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Heterometallic Complexes with Selenolate Ligands: Crystal Structures of $[(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]^-$, $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$, and $[(CO)_3Mn(\mu\text{-}SePh)_3Mn(CO)_3]^-$

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Oxidation of Co^{2+} by diphenyl diselenide in the presence of *cis*-$[PPN][Mn(CO)_4(SePh)_2]$, followed by carbonyl shift from Mn(I) to Co(III) and a benzeneselenolate group rearranging to bridge two metals, led directly to the thermally unstable $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$. Dropwise addition of [PPN][SePh] to the neutral $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ resulted in formation of a linear trinuclear complex possessing a hexaselenolatecobalt(III) core, $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]$. This complex crystallized in the triclinic space group $P\bar{1}$ with $a = 10.878(1)$ Å, $b = 15.095(2)$ Å, $c = 25.372(4)$ Å, $\alpha = 95.04(1)°$, $\beta = 95.00(1)°$, $\gamma = 91.52(2)°$, $V = 4132(2)$ Å^3, and $Z = 2$; final $R = 0.042$ and $R_w = 0.042$. In contrast, the thermally unstable *cis*-$[PPN][Mn(CO)_4(SeMe)_2]$, which was reacted with $Co(ClO_4)_2{\cdot}6H_2O$ and $(MeSe)_2$ in THF under a nitrogen atmosphere, led to the isolation of the stable heterometallic selenolate $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$. Crystal data: monoclinic space group $C2/c$, $a = 28.413(7)$ Å, $b = 11.091(3)$ Å, $c = 22.849(6)$ Å, $\beta = 125.06(3)°$, $V = 5894(3)$ Å^3, and $Z = 8$; final $R = 0.047$ and $R_w = 0.048$. The results indicated that the distinct electronic effects between methaneselenolate and benzeneselenolate play a key role in stabilizing the neutral Mn(I)−Co(III)−Mn(I)−selenolate complexes.

Introduction

The chemistry of complexes containing tellurolate/selenolate ligands is experiencing rapid development.[1] Interest in metal chalcogenolates stems not only from their potential application as precursors for M/Se and M/Te materials but also from the perspective of reactivity.[2−7] Recent work in this laboratory has shown that the complexes *cis*-$[Mn(CO)_4(ER)_2]^-$ (E = Te, Se; R = Ph, Me) which contain sites of latent reactivity (the delocalized lone pairs of electrons around chalcogen atoms) are useful in the syntheses of heterometallic Mn(I)−Co(III)−Mn(I)−chalcogenolate products such as $(CO)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}TePh)_3Mn(CO)_3$, and $(CO)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$.[8]

We further examined the reactivity of the manganese−selenolate species *cis*-$[Mn(CO)_4(SePh)_2]^-$ by reacting it with $Co(ClO_4)_2{\cdot}6H_2O$ and $(PhSe)_2$ in varying proportions. Specifically, the syntheses and characterization of a linear trinuclear anion containing a hexaselenolatocobalt(III) core $[(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]^-$, employing *cis*-$[Mn(CO)_4(SePh)_2]^-$ as a chelating ligand and intermetal ligand transfer reagent, are described. In addition, the synthesis and structure of the thermally stable $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$ are reported, see Scheme 1.

Results and Discussion

In the present work, we were interested to know how strongly the characteristics of the neutral heterotrimetallic Mn(I)−Co-

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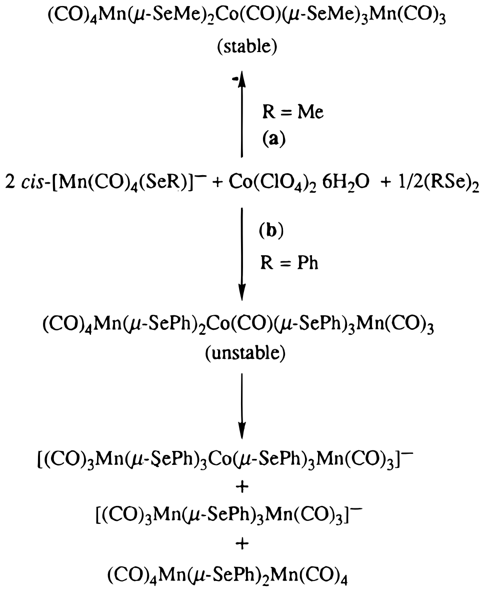
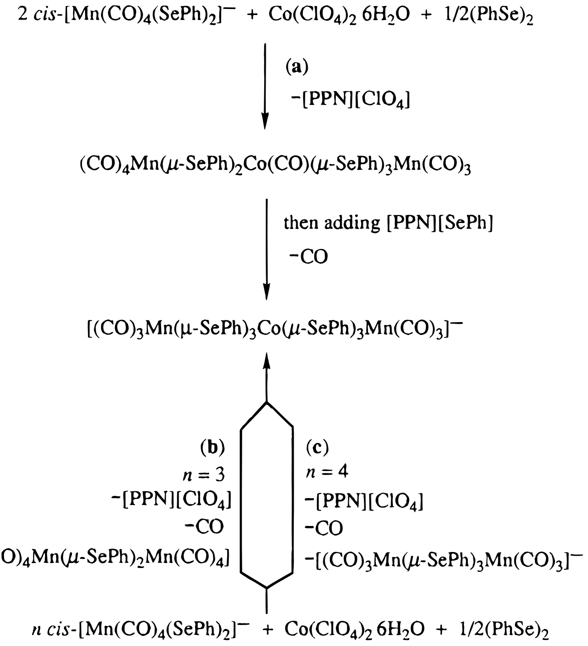
Scheme 1



Scheme 2



(III)−Mn(I)−chalcogenolate complexes depend on the substituents of the chalcogenolate ligands by using dialkyl dichalcogenide in place of the diphenyl dichalcogenide used earlier.[8] The IR carbonyl stretching spectra and X-ray diffraction confirm the formation of the neutral $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$ (**1**) in the reaction of *cis*-$[PPN][Mn(CO)_4(SeMe)_2]$, $(MeSe)_2$, and $Co(ClO_4)_2{\cdot}6H_2O$ (Scheme 1a). However, the reaction led to decomposition when reacting *cis*-$[Mn(CO)_4(SePh)_2]^-$ and $CoCl_2{\cdot}6H_2O$ in the presence of $(PhSe)_2$ in THF at room temperature. No decomposition was observed when stirring the neutral $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$ THF solution at ambient temperature for 2 days. The ^1H and ^{13}C NMR spectra of complex **1** show the expected signals for the methyl groups involved and display characteristics of diamagnetic d^6 Co(III) and d^6 Mn(I) species.

To evaluate the influence of the weaker electron-donating chalcogenolate ligand on the stability of the heterometallic Mn(I)−Co(III)−Mn(I)-chalcogenolate complexes, we surveyed the reactivity of diphenyl diselenide toward $Co(ClO_4)_2{\cdot}6H_2O$ in the presence of *cis*-$[Mn(CO)_4(SePh)_2]^-$ in stoichiometric proportions ($(PhSe)_2$:$Co(ClO_4)_2{\cdot}6H_2O$:*cis*-$[PPN][Mn(CO)_4(SePh)_2]$ = 0.5:1:2 molar ratio) in THF at ambient temperature (Scheme 1b).[8,9] An immediate reaction ensued under a nitrogen atmosphere. The IR carbonyl stretching (2074 w, 2033 w, 2006 s, 1991 sh, 1964 w, 1929 m cm^{-1} (THF)) spectra confirm the formation of the neutral $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$. However, the neutral complex is thermally unstable. Following extended periods of stirring in THF at ambient temperature, the dark purple solution of $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ converted into a dark purple brown solution. It is impossible to isolate the pure $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$, even if the reaction is run and crystallized at −10 °C. This transformation was indicated by the appearance of new bands for the ν_{CO} vibrations in THF (2068 w, 2008 m, 1983 vs, 1962 w, 1902 s cm^{-1} (THF)). The transformation products can be crystallized from THF−hexane as a mixture of dark purple crystals $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]$ (**2**) and red-brown crystals $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Mn(CO)_3]$ (**3**) after being separated from the hexane-soluble $(CO)_4Mn(\mu\text{-}SePh)_2Mn(CO)_4$ under nitrogen. We attribute the formation of the heterometallic anion **2** to the lability of "Co(III)−CO" carbonyl group in neutral $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ and rapid intermetal transfer of the benzeneselenolate group. These results indicate that the relative order of thermal stability of linear trinuclear Mn(I)−Co(III)−Mn(I)-selenolate complexes is $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3 > (CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$. This result may be accounted for by the distinct electronic effects between methaneselenolate and benzeneselenolate ligands. The trinuclear anion **2** and the dimeric anion **3**, individually, exhibit a two-band pattern in the ν_{CO} region of the infrared, but different pattern and positions, ν_{CO} 1983 vs, 1901 s cm^{-1} (THF) for **2** and ν_{CO} 1981 s, 1902 vs cm^{-1} (THF) for **3**, which is consistent with a tricarbonyl derivative of approximately C_{3v} symmetry. The electronic absorption spectra of the trinuclear anion **2** are dominated by four major bands in the region 305−664 nm. These bands are tentatively assigned as ligand-to-metal charge-transfer transitions.

In order to clarify the formation of heterotrimetallic anion **2** and the lability of the "Co(III)−CO" carbonyl group in neutral $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$, a straightforward synthetic reaction was conducted by employing $[PhSe]^-$ as a nucleophilic reagent as well as a bridging ligand. As illustrated in Scheme 2a, the dropwise addition of [PPN][SePh] to $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ in THF at ambient temperature led to the formation of a dark purple solution. The infrared spectrum shows carbonyl stretching bands (ν_{CO} (THF): 1983 vs, 1901 s cm^{-1}) attributable to the presence of the bis(benzeneselenolate-triply-bridged) species of composition $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]$. The trinuclear anion **2** is strongly colored and moderately sensitive to air and light; the crystalline solid was easily crystallized in 82.5% yield from THF-hexane at −10 °C.

In a similar fashion, *cis*-$[Mn(CO)_4(SePh)_2]^-$ was reacted in stoichiometric proportions with $Co(ClO_4)_2{\cdot}6H_2O$ and $(PhSe)_2$ (3:1:0.5 molar ratio) in THF under a nitrogen atmosphere, and the reaction mixture finally led to the isolation of red-brown dimer $(CO)_4Mn(\mu\text{-}SePh)_2Mn(CO)_4$ and the dark purple hetero-

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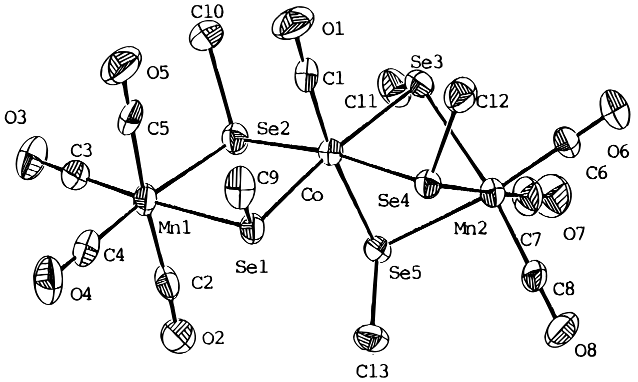

Figure 1. ORTEP drawing and labeling scheme of neutral $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$ with thermal ellipsoids drawn at the 50% probability level.

trimetallic selenolate **2** (Scheme 2b). Additionally, when the same reaction was carried out in a 4:1:0.5 (*cis*-$[Mn(CO)_4(SePh)_2]^-$:$Co(ClO_4)_2\cdot 6H_2O$:$(PhSe)_2$) molar ratio under similar experimental conditions, the complexes **2** and **3** were obtained after being recrystallized from THF-hexane (Scheme 2c). The most likely explanation for these results (Scheme 2b,c) is that *cis*-$[Mn(CO)_4(SePh)_2]^-$ was employed as a chelating ligand as well as an intermetal ligand transfer reagent.

The definitive assignment of the structure of the dark purple complex **1** was obtained by X-ray crystallography (Figure 1). The neutral trinuclear complex **1** has a linear chain of one Co atom and two Mn atoms; the distorted octahedral coordination geometry of the Co center is completed with five bridging methaneselenolates and a terminal carbonyl with Se(1)−Co−C(1), Se(2)−Co−C(1), Se(3)−Co−C(1), Se(4)−Co−C(1), and Se(5)−Co−C(1) angles of 93.5(5), 94.4(5), 90.8(5), 94.4(5), and 172.9(5)° respectively. The Co(III)−Se bond distances of 2.405(3) Å (average) observed in complex **1** are shorter than those of complex **2** (average distance 2.441(1) Å). The Co(III)−C(1)O bond of length 1.763(15) Å in complex **1** is comparable to the Co(III)−CO bond (1.75(3) Å) previously found in $(CO)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}TePh)_3Mn(CO)_3$.[8a] It is not surprising that the bite angle Se(1)−Co−Se(2) of the doubly-bridging methaneselenolates is 85.72(8)°, which is larger than the Se−Co−Se angles of the triply-bridging methaneselenolates (average 83.15(8)°) in complex **1**.

The X-ray crystal structure of the compound $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]\cdot 2THF$ consists of two crystallographically independent molecules and is composed of discrete cations, anions and two THF molecules; there are no exceptional cation−anion interactions (Figure 2). Complex **2** has a linear chain of one Co atom and two Mn atoms; each Mn(I) atom in a distorted octahedral arrangement is bonded to the three carbonyl ligands and to the three selenium atoms of the bridging SePh groups. The cobalt atom, which lies on an inversion centre, is surrounded by six homoleptic bridging benzeneselenolates. The cobalt component of the trinuclear anion **2** is thus an approximately octahedral hexaselenolate−Co^{III} complex. The six-coordinate polyhedron of D_3 symmetry can be defined by the two parameters ϕ and *s/h*, *i.e.* the twist angle between two parallel triangular faces of the polyhedron and the ratio of the side of the triangle to the distance between the triangles.[10] In the geometry of the $Co(\mu\text{-}SePh)_6$ core in complex **2**, ϕ is equal to 60° and *s/h* is equal to 1.03,[11,12] indicating that the structure is elongated along one of the pseudo-C_3 axes, and adopts a conformation in which two adjacent triangles (two parallel triangular-benzeneselenolate faces) are in almost perfectly staggered position. The staggered conformation would be the best for minimization of the interactions between the benzeneselenolate ligands.[13,14] The average bite angle (*cis* Se−Co(III)−Se angles) is 83.52(4)°. A further noteworthy result in the structure discussion is the *trans* Se−Co−Se angle which was found to average 180.0° (136 ± 1° in the known trigonal prism and 180° in the perfect octahedron) in complex **2**.

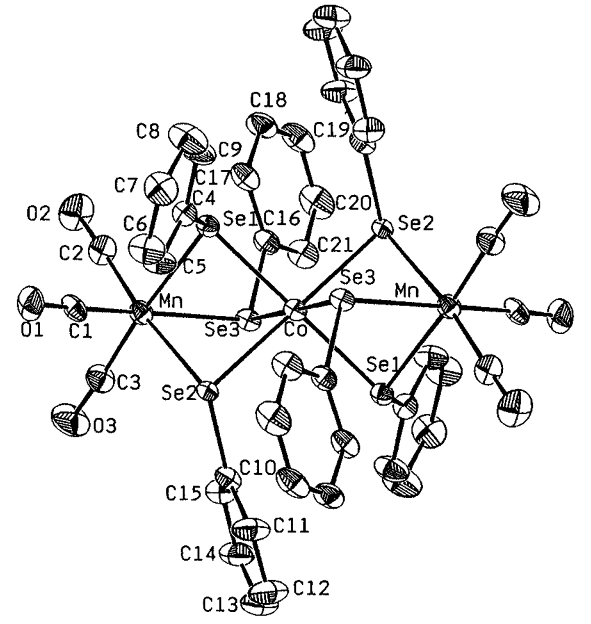

Figure 2. ORTEP drawing and labeling scheme of $[(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]^-$ with thermal ellipsoids drawn at the 50% probability level.

The Co(III)−Se distances ranging from 2.426(1) to 2.461(1) Å in complex **2** are considerably longer than that observed in $[(en)_2Co(SeCH_2CH_2NH_2)][(NO_3)_2]$ (2.378(1) Å).[15] This lengthening may be due to the presence of six benzeneselenolates which may cause the Co(III)−Se bonds to lengthen for steric reasons. The acute Mn(I)−Se−Co(III) angles range from 80.97(5) to 82.13(5)° in trinuclear anion **2**.

The structure of anion **3** is shown in Figure 3. The phenyl groups of three bridging μ_2-benzeneselenolates in **3** form a regular propeller-like arrangement around the Se_3 plane defined by the three seleniums. To a first approximation, the $Mn(Se)_3(CO)_3$ framework may be described as face-sharing octahedra. These Mn−Se distances (average 2.532(1) Å) in **3** are much shorter than the terminal Mn−Se bonds in the anion $[Mn(SePh)_4]^{2-}$ (average 2.567 Å).[16]

Conclusion. The heterotrimetallic selenolate $[(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]^-$ has been prepared by the reaction of $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ with $[PhSe]^-$ under mild conditions. It seems reasonable to state

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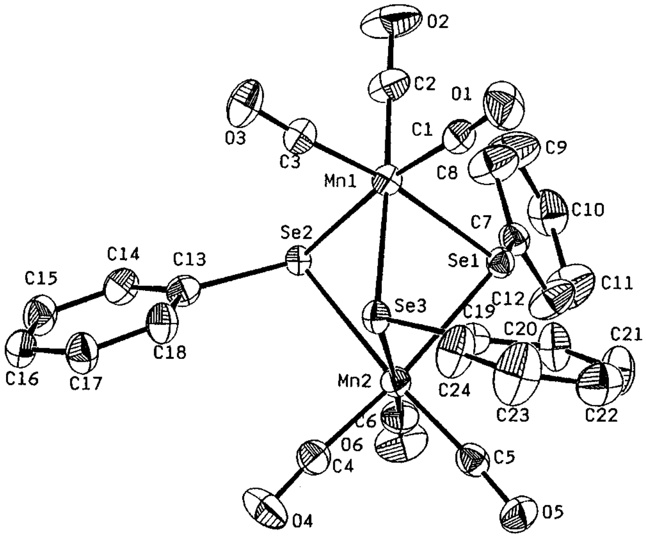

Figure 3. ORTEP drawing and labeling scheme of the $[(CO)_3Mn(\mu\text{-}SePh)_3Mn(CO)_3]^-$ anion with thermal ellipsoids drawn at the 50% probability level.

Table 1. Crystallographic Data of Complexes **1**−**3**

	1	2	3
chem formula	$C_{17}H_{23}O_9Mn_2CoSe_5$	$C_{86}H_{76}O_8NP_2Mn_2CoSe_6$	$C_{60}H_{45}O_6Mn_2Se_3NP_2$
fw	934.96	1956.06	1284.71
cryst syst	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
λ(Mo Kα), Å	0.7107	0.7107	0.7107
a, Å	28.413(7)	10.878(1)	10.644(3)
b, Å	11.091(3)	15.095(2)	14.946(3)
c, Å	22.849(6)	25.372(4)	19.541(3)
α, deg		95.04(1)	107.04(2)
β, deg	125.06(3)	95.00(1)	95.56(2)
γ, deg		91.52(2)	108.30(2)
V, Å^3	5894(3)	4132(1)	2760(1)
Z	8	2	2
d_{calcd}, g cm^{-3}	2.107	1.572	1.546
μ, cm^{-1}	76.597	31.951	37.061
T, °C	25	25	25
R^a	0.047	0.042	0.037
$R_w{}^b$	0.048	0.042	0.039
GOF^c	2.86	1.58	1.50

^{a} $R = \sum|(F_o - F_c)|/\sum F_o$. ^{b} $R_w = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$. ^{c} GOF $= [\sum[w(F_o - F_c)^2/(M - N)]^{1/2}$ where M = number of reflections and N = number of parameters.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$

Se(1)−Co	2.391(3)	Se(4)−Co	2.390(2)
Se(2)−Co	2.399(2)	Se(5)−Co	2.424(2)
Se(3)−Co	2.422(3)	C(1)−Co	1.763(2)
Se(1)−Mn(1)	2.483(3)	Se(4)−Mn(2)	2.477(3)
Se(2)−Mn(1)	2.491(3)	Se(5)−Mn(2)	2.492(3)
Se(3)−Mn(2)	2.478(3)	C(1)−O(1)	1.130(18)
Se(1)−Co−Se(2)	85.72(8)	Se(1)−Co−Se(4)	91.53(9)
Se(1)−Co−Se(3)	174.23(10)	Se(1)−Co−Se(5)	93.28(8)
Se(2)−Co−Se(3)	98.02(9)	Se(2)−Co−Se(4)	170.86(10)
Se(2)−Co−Se(5)	88.57(9)	Se(1)−Co−C(1)	93.3(5)
Se(4)−Co−C(1)	94.4(5)	Se(2)−Co−C(1)	94.4(5)
Se(5)−Co−C(1)	172.9(5)	Se(3)−Co−C(1)	90.8(5)
Se(1)−Mn(1)−Se(2)	81.81(8)	Se(3)−Mn(2)−Se(5)	79.96(8)
Se(3)−Mn(2)−Se(4)	81.14(8)	Se(4)−Mn(2)−Se(5)	79.74(8)
Co−Se(1)−Mn(1)	95.68(9)	Co−Se(4)−Mn(2)	82.42(9)
Co−Se(2)−Mn(1)	95.28(9)	Co−Se(5)−Mn(2)	81.43(8)
Co−Se(3)−Mn(2)	81.74(8)	Co−C(1)−O(1)	176.1(15)

that the weaker electron-donating chalcogenolate ligands decreasing the charge density around the Co(III) center may destabilize Co(III)−CO bond of $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$, resulting in displacement of "Co(III)−CO" carbonyl ligand by benzeneselenolate. This synthetic route provides an alternative method to obtain a heterometallic selenolate complex containing a hexaselenolatecobalt(III) core.

Experimental Section

Manipulations, transfers, and reactions of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from CaH_2/P_2O_5; hexane and tetrahydrofuran (THF) from Na/benzophenone) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use, and transfers to reaction vessels were via stainless-steel cannula under N_2 at a positive pressure. The reagents manganese decacarbonyl, diphenyl diselenide, bis(triphenylphosphoranylidene)ammonium chloride, dimethyl diselenide, cobalt dichloride, and cobalt perchlorate (Aldrich) were used as received. [PPN][SePh] was prepared by literature methods.[17] Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) with sealed solution cells (0.1 mm) and KBr windows. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of ^1H and ^{13}C are relative to tetramethylsilane. UV−visible spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of $(CO)_4Mn(\mu\text{-}SeMe)_2Co(CO)(\mu\text{-}SeMe)_3Mn(CO)_3$ (1). $[PPN][Mn(CO)_5]$ (0.293 g, 0.4 mmol) was added to $(MeSe)_2$ (0.094 g, 0.5 mmol, 50 μL) in THF (5 mL) at 15 °C. A vigorous reaction occurred immediately with evolution of CO gas. Over a period of 10 min, the reaction mixture was added to $Co(ClO_4)_2\cdot 6H_2O$ (73.2 mg, 0.2 mmol) by cannula under positive N_2 pressure. After 30 min of stirring at room temperature, the solvent was removed under vacuum. The residue was dissolved in 30 mL of diethyl ether, and the dark purple solution was filtered to remove $[PPN][ClO_4]$. The product, suitable for X-ray crystallography, was isolated by removing the solvent (diethyl ether) and recrystallized from vapor diffusion of hexane into concentrated THF solution at −15 °C. The yield was 0.156 g (90%). IR (ν_{CO}) (THF): 2068 w, 2027 sh, 1998 vs, 1981 sh, 1961 w, 1917 m cm^{-1}. ^1H NMR (C_4D_8O): δ 2.20 (s), 2.00 (s), 1.93 (s), 1.86 (s), 1.57 (s) ppm (Me); ^{13}C NMR (C_4D_8O): δ 5.88 (s), 4.19 (s), 3.41 (s), 3.36 (s), 2.20 (s) ppm (Me). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 507(3976), 451(5369), 398(7030), 281(20,143). Anal. Calcd for $C_{13}H_{15}O_8Se_5Mn_2Co$: C, 18.10; H, 1.75. Found: C, 18.81; H, 1.94.

Safety Note. *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.*

Preparation of $[PPN][(CO)_3Mn(\mu\text{-}SePh)_3Co(\mu\text{-}SePh)_3Mn(CO)_3]$ (2). The reaction mixture, *cis*-$[Mn(CO)_4(SePh)_2]^-$ (0.407 g, 0.4 mmol)[8b] and $(PhSe)_2$ (0.031 g, 0.1 mmol), was added to $Co(ClO_4)_2\cdot 6H_2O$ (73.2 mg, 0.2 mmol) in THF (5 mL) solution. A vigorous reaction which occurred immediately was monitored with FTIR at ambient temperature. IR spectrum, ν_{CO} (THF) 2074 w, 2033 w, 2006 s, 1991 sh, 1964 w, 1929 m cm^{-1},[8] indicated the formation of neutral $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$. To the dark purple solution of $(CO)_4Mn(\mu\text{-}SePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3$ was then added [PPN][SePh] (0.139 g, 0.2 mmol) THF/CH_3CN (4 mL/1 mL) solution drop by drop after removing the insoluble solid $[PPN][ClO_4]$. The reaction mixture was stirred for 3 h at room temperature. After the reaction was completed, the dark purple solution was then concentrated to 3 mL, and hexane was slowly added to precipitate a dark purple solid. The mother liquor was removed via cannula, and the solid was dried under vacuum. The isolated yield is 0.299 g (82.5%). IR (ν_{CO}) (THF): 1983 vs, 1901 s cm^{-1}. ^1H NMR (C_4D_8O): δ 7.03−7.67 (m) ppm (Ph); ^{13}C NMR (C_4D_8O): δ 137.6 (s), 134.6 (s), 133.2 (s), 132.2 (s), 130.5 (s), 130.2 (s), 128.0 (s), 126.9 (s). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 664(2750), 512(8150), 400(16,290), 305(20,860). Hexane was slowly diffused into dark purple THF solution under nitrogen atmo-

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[17] (a) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501. (b) Forde, C. E.; Morris, R. H.; Ramachandran, R. *Inorg. Chem.* **1994**, *33*, 5647.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (a) **2** and (b) **3**

(a) [PPN][(CO)$_3$Mn(μ-SePh)$_3$Co(μ-SePh)$_3$Mn(CO)$_3$]

Se(1)−Co	2.435(1)	Se(2)−Co	2.461(1)
Se(3)−Co	2.426(1)	Se(1)−Mn	2.513(2)
Se(2)−Mn	2.545(2)	Se(3)−Mn	2.521(2)

Se(1)−Co−Se(1)	180.0	Se(1)−Co−Se(2)	84.67(3)
Se(1)−Co−Se(2)	95.33(3)	Se(1)−Co−Se(3)	83.09(4)
Se(1)−Co−Se(3)	96.91(4)	Se(2)−Co−Se(2)	180.0
Se(2)−Co−Se(3)	82.79(3)	Se(2)−Co−Se(3)	97.21(3)
Se(3)−Co−Se(3)	180.0	Se(1)−Mn−Se(2)	81.37(6)
Se(1)−Mn−Se(3)	79.63(6)	Se(1)−Mn−C(1)	93.4(3)
Se(1)−Mn−C(2)	92.2(4)	Se(1)−Mn−C(3)	175.0(4)
Se(2)−Mn−Se(3)	79.27(6)	Co−Se(1)−Mn	82.13(5)
Co−Se(2)−Mn	80.97(5)	Co−Se(3)−Mn	82.13(5)

(b) [PPN][(CO)$_3$Mn(μ-SePh)$_3$Mn(CO)$_3$]

Se(1)−Mn(1)	2.526(1)	Se(1)−Mn(2)	2.522(1)
Se(2)−Mn(1)	2.556(1)	Se(2)−Mn(2)	2.557(1)
Se(3)−Mn(1)	2.521(1)	Se(3)−Mn(2)	2.511(1)

Mn(1)−Se(1)−C(7)	116.6(2)	Se(1)−Mn(1)−Se(2)	79.52(4)
Mn(2)−Se(1)−C(7)	107.5(2)	Se(1)−Mn(1)−Se(3)	81.40(4)
Mn(1)−Se(1)−Mn(2)	82.64(4)	Se(2)−Mn(1)−Se(3)	82.93(4)
Mn(1)−Se(2)−Mn(2)	81.37(4)	Mn(1)−Se(3)−Mn(2)	82.96(4)

sphere; storage for 4 weeks at −10 °C led to formation of dark purple crystals [PPN][(CO)$_3$Mn(μ-SePh)$_3$Co(μ-SePh)$_3$Mn(CO)$_3$] suitable for X-ray crystallography. Anal. Calcd for $C_{78}H_{60}O_6NP_2Mn_2CoSe_6$: N, 0.77; C, 51.71; H, 3.34. Found: N, 0.85; C, 51.87; H, 3.60.

Reaction of *cis*-[Mn(CO)$_4$(SePh)$_2$]$^-$, (PhSe)$_2$, and Co(ClO$_4$)$_2$·6H$_2$O. (PhSe)$_2$ (0.155 g, 0.5 mmol) was added to [PPN][Mn(CO)$_5$] (0.293 g, 0.4 mmol) in THF (5 mL) at ambient temperature. Over a period of 15 min, the reaction mixture was added to Co(ClO$_4$)$_2$·6H$_2$O (73.2 mg, 0.2 mmol) by cannula under positive N$_2$ pressure. The reaction was monitored with FTIR. The IR spectra, ν_{CO} (THF) 2074 w, 2033 w, 2006 s, 1991 sh, 1964 w, 1929 m cm^{-1}, indicated the formation of (CO)$_4$Mn(μ-SePh)$_2$Co(CO)(μ-SePh)$_3$Mn(CO)$_3$. The reaction mixture was stirred for 3 days at room temperature; the IR spectrum (ν_{CO} (THF) 2068 w, 2008 m, 1983 vs, 1962 w, 1902 s cm^{-1}) revealed that all (CO)$_4$Mn(μ-SePh)$_2$Co(CO)(μ-SePh)$_3$Mn(CO)$_3$ completely converted to [(CO)$_3$Mn(μ-SePh)$_3$Co(μ-SePh)$_3$Mn(CO)$_3$]$^-$ (**2**), [(CO)$_3$Mn(μ-SePh)$_3$Mn(CO)$_3$]$^-$ (**3**), and (CO)$_4$Mn(μ-SePh)$_2$Mn(CO)$_4$.[8] The dark purple brown solution was filtered to remove the unsoluble solid, and then dried under vacuum. Hexane was added to extract the known brown-red (CO)$_4$Mn(μ-SePh)$_2$Mn(CO)$_4$ (IR (ν_{CO}) (THF): 2066 m, 2012 vs, 1998 m, 1962 s cm^{-1}).[8b] The residue was dried again under vacuum, and then dissolved in 5 mL of THF. Recrystallization by vapor diffusion of hexane into THF solution at −10 °C afforded dark purple [PPN][(CO)$_3$Mn(μ-SePh)$_3$Co(μ-SePh)$_3$Mn(CO)$_3$] crystals suitable for X-ray crystallography (IR ν_{CO} (THF): 1983 vs, 1901 s cm^{-1}) and the known red-brown [PPN][(CO)$_3$Mn(μ-SePh)$_3$Mn(CO)$_3$] crystals (IR ν_{CO} (THF): 1981 s, 1902 vs cm^{-1}. Absorption spectrum (THF)[λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 409(2768), 312(7704), 273(20,128)).

Crystallography. Crystallographic data for the structures of complexes **1**, **2**, and **3** are collected in Table 1 and in the Supporting Information. All crystals of **1**, **2**, **3** are chunky. The dark purple crystal of **1** moderately sensitive to air chosen for diffraction measurement was *ca.* 0.20 × 0.50 × 0.50 mm; the dark purple crystal of **2** moderately sensitive to air and light had crystal dimensions 0.20 × 0.40 × 0.40 mm; the red-brown crystal of **3** had crystal dimensions 0.25 × 0.25 × 0.38 mm. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. The unit cell parameters were obtained from 25 reflections with 2θ between 19.00 and 32.00° for product **1**; $16.60° < 2\theta < 24.40°$ for product **2**, and $16.72° < 2\theta < 24.66°$ for product **3**. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode. A φ scan absorption correction was made.[18] Structural determinations were made using the NRCC-SDP-VAX package of programs.[19] [20] Selected bond distances and angles are listed in Tables 2 and 3.

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Supporting Information Available: Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, bond lengths and angles, and anisotropic temperature factors for (CO)$_4$Mn(μ-SeMe)$_2$Co(CO)(μ-SeMe)$_3$Mn(CO)$_3$, [PPN][(CO)$_3$Mn(μ-SePh)$_3$Co(μ-SePh)$_3$Mn(CO)$_3$], and [PPN][(CO)$_3$Mn(μ-SePh)$_3$Mn(CO)$_3$] (22 pages). Ordering information is given on any current masthead page.

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