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Reactivity of Bulky Alkyldichlorostibines and Alkyldichlorobismuthines toward $[\text{W}(\text{CO})_5]^{2-}$: Synthesis of Compounds Containing Stibinidene, Bismuthinidene, and Dibismuth Ligands

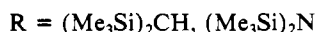
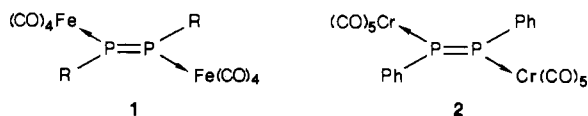
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The reaction of $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ with $[\text{W}(\text{CO})_5]^{2-}$ affords the stibinidene complex $[\text{W}_2(\text{CO})_{10}(\mu\text{-SbCH}(\text{SiMe}_3)_2)]$ (**3**). The "open" (i.e. non metal-metal bonded) structure of **3** was established by X-ray crystallography. Compound **3** crystallizes in the monoclinic space group $C2/c$ with $a = 17.450$ (4) Å, $b = 11.093$ (2) Å, $c = 15.654$ (2) Å, and $\beta = 113.51$ (2)°. The corresponding reaction of $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ with $[\text{W}(\text{CO})_5]^{2-}$ proceeds quite differently and produces two tungsten-bismuth cluster compounds, $[\text{W}(\text{CO})_5]_3(\mu_3\text{-}\eta^2\text{-Bi}_2)$ (**7**) and $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)(\mu\text{-BiMeW}(\text{CO})_5)]$ (**8**). Both compounds were characterized by X-ray crystallography. Compound **8** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.595$ (5) Å, $b = 16.130$ (8) Å, $c = 10.520$ (2) Å, $\alpha = 81.99$ (3)°, $\beta = 111.84$ (3)°, and $\gamma = 94.90$ (4)°. The interrelationships between the above structures and those of known compounds are discussed.

Introduction

The synthesis of stable compounds featuring unsupported double bonds between the heavier group 5 (group 15³⁴) elements has been achieved recently by the use of bulky ligands.¹ While this approach has been successful for diphosphenes ($\text{RP}=\text{PR}$), diarsenes ($\text{RAS}=\text{AsR}$), and phospharsenes ($\text{RP}=\text{AsR}$), only one such compound containing antimony, a phosphastibene ($\text{RP}=\text{SbR}$), has been observed.² Bismuth analogues are unknown. The reason for the apparent instability of compounds with multiple bonds to either antimony or bismuth is twofold, namely a decrease in bond energy as the group is descended and, because of increasing bond lengths, a relative decrease in the steric protection afforded by any particular R group. Little can be done to address the former problem. However, an approach to the latter was suggested by the fact that diphosphenes with smaller R groups can be stabilized by coordination of the lone pairs to transition-metal fragments as exemplified by **1**³ and **2**.⁴ We sought, therefore, to prepare



antimony and bismuth analogues of **1** and **2** by using the methodology of Power et al.,³ viz. treatment of the appropriate dihalides with transition-metal carbonyl dianions. The present paper is concerned with the reactions of $(\text{Me}_3\text{Si})_2\text{CHECl}_2$ ($\text{E} = \text{Sb}, \text{Bi}$) with $[\text{W}(\text{CO})_5]^{2-}$. Some aspects of the work have been the subject of preliminary communications.⁵

Results and Discussion

Treatment of $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ ⁶⁻⁸ with $\text{Na}_2[\text{W}(\text{CO})_5]^{2-}$ in THF solution at 25 °C, followed by column chromatography of the crude product, afforded a single dark blue compound, **3**, in 57% yield. Mass spectrometry and IR spectroscopy indicated the presence of $\text{W}(\text{CO})_5$ and $(\text{Me}_3\text{Si})_2\text{CHSb}$ moieties, but in order to determine the structure unambiguously, a single-crystal X-ray diffraction analysis was carried out. The results of this determination are represented in Figure 1 together with the atom-numbering protocol. Bond lengths, bond angles, and atomic positional parameters are presented in Tables I-III and pertinent crystallographic data are collected in Table IV. The structure of **3** comprises two $\text{W}(\text{CO})_5$ moieties bonded to a $(\text{Me}_3\text{Si})_2\text{CHSb}$ (stibinidene) unit. Each tungsten adopts an octahedral geometry, being bonded to five terminal carbonyl ligands and the central antimony atom. Within experimental error, the sum of bond

angles at Sb is 360°; hence, the stibinidene geometry is trigonal planar. The molecule resides on a crystallographic twofold axis coincident with a line through the antimony atom and the midpoint of the W-W vector. The two $\text{W}(\text{CO})_5$ and the two Me_3Si groups are thus related by symmetry. However, C(1), the unique carbon of the $(\text{Me}_3\text{Si})_2\text{CH}$ group, is disordered as a result of the existence of the C_2 axis. A detailed discussion of the disorder associated with C(1) is presented in the Experimental Section.

The precise geometries of the $\text{W}(\text{CO})_5$ and $(\text{Me}_3\text{Si})_2\text{CH}$ groups (apart from the disorder of C(1)) are unexceptional and merit no special comment. The nature of the W_2Sb core, however, is important in that it establishes **3** as an example of an "open" stibinidene complex. The term "open" has been introduced to define systems of the genre $\text{RE}(\text{ML}_n)_2$ ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$; $\text{ML}_n = 16e$ transition-metal fragment) in which there is no M-M bonding and the pnictogen atom assumes a trigonal-planar geometry.^{5,6,10} By contrast, the valence isomeric "closed" form involves a single M-M bond and a pyramidal geometry at E.⁶ The W-W separation in **3** is 4.907 (1) Å and is thus well outside the normal range of distances associated with W-W single bonding.¹¹ This observation, together with the trigonal-planar Sb geometry, clearly establishes **3** as a member of the "open" structure class.

Several other "open" stibinidene complexes have been synthesized by Huttner et al., two of which, **4** and **5**, have been

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- (7) Breunig, H. J.; Kanig, W.; Soltani-Neshan, A. *Polyhedron* **1983**, *2*, 291.
- (8) The choice of the $(\text{Me}_3\text{Si})_2\text{CH}$ group was dictated by synthetic considerations. See ref 6.
- (9) Recent work by Cooper et al. (Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354) indicates that sodium reduction of $\text{W}(\text{CO})_6$ generally leads to mixtures of $[\text{W}(\text{CO})_5]^{2-}$ and $[\text{W}_2(\text{CO})_{10}]^{2-}$. The precise nature of the reactive tungsten complex is thus somewhat uncertain.
- (10) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1267.
- (11) For example, the W-W bond length in $[\text{W}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ is 3.222 (1) Å. Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

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Table I. Bond Distances (Å) for $[\text{W}_2(\text{CO})_{10}\mu\text{-SbCH}(\text{SiMe}_3)_2] (3)^a$

Sb(1)–W(1)	2.687 (1)	W(1)–C(04)	1.98 (3)	O(01)–C(01)	1.23 (4)
Sb(1)–C(1)	2.11 (2)	W(1)–C(05)	2.01 (3)	O(02)–C(02)	1.15 (3)
W(1)–C(01)	1.98 (3)	Si(1)–C(1)	1.92 (3)	O(03)–C(03)	1.08 (3)
W(1)–C(02)	2.00 (2)	Si(1)–C(11)	1.82 (3)	O(04)–C(04)	1.16 (3)
W(1)–C(03)	2.01 (2)	Si(1)–C(12)	1.80 (3)	O(05)–C(05)	1.15 (4)
		Si(1)–C(13)	1.86 (3)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table II. Bond Angles (deg) for $[\text{W}_2(\text{CO})_{10}\mu\text{-SbCH}(\text{SiMe}_3)_2] (3)^a$

W(1)–Sb(1)–W(1')	131.88 (7)	C(01)–W(1)–C(04)	176.9 (8)
W(1')–Sb(1)–C(1)	102.5 (7)	C(01)–W(1)–C(05)	90 (1)
W(1)–Sb(1)–C(1)	125.6 (7)	C(02)–W(1)–C(03)	93.4 (8)
Sb(1)–W(1)–C(01)	91.3 (6)	C(02)–W(1)–C(04)	92 (1)
Sb(1)–W(1)–C(02)	88.0 (5)	C(02)–W(1)–C(05)	176.9 (9)
Sb(1)–W(1)–C(03)	177.4 (7)	C(03)–W(1)–C(04)	86 (1)
Sb(1)–W(1)–C(04)	91.8 (6)	C(03)–W(1)–C(05)	89.1 (9)
Sb(1)–W(1)–C(05)	89.7 (7)	C(04)–W(1)–C(05)	90 (1)
C(01)–W(1)–C(02)	88 (1)	Sb(1)–C(1)–Si(1)	114 (1)
C(01)–W(1)–C(03)	91 (1)	Si(1)–C(1)–Si(1)	118 (1)

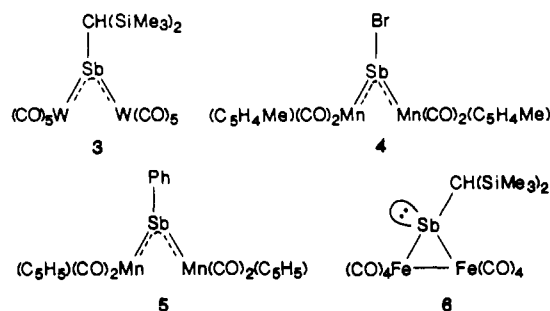
^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[\text{W}_2(\text{CO})_{10}\mu\text{-SbCH}(\text{SiMe}_3)_2] (3)$

atom	x	y	z	B_{11}^a Å ²
Sb(1)	0.500	0.0828 (2)	0.250	2.68 (4)
W(1)	0.36627 (5)	–0.01593 (9)	0.11387 (6)	3.80 (2)
Si(1)	0.4634 (4)	0.3496 (6)	0.3318 (4)	4.3 (2)
O(01)	0.307 (1)	–0.155 (3)	0.256 (1)	11.7 (8)
O(02)	0.477 (1)	–0.246 (2)	0.132 (1)	6.2 (5)
O(03)	0.216 (1)	–0.124 (2)	–0.050 (1)	8.7 (6)
O(04)	0.583 (1)	0.088 (2)	0.543 (1)	7.7 (6)
O(05)	0.259 (1)	0.217 (2)	0.106 (1)	8.6 (6)
C(01)	0.329 (2)	–0.089 (2)	0.206 (2)	5.9 (7)
C(02)	0.435 (1)	–0.164 (2)	0.126 (2)	4.4 (6)
C(03)	0.266 (1)	–0.084 (2)	0.008 (2)	5.2 (6)
C(04)	0.399 (1)	0.051 (2)	0.016 (1)	4.6 (6)
C(05)	0.300 (2)	0.134 (2)	0.110 (2)	6.4 (7)
C(1) ^b	0.475 (2)	0.269 (2)	0.229 (2)	1.6 (7)
C(11)	0.401 (2)	0.248 (2)	0.370 (1)	5.5 (6)
C(12)	0.601 (2)	0.477 (2)	0.224 (2)	6.4 (8)
C(13)	0.057 (2)	0.104 (3)	–0.063 (2)	10 (1)

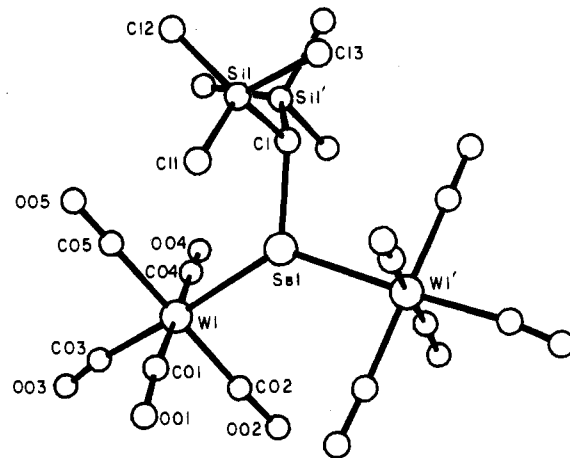
^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^b Isotropically refined atom.

characterized structurally.^{12,13} Pertinent structural details for 3–5 are presented in Table V together with those for the related



“closed” compound 6.^{5a,6} Possible reasons for the adoption of an “open” or “closed” structure will be reported elsewhere,¹⁴ but it is evident from Table V that marked structural differences exist

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**Figure 1.** Molecular structure of $[\text{W}_2(\text{CO})_{10}\mu\text{-SbCH}(\text{SiMe}_3)_2] (3)$, showing the atom-numbering scheme adopted.**Table IV.** Crystallographic, Data Collection, and Structure Refinement Parameters for $[\text{W}_2(\text{CO})_{10}\mu\text{-SbCH}(\text{SiMe}_3)_2] (3)$ and $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)(\mu\text{-BiMeW}(\text{CO})_5)] (8)$

	3	8
formula	$\text{C}_{17}\text{H}_{19}\text{O}_{10}\text{Si}_2\text{W}_2\text{Sb}$	$\text{C}_{14}\text{H}_3\text{O}_{13}\text{W}_3\text{Bi}_3\text{-C}_6\text{H}_6$
fw	928.95	1635.77
cryst class	monoclinic	triclinic
Space group	$\text{C}2/c$ (no. 15)	$\text{P}\bar{1}$ (no. 2)
$a/\text{Å}$	17.450 (4)	9.595 (5)
$b/\text{Å}$	11.093 (2)	16.130 (8)
$c/\text{Å}$	15.654 (2)	10.520 (2)
α/deg		81.99 (3)
β/deg	113.51 (2)	111.84 (3)
γ/deg		94.90 (4)
$V/\text{Å}^3$	2779 (2)	1494 (2)
Z	4	2
$\rho(\text{calcd})/\text{g cm}^{-3}$	2.221	3.454
$\lambda(\text{Mo K}\alpha)/\text{Å}$	0.71069	0.71069
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	95.4	293.4
time of data collection/h	39.4	41.8
% decay of stds	2.3	8.1
2θ range/deg	$2.0 \leq 2\theta \leq 50.0$	$3.0 \leq 2\theta \leq 46.0$
no. of reflns measd	2508	4818
no. of reflns obsd	1994	2523
data omissn factor	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$
R^a	0.0770	0.0550
R_w^b	0.0958	0.0672
no. of variables	155	252
QOF ^c	4.211	6.302
p^d	0.02	0.05

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|^2$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum|F_o|^2]^{1/2}$. ^c QOF = $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$; NO = number of observed data, and NV = number of variables. ^d The weighting scheme used was of the form $w = 4F_o^2 / \sigma^2(F_o)$ with $\sigma^2(F_o) = \sigma_o^2(F_o) + (pF)^2$; p is an empirical factor used to downweight intense reflections.

Table V. Summary of Structural Data for Stibinidene Complexes

compd	$\angle\text{MSbM}/\text{deg}$	av M–Sb/Å	sum of angles at Sb/deg	M–M/Å	ref
3	131.88 (7)	2.687 (1)	360.0 (7)	4.907 (1)	this work
4	138.6 (1)	2.404 (4)	359.6 (1)	4.50	13
5	140	2.457	360	4.62	12
6	64.15 (2)	2.637 (1)	287.1 (1)	2.801 (1)	6

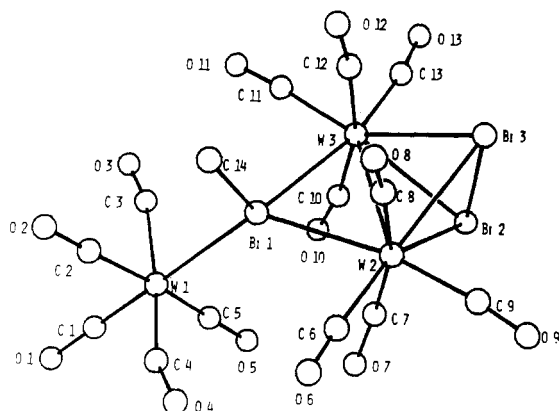
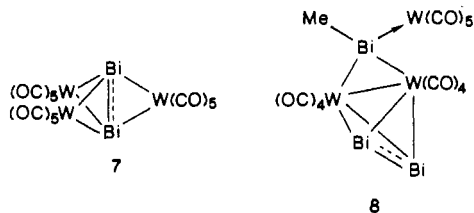


Figure 2. Molecular structure of $[W_2(CO)_8(\mu-\eta^2-Bi_2)(\mu-BiMeW(CO)_5)\cdot C_6H_6]$ (**8**), showing the atom-numbering scheme adopted.

between the two forms. In the "open" configuration the angle at antimony, $M-Sb-M$, is in the range $130-140^\circ$, while in the "closed" form, **6**, a much more acute angle of $64.15(2)^\circ$ is observed. The $M-M$ distances in compounds **3-5** are clearly non-bonding while that in **6**, although somewhat long, is within bonding distance.^{5a,6} Also noteworthy are the $M-Sb$ bond lengths. Comparison of the values for compounds **4-6**, which all feature first-row transition metals, reveals a significant shortening in the "open" form, consistent with a degree of $M-Sb$ multiple bonding. The presence of such bonding in "open" complexes has been discussed from a theoretical standpoint.^{10,15,16}

The corresponding chemistry with bismuth turned out to be quite different. Thus treatment of $(Me_3Si)_2CHBiCl_2$ ^{5b} with $Na_2[W(CO)_5]^{2-}$ in THF solution at $25^\circ C$ affords, after chromatographic workup, two compounds, **7** (5% yield) and **8** (12%



yield), as dark green and dark red crystalline materials respectively. Compounds **7** and **8** can also be prepared by treatment of $MeBiCl_2$ with $[W(CO)_5]^{2-}$. However, the yield of **8** is even lower from this reaction ($\sim 2\%$). Analysis by standard methods proved inconclusive, although for both compounds mass spectrometry indicated the presence of tungsten carbonyl and bismuth units. Accordingly, both materials were characterized by single-crystal X-ray diffraction methods. Compound **7** proved to be $\{[W(CO)_5]_3(\mu_3-\eta^2-Bi_2)\}$, which can be regarded as a Bi_2 molecule ligated to three $W(CO)_5$ fragments in an arrangement possessing approximate D_{3h} symmetry. This compound has, in fact, been prepared previously by Huttner et al.¹⁷ by treatment of $BiCl_3$ with $[W_2(CO)_{10}]^{2-}$. X-ray structure information is available for **7**¹⁷ as well as for analogous As_2 ¹⁸ and Sb_2 ¹⁹ compounds. A discussion of the bonding in these interesting clusters has also appeared.¹⁸

The structure of compound **8** is illustrated in Figure 2. Listings of bond lengths, bond angles, and atomic positional parameters are presented in Tables VI-VIII, and pertinent crystallographic data are collected in Table IV. The basic core of **8** comprises a

Table VI. Bond Distances (\AA) for $[W_2(CO)_8(\mu-\eta^2-Bi_2)(\mu-BiMeW(CO)_5)\cdot C_6H_6]$ (**8**)^a

W(2)-W(3)	3.142 (3)	Bi(2)-Bi(3)	2.796 (1)
Bi(1)-W(2)	2.881 (1)	Bi(2)-W(2)	2.987 (1)
Bi(1)-W(3)	2.864 (1)	Bi(2)-W(3)	3.001 (1)
Bi(1)-W(1)	2.851 (1)	Bi(3)-W(2)	2.990 (1)
Bi(1)-C(14)	2.339 (1)	Bi(3)-W(3)	2.997 (1)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Bond Angles (deg) for $[W_2(CO)_8(\mu-\eta^2-Bi_2)(\mu-BiMeW(CO)_5)\cdot C_6H_6]$ (**8**)^a

W(2)-Bi(1)-W(3)	66.33 (2)	Bi(2)-Bi(3)-W(3)	62.28 (2)
W(2)-Bi(1)-W(4)	129.66 (2)	W(2)-Bi(3)-W(3)	63.34 (2)
W(2)-Bi(1)-C(14)	106.6 (5)	Bi(1)-W(2)-Bi(2)	106.26 (2)
W(3)-Bi(1)-W(1)	128.46 (2)	Bi(1)-W(2)-Bi(3)	109.35 (2)
W(3)-Bi(1)-C(14)	111.7 (6)	Bi(1)-W(2)-C(9)	167.4 (5)
W(1)-Bi(1)-C(14)	109.3 (9)	Bi(2)-W(2)-Bi(3)	55.78 (2)
Bi(3)-Bi(2)-W(2)	62.16 (2)	Bi(1)-W(3)-Bi(2)	106.35 (2)
Bi(3)-Bi(2)-W(3)	62.15 (2)	Bi(1)-W(3)-Bi(3)	109.62 (2)
W(2)-Bi(2)-W(3)	63.33 (2)	Bi(2)-W(3)-Bi(3)	55.57 (2)
Bi(2)-Bi(3)-W(2)	62.06 (2)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Positional Parameters and Their Estimated Standard Deviations for $[W_2(CO)_8(\mu-\eta^2-Bi_2)(\mu-BiMeW(CO)_5)\cdot C_6H_6]$ (**8**)

atom	x	y	z	B_i^a , \AA^2
Bi(1)	-0.0033 (2)	0.7562 (1)	0.8568 (2)	1.31 (3)
Bi(2)	0.4692 (2)	0.8720 (1)	1.1086 (2)	2.85 (4)
Bi(3)	0.4663 (2)	0.7067 (1)	1.2306 (2)	2.80 (4)
W(1)	-0.2127 (2)	0.8572 (1)	0.6358 (2)	1.56 (4)
W(2)	0.3138 (2)	0.7403 (1)	0.9246 (2)	1.43 (4)
W(3)	0.1787 (2)	0.7980 (1)	1.1268 (2)	1.53 (4)
O(1) ^b	-0.450 (4)	0.966 (2)	0.388 (4)	12 (1)
O(2)	-0.446 (5)	0.706 (2)	0.593 (5)	14 (2)
O(3) ^b	-0.365 (4)	0.917 (3)	0.839 (4)	6 (1)
O(4) ^b	-0.111 (7)	0.793 (4)	0.445 (6)	22 (2)
O(5) ^b	-0.003 (5)	1.026 (3)	0.659 (4)	14 (1)
O(6)	0.189 (5)	0.676 (3)	0.628 (4)	7 (1)
O(7) ^b	0.269 (5)	0.921 (3)	0.726 (4)	14 (1)
O(8)	0.244 (5)	0.543 (3)	1.010 (5)	6 (1)
O(9)	0.625 (5)	0.714 (3)	0.920 (4)	15 (1)
O(10) ^b	0.117 (4)	0.982 (2)	0.954 (4)	13 (1)
O(11)	-0.140 (3)	0.825 (3)	1.133 (3)	13 (1)
O(12)	0.106 (5)	0.601 (3)	1.226 (4)	6 (1)
O(13)	0.278 (4)	0.858 (3)	1.422 (4)	16 (1)
C(1)	-0.350 (5)	0.921 (4)	0.493 (5)	8 (2)
C(2) ^b	-0.356 (5)	0.765 (3)	0.608 (5)	3 (1)
C(3) ^b	-0.297 (5)	0.905 (3)	0.787 (8)	14 (2)
C(4) ^b	-0.166 (1)	0.834 (7)	0.498 (1)	13 (5)
C(5)	-0.097 (7)	0.961 (3)	0.647 (7)	10 (2)
C(6) ^b	0.228 (6)	0.703 (4)	0.732 (6)	4 (1)
C(7) ^b	0.293 (7)	0.858 (4)	0.807 (7)	11 (2)
C(8)	0.274 (7)	0.615 (3)	0.988 (5)	5 (2)
C(9) ^b	0.513 (4)	0.722 (2)	0.930 (4)	1.1 (7)
C(10) ^b	0.157 (5)	0.914 (3)	1.025 (4)	1.9 (9)
C(11)	-0.020 (4)	0.812 (4)	1.137 (5)	8 (2)
C(12) ^a	0.140 (5)	0.673 (3)	1.196 (5)	6 (1)
C(13) ^a	0.254 (5)	0.831 (3)	1.314 (5)	3 (1)
C(14) ^a	-0.103 (5)	0.620 (3)	0.866 (5)	3 (1)
C(15) ^{a,c}	0.641 (7)	0.530 (4)	1.205 (6)	5 (1)
C(16) ^{a,c}	0.764 (7)	0.571 (4)	1.238 (6)	5 (1)
C(17) ^{a,c}	0.856 (8)	0.589 (4)	1.377 (7)	6 (2)
C(18) ^{a,c}	0.78 (1)	0.547 (5)	1.493 (9)	8 (2)
C(19) ^{a,c}	0.65 (1)	0.489 (6)	1.444 (9)	8 (2)
C(20) ^{a,c}	0.581 (8)	0.484 (5)	1.316 (8)	7 (2)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $1/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^b Isotropically refined atoms. ^c Carbon atoms of benzene of crystallization.

$W_2(CO)_8$ fragment, each tungsten atom being bonded to four terminal carbonyl ligands. The W-W separation of $3.142(3) \text{ \AA}$

(15) Kostic, N. M.; Fenske, R. F. *J. Organomet. Chem.* **1982**, *233*, 337.

(16) (a) Lang, H.; Mohr, G.; Scheidsteger, O.; Huttner, G. *Chem. Ber.* **1985**, *118*, 574. (b) Huttner, G.; Von Seyerl, J.; Marsili, M.; Schmid, H.-G. *Angew. Chem.* **1975**, *87*, 455; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 434.

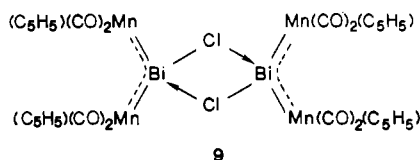
(17) Huttner, G.; Weber, U.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 707.

(18) Sigwarth, B.; Zsolnai, L.; Berke, H.; Huttner, G. *J. Organomet. Chem.* **1982**, *226*, C5.

(19) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O. *Angew. Chem.* **1982**, *94*, 210; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 215.

corresponds to that expected for a single bond.¹¹ The W_2 unit is bridged on one side by a Bi_2 fragment and on the other side by a MeBi (methylbismuthinidene) group. The former is transversely bonded in a manner akin to transverse-bonded alkyne complexes (such as $[\text{Co}_2(\text{CO})_6(\mu-\eta^2-\text{RC}\equiv\text{CR})]$) and can thus be considered to donate four electrons to the W_2 core. The Bi–Bi separation of 2.796 (1) Å is considerably shorter than that associated with a normal Bi–Bi single bond, e.g. 2.990 (2) Å in Ph_4Bi_2 ²⁰ and 2.936 (2) and 2.941 (2) Å in Bi_4 ²⁻²¹. A modicum of Bi–Bi multiple bonding is therefore implied. However, additional experiments are necessary to define more precisely the nature of the bismuth–bismuth interaction. The MeBi group is four-coordinate and adopts a distorted tetrahedral configuration. It is bonded to both tungsten atoms of the W_2 core ($\text{Bi}(1)–\text{W}(2) = 2.881$ (1) Å; $\text{Bi}(1)–\text{W}(3) = 2.864$ (1) Å), the carbon atom, C(14), of the methyl group, and, in addition, to a third tungsten atom ($\text{Bi}(1)–\text{W}(1) = 2.851$ (1) Å), this being part of a $\text{W}(\text{CO})_5$ fragment. Bismuth atom Bi(1) may thus be considered to form single bonds to W(2), W(3), and C(1), the remaining lone pair forming a donor bond to W(1) of the $\text{W}(\text{CO})_5$ group. On the basis of the foregoing discussion, it is apparent that each tungsten atom achieves an 18-electron configuration.

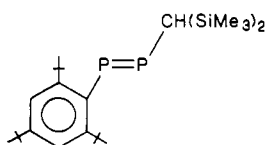
The solid-state structure of **8** also features a benzene of crystallization. Indeed, it was necessary to seal **8** under an atmosphere of benzene vapor to avoid degradation of the crystal. The benzene ring, however, is not bonded to the Bi_2 moiety since the distance between Bi(2) or Bi(3) and the benzene carbons exceeds the sum of the covalent radii of Bi and C. Only one previous bismuthinidene complex (**9**) has been reported,²² this being derived from



9

the reaction of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{THF})]$ with BiCl_3 . Unlike **8**, however, **9** may be considered to be an “open” compound, which has dimerized via Bi_2Cl_2 bridge formation. This constitutes a further example of the Lewis acidity of “open” $\text{RE}(\text{ML}_n)_2$ complexes.²³ By contrast, **8** may be regarded as a “closed” structure since if the $\text{W}(\text{CO})_5$ group is ignored, the bismuthinidene atom, Bi(1), is pyramidal and a W–W bond is present. It has been observed that such “closed” compounds are Lewis basic at the E center,^{5,24} which facet is evident in **8** by virtue of the coordination of the Bi(1) lone pair to a $\text{W}(\text{CO})_5$ group.

The origin of a Me group from a $(\text{Me}_3\text{Si})_2\text{CH}$ group in the case of **8** seems worthy of comment as indeed is the origin of the Bi_2 moiety group for both **7** and **8**. With regard to the former point, Me_3Si elimination is not uncommon in silylated alkyl groups under reducing conditions. This type of elimination has been observed, for example, in the formation of the diphosphene **10**, where the

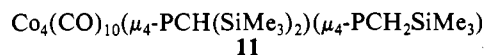


10

$(\text{Me}_3\text{Si})_3\text{C}$ group of the precursor dichlorophosphine,

- (20) Calderazzo, F.; Morrillo, A.; Pelizzi, G.; Poli, R. *J. Chem. Soc., Chem. Commun.* **1983**, 507.
 (21) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482.
 (22) Von Seyerl, J.; Huttner, G. *J. Organomet. Chem.* **1980**, *195*, 207.
 (23) Sigwarth, B.; Weber, U.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1985**, *118*, 3114 and references therein.
 (24) While **6** is the only example of a “closed” “inidene” compound in which the lone pair is chemically innocent,⁵ several complexes of such compounds are known. See, for example: (a) Weber, U.; Huttner, G.; Scheidsteiger, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *289*, 357. (b) Schneider, I.; Huttner, G. *Chem. Ber.* **1983**, *116*, 917.

$(\text{Me}_3\text{Si})_3\text{CPCl}_2$, appears as a $\text{CH}(\text{SiMe}_3)_2$ group in the isolated product.^{2b,25} A further example of this phenomenon occurs in the reaction of $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ with $[\text{Co}(\text{CO})_4]^-$, one product of which, **11**, contains a $\mu_4\text{-PCH}_2\text{SiMe}_3$ phosphinidene group.²⁶



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We suggest that in all cases, chloride ion, which is generated under the reaction conditions, removes Me_3SiCl , thus leaving a carbon ionic center that picks up the requisite number of protons from the solvent.

The origin of the bismuth atoms, which appear as Bi_2 molecules in both **7** and **8**, is mechanistically more obscure. However, their appearance is presumably a consequence of such factors as a low Bi–C bond energy and the stability of the $(\text{Me}_3\text{Si})_2\text{CH}^-$ anion, thereby rendering it a viable leaving group. The lability of Bi–C bonds toward organometallic anions has been noted previously by Panster and Malisch.²⁷

Finally, we draw attention to the fact that bismuth-containing transition-metal clusters are somewhat rare. Apart from the compounds discussed here, the only other examples of which we are aware are those containing iron,²⁸ cobalt,²⁹ and iridium.³⁰

Conclusions

The reaction of $[\text{W}(\text{CO})_5]^{2-}$ with $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ leads to a dinuclear stibinidene complex, **3**, while the reaction of this anion with $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ results in the WBi cluster compounds **7** and **8**. In neither case has it proved possible to isolate complexes analogous to **1** and **2**, which contain unsupported Sb=Sb or Bi=Bi double bonds.

It is possible that unsupported homonuclear double bonds between antimony and bismuth are too unstable to have more than a fleeting existence. Alternatively, however, such compounds, while stable in isolation, may decompose under the reaction conditions to form cluster compounds. Further studies are in progress to obtain more data relevant to this topic.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with standard Schlenk techniques. All solvents used were freshly distilled from either CaH_2 or Na/benzophenone immediately prior to use.

Spectroscopic Measurements. Medium-resolution mass spectra were measured on a Du Pont-Consolidated Model 21-491 instrument operating at an ionizing voltage of 70 eV. IR spectra were measured on a Perkin-Elmer 1330 spectrophotometer. UV/vis spectra were recorded on a Cary Model 14 spectrophotometer.

Starting Materials. The compounds $\text{Na}_2[\text{W}(\text{CO})_5]^{9,31}$ and $(\text{Me}_3\text{Si})_2\text{CHECl}_2$ (E = Sb,^{6,7} Bi^{5b}) were prepared according to literature methods. All other materials were procured commercially and used without further purification.

Reaction of $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ with $\text{Na}_2[\text{W}(\text{CO})_5]$. A solution of $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ (0.35 g, 1.0 mmol) in 15 mL of THF was added dropwise to 14.0 mL of a 0.14 M THF solution of $\text{Na}_2[\text{W}(\text{CO})_5]$ at 0 °C. After the reaction mixture was stirred for 2 h, the solvent was evaporated and the resulting residue was dissolved in *n*-hexane and subjected to column chromatography on silica gel. The first fraction eluted (*n*-hexane) was identified as unreacted $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ (0.07 g, 0.2 mmol) by X-ray crystallography.⁶ Dark blue $[\text{W}_2(\text{CO})_{10}(\mu\text{-SbCH}(\text{SiMe}_3)_2)]$ (**3**) (mp 105–106 °C) was eluted with 50/50 toluene/*n*-

- (25) Cowley, A. H.; Kilduff, J. E.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1983**, 528.
 (26) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Hursthouse, M. B.; Karaloz, A. *Organometallics* **1985**, *4*, 2227.
 (27) Panster, P.; Malisch, W. *J. Organomet. Chem.* **1977**, *134*, C32.
 (28) (a) Churchill, M. R.; Fettingner, J. C.; Whitmire, K. H. *J. Organomet. Chem.* **1985**, *284*, 13. (b) Whitmire, K. H.; Lagrone, C. B.; Churchill, M. R.; Fettingner, J. C.; Bondi, L. V. *Inorg. Chem.* **1984**, *23*, 4227. (c) Whitmire, K. H.; Churchill, M. R.; Fettingner, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1056.
 (29) Etzrodt, G.; Boese, R.; Schmid, G. *Chem. Ber.* **1979**, *112*, 2574.
 (30) Kruppa, W.; Bläser, D.; Boese, R.; Schmid, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 209.
 (31) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

hexane as the second fraction. On the basis of the $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ consumed, the yield of **3** was 57% (0.53 g, 0.57 mmol). X-ray quality crystals of **3** were grown by maintaining saturated *n*-hexane solutions at -20°C .

The highest mass peak observable in the EI-MS of **3** occurred at m/e 745, corresponding to the loss of six CO's and one Me group. Fragmentation characteristic of the $(\text{Me}_3\text{Si})_2\text{CH}$ group was evident from peaks at m/e 145, 129, and 73. Several other peaks featured the intensity pattern anticipated for fragments containing two tungsten atoms and one antimony atom. IR data for **3** (CH_2Cl_2): $\nu_{\text{CO}} = 2045, 1965\text{ cm}^{-1}$ (broad). UV/vis data for **3** (C_6H_{12}): $\lambda = 570\text{ nm}$ ($\epsilon = 15\,300\text{ cm}^{-1}\text{ M}^{-1}$), 403 nm ($\epsilon = 5100\text{ cm}^{-1}\text{ M}^{-1}$). Solutions of **3** were found to decompose rapidly, resulting in the appearance of new bands at 290 and 227 nm.

Reaction of $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ with $\text{Na}_2[\text{W}(\text{CO})_5]$. A solution of $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ (0.88 g, 2.0 mmol) in 30 mL of THF was added dropwise to 14.3 mL of a 0.14 M solution of $\text{Na}_2[\text{W}(\text{CO})_5]$ at 0°C . After the reaction mixture was stirred for 3 h, the solvent was evacuated and the resulting residue was dissolved in toluene and subjected to column chromatography on silica gel. The first fraction eluted (*n*-hexane) was **7** (0.07 g, 0.05 mmol, 5% yield based on the $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ consumed). As noted in the Results and Discussion section, this compound was identified as $[\{\text{W}(\text{CO})_5\}_3(\mu_3\text{-}\eta^2\text{-Bi}_2)]$ by X-ray crystallography. Moreover, the spectroscopic characteristics of **7** were identical with those published by Huttner et al.¹⁷ Red, crystalline **8** (0.125 g, 0.08 mmol, 12% yield) was isolated as the second fraction by elution with 2/1 *n*-hexane/toluene. Compound **8** decomposes without melting at $\sim 160^\circ\text{C}$. IR data for **8** (CH_2Cl_2): $\nu_{\text{CH}} = 3022, 2960\text{ cm}^{-1}$; $\nu_{\text{CO}} = 2070$ (shoulder), 2010 (shoulder), 1965 cm^{-1} (broad). UV/vis data for **8** (C_6H_{12}): $\lambda = 492\text{ nm}$ ($\epsilon = 20\,500\text{ cm}^{-1}\text{ M}^{-1}$). The mass spectra of **8** (EI or FAB) were not particularly useful for the characterization purposes due to extensive decomposition of this compound in the probe.

Reaction of MeBiCl_2 with $\text{Na}_2[\text{W}(\text{CO})_5]$. A solution of MeBiCl_2 was prepared in situ by treatment of BiCl_3 (0.315 g, 1.0 mmol) with 1.0 mmol of MeMgCl in 10 mL of Et_2O . This solution was added dropwise to 7.1 mL of a 0.14 M solution of $\text{Na}_2[\text{W}(\text{CO})_5]$ at 0°C . Separation of the reaction mixture as per the $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ reaction produced **7** and **8**. The yield of **8** from this reaction was very small (0.01 g, 1.9% yield).

X-ray Analysis of $[\text{W}_2(\text{CO})_{10}(\mu\text{-SbCH}(\text{SiMe}_3)_2)]$ (3**).** A suitable single crystal of **3** was sealed in a Lindemann capillary and mounted on an Enraf-Nonius CAD-4 diffractometer. Initial lattice parameters were determined from a least squares fit to 25 accurately centered reflections, $15 \leq 2\theta \leq 20^\circ$, and subsequently refined by using higher angle data. These data were indicative of a C-centered monoclinic lattice. Data were collected for one independent quadrant, $+h,+k,\pm l$, by using the ω - 2θ scan mode. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2–7° min^{-1} . ω -Scan angles and aperture settings were determined as described previously.⁶ Crystal stability was monitored every 30 min throughout data collection by means of two check reflections. Systematic absences observed were $h0l$ absent for l odd and hkl absent for $h+k$ odd, thus defining the space group as either *Cc* or *C2/c*.

Data were corrected for Lorentz, polarization, decay, and absorption effects, the latter by an empirical ψ -scan method. Transmission factors ranged from 58.43 to 99.90% (average 77.43%) and corrections factors from 0.7644 to 0.9995 (average 0.8800). Merging of equivalent reflec-

tions gave a total of 2508 unique measured data for which 1994 were considered observed, $I > 3.0\sigma(I)$. The positions of the tungsten and antimony atoms were determined from a Patterson map. This and subsequent refinement, which revealed all non-hydrogen atoms, indicated the centric space group *C2/c* to be the correct choice. As discussed in the Results and Discussion section, the molecule resides on a crystallographic twofold (C_2) axis that passes through the antimony atom and bisects the $\text{W}(1)\text{-Sb}(1)\text{-W}(1')$ angle. The resulting disorder associated with $\text{C}(1)$ was modeled by refining two isotropic carbon atoms 0.41 Å on either side of the C_2 axis with 50% occupancy factors. Other attempted models, including a single anisotropically refined carbon and an ordered structure in the noncentric space group *Cc* did not prove satisfactory. All remaining non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were neither located nor refined. Pertinent crystallographic data collection and structure refinement parameters are collected in Table IV.³²

X-ray Analysis of $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)(\mu\text{-BiMeW}(\text{CO})_5)\text{-C}_6\text{H}_6]$ (8**).** Details for the data collection for **8** are essentially the same as those described for **3**. The structure was solved by using MULTAN,³³ which revealed the positions of the W and Bi atoms. Subsequent refinement was carried out as described for **3**. There were a number of problems associated with this structure, which result directly from poor quality data due to a crystal of low quality. This is particularly apparent in some of the bond distance and angle parameters associated with the carbonyl ligands and with many of the derived thermal parameters. In the final difference Fourier map there were several peaks of high electron density (2.32 e \AA^{-3}), but all were close to the heavy atoms. This is also a result of bad data.

In neither case is the X-ray structure determination of high quality due mainly to problems in obtaining high-quality crystals. However, we consider that both structures are adequately determined by these experiments.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8506029) and the Robert A. Welch Foundation for generous financial support.

Supplementary Material Available: Tables bond distances and angles and of thermal parameters and ORTEP projections showing thermal ellipsoids for compounds **3** and **8** (8 pages); tables of observed and calculated structure factors for compounds **3** and **8** (22 pages). Ordering information is given on any current masthead page.

- (32) All programs used in the structure determination were from: *SDP Program Package*; B. A. Frenz and Associates, Inc.: College Station, TX. Scattering factor coefficients are taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vol. IV.
- (33) Main, P. "MULTAN 82", University of York, York, England, 1982.
- (34) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)