similarity in structure is also reflected in ^{15}N chemical shift; $HFeRu_3{}^{15}N(CO)_{12}$[17] and $Ph_3PAuFeRu_3{}^{15}N(CO)_{12}$ resonate at 530.9 and 533.0 ppm, respectively, a difference in chemical shift of only 2.1 ppm. The shifts of the two gold homonuclear clusters are also approximately 2 ppm downfield from the corresponding hydrides. These facts along with the IR data suggest the gold is also bridging the hinge M–M bonds in $Ph_3PAuFe_4N(CO)_{12}$ and $Ph_3PAuRu_4N(CO)_{12}$.

Removal of the Gold Phosphine Group. The three new compounds were reacted with $PPN(NO_2)$ in an attempt to synthesize new nitrido–nitrosyl clusters. We found, however, that reaction occurred immediately, not only wth $PPN(NO_2)$, but also with PPNCl, to remove the Ph_3PAu group from the cluster. Such reactivity is not unprecedented, as $[HBEt_3]^-$ and I^- have been used as a nucleophilic reagent to remove the gold ligand from other carbonyl clusters.[9]

Acknowledgment. This research was supported by a grant from the National Science Foundation (No. CHE-8410999).

Supplementary Material Available: Tables of isotropic and anisotropic thermal parameters and complete distances and angles (8 pages); calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry,
University of Delaware, Newark, Delaware 19716,
and Rice University, Houston, Texas 77251

Synthesis and Characterization of a Double-Spiro μ_4-Antimony Metal Carbonyl Complex, $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$

Arnold L. Rheingold,*[†] Steven J. Geib,[†] Minghuey Shieh,[‡] and Kenton H. Whitmire*[‡]

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Examples of clusters containing single "bare" or "naked" group 15 atoms (E) bridging transition-metal atoms have recently become more numerous.[1] However, the number of structurally confirmed examples in which the E atom links four or more metal atoms remains small. Examples include μ_4-spiro complexes $[Fe_2(CO)_8EFe_2(CO)_6Cl]$, E = P or As,[2] $[Co_4(\eta^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]BF_4$,[3] one μ_6-As structure, $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$,[4] and a few examples of partial[5] or complete encapsulation.[6] The isolobal analogy between E and CH makes understandable the more common μ_3-E, triangular-face capping properties of E atoms.[7]

Except for the encapsulated Sb atom in $[Rh_{12}Sb(CO)_{27}]^{3-}$,[6] no clusters containing four or more metal atoms linked by an Sb atom are known. In fact antimony atom clusters of any type are extremely rare; the only previously reported cluster is $Sb_2[W(CO)_5]_3$.[8] We now report the synthesis and characterization of $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (1) containing two spirolike μ_4-Sb(Fe_4) linkages.

Experimental Section

Synthesis of $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (1). Compound 1 was obtained by first treating 6.14 g of $[Et_4N]_2[Fe_2(CO)_8]$[9] (10.3 mmol) with 1.55 g of $SbCl_3$[10] (6.8 mmol) in dried acetone. This yielded a reddish brown solution, which was filtered and treated with 4.31 g of $[Cu(CH_3CN)_4][BF_4]$.[11] After being stirred overnight, the dark brown solution was filtered to remove precipitated copper and the solvent removed under vacuum. The solid residue was extracted into CH_2Cl_2/toluene (1:3) and chromatographed on Florisil by eluting with toluene to give brown $Sb_2Fe_6(CO)_{22}$ (1) in 8.5% yield. 1 is insoluble in hexane but soluble in most common organic solvents. IR (ν_{CO}, CH_2Cl_2): 2110 sh, 2090 m, 2060 m, 2038 s, 1995 w, 1960 w cm^{-1}. Mp: 232–233 °C dec.

Table I. Crystal Data Collection and Refinement Data for $Sb_2Fe_6(CO)_{22}$

(a) Crystal Parameters

formula	$C_{22}Fe_6O_{22}Sb_2$	Z	8
cryst system	orthorhombic	D(calcd), g cm^{-3}	2.27
space group	*Pbca*	μ, cm^{-1} (Mo Kα)	41.0
a, Å	18.016 (3)[a]	cryst size, mm	0.21 × 0.21 × 0.38
b, Å	16.414 (4)	color	deep red
c, Å	23.672 (6)	temp, °C	23
V, Å^3	7000 (3)		

(b) Data Collection

diffractometer	Nicolet R3m/μ	data collected	$+h,+k,+l$
radiation	Mo Kα (λ = 0.71073 Å)	rflns collected	6113
		obsd rflns ($F_o \geq 4\sigma(F_o)$)	3949
monochromator	graphite	std rflns	3 std/97 rflns
scan method	omega	decay	<1%
2θ scan limits, deg	$4 \leq 2\theta \leq 48$	T_{max}/T_{min}	0.288/0.210
scan speed, deg min^{-1}	var, 5–20		

(c) Refinement

R_F/R_{wF}, %	3.84/4.03	Δ/σ	0.075
g[b]	0.001	$\Delta\rho$(max), e Å^{-3}	0.58
GOF	1.009	$\Delta\rho$(min), e Å^{-3}	−0.49
data/param	8.40		

[a] Unit-cell parameters, least-squares best fit, angular settings of 25 reflections, $20° \leq 2\theta \leq 30°$. [b] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

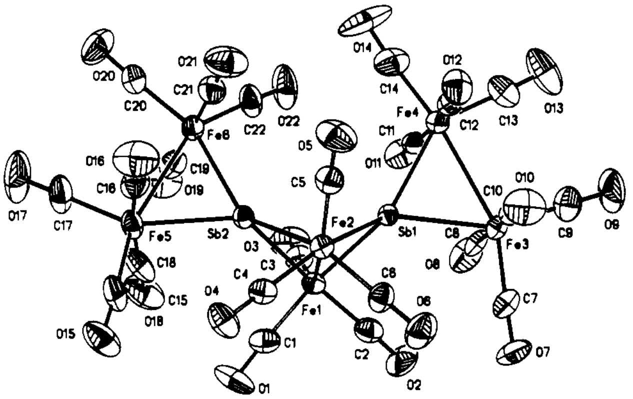

Figure 1. Molecular structure and labeling scheme for $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (1) with 45% probability thermal ellipsoids.

X-ray Structural Characterization. Crystals suitable for diffraction were recrystallized from CH_2Cl_2. Crystal data and parameters used

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[†] University of Delaware.

[‡] Rice University.

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U^a
Sb(1)	813.3 (3)	1374.8 (3)	1805.3 (2)	34.7 (2)
Sb(2)	1650.6 (3)	1822.4 (3)	580.0 (2)	37.4 (2)
Fe(1)	370.6 (6)	1343.0 (7)	805.7 (5)	40.1 (4)
Fe(2)	1072.0 (6)	2701.7 (6)	1322.9 (5)	37.3 (4)
Fe(3)	22.3 (6)	1099.4 (7)	2686.6 (5)	44.5 (4)
Fe(4)	1490.0 (6)	502.2 (7)	2542.2 (5)	42.7 (4)
Fe(5)	2230.3 (7)	2249.0 (7)	−355.9 (5)	52.4 (4)
Fe(6)	2866.9 (7)	1080.9 (7)	372.2 (5)	46.3 (4)
O(1)	−161 (4)	2254 (5)	−180 (3)	99 (3)
O(2)	−1146 (4)	1095 (5)	1208 (3)	94 (3)
O(3)	664 (4)	−322 (4)	430 (4)	93 (3)
O(4)	1023 (4)	3989 (4)	461 (3)	68 (2)
O(5)	2323 (4)	3259 (5)	2012 (3)	86 (3)
O(6)	−179 (4)	3427 (4)	1934 (3)	81 (3)
O(7)	−1343 (4)	1965 (5)	2407 (3)	93 (3)
O(8)	−528 (4)	−362 (4)	2091 (4)	92 (3)
O(9)	−308 (5)	401 (5)	3802 (3)	118 (4)
O(10)	511 (4)	2654 (4)	3181 (3)	91 (3)
O(11)	1049 (4)	−920 (4)	1861 (3)	79 (3)
O(12)	2050 (4)	2031 (4)	3032 (3)	73 (3)
O(13)	1366 (6)	−317 (5)	3648 (3)	122 (4)
O(14)	3051 (4)	179 (7)	2285 (5)	156 (5)
O(15)	1322 (5)	3586 (5)	−785 (3)	99 (3)
O(16)	3099 (4)	3432 (4)	302 (4)	105 (4)
O(17)	3379 (6)	2064 (6)	−1230 (4)	147 (5)
O(18)	1149 (5)	1146 (6)	−898 (3)	115 (4)
O(19)	2248 (5)	−70 (5)	−461 (4)	100 (4)
O(20)	4330 (4)	850 (6)	−177 (4)	104 (4)
O(21)	3545 (4)	2174 (5)	1205 (3)	102 (4)
O(22)	2671 (5)	−268 (5)	1161 (3)	116 (4)
C(1)	56 (5)	1890 (6)	196 (4)	63 (4)
C(2)	−544 (5)	1216 (6)	1066 (4)	64 (4)
C(3)	539 (5)	335 (5)	578 (4)	58 (3)
C(4)	1037 (4)	3485 (5)	792 (4)	44 (3)
C(5)	1846 (5)	3035 (5)	1736 (4)	52 (3)
C(6)	307 (5)	3137 (5)	1690 (4)	52 (3)
C(7)	−810 (5)	1633 (6)	2504 (4)	58 (3)
C(8)	−295 (4)	184 (5)	2312 (4)	55 (3)
C(9)	−171 (6)	663 (6)	3374 (4)	75 (4)
C(10)	356 (5)	2043 (6)	2991 (4)	62 (4)
C(11)	1202 (5)	−378 (6)	2120 (4)	55 (3)
C(12)	1809 (4)	1439 (5)	2841 (4)	49 (3)
C(13)	1404 (7)	−9 (6)	3220 (4)	76 (4)
C(14)	2433 (6)	313 (7)	2363 (5)	82 (4)
C(15)	1665 (6)	3062 (6)	−609 (4)	68 (4)
C(16)	2776 (5)	2950 (6)	54 (4)	68 (4)
C(17)	2948 (7)	2126 (7)	−898 (5)	88 (5)
C(18)	1583 (7)	1554 (6)	−684 (4)	75 (4)
C(19)	2455 (5)	402 (6)	−155 (5)	65 (4)
C(20)	3754 (5)	943 (7)	27 (4)	68 (4)
C(21)	3270 (5)	1771 (6)	874 (4)	66 (4)
C(22)	2766 (6)	284 (6)	875 (4)	75 (4)

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

during the collection of intensity data are given in Table I.

A deep red, roughly egg-shaped crystal of $C_{22}O_{22}Fe_6Sb_2$ was attached with epoxy cement to a fine glass fiber and found to crystallize in the orthorhombic space group *Pbca*. A profile-fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections. Intensity data were corrected for absorption by an empirical procedure that employs six refined parameters to define a pseudoellipsoid.

Table III. Selected Bond Distances and Angles for $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (**1**)

(a) Bond Distances (Å)

Fe(1)–Fe(2)	2.841 (1)	Sb(1)–Fe(4)	2.565 (1)
Fe(3)–Fe(4)	2.841 (1)	Sb(2)–Fe(1)	2.494 (1)
Fe(5)–Fe(6)	2.822 (2)	Sb(2)–Fe(2)	2.502 (1)
Sb(1)–Fe(1)	2.498 (1)	Sb(2)–Fe(5)	2.548 (1)
Sb(1)–Fe(2)	2.503 (1)	Sb(2)–Fe(6)	2.554 (1)
Sb(1)–Fe(3)	2.567 (1)		

(b) Bond Angles (deg)

Fe(1)–Sb(1)–Fe(2)	69.2 (1)	Fe(5)–Sb(2)–Fe(6)	67.2 (1)
Fe(1)–Sb(1)–Fe(3)	126.1 (1)	Sb(1)–Fe(1)–Fe(2)	55.5 (1)
Fe(1)–Sb(1)–Fe(4)	141.7 (1)	Sb(1)–Fe(2)–Fe(1)	55.3 (1)
Fe(2)–Sb(1)–Fe(3)	128.9 (1)	Sb(1)–Fe(3)–Fe(4)	56.4 (1)
Fe(2)–Sb(1)–Fe(4)	135.0 (1)	Sb(1)–Fe(4)–Fe(3)	56.4 (1)
Fe(3)–Sb(1)–Fe(4)	67.2 (1)	Sb(2)–Fe(1)–Fe(2)	55.5 (1)
Fe(1)–Sb(2)–Fe(2)	69.3 (1)	Sb(2)–Fe(2)–Fe(1)	55.2 (1)
Fe(1)–Sb(2)–Fe(5)	130.7 (1)	Sb(2)–Fe(5)–Fe(6)	56.5 (1)
Fe(1)–Sb(2)–Fe(6)	133.2 (1)	Sb(2)–Fe(6)–Fe(5)	56.3 (1)
Fe(2)–Sb(2)–Fe(5)	128.6 (1)	Sb(1)–Fe(1)–Sb(2)	84.3 (1)
Fe(2)–Sb(2)–Fe(6)	140.1 (1)	Sb(1)–Fe(2)–Sb(2)	84.0 (1)

Less than 1% decay occurred in three standard reflections over the course of the data collection.

The structure was solved by using the direct-methods program SOLV, which located the two Sb atoms. The remaining atoms were located from subsequent difference Fourier syntheses. All atoms were refined anisotropically. The final difference Fourier synthesis showed only a diffuse background (maximum 0.58 e/Å^3). An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet (Madison, WI) program packages P3 and SHELXTL (version 5.0).

The atomic coordinates are given in Table II and bond distances and angles in Table III. Additional crystallography data are available as supplementary material.

Results and Discussion

The treatment of $[NEt_4]_2[Fe_2(CO)_8]$ with $SbCl_3$ followed by Cu(I) oxidation produces $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (**1**) in low yield. The structure of **1** has been crystallographically characterized. The molecular structure and labeling scheme for **1** are shown in Figure 1. Compound **1** crystallizes as discrete molecules without significant intermolecular associations. The central complex core composed of the Fe(1), Fe(2), Sb(1), and Sb(2) rhombus may be viewed as a familiar "butterfly" (-ido)$_2$Fe$_2$(CO)$_6$ complex, i.e., $Fe_2(CO)_6(\mu\text{-}ER_2)_2$,[13] E = group 15 element, in which the $Sb[Fe(CO)_4]_2$ groups replace the "-ido" (ER_2) groups. The butterfly dihedral angle is 109.1 (1)° at the Fe–Fe crease. The overall molecular symmetry is approximately C_{2v}. The Sb(1)···Sb(2) distance, 3.351 (1) Å, precludes significant interaction. The Fe(1)–Fe(2) distance, 2.841 (2) Å, is rather long (cf. 2.623 (3) Å in $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$).[14] The Fe–Fe bonds in the $Fe_2(CO)_8$ groups are also long (average 2.831 (1) Å) but similar to Fe(1)–Fe(2). In $[PPN]_2[Fe_2(CO)_8]$,[15] the Fe–Fe distance is 2.787 (2) Å.

The naked Sb atoms serve as bridges between the inner $Fe_2(CO)_6$ group and the outer $Fe_2(CO)_8$ groups, with outer Sb–Fe bonds somewhat longer (average 2.559 (4) Å) than the inner set (average 2.499 (4) Å). In $[Fe_2(CO)_8\{\mu\text{-}SbCH(SiMe_3)_2\}]$ (**2**), the Sb–Fe distances are longer (average 2.637 Å)[15] than either set, but in the $Cl_2Sb[Fe(CO)_2Cp]_2^+$ ion, the Sb–Fe distances are shorter (average 2.440 Å).[17] Lastly, in the $\{ClSb[Fe(CO)_2Cp]_3\}_2^+$ ion, the Sb–Fe distances (average 2.539 Å)[18] are intermediate to

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the values in **1**, as is also that found in the simple stibine complex $\{Fe(CO)_4[Sb(t\text{-}Bu)_3]\}_3$, 2.547 (1) Å.[19]

The Sb atoms appear to apportion their five potential donor electrons, three to the central $Fe_2(CO)_6$ fragment and two to the outer $Fe_2(CO)_8$ fragments. This is in agreement with the isolobal principles used by Cowley et al. to describe the bonding in **2**[16] and the observed differences in the Sb–Fe distance in **1**. Each 34-electron diiron fragment is isoelectronic with $Fe_2(CO)_9$.

The acute Fe–Sb–Fe angles differ little whether involving inner or outer diiron units: inner average 69.25 (6)°; outer average 67.18 (6)°. These angles are similar to those found in $[Co_4(\eta^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ [average 70.1 (1)°], containing the related μ_4-$AsCo_4$ group,[3] and the $[Fe_2(CO)_8(\mu_4\text{-}E)Fe_2(CO)_6Cl]$ complexes, E = P or As.[2] The triangular Fe_2Sb planes in **1** have an inner/outer dihedral angle of 95.0 (1)° at Sb(1) and 85.1 (1)° at Sb(2) (if viewed from the same perspective). The expectation of more nearly perpendicular interplanar relationships is offset by intramolecular carbonyl repulsions between the $Fe_2(CO)_8$ units in the center of the complex; the O(22)···O(14) distance, 2.84 (1) Å, is within the sum of the van der Waals radii (3.04 Å).

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Registry No. 1, 105859-91-4; $[Et_4N]_2[Fe_2(CO)_8]$, 26024-88-4; $[Cu(CH_3CN)_4][BF_4]$, 15418-29-8; $SbCl_3$, 10025-91-9.

Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic temperature coefficients (3 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto di Chimica
e Tecnologia dei Radioelementi del CNR,
Padova, Italy, Institut für Anorganische
und Analytische Chemie, Freien Universität Berlin,
Berlin, West Germany, and Dipartimento di Chimica
Inorganica, Metallorganica ed Analitica,
Università di Padova, Padova, Italy

Electronic Structure of Nonacarbonylbis(μ_3-fluoromethylidyne)triiron by means of UV Photoelectron Spectroscopy and DV–Xα Quantum-Mechanical Calculations

Maurizio Casarin,*[1a] David Ajò,[1a] Dieter Lentz,*[1b]
Renzo Bertoncello,[1c] and Gaetano Granozzi[1c]

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Mono- and bis(methylidyne) complexes have been the object of several experimental and theoretical investigations in the near past,[2–4] not least because of suggestions that discrete metal clusters may serve as models for miniature metal surfaces or highly dispersed supported catalysts.[5] Some of the authors have already focused their attention on the electronic structure of nonacarbonyl-substituted mono(methylidyne)tricobalt clusters $(\mu_3\text{-}CY)[Co(CO)_3]_3$ (Y = H, CH_3, CF_3, $COOCH_3$, F, Cl, Br, I),[4] obtaining an experimental evaluation, along the investigated series, of the interaction extent between the metal triangle and the apical carbon atom.

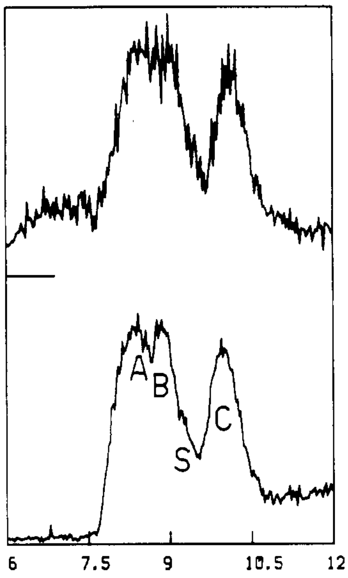

Figure 1. He I (below) and He II (above) excited PE spectra of $(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$. PE bands are labeled alphabetically.

In agreement with the EAN rule,[6] a further CY ligand could be incorporated into the analogous Fe cluster, leading to the $(\mu_3\text{-}CY)_2[Fe(CO)_3]_3$ series. At present, as a matter of fact, only two complexes containing the $Fe_3(CY)_2$ moiety have been synthesized to our knowledge.[3a] Further, two iron clusters of the type $(\mu_3\text{-}CCH_3)(\mu_3\text{-}COR)[Fe(CO)_3]_3$ (R = CH_3, C_2H_5), which have been described recently, show interesting reactions with CO and acetylenes, respectively.[3b–d]

In this note we report an experimental and theoretical analysis of the electronic structure of $(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$ combining He I/He II gas-phase UV photoelectron (PE) spectroscopy and Hartree–Fock–Slater first-principle DV–Xα calculations.[7]

$(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$ has been prepared according to the literature methods.[3] Its He I/He II excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified by inclusion of a hollow-cathode discharge lamp giving high output of He II photons. The spectrometer was connected on line with a MINC-23 computer (Digital Eq.). The ionization energy (IE) scale was calibrated by reference to admitted inert gases (Xe–Ar) and to the He $1s^{-1}$ self-ionization. A heated inlet probe system was used at 60–70 °C.

Figure 1, where bands have been labeled alphabetically, shows only the IE region below 12 eV. The higher IE one consists of

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