lower temperatures and that their exchange between the apical and equatorial sites of a trigonal bipyramid is rapid above this temperature.

The mass spectra (Table II) show a weak or nondetectable molecular ion. The fragments corresponding to the loss of F and OR are important. It is noteworthy that the loss of OR is generally extensive, while the loss of R is not detected; this is the opposite to what has been observed previously in the case of the analogous monoalkoxyfluorophenyl(or methyl)-phosphoranes, for which the breaking of the OR bond was an important feature.[4]

The infrared spectra show the expected ν_{as}(P–F) bands in the range of 920–800 cm^{-1}. These relatively low values are consistent with apical fluorines in a trigonal-bipyramidal structure[10] and comparable to those found in series of compounds R_3PF_2 having strongly electroattracting R groups.[11] The P–O–C linkage gives rise to three absorption bands near 1130, 1020, and 780 cm^{-1} [12]. The Ph–P linkage produces a characteristic vibration near 1450 cm^{-1}.[12] No vibrations assignable to ν(P=O) stretching vibrations were detected.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. $C_6H_5PF_2(OCH_2CCl_3)_2$, 43227-68-5; $C_6H_5PF_2(OCH_2CCl_2H)_2$, 63325-03-1; $C_6H_5PF_2(OCH(CH_3)(CN))_2$, 55509-54-1; $C_6H_5PF_2(OCH_2CF_3)_2$, 63325-04-2; $C_6H_5PF(OCH_2CF_3)_3$, 63325-05-3; $C_6H_5P(OCH_2CF_3)_4$, 63325-06-4; $CH_3PF_2(OCH_2CF_3)_2$, 63325-07-5; $CH_3PF(OCH_2CF_3)_3$, 63325-08-6; $CH_3P(OCH_2CF_3)_4$, 63325-09-7; $(CH_3)_3SiOCH_2CCl_2H$, 51209-79-1; $(CH_3)_3SiOCH(CH_3)(CN)$, 41309-99-3; $(CH_3)_3SiOCH_2CF_3$, 56859-55-3; $(CH_3)_3SiOCH_2CCl_3$, 41262-38-8; $C_6H_5PF_4$, 666-23-9.

References and Notes

(1) R. Schmutzler, *J. Chem. Soc.*, 4551 (1964).
(2) D. U. Robert, G. N. Flatau, A. Cambon, and J. G. Riess, *Tetrahedron*, **29**, 1877 (1973).
(3) D. U. Robert, G. N. Flatau, C. Demay, and J. G. Riess, *J. Chem. Soc., Chem. Commun.*, 1127 (1972).
(4) J. G. Riess and D. U. Robert, *Bull. Soc. Chim. Fr.*, 425 (1975).
(5) R. Schmutzler, "Halogen Chemistry", Vol. 2, V. Gutman Ed., Academic Press, New York, N.Y. 1967.
(6) E. D. Young and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **7**, 1033 (1971).
(7) I. L. Knunyants, V. V. Tynleneva, E. Y. Pervova, and R. N. Sterlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 1797 (1964).
(8) S. C. Peake, M. Fild, M. J. C. Hewson, and R. Schmutzler, *Inorg. Chem.*, **10**, 2723 (1971).
(9) L. Kolditz, K. Lehmann, W. Wiecker, and A. R. Grimmer, *Z. Anorg. Allg. Chem.*, **360**, 259 (1968).
(10) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).
(11) J. Grosse and R. Schmutzler, *Phosphorus*, **4**, 49 (1974).
(12) D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, (1969).

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Silicon–Transition Metal Chemistry. 9.[1] Synthesis, Properties, and Structure of the Rhenium Acylsilane Complex *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$

J. R. ANGLIN, H. P. CALHOUN, and W. A. G. GRAHAM*

Received November 9, 1976

AIC60815Q

The reaction of $[Re(CO)_4(diphos)]ClO_4$ with Ph_3SiLi yields the acylsilane complex *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**). A stereospecific synthesis of the ^{13}CO-enriched precursor [*fac*-$Re(CO)_3(^{13}CO)(diphos)]ClO_4$ is given. When **1** is prepared from this material, the majority of the enrichment remains mutually cis to phosphorus, although there is some scambling to positions trans to phosphorus. Treatment of **1** and the unisolated $SiMePh_2$ analogue with Et_3OPF_6 yields the cationic carbene species [*fac*-$Re(CO)_3(diphos)\{C(OEt)SiPh_3\}]^+$ and [*fac*-$Re(CO)_3(diphos)\{C(OEt)SiMePh_2\}]^+$, respectively. The thermal decarbonylation of **1** yields *mer*-$Re(CO)_3(diphos)SiPh_3$, with loss of CO mutually cis to phosphorus. The crystal and molecular structure of **1** has been determined from three-dimensional x-ray data collected by counter techniques. The material crystallizes in the space group $P2_1/n$ of the monoclinic system with $a = 20.675$ (4) Å, $b = 11.372$ (2) Å, $c = 18.271$ (2) Å, and $\beta = 108.04$ (9)°. The observed density 1.54 (1) g cm^{-3} may be compared with 1.554 g cm^{-3} calculated for $Z = 4$. The structure was refined by a full-matrix least-squares procedure to an R value of 0.0401 for 3604 observations having $I/\sigma(I) > 3.0$. The structure consists of discrete monomers of slightly distorted octahedral geometry having facial substitution. The $Ph_3SiC(O)$ ligand is bonded to rhenium through the acyl carbon and contains a planar SiC(O)Re group. This plane roughly bisects the P–Re–P angle and is such that the $SiPh_3$ group is remote from the diphos ligand. Bond distances in the acyl group are Si–C = 1.969 (10) Å, Re–C = 2.199 (9) Å, and O–C = 1.23 (1) Å. Bond angles are Re–C–Si = 127.9 (5)°, Re–C–O = 124.4 (6)°, and Si–C–O = 107.7 (6)°.

Introduction

Transition metal–acyl complexes are important organometallic intermediates that have deservedly received much study.[2,3] Related carbamoyl,[4] alkoxycarbonyl,[4] and formyl[5] complexes are also known, in which the metal-bonded carbonyl carbon is attached not to carbon but to N, O, or H, respectively. However, little attention has apparently been directed toward the study of transition metal–acyl derivatives of the heavier group 4 elements, although acylsilanes, acylgermanes, and acylstannanes are well-known.[6]

Transition metal–acyl complexes are most commonly prepared as shown in eq 1 and 2; however, it has not been

$$L_nM(CO)(R) + L' \rightarrow L_nL'M[C(O)R] \qquad (1)$$

$$L_nM(CO)_m^- + RC(O)X \rightarrow L_nM(CO)_m[C(O)R] + X^- \qquad (2)$$

feasible to extend these routes to the synthesis of acyl complexes of the heavier group 4 elements. The carbonyl insertion reaction (eq 1) has not been observed to occur in bonds between metals and heavier group 4 elements. The appropriate acyl halides and anhydrides for eq 2 are unknown for heavier group 4 elements, and our attempts to prepare such materials have proved unsuccessful.

Accordingly, we adopted the route (eq 3) where a transition

$$[L_nM(CO)_m]X + R_3M'Li \rightarrow L_nM(CO)_{m-1}[C(O)M'R_3] + LiX \qquad (3)$$

metal–carbonyl cation is treated with the appropriate lithium reagent, $R_3M'Li$. We reported recently the synthesis of *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**) by this route and noted its remarkable spectroscopic properties.[7] The cation $[Re(CO)_4(diphos)]^+$ had been chosen for this work because (i) rhenium acyls are known to have good thermal and photolytic stability,[3] (ii) the related cation [*trans*-$Re(CO)_4(PPh_3)_2]^+$ is known to undergo attack by nucleophiles at carbonyl carbon atoms,[8,9] (iii) the resulting trisubstituted octahedral complex, particularly with facial stereochemistry, would be expected to have relatively nonlabile CO ligands,[10] thereby inhibiting a decarbonylation pathway promoted by dissociation of CO cis to the acyl ligand,[11] and (iv) the steric bulk of the diphos ligand could provide stability to the resultant acyl complex by hindering subsequent attack of $R_3M'Li$ at the acyl carbon atom.[12,13] We now report the structure of **1** as determined by x-ray crystallography and discuss more fully its physical and chemical properties.

Experimental Section

General Data. Reactions were carried out under an atmosphere of prepurified nitrogen. Solvents were distilled from sodium benzophenone ketyl or P_4O_{10} and stored under nitrogen. Commercial reagents were generally used as received. Triphenylchlorosilane was found to contain large amounts of triphenylsilanol and was purified by treatment with anhydrous hydrochloric acid in ether, followed by recrystallization from hexane. Benzoyltriphenylsilane,[14] hexaphenyldisilane,[15] and *fac*-Re(CO)$_3$(diphos)Cl[16] were prepared by the reported procedures. The preparations of $Me_xPh_{3-x}SiLi$ ($x = 0$–2) were carried out from the $Me_xPh_{3-x}SiCl$ species essentially as described below for the preparation of Ph_3SiLi from hexaphenyldisilane in the synthesis of **1**; Me_3SiLi was prepared from bis(trimethylsilyl)mercury by the literature method.[17] Carbon monoxide containing 92% ^{13}CO was obtained from Monsanto Research Corp. Elemental analyses were performed by the microanalytical laboratory of this department.

Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer and calibrated using gaseous carbon monoxide in the carbonyl region and polystyrene in the acyl region. Raman spectra of rotating, solid samples were recorded on a Beckman 700 laser Raman spectrometer using a blue laser (488.0 nm). Electronic spectra were obtained with a Cary 15 spectrometer. Carbon-13 NMR spectra were recorded at 22.6 MHz and phosphorus-31 spectra at 36.4 MHz on a Bruker HFX-90-Nicolet 1085 system operating in the Fourier transform mode. Proton NMR spectra were recorded either at 60 MHz on a Varian A-56/60 spectrometer or at 90 MHz on a Perkin-Elmer R32 spectrometer. Mass spectra were obtained with AEI MS-2 and MS-12 spectrometers.

Preparation of [*fac*-Re(CO)$_3$(^{13}CO)(diphos)]ClO$_4$. A thick-walled tube with a Teflon stopcock was charged successively with *fac*-Re(CO)$_3$(diphos)Cl (2.50 g, 3.55 mmol), anhydrous $AlCl_3$ (0.95 g, 7.1 mmol), and benzene (40 mL). After freezing of the mixture, the nitrogen atmosphere was removed in vacuo, and an excess of enriched carbon monoxide (92% ^{13}CO) was admitted such that the pressure was ca. 2 atm. The mixture was then warmed to 60–65 °C with intermittent shaking. After ca. 20 min, a yellow-brown oil separated, and after 60 min the tube was cooled and the solvent removed in vacuo. The residue was then extracted in the air with 50% aqueous methanol and 70% perchloric acid (3 mL) was added to the filtered extracts causing a white solid to precipitate. This was collected by filtration, rinsed well with water and ether, and recrystallized from 1:2 methanol–ether to yield the pure product (2.4 g, 85%). Infrared spectrum (CH_2Cl_2): 2110 (vw), 2098 (s), 2028 (s), 1998 (s, sh), 1989 (s) cm^{-1}.

[Re(CO)$_4$(diphos)]ClO$_4$. This compound was prepared as above, except that the reaction was carried out in standard glassware under a slow stream of unenriched carbon monoxide and afforded the pure product in 85% yield. Infrared spectrum (CH_2Cl_2): 2111 (s), 2028 (s, sh), 2018 (s), 2000 (s) cm^{-1}. *The compound explodes at 200 °C (cf. ref 18) and was treated with caution.*

***fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$] (1).** A mixture of hexaphenyldisilane (0.22 g, 0.42 mmol) and excess lithium (3.2 mm wire, 1% sodium, Ventron) was vigorously stirred overnight in 8 mL of THF to yield a brown solution. This solution was filtered, cooled to 0 °C, and slowly added to a cold (0 °C) slurry of [Re(CO)$_4$(diphos)]ClO$_4$ (0.50 g, 0.63 mmol) in 5 mL of THF during 30 min. When all of the rhenium salt had dissolved, the addition was terminated and the red-purple solution was stirred for 60 min at 0 °C. The solution was evaporated in vacuo to a small volume, treated with 10 mL of acetone, and stored 24 h at 0 °C. The mother liquor was decanted from the purple solid, which was then rinsed with several portions of acetone and toluene and dried in vacuo to give 289 mg (48%) of crude product. As required, this was recrystallized by very slow evaporation of a 3:1 methylene chloride–acetone solution: mp 182–184 °C dec; IR (CH_2Cl_2) 2007 (s), 1924 (s), 1916 (s, sh), 1490 cm^{-1} (acyl C=O; this very weak band is located among several intense aromatic absorptions and could not be assigned routinely, as discussed below); mass spectrum m/e 928 ($M^+ - 28$).

Anal. Calcd for $C_{48}H_{39}O_4P_2ReSi$: C, 60.30; H, 4.11; O, 6.69. Found: C, 60.00; H, 4.23; O, 6.51.

[*fac*-Re(CO)$_3$(diphos){C(OEt)SiPh$_3$}]PF$_6$ (2). A solution of **1** (125 mg, 0.131 mmol) in 8 mL of methylene chloride was treated with Et_3OPF_6 (35.7 mg, 0.144 mmol). During 60 min, the solution changed from purple to yellow-orange. After 90 min, the solution was evaporated in vacuo to a small volume and treated with toluene (3 mL), and the volume was reduced to incipient crystallization. The yellow-orange crystals were recrystallized from CH_2Cl_2–toluene and dried overnight at 80 °C in vacuo: yield 71 mg (48%); mp 158–159 °C dec; IR (CH_2Cl_2) 2041 (s), 1972 (s), 1958 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.71 (t, 3, $J = 6.8$ Hz, CH_2CH_3), 3.68 ppm (quartet, 2, $J = 6.8$ Hz, CH_2CH_3).

Anal. Calcd for $C_{50}H_{44}F_6O_4P_3ReSi$: C, 53.14; H, 3.92. Found: C, 52.70; H, 3.84.

[*fac*-Re(CO)$_3$(diphos){C(OEt)SiMePh$_2$}]BPh$_4$ (3). A THF solution of $MePh_2SiCl$ was stirred vigorously overnight with excess lithium wire with formation of a deep red-brown color. This was added during 30 min to a −15 °C slurry of [Re(CO)$_4$(diphos)]ClO$_4$ (0.40 g, 0.50 mmol) in THF (5 mL) until all of the cation had dissolved. After stirring of the mixture at −10 °C for 60 min, the solvent was removed to yield a red-purple oil that could not be induced to crystallize: IR (CH_2Cl_2) 2005.5 (s), 1921 (s), ca. 1911 (s, sh) cm^{-1}. The oil was taken up in CH_2Cl_2 (8 mL) and treated with Et_3OPF_6 (0.193 g, 0.78 mmol). After stirring of the mixture for 60 min at 25 °C, a yellow-orange color formed, and the solution was evaporated in vacuo to ca. 3 mL. This was then applied to a very short column (~5 cm) of Florisil and rapidly eluted with CH_2Cl_2, although considerable material remained on the Florisil. The yellow-orange band was reduced to ~10 mL and treated with $NaBPh_4$ (0.173 g, 0.51 mmol) in 1:1 methanol–H_2O. The organic phase was separated, evaporated, and dried briefly in vacuo. The residue was dissolved in a minimum of CH_2Cl_2, treated with toluene, and reduced in volume to incipient crystallization. The yellow-orange crystals were rinsed with toluene and heptane before drying overnight at 80 °C in vacuo: yield 74 mg (12%); mp 90–97 °C; IR (CH_2Cl_2) 2039.5 (s), 1971.5 (s), 1951 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.35 (t, 3, $J = 7.0$ Hz, CH_2CH_3), 1.33 (s, 3, $SiCH_3$), 3.54 ppm (quartet, 2, $J = 7.0$ Hz, CH_2CH_3).

Anal. Calcd for $C_{69}H_{62}BO_4P_2ReSi$: C, 66.71; H, 5.03. Found: C, 66.15; H, 5.21.

***mer*-Re(CO)$_3$(diphos)SiPh$_3$.** An evacuated flask containing **1** (0.50 g) was immersed in an oil bath maintained at 200–205 °C. Within ca. 10 min, the purple solid had melted with gas evolution and decolorization to yield a pale yellow oil. After cooling to room temperature, the oil was dissolved in CH_2Cl_2 (10 mL), filtered, treated with 4 mL of heptane, and allowed to evaporate slowly. The product was crystallized a second time to yield 0.33 g (68%) of colorless crystals: mp 214.5–224 °C; IR (CH_2Cl_2) 2019.5 (w), 1927.5 (s) cm^{-1}; mass spectrum m/e 928 (M^+).

Anal. Calcd for $C_{47}H_{39}O_3P_2ReSi$: C, 60.83; H, 4.24. Found: C, 60.53; H, 4.29.

Collection and Reduction of X-Ray Data. Purple plates of **1** were grown from a dichloromethane–acetone solution of the complex. Preliminary Weissenberg and precession photographs showed the systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with the monoclinic space group $P2_1/n$ (C_{2h}^5). The unit cell dimensions $a = 20.675$ (4) Å, $b = 11.372$ (2) Å, $c = 18.271$ (2) Å, and $\beta = 108.04$ (9)° were obtained by a least-squares fit of the 2θ values of 12 general high-angle reflections accurately measured on a Picker FACS-I diffractometer using Mo Kα_1 (λ 0.709 26 Å) radiation at 23 °C. The density of the crystal was determined to be 1.54 (1) g cm^{-3} by flotation in a carbon tetrachloride–*n*-heptane mixture, and this value is in good agreement with the calculated value of 1.554 g cm^{-3} based on four molecules in the unit cell. The dimensions of the crystal used for intensity measurements were 0.126 × 0.076 × 0.376 mm, corresponding to separations between the faces (101) and ($\bar{1}0\bar{1}$), ($10\bar{1}$) and ($\bar{1}01$), and (010) and ($0\bar{1}0$), respectively. Intensity data were measured on a Picker FACS-I automatic four-circle diffractometer equipped with a graphite monochromator (002 reflection) using Mo Kα radiation (λ 0.710 69 Å). All reflections with $5° < 2\theta < 45°$ were measured at a scan speed of 1° min^{-1} using

Table I. Positional and Anisotropic Thermal Parameters[a] Excluding Those for Phenyl Carbon Atoms

Atom	x	y	z
Re	0.27502 (2)	0.16932 (3)	0.06427 (2)
P(1)	0.1806 (1)	0.3069 (2)	0.0153 (1)
P(2)	0.3248 (1)	0.2879 (2)	−0.0165 (1)
Si	0.2240 (1)	−0.1099 (2)	−0.0474 (1)
O(1)	0.2123 (3)	0.1026 (6)	−0.1058 (4)
O(2)	0.1880 (4)	0.0349 (6)	0.1460 (4)
O(3)	0.3399 (4)	0.3269 (8)	0.2066 (4)
O(4)	0.4014 (4)	0.0116 (7)	0.1229 (4)
C(1)	0.2330 (4)	0.0624 (8)	−0.0400 (5)
C(2)	0.2209 (5)	0.0830 (9)	0.1155 (5)
C(3)	0.3150 (5)	0.2694 (10)	0.1531 (6)
C(4)	0.3541 (5)	0.0666 (9)	0.0981 (5)
C(5)	0.2090 (5)	0.4212 (9)	−0.0394 (5)
C(6)	0.2553 (4)	0.3698 (8)	−0.0828 (5)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	320 (2)	340 (2)	310 (2)	48 (2)	101 (1)	39 (2)
P(1)	355 (13)	366 (18)	347 (13)	64 (12)	103 (11)	26 (12)
P(2)	379 (14)	398 (17)	399 (14)	32 (12)	152 (12)	44 (12)
Si	466 (16)	381 (16)	430 (18)	19 (14)	171 (14)	7 (13)
O(1)	725 (49)	374 (43)	525 (46)	−45 (38)	196 (38)	−13 (38)
O(2)	904 (56)	545 (52)	697 (51)	−103 (44)	489 (45)	67 (42)
O(3)	709 (51)	975 (64)	548 (47)	−210 (52)	77 (40)	−299 (52)
O(4)	566 (47)	881 (63)	845 (56)	403 (48)	254 (42)	383 (50)
C(1)	314 (54)	367 (62)	499 (63)	100 (46)	197 (51)	128 (49)
C(2)	534 (63)	377 (67)	315 (56)	110 (52)	130 (49)	8 (49)
C(3)	394 (60)	562 (72)	454 (65)	75 (54)	126 (52)	73 (59)
C(4)	442 (62)	512 (71)	433 (60)	63 (56)	158 (51)	125 (53)
C(5)	470 (62)	411 (67)	529 (64)	88 (51)	171 (50)	144 (53)
C(6)	423 (54)	352 (63)	400 (54)	24 (46)	159 (46)	93 (45)

[a] In this and all other tables the estimated standard deviation in the least significant figure(s) is given in parentheses. The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The units are Å^2 × 10^4.

the θ–2θ scan method with a scan width of 2° modified for α_1–α_2 dispersion. Background counts were taken for 40 s at both ends of the scan limits. Three standard reflections were measured every 100 reflections, and all three decreased linearly during the data collection by ~12%. The data were scaled to the same relative scale using the intensities of the standard reflections, corrected for Lorentz and polarization effects, and reduced to structure factor amplitudes with standard deviations estimated by the procedure of Doedens and Ibers[19a] using a p factor of 0.03. Of the 5719 independent reflections measured, 3604 were considered to be significantly above background using the criterion $I/\sigma(I) > 3.0$ where $\sigma(I)$ was estimated from counting statistics.

Structure Solution and Refinement. Data with $5° < 2\theta < 35°$ were used for solving the structure and for initial refinement. The rhenium atom was located from a sharpened Patterson map, and a structure factor calculation gave R = 38%. An electron density difference map gave the positions of the phosphorus and silicon atoms along with the positions of 3 oxygen and 13 carbon atoms, reducing R to 21%. A second electron density difference map gave the positions of the remaining nonhydrogen atoms.

An absorption correction (method of Gaussian integration[19b]) was applied to all of the data ($5° < 2\theta < 45°$) using a linear absorption coefficient of 32.94 cm^{-1}. The transmission factors ranged from 0.804 to 0.888.

Full-matrix least-squares refinement with the phenyl rings treated as rigid bodies (C–C = 1.397 Å) using anisotropic thermal parameters for Re, P(1), P(2), and Si and isotropic thermal parameters for O(1)–O(4) and C(1)–C(6) reduced R to 0.047. A difference map showed peaks of up to 1.0 e Å^{-3} which were in reasonable positions for most of the hydrogen atoms, along with some spurious peaks of up to 1.3 e Å^{-3} close to the phenyl rings. The hydrogen atoms were placed in calculated positions (C–H = 1.02 Å) and were given isotropic thermal parameters equal to those of the carbon atoms to which they are bonded. In subsequent cycles of refinement the hydrogen atom parameters were included in structure factor calculations but were not refined. Full-matrix least-squares refinement with all nonhydrogen atoms, excluding phenyl carbon atoms given anisotropic thermal parameters, phenyl rings treated as rigid bodies, and hydrogen atoms in fixed positions, converged at R = 0.0401 and R_w = 0.0405. On the final cycle of refinement no parameter shift was greater than 0.03 times its standard error. The standard deviation of an observation of unit weight based on 211 variables and 3604 observations was 1.53 electrons. The largest peaks on the final difference map were associated with the phenyl rings (up to 1.1 e Å^{-3}).

The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(|F_o|)$. R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The atomic scattering factors used for Re, P, Si, O, and C were taken from ref 20 and the values used for hydrogen were taken from ref 21. Anomalous dispersion terms from ref 22 for Re, P, and Si were applied. Major computer programs used were a local modification of SFLS5 by C. T. Prewitt, FORDAP by A. Zalkin, DATAP by P. Coppens, and ORTEP by C. K. Johnson.

Final atomic positional and thermal parameters are given in Table I. Rigid-body parameters for the seven phenyl rings and derived positional and isotropic thermal parameters for the phenyl carbon atoms are given in Table II.[23] Calculated hydrogen atom positions are given in Table III.[23] Calculated and observed structure factors ($10|F_o|$ and $10|F_c|$ in electrons) are given in Table IV.[23]

Results and Discussion

Preparation and Stability of *fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$] and Related Species. Purple crystals of the acylsilane complex **1** were isolated from the reaction of Ph$_3$SiLi with [Re(CO)$_4$(diphos)]ClO$_4$ in THF (eq 4). Similar reactions

$$[\mathrm{Re(CO)_4(diphos)}]^+ \xrightarrow{\mathrm{Ph_3SiLi}} \underset{\mathbf{1}}{fac\text{-}\mathrm{Re(CO)_3(diphos)[C(O)SiPh_3]}} \qquad (4)$$

of [Re(CO)$_4$(diphos)]ClO$_4$ with Me$_x$Ph$_{3-x}$SiLi (x = 1–3) have yielded products that have proven more difficult to isolate and characterize; although infrared spectra are consistent with the formation of acylsilane complexes in these reactions, strong supporting evidence is only present for the reaction with MePh$_2$SiLi as described below.

The purified solid **1** appears to be stable indefinitely in the air; however solutions of **1** decompose in the presence of air to yield [Re(CO)$_4$(diphos)]$^+$. The half-life varies from minutes to days and appears to be sensitive to the method of preparation of the Ph$_3$SiLi used in its synthesis. Thus, when hexaphenyldisilane rather than Ph$_3$SiCl was used as the

Table V. Phosphorus-31 and Carbon-13 NMR Data[a]

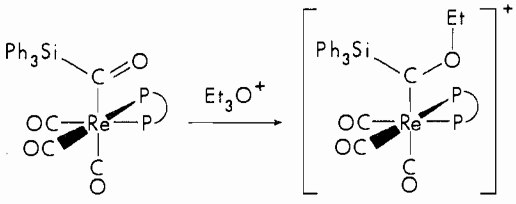
Compd	^{31}P NMR	^{13}C NMR: CO trans to P (J_{P-C})	^{13}C NMR: CO mutually cis to P (J_{P-C})	^{13}C NMR: Other (J_{P-C}) assignment
[Re(CO)$_4$(diphos)]ClO$_4$[b]	−27.8	184.1 (41, 8)	182.9 (8)	
fac-Re(CO)$_3$(diphos)[C(O)SiPh$_3$]	−35.4	196.1 (50, 9)	194.6 (6)	340.1 (10) acyl C
[*fac*-Re(CO)$_3$(diphos){C(OEt)SiPh$_3$}]PF$_6$	−33.4	192.5 (50, 9)	191.9 (7)	393.6 (9) carbenoid C
mer-Re(CO)$_3$(diphos)SiPh$_3$	−30.3[c] −39.9[c]	198.3[d]	198.9[d]	

[a] All spectra were run at ambient temperature unless otherwise noted, using CD$_2$Cl$_2$ as solvent and lock and proton broad-band decoupling. Phosphorus-31 NMR shifts are given relative to 85% H$_3$PO$_4$ with negative values being at lower field. Spectra were measured relative to P$_4$O$_6$ external reference and converted by taking 85% H$_3$PO$_4$ to be 112.5 ppm upfield from P$_4$O$_6$. Carbon-13 NMR shifts are quoted relative to Me$_4$Si following conversion, taking CD$_2$Cl$_2$ as 53.6 ppm downfield from Me$_4$Si and applying corrections for temperature as necessary. Positive shifts are downfield from Me$_4$Si. Coupling constants are quoted in Hz. [b] Carbon-13 NMR run at −60 °C. [c] J_{P-P} was not observed (≲2 Hz). [d] Coupling constants not resolved.

precursor for Ph$_3$SiLi, the resulting **1** showed improved air stability in CH$_2$Cl$_2$–acetone solution. However, the addition of LiBr or LiCl to these more stable solutions of **1** caused faster decolorization and implies that traces of LiCl may have been present in preparations of **1** utilizing Ph$_3$SiCl and accelerated the decomposition. Under nitrogen, solutions of **1** show no apparent sensitivity to normal room illumination. By contrast, acylsilanes[24] and particularly disilyl ketones[25] are known to be light sensitive in solution.

The use of silyl anions with methyl substitution in this reaction leads to products with different properties as indicated by preliminary results from the reaction with Me$_3$SiLi. The primary product is a colorless species with IR (THF) bands at 2020 (s), 1938 (s), and 1922 (s) cm^{-1}. This material readily decomposes to re-form [Re(CO)$_4$(diphos)]$^+$; however, an equilibrium between product and starting material is also apparent, since the relative proportions of the two species as observed by infrared spectroscopy depend upon the solvent. Thus, a THF spectrum of a portion of the product indicated an ca. 70:30 ratio of product to starting material. After removal of the solvent and dissolution of the solid in CH$_2$Cl$_2$, only starting material was observed; however, removal of the CH$_2$Cl$_2$ followed by redissolution in THF caused the reappearance of the original spectrum. Spectra of samples in acetone or hexamethylphosphoramide solution indicated intermediate proportions of product. Although this product has not been further characterized, the evidence would favor its identification as an acylsilane complex, particularly since equilibria have previously been studied in the corresponding reactions of amines with [*trans*-M(CO)$_4$L$_2$]$^+$ (M = Mn, Re; L = phosphine ligand).[8]

Alkylation of Acylsilane Complexes. The treatment of **1** with Et$_3$OPF$_6$ in CH$_2$Cl$_2$ yields a yellow-orange product formulated as the cationic carbene complex [*fac*-Re(CO)$_3$(diphos){C(OEt)SiPh$_3$}]PF$_6$ (**2**) (eq 5). The related species [*fac*-Re(CO)$_3$(diphos){C(OEt)SiMePh$_2$}]BPh$_4$ (**3**) was obtained from a similar alkylation of the unisolated red-violet product from the reaction of MePh$_2$SiLi with [Re(CO)$_4$(diphos)]ClO$_4$, followed by metathesis with NaBPh$_4$. The complexes **2** and **3** are air-stable solids, although solutions, particularly of compound **3**, decompose gradually upon exposure to the air. These cationic species are among the first examples of complexes with carbenoid ligands containing a silicon heteroatom.[26]



1 **2** (5)

Thermal Decarbonylation of 1. The acylsilane complex **1** decarbonylates at temperatures above the melting point (182–184 °C) with formation of *mer*-Re(CO)$_3$(diphos)SiPh$_3$. The stereochemistry of this complex was most readily assigned as meridional on the basis of the ^{31}P NMR spectrum (Table V). Thus, two signals were observed for this complex, whereas one signal was observed in the spectra of the facially substituted complexes **1** and **2**. It was of interest to determine whether this decarbonylation proceeded by a mechanism similar to that for the decarbonylation of Mn(CO)$_5$[C(O)Me], namely, loss of CO cis to the acyl accompanied by methyl migration. The geometry of *mer*-Re(CO)$_3$(diphos)SiPh$_3$ suggests a possible migration of the SiPh$_3$ moiety to a position cis to its original coordination site; however, preliminary results using stereospecifically enriched samples indicate that the CO is *not* released from a position cis to the acylsilane ligand. We are continuing our studies of the decarbonylation reaction and investigating the possible role of steric effects. Attempts to carbonylate CH$_2$Cl$_2$ solutions of *mer*-Re(CO)$_3$(diphos)SiPh$_3$ at pressures up to 300 atm have yielded no evidence of acylsilane species.

Preparations of Enriched [Re(CO)$_4$(diphos)]ClO$_4$. Samples of **1** with ^{13}CO enrichment were required in order to obtain infrared and carbon-13 NMR data for its characterization. In one method, Re(CO)$_5$Cl was enriched via an exchange process whereby a CH$_2$Cl$_2$ solution of Re(CO)$_5$Cl was subjected to ultraviolet irradiation in the presence of ^{13}CO. When this process is carried to equilibrium, starting material is obtained with a statistical distribution of ^{13}CO in the cis and trans positions. The derived *fac*-Re(CO)$_3$(diphos)Cl has an equal degree of enrichment in all carbonyls. In a second method, ^{13}CO could be incorporated as shown in eq 6. In agreement with previous work on rhenium,[8] we found the carbonylation did not require elevated CO pressures and proceeded smoothly in benzene at 60 °C. From ^{13}C NMR results as shown in trace A of Figure 1, it is apparent that this procedure yields a product in which the ^{13}CO enrichment occurs *exclusively* (>95%) in an axial position (mutually cis to phosphorus). Infrared spectral results are consistent with this conclusion.[27] Possible coincidence of the equatorial and axial carbonyl chemical shifts is ruled out by inspection of the ^{13}C NMR spectrum of the product isolated from the reaction of statistically enriched *fac*-Re(CO)$_3$(diphos)Cl with AlCl$_3$ and unenriched carbon monoxide having 1% ^{13}CO (Figure 1, trace C). The ca. 2:1 ratio of equatorial to axial carbonyl areas is consistent with selective axial incorporation of 1% ^{13}CO.

$$fac\text{-Re(CO)}_3\text{(diphos)Cl} \xrightarrow[\text{2. HClO}_4]{\text{1. AlCl}_3/^{13}\text{CO}} [fac\text{-Re(CO)}_3(^{13}\text{CO})\text{(diphos)}]\text{ClO}_4 \qquad (6)$$

Two independent reports have appeared during this study that discuss the stereospecificity of reactions in which halide is abstracted from a six-coordinate complex with AlCl$_3$ or

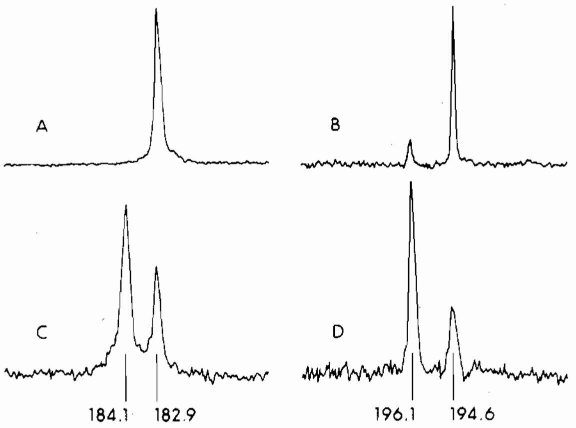


Figure 1. Carbon-13 NMR spectra of the carbonyl carbon atoms of $[Re(CO)_4(diphos)]ClO_4$ and *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**) under ^1H and ^{31}P decoupling. In each trace, the peak on the left corresponds to the equatorial carbonyl carbon atoms (trans to phosphorus) and the peak on the right corresponds to the axial carbonyl carbon atoms: (A) stereospecifically axially ^{13}CO-enriched $[Re(CO)_4(diphos)]ClO_4$; (B) *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ as prepared from A; (C) sample of $[Re(CO)_4(diphos)]ClO_4$ from the reaction of statistically ^{13}CO-enriched *fac*-$Re(CO)_3(diphos)Cl$ with natural abundance ^{13}CO and $AlCl_3$; (D) *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ as prepared from sample C. No $J(^{13}C–^{13}C)$ coupling was observed. Spectra were run in CD_2Cl_2 and referenced to Me_4Si as described in Table V.

Ag(I) in the presence of ligand.[28,29] On the basis of product stereochemistry, the very similar reactions of $Mn(CO)_{5-x}(CNMe)_xBr$ with $AlCl_3/CO$ in benzene were suggested[28] to occur such that the incoming ligand stereospecifically entered the coordination site initially occupied by the halide. Our results are consistent with this suggestion since an axial position is occupied by the entering ^{13}CO, but we cannot rule out the possibilities of ^{13}CO incorporation trans to the original chloride coordination site or the intermediacy of species that effectively average the two axial positions. Intuitively, however, we favor a mechanism that involves $AlCl_3$-assisted[30] displacement of the chloride by ^{13}CO without formation of a labile, coordinatively unsaturated intermediate and thus yields a product with ^{13}CO in the original coordination site of the chloride. The reactions with Ag(I) in THF are reported to give the same stereochemical result;[28,29] however the more polar solvent is likely to alter the detailed mechanism by facilitating the dissociative process.

The preparation of **1** from [*fac*-$Re(CO)_3(^{13}CO)(diphos)]ClO_4$ has in all cases been accompanied by some scrambling of the ^{13}CO to the equatorial positions as shown by a comparison of traces A and B in Figure 1. The degree of scrambling has varied widely from one preparation to another. When the starting material is the cation with an ca. 2:1 area ratio of equatorial to axial signals (trace C), the resulting **1** is expected to have an ca. 4:1 ratio of these two signals (trace D). However, the extent of scrambling cannot be measured as accurately when the starting cation is enriched in both equatorial and axial positions. The cause of the scrambling is not presently understood, but it apparently occurs during the synthesis since the ^{13}C NMR spectrum of the sealed sample corresponding to trace B showed no additional scrambling after storage for 6 months. The subsequent preparation of **2** caused no apparent increase in the degree of scrambling.

Spectroscopic Properties. In Table V are presented a series of ^{31}P and ^{13}C NMR data. The ^{13}C NMR data were obtained using ^{13}CO-enriched compounds, and chemical shifts for the metal carbonyl carbons are similar to those observed previously in rhenium carbonyl derivatives.[31] The other ^{13}C chemical shifts are discussed below.

Table VI. Spectral Properties of *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**) and Related Acyls

	ν(acyl CO),[a] cm^{-1}	λ_{max},[b] nm (ϵ)	^{13}C NMR[c] ($\delta(Me_4Si)$)
1	1490	557 (3.9×10^2)[d]	340.1
$Ph_3SiC(O)SiPh_3$	1558[e]	554[e,f]	
$Ph_3SiC(O)Ph$	1614	424 (2.9×10^2)	230.7
$PhC(O)Ph$	1654	345 (1.3×10^2)	196.4[g]

[a] KBr pellet. [b] CCl_4 solvent except as noted; most intense low-energy absorption. [c] CD_2Cl_2 except as noted. [d] CH_2Cl_2 solvent. [e] Reference 25. [f] Light sensitive; ϵ could not be accurately determined. [g] $CDCl_3$ solvent; ref 40.

The successive replacement of hydrocarbon substituents of a carbonyl group by silyl substituents leads to interesting trends in the spectroscopic properties of the carbonyl group (Table VI). The acyl carbonyl stretching frequency is lowered; the most intense low-energy electronic transition is shifted to lower energy; and the ^{13}C NMR chemical shift of the carbonyl carbon atom moves to lower field. No data are available, however, for the ^{13}C NMR of disilyl ketones. Similarly, transition metal acyls exhibit reduced carbonyl stretching frequencies and lower field ^{13}C NMR shifts compared to ketones (vide infra), while the effect upon the $n \rightarrow \pi^*$ electronic absorption has not been documented to our knowledge. The combination of a silyl and a transition metal substituent in **1** leads to very pronounced shifts in these parameters as shown in Table VI.

The decrease of the carbonyl stretching frequency in the series benzophenone, benzoyltriphenylsilane, and bis(triphenylsilyl) ketone is accompanied qualitatively by a decrease in band intensity. The carbonyl stretching frequency of **1** at 1490 cm^{-1} is very weak and was assigned only following comparison of the spectra (KBr disk) of a series of ^{13}C-enriched samples (Figure 2), which showed a very weak isotopically shifted band at 1453 cm^{-1}. The assignment was confirmed by a similar comparison of Raman spectra, in which the intensity is strong. The carbonyl stretching frequency of 1490 cm^{-1} is to our knowledge the lowest reported value for a formally neutral carbonyl group, which, as indicated below, has no additional bonding interactions. This value is considerably lower than values for rhenium–acyl species (1562–1645 cm^{-1})[32] or bis(triphenylsilyl) ketone (1558 cm^{-1}).[25] Values in this range have been reported, however, for transition metal acylate complexes[33] and for carbonyl groups in which the oxygen atom is coordinated to a metal.[34]

The successive substitution of silyl moieties into the carbonyl group of ketones (Table VI) or into certain other heteroatom-containing chromophores[35] is accompanied by the appearance of higher wavelength electronic absorptions. These bands have been assigned to $n \rightarrow \pi^*$ transitions, which in acylsilanes are red-shifted with respect to the corresponding ketones, but they have more recently been reassigned as $\sigma \rightarrow \pi^*$.[36] The band at 557 nm (ϵ 3.9×10^2) in **1** is similar in position to the most intense low-energy electronic absorption of bis(triphenylsilyl) ketone (554 nm), which is among the most red-shifted of the disilyl ketones.[25] The absorption in **1** is reasonably assigned to the metal–acylsilane chromophore,[37] since simple rhenium–acyl species are typically colorless to yellow,[32] and the derivative *mer*-$Re(CO)_3(diphos)SiPh_3$ is colorless.

A downfield shift of the ^{13}C NMR chemical shift of the acyl carbon atom occurs upon substitution of a silyl moiety into the carbonyl group. Thus, the chemical shift of the carbonyl carbon of benzophenone (196.4 ppm) is shifted to 230.7 ppm in benzoyltriphenylsilane. Some recently reported data for acetylsilanes (δ 251.5–254.1 ppm[38]) indicate a similar shift relative to acetone (δ 206.0 ppm). A similar effect obtains

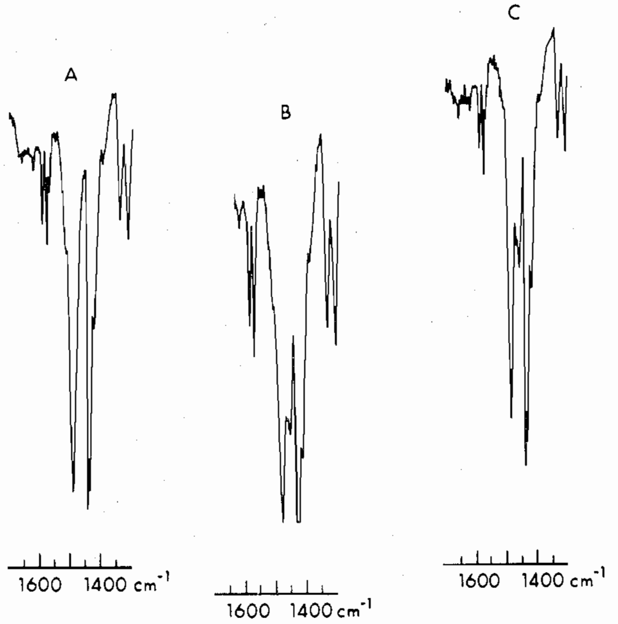


Figure 2. Acyl carbonyl stretching region of *fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$]: (A) natural abundance; (B) ca. 45% ^{13}C-enriched in acyl carbonyl; (C) ca. 70% ^{13}C enriched in acyl carbonyl. KBr-disk spectra are shown.

upon the substitution of rhenium into benzophenone, since the corresponding chemical shift for Re(CO)$_5$[C(O)Ph] is 245.4 ppm.[31] The combination of these substituents in **1** and in *fac*-Re(CO)$_3$(diphos)[C(O)SiMePh$_2$] results in the values 340.1 and 342.9 ppm,[39] respectively.

The carbenoid carbons of **2** and **3** have ^{13}C NMR chemical shifts of 393.6 and 393.7 ppm, respectively (Table V), and are presently the most deshielded values observed for rhenium organometallic species. By comparison, the corresponding value for *cis*-Me$_3$GeRe(CO)$_4$[C(OEt)Me] is 314.8 ppm.[40] It is apparent that the substitution of a silyl moiety for an alkyl group in the carbenoid ligand has resulted in a large downfield shift of the chemical shift of the carbon atom, although an assessment of this effect for precisely analogous carbon and silicon derivatives is not possible with available data. However, a comparison of the ^{13}C NMR chemical shifts of Cr(CO)$_5$[C(OEt)SiPh$_3$], which was reported during this work[26] (δ 431.1), and Cr(CO)$_5$[C(OEt)Me] (δ 357.3)[41] indicates a considerable downfield shift (73.8 ppm).

Description of the Structure. The crystal structure analysis of **1** confirms the presence of the acylsilane moiety Ph$_3$SiC(O) bonded to rhenium and verifies the facially substituted octahedral stereochemistry. A view of the molecule is shown in Figure 3, and Figure 4 depicts the packing of the molecules in the unit cell. Bond lengths, selected nonbonded contacts, and bond angles are given in Table VII. Intermolecular contacts are of the normal van der Waals type, and the closest contacts are listed in Table VII.

Although the geometry of **1** is essentially octahedral, substantial deviations from 90 and 180° bond angles occur. The P–Re–P angle (bite angle) of the diphos ligand is 82.20 (8)°, whereas the angle between the equatorial carbonyl groups C(2)–Re–C(4) is 95.5 (4)°. The angles P(1)–Re–C(4) and P(2)–Re–C(2) are 175.3 (3) and 170.2 (3)°, respectively. Other angles indicate the effects of nonbonded intra- and intermolecular steric interactions: P(2)–Re–C(1), 84.8 (2)°; C(1)–Re–C(3), 176.6 (3)°; C(2)–Re–C(3), 93.1 (4)°.

The ReC(O)Si group is planar as indicated by the 360.0° sum of the angles Re–C(1)–Si, Re–C(1)–O(1), and Si–C(1)–O(1), which are 127.9 (5), 124.4 (6), and 107.7 (6)°, respectively. These atoms show very little displacement from their weighted least-squares plane (Table VIII). There is, however, considerable deviation from the 120° bond angles expected for regular trigonal-planar geometry.

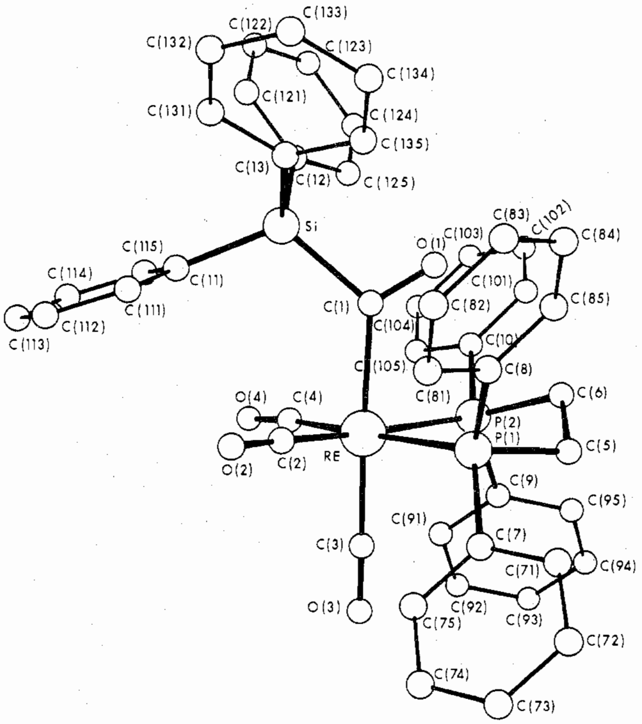


Figure 3. Molecular structure of *fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$] (**1**).

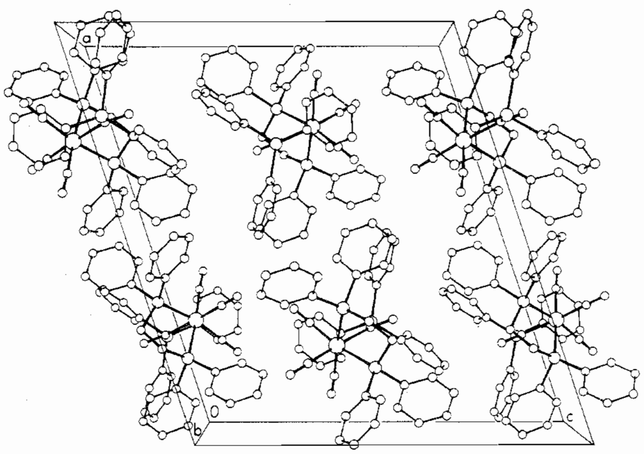


Figure 4. View of the unit cell down *b*.

The orientation of the Ph$_3$SiC(O) group as shown in Figure 5 minimizes intramolecular steric repulsions. Upon projection of this group onto the equatorial plane, O(1) lies near the bisector of the P–Re–P angle and Si lies near the bisector of the C(2)–Re–C(4) angle. The Ph$_3$SiC(O) group is displaced slightly toward P(2). This is shown by the smaller angle P(2)–Re–C(1), 84.8 (2)°, relative to P(1)–Re–C(1), 88.9 (3)°, and by the shorter nonbonded distances P(2)···C(1) and P(2)···O(1) of 3.14 and 3.19 Å relative to P(1)···C(1) and P(1)···O(1), which are 3.26 and 3.41 Å, respectively.

The Si–C(acyl) bond length of 1.969 (10) Å is 0.070 Å (7σ) longer than the average of the Si–C(Ph) bond lengths, 1.899 (11) Å. It is also significantly longer than the corresponding Si–C bond lengths of 1.926 (14) Å in Ph$_3$SiC(O)Me[42] and 1.93 (1) Å in Ph$_3$SiCH(OH)Ph.[43] Thus, a reduced Si–C(acyl) bond order in **1** seems probable.[44] The Si–C(Ph) average bond length of 1.899 (11) Å is similar to that for (η-C$_5$H$_5$)$_2$ZrCl(SiPh$_3$), 1.913 (4) Å,[45] but greater than those for

Table VII. Selected Distances (Å) and Angles (deg) in *fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$] (1)

Bond Distances

Re–C(1)	2.199 (9)	P(1)–C(5)	1.843 (10)
Re–C(2)	1.934 (9)	P(1)–C(7)	1.819 (7)
Re–C(3)	1.946 (10)	P(1)–C(8)	1.822 (8)
Re–C(4)	1.948 (10)	P(2)–C(6)	1.822 (9)
Re–P(1)	2.446 (2)	P(2)–C(9)	1.834 (7)
Re–P(2)	2.449 (2)	P(2)–C(10)	1.828 (12)
Si–C(1)	1.969 (10)	C(1)–O(1)	1.232 (12)
Si–C(11)	1.886 (7)	C(2)–O(2)	1.143 (12)
Si–C(12)	1.903 (8)	C(3)–O(3)	1.155 (13)
Si–C(13)	1.907 (6)	C(4)–O(4)	1.130 (12)
C(5)–C(6)	1.535 (13)		

Nonbonded Intramolecular Distances

Re···O(1)	3.069	Si···O(1)	2.62
Re···O(2)	3.077	O(1)···H(61)	2.48
Re···O(3)	3.100	O(1)···H(135)	2.42
P(1)···O(1)	3.41	C(1)···C(2)	2.94
P(2)···O(1)	3.19	C(1)···C(4)	2.95
Re···O(4)	3.075	C(2)···C(3)	2.82
P(1)···C(6)	2.80	C(2)···C(4)	2.87
P(1)···C(1)	3.26	C(3)···C(4)	2.74
P(1)···C(2)	3.10	C(3)···C(91)	3.19
P(1)···C(3)	3.15	C(3)···H(75)	2.53
P(1)···P(2)	3.218	C(5)···C(7)	2.88
P(2)···C(1)	3.14	C(5)···C(8)	2.94
P(2)···C(3)	3.18	H(52)···H(85)	2.24
P(2)···C(4)	3.21	H(61)···H(101)	2.25
P(2)···C(5)	2.75	H(62)···H(95)	1.97
Si···Re	3.745		

Angles

P(1)–Re–P(2)	82.20 (8)	Re–C(1)–O(1)	124.4 (6)
P(1)–Re–C(1)	88.9 (3)	Si–C(1)–O(1)	107.7 (6)
P(1)–Re–C(2)	89.2 (3)	Re–C(1)–Si	127.9 (5)
P(1)–Re–C(3)	90.9 (3)	Re–P(1)–C(5)	107.3 (3)
P(1)–Re–C(4)	175.3 (3)	Re–P(1)–C(7)	119.9 (3)
P(2)–Re–C(1)	84.8 (2)	Re–P(1)–C(8)	118.7 (2)
P(2)–Re–C(2)	170.2 (3)	C(5)–P(1)–C(7)	103.6 (4)
P(2)–Re–C(3)	91.8 (3)	C(5)–P(1)–C(8)	106.6 (4)
P(2)–Re–C(4)	93.1 (3)	C(7)–P(1)–C(8)	99.2 (3)
C(1)–Re–C(2)	90.3 (4)	Re–P(2)–C(6)	106.9 (3)
C(1)–Re–C(3)	176.6 (3)	Re–P(2)–C(9)	117.5 (2)
C(1)–Re–C(4)	90.6 (4)	Re–P(2)–C(10)	121.5 (4)
C(2)–Re–C(3)	93.1 (4)	C(6)–P(2)–C(9)	105.5 (4)
C(2)–Re–C(4)	95.5 (4)	C(6)–P(2)–C(10)	104.9 (4)
C(3)–Re–C(4)	89.3 (4)	C(9)–P(2)–C(10)	99.0 (3)
Re–C(2)–O(2)	178.0 (8)	C(1)–Si–C(11)	116.8 (4)
Re–C(3)–O(3)	178.4 (8)	C(1)–Si–C(12)	109.0 (4)
Re–C(4)–O(4)	174.7 (8)	C(1)–Si–C(13)	109.8 (4)
P(1)–C(5)–C(6)	111.5 (6)	C(11)–Si–C(12)	106.9 (4)
P(2)–C(6)–C(5)	110.0 (6)	C(11)–Si–C(13)	107.8 (3)
		C(12)–Si–C(13)	106.1 (3)

Nonbonded Intermolecular Distances[a]

C(72)···C(83)^{I}	3.60	C(94)···C(111)^{III}	3.44
C(93)···C(94)^{II}	3.43	C(94)···C(94)^{II}	3.46
C(93)···C(95)^{II}	3.44	C(95)···C(112)^{III}	3.56
C(94)···C(112)^{III}	3.38	C(101)···C(122)^{IV}	3.57

[a] The symmetry transformations are as follows: (I) $-x$, $1-y$, $-z$; (II) $1-x$, $1-y$, $-z$; (III) x, $1+y$, z; (IV) $^1/_2-x$, $^1/_2+y$, $-^1/_2-z$.

Table VIII

Weighted Least-Squares Planes through the Molecule[a]

Plane	Atoms	*A*	*B*	*C*	*D*
1	Si, C(1), O(1), Re	–0.9927	0.0743	0.0953	–5.0339
2	Re, P(1), P(2), C(2), C(4), O(2), O(4)	0.1620	0.6049	0.7797	2.8833
3	Re, P(1), P(2)	0.1769	0.6097	0.7727	2.9783

Distances of Atoms from Planes (Å)

Plane 1		Plane 2		Plane 3	
Re	0.000	Re	0.014	C(5)	0.22
Si	–0.001	P(1)	0.026	C(6)	–0.51
O(1)	–0.007	P(2)	–0.025		
C(1)	0.013	C(2)	–0.115		
		O(2)	–0.170		
		C(4)	0.000		
		O(4)	0.093		

Dihedral Angle between Plane 1 and Plane 2: 92.4°

[a] Equations of the planes are in the form $AX + BY + CZ = D$, where X, Y, and Z are orthogonal coordinates (Å) with respect to a, b, and c^*.

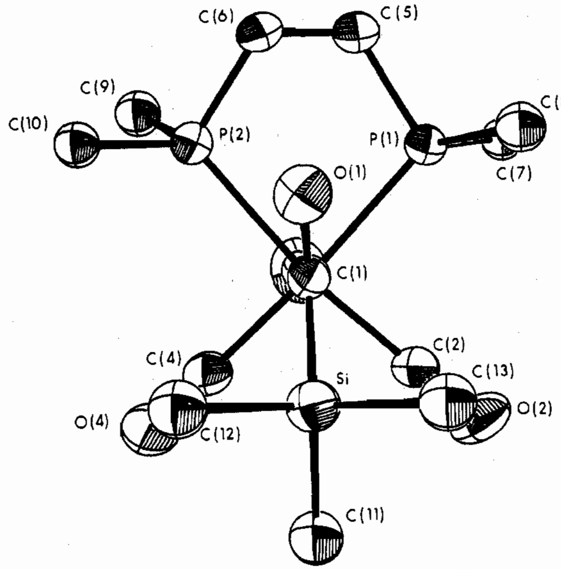


Figure 5. View of *fac*-Re(CO)$_3$(diphos)[C(O)SiPh$_3$] (**1**) down the Re–C(acyl) bond. For clarity, only the phenyl carbons bonded to Si or P are shown. Re, C(3), and O(3) are below C(1). Thermal ellipsoids are drawn at the 50% level.

Ph$_3$SiC(O)Me, 1.864 (8) Å,[42] and Ph$_3$SiCH(OH)Ph, 1.86 (1) Å.[43] The latter two values are in good agreement with the average values of 1.872 (7)[46] and 1.863 (7) Å[47] for the Si–C(Ph) bonds in Ph$_4$Si.

The Re–C(acyl) distance of 2.199 (9) Å is similar to the value 2.22 (2) Å reported for Re(CO)$_5$[C(O)(*p*-C$_6$H$_4$Cl)], the only simple rhenium–acyl complex to be characterized structurally.[48] This bond length is greater than the Re–C(carbene) distance of 2.14 (3) Å in [Me$_2$GeRe(CO)$_4$C(O)Me]$_2$[49] but shorter than the Re–C(alkyl) distance of 2.32 (4) Å in (η-C$_5$H$_5$)Re(CH$_3$)(CO)$_2$Br.[50] The shortening of M–C(acyl) bonds in transition metal–acetyl complexes relative to M–C(alkyl) bonds has been previously ascribed to d$_\pi$–p$_\pi$ back-donation from the metal to the acetyl group.[51b,c]

The acyl carbonyl bond length, C(1)–O(1), is 1.232 (12) Å. This value is slightly greater than that typical of ketones, 1.215 (5) Å,[52] or values found for transition metal–acetyl complexes, 1.193 (6)–1.206 (4) Å,[51] but the difference is not highly significant. Although lengthening has been observed in complexes where the acyl oxygen is coordinated,[53] there is no evidence for other than normal van der Waals contacts of the acyl oxygen in **1** with surrounding atoms.

The Re–C(carbonyl) bond lengths are all equal to within experimental error, with a mean value of 1.943 (7) Å. The trans-influencing properties of the Ph$_3$SiC(O) ligand and the phosphorus ligands of diphos would thus seem to be approximately equal. The carbonyl C–O bond lengths are also equal to their average distance of 1.143 (12) Å to within experimental error.

The geometry of the diphos ligand appears to be regular. The Re–P bonds are equal in length to within experimental error, mean 2.447 (2) Å. This value is greater than that in Re$_2$Cl$_6$(diphos)$_2$·2MeCN, 2.370 (3) Å,[54] but smaller than that in ReCl$_4$(diphos)·0.75CCl$_4$, 2.524 (5) Å.[55] The bond lengths

Table IX. Torsion Angles (deg) in the Five-membered Ring

P(2)–Re–P(1)–C(5)	+7.1	C(5)–C(6)–P(2)–Re	−44.0
Re–P(1)–C(5)–C(6)	−36.0	C(6)–P(2)–Re–P(1)	+16.9
P(1)–C(5)–C(6)–P(2)	+52.9		

in the diphos ligand are normal: mean P–C = 1.828 (9) Å, C–C = 1.535 (13) Å. The P–Re–P angle of 82.20 (8) Å is similar to those previously found in diphos complexes of rhenium.[54,55] Torsion angles in the diphos ligand are given in Table IX. The observed conformation of the rather flexible diphos ligand may be expected to reflect a minimum of intramolecular nonbonded interactions.

Conclusions

On the basis of the spectroscopic results above, we conclude that the electronic nature of the acyl carbonyl group in **1** differs considerably from that in simple transition metal acyls or acylsilanes. However, the limited available evidence indicates that the disilyl ketones are more closely related. Together, the infrared and ^{13}C NMR results are consistent with an acyl carbonyl group that has a relatively electron-rich oxygen atom and a relatively electron-deficient carbon atom. The structural results suggest a possible lengthening of the C(acyl)–O bond relative to known acetyl complexes. In addition, the Si–C(acyl) bond in **1** is 3σ longer than in Ph$_3$SiC(O)Me and is indicative of reduced bond order in **1**. Provided this bond lengthening persists in solution, involvement of silicon d orbitals in d_π–$p_{\pi*}$ interactions with the acyl carbonyl group is unlikely and therefore not a useful rationale to explain the low electronic transition energy in **1**.

The chemical properties of **1** are consistent with the above characterization. As observed previously in neutral compounds with carbonyl groups having low ν_{CO} values[56] and in acylate complexes,[57] alkylation occurs readily with Et$_3$O$^+$ salts, and so the oxygen atom is evidently electron rich. The effect of dissolved salts in solution is apparently to facilitate the dissociation of Ph$_3$Si$^-$, an observation consistent with the presence of polarization in the neutral complex **1**.

Acknowledgment. We thank the National Research Council of Canada for generous support of this research and for the award of Postdoctoral Fellowships to J.R.A. and H.P.C.

Registry No. **1**, 60482-65-7; **2**, 62549-79-5; **3**, 62549-77-3; [*fac*-Re(CO)$_3$(^{13}CO)(diphos)]ClO$_4$, 62521-08-8; [Re(CO)$_4$(diphos)]ClO$_4$, 25019-06-1; *mer*-Re(CO)$_3$(diphos)SiPh$_3$, 62521-09-9; *fac*-Re(CO)$_3$(diphos)Cl, 25257-38-9; hexaphenyldisilane, 1450-23-3; Et$_3$OPF$_6$, 17950-40-2; MePh$_2$SiCl, 144-79-6; Ph$_3$SiC(O)Ph, 1171-49-9; PhC(O)Ph, 119-61-9; ^{13}C, 14762-74-4.

Supplementary Material Available: Table II, rigid-body parameters for phenyl rings and positions of phenyl carbon atoms, Table III, calculated hydrogen atom positions, and Table IV, calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 8: W. Jetz and W. A. G. Graham, *J. Organomet. Chem.*, **69**, 383 (1974).

(2) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975); R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974; R. B. King, *Acc. Chem. Res.*, **3**, 417 (1970); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967; C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967.

(3) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).

(4) R. J. Angelici, *Acc. Chem. Res.*, **5**, 335 (1972).

(5) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973); C. P. Casey and S. M. Neumann, *ibid.*, **98**, 5395 (1976).

(6) A. G. Brook, *Adv. Organomet. Chem.*, **7**, 95 (1968).

(7) J. R. Anglin and W. A. G. Graham, *J. Am. Chem. Soc.*, **98**, 4678 (1976).

(8) R. J. Angelici and R. W. Brink, *Inorg. Chem.*, **12**, 1067 (1973).

(9) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

(10) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976); C. S. Kraihanzel and P. K. Maples, *J. Organomet. Chem.*, **117**, 159 (1976).

(11) K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10**, 101 (1967).

(12) The reaction of Re(CO)$_6^+$ with Ph$_3$SiLi leads to a mixture of products from which no acyl complexes have been isolated.

(13) G. J. D. Peddle, *J. Organomet. Chem.*, **14**, 139 (1968), and references therein.

(14) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

(15) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

(16) F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, **1**, 172 (1967); E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(17) E. Hengge and N. Holtschmidt, *J. Organomet. Chem.*, **12**, P5 (1968).

(18) E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, **47**, 4627 (1969).

(19) (a) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967); (b) P. Coppens, L. Leiserowitz, and D. Rabinovitch, *Acta Crystallogr.*, **18**, 1035 (1965).

(20) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(22) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(23) Supplementary material.

(24) A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965); A. G. Brook and J. B. Pierce, *J. Org. Chem.*, **30**, 2566 (1965).

(25) A. G. Brook, P. F. Jones, and G. J. D. Peddle, *Can. J. Chem.*, **46**, 2119 (1968).

(26) E. O. Fischer, H. Hollfelder, F. R. Kreissl, and W. Uedelhoven, *J. Organomet. Chem.*, **113**, C31 (1976).

(27) A comparison of the carbonyl stretching vibrations of unenriched [Re(CO)$_4$(diphos)]ClO$_4$ with those of [*fac*-Re(CO)$_3$(^{13}CO)(diphos)]ClO$_4$ in CH$_2$Cl$_2$ indicates that, upon enrichment, two bands at 2028 and 2000 cm^{-1} are essentially unchanged, whereas bands at 2111 and 2018 cm^{-1} are shifted to 2098 and 1989 cm^{-1}, respectively. A very weak band at 2110 cm^{-1} in the spectrum of [*fac*-Re(CO)$_3$(^{13}CO)(diphos)]ClO$_4$ can be attributed to residual ^{12}CO in the 92% ^{13}CO employed in the carbonylation.

(28) P. M. Treichel, H. J. Mueh, and B. E. Bursten, *J. Organomet. Chem.*, **110**, C49 (1976).

(29) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **98**, 4110 (1976).

(30) M. Pankowski, B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organomet. Chem.*, **35**, 155 (1972).

(31) M. J. Webb and W. A. G. Graham, *J. Organomet. Chem.*, **93**, 119 (1975).

(32) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961); E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(33) W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972); E. O. Fischer and V. Kiener, *J. Organomet. Chem.*, **23**, 215 (1970).

(34) R. J. McKinney and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3066 (1975); B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 308 (1970), and references therein.

(35) H. Bock, K. Wittel, M. Veith, and N. Wiberg, *J. Am. Chem. Soc.*, **98**, 109 (1976); L.-H. Chan and E. G. Rochow, *J. Organomet. Chem.*, **9**, 231 (1967).

(36) B. G. Ramsey, A. Brook, A. R. Bassindale, and H. Bock, *J. Organomet. Chem.*, **74**, C41 (1974), and references therein.

(37) Other transitions occur at 670 (ϵ 10) and 383 nm ($\epsilon \sim 3.4 \times 10^3$). The latter transition may be analogous to bands previously reported for transition metal acyls: R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, **2**, 15, (1964).

(38) E. M. Dexheimer and L. Spialter, *J. Organomet. Chem.*, **107**, 229 (1976).

(39) This value was obtained during measurement of the ^{13}C NMR spectrum of an unsealed sample of enriched [*fac*-Re(CO)$_3$(diphos){C(OEt)SiMePh$_2$}]BPh$_4$, which slowly decomposed to the acylsilane and [Re(CO)$_4$(diphos)]$^+$.

(40) M. J. Webb, Ph.D. Thesis, University of Alberta, 1975.

(41) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).

(42) P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 1778 (1969).

(43) K. T. Black and H. Hope, *J. Am. Chem. Soc.*, **93**, 3053 (1971).

(44) By contrast, no lengthening of C(acyl)–C(Me) bonds has (to our knowledge) been noted in the structures of acetyl complexes, whereas in the carbamoyl complex *cis*-Mn(CO)$_4$(NH$_2$CH$_3$)[C(O)NHCH$_3$] some *double*-bond character has been suggested to exist in the C(acyl)–N bond: D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, **1**, 393 (1967); G. L. Breneman, D. M. Chipman, C. J. Galles, and R. A. Jacobson, *ibid.*, **3**, 447 (1969).

(45) K. W. Muir, *J. Chem. Soc. A*, 2663 (1971).

(46) C. Glidewell and G. M. Sheldrick, *J. Chem. Soc. A*, 3127 (1971).

(47) L. Parkanyi and K. Sasvari, *Period. Polytech., Chem. Eng.*, **17**, 271 (1973).

(48) I. S. Astakhova, V. A. Semion, and Yu. T. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, **10**, 419 (1969).

(49) M. J. Webb, M. J. Bennett, L. Y. Y. Chan, and W. A. G. Graham, *J. Am. Chem. Soc.*, **96**, 5931 (1974).

(50) G. G. Aleksandrov, Yu. T. Struchkov, and Yu. V. Makarov, *J. Struct. Chem. (Engl. Transl.)*, **14**, 86 (1973).

(51) (a) M. R. Churchill and S. W.-Y. Chang, *Inorg. Chem.*, **14**, 1680 (1975); (b) F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, **7**, 161 (1973); (c) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(52) *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

(53) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **98**, 2365 (1976); R. J. McKinney, B. T. Huie, C. B. Knobler, and H. D. Kaesz, *ibid.*, **95**, 633 (1973); M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).

(54) J. A. Jaecker, W. R. Robinson, and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 306 (1974).
(55) J. A. Jaecker, W. R. Robinson, and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **10**, 93 (1974).
(56) A. Davison and D. L. Reger, *J. Am. Chem. Soc.*, **94**, 9237 (1972); M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 794 (1971).
(57) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).

Contribution from the Departments of Chemistry,
University of Windsor, Windsor, Ontario N9B 3P4, Canada, and Lewis University, Lockport, Illinois 60441

Phosphine–Borane Derivatives. 9. Vibrational Spectra of the Trimethylphosphine Adducts of Boron Trihalides

JOHN E. DRAKE,* J. LAWRENCE HENCHER, and BERNARD RAPP

Received December 28, 1976 AIC60910Z

The IR and Raman spectra of $Me_3P{\cdot}BCl_3$, $Me_3P{\cdot}BBr_3$, and $Me_3P{\cdot}BI_3$ are reported. A normal-coordinate analysis, utilizing a modified Urey–Bradley force field, supports the assignments. The values of K_{PB} obtained using this modified force field are consistent with the increase in relative Lewis acidity along the series $BCl_3 < BBr_3 < BI_3$. In all of the adducts, the P–B force constant is larger than in the corresponding $PH_3{\cdot}BX_3$ species.

One feature of studies of the vibrational properties of adducts containing the P–B bond has been the wide range of assigned P–B stretching frequencies.[1-5] Furthermore, significantly different values have been assigned to the magnitude of the P–B stretching force constant.[5-9] In our recent vibrational spectroscopic investigation of the $PH_3{\cdot}BX_3$ adducts,[6] we obtained reasonable agreement in the assignment of the P–B stretching mode and its corresponding force constant with that of an independently conducted study.[9] The values of the force constant vary only slightly from adduct to adduct. The relatively weak donor properties of phosphine as a Lewis base have prompted us to extend our investigation to the BX_3 (X = Cl, Br, I) adducts of progressively methyl-substituted phosphine in order to ascertain the effects of such substitution on the magnitude of the P–B force constant. (Our own ^{11}B NMR study of this adduct series[10] as well as that of Cowley and Damasco[11] on the adduct series $Me_{3-n}PH_n{\cdot}BH_3$ seems to indicate an increasing PB interaction with increasing donor strength.)

Of the various methyl-substituted phosphines, Me_3P was chosen as the appropriate base in this investigation because of its apparently superior donor properties[12] and because of the relative structural simplicity of its BX_3 adducts. These advantages should facilitate a conclusive vibrational assignment for the adduct series which will assist in our analysis of the partially methyl-substituted phosphine adducts of the boron trihalides.

Experimental Section

Starting Materials. Trimethylphosphine was prepared according to the method of Markham et al.[13] from the reaction of MeLi (Alfa Inorganics, Beverly, Mass.,) with PCl_3 (Anachemia, Toronto) in an ethereal solution. The product was checked for purity by vapor pressure measurement (160 mm at 0 °C; lit. 161.0 mm, 158 mm[14] at 0 °C) and by ^1H NMR spectrum.[15] The IR[16] and Raman[17,18] spectra were found to agree with those previously published. The boron trihalides were purified and checked in the manner reported previously.[19]

Formation of the Adducts. All reactions were carried out on a conventional Pyrex-glass vacuum system, employing the same type of reaction vessels and methods of addition with the trimethylphosphine systems as in our previous work with the phosphine–boron trihalide adducts.[6]

Spectroscopic Techniques. Raman spectra were recorded on both solid and solution samples of the adducts. Equipment type and employment were the same as in our previous study[6] except that CH_2Br_2 replaced MeI as one of the two solvents for the solution spectra of the adducts. It was found that methylene bromide had no Raman bands in the CH symmetric stretching and bending regions of the adducts, thus allowing us to obtain polarization data in these areas.

The IR spectra were recorded on both solid and solution samples of the adducts, using methods and equipment as previously reported.[6]

Table I. Description of Vibrational Assignments for $Me_3P{\cdot}BX_3$ Adducts[a] $\Gamma_v = 10\ A_1 + 5\ A_2 + 15\ E$

A_1	A_2	E	
ν_1	ν_{11}	ν_{16}, ν_{17}	CH_3 d str
ν_2		ν_{18}	CH_3 s str
ν_3	ν_{12}	ν_{19}, ν_{20}	CH_3 d def
ν_4		ν_{21}	CH_3 s def
ν_5	ν_{13}	ν_{22}, ν_{23}	CH_3 rock
ν_6			PB str
ν_7		ν_{24}	CP str
ν_8		ν_{25}	BX str
ν_9		ν_{26}	PC_3 def
		ν_{27}	PC_3 rock
ν_{10}		ν_{28}	BX_3 def
		ν_{29}	BX_3 rock
	ν_{14}	ν_{30}	CH_3 torsion
	ν_{15}		Frame torsion

[a] Descriptions of CH_3 modes are based on the local symmetry. Key: d, degenerate; s, symmetric.

Discussion

The molecules $Me_3P{\cdot}BX_3$ are assumed to be of C_{3v} symmetry in staggered conformation leading to 45 fundamental vibrations for which the conventional descriptions are given in Table I. The A_1 and E modes are active in both IR and Raman regions but the A_2 modes are inactive in both spectra and were not observed. The A_1 modes are polarized and the E modes depolarized in the Raman effect.

For comparison purposes, the values of the assigned and calculated frequencies for the three adducts are given in Table II.[20] Tables III–V provide the complete spectroscopic information on each adduct, together with the respective potential energy distributions.

(1) The Methyl Group Vibrations: ν_1–ν_5; ν_{16}–ν_{23}. By use of the previously assigned methyl group fundamental modes for Me_3P,[18] no difficulty was encountered in making the analogous assignments in the Me_3P adducts. Consistent with a previous investigation of $Me_3P{\cdot}BH_3$[21] all stretching modes are observed at higher wavenumber in the adducts than in the pure base. There is a general trend in these frequencies toward

---

* To whom correspondence should be addressed at the University of Windsor.