Table I. Structural Data for Three Crystalline Forms of Phosphorus(V) Oxides[a]

cryst form	P–O_{ext}	P–O_{bridge}	$\angle$POP	$\angle$$OPO_{ext}$	$\angle$$OPO_{bridge}$	ref
rhombohedral (trigonal) (H form)[c]	1.46 (3)	1.58 (3)	124 (2)	117 (2)	101 (2)	4
face-centered O form[b] (O form)[c]	1.4_0	1.6_5	124	117	96	5
primitive O form (O′ form)[c]	1.49 (3)	1.56 (3)	145 (2)	116	104 (2)	6

[a] Distances are in angstroms and angles in degrees. The esd's are enclosed in parentheses. The values are averages of the values in the asymmetric units unless indicated otherwise. [b] The values quoted are those assumed by deDecker.[5] The angles are calculated by this author on the basis of the assumed (by deDecker) P···P and O···O distances. [c] Previous label.

upon an electron diffraction study[8] of gaseous phosphorus(V) oxide, of which there is just one form. The crystals of this phosphorus(V) oxide containing discrete P_4O_{10} molecules belong to the rhombohedral crystal system (space group $R3c$, C_{3v}^6, No. 161) and should be correctly called the rhombohedral or trigonal form. The distinction between the hexagonal crystal system and the rhombohedral (trigonal) crystal system has been presented recently.[9,10] A reasonable name for this compound is "clovo tetraphosphorus decoxide" in any state. The Greek word "clovo" means cage. The existence of the discrete molecule P_4O_{10} cannot be overemphasized.

A second crystalline form of phosphorus(V) oxide has been labelled the O form,[1-3] based upon its orthorhombic crystal system as shown by single-crystal X-ray diffraction study.[5] The structure determination is the least precise among all the known crystalline phosphorus(V) oxides.[4-7,11] The space group is $Fdd2$ (C_{2v}^{19}, No. 43). The only definitive result is that there are 20-membered rings containing alternating P and O. The rings share POP linkages with other 20-membered rings to give a *three-dimensional network*; there are *no* discrete molecules. Hence, the crystals of the "clovo tetraphosphorus decoxide" and the crystalline form with the face-centered orthorhombic crystal system cannot be polymorphs. Just because two crystalline products show the same elemental composition does not mean that these are polymorphs. A precise definition of the term "polymorphs" has been presented elsewhere.[12] It is, therefore, necessary to name this orthorhombic crystalline form to distinguish it from the rhombohedral (trigonal) form. We name it "diktyo-icosogonal phosphorus(V) oxide". The Greek word "diktyo" means network. The crystals should be referred to as the face-centered O form.

The third crystalline form, labeled as O′ form, thought to be tetragonal by Hill, Faust, and Hendricks,[2] belongs in fact to the orthorhombic crystal system, space group $Pnam$ (D_{2h}^{16}, No. 62).[6,11] We suggest that this crystalline form be called the primitive O form. In this structure we have 12-membered rings with alternating P and O jointed with other 12-membered rings with common POP sides to give a pseudo-hexagonal-packed *layer* structure. Again, there are no discrete molecular entities. The POP angle linking the atoms in the ring and between rings is 145° as shown in Table I. This is clearly a different structural feature of significance compared to other similar values in the other two crystal forms. Hence, this crystal represents a different compound and is not a polymorph of either of the other two crystal forms. This requires that we give it a separate name. We suggest "phyllo-dodecagonal phosphorus(V) oxide". The Greek word "phyllo" means layer.

The distinctions suggested above are also supported by the fact that the three solids give different liquids upon melting.[2,3] In addition, the reaction of water with the rhombohedral (trigonal) form gives a clear solution with sudden evolution of heat, whereas the face-centered O form gives a suspension that dissolves slowly even at steam-bath temperature.[2,3] The electrical conductivities of the solutions of the rhombohedral (trigonal) form and face-centered O form in water, based upon the calculation of moles of the solute in terms of the formula P_4O_{10} in both cases, are different.[13] The primitive O form reacts with water to give a gel.[2,3]

There are other systems in inorganic chemistry that require the same kind of treatment. We hope to present these in the future.

Acknowledgment. I am grateful to the reviewers for suggestions that have made the presentation clearer.

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Light-Induced Excited-Spin-State Trapping (LIESST) in $[Fe(2\text{-}Y\text{-}phen)_3]X_2$ Spin-Crossover Compounds

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About 2 years ago we observed the first case of "light-induced excited-spin-state trapping (LIESST)" in the iron(II) spin-crossover compound $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole). This compound shows a thermally induced low-spin (LS) $\rightleftharpoons$ high-spin (HS) transition.[1-3] The $^1A_{1g}(O_h)$ ground state can be quantitatively converted into the $^5T_{2g}(O_h)$ state by irradiating the sample into the spin-allowed $^1A_1 \rightarrow {}^1T_1$ absorption band at temperatures much below the thermal transition temperature $T_c \sim 130$ K.[4,5] It could be shown that the trapped HS state has practically infinite lifetime below $T_c{}^L \sim 50$ K. We could also show that the mechanism of this LS → HS spin-state conversion involves a double intersystem crossing after the first spin-allowed transition, $^1A_1 \rightarrow {}^1T_1 \rightarrow {}^3T_1 \rightarrow {}^5T_2$. The back-relaxation from the trapped $^5T_2$ state to the $^1A_1$ ground state is thermally hindered.

More recently, we have reported on the occurrence of the LIESST effect in other iron(II) spin-crossover complexes such as $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline) and $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ (2-pic = 2-picolylamine).[6] The critical temperature $T_c{}^L$ for the $^5T_2 \rightarrow {}^1A_1$ back-relaxation was found to be ca. 55 K in the former and ca. 30 K in the latter case.

It is not clear as yet which conditions are to be fulfilled in order to see the LIESST effect. One important factor is the energetically favorable position of the spin-triplet levels,[5] which "catalyze" the population of the metastable spin-quintet state through spin–orbit coupling. Another important factor is the relative position, re-

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Table I. Isomer Shift (δ, Relative to the ^{57}Co/Rh Source), Quadrupole Splitting (ΔE_Q), Line Width (Γ), and Area Fraction of the HS and LS Resonance Lines of ^{57}Fe Mössbauer Spectra[a]

			δ, mm s^{-1}			ΔE_Q, mm s^{-1}			Γ, mm s^{-1}			A, %		
compd		T, K	HS1	HS2	LS	HS1	HS2	LS	HS1	HS2	LS	HS1	HS2	LS
$[Fe(2\text{-}CH_3\text{-}phen)_3](ClO_4)_2$	bb	5	1.033 ±0.181	1.210 ±0.270	0.398 ±0.021	1.982 ±0.369	1.587 ±0.575	0.669 ±0.046	0.391 ±0.261	0.640 ±0.334	0.360 ±0.017	12.4 ±11.3	6.8 ±13.2	80.8 ±3.7
	ab	5	0.990 ±0.005	0.992 ±0.005	0.415 ±0.011	1.919 ±0.018	1.280 ±0.019	0.511 ±0.020	0.388 ±0.023	0.353 ±0.025	0.281 ±0.029	47.0 ±3.8	38.0 ±4.1	15.0 ±1.1
$[Fe(2\text{-}CH_3\text{-}phen)_3](BO_4)_2$	bb	13	0.882 ±0.063	1.041 ±0.083	0.408 ±0.002	1.843 ±0.122	2.114 ±0.169	0.597 ±0.004	0.304 ±0.065	0.341 ±0.097	0.372 ±0.004	7.4 ±2.5	7.0 ±2.6	85.6 ±9.0
	ab	10	0.996 ±0.007	0.935 ±0.016	0.469 ±0.058	1.472 ±0.029	1.817 ±0.139	0.616 ±0.120	0.283 ±0.026	0.369 ±0.065	0.245 ±0.50	58.0 ±22.2	31.1 ±22.8	10.9 ±1.8
$[Fe(2\text{-}CH_3O\text{-}phen)_3]\text{-}(ClO_4)_2\cdot H_2O$	bb	25			0.390 ±0.001			0.529 ±0.001			0.261[b] ±0.003 0.272[c] ±0.003			100
	ab	13	1.026 ±0.006	1.000 ±0.004	0.385 ±0.002	1.544 ±0.030	2.149 ±0.020	0.532 ±0.005	0.407 ±0.030	0.396 ±0.021	0.296 ±0.005	21.9 ±3.2	32.6 ±3.2	45.5 ±0.7

[a] bb = before bleaching; ab = after bleaching. [b] High-velocity component. [c] Low-velocity component.

garding energy and nuclear coordinate, of the potential energy surfaces for the LS($^1A_1$) state and the HS($^5T_2$) state. The two main parameters determining the size of the energy barrier are (i) the difference in the ionic radii of the LS and the HS states ($r_{LS} < r_{HS}$, which is known from single-crystal X-ray diffraction measurements below and above T_c[7-9] and (ii) the free energy difference between the lowest vibronic levels of the LS and the HS states. In the course of searching for more systems in the realm of iron(II) spin-crossover compounds showing the LIESST effect, we have been successful with the class of complexes $[Fe(2\text{-}Y\text{-}phen)_3]X_2$ (Y = CH_3, X = ClO_4; Y = CH_3, X = BPh_4; Y = CH_3O, X_2 = $(ClO_4)_2\cdot H_2O$). The results are presented in the following.

Experimental Section

$[Fe(2\text{-}CH_3\text{-}phen)_3](ClO_4)_2$ was prepared by the procedure of Goodwin et al.[10] The dry material was recrystallized from a methanol/water (1:1) mixture according to Fleisch et al.[11]

$[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2$ was synthesized according to the description given by Goodwin et al.[12] One portion of the polycrystalline material was recrystallized from acetone; another portion, from nitromethane. The latter gave the better crystals (orange-yellow needles up to 3–4 mm long and ca. 0.5–1 mm thick), however, under inclusion of one molecule of nitromethane per formula unit yielding $[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2\cdot CH_3NO_2$.

$[Fe(2\text{-}CH_3O\text{-}phen)_3](ClO_4)_2\cdot H_2O$ was prepared the same way as described previously.[13] The material was recrystallized from CH_3OH/H_2O (9:1).

All samples were checked for chemical purity by elemental analysis.

The ^{57}Fe Mössbauer spectra were recorded in transmission geometry by using a conventional spectrometer operating in the constant-acceleration mode. The samples (up to ca. 100 mg each) were sealed into polished Plexiglas containers (2 cm^2; effective sample thickness <1 mm) and mounted in a helium bath cryostat equipped with a calibrated silicon diode and temperature controller. The temperature stability was better than ±1 K. The source (^{57}Co/Rh, ca. 30 mCi) was kept at room temperature. The spectra were fitted to Lorentzian lines with the least-squares fitting program MOSFUN.[14]

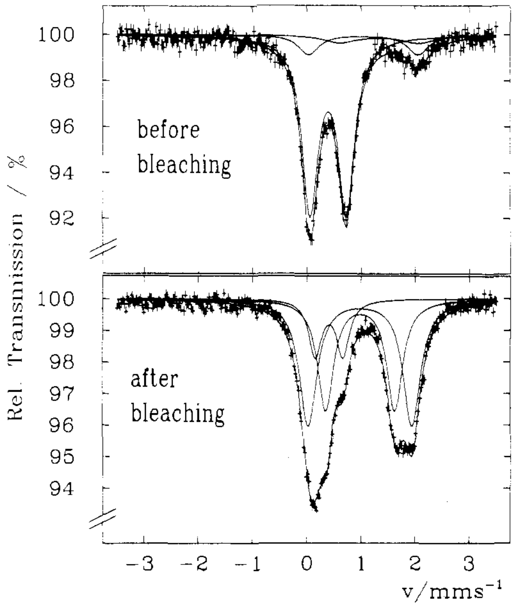

Figure 1. ^{57}Fe Mössbauer spectra of $[Fe(2\text{-}CH_3\text{-}phen)_3](ClO_4)_2$ at 4.2 K before bleaching (A) and after bleaching (B). Source: ^{57}Co/Rh at 295 K.

The absorbers were bleached for up to 2 h with a Xe arc lamp (XBO, 150 WM, Siemens). A heat absorption filter (KG 1, Schott, Mainz) was employed to cut off the IR part of the light source.

Results and Discussion

The existence of a temperature-dependent HS($^5T_2$) $\rightleftharpoons$ LS($^1A_1$) transition in $[Fe(2\text{-}CH_3\text{-}phen)_3](ClO_4)_2$ was well documented many years ago by Goodwin et al.[10] and by König et al.[15] In a later reinvestigation of this system we have detected two different spin-quintet quadrupole doublets in the Mössbauer spectra, which we have assigned to the $^5E(D_3)$ state (with the smaller splitting energy) and the $^5A_1(D_3)$ state (with the larger splitting energy) arising from the $^5T_{2g}(O_h)$ state upon trigonal field distortion.[11] In the present study we could confirm the existence of these two HS states. The compound shows a residual paramagnetism of up to 20% in the low-temperature region (see Figure 1A).

After bleaching of the sample with white light for ca. 2 h at 6 K, the LS($^1A_1$) state is nearly quantitatively converted into the two HS states, which are also observed in the high-temperature region (see Figure 1B). The Mössbauer parameters (isomer shift δ and quadrupole splitting ΔE_Q) of these light-induced metastable

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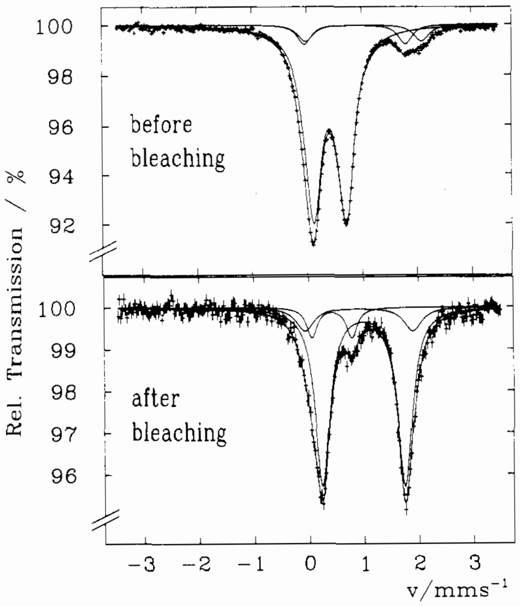

Figure 2. ^{57}Fe Mössbauer spectra of $[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2$ at 10 K before bleaching (A) and at 13 K after bleaching (B). Source: ^{57}Co/Rh at 295 K.

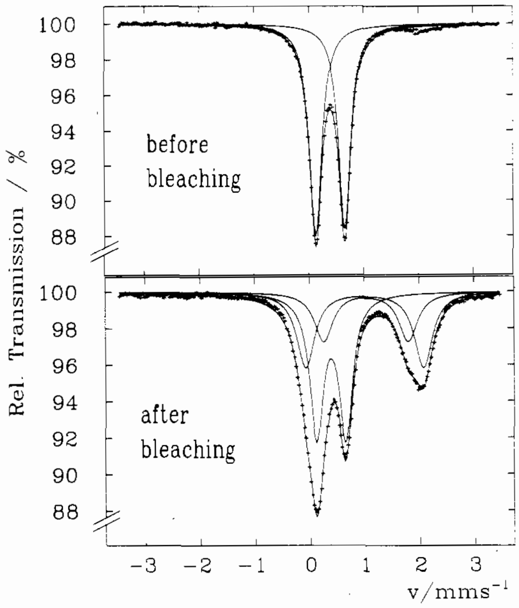

Figure 3. ^{57}Fe Mössbauer spectra of $[Fe(2\text{-}CH_3O\text{-}phen)_3](ClO_4)_2{\cdot}H_2O$ at 25 K before bleaching (A) and at 13 K after bleaching (B). Source: ^{57}Co/Rh at 295 K.

spin states are the same as those derived from the absorption spectra of the residual fraction of the HS states (see Table I and ref 11). Thermally induced back-relaxation to the LS($^1A_1$) ground state begins around 35 K; the Mössbauer spectrum shows a time-dependent increase in the intensity of the LS quadrupole doublet with the same parameters as found before bleaching. The back-relaxation behavior appears to be the same for both metastable HS states, as judged from the ratio A(HS1)/A(HS2) of the area fractions of the two Mössbauer quadrupole doublets; this ratio remains approximately constant during the relaxation process.

The compound $[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2$, first investigated by König et al.,[16] also exhibits temperature-dependent spin transition. However, a reinvestigation in the course of the present LIESST studies revealed the same kind of superposition of two HS quadrupole doublets, HS1($^5A_1$) and HS2(^5E), as seen in the perchlorate (see Figure 2); this was not known from the earlier work of König et al.[16] The room-temperature Mössbauer spectrum could be fitted with only one quadrupole doublet, most likely due to the fact that the Mössbauer parameters of the ^5A and ^5E states are similar. Up to now, only one crystal structure determination on $[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2$ at room temperature is known.[12] In that case there is no evidence for the existence of two crystallographically different iron sites, which agrees with the room-temperature Mössbauer spectrum. It is possible that a trigonal distortion, with both elongation and compression, becomes effective at lower temperatures.

The LIESST phenomenon occurs also in this compound, as can be seen from the Mössbauer spectra of the sample before and after bleaching at 10 K (see Figure 2). The HS resonances were fitted as a superposition of two quadrupole doublets HS1 and HS2 with an intensity ratio of ca. 1:2; the parameter values differ slightly from those derived from the absorption spectrum at 10 K before bleaching (see Table I). Thermally induced back-relaxation to the LS($^1A_1$) state occurs around 35 K, similar to the case of the perchlorate complex.

The compound $[Fe(2\text{-}CH_3\text{-}phen)_3](BPh_4)_2{\cdot}H_3CNO_2$ shows incomplete temperature-induced HS $\rightleftharpoons$ LS transition (e.g. LS fraction is 8% at 123 K and 35% at 27 K). On illumination with green light, the LS component is quantitatively converted into the HS state, as evidenced by optical spectroscopy (Cary 17, 10 K).

The compound $[Fe(2\text{-}CH_3O\text{-}phen)_3](ClO_4)_2{\cdot}H_2O$ has previously been characterized as a spin-crossover system.[13] The spin-transition behavior deviates somewhat from that of the 2-CH$_3$-phen complexes in that the HS state appears to be less favored. Spectrum A of Figure 3 was recorded at 25 K; it reflects nearly pure LS behavior (cf. Table I for the isomer shift and quadrupole splitting). After bleaching of the sample with green light at 13 K, spectrum B of Figure 3 was recorded. It shows a nearly 50% reduction of the LS state in favor of the light-induced production of the HS state. As in the case of the 2-CH$_3$-phen complexes, we note again that two HS states, presumably $^5A_1$ and ^5E under trigonal symmetry, are observed in both thermally induced and light-induced LS $\rightleftharpoons$ HS spin-state conversion.

It is noteworthy that the light-induced spin-state conversion is not complete in all cases. We notice that this is always the case when the spin-crossover compound under study has low-energy MLCT absorption bands overlapping with d–d transitions. In this case, light that is used to excite the $^1A_1$ ground state into spin-singlet ligand field and charge-transfer states (as the precursor processes for the population of the metastable $^5T_2$ state via double IC) simultaneously excites the metastable $^5T_2$ state to spin-quintet CT states. Relaxation from these states to the $^1A_1$ ground state by double IC is possible and causes the observed partial spin-state conversion.

It has been demonstrated[5,17] that the metastable $^5T_2$ state generated by LIESST can be pumped back to the $^1A_1$ ground state by selective irradiation into the $^5T_2 \rightarrow {}^5E$ absorption band using red light of ca. 750 nm (krypton laser or xenon arc lamp with filters, Schott RG 695). For this reason, it is necessary to use IR cutoff filters together with a xenon arc lamp to populate the $^5T_2$ state by LIESST. It has been suggested[17] that an iron(II) high-spin complex with ligand field strength close to the spin-crossover point could be converted to the LS($^1A_1$) state by illuminating with red light at sufficiently low temperature. This should be possible provided the overlap of the potential energy surfaces of the HS and LS states is such as to form an energy barrier preventing thermal back-relaxation from the LS to the HS state ("reverse LIESST effect"). We have done this experiment with $[Fe(2\text{-}Cl\text{-}phen)_3](ClO_4)_2$, which is high spin at all temperatures.[18,19] Irradiation with red light for 2 h at 12 K did not cause any change in the ^{57}Fe Mössbauer spectrum. The same experiment was carried out with $FeSO_4{\cdot}7H_2O$ and $[Fe(pyrazole)_6](ClO_4)_2$, again without success. Presumably, the relative

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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)$_5$Mn]$_3$Bi

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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)$_5$Mn]$_3$Bi, 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]

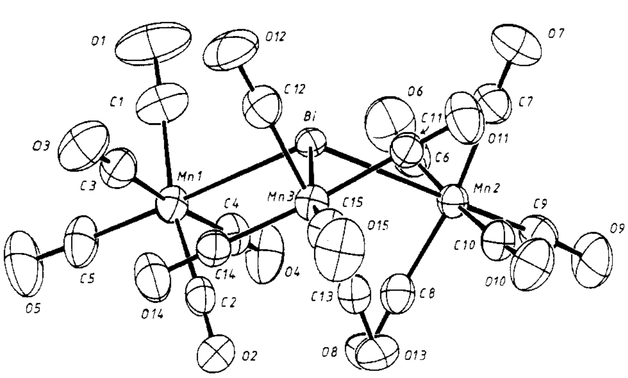

Figure 1. Molecular structure and atom-labeling scheme for [(CO)$_5$Mn]$_3$Bi. Atoms are drawn with 50% probability ellipsoids.

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)$_5$Mn]$_3$Bi (**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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