *P*2/*c*, $a = 20{\cdot}548(2)$, $b = 19{\cdot}988(2)$, $c = 11{\cdot}250(1)$ Å, $\beta = 102{\cdot}03(1)°$, $U = 4521$ Å^3, $Z = 4$, $D_c = 1{\cdot}51 \times 10^3$ kg/m^3 ($D_m = 1{\cdot}52 \times 10^3$ kg/m^3), μ(Mo-K_α) = 1·41 mm^{-1}. A crystal of dimensions *ca.* 0·7 × 0·7 × 0·15 mm ($\mu R = 0{\cdot}13$) was used for the data collection on a Nonius three-circle diffractometer (θ, 2θ scan, Mo-K_α radiation). Up to $\sin\theta/\lambda \leqslant 0{\cdot}4812$ Å^{-1} 3255 unique reflections with intensity well above background were observed. The normal Lorentz and polarisation corrections and an experimental azimuth dependent absorption correction were applied.[6]

The structure was solved with conventional Patterson, least squares, and difference density techniques. In the refinement neutral atomic scattering factors[7–9] and the anomalous dispersion correction for Ru, P, and Si were applied, whilst allowance was made for the insensity drop (13%) of the control reflection by using a time dependent correction for the scale factor for each reflection.[10] The final conventional agreement factors based on *F*(obs) are: $R = 0{\cdot}061$, $R_W = 0{\cdot}070$; error in observation of unit weight = 1·01. No attempt was made to locate the hydrogen atoms. The overall stereochemistry, together with important bond lengths and angles, is shown in the Figure.§

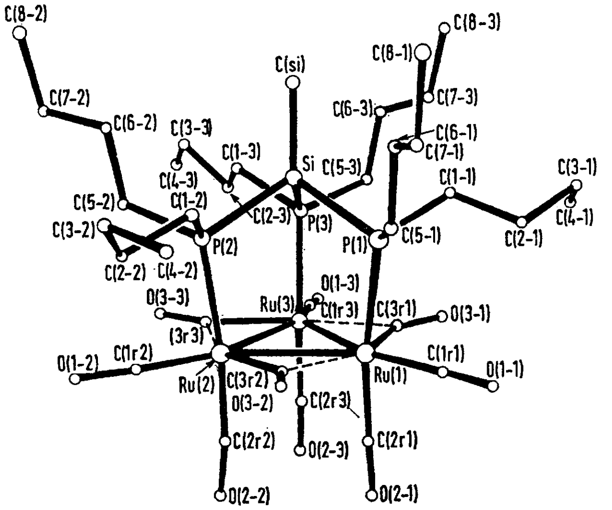


FIGURE. The molecular structure of $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$ (**2**) showing the atomic numbering scheme. Important bond lengths and angles are: Ru(1)–Ru(2), 2·915(1); Ru(2)–Ru(3), 2·917(1); Ru(1)–Ru(3), 2·918(1); Ru(3)–P(1), 2·403(3); Ru(2)–P(2), 2·402(3); Ru(3)–P(3), 2·406(3); Ru(1)–C(3r1), 2·031(12); Ru(3)–C(3r1), 2·229(12); Ru(1)–C(1r1), 1·828(13); and Ru(1)–C(2r1), 1·838(14) Å and ∠Ru(1)–Ru(2)–Ru(3), 60·06(3); P(1)–Ru(1)–Ru(2), 96·52(7); Ru(1)–C(3r1)–Ru(3), 86·3(4); C(1r1)–Ru(1)–C(3r1), 105·2(5); C(1r1)–Ru(1)–C(2r1), 86·6(5); Ru(1)–P(1)–Si, 110·04(13); and P(1)–Si–P(2), 100·29(14)°.

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‡ No attempt was made to optimize this yield.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table may be obtained as a Supplementary Publication (No. 22455; 21 pp.) from the British Library. For details of obtaining this material see Notice to Authors No. 7, Index Issues of *J.C.S. Dalton* or *Perkin I* or *II*.

The compound is somewhat unusual in that in spite of the bridging carbonyl ligands the ruthenium–ruthenium distance is longer than that found in other non-bridged ruthenium cluster compounds;[11] 2·917 compared to 2·85 Å in $Ru_3(CO)_{12}$,[12] 2·811 in $H_2Ru_4(CO)_{13}$,[11] 2·867 in $H_2Ru_6(CO)_{18}$,[13] and 2·80 Å in $H_2FeRu_3(CO)_{13}$.[14] Furthermore, the P–Si–P angle is significantly smaller, 100·32°, than the ideal tetrahedral angle of 109·45° expected. We attribute these two deviations from 'normality' to the imperfect tailoring of the cap ligand introducing strain into the complex.

Preliminary investigations of the catalytic properties of this and related systems[4] indicate that, compared to $Ru_3(CO)_{12}$, (**2**) is more resistant to dissociation into monomeric species when treated with mixtures of hydrogen and carbon monoxide at high (100 bar) pressure and temperature (300 °C).

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