positioning of the potential energy surfaces does not provide a thermal energy barrier in these examples.

It should be mentioned that a light-induced spin-state conversion from $^1A_1(O_h)$ to $^5T_2(O_h)$ was observed earlier by McGarvey et al.[20] with an iron(II) spin-crossover complex in solution. However, in that case the lifetime of the excited $^5T_2(O_h)$ state was very short (on the order of nanoseconds), whereas in the case of LIESST, which apparently occurs only in the crystalline state, the lifetime of the light-induced HS state is practically infinitely long. We wish to stress this point, because it opens the possibility of using such spin-crossover materials for optical data storage and optical filters. We have started extensive work in this direction.

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Organometallic Complexes of Bismuth: Preparation and Crystal and Molecular Structure of $[(CO)_5Mn]_3Bi$

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The incorporation of main-group elements into organometallic complexes is a field of current interest,[1] whereby the contrasting electronic requirements of the p-block elements can confer a variety of structural or reactivity changes on the transition-metal centers.[2] Conversely, the presence of transition-metal fragments as ligands to a main-group element can provide novel bonding modes for, and geometries about, the main-group central atom.[3] Bismuth, being not only the heaviest member of group 15 but also the heaviest stable element in the periodic table, can be expected to display effects that are related not only to the electropositive character but also to great size and mass in a pronounced way. These effects are exemplified by bismuthinidene[4] and dibismuthinidene[5] complexes, where oxidation states for Bi of 0 or I are obtainable, and where the Bi_2 unit can function as a four-π- or six-π-electron donor.[5] Cluster complexes of bismuth are also known, where the Bi atom can adjust from the freedom of capping a nonbonded triangle of metal atoms to the strain of occupying the apex of a closed tetrahedron, without problems.[6-9] Here we report the synthesis and structural characterization of $[(CO)_5Mn]_3Bi$, which contains the first example of a Mn–Bi single bond and should provide an entry to other MnBi cluster compounds. Finally, the ability of metal-complexed bismuth to form arene adducts was a further aspect of interest.[10]

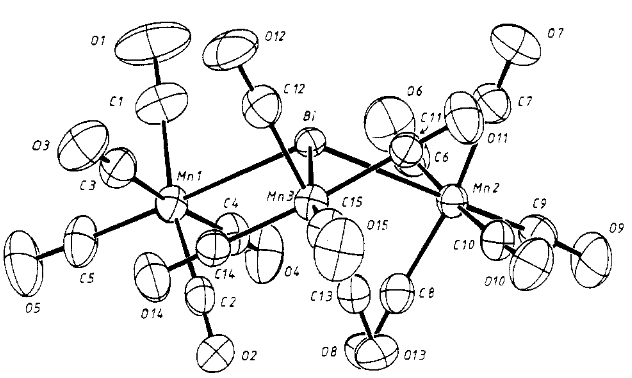

Figure 1. Molecular structure and atom-labeling scheme for $[(CO)_5Mn]_3Bi$. Atoms are drawn with 50% probability ellipsoids.

Table I. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Bi	0.0963 (1)	0.8110 (1)	0.1955 (1)	0.028
Mn1	−0.0946 (2)	0.6850 (1)	0.1137 (1)	0.035
Mn2	0.0090 (2)	0.8003 (1)	0.3346 (1)	0.032
Mn3	−0.0858 (2)	0.9545 (1)	0.1379 (1)	0.033
C1	0.1661 (13)	0.6435 (4)	0.1227 (4)	0.050
C2	−0.3279 (11)	0.7415 (4)	0.1164 (3)	0.036
C3	−0.0364 (11)	0.7430 (4)	0.0399 (3)	0.045
C4	−0.1355 (11)	0.6319 (4)	0.1918 (3)	0.044
C5	−0.2131 (13)	0.6088 (4)	0.0575 (4)	0.051
C6	0.1258 (12)	0.7037 (4)	0.3343 (3)	0.047
C7	0.2655 (12)	0.8425 (4)	0.3565 (3)	0.048
C8	−0.2431 (12)	0.7624 (4)	0.2959 (3)	0.040
C9	−0.0371 (11)	0.7863 (4)	0.4215 (3)	0.043
C10	−0.0931 (11)	0.8983 (4)	0.3372 (3)	0.040
C11	0.0811 (10)	0.9912 (4)	0.2138 (3)	0.039
C12	0.1383 (12)	0.9530 (4)	0.0925 (3)	0.047
C13	−0.2963 (11)	0.9335 (4)	0.1854 (3)	0.037
C14	−0.2351 (10)	0.9113 (4)	0.0608 (3)	0.038
C15	−0.1712 (12)	1.0522 (4)	0.1126 (3)	0.045
O1	0.3217 (10)	0.6182 (4)	0.1256 (4)	0.078
O2	−0.4751 (8)	0.7747 (3)	0.1169 (2)	0.050
O3	−0.0013 (10)	0.7754 (3)	−0.0062 (3)	0.065
O4	−0.1649 (9)	0.5973 (3)	0.2371 (2)	0.055
O5	−0.2844 (11)	0.5625 (3)	0.0213 (3)	0.075
O6	0.2102 (10)	0.6459 (3)	0.3383 (3)	0.072
O7	0.4217 (9)	0.8682 (4)	0.3701 (3)	0.070
O8	−0.4007 (8)	0.7413 (3)	0.2744 (3)	0.055
O9	−0.0791 (10)	0.7795 (3)	0.4748 (2)	0.062
O10	−0.1519 (9)	0.9607 (3)	0.3441 (3)	0.061
O11	0.1826 (9)	1.0155 (3)	0.2597 (2)	0.060
O12	0.2705 (9)	0.9523 (4)	0.0641 (3)	0.068
O13	−0.4338 (6)	0.9219 (3)	0.2109 (2)	0.052
O14	−0.3304 (8)	0.8891 (3)	0.0114 (2)	0.059
O15	−0.2265 (11)	1.1136 (3)	0.0989 (3)	0.067

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the U_{ij} matrix. Esd's are given in parentheses.

Results and Discussion

Treatment of $Na^+[Mn(CO)_5]^-$ with $^1/_3$ equiv of bismuth trichloride affords $[(CO)_5Mn]_3Bi$ (**1**) as green, air-sensitive needles, which were characterized by elemental analysis and infrared and mass spectroscopies. The solution IR spectrum of **1** (CH_2Cl_2) shows carbonyl bands only in the terminal region, and the mass spectrum displays a parent ion at 794 amu, together with a series of peaks corresponding to $BiMn_3(CO)_n$, n = 10–8, 6–0.

We were interested to know how sterically demanding $Mn(CO)_5$ units would influence the geometry at the Bi atom, and so we

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Table II. Selected Bond Distances (Å) and Angles (deg) for $[(CO)_5Mn]_3Bi$ (**1**)

		(a) Distances			
Bi–Mn1	2.884 (1)	Bi–Mn2	2.916 (1)	Bi–Mn3	2.911 (1)
Mn1–C1	1.866 (8)	Mn2–C6	1.843 (7)	Mn3–C11	1.838 (7)
Mn1–C2	1.846 (8)	Mn2–C7	1.848 (8)	Mn3–C12	1.867 (8)
Mn1–C3	1.864 (7)	Mn2–C8	1.855 (8)	Mn3–C13	1.851 (7)
Mn1–C4	1.858 (7)	Mn2–C9	1.814 (7)	Mn3–C14	1.843 (6)
Mn1–C5	1.821 (7)	Mn2–C10	1.826 (7)	Mn3–C15	1.823 (7)
		(b) Angles			
Mn1–Bi–Mn2	110.3 (1)	Mn2–Bi–Mn3	106.9 (1)	Mn3–Bi–Mn1	107.5 (1)
Bi–Mn1–C1	85.0 (3)	Bi–Mn2–C6	84.5 (2)	Bi–Mn3–C11	79.1 (2)
Bi–Mn1–C2	83.4 (2)	Bi–Mn2–C7	83.0 (2)	Bi–Mn3–C12	82.0 (2)
Bi–Mn1–C3	84.7 (2)	Bi–Mn2–C8	86.4 (2)	Bi–Mn3–C13	86.4 (2)
Bi–Mn1–C4	90.8 (2)	Bi–Mn2–C9	175.6 (2)	Bi–Mn3–C14	96.8 (2)
Bi–Mn1–C5	176.5 (2)	Bi–Mn2–C10	95.8 (2)	Bi–Mn3–C15	170.7 (2)

undertook a crystallographic investigation of **1**. The determination of the structure of **1** would also provide valuable structural data for this scarcely investigated class of compounds.[11]

Diffraction-quality crystals were obtained from a saturated benzene solution of **1**, and the result of the analysis is shown in Figure 1. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table I. Table II contains selected intramolecular bond distances and angles for **1**.

The monomeric **1** maintains a pyramidal geometry about the central bismuth atom, with each Mn atom having an approximate octahedral environment. The molecule relieves the possible steric interactions between the carbonyl groups of the $Mn(CO)_5$ units through conrotation about the three Mn–Bi vectors, such that the carbonyl ligands are interleaved. The average twist angle[13] of the four equatorial carbonyl ligands is 22.7°. The attainment of this relief results in the Mn–Bi–Mn′ angles being close to tetrahedral and only slightly greater than those found in $[(CO)_4Co]_3Bi$[7] (Co–Bi–Co′(av) = 106.8°). The conrotation of the $Mn(CO)_5$ units results in each molecule being chiral in the solid state; only one enantiomer is shown in Figure 1. The long Bi–Mn bonds also help to separate the manganese fragments, and in fact most of the Bi–Mn–C_{eq} angles are slightly less than 90°, indicating a distortion of the 12 equatorial carbonyl ligands *toward* the Bi atom. The axial carbonyl ligands show a shortening of 0.03 Å with respect to the equatorial carbonyls (averages: equatorial, 1.850 Å; axial, 1.819 Å), but all Mn–C–O angles are close to 180°, with no significant deviations from linearity.

Although structural data for first-row transition-metal–bismuth single bonds are scarce, the B–Mn distances in **1** (average 2.904 Å) are substantially longer than those for Bi–Co ($[(CO)_4Co]_3Bi$, Bi–Co(av) = 2.766 Å[7]) or those for Bi–Fe in open or closed clusters (e.g. in $\{[CpFe(CO)_2]_2BiCl\}_3$, Bi–Fe(av) = 2.687 (2) Å; $[BiFe_3(CO)_{10}]^-$, Bi–Fe = 2.650 (2) Å[8]). A dramatic difference in Bi–Mn bond lengths between **1** and the bismuthidene complex $\{[CpMn(CO)_2]_2BiCl\}_2$[4] also exists, where in the latter the dative Bi–Mn bond measures 2.469 Å. Comparative data for the heavy main-group elements Tl and Pb are also lacking[11] for cases where a single Mn–M bond is present. For the complexes $[(CO)_5Mn]_3M$, M = In,[14] Tl,[15] although synthesized, little reactivity has been explored. We can expect that these and the title compound should e.g. be photochemically active, providing routes to new closo cluster compounds incorporating heavy elements, as has been shown for iron.[9] Preliminary investigations indicate that intermediates in the reaction path leading to **1** are also isolable.

It is important to note that **1** does not crystallize from benzene as an arene adduct, while bismuth compounds with electronegative substituents have been found to form isolable π complexes with a variety of neutral arenes.[10]

Experimental Section

Synthesis of $[Mn(CO)_5]_3Bi$. The anion $Mn(CO)_5^-$ was prepared in thf solution (30 mL) from $Mn_2(CO)_{10}$ (0.69 g, 1.77 mmol) and sodium amalgam. The resulting solution was cooled to −30 °C, and a solution of $BiCl_3$ (0.19 g, 0.60 mmol) in thf (20 mL) was added dropwise over 15 min. The resulting golden brown solution was warmed to room temperature and evaporated to dryness under reduced pressure. The brown solid was washed with diethyl ether (3 × 25 mL) and the green residue recrystallized from CH_2Cl_2/ether (1:1), giving bright green needles: yield 0.45 g, 48%; mp 146 °C dec. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2052 s, 2005 sh, 1978 vs. Anal. Calcd for $C_{15}BiMn_3O_{15}$ (M_r = 793.94): C, 22.69; O, 30.2; Mn, 20.76. Found: C, 22.69; O, 30.6; Mn, 20.76.

X-ray structure determination: Enraf-Nonius CAD4 diffractometer; $C_{15}BiMn_3O_{15}$, $M_r = 793.94$; monoclinic, $P2_1/n$; $a = 6.682$ (1), $b = 17.255$ (2), $c = 19.830$ (2) Å; $\beta = 99.22$ (1)°; $V = 2256.82$ Å^3; $D_{calcd} = 2.34$ g cm^{-3} for $Z = 4$; $F(000) = 1472$; μ(Mo Kα) = 91.16 cm^{-1}; 7282 measured reflections, 6546 unique ($R_{int} = 0.014$) and 4301 observed ($I \geqslant 2.0\sigma(I)$); ϑ–2ϑ scan, $\Delta\omega = 0.80 + 0.35 \tan\theta$, $[(\sin\theta)/\lambda]_{max} = 0.702$; *hkl* +9,+24,±27; Mo K$\alpha$ radiation, $\lambda = 0.71069$ Å; graphite monochromator. The data were corrected for decay, Lp, and absorption effects (empirical, relative transmission 0.67–1.00). Solution was by a novel random start multisolution direct methods program (SHELXS-86[16]) and was completed by Fourier syntheses. All atoms were refined anisotropically by full-matrix least squares, with $R = 0.033$, $R_w = 0.028$ ($w = 1/\sigma^2(F_o)$), 307 refined parameters, and $\Delta\rho_{final} = +0.99/1.06$ with a maximum at Bi (SHELX-76).

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Registry No. **1**, 106213-52-9; $Mn_2(CO)_{10}$, 10170-69-1; Mn, 7439-96-5; Bi, 7440-69-9.

Supplementary Material Available: Tables of complete distances and angles and anisotropic thermal parameters for **1** (4 pages); a table of observed and calculated structure factors for **1** (24 pages). Ordering information is given on any current masthead page.

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(13) The twist angle gives a measure of the distortion from ideal C_{3v} symmetry. This angle is that between planes A and B. Plane A is defined by Bi, Mn, and the center of the Mn1, Mn2, and Mn3 triangle. Plane B is defined as Mn, the center of the 3 Mn triangle, and the two C_{eq} atoms closest to vertical. For C_{3v} symmetry this angle can be 0 or 45°.

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Preparation of Gold Derivatives of Nitrido Clusters. Structural Characterization of $Ph_3PAuFeRu_3N(CO)_{12}$

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Although the first transition-metal compounds containing $AuPR_3$ groups were synthesized over 20 years ago,[3] this area has

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