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Synthesis and Characterization of Neopentyl- and [(Trimethylsilyl)methyl]antimony Compounds. Molecular Structures of $(Me_3CCH_2)_3Sb$, $(Me_3CCH_2)_3SbI_2$, $(Me_3SiCH_2)_3Sb$, and $(Me_3SiCH_2)_3SbI_2$

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A series of substituted stibines of the general formula R_nSbI_{3-n} and R_mSbI_{5-m} (R = Me_3CCH_2 (neopentyl) and Me_3SiCH_2 ((trimethylsilyl)methyl); n = 1–3; m = 2, 3) have been prepared and characterized. The triorganostibines (neopentyl (**1a**) and (trimethylsilyl)methyl (**2a**)) have been synthesized in 80% yield by the reaction of the corresponding Grignard reagent with $SbCl_3$ in diethyl ether. Addition of iodine to a hydrocarbon solution of **1a** or **2a** affords the five-coordinate complexes R_3SbI_2 (**1b** or **2b**). Thermal decomposition of **1b** or **2b** at 170 °C results in the reductive elimination of RI along with the formation of R_2SbI (**1c** or **2c**). Compounds **1c** or **2c** will further react with iodine in an etheral solution at −78 °C to afford R_2SbI_3 (**1d** or **2d**). These triiodide complexes are thermally unstable at ambient temperature and will eliminate RI, giving rise to $RSbI_2$ (**1e** or **2e**). All compounds have been characterized by their physical properties, ^1H and ^{13}C NMR, elemental analysis, and infrared spectroscopy. In addition to the spectroscopic techniques, compounds **1a**, **1b**, **2a**, and **2b** have been subjected to single-crystal X-ray diffraction studies. Compounds **1a** and **2a** are virtually isomorphous and crystallize in the hexagonal space group $P6_3$ with unit cell parameters for **1a** of a = 10.069 (2) Å, c = 10.296 (3) Å, V, 904.0 (4) Å^3 for Z = 2. Unit cell parameters for **2a** are a = 10.692 (2) Å, c = 10.518 (4) Å, V = 1041.3 (5) Å^3 for Z = 2. Refinement of data for **2a** converged at R = 0.0211 (R_w = 0.0244) based on 691 observed reflections with $F \geq 3.0\sigma(F)$. Both compounds adopt a pyramidal geometry about the antimony center which lies on a crystallographic 3-fold axis. Compounds **1b** and **2b** are also nearly isomorphous and crystallize in the monoclinic space group Cc with unit cell parameters for **1b** of a = 10.012 (1) Å, b = 17.215 (4) Å, c = 12.828 (3) Å, β = 106.07 (1)°, V = 2124.6 (7) Å^3 for Z = 4. Unit cell parameters for **2b** are a = 10.647 (2) Å, b = 18.283 (4) Å, c = 13.124 (2) Å, β = 105.780 (10)°, V = 2458.4 (8) Å^3 for Z = 4. Structure refinement for **1b** converged at R = 0.0262 (R_w = 0.0286) based on 1878 observed reflections with $F \geq 3.0\sigma(F)$. These compounds deviate only slightly from the expected tbp geometry with an axial I–Sb–I bond angle of 179.0 (1)°. Average Sb–C and Sb–I bond distances are 2.171 (8) and 2.900 (1) Å, respectively.

Introduction

A growing interest in the production of specifically tailored, small-band-gap semiconductors has fostered increased interest in main-group organometallic chemistry. This interest has been manifested by the development of new precursors for MOCVD (metal organic chemical vapor deposition) such as t-$BuAsH_2$[2] and by reports of possible new single-source precursors.[3–7] Inherent to both types of MOCVD sources is the use of bulky ligands not only to stabilize these reactive species but also to provide a pathway for facile decomposition of the precursor when properly chosen. For example, the *tert*-butyl ligand has been shown to be an excellent ligand in the decomposition of organometallic complexes, possibly due to the presence of β-hydrogens.[4]

The use of sterically demanding ligands in order to stabilize highly reactive species or low-valent metal centers is a synthetic approach that has been utilized in many studies.[8–12] A number of ligands have been employed for this purpose such as *tert*-butyl, mesityl, and 2,4,6-(tri-*tert*-butyl)phenyl as well as the neopentyl (Me_3CCH_2) and the (trimethylsilyl)methyl (Me_3SiCH_2) moieties.

Our interest in the preparation of new organometallic sources for MOCVD has led us to explore the synthesis and characterization of new organoantimony complexes. Specifically, we have prepared five new neopentylantimony compounds and the analogous(trimethylsilyl)methyl complexes (some of which have been previously reported). From our studies, we hope to identify any similarities or

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dissimilarities between these two antimony systems and possibly evaluate how these two ligands may affect the properties of an antimony-based MOCVD precursor.

Experimental Section

General Considerations. The compounds described in this paper were synthesized by employing a combination of Schlenk and vacuum-line techniques. Other manipulations were performed in a helium-filled Vacuum Atmospheres glovebox. Pentane, toluene, and diethyl ether were all dried over sodium/benzophenone and distilled prior to use. Deuterated benzene and d_8-toluene (both Aldrich) were dried over Na/K alloy, degassed 3 times, and vacuum distilled. Neopentyl chloride (Aldrich) was stored over $\mathrm{P_2O_5}$ for at least 3 days and distilled at atmospheric pressure immediately before use. (Trimethylsilyl)methyl chloride (Petrarch), finely divided magnesium (Aldrich, 100 mesh), and antimony trichloride (Aldrich, 99.9%) were used as received. ^{1}H, variable-temperature ^{1}H, and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer at 300.13 MHz for ^{1}H and 75.468 MHz for ^{13}C and are given in ppm. Spectra were referenced to the residual protic peak of benzene (7.15 ppm for ^{1}H) and to the center of the benzene triplet (128.00 ppm for ^{13}C). Infrared spectra were obtained either as a solid film or as neat liquids between potassium bromide plates on a Perkin-Elmer 1430 spectrophotometer and are given in cm^{-1}. Absorption intensities were measured by the method of Durkin, DeHayes, and Glore[13] and are reported with the following abbreviations: w (weak), m (medium), sh (shoulder), s (strong), v (very), and br (broad). Melting points were obtained on a MEL-TEMP II from Laboratory Devices, USA, and are reported uncorrected. Elemental analyses were preformed by E & R Microanalytical Laboratories, Corona, NY.

Synthesis of $\mathbf{(Me_3CCH_2)_3Sb}$ (1a). Trineopentylstibine was synthesized by the addition of neopentyl Grignard to antimony trichloride. In a typical reaction, 11.7 g (13.5 mL, 0.110 mol) of neopentyl chloride was added slowly to 2.67 g (0.110 mol) of finely divided magnesium in 80 mL of diethyl ether. After heating and stirring for 24 h, the Grignard reaction was judged to be complete when little magnesium remained. This solution was then added slowly to an etheral solution of 6.84 g (0.030 mol) of $\mathrm{SbCl_3}$ maintained at 0 °C by an ice bath. Upon addition of the Grignard solution, an exothermic reaction and voluminous precipitate was observed. Following addition, the reaction mixture was allowed to reflux overnight (approximately 16–18 h). The ether was then removed in vacuo to leave a combination of salts and product. Trienopentylstibine was purified by extraction of the salts/product residue with pentane (4 × 150 mL) followed by sublimation of the pentane-soluble material at 70 °C (0.005 Torr) to afford 8.0 g (24.0 mmol, 80% yield) of a white crystalline solid. Mp 71–72 °C. ^{1}H NMR: 1.06 (s, 9 H, $\mathrm{SbCH_2C(C}\mathit{H}_3\mathrm{)_3}$), 1.54 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H} NMR: 31.98 (s, $\mathrm{SbCH_2}\mathit{C}\mathrm{(CH_3)_3}$), 32.43 (s, $\mathrm{SbCH_2C(}\mathit{C}\mathrm{H_3)_3}$), 37.81 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2C(CH_3)_3}$). IR (film): 2955 (s), 2900 (m), 2860 (m), 2700 (vw), 1475 (s), 1465 (s), 1385 (m), 1360 (s), 1260 (w), 1240 (m), 1215 (w), 1190 (vw), 1160 (m), 1135 (m), 1125 (w), 1090 (w), 1055 (s), 1015 (s), 930 (w), 915 (w), 785 (w), 750 (w), 730 (w), 675 (w), 640 (w), 600 (w), 560 (w), 450 (w). Elemental Anal. Calcd for $\mathrm{C_{15}H_{33}Sb}$: C, 53.75; H, 9.92; Sb, 36.32. Found: C, 54.15; H, 9.85; Sb, 36.36.

Synthesis of $\mathbf{(Me_3CCH_2)_3SbI_2}$ (1b). To 2.57 g (7.67 mmol) of $\mathrm{(Me_3CCH_2)_3Sb}$ in 50 mL pentane and 10 mL of toluene was added 1.94 g (7.67 mmol) of iodine slowly with stirring. Upon addition of the iodine to the hydrocarbon solution, the color of the iodine was immediately discharged until the reaction was complete. The mixture was allowed to stir for 1 h and then placed in a freezer at −20 °C. After the mixture stood overnight, colorless to slightly yellow crystals were obtained. Repeated concentrations of the mother liquor (two additional times) afforded 4.18 g (7.10 mmol, 92.6% yield) of product. Mp 155–157 °C (dec). ^{1}H NMR: 1.16 (s, 9 H, $\mathrm{SbCH_2C(C}\mathit{H}_3\mathrm{)_3}$), 3.73 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H} NMR: 33.21 (s, $\mathrm{SbCH_2C(}\mathit{C}\mathrm{H_3)_3}$), 36.06 (s, $\mathrm{SbCH_2}\mathit{C}\mathrm{(CH_3)_3}$), 67.11 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2C(CH_3)_3}$). IR (film): 2955 (s), 2920 (m), 2900 (m), 2860 (s), 1470 (s), 1460 (s), 1435 (m), 1405 (w), 1380 (s), 1360 (m), 1235 (s), 1150 (s), 1115 (s), 1020 (s), 895 (m), 790 (s), 740 (w), 605 (m). Elemental Anal. Calcd for $\mathrm{C_{15}H_{33}SbI_2}$: C, 30.59; H, 5.65; I, 43.09. Found: C, 30.91; H, 5.55; I, 43.28.

Synthesis of $\mathbf{(Me_3CCH_2)_2SbI}$ (1c). Dineopentyliodostibine was synthesized via the thermal decomposition of **1b**. A flask containing 4.18 g (7.09 mmol) of $\mathrm{Me_3CCH_2)_3SbI_2}$ was heated in an oil bath (170 °C) for 10 min. Upon heating, the slightly yellow solid quickly afforded a deep yellow oil. Following removal of all volatile materials (identified as $\mathrm{(Me_3CCH_2)I}$ by bp, 1.27 g, 90% theoretical), a light yellow oil was vacuum distilled through a short-path still to afford 2.50 g (6.39 mmol, 91.7% yield) of product. Bp 65–70 °C (0.006 Torr). ^{1}H NMR: 0.93 (s, 9 H, $\mathrm{SbCH_2C(C}\mathit{H}_3\mathrm{)_3}$), 2.04 (d, 1 H, J = 12.6 Hz, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$), 2.77 (d, 1 H, J = 12.6 Hz, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H} NMR: 32.31 (s, $\mathrm{SbCH_2C(}\mathit{C}\mathrm{H_3)_3}$), 32.76 (s, $\mathrm{SbCH_2}\mathit{C}\mathrm{(CH_3)_3}$), 42.37 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2C(CH_3)_3}$). IR (neat): 2950 (vs), 2930 (sh), 2900 (m), 2860 (m), 1470 (s), 1440 (w), 1385 (m), 1365 (s), 1265 (w), 1240 (s), 1135 (sh), 1130 (m), 1095 (w), 1020 (w), 1000 (w), 760 (w), 730 (m), 605 (m). Elemental Anal. Calcd for $\mathrm{C_{10}H_{22}SbI}$: C, 30.72; H, 5.67; I, 32.46. Found: C, 30.74; H, 5.41; I, 32.42.

Synthesis of $\mathbf{(Me_3CCH_2)_2SbI_3}$ (1d). To 1.30 g (3.33 mmol) of $\mathrm{(Me_3CCH_2)_2SbI}$ in 25 mL of $\mathrm{Et_2O}$ at −78 °C was added 0.844 g (3.33 mmol) of iodine. The solution was then allowed to warm to −50 °C and stirred for 3 h. During this period, the formation of an orange precipitate was observed. Removal of the ether in vacuo at −30 °C afforded 1.97 g (3.05 mmol, 91.7% yield) of a dark orange powder. This powder was unstable at ambient temperatures, decomposing in a period of hours. However, the solid was stable for a period of at least 6 months when stored under an inert atmosphere at −20 °C. Mp 47 °C (dec). ^{1}H NMR: 1.07 (s, 9 H, $\mathrm{SbCH_2C(C}\mathit{H}_3\mathrm{)_3}$), 3.44 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H} NMR: not observed due to low solubility and thermal decomposition at ambient temperatures in solution. Elemental Anal. Calcd for $\mathrm{C_{10}H_{22}SbI_3}$: C, 18.63; H, 3.44; I, 59.05. Found: C, 18.54; H, 3.23; I, 58.78.

Synthesis of $\mathbf{(Me_3CCH_2)SbI_2}$ (1e). Dineopentylantimony triiodide (**1d**) (3.8 g, 5.9 mmol) was warmed to 50 °C for 10 min. During that time the orange solid decomposed to a deep yellow, viscous oil. Removal of volatile materials, followed by vacuum distillation through a short-path still, afforded 1.90 g (4.26 mmol, 72.2% yield) of a viscous yellow oil. Bp 105–110 °C (0.01 Torr). ^{1}H NMR: 0.68 (s, 9 H, $\mathrm{SbCH_2C(C}\mathit{H}_3\mathrm{)_3}$), 3.21 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H} NMR: 31.93 (s, $\mathrm{SbCH_2C(}\mathit{C}\mathrm{H_3)_3}$), 33.90 (s, $\mathrm{SbCH_2}\mathit{C}\mathrm{(CH_3)_3}$), 48.73 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2C(CH_3)_3}$). IR (neat): 2960 (vs), 2930 (sh), 2880 (m), 2860 (m), 1465 (s), 1440 (w), 1405 (w), 1385 (m), 1265 (m), 1235 (s), 1160 (w), 1130 (m), 1095 (w), 1020 (w), 1000 (w), 790 (w), 745 (m), 600 (m). Elemental Anal. Calcd for $\mathrm{C_5H_{11}SbI_2}$: C, 13.44; H, 2.48; I, 56.82. Found: C, 13.13; H, 2.35; I, 57.18.

Synthesis of $\mathbf{(Me_3SiCH_2)_3Sb}$ (2a). Tris[(trimethylsilyl)methyl]stibine was prepared according to Seyferth[14] as a white, pyrophoric solid in an 80% yield. Mp 57–58 °C (lit.[14] 64–65 °C). ^{1}H NMR: 0.13 (s, 9 H, $\mathrm{SbCH_2Si(C}\mathit{H}_3\mathrm{)_3}$), 0.59 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR: 1.05 (s, $\mathrm{SbCH_2Si(}\mathit{C}\mathrm{H_3)_3}$), 4.62 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2Si(CH_3)_3}$). IR (film): 2955 (m), 2900 (w), 2840 (w), 1430 (m), 1250 (s), 1060 (m), 960 (m), 860 (s), 840 (vs), 780 (w), 760 (w), 720 (w), 690 (w), 670 (w), 640 (vw), 625 (vw), 540 (w), 485 (w). Elemental Anal. Calcd for $\mathrm{C_{12}H_{33}Si_3Sb}$: C, 37.59; H, 8.68; Sb, 31.76. Found: C, 37.60; H, 8.10; Sb, 30.88.

Synthesis of $\mathbf{(Me_3SiCH_2)_3SbI_2}$ (2b). To 1.05 g (2.74 mmol) of **2a** in 50 mL of pentane and 10 mL of toluene was added 0.695 g (2.74 mmol) of $\mathrm{I_2}$ with stirring. After the mixture was stirred for 3 h, the flask was cooled to −20 °C where 1.60 g (2.51 mmol, 91.6% yield) of **2b** was obtained. Mp 164–165 °C (dec). ^{1}H NMR: 0.25 (s, 9 H, $\mathrm{SbCH_2Si(C}\mathit{H}_3\mathrm{)_3}$), 2.78 (s, 2 H, $\mathrm{SbC}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR: 1.51 (s, $\mathrm{SbCH_2Si(}\mathit{C}\mathrm{H_3)_3}$), 37.02 (s, $\mathrm{Sb}\mathit{C}\mathrm{H_2Si(CH_3)_3}$). IR (film): 2955 (s), 2895 (w), 1410 (m), 1380 (w), 1340 (m), 1260 (s), 1250 (vs), 1055 (s), 1010 (m), 840 (vs), 780 (s), 760 (s), 705 (m), 690 (s), 635 (m), 530 (m). Elemental Anal. Calcd for $\mathrm{C_{12}H_{33}Si_3SbI_2}$: C, 22.62; H, 5.22; I, 39.83. Found: C, 22.66; H, 5.29; I, 39.85.

Synthesis of $\mathbf{(Me_3SiCH_2)_2SbI}$ (2c). In an analogous manner for **1c**, **2c** was prepared by thermally decomposing 3.50 g (5.49 mmol) of $\mathrm{(Me_3SiCH_2)_3SbI_2}$. Removal of volatile materials in vacuo, followed by vacuum distillation through a short-path still, afforded

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Table I. Crystal and Refinement Data for 1a, 1b, 2a, and 2b

formula	$C_{15}H_{33}Sb$	$C_{15}H_{33}SbI_2$	$C_{12}H_{33}SbSi_3$	$C_{12}H_{33}SbSi_3I_2$
cryst system	hexagonal	monoclinic	hexagonal	monoclinic
space group	$P6_3$	Cc	$P6_3$	Cc
a, Å	10.069 (2)	10.012 (1)	10.692 (2)	10.647 (2)
b, Å		17.215 (4)		18.283 (4)
c, Å	10.296 (3)	12.828 (3)	10.518 (4)	13.124 (2)
β, deg		106.1 (1)		105.78 (1)
γ, deg	120.0		120.0	
V, Å^3	904.0 (4)	2124.6 (7)	1041.3 (5)	2438.4 (8)
Z	2	4	2	4
fw	335.18	588.99	383.40	637.21
$F(000)$	348	1120	396	1216
ρ(calc), g cm^{-3}	1.231	1.841	1.223	1.722
temp, °C	−50	−50	22	22
cryst dimens, mm	0.03 × 0.42 × 0.66	0.34 × 0.36 × 0.44	0.42 × 0.46 × 0.70	0.30 × 0.42 × 0.56
λ, wavelength, Å	1.541 78	0.710 73	0.710 73	0.710 73
μ, abs coeff, cm^{-1}	122.1	41.7	14.9	37.5
2θ max, deg	110	50	55	55
ω scan speed, deg/min	constant 30	constant 15	variable 5.0–15.0	variable 7.5–30.0
2θ scan range, deg	$2.0 + \Delta_{\alpha1\alpha2}$	$1.8 + \Delta_{\alpha1\alpha2}$	$2.4 + \Delta_{\alpha1\alpha2}$	$2.0 + \Delta_{\alpha1\alpha2}$
data collected, hkl	−9 to 0, 0 to 9, −10 to 10	−11 to 11, 0 to 20, −15 to 0	0 to 13, −13 to 6, 0 to 13	0 to 13, 0 to 23, −17 to 16
unique data	662	1978	844	2997
R_{int}	0.075	0.01	0.022	0.014
unique data, $F_o > 3\sigma(F_o)$	469	1878	691	2637
std reflns	4.9% linear decay	3.8% linear decay	2.8% random	2.6% random
parameters refined	48	163	59	163
weighting function, g[a]	0.000 23	0.000 23	0.000 23	0.000 23
R,[b] wR,[c] S[d]	0.089, 0.094, 2.42	0.026, 0.029, 1.09	0.021, 0.024, 0.98	0.034, 0.037, 1.19
Fourier excursions, e Å^{-3}	0.76, −0.78	0.75, −0.79	0.44, −0.23	0.76, −0.70

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$. [b] $\sum|\Delta|/\sum|F_o|$. [c] $\sum[(w\Delta^2)/\sum(wF_o^2)]^{1/2}$. [d] $[\sum w(\Delta^2)/(N_o - N_p)]^{1/2}$.

2.11 g (4.99 mmol, 91% yield) of a yellow oil. Bp 58–62 °C (5 × 10^{-6} Torr). ^{1}H NMR: 0.06 (s, 9 H, $SbCH_2Si(CH_3)_3$), 1.38 (br, 2 H, $SbCH_2Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR: 0.90 (s, $SbCH_2Si(CH_3)_3$), 10.05 (s, $SbCH_2Si(CH_3)_3$). IR (neat): 2955 (s), 2895 (m), 1450 (w), 1405 (m), 1350 (m), 1300 (w), 1260 (s), 1250 (vs), 1020 (m), 1000 (m), 960 (m), 850 (vs), 835 (vs), 760 (s), 705 (s), 690 (s), 610 (m), 515 (m). Elemental Anal. Calcd for $C_8H_{22}Si_2SbI$: C, 22.71; H, 5.24; I, 30.00. Found: C, 22.59; H, 5.14; I, 29.70.

Synthesis of $(Me_3SiCH_2)_2SbI_3$ (2d). To 0.460 g (1.09 mmol) of **2c** in 10 mL of Et_2O at −78 °C was added 0.275 g (1.09 mmol) of I_2 with stirring. The solution was gradually warmed over a period of 2 h to −30 °C, and the ether was removed in vacuo to afford a deep orange powder in quantitative yield (1.09 mmol, 0.730 g). Mp 54–55 °C (dec). Similar to **1d**, this compound was stable under an inert atmosphere when stored at −20 °C. ^{1}H NMR: 0.27 (s, 9 H, $SbCH_2Si(CH_3)_3$), 3.28 (s, 2 H, $SbCH_2Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR: 0.44 (s, $SbCH_2Si(CH_3)_3$), 50.80 (s, $SbCH_2Si(CH_3)_3$). Elemental Anal. Calcd for $C_8H_{22}Si_2SbI_3$: C, 14.20; H, 3.28; I, 56.24. Found: C, 13.93; H, 2.96; I, 56.30.

Synthesis of $(Me_3SiCH_2)SbI_2$ (2e). An ethereal solution of 1.30 g (1.92 mmol) of **2d** was allowed to stir overnight (approximately 16 h) at ambient temperature. Following removal of volatile materials in vacuo, the remaining yellow oil was vacuum distilled through a short-path still to afford 0.451 g (50.6% yield) of a viscous yellow oil. Bp 70–75 °C (1 × 10^{-5} Torr). ^{1}H NMR: −0.08 (s, 9 H, $SbCH_2Si(CH_3)_3$), 2.02 (s, 2 H, $SbCH_2Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR: 0.62 (s, $SbCH_2Si(CH_3)_3$), 15.90 (s, $SbCH_2Si(CH_3)_3$). IR (neat): 2950 (s), 2890 (m), 1445 (w), 1405 (m), 1340 (m), 1300 (w), 1260 (s), 1250 (s), 1200 (vw), 1120 (vw), 1060 (w), 1035 (m), 1010 (s), 965 (m), 835 (s), 760 (s), 700 (s), 635 (vw), 610 (m), 600 (m), 510 (m), 475 (vw). Elemental Anal. Calcd for $C_4H_{11}SiSbI_2$: C, 10.38; H, 2.40; I, 54.85. Found: C, 10.85; H, 2.45; I, 54.54.

Crystallographic Studies. Suitable crystals of $(Me_3CCH_2)_3Sb$, $(Me_3SiCH_2)_3Sb$ (both grown by sublimation), $(Me_3CCH_2)_3SbI_2$, and $(Me_3SiCH_2)_3SbI_2$ (both grown from a pentane/toluene solution) were mounted under a helium atmosphere in thin-walled capillaries and flame sealed. Data collection for all four structures utilized automated Siemens R3m/V diffractometers with incident beam graphite monochromators; Mo Kα radiation was used for **1b**, **2a**, and **2b** and Cu Kα for **1a**. Several attempts to collect data for **1a** using Mo Kα radiation at −50 °C were unsuccessful due to unexpected and rapid decay of the crystals. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on the φ dependence of 10–12 reflections with χ ca. 90° were applied for **1b**, **2a**, and **2b**; with a maximum and minimum transmittance of 0.59 and 0.48, 0.89 and 0.74, and 0.87 and 0.43, respectively. Identification of the crystal faces permitted a numerical absorption correction based on the Gaussian integration method to be applied for **1a**; maximum and minimum transmittance was 0.68 and 0.07. The space group determinations were based on extinctions present and were confirmed by the structure solution. In each case, the structures were determined by direct methods with the aid of the program SHELXTL[15] and refined using a full-matrix least-squares program.[15] In each structure, the parameters refined include the atomic coordinates and anisotropic thermal parameters for all but the hydrogens. For **1a**, **1b** and **2b**, hydrogens were placed in idealized positions (C–H = 0.96 Å) and coordinate shifts of the carbon atom were applied to the bonded hydrogens. For **2a**, the methyl groups were treated as rigid groups and allowed to rotate about the C–C bond. In all cases, the isotropic thermal parameters assigned to the hydrogens were fixed. The determination of the absolute configuration using the method suggested by Rogers[16] proved inconclusive. Table I contains additional data collection and refinement parameters.

Results and Discussion

The triorganostibines (**1a** and **2a**) were synthesized by the reaction of the corresponding Grignard reagent with antimony trichloride in diethyl ether (eq 1). The com-

$$3RMgCl + SbCl_3 \xrightarrow[\text{reflux 18 h}]{Et_2O,\ 0\ °C} R_3Sb + 3MgCl_2 \qquad (1)$$

1a, R = Me_3CCH_2
2a, R = Me_3SiCH_2

pounds are both white, air-sensitive solids that sublime slowly at ambient temperature under dynamic vacuum (10^{-5}–10^{-6} Torr) and are quite soluble in aliphatic and aromatic hydrocarbons as well as ethers. Examination of

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[16] Rogers, D. *Acta. Crystallogr.* **1981**, *A37*, 734.

Table II. Bond Lengths (Å) and Bond Angles (deg) for 1a

Sb–C(1)	2.18 (3)	C(1)–C(2)	1.57 (5)
C(2)–C(3)	1.51 (5)	C(2)–C(4)	1.52 (4)
C(2)–C(5)	1.51 (4)		
C(1)–Sb–C(1A)	93.5 (9)	Sb–C(1)–C(2)	117.1 (18)
C(1)–C(2)–C(3)	107.2 (32)	C(1)–C(2)–C(4)	109.2 (24)
C(3)–C(2)–C(4)	116.2 (34)	C(1)–C(2)–C(5)	107.3 (26)
C(3)–C(2)–C(5)	107.5 (21)	C(4)–C(2)–C(5)	109.0 (32)

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 1a[a]

	x	y	z	U(eq)
Sb	0	0	1815	38 (1)
C(1)	-2032 (33)	-538 (46)	668 (23)	55 (19)
C(2)	-3238 (3)	-171 (31)	1298 (31)	48 (15)
C(3)	-3950 (37)	-1247 (46)	2430 (33)	89 (25)
C(4)	-2464 (36)	1532 (29)	1604 (60)	69 (18)
C(5)	-4489 (32)	-565 (36)	303 (32)	59 (18)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Bond Lengths (Å) and Bond Angles (deg) for 2a

Sb(1)–C(1)	2.153 (5)	C(1)–Si(1)	1.859 (5)
Si(1)–C(2)	1.866 (9)	Si(1)–C(3)	1.858 (8)
Si(1)–C(4)	1.856 (9)		
C(1)–Sb(1)–C(1A)	95.9 (2)	Sb(1)–C(1)–Si(1)	114.8 (3)
C(1)–Si(1)–C(2)	108.0 (3)	C(1)–Si(1)–C(3)	109.9 (4)
C(2)–Si(1)–C(3)	110.0 (3)	C(1)–Si(1)–C(4)	111.1 (3)
C(2)–Si(1)–C(4)	109.3 (5)	C(3)–Si(1)–C(4)	108.5 (3)

the two stibines by ^1H and ^{13}C NMR spectroscopy reveals spectra that are consistent with our formulation. The ^1H spectra for both **1a** and **2a** show only two resonances in a ratio of 2:9, with the resonance for the methylene hydrogens occurring approximately 0.5 ppm downfield from the methyl resonance. Proton-decoupled ^{13}C spectra show the expected three resonances for **1a** and two resonances for **2a**.

Both $(Me_3CCH_2)_3Sb$ (**1a**) and $(Me_3SiCH_2)_3Sb$ (**2a**) have been examined by single-crystal X-ray analysis. The two species are isomorphous and crystallize in the hexagonal space group $P6_3$ with c/a ratios of 1.022 and 0.983, respectively. Figure 1 shows a thermal ellipsoid plot of **2a** (a plot of **2a** is also representative of **1a**). Selected bond distances and bond angles and atomic coordinates for non-hydrogen atoms (with equivalent isotropic thermal parameters) are given in Tables II and III (**1a**) and IV and V (**2a**).

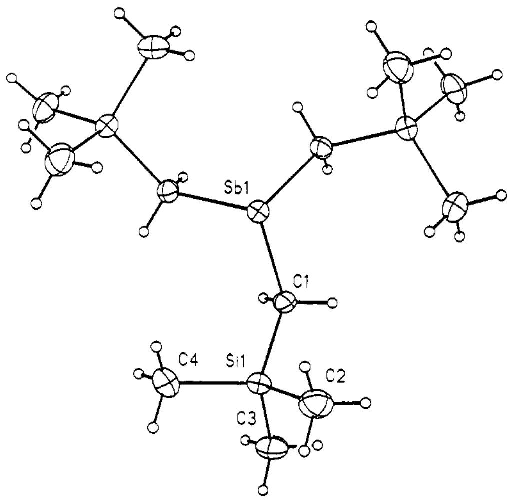

Figure 1. Thermal ellipsoid plot of $(Me_3SiCH_2)_3Sb$. Atoms are shown as 20% probability thermal ellipsoids.

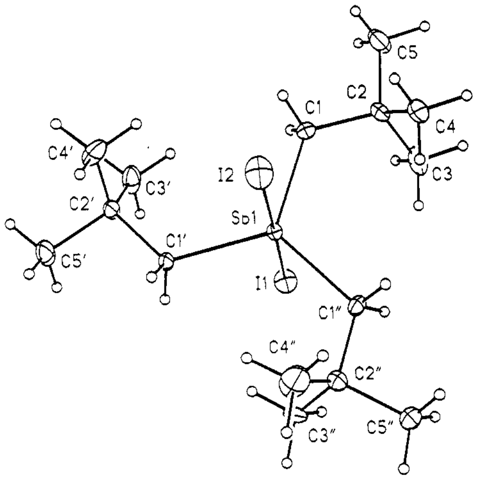

Figure 2. Thermal ellipsoid plot of $(Me_3CCH_2)_3SbI_2$. Atoms are shown as 20% probability thermal ellipsoids.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2a[a]

	x	y	z	U(eq)
Sb(1)	0	0	2745	46 (1)
C(1)	1237 (4)	1974 (4)	1692 (7)	53 (2)
Si(1)	2970 (1)	3304 (1)	2448 (4)	57 (1)
C(2)	2544 (7)	4016 (7)	3905 (8)	86 (3)
C(3)	4049 (6)	4806 (6)	1325 (9)	89 (3)
C(4)	4050 (6)	2450 (7)	2897 (10)	92 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In both **1a** and **2a**, the pyramidal antimony(III) lies on a crystallographic 3-fold axis. The molecular C_{3v} symmetry is not present due to a rotation of the Me_3CCH_2 and Me_3SiCH_2 groups from the 3-fold axis of approximately 24 and 29°, respectively, and in that respect **1a** and **2a** are similar to $(Me_3CCH_2)_3As$[17] to which they are also isomorphous. The C–Sb–C angles are 93.5 (12) (**1a**) and 95.9 (2)° (**2a**) and the respective Sb–C distances are 2.18 (3) and 2.153 (5) Å, which are in accordance with the values 94.2° and 2.169 Å observed in Me_3Sb.[18] In the complexes tris(cyclopentadienyl)antimony,[19] tri-*p*-tolylantimony,[20] and tris(2,6-dimethylphenyl)antimony,[21] the mean value of the C–Sb–C angle grows to 96.4, 97.3, and 104.7° as the substituents become more sterically demanding. Other bond distances and angles are normal. There are few close contacts, and the intermolecular ones are greater than van der Waals separations.

Both **1a** and **2a** oxidatively add iodine to give the five-coordinate diiodide species. The products (R_3SbI_2 for **1b** and **2b**) are pale yellow, air-sensitive solids and are markedly less soluble than their R_3Sb counterparts. Spectroscopic characterization of the two species reveal no unusual anomalies.

The X-ray analysis of **1b** and **2b** shows that the two compounds are also isomorphous and crystallize in the monoclinic space group Cc. The structure of both complexes may be represented by that shown in Figure 2. Selected bond distances and angles for **1b** are given in Table VI, with atomic coordinates for the non-hydrogen atoms given in Table VII. The respective information for

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Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 1b

I(1)–Sb(1)	2.922 (1)	I(2)–Sb(1)	2.878 (1)
Sb(1)–C(1)	2.183 (8)	Sb(1)–C(1′)	2.167 (8)
Sb(1)–C(1″)	2.172 (9)	C–C (av)	1.533 (17)

I(1)–Sb(1)–I(2)	179.0 (1)	I(1)–Sb(1)–C(1)	90.0 (3)
I(2)–Sb(1)–C(1)	90.3 (3)	I(1)–Sb(1)–C(1′)	88.6 (2)
I(2)–Sb(1)–C(1′)	90.5 (2)	C(1)–Sb(1)–C(1′)	121.3 (3)
I(1)–Sb(1)–C(1″)	90.0 (2)	I(2)–Sb(1)–C(1″)	90.8 (2)
C(1)–Sb(1)–C(1″)	118.0 (3)	C(1′)–Sb(1)–C(1″)	120.7 (3)
Sb(1)–C(1)–C(2)	120.0 (6)	Sb(1)–C(1′)–C(2′)	120.5 (5)
Sb(1)–C(1″)–C(2″)	119.8 (6)	C–C–C (av)	109.4 (28)

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 1b[a]

	x	*y*	*z*	*U*(eq)
I(1)	2831 (1)	1825 (1)	7057 (1)	50 (1)
I(2)	4291 (1)	981 (1)	11610 (1)	62 (1)
Sb(1)	3542	1399 (1)	9350	26 (1)
C(1)	3005 (9)	192 (5)	8901 (9)	41 (3)
C(2)	1543 (9)	−95 (5)	8777 (8)	42 (3)
C(3)	482 (10)	324 (6)	7837 (9)	60 (4)
C(4)	1084 (10)	1 (6)	9804 (9)	54 (4)
C(5)	1611 (13)	−971 (6)	8545 (12)	73 (6)
C(1′)	5620 (8)	1839 (5)	9525 (8)	31 (3)
C(2′)	6778 (8)	1297 (5)	9401 (9)	40 (3)
C(3′)	6382 (10)	839 (7)	8342 (9)	62 (4)
C(4′)	7245 (12)	762 (7)	10383 (10)	69 (5)
C(5′)	8002 (10)	1840 (6)	9388 (12)	65 (5)
C(1″)	1912 (8)	2159 (5)	9574 (8)	36 (3)
C(2″)	2260 (10)	3028 (5)	9931 (10)	47 (4)
C(3″)	2809 (12)	3449 (5)	9090 (12)	72 (6)
C(4″)	3272 (13)	3081 (8)	11066 (12)	88 (6)
C(5″)	870 (11)	3362 (6)	9967 (11)	60 (5)

[a] Equivalent isotopic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VIII. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b

Sb(1)–I(1)	2.877 (1)	Sb(1)–I(2)	2.902 (1)
Sb(1)–C(1)	2.134 (9)	Sb(1)–C(1′)	2.139 (8)
Sb(1)–C(1″)	2.129 (9)	C(1)–Si(1)	1.888 (9)
C(1′)–Si(1′)	1.898 (9)	C(1″)–Si(1″)	1.889 (9)
Si–C (av)	1.864 (25)		

I(1)–Sb(1)–I(2)	179.0 (1)	I(1)–Sb(1)–C(1)	90.4 (3)
I(2)–Sb(1)–C(1)	90.6 (3)	I(1)–Sb(1)–C(1′)	90.1 (3)
I(2)–Sb(1)–C(1′)	89.2 (3)	C(1)–Sb(1)–C(1′)	120.8 (3)
I(1)–Sb(1)–C(1″)	90.1 (2)	I(2)–Sb(1)–C(1″)	89.6 (2)
C(1)–Sb(1)–C(1″)	119.1 (3)	C(1′)–Sb(1)–C(1″)	120.1 (3)
Sb(1)–C(1)–Si(1)	118.7 (4)	Sb(1)–C(1′)–Si(1′)	117.7 (5)
Sb(1)–C(1″)–Si(1″)	119.1 (4)	C–Si–C (av)	109.5 (22)

Table IX. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2b[a]

	x	*y*	*z*	*U*(eq)
Sb(1)	6852	1386 (1)	3903	42 (1)
I(1)	6220 (1)	1042 (1)	1682 (1)	93 (1)
I(2)	7469 (1)	1758 (1)	6133 (1)	83 (1)
C(1)	7187 (7)	256 (5)	4288 (8)	58 (3)
Si(1)	8856 (3)	−139 (1)	4389 (2)	55 (1)
C(2)	10113 (11)	336 (7)	5461 (7)	84 (4)
C(3)	9342 (12)	−26 (7)	3143 (8)	82 (4)
C(4)	8754 (13)	−1121 (6)	4695 (12)	122 (8)
C(1′)	4957 (8)	1856 (5)	3686 (8)	58 (3)
Si(1′)	3577 (3)	1225 (1)	3777 (3)	65 (1)
C(2′)	3994 (11)	719 (7)	5024 (11)	108 (6)
C(3′)	3147 (13)	592 (9)	2667 (14)	126 (7)
C(4′)	2149 (11)	1855 (8)	3697 (15)	123 (7)
C(1″)	8436 (8)	2047 (5)	3750 (7)	55 (3)
Si(1″)	8133 (3)	3043 (2)	3383 (3)	75 (1)
C(2″)	7471 (15)	3521 (7)	4371 (15)	135 (9)
C(3″)	6961 (14)	3125 (8)	2039 (14)	144 (8)
C(4″)	9758 (10)	3427 (7)	3390 (11)	88 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2b is given in Tables VIII and IX.

The geometry about the Sb atoms is trigonal bipyramidal (TBP) with only minor deviations from ideal TBP. This is also the geometry observed in $(Me_3CCH_2)_3AsI_2$,[17] Me_3SbX_2,[22,23] (X = Cl, Br, I, and F), and $(C_6H_5)_3SbCl_2$.[24] The I–Sb–I angle is 179.0 (1)° for both **1b** and **2b**, and the Sb–I distances are 2.922 (1) and 2.878 (1) Å (**1b**) and 2.877 (1) and 2.902 (1) Å (**2b**). The 2.895-Å average agrees well with the 2.88-Å average observed in Me_3SbI_2.[22] Overall, the methyl groups of the Me_3CCH_2 and Me_3SiCH_2 substituents are oriented so that there is a rough 3-fold symmetry about the I–Sb–I axis in that a least-squares plane including the Sb atom, methylene carbons, and the Si (**2b**) or quaternary carbon (**1b**) has a mean deviation from the plane of 0.016 (**1b**) and 0.037 Å (**2b**), while C5, C5′, and C5″ are 0.11, −0.25, and −0.04 Å from the plane (**1b**) and C4, C4′, and C4″ are 0.04, 0.07, and 0.09 Å out-of-plane (**2b**). There are a number of intermolecular contacts[25] (H--I) in the ranges 3.20–3.42 (**1b**) and 3.38–3.44 Å (**2b**), and the deviations from the C_{3h} molecular symmetry are likely due to packing forces.

The decomposition of five-coordinate triorganoantimony dihalides is a well-known reaction.[26] From our studies of the five-coordinate trineopentyl species, we have found that iodine is the preferred halogen for this system. This is based on the observation that the decomposition temperature of the five-coordinate dihalide species increases with increasing electronegativity of the halogen (Cl > Br > I) for this system.[27] Both **1b** and **2b** decompose cleanly at 170 °C to exclusively give R_2SbI and RI. The corresponding five-coordinate dibromide compounds decompose at much higher temperatures than the iodides (250 °C) and yield a mixture of decomposition products containing primarily $RSbBr_2$ with smaller amounts of R_2SbBr. Therefore, the choice of halogen is crucial in producing a diorgano(monohalo)antimony species by the reductive elimination route. We have utilized this approach for the synthesis of R_2SbI (**1c** and **2c**). It is of interest to note that in the case of **2c**, no cleavage of the Si–C bond occurred during the decomposition of $(Me_3SiCH_2)_3SbI_2$. Observations by Malisch and co-workers indicate that $(Me_3SiCH_2)_3AsBr_2$, when thermally decomposed at 170–80 °C (10^{-4} Torr), eliminates Me_3SiBr and results in the formation of $(Me_3SiCH_2)_2AsCH_2Br$ in 70% yield.[28] Examination by ^1H NMR of the decomposition of **2b** shows no cleavage of the Si–C bond. This may be attributed to the difference in silicon's affinity for bromine over iodine or in the difference between the two metal centers (arsenic vs antimony).

The two dialkylantimony iodides are both yellow, slightly air-sensitive oils that exhibit marked solubility in nonpolar hydrocarbons (aliphatic and aromatic) and polar ethers. Both **1c** and **2c** have been characterized by ^1H NMR. In the case of **1c**, an AB pattern for the methylene hydrogens (J = 12.6 Hz) is observed at room temperature. This magnetic inequivalence of the methylene hydrogens (diastereotopic) arises out of the reduction of symmetry

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(replacing a like R group in R_3Sb with a halogen atom) about the antimony center as well as the inability of $(Me_3CCH_2)_2SbI$ to invert about the antimony center at ambient temperature. However, for **2c**, a room-temperature ^1H spectrum reveals a broadened resonance for the methylene hydrogens ($\nu_{1/2}$ = 7.1 Hz) located midway between where expected diastereotopic resonances for this complex would occur. This anomaly led us to examine **1c** and **2c** by variable-temperature ^1H NMR. For **2c**, as the temperature is lowered from ambient to −70 °C, the methylene resonance continues to broaden ($\nu_{1/2} > 30$ Hz). Even at −70 °C, an AB pattern is not observed. Warming the sample from −70 °C to ambient and continuing to 50 °C produces only a narrowing of the methylene resonance with $\nu_{1/2}$ = 3.1 Hz at 50 °C. This system shows no concentration dependence. Examination of the analogous neopentyl system shows only a slight broadening of the AB pattern at elevated temperatures. We believe the difference in the NMR spectra of these two systems results from $(Me_3CCH_2)_2SbI$ adopting a pyramidal structure and $(Me_3SiCH_2)_2$ SbI one that is intermediate between pyramidal and planar. Because of intramolecular crowding between the Me_3Si groups of the two Me_3SiCH_2 ligands, **2c** could be forced to expand its C–Sb–C angle beyond ca. 95°. The opening of this angle would force a "flattening" of the molecule (a more planar structure). Heating such a system would tend to increase the rate of inversion about the antimony center, thus giving rise to a "time-averaged" (on the NMR time scale) planar geometry and a single, narrow resonance for the methylene hydrogens. If the temperature is lowered in this system, the inversion rate would decrease and a more pyramidal geometry would be favored. However, if internal repulsion forces between the two Me_3SiCH_2 groups were significant, a true pyramidal structure would be energetically unfavorable and a structure intermediate between pyramidal and planar would result. This would account for our observation of only a broadened resonance for the methylene hydrogens, rather than a resolved AB pattern, at low temperatures. Examination of the ^{13}C spectra shows three resonances for **1c** and two resonances for **2c**. The methylene carbon (or α-carbon) exhibits an expected downfield shift of 4.5 ppm for **1c** and 5.4 ppm for **2c** as compared to the parent triorgano compounds **1a** and **2a** due to the presence of the iodine.

A further iteration of the reactions starting with **1c** or **2c** produces the five-coordinate triiodide species (R_2SbI_3 for **1d** or **2d**) and the alkyl(diiodo)stibines ($RSbI_2$ for **1e** or **2e**). The triiodide compounds are dark orange, air-sensitive solids. They also show diminished stability in the presence of light or when stored at ambient temperature. Under either of these conditions, the triiodidies reductively eliminate RI to afford $RSbI_2$ (**1e** or **2e**). However, both **1d** and **2d** are indefinitely stable when stored under an inert atmosphere at −20 °C in the absence of light. The alkyl(diiodo)stibines ($RSbI_2$) are bright yellow, highly viscous, air-sensitive oils. Unlike the monoiodo complexes, these species exhibit simple ^1H NMR spectra (no diastereotopic hydrogens).

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Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and H-atom coordinates with isotropic parameters for **1a**, **1b**, **2a**, and **2b** and packing diagrams for **1b** and **2a** (6 pages). Ordering information is given on any current masthead page.

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(η^2-Vinyl)- and (η^3-Allyl)tungsten(II) Complexes Containing a Hydridotris(3,5-dimethylpyrazolyl)borate Ligand

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Cationic alkyne complexes react with anionic nucleophiles to generate the η^2-vinyl complexes $Tp'(CO)_2W(\eta^2\text{-}RC{=}CRR')$. Reaction of $[Tp'(CO)_2W(PhC{\equiv}CH)][BF_4]$ with $P(OMe)_3$ produces a $P(O)(OMe)_2$-substituted η^2-vinyl complex, $Tp'(CO)_2W[\eta^2\text{-}CPh{=}CHP(O)(OMe)_2]$, which can be protonated at the oxygen to generate a cationic $P(OH)(OMe)_2$-substituted η^2-vinyl complex, $\{Tp'(CO)_2W[\eta^2\text{-}CPh{=}CHP(OH)(OMe)_2]\}[BF_4]$. Reaction of $[Tp'(CO)_2W(RC{\equiv}CMe)][BF_4]$ (R = Me, Ph) with $LiBEt_3H$ generates η^3-allyl complexes via an η^2-vinyl intermediate. Reaction of $[Tp'(CO)_2W(PhC{\equiv}CMe)][BF_4]$ with $LiCu(Bu^n)_2$ yields an η^1-acyl complex, $Tp'(CO)W(PhC{\equiv}CMe)[\eta^1\text{-}C(O)Bu^n]$, in which the alkyne ligand acts as a four-electron donor.

Introduction

Isolation and characterization of η^2-vinyl complexes have important mechanistic implications since such results imply that vinyl ligands may stabilize unsaturated intermediates. Molecular orbital analyses, which can serve as a guide to synthetic efforts, indicate that four-electron-donor alkyne and η^2-vinyl ligands will bind to similar metal fragments (Chart I); they are isolobal ligands.[1] The three fundamental metal–ligand interactions (σ donation, $\pi_\perp$ donation, and π* acceptance) identified in monomeric d^4 alkyne complexes have orbital analogies in η^2-$RC{=}CR_2$ ligands. These isolobal relationships are germane to synthetic transformations of alkyne ligands.

Four-electron-donor alkyne ligands have been converted to η^2-vinyl ligands, $RC{=}CR_2$, by addition of nucleophiles. Green and co-workers have reported that reactions of cationic alkyne complexes of the type $[CpL_2M(RC_2R)]^+$ with anionic nucleophiles generate neutral η^2-vinyl complexes, $[CpL_2Mo(\eta^2\text{-}RC{=}CRR')]$ (eq 1).[2] Note that

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[1] Brower, D. C.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1986**, *5*, 94.