direct observation of metal hydride carbonylation (eq 2) might in some cases be rendered impossible by a competing reaction between the product $L_nMCHO$ and starting $L_nMH$.[19] The thermal decomposition of neutral formyl complexes by the reverse of eq 2 could also in some cases be complicated by such a competing back reaction.

**Summary.** The $Li(C_2H_5)_3BH$ reduction of metal carbonyl cations and subsequent reductive transformations of the resulting neutral formyl complexes have served to define numerous new model compounds and reactions which may bear important relationships to operative features of Fischer-Tropsch type catalysts. More detailed investigations of the complexes and reactions reported herein are actively being pursued.

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(15) IR (22 °C, THF, $cm^{-1}$): 1655 (s), 1524 (m, br). $^1H$ NMR (−23 °C, THF, $\delta$): 14.23 (s, 2 H), 5.35 (s, 5 H). $^{13}C$ NMR (−60 °C, THF-$d_8$, 0.02 M $(Cr(acac)_3)$: 265.8, 96.8 ppm.

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(18) Reactions of $HMn(CO)_5$ are known to be highly dependent upon conditions.[6b] For this experiment, $HMn(CO)_5$ was generated in situ in THF and contained equivalent amounts of $(C_2H_5)_3B$ and $CF_3SO_3Li$. J. A. Gladysz, W. Tam, G. M. Williams, D. L. Johnson, and D. W. Parker, *Inorg. Chem.*, in press.

(19) This statement is made without regard to the thermochemistry of eq 2. However, considering that the migration of metal hydrides to coordinated olefins has been observed but not the migration of metal alkyls to coordinated olefins (see K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978)), we believe it premature to regard eq 2 as universally endothermic.

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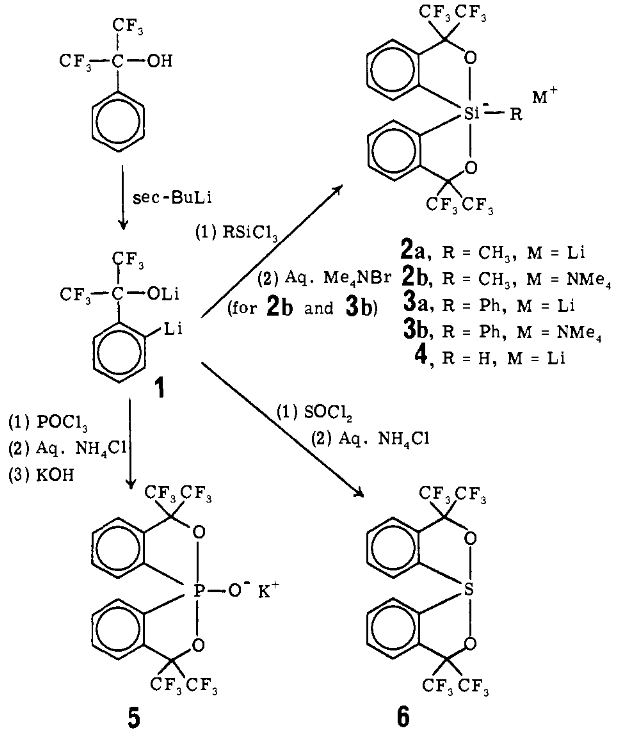
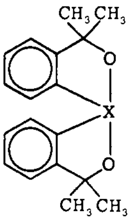
# Facile Syntheses of Isolable Organic Derivatives of Hypervalent Sulfur, Phosphorus, and Silicon. Introduction of a Stabilizing Bidentate Ligand via Its Dilithio Derivative

*Sir:*

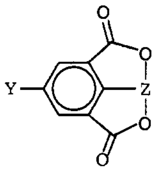
We report a very convenient preparation of dilithio derivative **1** by the reaction of *sec*-butyllithium with hexafluorocumyl alcohol. This reagent is used to prepare siliconates[1] **2**, **3**, and **4** (anionic pentacoordinate silicon species); potassium phosphoranoxide[2] **5**; and spirosulfurane[3] **6**. These compounds share structural features which have been credited with the extraordinary stabilities earlier noted[4] for certain derivatives of hypervalent sulfur.



Recent success in the isolation of novel anionic hypervalent phosphorus species, phosphoranides[5] (**7c**) and phosphoranoxides[2] (**7d**), isoelectronic with the analogous stable sulfuranes[6] (**7a**) and sulfurane oxides[6] (**7b**), has underscored the postulate[2] that one can, at least qualitatively, assess the probability that a hypervalent species will be stable enough to isolate by extrapolations from a knowledge of stabilities of analogous derivatives of atoms from adjacent columns of the periodic table. Closely analogous (essentially isoelectronic) derivatives of tetracoordinate sulfur(IV)[6] (**7a**), selenium(IV)[7] (**7e**), and anionic phosphorus[2] (**7c**); of pentacoordinate sulfur (VI)[6] (**7b**) and anionic phosphorus(V)[5] (**7d**); and of tricoordinate iodine(III)[8] (**8a**) and anionic sulfur(IV)[9] (**8b**) have been studied with results supporting this postulate.



**7a**, X = S
**b**, X = SO
**c**, X = P$^-$
**d**, X = PO$^-$
**e**, X = Se



**8a**, X = I, Y = H
**b**, X = S$^-$, Y = t-Bu

The isolation of siliconates **2** and **3** provides an opportunity for the comparison of such group 4a species with analogous group 5a or 6a species with identical bidentate ligands. Several other pentacoordinate silicon species have been described including complexes of fluoride ion,[10] amines,[11] pyridine,[12] and bipyridyl;[13] the bicyclic silatranes[14] (bicyclic intramolecular amine adducts); tetraoxyspirosiliconates[1,15] and pentaoxysiliconates[16] as examples.[17]

The bidentate ligand introduced by dilithio derivative **1** is extraordinarily well suited for the synthesis of stable hypervalent species. The enhanced electronegativity of the apical oxygen in the fluoroalkoxy ligand and the electropositive carbon equatorial ligand to the central atom enhances the difference in electronegativity between central atom and apical ligand which makes for a stable hypervalent bond.[18] The ligand also provides stabilization by the five-membered ring effect[4] and a *gem*-dialkyl (Thorpe-Ingold) effect[19] favoring the ring-closed hypervalent species.

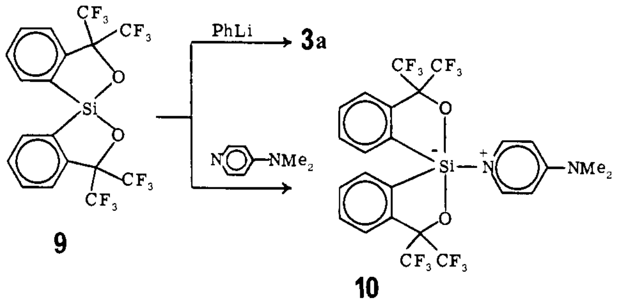
Lithium reagent **1** is prepared by dropwise addition of 2.1 equiv of a cyclohexane solution of *sec*-butyllithium to a concentrated solution of 1,1,1,3,3,3-hexafluoro-2-propanol ($R_FOH$) in tetrahydrofuran (typically 4.38 g of $R_FOH$ in 5 mL of dry tetrahydrofuran) at 0 °C, followed by stirring for 12-14 h at room temperature. Dropwise addition of $CH_3SiCl_3$, $C_6H_5SiCl_3$, $SOCl_2$, or $POCl_3$ at 0 °C in tetrahydrofuran is followed by stirring the mixture at room temperature for 1, 3, 33.5 and 6 h, respectively.

High-melting (>355 °C) **2a** (79.1%) and **3a** (70.4%) were isolated by crystallization of the oil initially formed in these reactions. Recrystallization from water or ether-chloroform-pentane failed to remove traces of LiCl (determined by analysis for ionic chloride).[20] Precipitation of the tetramethylammonium salts **2b** (mp 267.5-268.5 °C) or **3b** (mp 323-328 °C, resolidifies, then mp >355 °C) from an aqueous solution of **2a** or **3a** upon addition of tetramethylammonium bromide gave analytically pure materials,[20,21] however. Notable among the lines of evidence for these structures is the low-field chemical shift seen for protons ortho to silicon ($\delta$ 8.05-8.25) which has been shown to be characteristic of such protons in many sulfuranes,[22] iodinanes,[23] and phosphoranes.[2,5]

The reaction of **1** with $HSiCl_3$ gives a white hygroscopic solid, mp >355 °C, postulated to have the intriguing structure **4**. This material gives spectra consistent with the postulated structure,[24] except for our failure to locate the Si-H proton in the NMR, but could not be obtained analytically pure.[24] Further work will be required to establish this structure.

The reaction of **1** with $SiCl_4$ gives silane **9**, isolated (10.9%) by sublimation, mp 131-131.5 °C. Silane **9** shows a remarkable level of electrophilicity, reacting with a number of nucleophiles including phenyllithium (to give **3a**, 71.0%) and 4-dimethylaminopyridine (to give **10**, 47.2%, mp 192-195 °C, sublimes).[25]

The isolation of sulfurane **6** was effected by washing the reaction mixture with aqueous $NH_4Cl$, then aqueous KOH, and then chromatography to give 45% of material of mp 161-162.4 °C. A similar process (washing with aqueous $NH_4Cl$, pentane, and aqueous KOH) gave phosphoranoxide **5**.



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(20) Anal. Calcd for **2b,** $C_{23}H_{23}F_{12}NO_2Si$: C, 45.93; H, 3.85; N, 2.33. Found: C, 46.04; H, 3.87; N, 2.27. Anal. Calcd for **3b,** $C_{28}H_{25}F_{12}NO_2Si$: C, 50.68; H, 3.80; N, 2.11. Found: C, 50.57; H, 3.85; N, 2.09. Analyses for the lithium compounds contaminated with lithium chloride follow. Calcd for **2a,** $C_{19}H_{11}F_{12}LiO_2Si \cdot 0 \cdot 1649LiCl$: C, 42.15; H, 2.04; Li, 1.50; Cl, 1.08. Found: C, 41.63; H, 2.32; Li, 1.24; Cl, 1.08. Calcd for **3a,** $C_{24}H_{13}F_{12}LiO_2Si \cdot 0.3164LiCl$: C, 47.27; H, 2.15; F, 37.39; Li, 1.50; Cl, 1.84. Found: C, 47.42; H, 2.02; F, 35.58; Li, 1.15; Cl, 1.84.

(21) $^1H$ NMR for **2b** ($Me_2SO$-$d_6$, 90 MHz): $\delta$ 8.05 (m, 2.0, H ortho to Si), 7.32 (m, 6.2, HAr), 3.11 (s, 12.0, $^+NMe_4$), 0.12 (s, 3.0, Me). $^{19}F$ NMR for **2b** ($Me_2SO$-$d_6$, 84.6 MHz) shows two closely spaced quartets at 73.9 and 74.2 ppm upfield from $CFCl_3$, $J_{FF} = 7.8$ Hz. $^1H$ NMR for **3b** ($Me_2SO$-$d_6$, 90 MHz): $\delta$ 8.27 (m, 2.0, H, ortho to Si on spirobicyclic rings), 7.80 (m, 2.0, H ortho to Si on nonspirobicyclic ring), 7.34 (m, 6.3, remaining H on spirobicyclic

rings), 6.98 (m, 2.9, remaining H on nonspirobicyclic ring), 3.11 (s, 12.4, $^{+}NMe_4$). $^{19}F$ NMR for **3b** ($Me_2SO$-$d_6$, 84.6 MHz) shows two quartets, at 72.9 and 74.3 ppm upfield from $CFCl_3$, $J_{FF} = 8.5$ Hz. The $^{1}H$ and $^{19}F$ NMR data for **2a** and **3a** are very similar to those given above.

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(24) $^{1}H$ NMR ($Me_2SO$-$d_6$): $\delta$ 7.93 (m, 2.0, H ortho to Si), 7.27 (m, 6.3 ArH). $^{19}F$ NMR: $\phi$ 74.2 and 74.6 (q, $J_{FF} = 8.5$ Hz). Mass spectrum: *m/e* 512 ($M^{+\cdot}$ − LiH). Anal. Calcd for $C_{16}H_9F_{12}LiO_2Si\cdot0.4994LiCl$: C, 39.93; H, 1.68; Li, 1.92; Cl, 3.27. Found: C, 40.77; H, 2.01; Li, 1.48; Cl, 3.27.

(25) Anal. Calcd for **10,** $C_{25}H_{16}F_{12}N_2O_2Si$: C, 47.32; H, 2.86; N, 4.42. Found: C, 46.83; H, 3.05; N, 4.20. All other analyses are within 0.4% of the calculated values *unless* otherwise reported.

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## Interaction of Hydrogen and Hydrocarbons with Transition Metals. Neutron Diffraction Evidence for an Activated C-H Bond in an Electron-Deficient Tantalum-Neopentylidene Complex

*Sir:*

For some time we have observed two peculiarities in the $^{13}C$ NMR and IR spectra of electron-deficient niobium- and tantalum-benzylidene and -neopentylidene complexes: both $^{1}J_{CH_\alpha}$ (75-100 Hz) and $\nu_{CH_\alpha}$ (2400-2600 $cm^{-1}$) are unexpectedly low.[1] In the more sterically crowded 18-electron complexes $TaCp_2(CHR)X$ (R = H, Ph, or $CMe_3$ and X = $CH_3$, $CH_2Ph$, or Cl, respectively), whose structures are known, $^{1}J_{CH_\alpha}$ = 135, 127, and 121 Hz, respectively. Interestingly, the M-$C_\alpha$-R angle varies *inversely* with $^{1}J_{CH_\alpha}$, from 126 (4)° when R = H,[5a] to 135.2 (7)° when R = Ph,[5b] to 150.4 (5)° when R = $CMe_3$.[5c,d] Therefore, it seems likely that the even lower values for $^{1}J_{CH_\alpha}$ and $\nu_{CH_\alpha}$ in the electron-deficient complexes are characteristic of even larger M-$C_\alpha$-R angles and, consequently, smaller M-$C_\alpha$-$H_\alpha$ angles. The previous structural studies were all determined by X-ray diffraction methods, from which the location of the $\alpha$-hydrogen atom cannot be accurately obtained. In order to characterize precisely the molecular structure of an alkylidene complex, we have determined the structure of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ by neutron diffraction.

$Ta(CH_2CMe_3)_2Cl_3$ in toluene reacts with 1 mol of $PMe_3$ to give $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$, which then disproportionates to **1** and starting material (eq 1). All **1** and starting material are converted to **2**, the final product, which slowly crystallizes as large red nuggets, in 24 h.[6,7] In electron-deficient **2** (14 electrons per Ta assuming bridging Cl ligands), $^{1}J_{CH_\alpha}$ = 101 Hz and $\nu_{CH_\alpha}$ = 2605 $cm^{-1}$.

$$Ta(CH_2CMe_3)_2Cl_2 + PMe_3 \xrightarrow{\text{rapid}}$$

$$Ta(CH_2CMe_3)_2(PMe_3)Cl_3 \xrightarrow[-0.5CMe_4]{1\text{ h, }25\,^\circ C}$$

$$\underset{\mathbf{1}}{0.5\,Ta(CHCMe_3)(PMe_3)_2Cl_3} + 0.5\,Ta(CH_2CMe_3)_2Cl_3$$

$$\xrightarrow[-0.5CMe_4]{24\text{h, }25\,^\circ C} \underset{\mathbf{2}}{0.5[Ta(CHCMe_3)(PMe_3)Cl_3]_2} \qquad (1)$$

The compound crystallizes in the monoclinic space group $P2_1/n$ with refined cell dimensions at 110 K of $a$ = 10.920 (6) Å, $b$ = 12.827 (7) Å, $c$ = 10.553(6) Å, $\beta$ = 91.05 (2)°, and $Z$ = 2, which imposes a crystallographic center of inversion on the molecule. A 30-mg crystal of **2** was sealed in a lead-glass capillary under a nitrogen atmosphere and transferred to the computer-controlled diffractometer at the CP-5 reactor.[9] The crystal was cooled by a cold stream of nitrogen gas[10] and all data were measured at 110 K. Data were measured out to (sin $\theta$)/$\lambda$ = 0.62 $Å^{-1}$ ($\lambda$ 1.142 (1) Å) using the $\theta$-$2\theta$ step scan mode with 0.1° steps. Each of the data was corrected for its Lorentz factor and absorption ($\mu$ = 2.37 $cm^{-1}$) to yield a set of 2930 $F_o^2$ values. The initial positions of all independent nonhydrogen atoms were obtained by direct methods using the program MULTAN.[11] The 19 hydrogen atoms were located on a Fourier map with phases calculated from the refined coordinates of the nonhydrogen atoms. In the final stages of full-matrix least-squares refinement, the thermal motion of all atoms was treated anisotropically and the data were corrected for secondary extinction[12] ($g$ = 0.56 (3) × $10^{-4}$). The final discrepancy indices for all 2930 reflections are $R(F_o^2)$ = 0.079 and $R_w(F_o^2)$ = 0.095.

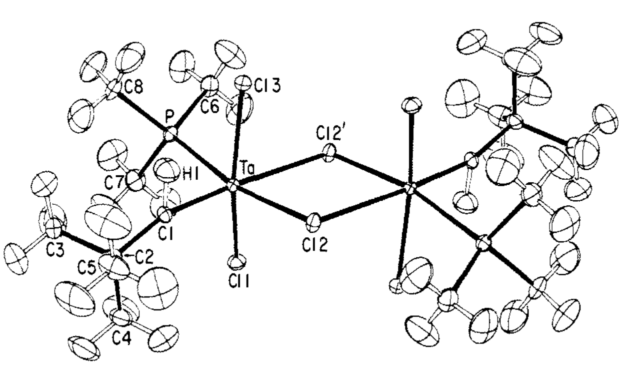

**Figure 1.** Drawing of the molecular structure of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ determined by neutron diffraction at 110 K. A crystallographic inversion center is located midway between the two Ta atoms. The ellipsoids of thermal motion for all atoms are scaled to enclose 50% probability.

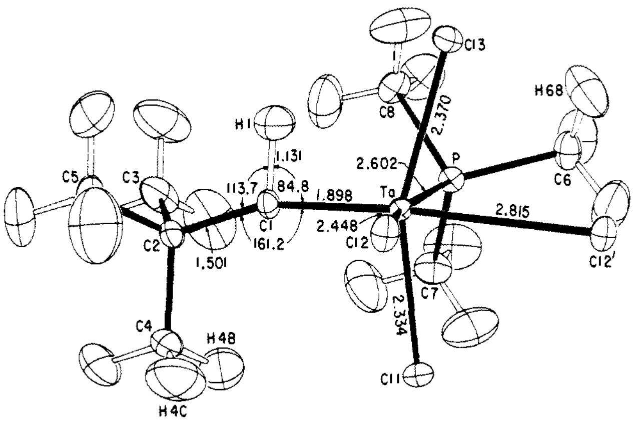

**Figure 2.** A view of the pseudooctahedral coordination geometry of one Ta atom with emphasis on the configuration of the neopentylidene ligand. The C(1)-H(1) distance of 1.131 (3) Å may be compared with the average methyl C-H distance of 1.083 (2) Å (see text).

As illustrated in Figure 1, each Ta atom possesses distorted octahedral geometry and forms an edge-sharing dimer with a center of inversion located midway between the two Ta atoms. The Ta-Ta distance (4.061 (2) Å) is much greater than that in Ta metal (2.86 Å) and precludes any direct metal-metal interaction. The distance and angles associated with the $PMe_3$ ligand are within normal ranges. Figure 2 is a view of half of the dimer molecule which emphasizes several important features of the neopentylidene ligand.

In the neopentylidene ligand, C(2), C(1), H(1), and Ta form a plane which is oriented perpendicular to the C(1)-Ta-P plane (dihedral angle = 89.8 (2)°). The short hydrogen-chlorine contacts (H(1)··Cl(3) = 2.657 (4), H(4B)··Cl(1) = 3.061 (5), and H(4C)··Cl(1) = 3.291 (5) Å) and the bending of the chloride ligands away from the alkylidene coordination site (C(1)-Ta-Cl(3) = 104.01 (7) and C(1)-Ta-Cl(1) = 95.13 (7)°) provide evidence that the alkylidene ligand is coordinated in this position by multiple bonding between Ta

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