composite, containing, for example, a high-energy d → d transition and the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition. Further study of this transition is clearly necessary.

We conclude that the MCD of bands 4 and 5 fits nicely with Gray and Ballhausen's assignments, but we have no detailed explanation for the behavior of band 3.

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Organotellurium, -selenium, and -sulfur Derivatives of π-Cyclopentadienylmolybdenum Tricarbonyl

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The donor properties of most of the heavier elements of groups IVa, Va, and VIa of the periodic table toward transitional metal substrates have been investigated a great deal in the past decade. However, little interest in the donor properties of tellurium has been shown, as evidenced by the fact that only a dozen or so complexes containing transitional metal–tellurium bonds have been described in the literature.[3]

We have, in this laboratory, commenced an investigation of the donor properties of tellurium in transitional metal complexes, and report herein results obtained for the reactions of diphenyl ditelluride, and the analogous selenium and sulfur compounds, with π-cyclopentadienylmolybdenum tricarbonyl dimer.

Experimental Section

I. **Materials.**—All reactions and work-ups were performed in a nitrogen atmosphere. Solvents were degassed with nitrogen prior to use.

Cyclopentadienylmolybdenum tricarbonyl dimer was prepared by a literature method.[4] Diphenyl disulfide, diphenyl diselenide, and diphenyl ditelluride were obtained from commercial sources and used without further purification. Merck acid-washed alumina was used for chromatography.

II. **Reactions of $(C_6H_5)_2Te_2$ with $[\pi\text{-CpMo(CO)}_3]_2$. (A) Preparation of $\pi\text{-CpMo(CO)}_3TeC_6H_5$.**—Diphenyl ditelluride (0.63 g, 1.5 mmol), $[\pi\text{-CpMo(CO)}_3]_2$ (0.73 g, 1.5 mmol), and benzene (100 ml) were placed in a reaction flask which was maintained at 25° with a water bath. The mixture was stirred for 3 hr and irradiated during this period with a 250-W infrared heating lamp. The violet solution was filtered, and solvent was removed under reduced pressure from the filtrate to yield a dark, gummy solid. Recrystallization from benzene–hexane gave dark violet, air-stable crystals, mp 80–82° dec. *Anal.* Calcd for $C_{14}H_{10}O_3TeMo$: C, 37.39; H, 2.24; mol wt, 450. Found: C, 38.18; H, 2.62; mol wt, 500. Attempts to purify the compound by sublimation resulted in decomposition to $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$. Mononuclear $\pi\text{-CpMo(CO)}_3TeC_6H_5$ is soluble in benzene, CS_2, and $CHCl_3$. Solutions of the complex undergo slow decomposition in a nitrogen atmosphere at room temperature. The infrared spectrum[5] of a CS_2 solution of the complex includes bands at 2016 (vs, sp), 1948 (sh), and 1937 (vs) cm^{-1}. The proton nmr spectrum includes a singlet at τ 4.72 due to the cyclopentadienyl protons and a complicated phenyl-hydrogen resonance with a 1:1 ratio of cyclopentadienyl to phenyl hydrogens.

(B) **Preparation of $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$.**—Diphenyl ditelluride (1.15 g, 2.8 mmol) and $[\pi\text{-CpMo(CO)}_3]_2$ (1.25 g, 2.5 mmol) were added to 100 ml of benzene and the mixture was refluxed for 14 hr to give a dark brown solution. After the mixture had cooled, it was filtered, and the filtrate was taken to near dryness, resulting in a dark brown, gummy solid. This material was dissolved in a small amount of benzene, hexane was added, and dark brown crystals formed as the solvent slowly evaporated in a stream of nitrogen. The crystals, which are stable in air and melt at 175–176°, were obtained in 80% yield. *Anal.* Calcd for $C_{26}H_{20}O_4Te_2Mo_2$: C, 37.02; H, 2.39; Te, 30.25; Mo, 22.75; mol wt, 843. Found: C, 37.14; H, 2.49; Te, 31.16; Mo, 23.37; mol wt, 840. The dinuclear compound $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$ is soluble in aromatic hydrocarbons, carbon disulfide, and chloroform, but only sparingly soluble in hexane. Solutions of the complex are slightly air sensitive and deposit a fine, black precipitate. The infrared spectrum in CS_2 includes bands at 1960 (s), 1935 (vs), 1876 (vs), and 1860 (s) cm^{-1} in the carbonyl stretching region. The ^{1}H nmr spectrum shows a singlet at τ 4.88 in addition to the phenyl multiplet.

(C) **Preparation of $[\pi\text{-CpMo(TeC}_6H_5)_2]_x$.**—Diphenyl ditelluride (0.5 g, 1.2 mmol) and $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$ (1 g, 1 mmol) were added to 100 ml of xylene and the mixture was refluxed for 5 hr. After the solution had cooled, the dark brown solid which had formed was collected on a filter and washed with hexane. The yield of the amorphous solid was 0.6 g. *Anal.* Calcd for $C_{17}H_{15}Te_2Mo$: C, 35.79; H, 2.65; Mo, 16.82. Found: C, 35.52; H, 2.91; Mo, 16.30. An infrared spectrum of a Nujol mull of the solid showed no absorptions in the 1700–2200-cm^{-1} region. The material is very insoluble in organic solvents and water, is not volatile, and decomposes at temperatures greater than 190°. A molecular weight measurement was not possible owing to the insoluble nature of the compound.

III. **Reactions of $(C_6H_5)_2Se_2$ with $[\pi\text{-CpMo(CO)}_3]_2$. (A) Preparation of $\pi\text{-CpMo(CO)}_3SeC_6H_5$.**—Diphenyl diselenide (0.5 g, 1.6 mmol) and $[\pi\text{-CpMo(CO)}_3]_2$ (0.79 g, 1.6 mmol) were added to 100 ml of benzene, and the reaction mixture was maintained at 10° with an ice–water bath. The mixture was stirred, and samples were removed periodically to record an infrared spectrum. After 2 hr of stirring, an infrared spectrum indicated that the principal carbonyl-containing species in solution was a material analogous to mononuclear $\pi\text{-CpMo(CO)}_3TeC_6H_5$. The reaction mixture was then filtered, and the filtrate was taken to dryness under reduced pressure, yielding a red solid which had a tendency to change to an oil. The material, which from its infrared spectrum appeared to be a mixture of $\pi\text{-CpMo(CO)}_3SeC_6H_5$ and $[\pi\text{-CpMo(CO)}_2SeC_6H_5]_2$, was dissolved in toluene and the solution was chromatographed on a 50-cm alumina column by elution with a 2:1 mixture of hexane and toluene. A partial separation of the compounds was achieved as a band developed whose upper por-

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[3] E. Fritzmann, *Z. Anorg. Allgem. Chem.*, **133**, 119 (1924); K. S. Jensen, *ibid.*, **231**, 365 (1937); J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2787 (1955); J. Chatt and L. M. Venanzi, *ibid.*, 2351 (1957); J. Chatt and L. M. Venanzi, *ibid.*, 2445 (1957); W. Hieber and J. Gruber, *Z. Anorg. Allgem. Chem.*, **296**, 91 (1958); E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961); W. Hieber and K. Wallman, *Chem. Ber.*, **95**, 1552 (1962); W. Hieber and T. Kruck, *ibid.*, **95**, 2027 (1962); W. Hieber and R. Kramolowsky, *Z. Anorg. Allgem. Chem.*, **321**, 94 (1963); T. Kruck and M. Hoffler, *Chem. Ber.*, **96**, 3035 (1963).

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[5] Abbreviations used in this paper to describe infrared band intensities and widths are: s, strong; vs, very strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder. All infrared band positions are given in reciprocal centimeters.

tion was red and whose lower portion was brown. A solution was collected corresponding to the red portion of the band, and this solution was again chromatographed. Evaporation of the eluted solution gave a small amount of red solid, mp 92–94°. *Anal.* Calcd for $C_{14}H_{10}O_3MoSe$: C, 41.92; H, 2.61; mol wt, 401. Found: C, 41.59; H, 2.91; mol wt, 465. The infrared spectrum of the compound in CS_2 includes bands at 2026 (vs, sp) and 1948 (vs) cm^{-1}. In solution the mononuclear compound is unstable and is transformed to dinuclear $[\pi$-CpMo(CO)$_2$SeC$_6$H$_5]_2$, as evidenced by appearances in the infrared spectrum of bands at 1865 and 1874 cm^{-1} and also by the slightly high molecular weight.

(B) **Preparation of $[\pi$-CpMo(SeC$_6$H$_5$)$_2]_x$.**—Diphenyl diselenide (0.64 g, 2 mmol) and $[\pi$-CpMo(CO)$_3]_2$ (0.5 g, 1 mmol) were refluxed in benzene for 9 hr. The reaction mixture was filtered, and 0.3 g of an amorphous, red-brown solid was collected on the filter. *Anal.* Calcd for $C_{17}H_{15}Se_2Mo$: C, 43.15; H, 3.20. Found: C, 42.90; H, 3.40. The compound is highly insoluble in organic solvents and decomposed at temperatures greater than 200°; no bands were observed in the carbonyl region of the infrared spectrum.

IV. **Reactions of $(C_6H_5)_2S_2$ with $[\pi$-CpMo(CO)$_3]_2$. Preparation of $[\pi$-CpMo(SC$_6$H$_5$)$_2]_x$.**—Diphenyl disulfide (6.6 g, 30 mmol) and $[\pi$-CpMo(CO)$_3]_2$ (3.0 g, 6 mmol) were dissolved in 125 ml of toluene and the mixture was refluxed for 4 hr. A light brown solid separated, and this was collected on a filter. The yield of the amorphous solid was 85%. *Anal.* Calcd for $C_{17}H_{15}S_2Mo$: C, 53.83; H, 3.96; Mo, 25.29; S, 16.90. Found: C, 53.34; H, 4.23; Mo, 24.94; S, 16.15. The air-stable solid, like its selenium and tellurium analogs, was too insoluble in organic solvents for molecular weight and nmr measurements. Also, the infrared spectrum showed no absorption in the carbonyl stretching region. The compound decomposes at temperatures greater than 200°.

V. **Analyses and Instrumentation.**—Analyses for carbon and hydrogen were carried out by Mr. R. Seab of the Department of Chemistry, The Louisiana State University. Analyses for sulfur, tellurium, and molybdenum were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and/or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Infrared spectra were recorded on a Beckman IR-7 spectrophotometer using carbon disulfide solutions in 0.5-mm NaCl cells, KBr disks, or Nujol mulls.

Proton nmr spectra were measured with a Varian A-60A instrument in CS_2 solutions.

Molecular weight measurements were made in benzene or chloroform with a Mechrolab osmometer, Model 302, with a 37° probe.

Melting points were observed with a Hoover instrument in open capillaries.

Results

Reactions of diphenyl ditelluride with $[\pi$-CpMo(CO)$_3]_2$ have yielded several complexes, depending on the conditions employed. The first compound isolated was a dark brown crystalline material with a metallic sheen. This substance, which is formulated as a dinuclear species with phenyltellurido bridging groups, $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$, was obtained under rather rigorous conditions involving refluxing of the reactants in benzene for 14 hr. Formation of dinuclear $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$ appeared to proceed *via* initial formation of mononuclear π-CpMo(CO)$_3$TeC$_6$H$_5$ in the reaction mixture, as was ascertained by monitoring the progress of the reaction by occasional withdrawal of samples for infrared examination. The mononuclear complex, π-CpMo(CO)$_3$TeC$_6$H$_5$, was then isolated by employing very mild reaction conditions, *i.e.*, stirring the reactants in benzene at 25° for 2.5 hr. Dinuclear $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$ was formed when π-CpMo(CO)$_3$TeC$_6$H$_5$ was thermally decomposed, and also it was observed that solutions of π-CpMo(CO)$_3$TeC$_6$H$_5$ decomposed at room temperature to give $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$. With even more rigorous conditions than were employed in preparing $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$, *i.e.*, 12 hr of refluxing in toluene, a third carbonyl-containing complex was formed in the reaction mixture as indicated by infrared monitoring, but the compound was not isolated. The major product of the prolonged reaction of $[\pi$-CpMo(CO)$_3]_2$ and $(C_6H_5)_2Te_2$ in refluxing xylene was the completely decarbonylated compound $[\pi$-CpMo(TeC$_6$H$_5$)$_2]_x$, an amorphous highly insoluble material.

Diphenyl diselenide reacted with $[\pi$-CpMo(CO)$_3]_2$ under somewhat milder conditions than did diphenyl ditelluride. Two complexes, mononuclear π-CpMo(CO)$_3$SeC$_6$H$_5$ and completely decarbonylated $[\pi$-CpMo(SeC$_6$H$_5$)$_2]_x$, were isolated, and there was evidence from infrared monitoring that several other complexes, including dinuclear $[\pi$-CpMo(CO)$_2$SeC$_6$H$_5]_2$, were present in the reaction mixtures. The violet solid, π-CpMo(CO)$_3$SeC$_6$H$_5$, was isolated from an equimolar reaction mixture of $[\pi$-CpMo(CO)$_3]_2$ and $(C_6H_5)_2Se_2$ in benzene which had been stirred at 10° for 2 hr. When a mixture of $[\pi$-CpMo(CO)$_3]_2$ and $(C_6H_5)_2Se_2$ in benzene was refluxed for several hours, infrared sampling indicated that the selenium analog of $[\pi$-CpMo(CO)$_2$TeC$_6$H$_5]_2$ was present in solution, but, unlike the tellurium complex, it seemed to be transformed fairly rapidly into other carbonyl-containing complexes and was not isolated. As with the tellurium reactions, a very insoluble, amorphous product was also obtained after prolonged reaction periods and is similarly formulated as $[\pi$-CpMo(SeC$_6$H$_5$)$_2]_x$.

Diphenyl disulfide reacted more rapidly with $[\pi$-CpMo(CO)$_3]_2$ than did $(C_6H_5)_2Se_2$ or $(C_6H_5)_2Te_2$, and the only product which could be isolated was the completely decarbonylated material $[\pi$-CpMo(SC$_6$H$_5$)$_2]_x$. Infrared evidence suggested that several carbonyl-containing species were present in the reaction mixture of $[\pi$-CpMo(CO)$_3]_2$ and $(C_6H_5)_2S_2$. After the reactants had been stirred in benzene at 10° for 10 min, the infrared spectrum of a withdrawn sample showed a sharp band at 2033 cm^{-1}, indicative of mononuclear π-CpMo(CO)$_3$SC$_6$H$_5$. Various means failed to enhance the concentration of this species, and it could not be isolated.[6] Infrared monitoring showed no evidence for the presence of dinuclear $[\pi$-CpMo(CO)$_2$SC$_6$H$_5]_2$ in reaction mixtures.

Discussion

The new tellurium complexes of molybdenum reported herein are the first examples of compounds in which this chalcogen is a donor atom for cyclopentadienyl derivatives of transitional metals. Several deriv-

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[6] Preparation of mononuclear π-CpMo(CO)$_3$SC$_6$H$_5$ and dinuclear $[\pi$-CpMo(CO)$_2$SC$_6$H$_5]_2$ has been mentioned in a note: R. Havlin and G. R. Knox, *Z. Naturforsch.*, **21b**, 1108 (1966).

atives of metal carbonyls have, however, been previously reported.[3] Furthermore, these are the first examples of complexes in which there exist molybdenum–selenium and molybdenum–tellurium bonds.

Mononuclear complexes of the type π-CpMo(CO)$_3$X (X = H, halogen, CH$_3$, Sn(C$_6$H$_5$)$_3$, etc.) are well known, and the volatility, low melting points, and infrared spectra of π-CpMo(CO)$_3$EC$_6$H$_5$ (E = Se, Te) are as expected for compounds of this type. It is of interest that the highest energy carbonyl stretching absorptions in the complexes π-CpMo(CO)$_3$X are 2055, 2049, 2040, 2033, 2026, and 2016 cm^{-1} for X = Cl,[7] Br,[7] I,[7] SC$_6$H$_5$, SeC$_6$H$_5$, and TeC$_6$H$_5$, respectively. These data suggest that π bonding between molybdenum and carbon monoxide is strongest in the tellurium complex, and the stabilities of π-CpMo(CO)$_3$EC$_6$H$_5$ (E = S, Se, Te) as observed in the preparative experiments indicate that the ability of the chalcogen to stabilize the mononuclear species decreases in the order of E: Te > Se > S. Thus the greater "softness" of tellurium and selenium relative to sulfur results in a less positive charge on the molybdenum, and π bonding to CO is thereby enhanced. Decomposition of π-CpMo(CO)$_3$EC$_6$H$_5$ by loss of carbon monoxide to form [π-CpMo(CO)$_2$EC$_6$H$_5$]$_2$ therefore decreases in the order of E: S > Se > Te.

As noted in the Results section, the only dinuclear complex of the type [π-CpMo(CO)$_2$EC$_6$H$_5$]$_2$ which was isolated and characterized was that for E = Te. The selenium analog was undoubtedly present in the reaction mixtures, but the sulfur analog was not detected. Thus, as with the mononuclear derivatives, the gross stability of the dinuclear species may be correlated with the "softness" of the chalcogen donor atom. The infrared spectra of [π-CpMo(CO)$_2$EC$_6$H$_5$]$_2$ (E = Te, Se) show four bands in the carbonyl stretching region and are similar to the reported spectrum of [π-CpMo(CO)$_2$SCH$_3$]$_2$.[8] A similar structure with C$_6$H$_5$E briding units is proposed.[9] Although several geometrical isomers may be envisioned for [π-CpMo(CO)$_2$TeC$_6$H$_5$]$_2$, the H nmr spectrum shows only one kind of cyclopentadienyl proton.

Prolonged reaction of (C$_6$H$_5$)$_2$E$_2$ (E = S, Se, Te) with [π-CpMo(CO)$_3$]$_2$ gave highly insoluble materials whose elemental analyses suggest the formulation [π-CpMo(EC$_6$H$_5$)$_2$]$_x$. The nature of these compounds has prevented a determination of the value of x in the formula.

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(9) An X-ray crystallographic examination of [π-CpMo(CO)$_2$TeC$_6$H$_5$]$_2$ is underway: C. J. Fritchie, private communication.

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Coordination Compounds of Thallium(III). V. The Vibrational Spectra of Mixed Tetrahalothallates of the Type (C$_2$H$_5$)$_4$NTlX$_{4-n}$Y$_n$, where n = 1, 2, or 3[1]

BY R. A. WALTON

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The complete series of tetrahalothallates of the type (C$_2$H$_5$)$_4$NTlX$_{4-n}$Y$_n$, where X = Cl when Y = Br or I and X = Br when Y = I, and n = 1, 2, or 3, have recently been synthesized[1,2] and shown[1] from X-ray powder data and electronic absorption spectra measurements to contain the authentic TlX$_{4-n}$Y$_n^-$ species. This has provided an ideal opportunity to investigate in detail the vibrational spectra of a complete series of tetrahedral anions of the type MX$_{4-n}$Y$_n^-$. To date, no such investigation appears to have geen reported, although the far-infrared spectra of the related zinc(II) anions (except ZnCl$_3$I^{2-}) have recently been described.[3] The tetrahalothallates are particularly suitable for such an investigation since they are air stable and very soluble in acetonitrile, an ideal spectroscopic solvent below 380 cm^{-1}, thus facilitating polarization measurements and providing a useful check on the possibility that some absorption bands might arise from solid-state effects.

The spectra of the TlCl$_3$I$^-$ (infrared and Raman) and TlCl$_3$Br$^-$ (infrared) anions have been reported in an earlier paper.[2] These results are compared with those described in the present report for the remaining mixed-halo species, as are the literature data for the TlCl$_4^-$, TlBr$_4^-$, and TlI$_4^-$ anions.[4]

Experimental Section

The preparation of the complexes has been described previously.[1,2] The samples used in the present spectroscopic investigation were those whose analytical data, X-ray powder photographs, and electronic absorption spectra have already been measured.[1,2]

Raman spectra were recorded on a Cary 81 spectrophotometer equipped with an He–Ne laser source. The characteristics of this particular instrument have been described elsewhere.[5] Good-quality spectra of the crystalline solids were obtained with the sample contained in a stoppered Pyrex tube. Solution measurements were carried out on saturated acetonitrile solutions of several of the complexes. Infrared spectra were recorded on Nujol mulls using a Beckman IR-11 infrared spectrophotometer in the region 350–33 cm^{-1}.

Results and Discussion

Complex Anions TlX$_3$Y$^-$ and TlXY$_3^-$.—Data for these particular anions are listed in Table I, and assignments

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