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SYNTHESIS OF HETEROMETALLIC CLUSTER COMPOUNDS FROM $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ AND COMPARISONS WITH ANALOGOUS SULFIDE CLUSTERS

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Summary

$Fe_3Te_2(CO)_9$ is shown to be a useful precursor to a variety of heterometallic carbonyl clusters in reactions which appear to proceed via the intermediacy of $Fe_2(Te_2)(CO)_6$. $Fe_3Te_2(CO)_9$ decomposed in polar solvents to give $Fe_2(Te_2)(CO)_6$ which could be dimerized to $Fe_4Te_4(CO)_{12}$. $Fe_3Te_2(CO)_9$ reacted with $C_5H_5Co(CO)_2$ and $Pt(C_2H_4)(PPh_3)_2$ to give good yields of $(C_5H_5Co)Fe_2Te_2(CO)_7$ and $Fe_2PtTe_2(CO)_6(PPh_3)_2$, respectively. $(C_5H_5Co)Fe_2Te_2(CO)_7$ underwent reversible decarbonylation to give a mixture of two isomers of $(C_5H_5Co)Fe_2Te_2(CO)_6$ as established by ^{125}Te NMR spectroscopy. Upon reaction with $Co_2(CO)_8$, $Fe_3Te_2(CO)_9$ gave $Co_2FeTe(CO)_9$ or $Co_4Te_2(CO)_{11}$ depending on the reaction conditions. $Co_4Te_2(CO)_{11}$, like $Fe_3Te_2(CO)_{10}$ and $(C_5H_5Co)Fe_2Te_2(CO)_7$, can be reversibly decarbonylated. The assembly of $Co_2FeTe(CO)_9$ may be mechanistically related to the conversion of $Fe_2(S_2)(CO)_6$ to $FeCo_2S(CO)_9$ which was found to proceed via $Co_2Fe_2S_2(CO)_{11}$. Alternatively, $Co_2Fe_2S_2(CO)_{11}$ reacted photochemically with $[C_5H_5Mo(CO)_3]_2$ to give the known, chiral cluster $(C_5H_5Mo)CoFeS(CO)_8$. While $Fe_2(Te_2)(CO)_6$ thermally dimerized to $Fe_4Te_4(CO)_{12}$, $Fe_2(S_2)(CO)_6$ gave the analogous dimer only upon photolysis. In contrast to the stability of $(C_5H_5Co)Fe_2Te_2(CO)_7$, the reaction of $C_5H_5Co(CO)_2$ with $Fe_2(S_2)(CO)_6$ gave only $(C_5H_5Co)Fe_2S_2(CO)_6$ which is proposed to be structurally related to $Fe_3S_2(CO)_9$ and not $(C_5H_5Co)_3S_2$ or $Fe_2PtS_2(CO)_6(PPh_3)_2$.

Introduction

We recently reported an efficient, high yield synthesis of $Fe_3Te_2(CO)_9$ from inexpensive materials [1]. Based on synthetic simplicity and expense, $Fe_3Te_2(CO)_9$ is

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certainly one of the most readily accessible transition metal carbonyl clusters known. For this reason we have explored its utility as a precursor to other Te-containing carbonyl cluster compounds including several heterometallic derivatives. An additional objective of the present study was the comparison of the syntheses and hence the reactivity of analogous S- and Te- containing clusters. This study has demonstrated that the reactivity and structural characteristics of sulfur clusters are a useful complement but an unreliable guide to the behavior of the corresponding tellurium clusters.

Experimental section

Reactions were performed under an atmosphere of nitrogen in reagent grade solvents. Workups were done aerobically unless otherwise noted. Thin layer chromatography was performed on 2 × 10 cm plates cut from sheets of Eastman silica gel coated polyvinylchloride. Column chromatography was done with 30–60 μm Woelm silica gel or Florisil. Unless otherwise indicated, organometallic starting materials were purchased commercially or were prepared according to procedures described in Inorganic Syntheses.

^{125}Te NMR spectra were recorded on a Varian XL-100 spectrometer at 31.583 or 31.547 MHz. Spectra were referenced to neat $Te(CH_3)_2$, upfield shifts being negative. ^{1}H NMR spectra were recorded on a Varian EM-390 instrument and referenced to TMS. IR spectra were measured on cyclohexane solutions (unless otherwise indicated) using a Nicolet 7199C FT-IR spectrometer. Field desorption mass spectra (FDMS) were measured by Mr. Carter Cook on a Varian 731 spectrometer. Electron impact mass spectra (EIMS) were measured on a Varian CH-5 spectrometer. Analyses were performed as a departmental service.

$Fe_2(Te_2)(CO)_6$. $Fe_3Te_2(CO)_9$ [1] (2.01 g, 2.98 mmol) and $NaOCH_3$ (0.645 g, 11.9 mmol) were stirred in CH_3OH (800 ml) until complete dissolution. The solution was diluted with pentane (200 ml) and water (200 ml) and acidified with 6 *M* HCl (4 ml). After separation of the layers, the aqueous phase was further extracted with hexane (100 ml) and the combined organic extracts were washed with H_2O (200 ml) and dried over $MgSO_4$. The organic solution was concentrated to ~ 10 ml and filtered. A standard aliquot was further purified by flash chromatography. Based on $\varepsilon_{345} = 1.15 \times 10^4$ cm^2 mol^{-1}, the yield was 40% (1.18 mmol).

$Fe_4Te_4(CO)_{12}$. In a 40 ml autoclave were placed $Fe_3Te_2(CO)_9$ (2.0 g, 3.0 mmol) and MeCN (30 ml). After evacuation, the vessel was pressurized to 2000 psi with CO then was heated to 80–90°C for 42 h. After venting and cooling, the solution was filtered and the remaining black crystals were extensively washed with CH_2Cl_2 to remove the $Fe_3Te_2(CO)_{10}$, which was the only other tellurium compound present. Yield: 69% (2.0 g). Anal. Found: C, 13.33; Fe, 20.75. $C_{12}Fe_4O_{12}Te_4$ calcd.: C, 13.46; Fe, 20.88%. IR (mineral oil mull): 2043vs, 2035sh, 1994sh, 1988sh, 1982s, 1968w.

$Fe_2PtTe_2(CO)_6(PPh_3)_2$. $Fe_3Te_2(CO)_9$ (0.29 g, 0.43 mmol) and $Pt(C_2H_4)(PPh_3)_2$ (0.32 g, 0.43 mmol) in CH_3CN (60 ml) were stirred for 1 h at room temperature. The red precipitate was filtered and recrystallized from CH_2Cl_2/hexane. Yield: 76% (0.41 g). This compound was identified by comparison of its IR and TLC behavior with samples prepared previously [2].

$(C_5H_5Co)Fe_2Te_2(CO)_7$. Excess $C_5H_5Co(CO)_2$ (0.40 ml) was added to an acetonitrile solution (100 ml) of $Fe_3Te_2(CO)_9$ (1.0 g, 1.5 mmol). The solution was

refluxed for 2 h and evaporated to dryness. The crude product was dissolved in CH_2Cl_2, filtered through a plug of Florisil, and crystallized by the addition of hexane. Yield: 70% (0.69 g). Anal. Found: C, 20.42; H, 0.60; Fe, 15.99. $C_{12}H_5CoFe_2O_7Te_2$ calcd.: C, 20.98; H, 0.73; Fe, 16.26%. FDMS: m/z 687 (M^+). IR: 2054s, 2028vs, 2008s, 1985s, 1969m, 1952m. ^{125}Te NMR: −825 ppm (broad).

$(C_5H_5Co)Fe_2Te_2(CO)_6$. Me_3NO (0.022 g, 0.29 mmol) in CH_2Cl_2 (10 ml) was added to a CH_2Cl_2 solution (20 ml) of $(C_5H_5Co)Fe_2Te_2(CO)_7$ (0.20 g, 0.29 mmol). After stirring at ambient temperature for 15 min, the solution was concentrated to 2 ml and diluted with an equal volume of hexane. The resultant solution was chromatographed on Florisil (30 ml) eluting with hexane. The first fraction was intensely purple black and was collected, evaporated and crystallized from CH_2Cl_2/CH_3OH. Yield: 34% (0.065 g). Anal. Found: C, 20.12; H, 0.71. Fe, 16.71. $C_{11}H_5CoFe_2O_6Te_2$ calcd.: C, 20.05; H, 0.76; Fe, 16.95%. FDMS: m/z 659 (M^+). IR: 2053m, 2046m, 2024vs, 2014m, 1991w, 1982s, 1974sh, 1971s. ^{125}Te NMR: 1103, 1087 ppm.

Carbonylation of $(C_5H_5Co)Fe_2Te_2(CO)_6$. A CH_2Cl_2 solution (15 ml) of $(C_5H_5Co)Fe_2Te_2(CO)_6$ (0.15 g) was stirred for 1 h under 2000 psi CO. TLC of the crude reaction mixture showed only $(C_5H_5Co)Fe_2Te_2(CO)_7$ which proved identical to samples prepared from $C_5H_5Co(CO)_2$ and $Fe_3Te_2(CO)_9$ as judged by IR and ^{125}Te NMR spectroscopy.

$Co_2FeTe(CO)_9$ from $Fe_3Te_2(CO)_9$. $Fe_3Te_2(CO)_9$ (0.350 g, 0.518 mmol), $Co_2(CO)_8$ (0.354 g, 1.036 mmol), and hexane (35 ml) were heated at 180°C under 1700 psi CO for 4 h. After cooling and venting the autoclave, the reaction mixture was filtered and the residue was extracted with hexane. The hexane extracts were purged with air for 36 h to destroy any $Fe_3Te_2(CO)_9$; a second filtration followed by evaporation gave black crystals of $Co_2FeTe(CO)_9$ [3]. Yield: 76% (0.433 g). IR: 2095w, 2054s, 2046vs, 2033m, 2021w, 1978w.

$Co_2FeTe(CO)_9$ from $Co_4Te_2(CO)_{11}$. $Co_4Te_2(CO)_{11}$ (0.189 g, 0.236 mmol), $Fe(CO)_5$ (0.48 ml, 3.6 mmol), and hexane (35 ml) were heated at 180°C under an initial pressure of 1300 psi CO which rose during the reaction to 1480 psi. After 4 h the autoclave was cooled and vented and the reaction was worked up in the manner described for the preceding preparation. Yield: 81% (0.212 g).

$Co_4Te_2(CO)_{11}$ from $Fe_3Te_2(CO)_9$. $Fe_3Te_2(CO)_9$ (0.228 g, 0.427 mmol), $Co_2(CO)_8$ (0.292 g, 0.854 mmol), and CH_2Cl_2 (40 ml) were heated at 150°C under 2000 psi CO for 24 h. After cooling and venting the autoclave, the crude reaction mixture was filtered and the residue was extracted with hexane. The hexane-insoluble residue was then extracted with CH_2Cl_2, filtered, and evaporated giving purple crystals of $Co_4Te_2(CO)_{11}$ [3]. Yield: 64% (0.220 g). Lower yields are obtained at 1700 psi, in hexane. IR (CH_2Cl_2 soln.): 2050vs, 2039s, 2020m, 1838w,br. As noted previously, purple solutions of this compound slowly deposit a black precipitate of $Co_4Te_2(CO)_{10}$ [3,4]. IR (KBr): 2068s, 2027vs, 1994vs, 1859w, 1841vs, 1810w. The black decacarbonyl is reconverted to $Co_4Te_2(CO)_{11}$ when slurried in CH_2Cl_2 under 2000 psi CO.

$Co_4Te_2(CO)_{11}$ from $Co_2FeTe(CO)_9$. $Co_2FeTe(CO)_9$ (0.261 g, 0.471 mmol), $Co_2(CO)_8$ (0.272 g, 0.796 mmol), and hexane (40 ml) were heated at 140°C under 1900 psi CO for 48 h. The reaction was worked up in the manner described for the preceding preparation. Yield: 71% (0.133 g).

$Co_3S(CO)_9$ from $Co_2FeS(CO)_9$. $Co_2FeS(CO)_9$ (0.188 g, 0.411 mmol), $Co_2(CO)_8$

(0.140 g, 0.411 mmol), and cyclohexane (35 ml) were heated at 150°C under 1700 psi CO for 4 h. After cooling and venting the autoclave, an aliquot was taken and its FT IR spectrum recorded. From the spectrum were subtracted successively spectra of $Co_2(CO)_8$, $Co_2FeS(CO)_9$, and $Fe(CO)_5$. The resulting IR matched that reported for $Co_3S(CO)_9$: 2103vw, 2048vs, 2037m, although the very weak peak expected at 2024 cm^{-1} was not significantly more intense than noise, possibly because of overcompensation for $Co_2(CO)_8$ and $Co_2FeS(CO)_9$.

$Fe_2PtSe_2(CO)_6(PPh_3)_2$ from $Fe_3S_2(CO)_9$. A solution of $Fe_3S_2(CO)_9$ (50 mg, 0.10 mmol) and $Pt(C_2H_4)PPh_3)_2$ (77 mg, 0.10 mmol) in benzene (15 ml) was stirred for 21 h at room temperature and then refluxed for 2 h. After concentrating, the solution was chromatographed on silica gel. Eluting with 1/1 benzene/hexane gave five bands. The fourth (orange) band was identified as $Fe_2PtS_2(CO)_6(PPh_3)_2$ by IR spectroscopy [2]; yield: 25%. The other products were present in lesser abundance, two were identified by IR spectroscopy as $Fe_3S_2(CO)_8PPh_3$ and $Fe_3S_2(CO)_7(PPh_3)_2$ [5].

$Fe_2(S_2)(CO)_6$. This procedure is easier and gives higher yields than older methods [6]. $Fe(CO)_5$ (10 ml, 73 mmol) was added to a degassed solution of 50% aqueous KOH (40 ml, 480 mmol) in CH_3OH (100 ml). After 15 min, the solution was cooled to 0°C and sulfur (23 g, 0.73 mmol) was added in one portion. The mixture became very warm and instantly turned black. After 15 min, H_2O (250 ml) and pentane (500 ml) were added and the mixture was cautiously acidified with 25% HCl (200 ml). (*Caution:* Evolution of H_2S and foaming occurs.) The mixture was filtered and the solid was rinsed with additional pentane. The pentane layer was washed with H_2O and dried over Na_2SO_4. Evaporation of this pentane solution gave a red oil which crystallized in vacuo. The product is pure by TLC (silica gel, hexane eluent) and IR spectroscopy [6]. Yield: 52% (6.5 g). Sublimation gives a more crystalline product but the yield is decreased.

$Co_2FeS(CO)_9$ from $Co_2Fe_2S_2(CO)_{11}$. $Co_2Fe_2S_2(CO)_{11}$ [7] (0.190 g, 0.316 mmol) and $Co_2(CO)_8$ (0.121 g, 0.354 mmol) were allowed to react in CH_2Cl_2 (54 ml) at 25°C for 24 h. The reaction mixture was then filtered and evaporated. The hexane extract of this material was purged with air, filtered, and evaporated to afford black microcrystalline $Co_2FeS(CO)_9$ identified by IR and microanalysis. Yield: 57% (0.166 g).

$(C_5H_5Mo)CoFeS(CO)_8$. $Co_2Fe_2S_2(CO)_{11}$ (137.6 mg, 0.229 mmol) and $[C_5H_5Mo(CO)_3]_2$ (224.1 mg, 0.457 mmol) were irradiated in CH_2Cl_2 (25 ml) with a 200 W Hg arc lamp for 1 day at 25°C. The reaction mixture was then filtered, evaporated, and extracted with hexane. The hexane-soluble products were then chromatographed on a 3 × 30 cm column of silica gel. Elution with 1/9 CH_2Cl_2/hexane gave $Co_2Fe_2S_2(CO)_{11}$ followed by two unidentified bands. Elution with 1/3 CH_2Cl_2/hexane gave $(C_5H_5Mo)CoFeS(CO)_8$. The product was crystallized from concentrated hexane solution. Yield: 42% (50.5 mg). The product was identified by IR and EIMS [8].

$Fe_4S_4(CO)_{12}$. A CH_2Cl_2 solution (100 ml) of $Fe_2S_2(CO)_6$ (0.80 g, 2.3 mmol) was placed in a stoppered flask and allowed to stand in sunlight for eight days. The resulting red crystals were filtered and washed with CH_2Cl_2. Yield: 20% (0.16 g). Anal. Found: C, 20.50; Fe, 32.38. $C_{12}Fe_4O_{12}S_4$ calcd.: C, 20.96; Fe, 32.48%. IR (mineral oil mull): 2071vs, 2060sh, 2033m, 2011sh, 2008s, 1980w.

$(C_5H_5Co)Fe_2S_2(CO)_6$. $Fe_2(S_2)(CO)_5$ (1.0 g, 2.9 mmol) and $C_5H_5Co(CO)_2$ (0.8

ml) were refluxed in 100 ml of hexane for 2 h. Flash chromatography of the crude product on silica gel with hexane gave a small amount of starting material; CH_2Cl_2 eluted the intensely purple product. The major band was evaporated to dryness. Yield: 81% (1.1 g). IR: 2065w, 2039s, 1990m. ^1H NMR: 5.74 ppm.

Results and discussion

Interconversion reactions of iron-tellurium clusters

An improved synthesis now furnishes a 1/2 mixture of $Fe_3Te_2(CO)_n$ ($n = 9$, 10) in 70% yield from the reaction of $Fe(CO)_5$, KOH, and TeO_2 followed by acidification [1]. For many purposes the mixture of nona- and decacarbonyls can be used without separation although the decacarbonyl is quantitatively converted in refluxing benzene to $Fe_3Te_2(CO)_9$. $Fe_3Te_2(CO)_9$ itself is a black, easily crystallized material which is quite soluble in most organic solvents wherein it gives brown, mildly air sensitive solutions. It is also possible to isolate ~ 5% yields of $Fe_2(Te_2)(CO)_6$ from preparations of $Fe_3Te_2(CO)_9$ [1]. While the high reactivity and thermal instability of this Fe_2Te_2 cluster are of interest from the perspective of structure-reactivity correlations, synthetic studies are severely hampered by this inefficient synthesis. We have now found that $Fe_3Te_2(CO)_9$ can be readily converted to $Fe_2(Te_2)(CO)_6$ in good yield. Our initial breakthrough in this direction involved the observation that $Fe_3Te_2(CO)_n$ decomposed in polar solvents, e.g. acetonitrile, to give $Fe_2(Te_2)(CO)_6$. A series of optimization experiments has led to a useful synthesis of $Fe_2(Te_2)(CO)_6$ free of any contaminating triiron clusters. Thus, treatment of a methanolic suspension of $Fe_3Te_2(CO)_9$ with sodium methoxide followed by acidification, hexane extraction, and silica gel chromatography gave $Fe_2(Te_2)(CO)_6$ in ca. 40% yield (eq. 1).

$$Fe_3Te_2(CO)_9 \xrightarrow{\text{NaOMe, H}^+} Fe_2(Te_2)(CO)_6 \quad (1)$$

When acetonitrile solutions of $Fe_3Te_2(CO)_9$ are heated under a CO atmosphere, one obtains instead of $Fe_2(Te_2)(CO)_6$, a black, insoluble, crystalline product which analyzes as $[FeTe(CO)_3]_n$. The IR spectrum of this compound is very similar to that reported for the cubane clusters $Co_4Sb_4(CO)_{12}$ [9], $Fe_4S_4(CO)_{12}$, and $Fe_4Se_4(CO)_{12}$ [10]. Since we have shown that $Fe_2(Te_2)(CO)_6$ is formed by the decomposition of $Fe_3Te_2(CO)_9$ in acetonitrile, we propose that $Fe_2(Te_2)(CO)_6$ dimerizes under more vigorous conditions to give the cubane cluster (eq. 2).

$$2Fe_2(Te_2)(CO)_6 \xrightarrow{\Delta} Fe_4Te_4(CO)_{12} \quad (2)$$

This observation suggests that the previously reported synthesis of $Co_4Sb_4(CO)_{12}$ may proceed via a similar pathway.

In view of the fact that $Fe_2(Te_2)(CO)_6$ undergoes facile oxidative addition to low valent metals, the observation that $Fe_2(Te_2)(CO)_6$ can be obtained from $Fe_3Te_2(CO)_9$ suggests that the latter should undergo facile transmetallation. Indeed $Fe_3Te_2(CO)_9$ was found to react with $Pt(C_2H_4)(PPh_3)_2$ to give the known $Fe_2PtTe_2(CO)_6(PPh_3)_2$ [2] (eq. 3).

$$Fe_3Te_2(CO)_9 + Pt(C_2H_4)(PPh_3)_2 \xrightarrow{-Fe(CO)_3} Fe_2PtTe_2(CO)_6(PPh_3)_2 + C_2H_4 \quad (3)$$

This process is very solvent dependent, occuring rapidly in acetonitrile but slowly in benzene.

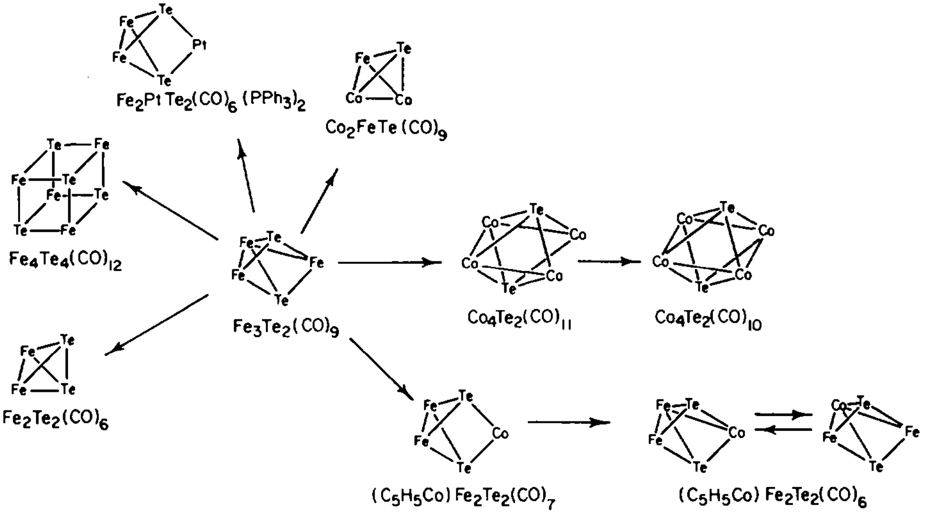
A closely related transmetallation afforded $(C_5H_5Co)Fe_2Te_2(CO)_7$ from the reaction of $Fe_3Te_2(CO)_9$ and $C_5H_5Co(CO)_2$ (eq. 4).

$$Fe_3Te_2(CO)_9 + C_5H_5Co(CO)_2 \rightarrow (C_5H_5Co)Fe_2Te_2(CO)_7 \qquad (4)$$

Both the orange color of its solutions and its formula suggest a close similarity of $(C_5H_5Co)Fe_2Te_2(CO)_7$ to the arachno clusters, $Fe_3Te_2(CO)_{10-n}L_n$ [11]. The ^{125}Te NMR spectrum of the iron-cobalt cluster established the presence of a single (arachno) Te cluster consistent with the structure depicted in Scheme 1. The formation of this species from $Fe_3Te_2(CO)_9$ is proposed to occur via the intermediacy of $Fe_2(Te_2)(CO)_6$ followed by oxidative addition to "$C_5H_5Co(CO)$".

$(C_5H_5Co)Fe_2Te_2(CO)_7$ reacted with Me_3NO in hot acetonitrile solution to give $(C_5H_5Co)Fe_2Te_2(CO)_6$ in excellent yield. This behavior is again completely comparable to the decarbonylation of $Fe_3Te_2(CO)_{10-n}L_n$. In the reverse reaction, $(C_5H_5Co)Fe_2Te_2(CO)_6$ reformed the aforementioned isomer of (C_5H_5Co)-$Fe_2Te_2(CO)_7$ upon treatment with 2000 psi of CO. ^{125}Te NMR measurements demonstrate that $(C_5H_5Co)Fe_2Te_2(CO)_6$, which is isoelectronic with $Fe_3Te_2(CO)_9$, exists in solution as a mixture of two isomers, suggested structures for which are depicted in Scheme 1. The observed ^{125}Te NMR shifts for these isomers are quite close to that previously reported for $Fe_3Te_2(CO)_9$ [1].

SCHEME 1



The clusters $Co_2FeTe(CO)_9$ and $Co_4Te_2(CO)_{11}$ have been previously prepared by the reaction of Et_2Te or Ph_2Te with the appropriate metal carbonyls under carbon monoxide [3,4]. We have found that these same tellurium clusters can be prepared readily from $Fe_3Te_2(CO)_9$. While this modification is of preparative value, the overall transmetallation process is particularly intriguing mechanistically. $Fe_3Te_2(CO)_9$ was found to react with 2 equivalents of $Co_2(CO)_8$ under carbon monoxide at elevated temperatures to give $Co_2FeTe(CO)_9$, or $Co_4Te_2(CO)_{11}$, or both, depending on the conditions used (eqs. 5 and 6).

$$Fe_3Te_2(CO)_9 + 2Co_2(CO)_8 \xrightarrow{CO} 2Co_2FeTe(CO)_9 + Fe(CO)_5 \qquad (5)$$

$$Fe_3Te_2(CO)_9 + 2Co_2(CO)_8 \xrightarrow{CO} Co_4Te_2(CO)_{11} + 3Fe(CO)_5 \quad (6)$$

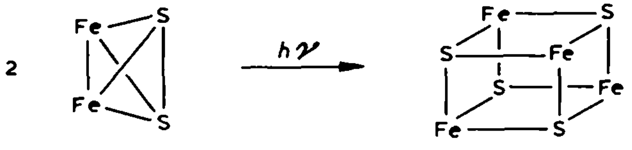
$Fe(CO)_5$ distilled from the reaction mixture in the work-up and was identified by IR. Within limits, higher temperatures and lower pressures favor formation of $Co_2FeTe(CO)_9$, while lower temperatures and higher pressures favor formation of $Co_4Te_2(CO)_{11}$.

The isolation of $Co_2FeTe(CO)_9$ was facilitated by its exceptional aerobic stability. Little is known of the chemical reactivity of this tetrahedral cluster although the isostructural $Co_2FeS(CO)_9$ has received considerable attention [8,12]. Under the conditions used in eq. 6, $Co_2FeTe(CO)_9$ was found to react further with one equivalent of $Co_2(CO)_8$ to afford $Co_4Te_2(CO)_{11}$ in good yield. The role of the additional $Co_2(CO)_8$ is not understood. In the absence of $Co_2(CO)_8$ or with only a catalytic amount of it, the reaction does not proceed. The reverse reaction however, gives an 81% yield of $Co_2FeTe(CO)_9$ from $Co_4Te_2(CO)_{11}$ and $Fe(CO)_5$, employing the conditions used in eq. 5. A mechanistic study of these conversions is the subject of ongoing investigations. Like $Fe_3Te_2(CO)_{10}$ and $(C_5H_5Co)Fe_2Te_2(CO)_7$, $Co_4Te_2(CO)_{11}$ undergoes reversible decarbonylation (Scheme 1).

Comparisons of the chemistry of sulfur and tellurium-containing iron carbonyl clusters

In the following paragraphs we elaborate upon aspects of iron chalcogenide carbonyl chemistry with special attention to the relationship between the corresponding sulfide and telluride clusters.

The greater thermal stability of $Fe_2(S_2)(CO)_6$ relative to $Fe_2(Te_2)(CO)_6$ is well illustrated by their lifetimes in hexane solution. Whereas $Fe_2(S_2)(CO)_6$ is stable for weeks in solution, $Fe_2(Te_2)(CO)_6$ converts in hours to a brown insoluble material which, based in IR spectroscopy, is mostly $Fe_4Te_4(CO)_{12}$. It is interesting to note however that although $Fe_2(S_2)(CO)_6$ is quite stable thermally, we found that it dimerizes photochemically to give $Fe_4S_4(CO)_{12}$ (eq. 7), which like $Fe_4Te_4(CO)_{12}$ is completely insoluble in common organic solvents.



(7)

$Fe_2(S_2)(CO)_6$ $\quad$ $Fe_4S_4(CO)_{12}$

This represents an unusual example of photochemically induced clusterification; it bears some similarity to the photochemical reaction of hexafluorobutyne with $Fe_2(S_2)(CO)_6$ giving $Fe_2(S_2C_2(CF_3)_2)(CO)_6$ [13]. The previous synthesis of $Fe_4S_4(CO)_{12}$ involved the high pressure carbonylation of $Fe_4S_4(NO)_4$ [10].

In contrast to the fact that $Fe_2(S_2)(CO)_6$ is synthetically versatile, preliminary indications are that $Fe_3S_2(CO)_9$ is not as useful synthetically. Thus while $Fe_3S_2(CO)_9$ does react with $Co_2(CO)_8$ to give the very stable $Co_2FeS(CO)_9$, treatment with $Pt(C_2H_4)(PPh_3)_2$ gives at least five products, one of which corresponded to a low yield of the known $Fe_2PtS_2(CO)_6(PPh_3)_2$.

We have reconfirmed an earlier report that $(C_5H_5Co)Fe_2S_2(CO)_6$ results from the action of $C_5H_5Co(CO)_2$ on $Fe_2(S_2)(CO)_6$ [14]. It is conceivable that this species

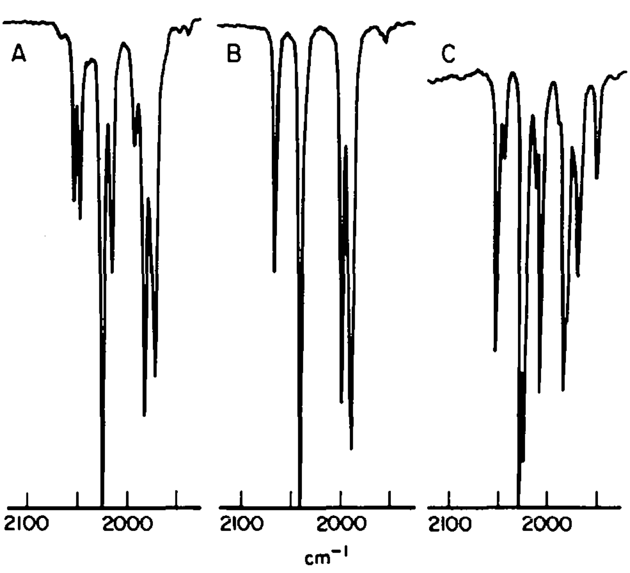
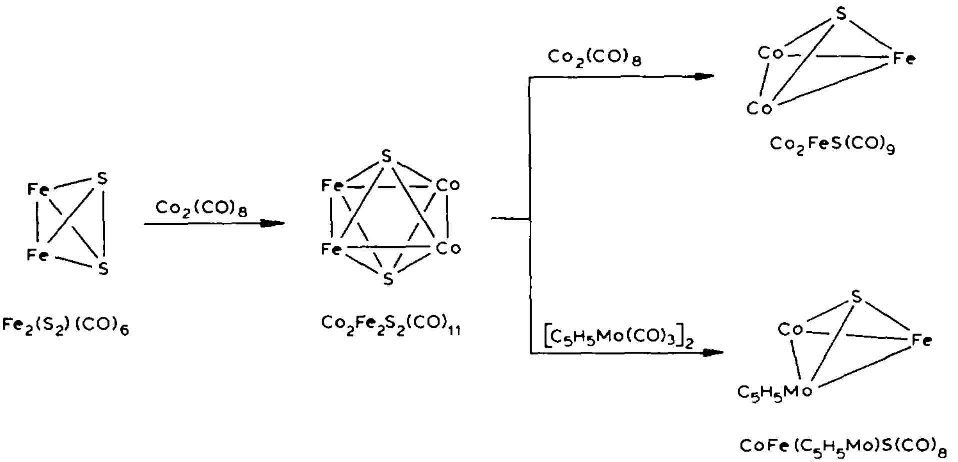


Fig. 1. IR spectra of cyclohexane solutions of $(C_5H_5Co)Fe_2Te_2(CO)_6$ (A); $(C_5H_5Co)Fe_2S_2(CO)_6$ (B), and $(C_5H_5Co)Fe_2Te_2(CO)_7$ (C).

could possess a trigonal core structure akin to that found for $(C_5H_5Co)_3S_2$ [15], although based on its physical properties (color, stability, diamagnetism) we feel that it is more likely that $(C_5H_5Co)Fe_2S_2(CO)_6$ structurally resembles $Fe_3S_2(CO)_9$ [16]. Earlier in this paper we had concluded from ^{125}Te NMR shift data that $(C_5H_5Co)Fe_2Te_2(CO)_6$ exists as a mixture of two isomeric nido clusters which like $Fe_3Te_2(CO)_9$ [17] possess square pyramidal M_3Te_2 cores (Scheme 1); a similar argument applies to the corresponding $RhFe_2Te_2$ clusters [18]. High resolution IR spectra suggest that $(C_5H_5Co)Fe_2S_2(CO)_6$ and $(C_5H_5Co)Fe_2Te_2(CO)_6$ are structurally closely related although the sulfide cluster is isomerically less complex (Fig. 1). We note that our structural assignment of $(C_5H_5Co)Fe_2S_2(CO)_6$ as a nido cluster with two metal–metal bonds differs from that proposed by those who originally prepared this compound [14]. The same square pyramidal core structure also appears to obtain for $(C_5H_5Co)_2FeS_2(CO)_3$ which can be prepared from $(C_5H_5Co)_3S_2$ and $Fe(CO)_5$ [19].

Markó and coworkers prepared the first mixed-metal sulfide cluster compound by the reaction of $Co_2(CO)_8$ and $Fe_2(S_2)(CO)_6$ [20]. More recently Vahrenkamp and coworkers have isolated $Co_2Fe_2S_2(CO)_{11}$ from the low temperature reaction of $Co_2(CO)_8$ and $Fe_2(S_2)(CO)_6$ [7]. The analogous $Co_2Fe_2Te_2(CO)_{11}$ may be an intermediate in the reaction of $Fe_3Te_2(CO)_9$ with $Co_2(CO)_8$, although attempts to isolate this cluster from the reactions of $Fe_2(Te_2)(CO)_6$ and $Co_2(CO)_8$ were unsuccessful. We have found that $Co_2Fe_2S_2(CO)_{11}$ indeed reacted with $Co_2(CO)_8$ and $[C_5H_5Mo(CO)_3]_2$ to give $Co_2FeS(CO)_9$ and $(C_5H_5Mo)CoFeS(CO)_8$, respectively (Scheme 2). At elevated temperatures and carbon monoxide pressures, $Co_2FeS(CO)_9$

SCHEME 2



reacts further with $Co_2(CO)_8$ to give detectable quantities of $Co_3S(CO)_9$ [21], which is known to be formed from $Co_4S_2(CO)_{10}$ under these conditions.

Acknowledgments

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