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Transition-Metal-Substituted Dichlorobismuthanes as Starting Materials for Novel Bismuth−Transition-Metal Clusters[†]

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The reaction of [{Cp(CO)$_2$Fe}BiCl$_2$] (**1a**) with [Co(CO)$_4$]$^-$ leads to the formation of the first heteroleptic substituted bismuthane, [(μ_3-Bi){Co(CO)$_4$}$_2${Fe(CO)$_2$Cp}] (**2**). When the "open" complex **2** is irradiated, the heterocubane [Bi$_4${Co(CO)$_3$}$_4$] (**3**) is formed. [{Cp″(CO)$_2$Fe}BiCl$_2$] (**1b**; Cp″ = η^5-C$_5$H$_3$-*t*Bu$_2$) reacts with [Fe(CO)$_4$]$^{2-}$ to give the *nido* cluster [{Fe$_3$(CO)$_9$}{μ-BiFe(CO)$_2$Cp″}$_2$] (**4**) and to give the complex [Bi$_4${μ_3-Fe(CO)$_3$}$_3${Fe(CO)$_2$Cp″}$_2$] (**5**); the latter contains a distorted-tetrahedral Bi$_4$ cluster core in which three of the faces are capped by Fe(CO)$_3$ moieties. The reaction of **1b** with Na$_2$[W$_2$(CO)$_{10}$] yields the Bi-bridged tetrahedral W$_2$Bi$_2$ cluster [{W$_2$(CO)$_8$}(μ,η^2-Bi$_2$){μ-BiFe(CO)$_2$Cp″}] (**6**). In contrast to this, the molybdenum-substituted analogue [{Cp″(CO)$_3$Mo}BiCl$_2$] (**7**) reacts with Na$_2$[Fe(CO)$_4$] to yield the *arachno* cluster [{Fe$_2$(CO)$_6$}{Fe(CO)$_4$}{μ_3-BiMo(CO)$_3$Cp″}$_2$] (**9**). When **7** is reacted with Na$_2$[W(CO)$_5$], the complex [{Cp″(CO)$_3$Mo}$_2$BiCl] (**10**) is obtained. The decomposition of compound **7** in THF leads to the ionic complex [(Cp″MoCO)$_2$(μ-Cl)$_3$]$_2$[Bi$_2$Cl$_8$(thf)$_2$] (**8**). The crystal structures of all products are presented.

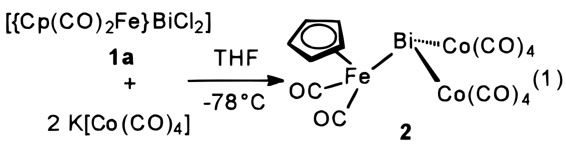
Introduction

Organometallic complexes incorporating heavy main-group elements are attracting increasing attention. A large variety of those complexes can be obtained, using the reactivity of group 15 halogenides toward complex metalates as well as to metal dimers. This field of research is well-established, as is the chemistry of dimetal-substituted halogeno pnictogenides. Many examples of these species and their synthetic potential can be found in the literature.[1] However, organotransition-metal complexes containing bismuth are still rare and only a few research groups are concerned with this field of chemistry.

Recently we reported on the synthesis, structure, and properties of [{Cp^x(CO)$_2$Fe}BiCl$_2$] (**1a,** Cp^x = Cp; **1b**, Cp^x = η^5-C$_5$H$_3$*t*Bu$_2$ (Cp″)),[2] whose reactivity had hitherto not been investigated, though the Cp-containing complex has been known since 1971.[3] We found that reactions of these complexes with magnesium yield transition-metal substituted μ_3-Bi complexes, whereas the reactivity of **1a,b** toward metalates has not yet been investigated. Thus, we herein describe the reaction of these compounds, as well as the molybdenum-substituted analogue [{Cp″(CO)$_3$Mo}BiCl$_2$] (**7**), with transition metalates and discuss the crystal structures of the obtained mixed transition-metal−main-group-element clusters.

Results and Discussion

Reactions Starting from [{Cp^x(CO)$_2$Fe}BiCl$_2$] (1a, Cp^x = Cp; 1b, Cp^x = η^5-C$_5$H$_3$*t*Bu$_2$ (Cp″)). The reaction of [{Cp(CO)$_2$Fe}BiCl$_2$] (**1a**) with K[Co(CO)$_4$] at low temperature in a molar ratio of 1:2 leads quantitatively to [(μ_3-Bi){Co(CO)$_4$}$_2${Fe(CO)$_2$Cp}] (**2**) (eq 1), which is a brown crystalline compound readily soluble in *n*-hexane, toluene, CH$_2$Cl$_2$ and THF.



The X-ray structure analysis of **2** (Figure 1) reveals a central bismuth atom bonded via single bonds to the iron atom of an Fe(CO)$_2$Cp″ group and to two cobalt atoms of tetracarbonylcobalt groups. No bonding interaction between the transition metals is observed. The coordination geometry around the bismuth is trigonal pyramidal, with angles close to the tetrahedral angle. This indicates the presence of a stereochemically active lone pair. Complex **2** is the first example of a heteroleptic trimetal-substituted bismuthane. Pnictogenides coordinated in a trigonal-pyramidal fashion have been known for many years now, and many examples of those have been prepared, yet all of these compounds only bear homoleptic substituents.[1] For trigonal-planar phosphinidenes, arsinidenes, and stibinidenes, only complexes with heteroleptic metal substituents are known.[4] To find out whether it was possible to connect the

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[†] Dedicated to Professor H. Vahrenkamp on the occasion of his 60th birthday.

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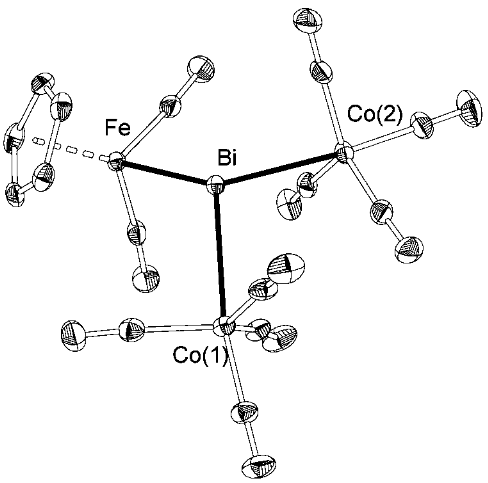
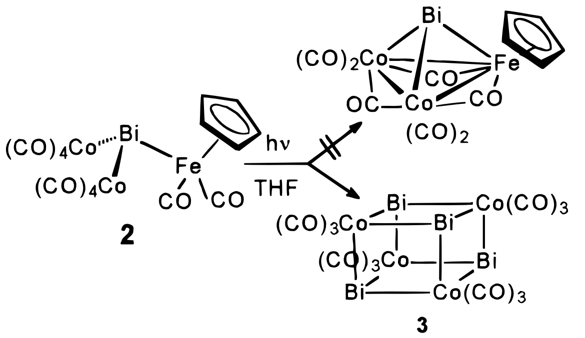


Figure 1. Molecular structure of $[(\mu_3\text{-Bi})\{Co(CO)_4\}_2\{Fe(CO)_2Cp\}]$ (**2**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Bi−Fe = 2.6619(12), Bi−Co(1) = 2.8360(13), Bi−Co(2) = 2.8177(10); Fe−Bi−Co(1) = 110.03(3), Fe−Bi−Co(2) = 110.25(3), Co(1)−Bi−Co(2) = 104.18(3).

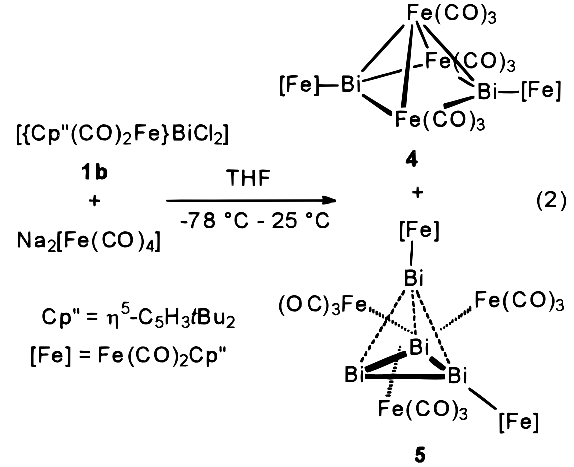
Scheme 1. Photolysis of Complex 2 in THF



transition-metal atoms in **2** to form a tetrahedron of the type $[Bi\{Co(CO)_2\}_2(FeCp)(\mu\text{-CO})_3]$, a solution of **2** in THF was irradiated. However, no tetrahedron was formed; only the heterocubane $[Bi_4\{Co(CO)_3\}_4]$ (**3**) could be isolated (Scheme 1), and it was characterized by X-ray diffraction studies. A side product of this reaction is $[Fe(CO)_2Cp]_2$, which was detected by ^1H NMR spectroscopy (^1H NMR ($CDCl_3$): δ 4.28 ppm (s)).

The heterocubane $[Bi_4\{Co(CO)_3\}_4]$ (**3**) crystallizes in the monoclinic space group $P2_1/m$ together with one molecule of CH_2Cl_2 (Table 1). The cell dimensions are a = 9.796(2) Å, b = 11.1900(22) Å, c = 12.2120(24) Å, β = 104.51(3)°, and V = 1295.9(4) Å^3. The crystal structure of **3** has already been described by Ciani et al., who prepared the cluster by thermolysis of $[Bi\{Co(CO)_4\}_3]$.[5] In their case, however, the heterocubane $[Bi_4\{Co(CO)_3\}_4]$ crystallized solvent-free, making the space group and cell dimensions different from our data (tetragonal, $I4/amd$, $a = b$ = 14.731(3) Å, c = 10.574(3) Å, V = 2294.58 Å^3, Z = 4). Owing to the solvent molecules in the crystal structure of $[Bi_4\{Co(CO)_3\}_4]$ (**3**), D_{2d} symmetry, as found in the complex of Ciani, cannot be achieved in compound **3**. The Bi_4Co_4 cluster in **3** is only of C_s symmetry, leading to four different Bi···Bi distances (3.245(12)−3.3758(10) Å) and six different Bi−Co bond lengths (2.746(2)−2.763(3) Å) within the cluster. These distances are similar to those described by Ciani et al. (Bi···Bi = 3.351(1) and 3.364(1) Å; Bi−Co = 2.742(2) and 2.751(2) Å).

The reaction of **1b** with $Na_2[Fe(CO)_4]$ leads to the formation of two different transition-metal−bismuth compounds, the *nido* cluster $[\{Fe_3(CO)_9\}\{\mu\text{-BiFe(CO)}_2\text{-Cp}''\}_2]$ (**4**) and the major product $[Bi_4\{\mu_3\text{-Fe(CO)}_3\}_3\{Fe(CO)_2Cp''\}_2]$ (**5**), which can be partially separated by fractionating crystallization (eq 2). Both compounds are red crystalline complexes readily soluble in *n*-hexane and toluene.



The predominant structural feature of **4** is a square-planar pyramid consisting of two bismuth and three iron atoms (Figure 2). The vertex of the pyramid is occupied by an iron atom which is bonded to two bismuth atoms and two iron atoms of the pyramidal plane by single bonds. Each iron atom in the square pyramid is further bonded to three carbonyl ligands, resulting in an electron count of 18 for each iron atom within the cluster, assuming that the bismuth atoms donate four electrons each to the cluster core, three of which count for each basal iron atom and one for the apical. The cluster core itself obeys Wade's rules and, hence, is a *nido* cluster with a characteristic skeletal electron count of 14 (n + 2 skeletal electron pairs).[6] The two bismuth atoms are further connected to two cyclopentadienyl−iron fragments with almost equal distances (2.6177(14) and 2.6199(13) Å). If the latter feature is missing, a dianionic complex of the formula $[\{Fe_3(CO)_9\}\{\mu_3\text{-Bi}\}_2]^{2-}$ results, which was recently structurally characterized by Whitmire et al.[7] Its structural comparison with **4** shows slightly shorter Fe−Fe bonds and longer Bi−Fe bonds as in **4**. *nido* clusters, similar to **4**, are known for elements of group 15, such as $[\{Fe_3(CO)_9\}\{\mu_3\text{-AsMo(CO)}_3\text{-Cp}\}_2]$[8] and $[\{Fe_3(CO)_9\}\{\mu_3\text{-PFe(CO)}_2\text{Cp}\}_2]$,[9] which are the only neutral *nido* type clusters bearing no organic ligand at the pnictogenide atom. Charged examples of this type are $[\{Fe_3(CO)_9\}\{\mu_3\text{-EML}_n\}_2]^{2-}$ (EML_n = PMn(CO)$_2$Cp,[10] AsFe(CO)$_4$,[11] SbFe(CO)$_4$[12]) and $[\{Fe_3(CO)_9\}$-

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Table 1. Crystallographic Data for the Compounds 2−5 and 8−10

	2	**3**·CH_2Cl_2	**4**	**5**	**8**	**9**	**10**·C_7H_8
formula	$C_{15}H_5BiCo_2$-FeO_{10}	$C_{13}H_2Bi_4Cl_2$-Co_4O_{12}	$C_{39}H_{42}Bi_2$-Fe_5O_{13}	$C_{39}H_{42}Bi_4$-Fe_5O_{13}	$C_{32}H_{50}Bi$-$Cl_7Mo_2O_3$	$C_{42}H_{42}Bi_2Fe_3$-Mo_2O_{16}	$C_{39}H_{50}BiCl$-Mo_2O_6
fw	727.88	1492.69	1415.94	1833.90	1131.73	1580.15	1051.10
cryst size, mm	0.45 × 0.38 × 0.08	0.08 × 0.06 × 0.02	0.22 × 0.11 × 0.22	0.15 × 0.08 × 0.02	0.23 × 0.23 × 0.04	0.08 × 0.08 × 0.02	0.40 × 0.35 × 0.10
T, K	203(2)	200(2)	200(1)	200(1)	200(1)	200(2)	200(1)
space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$Pcca$	$P2_1/n$
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
a, Å	7.2160(14)	9.796(2)	9.654(2)	18.315(4)	17.835(3)	19.453(4)	9.968(2)
b, Å	9.698(2)	11.190(2)	9.756(2)	20.944(4)	13.276(2)	14.383(3)	15.862(3)
c, Å	15.022(3)	12.212(2)	27.598(4)	13.186(3)	18.353(4)	18.546(4)	26.481(5)
α, deg	81.20(3)	90	83.25(3)	90	90	90	90.00
β, deg	84.06(3)	104.51(3)	81.25(3)	105.31(3)	112.88(3)	90	90.56(3)
γ, deg	71.59(3)	90	63.90(3)	90	90	90	90.00
V, Å^3	984.0(3)	1295.9(4)	2303.3(7)	4879(2)	4003.6(14)	5189.0(18)	4187.0(15)
Z	2	2	2	4	4	4	4
d_c, g/cm^3	2.457	3.825	2.042	2.497	1.878	2.023	1.667
μ, mm^{-1}	11.344	29.806	9.199	15.869	5.499	8.102	4.887
diffractometer	STOE STADI IV	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
2θ range, deg	$4.46 \leq 2\theta \leq 58$	$4.78 \leq 2\theta \leq 52$	$4.48 \leq 2\theta \leq 51.68$	$3.74 \leq 2\theta \leq 51.72$	$3.94 \leq 2\theta \leq 53.34$	$4.16 \leq 2\theta \leq 51.90$	$4.00 \leq 2\theta \leq 51.78$
hkl range	$-9 \leq h \leq 9$ $-12 \leq k \leq 12$ $0 \leq l \leq 20$	$-12 \leq h \leq 11$ $-13 \leq k \leq 13$ $-13 \leq l \leq 15$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-33 \leq l \leq 33$	$-22 \leq h \leq 14$ $-25 \leq k \leq 25$ $-13 \leq l \leq 16$	$-20 \leq h \leq 21$ $-16 \leq k \leq 16$ $-23 \leq l \leq 23$	$-22 \leq h \leq 23$ $-17 \leq k \leq 17$ $-22 \leq l \leq 20$	$-9 \leq h \leq 12$ $-17 \leq k \leq 19$ $-32 \leq l \leq 29$
no. of rflns collected	4987	8658	16580	24164	31289	22472	14365
no. of data/restraints/params	4987/0/262	2625/0/167	8271/0/544	8883/0/552	7928/0/418	5026/0/300	7830/0/455
no. of indep rflns with $I > 2\sigma(I)$	4552	2239 (R_{int}= 0.0770)	6665 (R_{int}= 0.0341)	5167 (R_{int}= 0.0873)	6494 (R_{int}= 0.0715)	1785 (R_{int} = 0.3002)	6123 (R_{int}= 0.0947)
GOF on F^2	1.077	1.092	1.064	0.857	0.954	0.772	1.050
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0302, 0.0685	0.0551, 0.1367	0.0333, 0.0796	0.0495, 0.0953	0.0430, 0.1047	0.0630, 0.1344	0.0643, 0.1549
R1,[a] wR2[b] (all data)	0.0368, 0.0744	0.0630, 0.1426	0.0460, 0.0833	0.0984, 0.1076	0.0523, 0.1086	0.1878, 0.1765	0.0762, 0.1612
largest diff peak, hole, e/Å^3	2.197, −2.138	4.494, −5.477	1.036, −1.084	5.209, −2.452	1.755, −2.474	1.228, −2.487	3.926; −3.383

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [[\sum w(F_o^2 - F_c^2)^2]/[\sum(F_o^2)^2]]^{1/2}$.

(μ_3-Bi{Fe(CO)$_4$})(μ_3-Bi)]$^{2-}$,[13] whereas other known clusters of similar composition such as [{$Fe_3(CO)_9$}{μ_3-EML$_n$}$_2$] (EML$_n$ = PMn(CO)$_2$Cp,[14] AsMn(CO)$_2$Cp, SbMn(CO)$_2$Cp, AsCr(CO)$_5$[10b]) tend to have two skeletal electrons less, thus being *closo* clusters building a trigonal bipyramid.

The crystal structure analysis of **5** reveals four monomeric units of [Bi_4{μ_3-Fe(CO)$_3$}$_3${Fe(CO)$_2$Cp″}$_2$] in the monoclinic cell (Figure 3). The structural features of the neutral compound **5** are similar to those of the ionic complex [$Bi_4Fe_4(CO)_{13}$]$^{2-}$ described by Whitmire et al.[15] but exhibit some significant differences. The main structural feature of **5** is a Bi_4 tetrahedron. Three of the four tetrahedral faces are capped by μ_3-Fe(CO)$_3$ fragments, whereas the fourth is left bare. As in [$Bi_4Fe_4(CO)_{13}$]$^{2-}$ there are substantial differences in Bi−Bi bond lengths within the cluster core of **5** but there are also lengths comparable to those in the former as well. Hence, all Bi−Bi distances around the basal face (3.0893(11)−3.1949(12) Å) are systematically shortened by 0.2−0.4 Å relative to the other three Bi−Bi distances to the apical Bi atom (3.4226(10)−3.5298(9) Å). The Fe−Bi bonds from the μ_3-Fe(CO)$_3$ fragments to the Bi_4 tetrahedron (2.686(2)−2.782(2) Å) are in the same region as those reported by Whitmire, with the exception of all Bi(2)−Fe(3/5) bond lengths, which are shortened by 0.1 Å (2.651(2) and 2.647(3) Å). Bi(2) is the only basal Bi atom which is σ-bound to a Cp″Fe(CO)$_2$ unit. The bond lengths of the iron atoms Fe(1) and Fe(2), which are σ-bonded to Bi(1) and Bi(2), behave in the same way; hence, Bi(2)−Fe(2) (2.643(2) Å) is 0.06 Å

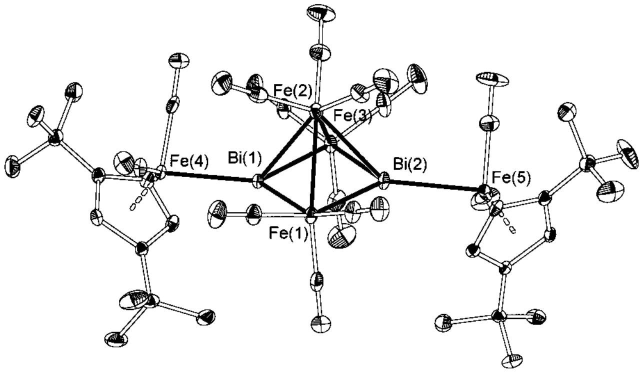

Figure 2. Molecular structure of [{$Fe_3(CO)_9$}{μ-BiFe(CO)$_2$Cp″}$_2$] (**4**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.841(2), Fe(2)−Fe(3) = 2.852(2), Bi(1)···Bi(2) = 3.3030(12), Bi(1)−Fe(1) = 2.6111(2), Bi(1)−Fe(2) = 2.6460(13), Bi(1)−Fe(3) = 2.5933(12), Bi(1)−Fe(4) = 2.6177(14), Bi(2)−Fe(1) = 2.6034(12), Bi(2)−Fe(2) = 2.6278(13), Bi(2)−Fe(3) = 2.595(2), Bi(2)−Fe(5) = 2.6199(13); Fe(1)−Bi(1)−Fe(3) = 101.05(5), Bi(1)−Fe(1)−Bi(2) = 78.62(5), Fe(1)−Bi(2)−Fe(3) = 101.20(5), Bi(1)−Fe(3)−Bi(2) = 79.08(5).

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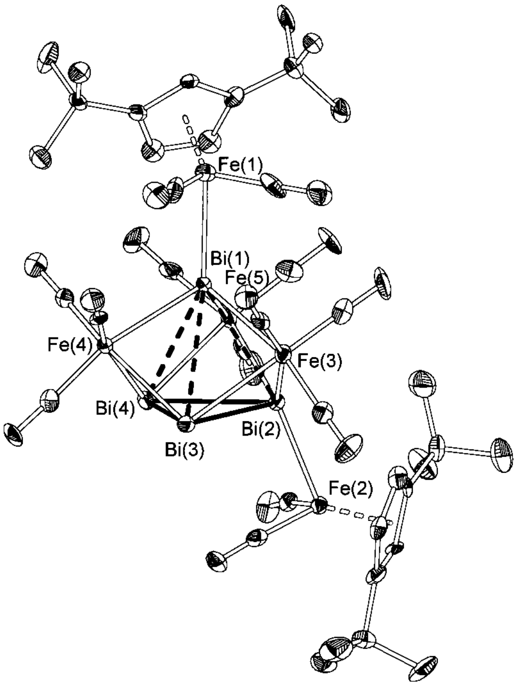
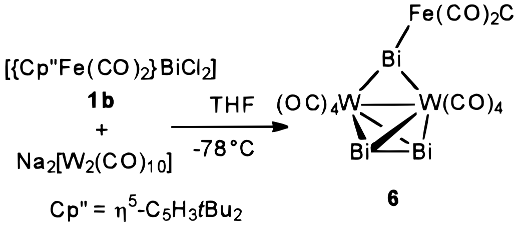


Figure 3. Molecular structure of $[Bi_4\{\mu_3\text{-}Fe(CO)_3\}_3\{Fe(CO)_2Cp''\}_2]$ (**5**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å): Bi(1)−Bi(2) = 3.4226(10), Bi(1)−Bi(3) = 3.4466(10), Bi(1)−Bi(4) = 3.5298(9), Bi(2)−Bi(3) = 3.1634(9), Bi(2)−Bi(4) = 3.0893(11), Bi(3)−Bi(4) = 3.1949(12), Bi(2)−Fe(2) = 2.643(2), Bi(2)−Fe(3) = 2.651(2), Bi(2)−Fe(5) = 2.647(3), Bi(1)−Fe(1) = 2.709(2), Bi(1)−Fe(3) = 2.738(3), Bi(1)−Fe(4) = 2.686(2), Bi(1)−Fe(5) = 2.769(3), Bi(3)−Fe(3) = 2.748(2), Bi(3)−Fe(4) = 2.703(2), Bi(4)−Fe(4) = 2.717(2), Bi(4)−Fe(5) = 2.782(2).

shorter than Bi(1)−Fe(1) (2.709(2) Å). The Bi−Bi distances of the basal Bi(2)−Bi(3)−Bi(4) face (3.0893(11)−3.1949(12) Å) are within the range of known bonding Bi−Bi interactions. The other three longer Bi···Bi distances (3.4226(10)−3.5298(9) Å) are still short enough to be comparable to the second shortest interactions within elemental bismuth[16] yet are too long to be considered bonding in the sense of a two-center−two-electron bond. The molecules in complex **5** are linked to chains by long-range Bi···Bi interactions of 3.725(2) Å between the atoms Bi(3) and Bi(4) (Figure 4). Since in **5** the coordination spheres of two of the four Bi atoms are completed by the σ-bond iron moieties, a one-dimensional connectivity is formed. In the complex $[Bi_4Fe_4(CO)_{13}]^{2-}$, in contrast, where only the apical Bi atom is connected to a further Fe atom of a terminal $Fe(CO)_4$ group, two-dimensional sheets (Bi···Bi 3.98 Å) are formed.

The most striking difference of complex **5** from $[Bi_4Fe_4(CO)_{13}]^{2-}$ is the fact that it is a neutral molecule, whereas $[Bi_4Fe_4(CO)_{13}]^{2-}$ is dianionic and crystallizes with two $[Et_4N]^+$ cations per molecule.[15] However, the cluster shape, buildup, and dimensions of the two complexes are similar, and therefore, the electronic structures of both should not differ much either. Considering the cluster core itself in the same manner as done in a theoretical discussion in the report by Whitmire et al. (which also gives an MO-based explanation on why there are substantial differences in the Bi−Bi bond lengths),[15] an electron count will miss two electrons which, in the case of complex $[Bi_4Fe_4(CO)_{13}]^{2-}$, come from the two negative charges on the dianion, making an overall skeletal electron number of 20. In the case of **5**, however, the also two missing electrons are localized in the two two-center−two-electron σ-bonds between Bi(1), Bi(2), and the fragment $Fe(CO)_2Cp''$.

Reacting **1b** with an equimolar amount of $Na_2[W_2(CO)_{10}]$ yields the compound $[\{W_2(CO)_8\}(\mu,\eta^2\text{-}Bi_2)\{\mu\text{-}BiFe(CO)_2Cp''\}]$ (**6**) (eq 3) as green crystals, which is readily soluble in *n*-hexane and toluene.



(3)

The X-ray analysis of **6** reveals a Bi_2W_2 tetrahedron, whose W−W edge is capped by a $[\mu\text{-}BiFe(CO)_2Cp'']$ moiety (Figure 5). All framework distances are within the usual range and represent single bonds. The tetrahedron is close to regular (all facial angles are within the range of 55.81(7)−63.92(6)°). Owing to its bridging function, the angles at Bi(1) split into two large angles (Fe−Bi(1)−W(1) = 117.71(14)° and Fe−Bi(1)−W(2) = 117.71(14)°) and one small one (W(1)−Bi(1)−W(2) = 64.90(6)°). A similar Bi_3W_2 unit can be found in the complex $[\{Bi_2W_2(CO)_8\}(\mu\text{-}BiMe)\{W(CO)_5\}]$, which was reported by Norman et al.[17] It was prepared by the reaction of $MeBiCl_2$ with $Na_2[W_2(CO)_{10}]$. In contrast to **6**, there a MeBi unit bridges the W−W edge of a Bi_2W_2 tetrahedron and coordinates additionally to a $W(CO)_5$ moiety, whereas in **6** a $BiFe(CO)_2Cp''$ group bridges this edge.

Reactions Starting from $[\{Cp''(CO)_3Mo\}BiCl_2]$ (7). To investigate in which way reactions would differ if one were to exchange the $Fe(CO)_2Cp''$ group in $[\{Cp''(CO)_2Fe\}BiCl_2]$ (**1b**) with a $Mo(CO)_3Cp''$ unit, we investigated the molybdenum-substituted analogue $[\{Cp''(CO)_3Mo\}BiCl_2]$ (**7**) as a starting material as well in the reactions with two of the above-mentioned metalates. Compound **7** was prepared in high yields according to a two-step synthesis described by Norman et al. for the preparation of $[\{Cp(CO)_3Mo\}BiCl_2]$.[18] First, $BiCl_3$ is reacted with 2 equiv of $Na[Mo(CO)_3Cp'']$ to yield $[\{Cp''(CO)_3Mo\}_2BiCl]$. In the second step, an additional 1 equiv of $BiCl_3$ reacts with $[\{Cp''(CO)_3Mo\}_2BiCl]$ under ligand exchange to afford $[\{Cp''(CO)_3Mo\}BiCl_2]$ (eqs 4 and 5).

Compound **7** is insoluble in hydrocarbons but exhibits very low solubility in CH_2Cl_2. In THF **7** dissolves readily with decomposition to yield an ionic compound of the formula $[(Cp''MoCO)_2(\mu\text{-}Cl)_3]_2[Bi_2Cl_8(thf)_2]$ (**8**). This as well is the reason **7** could not be prepared from $BiCl_3$ and the molybdenum dimer $[Mo(CO)_3Cp'']_2$, analogous to the preparation of **1**. The reaction proved to be

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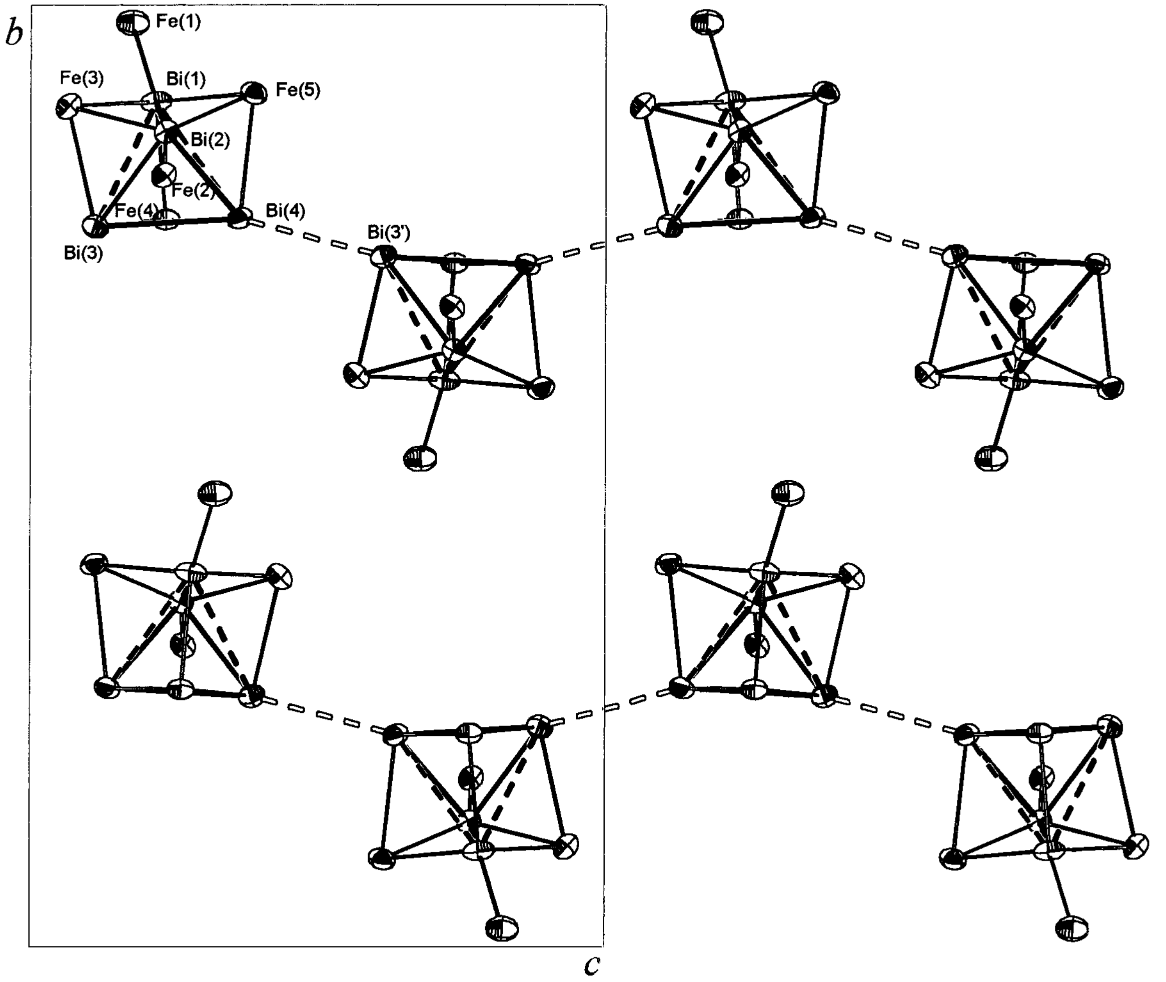
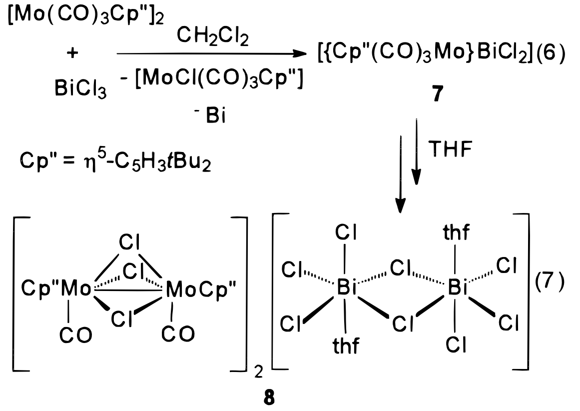


Figure 4. Molecules of **5** linked to infinite chains by long-range Bi···Bi interactions (Bi(4)···Bi(3′) = 3.725 Å); view along the *a*-axis (showing 30% probability ellipsoids; C, H, and O are omitted for clarity).

$$2\,K[Mo(CO)_3Cp''] + BiCl_3 \xrightarrow[-\,2\,KCl]{Et_2O} [\{Cp''(CO)_3Mo\}_2BiCl] \quad (4)$$

$$[\{Cp''(CO)_3Mo\}_2BiCl] + BiCl_3 \xrightarrow[CH_2Cl_2]{} 2\,\underset{\mathbf{7}}{[\{Cp''(CO)_3Mo\}BiCl_2]} \quad (5)$$

$Cp'' = \eta^5\text{-}C_5H_3tBu_2$



feasible, yet elemental Bi formed as a black precipitate from which the orange microcrystalline **7** could not be separated, owing to the low solubility of **7** even in CH_2Cl_2 (eqs 6 and 7).

The X-ray structure analysis reveals compound **8** to be ionic, consisting of two $[(Cp''MoCO)_2(\mu\text{-}Cl)_3]^+$ cations and one $[Bi_2Cl_8(thf)_2]^{2-}$ dianion (Figure 6). The structure is centrosymmetric, and the center of inversion lies within the four-membered $Bi_2(\mu\text{-}Cl)_2$ ring. The dianion $[Bi_2Cl_8(thf)_2]^{2-}$ is known from the ionic compound $[Li(thf)_4]_2[Bi_2Cl_8(thf)_2]$, which recently was synthesized and characterized independently by Norman[19] and Breunig,[20] respectively. The Bi atom in **6** has a distorted-octahedral environment of five chlorine atoms and one oxygen atom of the THF ligand. All Bi−Cl distances in **8** (2.487(2)−2.886(2) Å) are similar to those reported for $[Li(thf)_4]_2[Bi_2Cl_8(thf)_2]$ (2.551(3)−2.902(3) Å). The association of the THF molecule in **8** (Bi−O = 2.739(5) Å) is weaker than in $[Li(thf)_4]_2[Bi_2Cl_8(thf)_2]$ (Bi−O = 2.588 Å),[19] and in comparison with Bi−O bond distances of other bismuth−chloro complexes with donating oxygen ligands (2.55−2.67 Å),[21,22] the Bi−O distance in **8** is exceedingly long.

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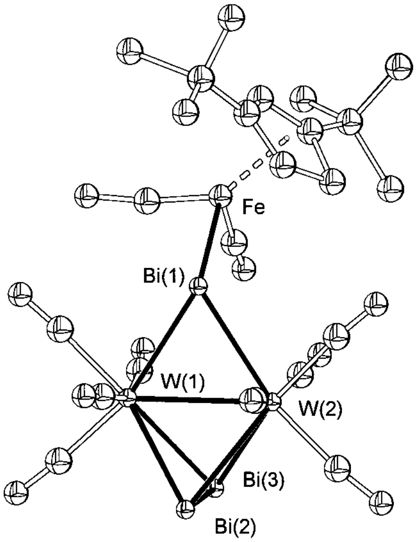
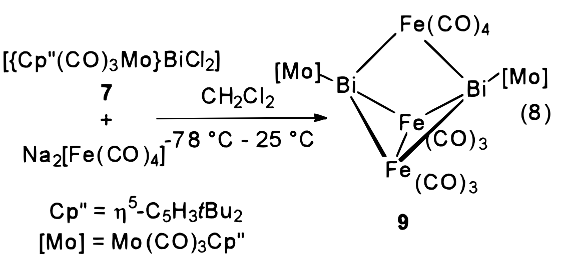


Figure 5. Molecular structure of [{W$_2$(CO)$_8$}(μ,η^2-Bi$_2$){μ-BiFe(CO)$_2$Cp″}] (**6**) (no ellipsoidal representation; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(1)−W(2) = 3.1501(18), W(1)−Bi(1) = 2.936(2), W(1)−Bi(2) = 3.017(2), W(1)−Bi(3) = 2.976(2), W(2)−Bi(1) = 2.936(2), W(2)−Bi(2) = 3.017(2), W(2)−Bi(3) = 2.975(2), Bi(1)−Fe = 2.723(7), Bi(2)−Bi(3) = 2.805(3); Bi(1)−W(1)−Bi(2) = 107.27(5), Bi(1)−W(1)−Bi(3) = 109.62(5), Bi(2)−W(1)−Bi(3) = 55.81(7), Bi(1)−W(1)−W(2) = 57.55(3), Bi(2)−W(1)−W(2) = 58.53(3), Bi(3)−W(1)−W(2) = 58.04(3), Fe−Bi(1)−W(1) = 117.71(14), Fe−Bi(1)−W(2) = 117.71(14), W(1)−Bi(1)−W(2) = 64.90(6), Bi(3)−Bi(2)−W(1) = 61.34(6), Bi(3)−Bi(2)−W(2) = 61.34(6), W(2)−Bi(2)−W(1) = 62.94(5), Bi(2)−Bi(3)−W(1) = 62.85(6), Bi(2)−Bi(3)−W(2) = 62.85(6), W(1)−Bi(3)−W(2) = 63.92(6).

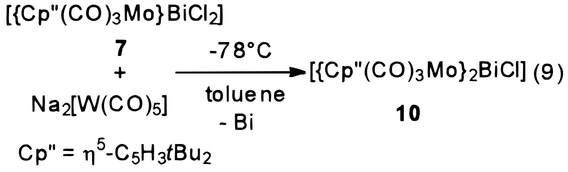
The cation in **8** consists of two Mo(CO)Cp″ fragments bridged by three Cl atoms (Figure 6). The structural motif of three bridging halogen atoms between two metal centers is known in the literature, whereas cationic molybdenum species of this kind are restricted to a few examples;[23] however, only one example bearing a cyclopentadienyl ligand is known within the complex [{Cp*MoCl}$_2$(μ-Cl)$_3$]$^+$[AlCl$_4$]$^-$.[23d] In contrast to compound **8**, however, where molybdenum is in the formal oxidation state +3, in [{Cp*MoCl}$_2$(μ-Cl)$_3$]$^+$[AlCl$_4$]$^-$ molybdenum is in the oxidation state +4. Mo−Cl distances in **7** (2.3942(14)−2.496(2) Å) are similar to those in the cation [(Cp*MoCl)$_2$(μ-Cl)$_3$]$^+$ (2.422−2.460 Å) and are in the usual range for bridging chlorine atoms. The Mo−Mo contact of 2.7717(8) Å is in the upper range of Mo(III)−Mo(III) bonds (from 2.573 Å in [(MoCp^{Me})(μ-S)(μ-SCH$_3$)]$_2$[24] to 2.743 Å in [(MoCl$_3$)$_2$(μ-Cl)$_3$]$^{3-}$)[25] but can be regarded as bonding, which is proven by the diamagnetism of compound **8**.

To compare the reaction behavior of the Fe-substituted complex **1b** with that of the Mo derivative [{Cp″(CO)$_3$Mo}BiCl$_2$] (**7**), the reaction of **7** with Na$_2$[Fe(CO)$_4$] was carried out under the same conditions. However, a different product, [{Fe$_2$(CO)$_6$}{Fe(CO)$_4$}{μ_3-BiMo(CO)$_3$Cp″}$_2$] (**9**), was afforded as a green crystalline compound (eq 8) which is readily soluble in *n*-hexane and toluene.



Although the compositions of the compounds [{Fe$_3$(CO)$_9$}{μ-BiFe(CO)$_2$Cp″}$_2$] (**4**) and [{Fe$_2$(CO)$_6$}{Fe(CO)$_4$}{μ_3-BiMo(CO)$_3$Cp″}$_2$] (**9**) (Figure 7) appears on first view to be similar (except for the difference in the CO group content)—in both compounds the central structural feature is a Bi$_2$Fe$_3$ cage—there are substantial differences between these clusters. Owing to the four carbonyl groups at Fe(2), the Fe$_3$Bi$_2$ cluster in **9** contains 16 skeletal electrons, 2 more than in the Fe$_3$Bi$_2$ core in **4**. This results, according to Wade's rules, in the formation of a formal *arachno* type cluster with an open "butterfly-type" structure in **9**, in contrast to the *nido* tetragonal pyramid in **4**. However, the cluster core of **9** does not correspond to the *arachno*-B$_5$H$_{11}$ structure. The cluster in **9** consists of a bent Fe$_2$Bi$_2$ ring capped by the Fe(CO)$_4$ group. Within this ring the bond distances (Bi−Fe(1) = 2.624(3) Å, Bi−Fe(1′) = 2.639(3) Å, Fe(1)−Fe(1′) = 2.710(7) Å) are within the usual range. Owing to the bridging Fe(CO)$_4$ group, the Fe$_2$Bi$_2$ ring is bent by 88.91° (angle between the faces Fe(1)−Bi−Fe(1′) and Fe(1′)-Bi′−Fe(1)), making the Bi···Bi distance in **9** (3.1595(15) Å) shorter by almost 0.15 Å than the Bi···Bi contact in **4** (3.3030(12) Å). The cluster core of **9** shows some structural similarities to that of the monoanionic complex [(μ-H)Fe$_2$(CO)$_6$Bi$_2${Fe(CO)$_4$}]$^-$, containing an additional H-bridge between the Fe atoms.[26] The Bi−Mo bond length of 2.915(2) Å in **9** is consistent with the few examples of structurally characterized molecules containing molybdenum−bismuth bonds, such as [{Cp(CO)$_3$Mo}$_2$BiCl] (average Bi−Mo = 2.951 Å).[18]

The reaction of **7** with Na$_2$[W(CO)$_5$] (eq 9) yields the complex [{Cp″(CO)$_3$Mo}$_2$BiCl] (**10**) as green needles which are readily soluble in *n*-hexane and toluene. In



$$\underset{\mathbf{7}}{[\{Cp''(CO)_3Mo\}BiCl_2]} + Na_2[W(CO)_5] \xrightarrow[\text{toluene}\ -\ \text{Bi}]{-78\,°C} \underset{\mathbf{10}}{[\{Cp''(CO)_3Mo\}_2BiCl]} \quad (9)$$

$$Cp'' = \eta^5\text{-}C_5H_3tBu_2$$

this case we find that no fragment of the metalate is incorporated within the structure of the product. Here the metalate causes the reduction of [{Cp″(CO)$_3$Mo}BiCl$_2$] (**7**) in a manner we have already found for the reaction of **1** with magnesium.[2]

The crystal structure analysis of **10** reveals a central bismuth atom coordinated in a trigonal-pyramidal way by two Mo(CO)$_3$Cp″ moieties and one chlorine atom (sum of angles 318.2°) (Figure 8). The Bi−Mo bond distances (2.9230(9) and 2.9654(9) Å) are within the

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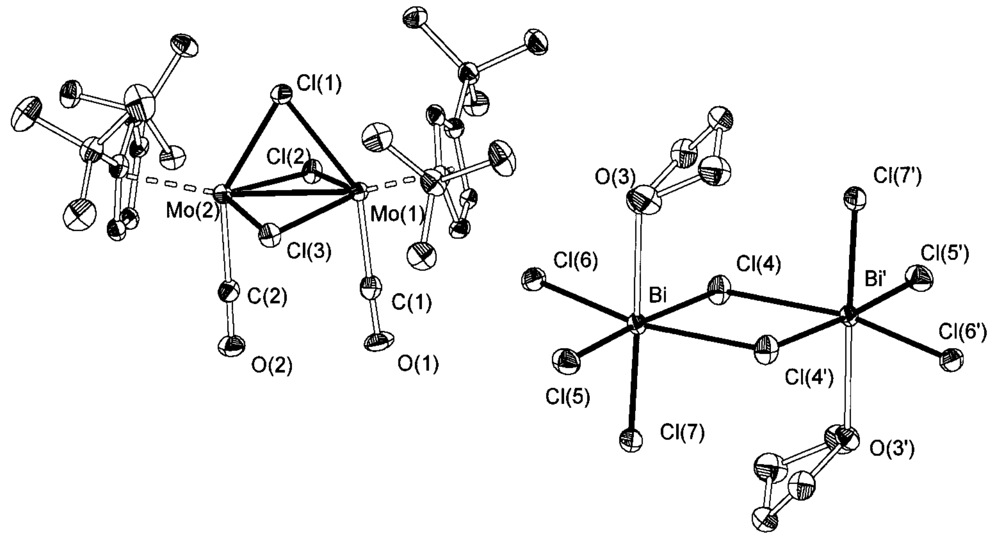

Figure 6. Molecular structure of $[(\mathrm{Cp''MoCO})_2(\mu\text{-Cl})_3]_2[\mathrm{Bi_2Cl_8(thf)_2}]$ (**8**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity; only one of the two cations is presented). Selected bond distances (Å) and angles (deg): Bi−Cl(4) = 2.886(2), Bi−Cl(4′) = 2.879(2), Bi−Cl(5) = 2.576(2), Bi−Cl(6) = 2.541(2), Bi−Cl(7) = 2.487(2), Bi−O(3) = 2.739(5), Mo(1)−Cl(1) = 2.484(2), Mo(1)−Cl(2) = 2.3942(14), Mo(1)−Cl(3) = 2.496(2), Mo(2)−Cl(1) = 2.443(2), Mo(2)−Cl(2) = 2.456(2), Mo(2)−Cl(3) = 2.4234(14), Mo(1)−Mo(2) = 2.7717(8); O(3)−Bi−Cl(4) = 88.71(11), O(3)−Bi−Cl(4′) = 98.34(11), O(3)−Bi−Cl(5) = 84.55(11), O(3)−Bi−Cl(6) = 84.78(11), O(3)−Bi−Cl(7) = 173.20(11), Cl(6)−Bi−Cl(7) = 97.14(6), Cl(6)−Bi−Cl(5) = 90.98(7), Cl(6)−Bi−Cl(4′) = 90.98(6), Cl(6)−Bi−Cl(4) = 168.22(6), Cl(5)−Bi−Cl(7) = 88.89(7), Cl(5)−Bi−Cl(4) = 98.17(6), Cl(5)−Bi−Cl(4′) = 176.65(6).

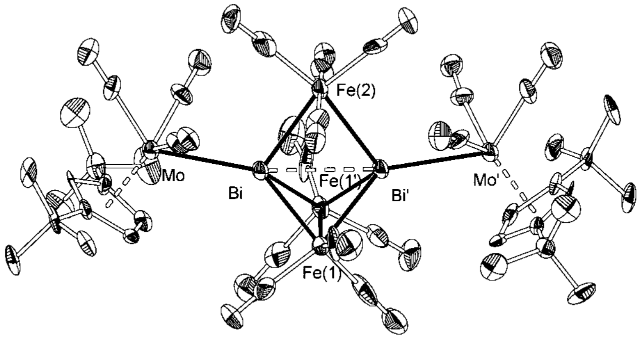

Figure 7. Molecular structure of $[\{\mathrm{Fe_2(CO)_6}\}\{\mathrm{Fe(CO)_4}\}\{\mu_3\text{-}\mathrm{BiMo(CO)_3Cp''}\}_2]$ (**9**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Bi−Bi′ = 3.1595(15), Bi−Fe(1) = 2.624(3), Bi−Fe(1′) = 2.639(3), Bi−Fe(2) = 2.769(4), Bi−Mo = 2.915(2), Fe(1)−Fe(1′) = 2.710(7); Fe(1)−Bi−Fe(2) = 99.38(9), Fe(1′)−Bi−Fe(2) = 99.03(8), Fe(1)′−Bi−Fe(1) = 62.00(15), Bi−Fe(2)−Bi′ = 69.57(11).

usual range, as is the Bi−Cl distance (2.555(3) Å). As for the similar complex $[\{\mathrm{Cp''(CO)_2Fe}\}_2\mathrm{BiCl}]$,[2] there are no intermolecular Bi−Cl distances observed as they are usually found for bismuth−halogenides of the type $[\{\mathrm{L}_n\mathrm{M}\}_2\mathrm{BiX}]$ (M = Fe, Mo, W; X = Cl, Br, I). The shortest intermolecular Bi···Cl distance is 5.314(3) Å. This is due to the steric demand of the di-*tert*-butylcyclopentadienyl ligands. Hence, compound **10**, together with $[\{\mathrm{Cp''(CO)_2Fe}\}_2\mathrm{BiCl}]$ and $[\{\mathrm{Cp(CN}t\mathrm{Bu)(CO)_2Mo}\}_2\mathrm{BiCl}]$,[18] is the only example of a structurally characterized monomeric chlorobismuth complex.

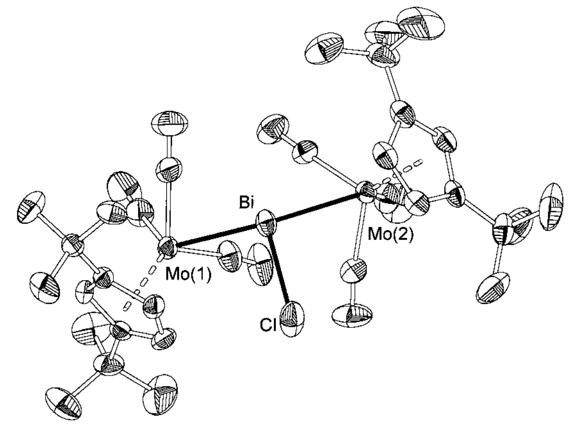

Figure 8. Molecular structure of $[\{\mathrm{Cp''(CO)_3Mo}\}_2\mathrm{BiCl}]$ (**10**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Bi−Cl = 2.555(3), Bi−Mo(1) = 2.9654(9), Bi−Mo(2) = 2.9230(9); Cl−Bi−Mo(1) = 100.65(7), Cl−Bi−Mo(2) = 100.46(6), Mo(1)−Bi−Mo(2) = 117.09(2).

Conclusions

In contrast to reactions of $[\{\mathrm{Cp(CO)_2Fe}\}\mathrm{BiCl_2}]$ (**1a**) with magnesium, which yielded μ_3-Bi bridged binary bismuth−transition-metal complexes,[2] compounds **1a**,**b** react with transition metalates with incorporation of a transition-metal moiety within a cluster core. Remarkably, the differences in the reaction behavior between the iron- and molybdenum-substituted starting materials **1a**,**b** and **7**, respectively. Thus, $[\{\mathrm{Cp''(CO)_3Mo}\}\mathrm{BiCl_2}]$ (**7**) reacts with $\mathrm{Na_2[Fe(CO)_4]}$ in a different way than **1b**. Instead of an $[(\mathrm{L}_n\mathrm{ME})_2\{\mathrm{Fe(CO)_3}\}_3]$ *nido* cluster (**4**) an $[(\mathrm{L}_n\mathrm{ME})_2\{\mathrm{Fe(CO)_3}\}_2\{\mathrm{Fe(CO)_4}\}]$ *arachno* type cluster (**9**) is formed. Furthermore, the reaction products with $\mathrm{Na_2[W(CO)_5]}$ are different as well.

In most of the reactions, however, no E−E bond formation was observed, in contrast to similar reactions of phosphorus-containing starting materials of the formula $[\mathrm{L}_n\mathrm{MPCl_2}]$.[27] The reason for this can probably be found in the stronger metallic character of Bi and, hence, the higher tendency for element formation.

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Generally, these types of reactions open a facile and rational way to generate novel main-group-transition-metal clusters. Starting from halogenated main-group elements which already bear a transition-metal function might even serve as a good approach to preparing cluster compounds with different man-group elements and different transition metals as well in a specified manner.

Experimental Section

General Comments. Unless otherwise stated, commercial-grade reagents were used without further purification. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying reagents immediately prior to use. The compounds $[Mo(CO)_3Cp'']_2$,[28] $[Fe(CO)_2Cp^x]_2$ ($Cp^x = Cp$, Cp''),[29] $K[Mo(CO)_3Cp'']$,[30] $K[Co(CO)_4]$,[30] $Na_2[Fe(CO)_4]$,[31] $Na_2[W_2(CO)_{10}]$,[32] and $Na_2[W(CO)_5]$[33] and the dichlorobismuthanes $[\{Cp^x(CO)_2Fe\}BiCl_2]$ (Cp^x = Cp (**1a**),[34] Cp'' (**1b**)[2]) were synthesized by literature methods.

Synthesis of $[(\mu_3\text{-Bi})\{Co(CO)_4\}_2\{Fe(CO)_2Cp\}]$ (2). To a solution of **1a** (0.29 g, 0.63 mmol) in THF at −78 °C was added solid $K[Co(CO)_4]$ (0.26 g, 1.26 mmol), resulting in a brown solution. After 1 h the mixture was warmed to room temperature and stirred for another 1 h. After removal of all volatiles the brown residue was redissolved in *n*-hexane and the solution filtered. Storing at 0 °C yielded **2** as brown needles. Isolated yield: 429 mg (92%). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2081 (w), 2070 (m), 2057 (m), 2040 (m), 2029 (m), 2009 (s), 1982 (m). ^{1}H NMR (C_6D_6): δ 4.00 (s). MS (70 eV, EI; *m/e* (%)): 727.8 (3.5) [M$^+$], 556.9 (13.1) [M$^+$ − $Co(CO)_4$], 386.0 (100) [$CpFe(CO)_2Bi^+$], 353.9 (5.7) [$Cp_2Fe_2(CO)_4{}^+$], 341.8 (0.3) [$Co_2(CO)_8{}^+$]. Anal. Calcd for $C_{15}H_5BiFeCo_2O_{10}$: C, 24.75; H, 0.69; Found: C, 25.01; H, 0.80.

UV Reaction of $[(\mu_3\text{-Bi})\{Co(CO)_4\}_2\{Fe(CO)_2Cp\}]$ (2). A solution of $[(\mu_3\text{-Bi})\{Co(CO)_4\}_2\{Fe(CO)_2Cp\}]$ (**2**; 143 mg, 0.2 mmol) in 50 mL of THF is irradiated for 45 min with a low-pressure mercury lamp (125 W). Subsequently all volatiles are removed in vacuo and the red-brown residue is dissolved in 20 mL of CH_2Cl_2. Storing the solution at −20 °C affords $[Bi_4\{Co(CO)_3\}_4]$ (**3**) as brown crystals. Isolated yield: 67 mg (23%). Analytical and spectroscopic data are in agreement with literature values.[5]

Reaction of $[\{Cp''(CO)_2Fe\}BiCl_2]$ (1b) with $Na_2[Fe(CO)_4]$. To a solution of **1b** (0.335 g, 0.59 mmol) in 50 mL of THF at −78 °C was added at once solid $Na_2[Fe(CO)_4]$ (0.126 g, 0.59 mmol). The mixture was stirred at −78 °C for 1 h and afterward warmed to room temperature within 2 h. When it was warmed, the solution darkened and changed color from orange to dark green to brown. After 1 h of stirring at room temperature, the solvent was removed in vacuo to dryness. The brown residue was extracted with 50 mL of *n*-hexane over a column of dry SiO_2. The resulting solution was reduced to 20 mL. First, a few crystals of $[\{Fe_3(CO)_9\}\{\mu\text{-BiFe(CO)}_2Cp''\}_2]$ (**4**) crystallized, followed by the red crystals of the major product $[Bi_4\{\mu_3\text{-Fe(CO)}_3\}_3\{Fe(CO)_2Cp''\}_2]$ (**5**). Since fractionating crystallization does not lead to a complete separation of the compounds **4** and **5**, and separation by column chromatography was not feasible due to decomposition of the compounds, no elemental analysis could be performed. Isolated yield: 316 mg (of a mixture of **4** and **5**). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2022 (m), 2003 (s), 1984 (vs), 1968 (vs), 1947 (sh), 1943 (s), 1927 (s). Data for **4**: ^{1}H NMR (C_6D_6) δ 1.06 (s, 18H), 4.23 (t, 1H, $^4J_{HH}$ = 1.8 Hz), 4.51 (d, 2H, $^4J_{HH}$ = 1.8 Hz); MS (70 eV, EI; *m/z* (%)) 1444.1 (2) [M$^+$ + CO], 1182.7 (5) [M$^+$ − Cp'' − 2CO], 834.2 (12) [M$^+$ − $FeCp''Bi(CO)_5$]. Data for **5**: ^{1}H NMR (C_6D_6) δ 1.07 (s, 18H), 4.27 (t, 1H, $^4J_{HH}$ = 1.9 Hz), 4.54 (d, 2H, $^4J_{HH}$ = 1.9 Hz).

Synthesis of $[\{W_2(CO)_8\}(\mu,\eta^2\text{-Bi}_2)\{\mu\text{-BiFe(CO)}_2Cp''\}]$ (6). To a solution of **1b** (0.335 g, 0.59 mmol) in 50 mL of THF, which was cooled to −78 °C, was added at once solid $Na_2[W_2(CO)_{10}]$ (0.409 g, 0.59 mmol). The mixture was stirred at −78 °C for 1 h and afterward warmed to room temperature within 2 h. When it was warmed, the solution darkened and changed color from orange to dark green to brown. After 1 h of stirring at room temperature, the solvent was removed in vacuo to dryness. The brown residue was extracted with 50 mL of *n*-hexane over a column of dry SiO_2. From this solution green crystals of $[\{W_2(CO)_8\}(\mu,\eta^2\text{-Bi}_2)\{\mu\text{-BiFe(CO)}_2Cp''\}]$ (**6**) were obtained at −20 °C. Isolated yield: 241 mg (27%). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2022 (w), 1976 (vs), 1962 (m), 1934 (s), 1932 (sh), 1901(m), 1895 (sh), 1889 (s). ^{1}H NMR (C_6D_6): δ 1.08 (s, 18H), 4.35 (d, 2H, $^4J_{HH}$ = 1.9 Hz), 4.58 (t, 1H, $^4J_{HH}$ = 1.9 Hz). MS (70 eV, EI, 120 °C; *m/e* (%)): 1367.2 (2) [M$^+$ − 5CO], 1162.8 (4) [M$^+$ − Cp'' − 7CO], 178 (65) [Cp'']. Anal. Calcd for $C_{23}H_{21}Bi_3FeO_{10}W_2$: C, 18.32; H, 1.40. Found: C, 18.12; H, 1.35.

Synthesis of $[\{Cp''(CO)_3Mo\}BiCl_2]$ (7). To a mixture of $BiCl_3$ (3.16 g, 10 mmol) in 150 mL of Et_2O at 0 °C was added 2 equiv of $K[Mo(CO)_3Cp'']$ (7.92 g, 20 mmol) within 1 h. After a further 1 h of stirring the solution was warmed to room temperature. After filtration the solution was reduced to dryness in vacuo and the residue redissolved in 50 mL of CH_2Cl_2. To the green solution was added a further 1 equiv of $BiCl_3$ (3.15 g, 10 mmol), and within 2 h of stirring the color changed from green to red and an orange precipitate formed. The orange solid was filtered off and dried in vacuo. Isolated yield: 8.538 g (67%). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2012 (s), 1952 (m), 1930 (s), 1910 (vs), 1880 (s). ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 18H), 5.12 (t, 1H, *J* = 1.6 Hz), 5.33 (d, 2H, *J* = 1.6 Hz). MS (70 eV, EI; *m/e* (%)): 637.9 (5.4) [M$^+$], 651.0 (1.51) [M$^+$ − Cl], 386 (6.01) [$BiCp''^+$], 309.9 (100) [$Cp''MoCl^+$]. Anal. Calcd for $C_{16}H_{21}BiCl_2MoO_3$: C, 30.16; H, 3.32. Found: C, 30.12; H, 3.35.

Synthesis of $[(Cp''MoCO)_2(\mu\text{-Cl})_3]_2[Bi_2Cl_8(thf)_2]$ (8). A mixture of $BiCl_3$ (0.473 g, 3 mmol) and $[Mo(CO)_3Cp'']_2$ (1.5 mmol) was refluxed for 14 h in 50 mL of CH_2Cl_2. During this time $BiCl_3$ dissolved and an orange precipitate of **7** and amorphous elemental Bi formed. Filtration left an brownish residue, which was extracted with hot THF until the extract was colorless and the residue crystalline black. Over 2 h the former red extract changed color to green. After the green solution was reduced to half of its original volume and 10 mL of hexane was added, green crystals of **8** formed. Isolated yield: 1.268 g (18.7%, based on $BiCl_3$). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2001 (vs), 1997 (sh). ^{1}H NMR ($CDCl_3$): 1.25 (s, 36H), 1.76 (m, 4H), 3.61 (m, 4H), 5.44 (d, 4H, $^4J_{HH}$ = 2.2 Hz), 5.52 (t, 2H, $^4J_{HH}$ = 2.2 Hz). Anal. Calcd for $C_{64}H_{100}Bi_2Cl_{14}Mo_4O_6$: C, 33.96; H, 4.45. Found: C, 34.15; H, 4.42.

Reaction of $[\{Cp''(CO)_3Mo\}BiCl_2]$ (7) with $Na_2[Fe(CO)_4]$. To a slurry of **7** (0.37 g, 0.58 mmol) in 50 mL of CH_2Cl_2 at −78 °C was added solid $Na_2[Fe(CO)_4]$. After 0.5 h the reaction mixture was warmed to room temperature. It took several hours of stirring at room temperature until all orange solid had disappeared and the solution changed in color to dark green. Workup was as for the preparation of **4**, and $[\{Fe_2(CO)_6\}\{Fe(CO)_4\}\{\mu_3\text{-BiMo(CO)}_3Cp''\}_2]$ (**9**) was obtained as green needles from *n*-hexane solution at −20 °C. Isolated yield: 284 mg (31%, based on **7**). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2040 (w), 2000 (s), 1987 (vs) 1963 (vs), 1938 (sh), 1933 (s), 1915 (s). ^{1}H NMR (C_6D_6): δ 1.00 (s, 18H), 5.13 (t, 1H, *J* = 2.0 Hz), 5.35 (d, 2H,

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$J = 2.0$ Hz). Anal. Calcd for $C_{42}H_{42}Bi_2Fe_3Mo_2O_{16}$: C, 31.92; H, 2.68. Found: C, 32.01; H, 2.80.

Reaction of [{Cp″(CO)$_3$Mo}BiCl$_2$] (7) with Na$_2$[W(CO)$_5$]. To a slurry of **7** (0.37 g, 0.58 mmol) in 50 mL of toluene at −78 °C was added freshly prepared $Na_2[W(CO)_5]$ (0.215 g, 0.58 mmol). After 1 h the reaction mixture was warmed to room temperature and the solution changed in color to dark green. Workup was as before, and [{Cp″(CO)$_3$Mo}$_2$BiCl] (**10**) was obtained as green needles from *n*-hexane solution at −20 °C. Isolated yield: 240 mg (43%, based on **7**). IR (KBr; $\tilde{\nu}$(CO), cm^{-1}): 2042 (w), 1999 (vs), 1967 (m), 1932 (m), 1921 (m), 1896 (s), 1877 (m). ^{1}H NMR (C_6D_6): δ 1.00 (s, 18H), 5.15 (d, 2H, $^4J = 2.3$ Hz), 5.35 (t, 1H, $^4J = 2.3$ Hz). MS (70 eV, EI; *m*/*e* (%)): 960.0 (13.4) [M$^+$], 902.1 (7.3) [M$^+$ − 2(CO)], 846.1 (1.5) [M$^+$ − 4(CO)], 687.9 (47.8) [Cp″$_2$Mo$_2$Cl$_4$$^+$], 309.9 (100) [Cp″MoCl$^+$]. Anal. Calcd for $C_{32}H_{42}BiClMo_2O_6$: C, 40.08; H, 4.41. Found: C, 40.20; H, 4.40.

X-ray Structure Determination and Details of Refinement. Crystal structure analyses were performed on STOE STADI IV (**2**) and STOE IPDS (**3**−**6**, **8**−**10**) diffractometers using Mo Kα (λ = 0.710 69 Å) radiation with empirical absorption corrections for **2** (λ scans). The structures were solved by direct methods using SHELXS-86[35a] and refined using the method of least-squares refinement on F^2 in SHELXL-93.[35b] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed in calculated positions and were refined isotropically. For **5** the quality of the obtained data set was limited; thus, the atoms C(16) and C(17) were solely refined isotropically and the remaining residue electron densities were located close to the atoms Fe(1) and Bi(1), respectively. Crystallographic data are given in Table 1. X-ray structure analysis of **6**: formula $C_{23}H_{21}Bi_3FeO_{10}W_2$, M_r = 1507.89, 0.10 × 0.10 × 0.01 mm, $a = 17.677(4)$ Å, $b = 13.518(3)$ Å, $c = 12.950(3)$ Å, $V = 3094.5(12)$ Å^3, $d_c = 3.237$ g/cm^3, $Z = 4$, orthorhombic, space group *Abm*2, 8855 reflections collected ($-21 \le h \le 19$, $-16 \le k \le 16$, $-15 \le l \le 15$), 3123 independent and 2281 observed reflections ($I > 2\sigma(I)$), 96 refined parameters, maximum residual electron density 7.925 (−8.218) e Å^{-3}. In summary, the quality of different crystals of **6** was very poor and the habit of the crystals as very thin plates gave unfortunately a final R_{int} value of 0.2561. The refinement of the structure of **6** in the acentric orthorhombic space group *Abm*2 did yield a value of R1 = 0.1171 with an absolute structure parameter of −0.09(5). The Cp″ group was found to be disordered along the mirror plane of the atoms Bi(1), Bi(2), and Bi(3). Finally, in **6** only the atoms Bi, W, and Fe were refined anisotropically and the remaining residual electron density was found to be close to the heavy atoms Bi and W, respectively.

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Supporting Information Available: Complete tables of crystal data, atomic coordinates, H-atom parameters, bond distances, and anisotropic displacement parameters and fully labeled figures for **2**−**6** and **8**−**10**; data for these compounds are also available as electronic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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