of K-**1** containing organic cations. Curiously, the replacement of KCN by tetraalkylammonium cyanide in the synthesis of K-**1** gave none of the desired product in either aqueous or acetonitrile solvent. Cation metathesis reactions with R_4NBF_4 gave complex mixtures of incompletely exchanged salts.[22]

Success was achieved by precipitation of $([(C_6H_5)_3P]_2N)_6[(NC)_5CoC(CO_2Me){=}C(CO_2Me)Co(CN)_5]$ (PPN-**1**) from aqueous solution using bis(triphenylphosphine)nitrogen(1+) chloride (PPN^+Cl^-). Surprisingly, PPN-**1** proved to be far less stable thermally than K-**1** both as a solid and in solution. It also proved impossible to completely dry PPN-**1** without significant decomposition.

The reaction chemistry of **1** proved to be quite limited. Nucleophiles such as CN^- and OH^- reacted only with the ester functionalities of **1**; no evidence was observed for conjugate addition products. The double bond of **1** also proved inert to Diels–Alder dienes.[23]

Comments on the Mechanism of Cobalt-Catalyzed Cyanation. Our attention was initially drawn to K-**1** because of its potential for modeling the (σ-vinyl)cobalt cyanide complexes proposed to be intermediates in the cobalt-catalyzed cyanation of vinyl halides.[3] Wilkinson et al.[4] have reported that the unsubstituted analogue of K-**1** derived from acetylene and $Co(CN)_5^{3-}$ decomposes in solution to an uncharacterized organic nitrile. Since this was the only known example of a characterized organocobalt cyanide undergoing thermal decomposition to a nitrile product, a key step in the mechanism proposed for the aforementioned cobalt-catalyzed cyanation, the thermal reactivity of K-**1** was of great interest. Both K-**1** and PPN-**1** decompose in solution at moderate temperatures. The decomposition mixtures were examined by NMR and infrared spectroscopy and found to be quite complex, with no evidence for significant amounts of nitriles in the mixture.[24] An alternate mechanistic hypothesis for the nitrile formation step of the cobalt-catalyzed reaction would be a bimolecular reaction between the (σ-vinyl)cobalt cyanide intermediate and some other cyanide-containing species in the reaction mixture. To test the feasibility of this idea, K-**1** was exposed to the catalytic mixture; it proved to be unreactive and could be recovered in good yield.[25]

Acknowledgment[26] is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for partial support of this research.

Registry No. K-1·6H_2O, 85439-49-2; PPN-1, 85439-51-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, nonessential bond lengths and angles, hydrogen bonds, angles subtended at potassium ions, and observed and calculated structure factors and Figure 3, showing the coordination geometry of the potassium ions (18 pages). Ordering information is given on any current masthead page.

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(22) With a substantial excess of tetraalkylammonium ion in the solution $(R_4N)_6[(NC)_5CoC(COOMe){=}C(COOMe)Co(CN)_5]$ could be isolated but in unsatisfactory yield.

(23) Iodine has been reported to effect cobalt–carbon bond cleavage of K-**1** rather than addition to the double bond.[3] Another electrophile, benzyl bromide, was found to be unreactive with K-**1**. Cyclopentadiene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene were chosen as sterically unencumbered representative Diels–Alder substrates with extreme electronic qualities, electron rich vs. electron poor. No reaction was observed with either.

(24) Attempts to extract organic products from aqueous solutions of decomposed K-**1** were unsuccessful.

(25) Hydrogenolysis and hydrogenation products are observed as byproducts of the β-bromostyrene cyanation reaction.[2a] However, compound K-**1** was found to be inert to $NaBH_4$ and also to the Funabiki cyanation reaction mixture (sans β-bromostyrene).

(26) This work has been abstracted in part from the Senior Honors Theses of A.J.K. and K.D.G.

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Cadmium Thiolates. Tetrahedral CdS_4 and Dodecahedral CdS_4O_4 Coordination in *catena*-Bis(carbethoxymethanethiolato)cadmium(II)

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Crystals of $Cd(SCH_2COOCH_2CH_3)_2$ from ethanol solution contain $[Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$ linear chains, along which cadmium atoms of two different coordination stereochemistries alternate. Cadmium atoms are separated by 344 pm and bridged by two thiolate functions. At each cadmium atom the primary coordination is $(\mu\text{-}SR)_4$: additional, secondary, coordination at one cadmium atom is by four carbonyl oxygen atoms (Cd1–S = 262 pm, Cd1–O = 288 pm) in stereochemistry idealized as dodecahedral, and at the other cadmium the secondary carbonyl oxygen coordination is very weak (Cd2–S = 253 pm, Cd2–O = 323 pm) in tetracapped-tetrahedral stereochemistry. Crystal data: $CdS_2C_8H_{14}O_4$, space group $I4_1/acd$, $a = 1937.1\ (3)$ pm, $c = 1376.4\ (3)$ pm, $Z = 16$, $d_{obsd} = 1.81\ (2)$ g cm^{-3}, $d_{calcd} = 1.80$ g cm^{-3}, 509 observed reflections, Cu Kα, $R = 0.055$.

A variety of structure types have been found for cadmium complexes in which the coordination is exclusively or predominantly by the thiolate function. Observed molecular structures range in size from $[Cd(SPh)_4]^{2-}$ [1] through $[Cd_4(SR)_{10}]^{2-}$ [2] to $[ICd_8(SCH_2CH_2OH)_{12}]^{3+}$,[3] $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$,[4] and $[S_4Cd_{10}(SPh)_{16}]^{4-}$,[5] while one-dimensional nonmolecularity occurs in $\{Cd[SCH(CH_2CH_2)_2NHCH_3]_2^{2+}\}_\infty$[6] and two-dimensional nonmolecularity occurs in $[Cd(SCH_2CH_2OH)_2]_\infty$.[7]

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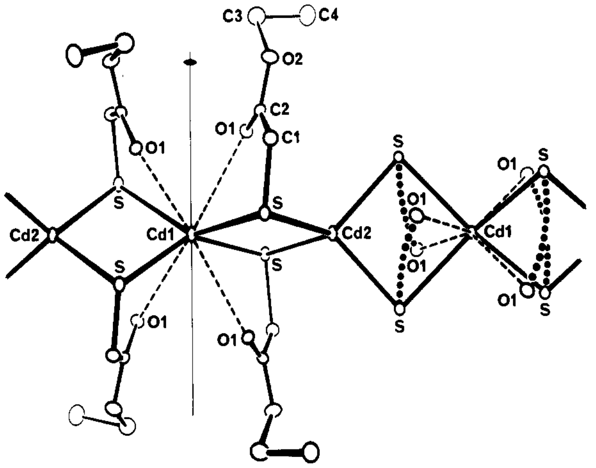

Figure 1. Repeat unit of the $Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2$ chain, with carbon atoms from some ligands omitted. The marked twofold axis at Cd1 is the principal twofold axis of the coordination dodecahedron at Cd1.

Homoleptic cadmium thiolate coordination occurs also in the metallothionein proteins.[8] The most advanced current structural model for metallothionein from cadmium-loaded rabbit liver involves $[Cd_3(S\text{-cys})_9]^{3-}$ and $[Cd_4(S\text{-cys})_{11}]^{3-}$ molecular cages.[9]

No more than four thiolate ligands are known to enter the cadmium(II) coordination sphere, consistent with the widely applicable model of RS^- as a strongly electron-releasing ligand,[10] but additional heteroligands may be present and reduce the coordination symmetry.[3,4,7,11] As part of a research program on the syntheses and structures of metal thiolates we have investigated the metal complexes of $^-SCH_2COOCH_2CH_3$. With nickel(II) this ligand functions only as a thiolate which doubly bridges metal atoms to form the unusual molecular octagonal toroid $Ni_8(SCH_2COOCH_2CH_3)_{16}$.[12] We here report the structure of $Cd(SCH_2COOCH_2CH_3)_2$, which is one-dimensionally nonmolecular with two different cadmium coordination spheres.

Results

Colorless prismatic crystals of $Cd(SCH_2COOCH_2CH_3)_2$ are readily obtained from alcohol solutions of cadmium salts plus 2–4 equiv of ethyl 2-mercaptoacetate and base.

In the tetragonal crystal structure the cadmium atoms and their associated ligands occur in separated chains parallel to the unique *c* axis. The chains are separated by 969 pm ($a/2$).[13] As shown in Figure 1, cadmium atoms with two different coordination environments alternate along these chains, separated by 344 pm ($c/4$): two cadmium atoms of each type constitute the repeat unit along the chain. The crystallographic site symmetries of the cadmium locations are 222 (D_2) at Cd1 and $\bar{4}$ (S_4) at Cd2. The ligands function mainly as bridging thiolates, occurring in pairs between cadmium atoms, such that the primary coordination of each cadmium atom is $Cd(\mu\text{-}SR)_4$. The carbonyl oxygen atoms provide secondary coordination of cadmium, four such oxygen atoms being 288 pm from Cd1 and four being 323 pm from Cd2. The coordination stereochemistries are described fully below.

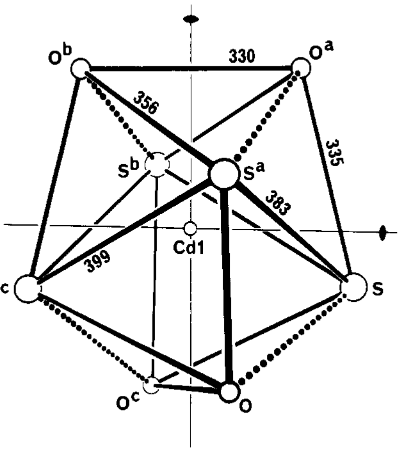

Figure 2. Coordination polyhedron at Cd1, with the dodecahedral (D_{2d}) principal twofold axis vertical. Only one of the subsidiary twofold axes is shown. Distances are in picometers.

The bridging CdS_2Cd units are strictly planar, being inclined 18 and 72° to the *a*, *b* axes. Fourfold rotary inversion and twofold rotary axes are collinear with the chain axis. At the D_2 site (Cd1) the additional twofold rotation axes are crystallographic and are parallel to the crystal axes [110] (the *ab* diagonals). However, at the S_4 site (Cd2), where there are also secondary twofold rotation axes perpendicular to the primary unique axis, they are not crystallographic and are inclined at 27 and 63° to the *a*, *b* axes.[13]

The two independent cadmium atoms differ substantially in coordination stereochemistry. The supplementary material[13] includes a full tabulation of bond distances and angles. At Cd2 (S_4 site) the primary coordination of four sulfur atoms occurs at Cd2–S = 253 pm, which is comparable with that distance in other CdS_4 entities.[14] Concomitant with this the secondary coordination is distant, Cd2–O1 = 328 pm, almost to the point of being nonexistent. The tetrahedral Cd2–S_4 primary coordination is elongated slightly along the chain axis, the independent angles being 98.5 and 115.2°. The stereochemistry of the secondary coordination at Cd2 is approximately that of four caps to the primary CdS_4 tetrahedron.[13]

At Cd1 (D_2 symmetry) the primary coordination of four sulfur atoms is 9 pm more distant (262 pm) than that at Cd2, whereas the secondary coordination occurs at Cd1–O1 = 288 pm. Considering the ca. 35-pm difference in O and S radii, the radial differentiation of the primary and secondary coordination at Cd1 is effectively 60 pm. The S_4O_4 coordination polyhedron, shown in Figure 2, is best described as bisphenoidal, approximating a triangulated dodecahedron, with idealized point group D_{2d}. It should be noted that this dodecahedron is oriented with its principal twofold axis in the D_{2d} ideal along a [110] diagonal crystal direction, not along the chain axis (*c*) of the crystal.

In the description of an eight-coordinate polyhedron containing two radially distinct types of donor atom, the best criterion for assignment as dodecahedral is the occurrence of the two orthogonal planar trapezoids required of point group D_{2d}. The plane calculations reported in the supplementary material show that the two CdS_2 primary coordination planes are almost orthogonal (87.1°) but that the CdO_2 secondary coordination planes are twisted, by 9.0° with respect to the corresponding CdS_2 planes and by 20.9° from mutual orthogonality. Consequently, the overall CdS_4O_4 coordination

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(14) Mean values are 253.5 pm in $[Cd(SPh)_4]^{2-}$,[1] 254.8 pm in $[Cd(SCH(CH_2CH_2)_2NHCH_3)_2]^{2+}$,[6] 251 pm in $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$,[4] and 256 pm in $Cd(SCH_2CH_2OH)_2$.[7]

at Cd1 is appreciably distorted from the idealized D_{2d} symmetry, with atom displacements of ±12 and ±18 pm from the two best planar trapezoids, between which the angle is 81.6°. The reason for this twisting is the limited S- - -O separation of the chelating ligand. These S- - -O chelated edges of the dodecahedron, shortened from the average by 25 pm, are marked on Figure 2.

A coordination dodecahedron is also characterized by the two independent inclinations (θ) of metal ligand vectors with the principal axis in point group D_{2d}.[15] At Cd1 these angles are 70.4° for Cd–S and 35.0° for Cd–O, which are not significantly different from "idealized" values.[15]

At the bridging thiolate function the S–C vector is inclined 72.2° to the CdSCd plane, substantially more than the value of 54.7° for tetrahedral stereochemistry at sulfur. All nonhydrogen atoms of the ligand, except C4, are almost coplanar.[13]

Discussion

The crystal structure of *catena*-Cd(SCH$_2$COOCH$_2$CH$_3$)$_2$ resembles that of *catena*-bis[(μ-*N*-methylpiperidinium-4-thiolato)]cadmium(II) perchlorate dihydrate,[6] in which cadmium atoms on $S_4(\bar{4})$ crystallographic sites are linked in chains by pairs of doubly bridging thiolate ligands. In the latter compound the cadmium is only four-coordinate, Cd–S = 255 pm, the tetrahedron being elongated along the chain axis such that the unique S–Cd–S angles are 98.5 and 115.2°, which are identical with the values at Cd2 in the present structure. A similar chain structure has been reported for *catena*-Hg(S-*t*-Bu)$_2$.[16]

Since four doubly bridging alkanethiolate sulfur atoms can satisfy the coordination requirements of cadmium(II), and indeed do so at Cd2 in the present compound, the question arises as to why the carbonyl oxygen atom O1 enters the coordination sphere of Cd1. There is no apparent steric reason: the ligand could rotate away about the S–C vector. The 9-pm extension of Cd1–S over Cd2–S is consistent with but does not rationalize the entrance of O1 into the coordination sphere.

It can be asked further why O1 is not equidistant from Cd1 and Cd2. This would require an approach to square-antiprismatic coordination at each cadmium atom. It is not possible to link convex triangulated eight-coordinate polyhedra along a linear chain using only bridging ligands: in the structure adopted by *catena*-Cd(SCH$_2$COOCH$_2$CH$_3$)$_2$ the *convex* triangulated dodecahedron at Cd1 is linked to the *concave* tetracapped tetrahedron at Cd2.

Experimental Section

Preparation. Solutions were deoxygenated with nitrogen. A solution of Cd(NO$_3$)$_2$·4H$_2$O (6.0 g, 19 mmol) in warm absolute ethanol (30 mL) was added slowly to a stirred solution of ethyl 2-mercaptoacetate (4.8 g, 40 mmol) and triethylamine (4.0 g, 40 mmol) in absolute ethanol (50 mL). The mixture was sealed and allowed to crystallize during 3 days. The product was filtered, washed with methanol, and dried under vacuum; yield 6.65 g. The compound is soluble in chloroform, slightly soluble in the lower alcohols, acetone, acetonitrile, and THF, and insoluble in ether and petroleum ether. Recrystallization was from chloroform/methanol; mp 172–173 °C. Anal. Calcd for $C_8H_{14}CdS_2O_4$: C, 27.40; H, 4.02; S, 18.26. Found: C, 27.20, 27.04; H, 4.24, 4.37; S, 17.57. Infrared: broad intense CO absorption at 1713 cm^{-1}, overtone at 3403 cm^{-1}.

Similar reactions with Cd/HSCH$_2$COOEt/Et$_3$N in a ratio of 1:4:4 crystallized Cd(SCH$_2$COOEt)$_2$ in much reduced yield, only in the presence of higher alcohols propanol or butanol. The well-formed needles used in the crystal structure determination were from such a reaction in ethanol plus butanol.

Diffraction Analysis. Numerical details are set out in Table I. The crystals investigated were well-developed prisms directly from the preparation. The space group was established photographically. Unit-cell dimensions and intensity data were measured with an Enraf-Nonius CAD4 diffractometer. Corrections for intensity decay (assessed from three intensity standards) during irradiation were applied, as were absorption corrections calculated by numerical integration over a 6 × 6 × 6 grid.

Table I. Details of Diffraction Analysis

formula, formula mass	$C_8H_{14}O_4CdS_2$, 350.4
cryst descripn	colorless needles, elongated along *c* {100}, {010}, {001}, (021)
space group	$I4_1/acd$
a, b, pm	1937.1 (3)
c, pm	1376.4 (3)
V, nm^3	5.163 (3)
temp, °C	21
d_{obsd}, g cm^{-3}	1.81 (2)
Z	16
d_{calcd}, g cm^{-3}	1.80
radiation, λ, pm	CuKα, 154.18
μ, cm^{-1}	168.8
cryst dimens, mm	0.14 × 0.12 × 0.49
scan mode	$\theta/2\theta$
$2\theta_{\mathrm{max}}$, deg	120
no. of intens measmts	2153
max, mean, and min values of the transmission coeff	0.252, 0.135, 0.020
std intens decay	1 → 0.81
criterion for obsd reflctn	$I/\sigma(I) > 3$
no. of indep obsd reflctns	509
no. of reflctns (*m*) and variables (*n*) in final refinement	509, 71
$R = \Sigma^m \lvert\Delta F\rvert / \Sigma^m \lvert F_o\rvert$	0.055
$R_w = [\Sigma^m w \lvert\Delta F\rvert^2 / \Sigma^m w \lvert F_o\rvert^2]^{1/2}$	0.068
$[\Sigma^m w \lvert\Delta F\rvert^2/(m-n)]^{1/2}$	2.28

Table II. Atomic Coordinates for Cd(SCH$_2$COOC$_2$H$_5$)$_2$

	x	*y*	*z*
Cd1	0.0000	0.2500	0.1250
Cd2	0.0000	0.2500	0.3750
S	0.0301 (2)	0.1558 (2)	0.2551 (2)
C1	−0.0469 (7)	0.1025 (6)	0.2675 (9)
C2	−0.1137 (6)	0.1393 (6)	0.2482 (10)
O1	−0.1205 (4)	0.1977 (5)	0.2236 (7)
O2	−0.1647 (5)	0.0968 (5)	0.2675 (8)
C3	−0.2372 (10)	0.1195 (12)	0.2456 (19)
C4	−0.2594 (11)	0.1515 (13)	0.3310 (20)
H1C1	−0.0482	0.0797	0.3408
H1C1	−0.0426	0.0573	0.2196
H3C3	−0.2696	0.0737	0.2312
H4C3	−0.2365	0.1571	0.1856
H5C4	−0.3125	0.1703	0.3215
H6C4	−0.2251	0.1956	0.3470
H7C4	−0.2573	0.1146	0.3913

Structure solution and least-squares refinement, minimizing $\sum w \lvert\Delta F\rvert^2$ with $w = [\sigma(F_o)]^{-2}$, proceeded normally. Hydrogen atoms appeared on a difference map and were subsequently included at idealized positions with temperature factors equal to those of the bonded carbon atoms.

In the final difference map there were peaks of height 3 × 10^3 e nm^{-3} (3 e Å^{-3}) distant 90 pm from the cadmium atoms and others of height 2.5 × 10^3 e nm^{-3} at the cadmium positions. These were probably due to errors in the intensity data introduced by the radiation damage and the high absorption coefficient. All other peaks in the difference map were less than 8 × 10^2 e nm^{-3} and had no chemical significance.

Scattering factors for neutral atoms, with real and imaginary anomalous dispersion corrections for cadmium and sulfur, were taken from standard sources.[17]

Coordinates for non-hydrogen atoms are listed in Table II.

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Registry No. *catena*-$Cd(SCH_2COOCH_2CH_3)_2$, 85585-31-5.

Supplementary Material Available: Figures showing a projection of the structure along the chain (*c*) axis and the coordination stereochemistry at Cd2, a full tabulation of atomic parameters, and listings of bond distances and angles, plane calculations, and F_o and F_c values (12 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486,
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Studies on Organometallic Hetero-Multiple-Bridged Molecules. 8. Preparation and Crystal and Molecular Structures of Diphenyl Dichalcogenide Complexes of Manganese(I). Kinetic, Spectroscopic, and Equilibrium Data: A Quantitative Assessment of the Solid-State and Solution Properties within Members of Homogeneous Families of Chalcogenide Low-Valent Metal Complexes

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The first organic dichalcogenide complexes of manganese(I), $Mn_2Br_2(CO)_6Se_2Ph_2$ (I) and $Mn_2Br_2(CO)_6Te_2Ph_2$ (II), have been prepared by the reaction of halo carbonyl derivatives of manganese(I) with the appropriate dichalcogenide in diethyl or diisopropyl ether as solvent. The crystal and molecular structure of I has been solved by X-ray diffraction methods. The compound belongs to the monoclinic space group *C2/c* with $a = 11.618$ (3) Å, $b = 10.576$ (3) Å, $c = 10.456$ (4) Å, $\beta = 106.94$ (2)°, $V = 2286.9$ Å^3, and $D_{calcd} = 2.18$ g cm^{-3} for $Z = 4$. Both I and II are hetero-multiple-bridged (HMB) molecules consisting of two hexacoordinated metal centers sharing a common edge composed of two bridging bromides and joined by a bidentate E–E bridge. For the manganese complexes and for the corresponding rhenium(I) complexes the ligand displacement reactions by carbon monoxide, tetrahydrofuran, and E'_2Ph_2 have been studied and kinetic or equilibrium data have been collected by gas volumetry, by IR spectrophotometry, and by ^{13}C NMR spectrometry, respectively. The results establish increased stability of these complexes in the sequence S < Se < Te.

Introduction

Earlier papers in this series have reported the preparation of $M_2Br_2(CO)_6E_2Ph_{2n}$ complexes[4] (M = Mn,[4a] Re,[4b] $n = 2$, E = P; M = Re, $n = 1$, E = S,[4c] Se,[4d] Te[4e]). All of these compounds have been shown to possess the HMB (hetero-multiple-bridged) type of molecular structure, consisting of two hexacoordinated metal centers sharing a common edge composed of two bridging bromides and joined by a bidentate E–E bridge (see Figure 1). Oxidative cleavage of the E–E bond has not been observed in these complexes.

In the course of these studies it became clear that the new compounds could provide a powerful tool for a better understanding of the "vertical sequence effect". By this is meant the modification of bond strengths and chemical properties in low-valent metal complexes that occurs when the ligand donor atoms are changed in the same group beyond the second-period threshold. The parallel question of how the same properties behave when the metal is changed may also be addressed. Since the dichalcogenide complexes of rhenium(I) had been prepared earlier,[4c-e] the first step was to prepare the corresponding manganese(I) derivatives.

We now report (a) the isolation of the first HMB complexes of manganese(I) having dichalcogenides as bridging ligands and (b) structural and kinetic data that permit generalizations on comparative stabilities of these dichalcogenide complexes.

Experimental Section

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried and purified by conventional methods prior to use. The IR spectra were measured with a Perkin-Elmer 283 instrument equipped with grating, and each spectrum was calibrated with both CO and water vapor; the wavenumber values are believed to be accurate to ±1 cm^{-1}. The compound Te_2Ph_2 was prepared according to the literature method[5] by the reaction of PhMgBr with elemental tellurium and then with dry oxygen. Decacarbonyldimanganese(0)[6] and $MnBr(CO)_5$[7] were prepared according to literature methods. $MnI(CO)_5$ was synthesized[8] by oxidizing $NaMn(CO)_5$ with diiodine in tetrahydrofuran as solvent. $ReI(CO)_5$ and $Re_2I_2(CO)_8$ were prepared by a slight modification of a literature procedure,[10] by UV irradiation of benzene solution of $Re_2(CO)_{10}$ containing the stoichiometric amount of I_2 at 20 °C. Solutions about 10 times more concentrated than those in the literature method were used. After filtration the resulting solid was recrystallized from chloroform to obtain a 31% yield of $Re_2I_2(CO)_8$. From the mother liquor a 51% yield of $ReI(CO)_5$ was obtained

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