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Crystal Structures of $HM(SiPh_3)(CO)_3(PPh_3)$ (M = Fe, Ru) Formed from Photolysis of $M(CO)_4PPh_3$ in the Presence of $HSiPh_3$

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Abstract

Near-UV irradiation of $M(CO)_4PPh_3$ (M = Fe, Ru) at 298 K in deoxygenated hydrocarbon solutions containing molecules having a Si–H bond gives clean formation of products of the formula $HM(CO)_3(PPh_3)(\mathrm{Si}{\lessdot})$. Several isomers of such species are possible and X-ray crystallography has been used to unambiguously establish the isomer formed in the photochemical reaction. The crystal structure of the isomer of $HM(SiPh_3)(CO)_3(PPh_3)$ formed by the photochemical reaction of $M(CO)_4PPh_3$ with $HSiPh_3$ is reported for M = Fe (**1**) and Ru (**2**). Both complexes have the same geometry, a distorted octahedron with the COs meridional and the H *cis* to both the $SiPh_3$ and the PPh_3. The crystals are triclinic, space group $P\bar{1}$. Crystal parameters for **2**, (followed in square brackets by those for **1**), are: $a = 12.535(3)$ [12.32(2)], $b = 14.244(3)$ [14.50(4)], $c = 10.174(3)$ [10.06(2)] Å, $\alpha = 104.98(2)$ [106.3(2)], $\beta = 98.52(2)$ [98.2(2)], $\gamma = 71.92(2)^\circ$ [72.0(2)°], $V = 1663.63$ [1637.38] Å^3.

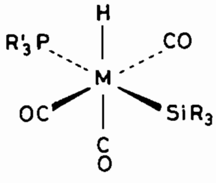
Introduction

We wish to report the molecular structure of $HM(SiPh_3)(CO)_3(PPh_3)$ (M = Fe, Ru) formed by the photochemical reaction represented by eqn. (1) [1]. There have been several recent studies concerning the chemistry of various isomers of compounds

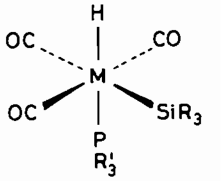
$$M(CO)_4PPh_3 + HSiPh_3 \xrightarrow[\text{alkane}]{\text{near-UV}} HM(SiPh_3)(CO)_3(PPh_3) + CO \quad (1)$$

$$\mathbf{1},\ M = Fe;\ \mathbf{2},\ M = Ru$$

having the formula $HM(SiR_3)(CO)_3(PR'_3)$ (M = Fe, Ru; various R and R′ groups) [1–3]. Four possible isomers exist for these compounds (**A**–**D** below). The structural assignment of the $HM(SiR_3)(CO)_3(PR'_3)$ species has been based on IR and NMR spectroscopic data, particularly on the values of NMR coupling constants [1–3]. To this point no crystal structures have been reported.



A



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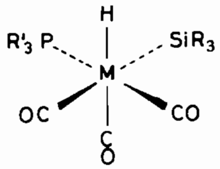

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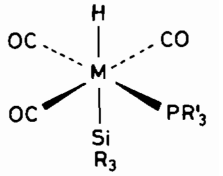

D

Complexes of structure **A** are reportedly [1] formed by photolysis at 298 K of $M(CO)_4PPh_3$ in the presence of $HSiR_3$ ($R_3 = Et_3$, Ph_3, $MeCl_2$). However, at 100 K photolysis of $M(CO)_4PPh_3$ in the presence of $HSiEt_3$ yields an isomer of $HM(SiEt_3)(CO)_3(PPh_3)$ assigned as structure **C**, which upon warming yields the isomer assigned to be structure **A**. The low temperature structure **C** was assigned only on the basis of its IR spectrum. Thermal reaction of *cis*-$HRu(SiCl_2R)(CO)_4$ with PR'_3 (R = Me, Cl) yields complexes assigned to structure **A** [2]. In contrast, thermal reaction of *cis*-$HFe(SiPh_3)(CO)_4$ with PPh_3 results in the formation of a compound assigned to structure **B** [3]. This compound is labile, and quickly reacts further to give a mixture of $Fe(CO)_3(PPh_3)_2$ and $Fe(CO)_4(PPh_3)$ [3]. To our knowledge, isomer **D** has not been claimed for any of the systems investigated.

The $HM(SiR_3)(CO)_3(PPh_3)$ compounds are of interest because of their possible role in the $M(CO)_4(PPh_3)$-photocatalyzed hydrosilation of olefins [4]. In view of the interest in these compounds, and the structural diversity that they might exhibit, we have determined the crystal structure of the isomer

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of $HM(SiPh_3)(CO)_3(PPh_3)$ (1, M = Fe; 2, M = Ru) that is formed from photolysis of $M(CO)_4(PPh_3)$ with $HSiPh_3$, eqn. (1). The structures reported herein comprise a firm foundation for the assignment of various derivatives on the basis of spectroscopic (IR and NMR) information.

Experimental

Preparation and Crystallization of 1 and 2

Compounds 1 and 2 were prepared by near-UV irradiation of $M(CO)_4PPh_3$ in deoxygenated alkane solution at 298 K in the presence of an excess of $HSiPh_3$ [1]. The product precipitated from the solution during irradiation and was collected by filtration, washed with hexane, and dried under vacuum at room temperature. Elemental analyses were performed by Galbraith Laboratories. *Anal.* Calc. (found) for $FeC_{39}H_{31}O_3SiP$: C, 70.69(70.61); H, 4.72(4.75); Fe, 8.43(7.57); Si, 4.24(4.15); P, 4.67(4.31)%. Calc. (found), for $RuC_{39}H_{31}O_3SiP$: C, 66.18(65.88); H, 4.42(4.29); P, 4.38(4.41); Si, 3.97(4.03)%. Crystals of 2 suitable for X-ray analysis were grown by slow evaporation from a benzene solution. Attempts to grow suitable crystals of 1 by slow evaporation from several solvents resulted only in the decomposition of 1. Very small crystals of 1 were prepared by irradiation (General Electric blacklight) of a saturated solution of $Fe(CO)_4PPh_3$ in hexane containing an excess of $HSiPh_3$. The needle-shaped crystals of 1 precipitated from the irradiated solution and were collected by filtration.

IR and NMR Spectroscopy

IR spectra were recorded using a Nicolet 7199 FTIR spectrometer. NMR spectra were obtained with a Bruker 250 or 270 MHz Fourier transform NMR spectrometer. Some of the ^{13}C NMR spectra were obtained for samples at natural abundance, and others were recorded for ^{13}CO-enriched samples of 1 and 2. The ^{13}CO-enriched samples of 1 and 2 were prepared as described above, starting with ^{13}CO-enriched $M(CO)_4PPh_3$ made via the photolysis of $M(CO)_4PPh_3$ in the presence of ^{13}CO.

X-ray Crystallography

The crystals of 1 and 2 are triclinic, space group $P\bar{1}$. Crystal parameters for 2, (followed in square brackets by those for 1), are: $a = 12.535(3)$ [12.32(2)], $b = 14.244(3)$ [14.50(4)], $c = 10.174(3)$ [10.06(2)] Å, $\alpha = 104.98(2)$ [106.3(2)], $\beta = 98.52(2)$ [98.2(2)], $\gamma = 71.92(2)°$ [72.0(2)°], $V = 1663.63$ [1637.38] Å^3, $D_c = 1.413$ [1.344] g cm^{-3} with $Z = 2$, $\mu = 47.03$ [5.45 cm^{-1}] (an empirical absorption correction was applied to 2). Data were collected at -50 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid N_2 low temperature device, using Mo Kα radiation for 1 and Cu Kα radiation for 2. Data collection, reduction and refinement procedures have been described in detail elsewhere [5]. A total of 4142 [4277 for 1] reflections ($\pm h$, $\pm k$, $+1$) were collected in the range $3° \leqslant 2\theta \leqslant 110°$ [45° for 1] with the 3678 [1619] having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (227 [181] variables) using SHELX-76. Final $R_1 = 0.051$ [0.173] and $R_2 = 0.064$ [0.173].

For 2, the Ru, P, and Si atoms, and atoms of the carbonyl groups were refined anisotropically. The hydride atom was not included in the model, but all remaining hydrogen atoms were placed in calculated positions (C H = 0.95 Å) and constrained to 'ride' on their respective carbon atoms. The largest peak on the final difference-Fourier map was 0.75 e/Å^3. Some difficulty was encountered in determining which atom was Si and which was P. Attempts were made to solve this problem by comparing the observed Ru–L bond lengths, finally assigned as Ru–P = 2.402(2) Å and Ru–Si = 2.446(2) Å, to those of Ru–PPh_3 and Ru–SiR_3 compounds in the Cambridge Crystallographic Data Base [6].

Only poor quality crystals of 1 could be obtained. Initially, only the Fe, Si, and P atoms could be located in difference-Fourier maps. Therefore, the structure of the Ru analog was used as a starting point for the refinement of 1. All atoms were refined isotropically, and hydrogen atoms were ignored. As with compound 2, the decision as to which atom was Si and which was P was based on Fe–PPh_3 and Fe–SiR_3 bond lengths of compounds reported in the Cambridge Crystallographic Data Base [6]. The structure of 1 is in no sense an accurate determination, but the refinement does serve to show that the Fe and Ru compounds are isomorphous and isostructural, as had been predicted from the similarities between their IR spectra [1].

Results and Discussion

NMR Spectroscopy

In the ^1H NMR of 1, the hydride ligand is coupled to the phosphorus with $^2J(P–H) = 25$ Hz [1]. This coupling constant is consistent with a *cis* arrangement of the phosphorus and the hydride [7], a condition that is fulfilled by structure A, C, and D. The ^{13}C NMR spectrum of 1 shows only one resonance in the region where M–CO groups are expected, a doublet at 212.1 ppm with $^2J(P–C) = 12$ Hz. This indicates that all three CO groups are equivalent on the NMR time scale. To confirm this, the splitting of the hydride peak in the ^1H NMR of a partially ^{13}CO-enriched sample of 1 was examined. The hydride peak is at -8.44 ppm and is split by coupling to the phosphorus and to the ^{13}COs. The splitting of the hydride peak is consistent with coupling to equivalent ^{13}Cs with ^2J(C–H) = 9 Hz where some molecules contain one ^{13}CO, some two ^{13}COs and some three ^{13}COs. Fourteen peaks are actually observed in the hydride region, with relative intensities and splittings in accord with the information given. Since none of the possible isomers **A**–**D** have three equivalent CO groups, we conclude that at room temperature, **1** is a fluxional molecule on the NMR time scale. The ^{13}C NMR is therefore not helpful in trying to determine the structure of **1**.

The ^{13}C NMR of **2** shows two resonances in the region where M–CO peaks are expected, a doublet at 200.3 ppm with ^2J(P–C) = 10 Hz and a broad peak at 119.0 ppm that seems to be an unresolved doublet [1]. Thus, compound **2** contains at least two nonequivalent COs. Both structures **A** and **B** could fit this spectrum, but the P–H coupling observed for the hydride peak in the ^{1}H NMR, ^2J(P–H) = 16 Hz, is more consistent with a *cis* arrangement of the hydride and the phosphorus [7], suggesting structure A as the most likely structure.

The ^{1}H NMR coupling constants for $HRu(SiMeCl_2)(CO)_3[P(OCH_2)_3CC_2H_5]$, formed by the thermal reaction of $P(OCH_2)_3CC_2H_5$ with $HRu(SiMeCl_2)(CO)_4$, have been reported by Pomeroy and Hu [2]. They report a coupling constant of 0.5 Hz between the hydride and the protons of the methyl group on the Si, indicating a *cis* arrangement of the hydride and $-SiMeCl_2$ groups [2]. The coupling constant between the phosphorus and the Si methyl protons was reported to be 1.4 Hz, which they concluded to be indicative of a *trans* arrangement of the P and the Si [2]. On the basis of this study, Pomeroy and Hu concluded that $HRu(SiMeCl_2)(CO)_3[P(OCH_2)_3CC_2H_5]$ has structure **A**. The CO-stretching absorbances in the IR for this molecule have relative intensities [2] similar to those of **1** and **2** [1], indicating that these molecules have the same geometry. However, although the different isomers would be expected to have different IR spectra, one cannot predict with certainty which isomer would have which spectrum. Therefore, although the IR spectra allow one to determine whether two compounds have the same geometry, they do not enable one to assign a particular geometry to a particular compound in the case at hand.

X-ray Crystallography

The geometry and atom labeling scheme for **1** and **2** are shown in Fig. 1. The principal bond lengths and bond angles for **1** and **2** are given in Tables I and II. Although the hydride ligand was not located, it is clear that the geometry of both $HM(SiPh_3)(CO)_3(PPh_3)$ compounds is that of structure **A**, as had been predicted from their IR and NMR spectra [1, 2]. The positional parameters for the atoms of the two compounds are listed in Table III. The structure of **2** is of high quality, but the structure of **1** cannot be so regarded because only poor quality crystals were available. As outlined in the 'Experimental', however, compounds **1** and **2** are isostructural.

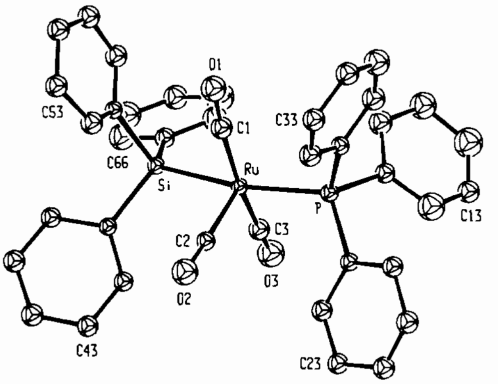

Fig. 1. ORTEP diagram of $HRu(SiPh_3)(CO)_3(PPh_3)$, **2**, showing the 30% probability thermal ellipsoids and the atom numbering scheme. The analogous Fe compound, **1**, is isostructural, and the same numbering scheme was used. *cf.* Tables I–III for bond distances, angles and positional parameters for **1** and **2**.

TABLE I. Bond Lengths (Å) for $HM(SiPh_3)(CO)_3(PPh_3)$

Bond	M = Ru	M = Fe
M–P	2.406(2)	2.271(12)
M–Si	2.446(2)	2.343(12)
M–C(1)	1.914(8)	1.724(37)
M–C(2)	1.935(7)	1.798(46)
M–C(3)	1.908(7)	1.762(46)
P–C(11)	1.841(6)	1.928(36)
P–C(21)	1.838(6)	1.938(31)
P–C(31)	1.841(6)	1.791(37)
Si–C(41)	1.898(6)	1.854(34)
Si–C(51)	1.875(6)	1.899(30)
Si–C(61)	1.884(6)	1.878(32)
C(1)–O(1)	1.141(8)	1.156(38)
C(2)–O(2)	1.139(8)	1.151(44)
C(3)–O(3)	1.145(8)	1.154(44)

TABLE II. Bond Angles (°) for $HM(SiPh_3)(CO)_3(PPh_3)$

	M = Ru	M = Fe
P–M–Si	168.4(1)	168.0(4)
C(1)–M–Si	88.2(2)	88.8(12)
C(1)–M–P	91.2(2)	89.6(12)
C(2)–M–Si	93.9(2)	95.1(15)
C(3)–M–Si	86.5(2)	87.2(14)
C(2)–M–P	97.7(2)	96.9(15)
C(3)–M–P	91.1(2)	90.1(14)
C(1)–M–C(2)	93.5(3)	101.5(18)
C(2)–M–C(3)	100.9(3)	99.8(20)
C(1)–M–C(3)	165.0(3)	158.6(17)

TABLE III. Positional Parameters for $HM(SiPh_3)(CO)_3(PPh_3)$ (M = Fe, Ru). Values for the Fe Compound Appear Below Those for the Ru Compound[a]

Atom	*x*	*y*	*z*
Ru	0.49029(4)	0.26315(4)	0.18958(5)
	0.4909(5)	0.2597(4)	0.1875(6)
P	0.30230(13)	0.30067(12)	0.25547(16)
	0.3095(9)	0.2951(7)	0.2497(10)
Si	0.66873(14)	0.26016(12)	0.11609(17)
	0.6657(9)	0.2577(7)	0.1190(10)
O(1)	0.4112(5)	0.1988(4)	−0.1099(5)
	0.410(2)	0.2220(19)	−0.100(3)
O(2)	0.5772(5)	0.0439(4)	0.2260(6)
	0.565(2)	0.050(2)	0.204(3)
O(3)	0.5597(6)	0.3867(4)	0.4633(6)
	0.557(2)	0.3789(20)	0.453(3)
C(1)	0.4428(6)	0.2208(5)	0.0016(8)
	0.442(3)	0.237(2)	0.015(4)
C(2)	0.5455(6)	0.1261(6)	0.2162(7)
	0.541(4)	0.135(3)	0.213(5)
C(3)	0.5340(6)	0.3373(5)	0.3631(7)
	0.528(4)	0.328(3)	0.353(5)
C(11)	0.2345(5)	0.4359(5)	0.3245(7)
	0.241(3)	0.437(3)	0.318(4)
C(12)	0.1842(7)	0.4700(7)	0.4438(9)
	0.190(4)	0.463(3)	0.448(5)
C(13)	0.1312(9)	0.5766(9)	0.4889(12)
	0.144(4)	0.577(4)	0.495(5)
C(14)	0.1324(8)	0.6401(8)	0.4174(10)
	0.137(4)	0.633(3)	0.414(5)
C(15)	0.1827(7)	0.6084(7)	0.2959(9)
	0.187(4)	0.602(4)	0.283(6)
C(16)	0.2373(6)	0.5044(6)	0.2501(8)
	0.243(4)	0.495(3)	0.234(5)
C(21)	0.2859(5)	0.2375(5)	0.3844(6)
	0.297(3)	0.231(2)	0.390(3)
C(22)	0.3782(6)	0.2004(5)	0.4706(7)
	0.392(3)	0.197(2)	0.470(4)
C(23)	0.3666(6)	0.1546(5)	0.5715(7)
	0.371(3)	0.154(2)	0.568(3)
C(24)	0.2636(6)	0.1455(5)	0.5869(7)
	0.262(3)	0.154(2)	0.590(4)
C(25)	0.1719(6)	0.1816(5)	0.5032(7)
	0.170(3)	0.186(2)	0.507(4)
C(26)	0.1823(6)	0.2269(5)	0.4013(7)
	0.182(3)	0.234(2)	0.403(3)
C(31)	0.2047(5)	0.2637(5)	0.1115(6)
	0.209(3)	0.260(3)	0.113(4)
C(32)	0.2215(6)	0.1619(5)	0.0511(7)
	0.229(3)	0.153(3)	0.043(4)
C(33)	0.1549(6)	0.1303(6)	−0.0622(8)
	0.157(4)	0.125(3)	−0.063(4)
C(34)	0.0737(6)	0.1990(6)	−0.1192(8)
	0.071(4)	0.185(3)	−0.124(5)
C(35)	0.0570(7)	0.2998(7)	−0.0627(9)
	0.055(4)	0.291(3)	−0.067(5)
C(36)	0.1215(6)	0.3340(6)	0.0545(8)
	0.122(3)	0.320(3)	0.052(4)
C(41)	0.7978(5)	0.1750(5)	0.1932(6)
	0.791(3)	0.177(2)	0.199(3)
C(42)	0.7980(5)	0.1493(5)	0.3157(7)
	0.793(3)	0.153(3)	0.322(4)
C(43)	0.8939(6)	0.0860(5)	0.3705(7)
	0.894(4)	0.095(3)	0.382(4)
C(44)	0.9903(6)	0.0459(5)	0.3014(7)
	0.996(3)	0.056(2)	0.304(4)
C(45)	0.9928(6)	0.0710(5)	0.1806(7)
	0.997(3)	0.080(3)	0.184(4)
C(46)	0.8970(5)	0.1344(5)	0.1270(7)
	0.897(3)	0.138(3)	0.129(4)
C(51)	0.6780(5)	0.2061(5)	−0.0720(6)
	0.680(3)	0.199(2)	−0.074(3)
C(52)	0.6907(6)	0.1030(5)	−0.1249(7)
	0.686(3)	0.094(2)	−0.126(4)
C(53)	0.6898(6)	0.0597(6)	−0.2627(7)
	0.693(3)	0.056(3)	−0.269(4)
C(54)	0.6767(6)	0.1194(6)	−0.3542(8)
	0.680(3)	0.110(2)	−0.364(4)
C(55)	0.6633(6)	0.2206(6)	−0.3066(8)
	0.668(3)	0.215(3)	−0.316(4)
C(56)	0.6619(6)	0.2643(6)	−0.1668(7)
	0.670(3)	0.260(2)	−0.161(4)
C(61)	0.6979(5)	0.3865(5)	0.1483(7)
	0.692(3)	0.383(2)	0.147(3)
C(62)	0.8035(7)	0.3916(6)	0.1377(8)
	0.801(4)	0.388(3)	0.146(4)
C(63)	0.8268(8)	0.4855(7)	0.1589(9)
	0.839(4)	0.479(4)	0.174(5)
C(64)	0.7455(7)	0.5727(6)	0.1922(8)
	0.746(3)	0.569(3)	0.195(4)
C(65)	0.6410(8)	0.5705(7)	0.2024(9)
	0.635(4)	0.564(3)	0.198(4)
C(66)	0.6152(7)	0.4789(6)	0.1815(8)
	0.604(4)	0.478(3)	0.188(4)

[a] Numbers in parentheses are errors in the last significant digit(s).

One minor difficulty in establishing the structures of 1 and 2 stems from the similarity of the $-SiPh_3$ and PPh_3 ligands. The assignment of the structure has involved comparison of the observed Ru–L (L = PPh_3, $-SiPh_3$) distances with reported values for related complexes (Table IV). The reported Ru–PPh_3 bond lengths [8] vary from 2.335 to 2.416 Å, the average for twelve entries being 2.371 Å (Table IV). No Ru–$SiPh_3$ compounds were found in a search of the literature. The only reported Ru–SiR_3 bond lengths (Table V) were for R = Me or Cl, and only one of these was Ru–$SiCl_3$. The Ru–$SiMe_3$ bond lengths vary from 2.414 to 2.507 Å, the average being 2.45 Å for the five compounds reported [9]. The one Ru–$SiCl_3$ compound [9f] has much shorter Ru–Si bonds, averaging 2.339 Å, so the bond length depends significantly on the R group. Based on this data, the shorter of the two Ru–L bond lengths observed in 2, 2.406(2) Å, seems more consistent with

TABLE IV. Reported Ru–PPh_3 Bond Lengths (Å) [8]

Compound	Ru–P bond length	Reference
$CH_3C(O)C_6H_4RuCl(CO)(PPh_3)_2$	P(1) 2.373(4) P(2) 2.381(4)	8a
$[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4 \cdot EtOH$	P(1) 2.416(5) P(2) 2.329(5)	8b
$(\eta^5\text{-}C_5H_5)Ru(Cl)(PPh_3)_2$	P(1) 2.337(1) P(2) 2.335(1)	8c
$Ru(OAc)(p\text{-}MeC_6H_4NCH)(CO)(PPh_2)_2$	P(1) 2.373(3) P(2) 2.383(3)	8d
$Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$	P(1) 2.391(4) P(2) 2.344(3)	8e
$RuCl[CH_2C(Me)NCHNCHMe_2]CO(PPh_3)_2$	P(1) 2.400(4) P(2) 2.383(4)	8f

TABLE V. Reported Ru–SiR_3 Bond Lengths (Å) [9]

Compound	Ru–Si bond length	Reference
$Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4$	2.439(4)	9a
$[(Me_3Si)(CO)_3Ru(SiMe_2)]_2$	2.507(8)	9b
$Ru(SiMe_3)(CO)_2[C_7H_7(C_6F_5)(SiMe_3)]$	2.43	9c
$Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$	2.452(3)	9d
$Ru(SiMe_3)(CO)_2[C_8H_8(SiMe_3)]$	2.414(2)	9e
$[p\text{-}(tBu)_2C_6H_4]Ru(CO)(SiCl_3)_2$	Si(1) 2.338(1) Si(2) 2.340(1)	9f

TABLE VI. Reported Fe–PPh_3 Bond Lengths (Å) [10]

Compound	Fe–P bond length	Reference
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[Si(Ph)(CH_2)_4CH_2]$	2.191(2)	10a
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]Cl \cdot 3H_2O$	2.242(1)	10b
$(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)[COCH(Me)(Et)]$	2.193(1)	10c
$[(\eta^5\text{-}1\text{-}CH_3\text{–}3C_6H_5C_5H_3)Fe(CO)(PPh_3)]I$	2.223(4)	10d
$[(\eta^5\text{-}1\text{-}CH_3\text{–}3C_6H_5C_5H_3)Fe(CO)(PPh_3)]C(O)CH_3$	2.216(3)	10d
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}C(CO_2Et){=}CMe_2)$	2.2236(8)	10e
$Fe(CO)_4PPh_3$	2.244(1)	10f
$(\eta^4\text{-}C_8H_8)Fe(CO)_2PPh_3$	2.241(2)	10g
$(\eta^4\text{-}C_6H_8)Fe(CO)_2PPh_3$	2.232(1)	10h
$(\eta^4\text{-}C_6H_7OMe)Fe(CO)_2PPh_3$	2.225(1)	10h
$Fe(NO)_2(PPh_3)Cl$	2.339(2)	10i
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)S(O)_2CH_2CH(CH_3)_2$	2.237(2)	10j

the reported Ru–PPh_3 bond lengths than does the longer distance of 2.446(2) Å. Therefore we have assigned the shorter bond as Ru–P and the longer one as Ru–Si. The Ru–Si bond length of 2.446(2) Å is quite similar to the bond lengths reported for Ru–$SiMe_3$ compounds, but it is difficult to predict how the Ru–SiR_3 bond length would be affected by changing R from Me to Ph.

In solving the structure of **1** literature data were again consulted in order to assign the Fe–PPh_3 and Fe–$SiPh_3$ distances. Table VI lists the Fe–P bond lengths for twelve compounds containing Fe–PPh_3 bonds [10]. The bond lengths vary from 2.191(2) Å to 2.339(2) Å, with the average for the twelve values being 2.234 Å [10]. As with Ru, no Fe–$SiPh_3$ compounds were found in a search of the literature, but the structures of several compounds containing Fe-SiRR′R″ groups have been determined and these are listed in Table VII [10, 11]. The nine Fe–Si bond lengths range from 2.224(9) Å to 2.456-

TABLE VII. Reported Fe–SiR$_3$ Bond Lengths (Å) [10, 11]

Compound	Fe–Si bond length	Reference
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[\overline{Si(Ph)(CH_2)CH_2}]$	2.366(2)	10a
$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2\text{-}SiPh_3$	2.346(1)	11a
cis-$Fe(CO)_4(SiMe_3)_2$	2.456(2)	11b
cyclo-$Si_5Me_9SiMe_2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$	2.350(1)	11c
$(C_3H_6Si_3Cl_5)Fe(CO)_2(\eta^5\text{-}C_5H_5)$	2.264(2)	11d
$(\eta^5\text{-}C_5H_5)Fe(CO)(H)(SiF_2CH_3)_2$	2.249(1)	11e
$(\eta^5\text{-}C_5H_5)Fe(CO)(H)(SiCl_3)_2$	2.252(3)	11e
$(\eta^5\text{-}C_5H_5)Fe(CO)(H)(SiMe_2Ph)_2$	2.336(3)	11e
$[Fe(CO)_4(SiCl_3)]^-[NEt_4]^+$	2.224(9)	11f

(2) Å, the average being 2.316 Å [10, 11]. Thus, as with Ru, the Fe–P bonds are significantly shorter than the Fe–Si bonds. Of particular interest is the compound $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[\overline{Si(Ph)(CH_2)_4\text{-}CH_2}]$ [10a] which has both an Fe–PPh$_3$ and an Fe–Si bond. In this compound, the Fe–P bond (2.191(2) Å) is considerably shorter than the Fe–Si bond (2.366(2) Å) [10a]. Based on this evidence, we have assigned the Fe–L bond lengths of **1** as Fe–P = 2.271(12) Å and Fe–Si = 2.343(12) Å.

Conclusion

X-ray structures of **1** and **2** establish the coordination geometry for a number of products from the photolysis of M(CO)$_4$(P-donor) (M = Fe, Ru) in the presence of HSiR$_3$ to be as represented in structure A. Based on the IR spectral properties of a variety of HM(SiR$_3$)(CO)$_3$(P-donor) complexes this coordination geometry appears to be commonplace [1, 2]. The *cis* arrangement of the –SiR$_3$ and the hydride is in accord with the finding that light-induced reductive elimination of HSiR$_3$ occurs from HM(SiR$_3$)(CO)$_3$(PPh$_3$) complexes [1].

Supplementary Material

Atomic coordinates, thermal parameters and structure factors for **1** and **2** have been placed on file (26 pages) with the Editor-in-Chief.

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