Reactions of $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ with Alkyl Halides and Dihalides: Formation of the Alkyl- and the Dialkylantimony−Iron Carbonyl Complexes

Minghuey Shieh,* Chii-maw Sheu, Li-Fang Ho, Jiann-Jang Cherng, Li-Fing Jang, and Chuen-Her Ueng

Department of Chemistry, National Taiwan Normal University,
Taipei 11718, Taiwan, Republic of China

Shie-Ming Peng and Gene-Hsiang Lee

Department of Chemistry, National Taiwan University, Taipei 10764, Taiwan, Republic of China

Received October 18, 1995[⊗]

The reactions of $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ (**1**) with RX (R = Me, Et, *n*-Pr; X = I) in MeCN form the monoalkylated antimony complexes $[Et_4N]_2[RSb\{Fe(CO)_4\}_3]$ (R = Me, **2**; R = Et, **4**; R = *n*-Pr, **6**) and the dialkylated antimony clusters $[Et_4N][R_2Sb\{Fe(CO)_4\}_2]$ (R = Me, **3**; R = Et, **5**; R = *n*-Pr, **7**), respectively. When $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ reacts with *i*-PrI, only the monoalkylated antimony complex $[Et_4N]_2[i\text{-}PrSb\{Fe(CO)_4\}_3]$ (**8**) is obtained. The mixed dialkylantimony complex $[Et_4N][MeEtSb\{Fe(CO)_4\}_2]$ (**9**) also can be synthesized from the reaction of **2** with EtI. While the reaction with $Br(CH_2)_2Br$ produces $[Et_4N]_2[BrSb\{Fe(CO)_4\}_3]$ (**10**), treatment with $Cl(CH_2)_3Br$ forms the monoalkylated product $[Et_4N]_2[Cl(CH_2)_3Sb\{Fe(CO)_4\}_3]$ (**11**) and a dialkylated novel antimony−iron complex $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**). On the other hand, the reaction with $Br(CH_2)_4Br$ forms the monoalkylated antimony product and the dialkylated antimony complex $[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$ (**13**). Complexes **2**−**13** are characterized by spectroscopic methods or/and X-ray analyses. On the basis of these analyses, the core of the monoalkyl clusters consists of a central antimony atom tetrahedrally bonded to one alkyl group and three $Fe(CO)_4$ fragments and the dialkyl products are structurally similar to the monoalkyl clusters, with the central antimony bonded to two alkyl groups and two $Fe(CO)_4$ moieties in each case. The dialkyl complex **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.014(8)$ Å, $b = 11.527(8)$ Å, $c = 17.085(5)$ Å, $\beta = 105.04(3)°$, $V = 2475(2)$ Å^3, and $Z = 4$. Crystals of **12** are orthorhombic, of space group *Pbca*, with $a = 14.791(4)$ Å, $b = 15.555(4)$ Å, $c = 27.118(8)$ Å, $V = 6239(3)$ Å^3, and $Z = 8$. The anion of cluster **12** exhibits a central antimony atom bonded to three $Fe(CO)_4$ fragments with a $-(CH_2)_3-$ group bridging between the Sb atom and one $Fe(CO)_4$ fragment. This paper discusses the details of the reactions of $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ with a series of alkyl halides and dihalides. These reactions basically proceed via a novel double-alkylation pathway, and this facile methodology can as well provide a convenient route to a series of alkylated antimony−iron carbonyl clusters.

Introduction

Main group−transition metal carbonyl clusters attract extensive attention because of their interesting bonding modes and reactivity patterns.[1] The role of the main group elements has been increasingly probed because of their significant influence on the reactivity of the mixed main group−transition metal clusters. Regarding the effects of main group elements in the catalysts,[2] it is of great importance to understand how the main group element affects the interaction of main group−transition metal clusters with organic substrates.

The alkylation at the main group centers has been observed for group-16-element-containing complexes such as $[S_2Fe_2(CO)_6]^{2-}$,[3] $[S_2Fe_2(NO)_4]^{2-}$,[4] $[Te_6Fe_8(CO)_{24}]^{2-}$,[5] and $[Se_6Fe_6(CO)_{12}]^{2-}$.[6] The recent study of the reactivity of the group-15-element-containing cluster $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ toward a series of alkyl halides shows that bismuth alkyl products of the type $[RBi\{Fe(CO)_4\}_3]^{2-}$ are isolated from the reactions.[7] These alkylations clearly demonstrate that the main group elements are active toward the incoming organo ligands. Nevertheless, the effects of the main group elements of the mixed main group−transition metal carbonyl clusters on the alkylation reactions have been little explored. To study this aspect, we investigate the alkylation reactions of the lighter analog $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ (**1**)[8] with a series of alkyl halides and dihalides.

---

* To whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

(1) For recent reviews of transition-metal/main-group compounds, see: (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (b) Vaira, M. D.; Stoppioni, P.; Peruzzini, M. *Polyhedron* **1987**, *6*, 351. (c) Scherer, O. J. *Comments Inorg. Chem.* **1987**, *6*, 1. (d) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924. (e) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95. (f) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Ed. Engl.* **1987**, *26*, 743. (g) Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406. (h) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (i) Scherer, O. J. *Angew. Chem.* **1990**, *102*, 1137. (j) Cowley, A. H. *J. Organomet. Chem.* **1990**, *400*, 71. (k) Dimaio, A.-J.; Rheingold, A. L. *Chem. Rev.* **1990**, *90*, 169. (l) Whitmire, K. H. *J. Cluster Sci.* **1991**, *2*, 231. (m) Shriver, D. F.; Kasez, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Complexes*; VCH Publishers: New York, 1990.

(2) (a) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133. (b) Grasselli, R. K. *J. Chem. Educ.* **1986**, *63*, 216. (c) Sposito, G. *The Surface Chemistry of Soil*; Oxford University Press: New York, 1984.

(3) (a) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(4) (a) Seyferth, D.; Gallagher, M. K.; Cowie, M. *Organometallics* **1986**, *5*, 539. (b) Seyferth, D.; Gallagher, M. K. *J. Organomet. Chem.* **1981**, *218*, C5.

(5) (a) Shieh, M.; Shieh, M.-H. *Organometallics* **1994**, *13*, 920. (b) Shieh, M.; Chen, P.-F.; Tsai, Y.-C.; Shieh, M.-H.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1995**, *34*, 2251.

(6) Shieh, M.; Shieh, M.-H. Unpublished results.

(7) (a) Shieh, M.; Liou, Y.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1993**, *32*, 2212. (b) Shieh, M.; Liou, Y.; Jeng, B.-W. *Organometallics* **1993**, *12*, 4926.

(8) Luo, S.; Whitmire, K. H. *Inorg. Chem.* **1989**, *28*, 1424.

S0020-1669(95)01339-5 CCC: $12.00

The reactions of **1** with alkyl halides mainly proceed through a double-alkylation mechanism to form the alkylated antimony complexes of the type $[Et_4N]_2[RSb\{Fe(CO)_4\}_3]$ and the dialkylated antimony complexes $[Et_4N][R_2Sb\{Fe(CO)_4\}_2]$. In addition, a novel dialkylated antimony−iron complex $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**) is obtained from the reaction with $Cl(CH_2)_3Br$.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[9] Solvents were purified, dried, and distilled under nitrogen prior to use. The compound $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ (**1**) was prepared according to the published method.[8] Infrared spectra were recorded on a JASCO 5300 IR spectrometer for solutions in CaF_2 cells. ESI mass spectra were obtained on a Fision (VG platform) mass spectrometer. ^{1}H NMR spectra were taken on a JEOL 400 (400 MHz) instrument. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

Reaction of 1 with MeI. To a solution of 1.60 g (1.35 mmol) of **1** in 20 mL of MeCN was added 1.80 mL (28.9 mmol) of MeI. The resulting solution was stirred in an ice/water bath for 20 min to give a reddish-brown solution. The latter was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and ether and then extracted with THF. The product in the THF extract was recrystallized with CH_2Cl_2/MeOH to give 1.00 g (1.11 mmol) of $[Et_4N]_2[MeSb\{Fe(CO)_4\}_3]$ (**2**) (82% based on Sb). IR (ν_{CO}, CH_2Cl_2): 2017 w, 1986 s, 1901 vs, br cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 1.71 (s) (chemical shifts not given for $[Et_4N]^+$). Negative ion *m*/*z* (FABMS): 640. Anal. Calcd for $[Et_4N]_2[MeSb\{Fe(CO)_4\}_3]$: C, 38.66; H, 4.81; N, 3.11. Found: C, 37.10; H, 4.54; N, 2.95.

In a similar procedure, 0.50 g (0.42 mmol) of **1** and 0.56 mL (9.0 mmol) of MeI in 20 mL of MeCN were stirred at room temperature for 4.5 h to give a brown solution. The solution was filtered and solvent was removed under vacuum. The residue was washed with hexanes and extracted with ether to give 0.15 g (0.24 mmol) of $[Et_4N][Me_2Sb\{Fe(CO)_4\}_2]$ (**3**) (57% based on Sb). Crystals suitable for X-ray analysis were grown from ether solution. IR (ν_{CO}, ether): 2027 w, 2004 s, 1915 vs, br cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 1.36 (s) (chemical shifts not given for $[Et_4N]^+$). Negative ion *m*/*z* (ESIMS): 487. Anal. Calcd for $[Et_4N][Me_2Sb\{Fe(CO)_4\}_2]$: C, 34.99; H, 4.24; N, 2.27. Found: C, 35.02; H, 4.21; N, 2.31.

In a similar reaction, a mixture of 1.00 g (0.84 mmol) of **1** with 1.12 mL (18.0 mmol) of MeI in 20 mL of MeCN stirred at room temperature for 10 min gave 0.15 g (0.24 mmol) of **3** (29% based on Sb) and 0.15 g (0.17 mmol) of **2** (20% based on Sb).

Reaction of 1 with EtI. To a solution of 0.80 g (0.68 mmol) of **1** in 20 mL of MeCN was added 0.64 mL (7.92 mmol) of EtI. The resulting solution was stirred at room temperature for 6 days to give a reddish-brown solution. The latter was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with ether to give 0.14 g (0.22 mmol) of $[Et_4N][Et_2Sb\{Fe(CO)_4\}_2]$ (**5**) (32% based on Sb). IR (ν_{CO}, ether): 2025 w, 2002 s, 1925 vs, 1911 vs cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 1.89 (q, 4H, $J = 7.9$ Hz), 1.28 (t, 6H, $J = 7.9$ Hz) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N][Et_2Sb\{Fe(CO)_4\}_2]$: C, 37.19; H, 4.69; N, 2.17. Found: C, 36.80; H, 4.65; N, 2.19. The residue was then extracted with THF, and product in the THF extract was recrystallized with THF/ether/hexane and then with CH_2Cl_2/MeOH to give 0.35 g (0.38 mmol) of $[Et_4N]_2[EtSb\{Fe(CO)_4\}_3]$ (**4**) (56% based on Sb). IR (νCO, MeCN): 2017 w, 1984 s, 1898 vs cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 2.32 (q, 2H, $J = 7.3$ Hz), 1.42 (t, 3H, $J = 7.3$ Hz) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N]_2[EtSb\{Fe(CO)_4\}_3]$: C, 39.38; H, 4.96; N, 3.06. Found: C, 39.13; H, 4.93; N, 3.04.

Reaction of 1 with *n*-PrI. To a solution of 0.80 g (0.68 mmol) of **1** in 25 mL of MeCN was added 0.80 mL (8.0 mmol) of *n*-PrI. The mixed solution was stirred at room temperature for 36 h to give a reddish-brown solution, which was then filtered. The solvent was removed under vacuum, and $Fe(CO)_5$ was collected and detected by IR. The residue was washed with hexane and ether and extracted with CH_2Cl_2. The product in the CH_2Cl_2 extract was recrystallized with CH_2Cl_2/MeOH to give 0.57 g (0.61 mmol) of $[Et_4N]_2[n\text{-}PrSb\{Fe(CO)_4\}_3]$ (**6**) (90% based on Sb). IR (ν_{CO}, MeCN): 2015 w, 1984 s, 1898 vs, br cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 2.31 (t, 2H, $J = 8.5$ Hz), 1.84 (m, 2H), 0.91 (t, 3H, $J = 7.3$ Hz) (chemical shifts not given for $[Et_4N]^+$). Negative ion *m*/*z* (FABMS): 668. Anal. Calcd for $[Et_4N]_2[n\text{-}PrSb\{Fe(CO)_4\}_3]$: C, 40.06; H, 5.10; N, 3.02. Found: C, 38.30; H, 4.95; N, 2.99.

In a similar procedure, the reaction mixture was refluxed overnight and the residue was extracted into ether. IR (ν_{CO}, ether): 2025 w, 2002 s, 1921 vs, br cm^{-1}. The IR spectrum of the ether extract showed it to contain $[Et_4N][(n\text{-}Pr)_2Sb\{Fe(CO)_4\}_2]$ (**7**). However, this product formed an oil and further characterization was difficult.

Reaction of 1 with *i*-PrI. To a solution of 0.84 g (0.71 mmol) of **1** in 20 mL of MeCN was added 1.00 mL (10.0 mmol) of *i*-PrI. The mixed solution was stirred at room temperature for 22 h to give a reddish-brown solution, which was then filtered, and the solvent was removed under vacuum. The residue was washed with hexane and ether and extracted with THF. The product in the THF extract was recrystallized with hexane/ether/THF and then with CH_2Cl_2/MeOH to give 0.35 g (0.38 mmol) of $[Et_4N]_2[i\text{-}PrSb\{Fe(CO)_4\}_3]$ (**8**) (54% based on Sb). IR (νCO, MeCN): 2027 w, 1994 s, 1911 s cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 2.80 (m, 1H), 1.51 (d, 6H, $J = 6.8$ Hz) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N]_2[i\text{-}PrSb\{Fe(CO)_4\}_3]$: C, 40.06; H, 5.10; N, 3.02. Found: C, 39.19; H, 4.80; N, 2.87.

Reaction of 2 with EtI. To a solution of 0.91 g (1.0 mmol) of **2** in 20 mL of MeCN was added 0.87 mL (11 mmol) of EtI. The mixed solution was stirred and heated at 45 °C for 54 h to give a reddish-brown solution, which was then filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with ether. The ether extract was cooled at −20 °C to give 0.52 g (0.82 mmol) of $[Et_4N][MeEtSb\{Fe(CO)_4\}_2]$ (**9**) (81% based on Sb). IR (ν_{CO}, MeCN): 2027 w, 2004 s, 1913 vs, br cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 1.89 (q, 2H, $J = 6.8$ Hz), 1.29 (m, 6H) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N][MeEtSb\{Fe(CO)_4\}_2]$: C, 36.12; H, 4.47; N, 2.22. Found: C, 36.21; H, 4.34; N, 2.13.

Reaction of 1 with $Br(CH_2)_2Br$. To a solution of 0.50 g (0.42 mmol) of **1** in 20 mL of MeCN was added 0.11 mL (1.3 mmol) of $Br(CH_2)_2Br$. The mixed solution was stirred at room temperature for 30 h to give a reddish-brown solution, which was then filtered, and the solvent was removed under vacuum. The residue was washed with hexane and ether and extracted with THF. The product in the THF extract was recrystallized with hexane/ether/THF and then with MeOH at −20 °C to give 0.31 g (0.32 mmol) of $[Et_4N]_2[BrSb\{Fe(CO)_4\}_3]$ (**10**) (76% based on Sb). IR (ν_{CO}, DMSO-d_6): 1990 s, 1913 vs cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 3.19 (q, 16 H, $J = 7.3$ Hz), 1.15 (t, 24H, $J = 7.3$ Hz). Anal. Calcd for $[Et_4N]_2[BrSb\{Fe(CO)_4\}_3]$: C, 34.82; H, 4.17; N, 2.90. Found: C, 35.05; H, 4.13; N, 2.90.

Reaction of 1 with $Cl(CH_2)_3Br$. To a solution of 1.0 g (0.84 mmol) of **1** in 20 mL of MeCN was added 0.25 mL (2.53 mmol) of $Cl(CH_2)_3Br$. The resulting solution was stirred and heated at 45 °C for 42 h to give a reddish-brown solution. The latter was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with ether to give 0.06 g (0.08 mmol) of $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**) (10% based on Sb). The crystals of **12** suitable for X-ray analysis were grown from ether solution. IR (ν_{CO}, MeCN): 2087 w, 2019 s, 2004 sh, 1915 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.99 (2H, t, $J = 5.8$ Hz), 2.68 (4H, m) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$: C, 34.63; H, 3.29; N, 1.76. Found: C, 34.42; H, 3.32; N, 1.79. The residue was then extracted with THF, and the THF extract was recrystallized with THF/ether/hexane and then with ether/MeOH to give 0.63 g (0.65 mmol) of $[Et_4N]_2[Cl(CH_2)_3Sb\{Fe(CO)_4\}_3]$ (**11**) (78% based on Sb). IR (ν_{CO}, MeCN): 2017 w, 1986 s, 1901 vs cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 3.55 (t, 2H, $J = 6.4$ Hz), 2.29 (m, 4H) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N]_2[Cl(CH_2)_3Sb\{Fe(CO)_4\}_3]$: C, 38.65; H, 4.81; N, 2.91. Found: C, 36.69; H, 4.71; N, 2.92.

---

(9) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986.

Table 1. Crystallographic Data for $[Et_4N][Me_2Sb\{Fe(CO))_4\}_2]$ (**3**) and $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**)

	3	**12**
empirical formula	$SbFe_2C_{18}H_{26}O_8N$	$SbFe_3C_{23}H_{26}O_{12}N$
fw	617.85	797.74
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbca*
a, Å	13.014(8)	14.791(4)
b, Å	11.527(8)	15.555(4)
c, Å	17.085(5)	27.118(8)
β, deg	105.04(3)	
V, Å^3	2475(2)	6239(3)
Z	4	8
D(calc), Mg m^{-3}	1.658	1.699
abs coeff, cm^{-1}	22.86	22.848
diffractometer	Nonius (CAD-4)	Nonius (CAD-4)
radiation, λ(Mo Kα), Å	0.7107	0.7107
temp, °C	25	25
T_{min}/T_{max}	0.71/1.00	0.77/1.00
residuals: R, R_w[a]	0.044, 0.045	0.055, 0.058

[a] The functions minimized during least squares cycles were $R = \Sigma|F_o - F_c|/\Sigma F_o$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Reaction of 1 with $Br(CH_2)_4Br$. To a solution of 1.00 g (0.84 mmol) of **1** in 20 mL of MeCN was added 0.30 mL (2.5 mmol) of $Br(CH_2)_4Br$. The resulting solution was stirred and heated at 55 °C for 70 h to give a reddish-brown solution. The latter was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with ether to give 0.11 g (0.17 mmol) of $[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$ (**13**) (20% based on Sb). IR (ν_{CO}, CH_2Cl_2): 2025 w, 2002 s, 1913 s, br cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 298 K): δ 1.81 (4H, m), 2.15 (4H, t, $J = 5.4$ Hz) (chemical shifts not given for $[Et_4N]^+$). Anal. Calcd for $[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$: C, 37.31; H, 4.38; N, 2.18. Found: C, 37.34; H, 4.42; N, 2.08. The residue was then extracted with THF to give about 0.50 g (0.49 mmol) of $[Et_4N]_2[Br(CH_2)_4Sb\{Fe(CO)_4\}_3]$ (58% based on Sb). IR (νCO, THF): 1990 s, 1913 s, br cm^{-1}. This compound formed an oil, and further characterization was not carried out.

X-ray Structural Characterization of Complexes 3 and 12. A summary of selected crystallographic data for **3** and **12** is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 25 °C. All crystals were mounted on glass fibers with epoxy cement. Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,[10] and atomic scattering factors were taken from ref 11.

Structures of 3 and 12. The deep brown crystal of **3** chosen for diffraction measurements was ca. 0.20 × 0.50 × 0.50 mm, and the deep brown crystal of **12** had dimensions 0.20 × 0.40 × 0.50 mm. Cell parameters were obtained from 25 reflections with 2θ in the ranges 16.12−28.46° for **3** and 15.46−23.00° for **12**. A total of 3286 reflections with $I > 2.0\sigma(I)$ for **3** (1626 reflections with $I > 2.0\sigma(I)$ for **12**) were used in the refinement. The structures were solved by the heavy-atom method and refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement led to convergence with $R = 4.4\%$ and $R_w = 4.5\%$ for **3** and with $R = 5.5\%$ and $R_w = 5.8\%$ for **12**.

The selected distances and angles of **3** and **12** are given in Tables 2 and 3, respectively. Additional crystallographic data for **3** and **12** and the crystallographic data for **2**, **9**, **10**, and **13** are available as supporting information.

Results

Reactions with MeI, EtI, *n*-PrI, and *i*-PrI. The alkylation products $[Et_4N]_2[MeSb\{Fe(CO)_4\}_3]$ (**2**) and $[Et_4N][Me_2Sb\{Fe(CO)_4\}_2]$ (**3**) are produced in almost equal amounts from the reaction of $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ (**1**) with an excess of MeI in MeCN at room temperature for 10 min. Under milder conditions, the monoalkyl derivative **2** is produced as the only product from the reaction with MeI. When monitored by infrared spectroscopy, the reaction proceeds to form cluster **2** first, and continued stirring gives the dialkyl complex **3**. It clearly indicates that the dialkyl cluster **3** results from the further alkylation of the alkyl complex **2**. In support, we found that **2** reacts readily with MeI to form **3**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][Me_2Sb\{Fe(CO)_4\}_2]$ (**3**)

(A) Distances			
Sb−Fe(1)	2.522(2)	Sb−Fe(2)	2.538(1)
Sb−C(9)	2.150(7)	Sb−C(10)	2.142(6)
(B) Angles			
Fe(1)−Sb−Fe(2)	123.95(4)	Fe(1)−Sb−C(9)	106.0(2)
Fe(2)−Sb−C(9)	110.1(2)	Fe(2)−Sb−C(10)	107.1(2)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**)

(A) Distances			
Sb−Fe(1)	2.671(3)	Sb−Fe(2)	2.585(3)
Sb−Fe(3)	2.595(4)	Sb−C(13)	2.12(2)
(B) Angles			
Fe(1)−Sb−Fe(2)	114.8(1)	Fe(1)−Sb−Fe(3)	115.2(1)
Fe(1)−Sb−C(13)	93.5(8)	Fe(2)−Sb−Fe(3)	115.0(1)
Fe(2)−Sb−C(13)	109.8(6)	Fe(3)−Sb−C(13)	105.7(7)

As the reactivity of the reagent decreases, the reaction proceeds in a similar manner but under an elevated temperature. The reaction with EtI forms the monoalkylated complex $[Et_4N]_2[EtSb\{Fe(CO)_4\}_3]$ (**4**) and the dialkylated product $[Et_4N][Et_2Sb\{Fe(CO)_4\}_2]$ (**5**). Similarly, the treatment with *n*-PrI forms $[Et_4N]_2[n\text{-}PrSb\{Fe(CO)_4\}_3]$ (**6**) and an undentified species proposed to be $[Et_4N][(n\text{-}Pr)_2Sb\{Fe(CO)_4\}_2]$ (**7**) on the basis of its IR spectrum. As expected, only the monoalkylated cluster $[Et_4N]_2[i\text{-}PrSb\{Fe(CO)_4\}_3]$ (**8**) is produced in the reaction with *i*-PrI and no dialkylated product is observed because of the steric effect.

Synthesis of the Mixed Dialkylantimony Cluster. Noteworthy is that different alkyl groups can be introduced into **1**. The synthesis of dialkyl complexes of the type $[RR'Sb\{Fe(CO)_4\}_2]^-$ can be accomplished under suitable conditions. We have successfully isolated a mixed dialkylantimony complex $[Et_4N][MeEtSb\{Fe(CO)_4\}_2]$ (**9**) by treatment of the methylantimony cluster **2** with EtI. However, when the ethylantimony cluster **4** reacted with MeI, a mixture of **9** and the oxidized products was obtained. It is believed that MeI acts not only as an alkylation agent but also as an oxidizing agent in the latter case due to the reactive nature of MeI and the steric hindrance of the Et group in cluster **4**. The less steric effect of the methyl group in complex **2** compared to the incoming agent EtI favors the formation of cluster **9**. Other mixed dialkylated antimony clusters also can be designed and synthesized along these lines.

Reactions with $Br(CH_2)_2Br$, $Cl(CH_2)_3Br$, and $Br(CH_2)_4Br$. The extended reactions with dihalides were also investigated. The reaction with $Br(CH_2)_2Br$ forms a bromoantimony complex $[Et_4N]_2[BrSb\{Fe(CO)_4\}_3]$ (**10**). Notably, the treatment with $Cl(CH_2)_3Br$ forms the monoalkylated product $[Et_4N][Cl(CH_2)_3Sb\{Fe(CO)_4\}_3]$ (**11**) and a novel antimony−iron dialkylated complex $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**). The formation of **12** indicates that the alkylation of **1** with $Cl(CH_2)_3Br$ occurs at both the central antimony and one iron center. On the other hand, the reaction with $Br(CH_2)_4Br$ forms the monoalkylated antimony product and the dialkylated antimony complex $[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$ (**13**). Cluster **13** results from the double alkylation at the central antimony.

The reactions of **1** with alkyl halides and dihalides are summarized in Scheme 1.

---

(10) Gabe, E. J.; Lepage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(11) *International Tables for X-ray Crystallography*; Kynoch press: Birmingham, England, 1974; Vol. IV.

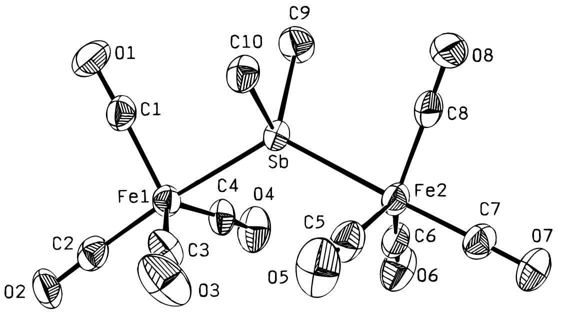
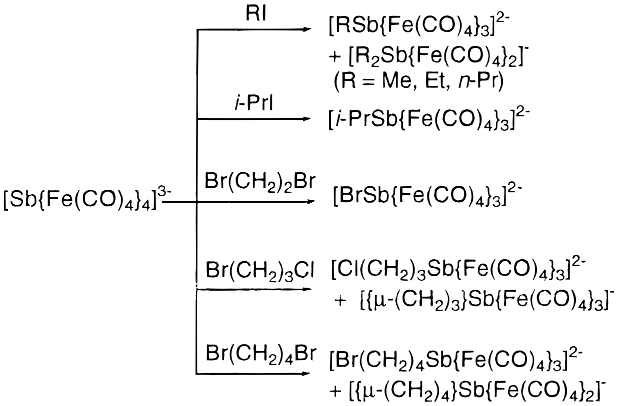


Figure 1. ORTEP diagram showing the structure and atom labeling for the anion of **3**.

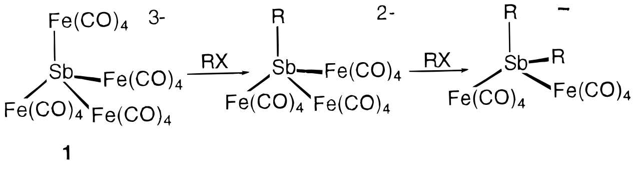
Scheme 1



Structures of 2−13. Clusters **2**−**13** are characterized by spectroscopic methods and/or X-ray analysis. On the basis of the spectroscopic data and X-ray analyses, the dianions of the monoalkylated clusters **2**, **4**, **6**, **8**, and **11** are isostructural species and each bears a central antimony tetrahedrally coordinated to one alkyl group and three $Fe(CO)_4$ groups; the dialkylated clusters **3** (Figure 1), **5**, **7**, and **9** are structurally similar to the monoalkylated cluster except that one $Fe(CO)_4$ fragment is further replaced by another alkyl group in each case. The dianion of cluster **10** is isostructural with that of cluster **2** with the central antimony bonded to one Br and three $Fe(CO)_4$ groups. Cluster **13** is a dialkylated product in which the antimony atom and the $-(CH_2)_4-$ fragment form a cyclic ring with the Sb atom bonded to two $Fe(CO)_4$ moieties. The metal core of the novel dialkylated cluster **12** consists of the central antimony and one $Fe(CO)_4$ bridged by a $-(CH_2)_3-$ group, and the coordination of the Sb atom is completed by bonding to the other two $Fe(CO)_4$ fragments (Figure 2).

Discussion

Alkylations of 1 with Alkyl Halides. Our results show that the reactions of **1** with alkyl halides basically undergo a two-step alkylation to give the monoalkylated products of the type $[Et_4N]_2[RSb\{Fe(CO)_4\}_3]$ and the dialkylated antimony clusters $[Et_4N][R_2Sb\{Fe(CO)_4\}_2]$. The alkylation of **1** can be considered to occur via substitution of the $Fe(CO)_4$ moiety with the incoming alkyl group in two successive processes. This reactivity pattern represents an unprecedented reaction type in the heavier group-15-element-containing metal carbonyl chemistry and can be compared to that found for the bismuth system. In the bismuth case, only the monoalkylated products $[RBi\{Fe(CO)_4\}_3]^{2-}$ were isolated in the analogous alkylations and no dialkylated bismuth complexes were observed.[7] The greater thermal stability for the dialkylantimony clusters of the type $[R_2Sb\{Fe(CO)_4\}_2]^-$ may be ascribed to the increased basicity of the antimony and the stronger antimony−carbon bond.



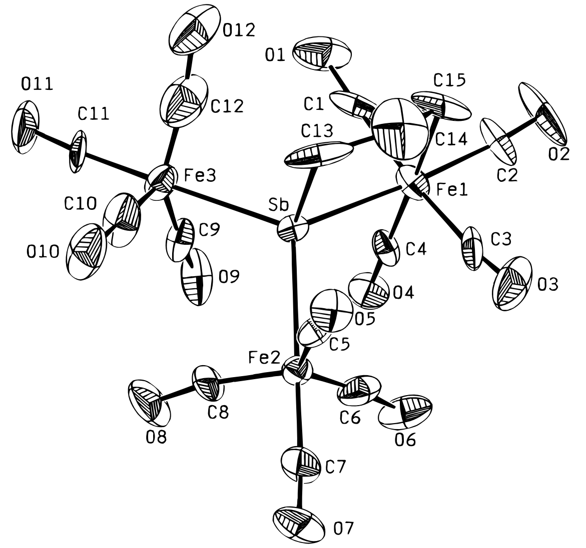
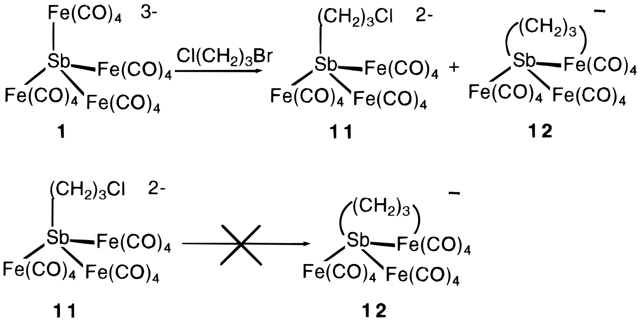


Figure 2. ORTEP diagram showing the structure and atom labeling for the anion of **12**.

Alkylations of 1 with Dihalides. Some unexpected outcomes were found in the reactions with dihalides. Instead of the alkylated products, the reaction with $Br(CH_2)_2Br$ produces the bromoantimony $[Et_4N]_2[BrSb\{Fe(CO)_4\}_3]$ (**10**) probably due to the reactive nature of $Br(CH_2)_2Br$. Cluster **10** may be considered as a result of substitution of $Fe(CO)_4$ by Br. In the analogous bismuth system, the oxidized product is found in the reaction with $Br(CH_2)_2Br$.[7b] Cluster **10** decomposes slowly in the solution to form the known cluster $[Sb_2Fe_6(CO)_{20}]^{2-}$,[12] owing to the weak bond between Sb and Br.

Of particular interest, the treatment with $Cl(CH_2)_3Br$ forms the monoalkylated product **11** and a novel dialkylated complex $[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**), in which the $-(CH_2)_3-$ group bridges between the Sb and Fe atoms, as a result of dialkylation at the central Sb and one Fe atom. The absence of the dialkylated antimony product containing an SbC_3 cyclic ring may be attributed to the high strained energy of the four-membered ring. It is curious to know if cluster **12** arises from the further alkylation of **11**. However, refluxing cluster **11**, premade, in acetonitrile does not form the novel cluster **12**, which rules out the formation of cluster **12** from the alkylation of **11** at the iron center. Upon alkylation with $Cl(CH_2)_3Cl$, only the monoalkylated complex **11** was isolated with no observation of cluster **12**, and the reaction with $Br(CH_2)_3Br$ leads to the



---

(12) Luo, S.; Whitmire, K. H. *J. Organomet. Chem.* **1989**, *376*, 297.

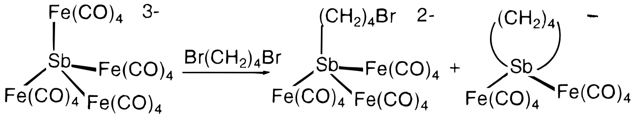
Table 4. Comparison of the Average Fe−Sb−Fe Angles and the Average Sb−Fe and Sb−C Distances in Related Clusters

complex	Fe−Sb−Fe, deg	Sb−Fe, Å	Sb−C, Å
$[Sb\{Fe(CO)_4\}_4]^{3-}$ (**1**)[8]	109.56	2.666	
$[Et_4N]_2[MeSb\{Fe(CO)_4\}_3]$ (**2**)[a]	114.43	2.614	2.160(7)
$[Et_4N][Me_2Sb\{Fe(CO)_4\}_2]$ (**3**)[a]	123.95	2.53	2.146
$[Et_4N][MeEtSb\{Fe(CO)_4\}_2]$ (**9**)[a]	120.8	2.545	2.22
$[Et_4N][\{\mu\text{-}(CH_2)_3\}Sb\{Fe(CO)_4\}_3]$ (**12**)[a]	115.0	2.617	2.12(2)
$[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$ (**13**)[a]	120.08	2.542	2.160

[a] This work; the detailed crystallographic data for **2**, **9**, and **13** are provided in the Supporting Information.

formation of the sole product **10**. The results indicate that the reactivity of dihalides plays an important role in the formation of **12**. However, the detailed mechanism is not very clear, and further investigation may be worthwhile.

To compare the stability of the five-membered ring SbC_4 and the six-membered ring $SbFeC_4$, we conducted the reaction with $Br(CH_2)_4Br$ in refluxing MeCN. The reaction only yields the monoalkylated antimony product and the dialkylated antimony complex $[Et_4N][\{\mu\text{-}(CH_2)_4\}Sb\{Fe(CO)_4\}_2]$ (**13**), suggesting the better stability of the SbC_4 ring than of the $SbFeC_4$ ring under this condition.



1 **13**

Structures of Complexes 2, 3, 9 10, 12, and 13. The antimony atoms in the clusters **2**, **3**, **9**, **10**, **12**, and **13** are all in distorted tetrahedral environments. For comparison, the average Fe−Sb−Fe angle, the Sb−Fe distance, and the Sb−C length in these tetrahedral clusters and the related cluster **1** are listed in Table 4. The Sb−C distances in **2** (2.16 Å), **3** (2.15 Å, average), **12** (2.12 Å), and **13** (2.16 Å, average) are close to the sum of single-bond covalent radii (2.2 Å),[13] and the longer Sb−C(9) length (2.34 Å) for **9** is probably due to the repulsion between the Me and Et groups. As shown, the average Fe−Sb−Fe angle becomes larger and the Sb−Fe distance becomes shorter as the number of the alkyl groups increases (i.e., the number of the $Fe(CO)_4$ groups decreases) attributable to the steric hindrance of the $Fe(CO)_4$ fragments. The Sb−Fe distances in these clusters fall in the range of other known Sb−$Fe(CO)_4$ distances (2.460−2.715 Å)[8,14,15] and are compared to those found in other structurally characterized antimony complexes such as $[ClSb\{Fe(CO)_2Cp\}_3]_2^{2+}$ (2.539 Å, average)[16] and $[Cl_2Sb\{Fe(CO)_2Cp\}_2]^+$ (2.440 Å, average).[17]

The dianion of complex **10** is isostructural with the previously reported chloroantimony clusters $[ClE\{Fe(CO)_4\}_3]^{2-}$ (E = Sb, Bi).[8,18] The bond distance of Sb(a)−Br(a) is 2.606 (3) Å, which is normal.[13] The average Fe−Sb(a)−Fe angle in **10** (115.07°) is a bit smaller than that in the analogous complex $[ClSb\{Fe(CO)_4\}_3]^{2-}$ (115.35°)[8] due to the larger size of Br. Cluster **12** represents an unprecedented bonding mode in the mixed group 15 element−iron carbonyl clusters. In **12**, the Sb and Fe atoms are linked by a $-(CH_2)_3-$ group to form a five-membered $SbFeC_3$ ring. The average Fe−Sb−Fe angle in **12** is close to that of **2**, indicative of the little influence of the ring on the Fe−Sb−Fe tetrahedral angles. While the Sb−Fe distance in **2** is about the same, in **12** the Sb−Fe(1) bond distance, the one involving the alkyl bridge, is longer than the other Sb−Fe bonds because of the effect of the ring. The C(13)−Sb−Fe(1) angle is 93.5 (8)°, which deviates greatly from the tetrahedral angle to fit the requirement of formation of the $SbFeC_3$ ring.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 85-2113-M-003-003).

Supporting Information Available: Listings of complete crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for **2**, **3**, **9**, **10**, **12**, and **13** (39 pages). Ordering information is given on any current masthead page.

IC9513393

---

(13) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper Collins College Publishers: New York, 1993.

(14) (a) Cowley, A. H.; Norman, N. C.; Pakulski, M.; Bricker, D. L.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 8211. (b) Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 622.

(15) (a) Luo, S.; Whitmire, K. H. *J. Organomet. Chem.* **1989**, *376*, 297. (b) Whitmire, K. H.; Leigh, J. S.; Luo, S.; Shieh, M.; Fabiano, M. D. *New J. Chem.* **1988**, *12*, 397. (c) Rheingold, A. L.; Gieb, S. J.; Shieh, M.; Whitmire, K. H. *Inorg. Chem.* **1987**, *26*, 463.

(16) Trinh-Toan; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 2654.

(17) Einstein, F. W. B.; Jones, R. D. G. *Inorg. Chem.* **1973**, *12*, 1690.

(18) Ferrer, M.; Rossell, O.; Seco, M.; Braunstein, P. *J. Organomet. Chem.* **1989**, *364*, C5.