The Phosphinomethylsilyl Group as a Bifunctional Bridging Ligand. *X*-Ray Crystal Structure of Hexacarbonylbis(μ-diphenylphosphinomethyldimethylsilyl)diruthenium(II), and of its Reaction Product with Trifluoroacetic Acid, a Mononuclear Ruthenium(II) Complex incorporating a Unique Co-ordinated Silanol

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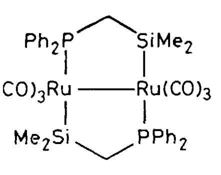
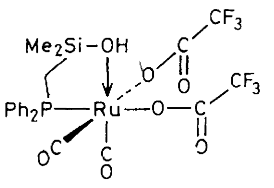
Reaction between $Ru_3(CO)_{12}$ and $Ph_2PCH_2SiMe_2H$ affords the symmetrical bridged diruthenium complex $[Ru_2(\mu\text{-}PPh_2CH_2SiMe_2)_2(CO)_6]$ in which Ru–Ru = 3.056(1) Å; treatment of this dimer with CF_3CO_2H leads to formation of a mononuclear phosphinomethyldimethylsilanol complex $[Ru(PPh_2CH_2SiMe_2OH)(CO)_2(CO_2CF_3)_2{\cdot}Et_2O]$ in which $Ru\text{–}O_{Si}$ = 2.19 Å, δ(O*H*) = 12.12, and the solvating Et_2O molecule is H-bonded to the silanol-*O* with O $\cdots$ O 2.64 Å.

We have recently developed[1] a systematic approach to the synthesis of phosphinoalkylsilanes $\{R_2P[CH_2]_nSiR^1R^2H$; R, R^1, or R^2 = Me or Ph; n = 1, 2, or 3$\}$ and have shown that where n = 2 these modified silanes will oxidatively add to



(A)



(B)

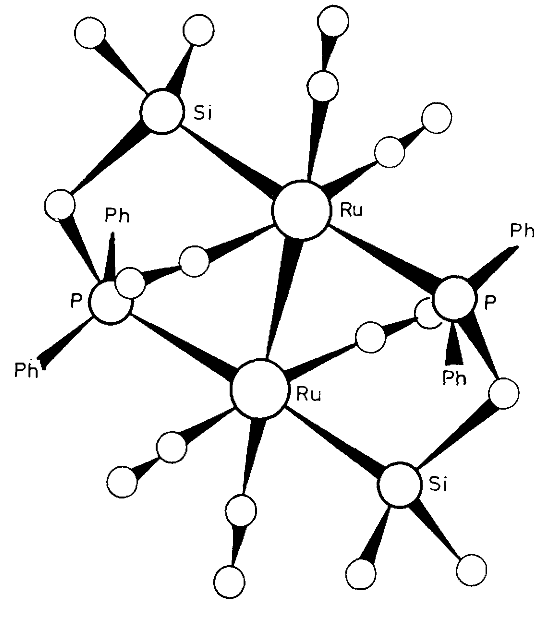


Figure 1. Molecular structure of compound (**1**). Ru–Ru 3.056(1), Ru–P 2.426(1), Ru–Si 2.465(1); Ru–C(6) 1.921(3) and Ru–C(8) 1.914(3) Å with C(6)–Ru–C(8) 165.6(2)°; Ru–C(9) 1.869(4) Å with C(6)–Ru–C(9) 92.8(2)°.

suitable low-valent transition-metal species *via* 'chelate-assisted' hydrosilylation, to afford complexes[2] of the bidentate bifunctional phosphinoethylsilyl ($R_2PCH_2CH_2$-SiR^1R^2–) ligand family. We have also observed that the phosphinomethylsilyl fragment (*i.e.* $n = 1$) can enter as an unsymmetrical bridging group into a bimetallic configuration. Typically prolonged heating (72 h, 145 °C) in a sealed, evacuated glass reaction-tube of $Ru_3(CO)_{12}$ with PPh_2CH_2-$SiMe_2H$ (6 mol. equiv.) in hexane afforded a yellow solution which on cooling began to deposit pale yellow crystals, (**1**); these were recovered and washed with Et_2O. A symmetrical structure (A) was implied by the presence of only three absorptions due to ν(CO) (2010s, 1975vs, and 1955s cm^{-1}) in the i.r. spectrum, and by single $SiCH_3$ and PPh_2 n.m.r. signals [δ 0.34, ^{1}H; δ −125.2 p.p.m. *vs.* trimethyl phosphite (TMP), ^{31}P], as well as by appropriate analytical data. Confirmation of such a formulation was sought using *X*-ray crystallography, since suitable crystals were available and because of our interest in the disposition of the novel bridging framework. The structure† is illustrated in Figure 1; the complex is indeed a symmetrical dimer, molecular point group C_{2h} predicting 3 i.r.-active ν(CO) modes ($a_u + 2b_u$) as observed. In terms of the 18-electron rule, configuration (A) requires the existence of a Ru–Ru bond, making the Ru_2 separation which at 3.056(1) Å is considerably longer (by *ca.* 0.30 Å) than established[3] Ru–Ru bonding distances the most interesting structural parameter. Unequivocal evidence for significant metal–metal interaction is provided however by the observation of an extremely intense feature in the Raman spectrum at 136 cm^{-1} attributable to ν(Ru–Ru), and by the unusual shape of the CH_2 resonance (broad feature δ 2.33 flanked symmetrically by sharp single lines), which is accountable for as the A part of a virtually-coupled A_2XX' system, consistent with a large ^3J(PP) term. Corresponding reactions using $Os_3(CO)_{12}$ afforded a yellow product (**2**) for which spectroscopic characteristics were extremely similar to those of the diruthenium complex (**1**) and which has been shown to be isomorphous with the latter [a = 20.345(2), b = 9.739(2), c = 9.400(1) Å, β = 94.88(1)°].

Protonation is a characteristic reaction of a range of metal–metal bonded compounds[4] but has been observed to occur only very slowly[5] for $[Mn_2(dpm)_2(CO)_6]$ [(**3**) dpm = $Ph_2PCH_2PPh_2$] which is co-ordinatively saturated at both metal centres. Complex (**1**), which possesses a structure very similar to that of (**3**) and is isoelectronic with it, was unaffected by HBF_4–Et_2O (36 h, 20 °C); however with an excess of CF_3CO_2H in CH_2Cl_2 the yellow colour of the solution gradually faded over 24 h (20 °C), when concentration afforded a white solid (**4**) which was recrystallized from Et_2O–heptane. The i.r. spectrum showed ν(CO) at 2072vs, 2003s with intense bands at 1700, 1200, and 1120 cm^{-1} assigned to CF_3CO_2 modes, while n.m.r. spectra demonstrated the existence of inequivalent $SiCH_3$ groups and CH_2 protons, the presence of one Et_2O molecule, and a single P environment (δ −92.0 p.p.m. *vs.* TMP). Further experiments using ^{31}P n.m.r. spectroscopy confirmed that the reaction was slow, as well as clearly distinguishing (**1**) and (**4**) as the only P-containing species in solution providing no evidence for any other detectable intermediate species. The identity of compound (**4**) was established‡ using *X*-ray crystallography. The unexpected result is depicted in Figure 2.

$[Os_2(\mu\text{-}PPh_2CH_2SiMe_2)_2(CO)_6]$
(**2**)

$[Mn_2(Ph_2PCH_2PPh_2)_2(CO)_6]$
(**3**)

Complex (**4**) is mononuclear, a *cis*-dicarbonyl arrangement at Ru accompanying a pair of ester groups which are also *cis*; octahedral co-ordination about the metal is completed by a novel chelating unit (constructing a cyclic sequence of five different atoms) derived from the (originally bridging) $Ph_2PCH_2SiMe_2$ unit by introduction of an O atom. The presence of a hydrogen atom attached to the latter was

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† *Crystal data* for (**1**): $Ru_2P_2Si_2O_6C_{36}H_{36}$, M = 884.62, monoclinic, space group $P2_1/n$, a = 20.383(2), b = 9.784(2), c = 9.403(2) Å, β = 94.90(1)°, D_c = 1.573 g cm^{-3}, Cu-K_α radiation (λ = 1.54178 Å), μ = 85.32 cm^{-1}, Picker FACS1 four-circle diffractometer, 3177 unique reflections, 2491 with $I > \sigma(I)$. Solution by Patterson and Fourier methods led to a conventional R of 0.028.

‡ *Crystal data* for (**4**): $RuPSiF_6O_8C_{25}H_{29}$, M = 730.6, monoclinic, space group $C2/c$, a = 14.694(5), b = 11.780(4), c = 37.371(13) Å, β = 95.83(4)°, D_c = 1.51 g cm^{-3}, Z = 8, Mo-$K_{\alpha 2}$ radiation (λ 0.71069 Å), μ = 6.5 cm^{-1}, Picker four-circle diffractometer, 995 independent, observable reflections with $I > 3\sigma(I)$ leading to current conventional R 0.077.

The atomic co-ordinates for the structures of (**1**) and (**4**) 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.

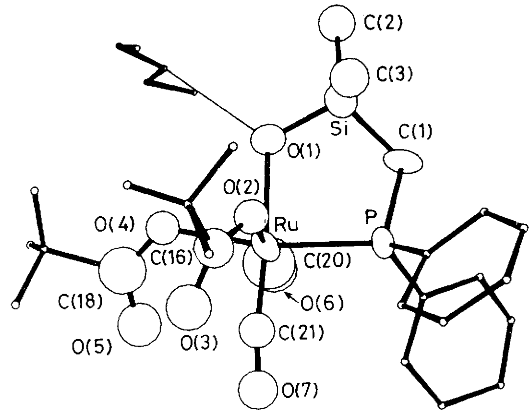

Figure 2. Geometry of compound (**4**). Phenyl rings at P, CF_3 groups at C(16) and C(18), and the solvating Et_2O molecule have been simplified for clarity. Ru–P 2.348(10), Ru–O(1) 2.192(19), Ru–C(20) 1.833(68), Ru–C(21) 1.707(37), Ru–O(2) 2.079(26), Ru–O(4) 2.096(23), Si–O(1) 1.692(21) Å.

suggested by the diamagnetism of the complex (*i.e.* Ru^{II} not Ru^{III}) and the Ru–O distance of 2.19 Å, considerably longer than $Ru–O_{ester}$ (mean 2.09 Å). This was confirmed by (i) the resolution in the *X*-ray structure of the solvating diethyl ether molecule at O • • • O 2.64 Å (Figure 2), typical[6] of a short hydrogen-bonded contact; (ii) the appearance of the 250 MHz ^1H n.m.r. spectrum, which includes a characteristically broadened signal at extremely low field (δ 12.12). The configuration (B) of this very unusual molecule therefore represents intramolecular co-ordination to Ru^{II} *via* the O-atom of a trimethylsilanol derivative, such stabilization of which appears to be without precedent. Accordingly we are continuing to explore the chemistry of the unique proton in compound (**4**) and to elucidate (a) the course of the reaction whereby the latter is formed from (**1**); (b) how the Ph_2PCH_2-$SiMe_2$ bridging unit in complexes (**1**) and (**2**) is formed since loss of H following oxidative addition of Si–H to Ru may implicate a binuclear 1,2-dihydrogen elimination.

We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support of this research, and Dr. W. H. Woodruff (University of Texas) for providing the Raman spectrum of a solid sample of compound (**1**).

Received, 8th August 1983; Com. 1070

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