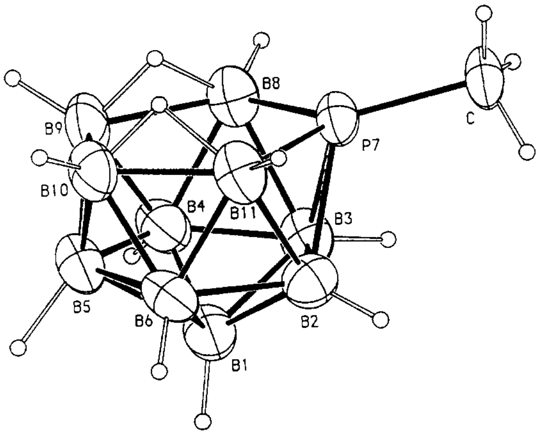

Figure 2. Molecular structure of $B_{10}H_{12}PCH_3$ (ORTEP plot with 50% probability ellipsoids).

protonation to form the $[B_{11}H_{14}]^-$ analogue $[B_{10}H_{12}PHCH_3]^+$. However, attempts to protonate the phosphaborane molecule by HCl, HBF_4, and $HCl-BCl_3$ were unsuccessful.

Acknowledgment. This work was supported by the Army Research Office through Grants DAAL03-88-K-0176 and DAAG29-85-K0187. We thank the NSF for a grant (CHE84-11630) for an X-ray diffractometer. NMR spectra were obtained at The Ohio State University Campus Instrument Center (funded in part by NSF Grant 79-100019 and NIH Grant 1 S10 PRO140518-01A).

Registry No. $Na_2[B_{11}H_{13}]$, 55624-52-7; $K_2[B_{11}H_{13}]$, 122213-27-8; $B_{11}H_{11}PCH_3$, 119203-72-4; $B_{10}H_{12}PCH_3$, 57108-87-9; $Na[B_{11}H_{14}]$, 52261-23-1.

Supplementary Material Available: Full listings of positional parameters, bond distances, bond angles, and anisotropic thermal parameters (18 pages); tables of calculated and observed structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Facile Synthesis of $M_3(CO)_9(\mu_3\text{-Te})_2$ (M = Ru, Os) and the Synthesis and Characterization of the Novel Cluster $Fe_2Os_3(CO)_{17}(\mu_4\text{-Te})(\mu_3\text{-Te})$

Pradeep Mathur,* Ipe J. Mavunkal, and V. Rugmini

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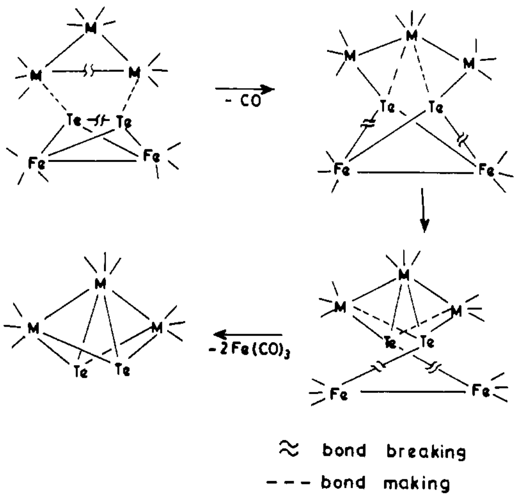
Cluster compounds incorporating single-atom ligands have received considerable attention recently, largely because of their utility in the synthesis of high-nuclearity clusters.[1,2] The ligands act as the initial point of contact when treated with coordinatively unsaturated metal fragments. Numerous sulfido-osmium and -ruthenium clusters have been synthesized and characterized, demonstrating the potential of this synthetic approach.[3-9] The lone pair of electrons on the triply bridging sulfido ligands in $Os_3(CO)_9(\mu_3\text{-S})_2$ have been used to coordinate to an additional metal atom, thereby providing a facile first step in cluster-growth sequences.[10-13] The molecule $Os_4(CO)_{12}(\mu_3\text{-S})_2$, obtained from $Os_3(CO)_9(\mu_3\text{-S})_2$ and $Os(CO)_5$,[10] is one of several examples highlighting the ability of the sulfido ligands to aid cluster growth. Synthesis of the selenido-osmium carbonyl cluster $Os_4(CO)_{12}(\mu_3\text{-Se})_2$ from $Os_3(CO)_9(\mu_3\text{-Se})_2$ and $Os(CO)_5$ suggests that selenium behaves in a manner similar to that of sulfur in cluster-growth reactions.[14]

Scheme I. Proposed Mechanism of Formation of $Me_3Te_2(CO)_9$



Reports by Rauchfuss and co-workers[15,16] and recent work in our laboratory[17-19] suggest that the much larger tellurium is markedly different from sulfur or selenium in reactions of the above type, and it is expected that the tellurium-containing clusters may exhibit unusual bonding properties and reactivity. Herein, we report a new route for the synthesis of the compounds $Os_3(CO)_9(\mu_3\text{-Te})_2$ (**1**) and $Ru_3(CO)_9(\mu_3\text{-Te})_2$ (**2**) and the synthesis and characterization of the new trimetallic cluster $Fe_2Os_3(CO)_{17}(\mu_4\text{-Te})(\mu_3\text{-Te})$ (**3**). It is significant that they have been made at room temperature from the readily available compounds $Fe_2Te_2(CO)_6$, $M_3(CO)_{10}(NCMe)_2$ (M = Ru, Os), and $Os_3(CO)_{11}(NCMe)$.

Results

Room-temperature stirring of a benzene solution of $Os_3(CO)_{10}(CH_3CN)_2$ and $Fe_2Te_2(CO)_6$ (**4**) formed the cluster **1** along with a maroon compound, which in solution slowly converted to **1**. When the maroon compound was refluxed in benzene solvent for 3 h, it converted to the yellow **1**. UV irradiation of a benzene solution of the maroon compound for 30 min also led to a conversion to **1**. The conversion of the maroon compound to **1** by photolysis or thermolysis was always found to be accompanied by the formation of traces of $Fe_3(CO)_9(\mu_3\text{-Te})_2$, suggesting that the maroon compound is a mixed-metal intermediate. The ruthenium analogue **2** was obtained similarly from the reaction of $Ru_3(CO)_{10}(CH_3CN)_2$ and **4**. Both **1** and **2** have been obtained previously from the high-temperature and high-CO-pressure reactions of $M_3(CO)_{12}$ (M = Ru, Os) and tellurium.[20] Our method provides an ambient-pressure route for an improved-yield synthesis of $M_3(CO)_9(\mu_3\text{-Te})_2$ (M = Ru, Os). It has been amply demon-

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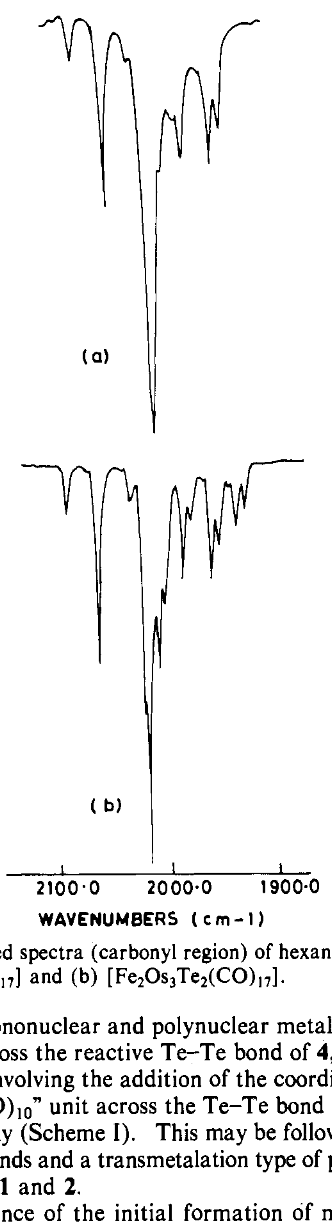


Figure 1. Infrared spectra (carbonyl region) of hexane solutions of (a) $[Fe_2Ru_3Te_2(CO)_{17}]$ and (b) $[Fe_2Os_3Te_2(CO)_{17}]$.

strated that mononuclear and polynuclear metal fragments can readily add across the reactive Te–Te bond of **4**, and therefore, a mechanism involving the addition of the coordinatively unsaturated "$M_3(CO)_{10}$" unit across the Te–Te bond of **4** as the first step is very likely (Scheme I). This may be followed by cleavage of the Fe–Te bonds and a transmetalation type of process, yielding the complexes **1** and **2**.

The importance of the initial formation of metal–tellurium bonds is more apparent from the reaction of $Os_3(CO)_{11}(NCMe)$ with **4** to give $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$ (**3**). Compound **3** has been characterized by infrared spectroscopy, mass spectrometry, and microanalysis. The infrared spectrum of **3** in the carbonyl region is similar to that of the related compound $Fe_2Ru_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$ (Figure 1), whose structure has been determined by single-crystal X-ray diffraction techniques.[19] The mass spectrum of **3** shows a molecular ion peak at *m/e* 1420 and peaks at *m/e* 1392, 1364, 1336, 1308, 1280, 1252, 1224, 1196, 1168, 1140, 1112, 1084, 1056, 1028, 1000, 972, and 944, corresponding to the successive loss of 17 carbonyl ligands. There is also good agreement between the experimentally obtained and the computer-simulated distribution patterns for the $Fe_2Os_3Te_2^+$ ion (Figure 2). The formation of **3** from $Os_3(CO)_{11}(NCMe)$ and **4** seems to be that of straightforward addition involving the cleavage of one Os–Os bond and the Te–Te bond (Scheme II). Three new Os–Te bonds are formed, and 1 mol of MeCN is eliminated. There is no loss of CO, and also there is no shift of carbonyl ligands between the iron atoms and the osmium atoms. This is in contrast to the formation of higher nuclearity sulfido–osmium clusters, whereby the initial contact of the coordinatively unsaturated metal fragments with the sulfido ligands is accompanied quite often by CO rearrangements and new metal–metal bond formations. The absence of new Fe–Os bonds in **3** may be attributed to the much larger size of the bridging tellurium ligands, and therefore, it may be anticipated that higher nuclearity mixed-metal clusters with bridging tellurium ligands should prefer to adopt open types of structures.

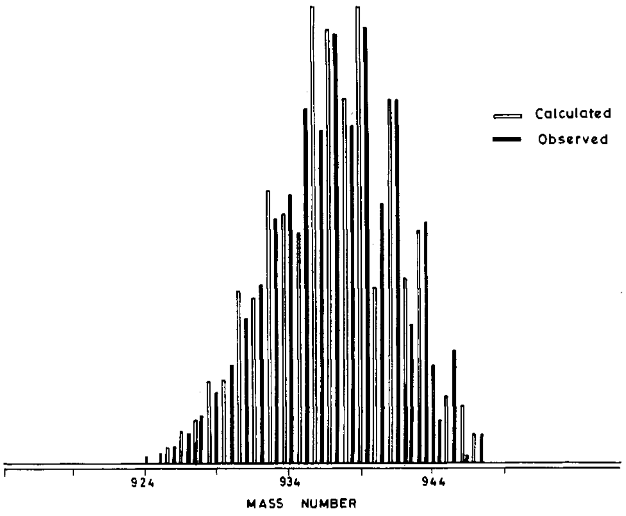
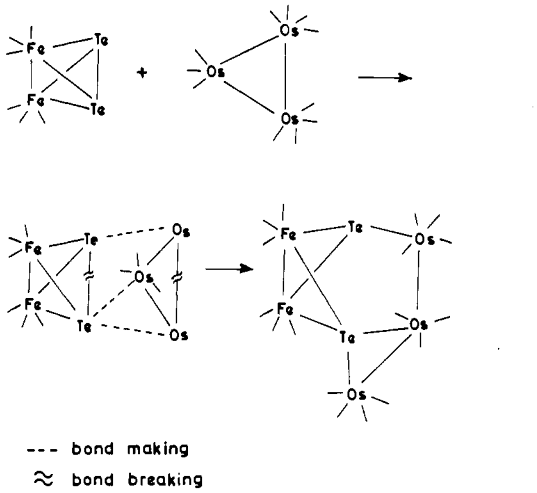


Figure 2. Comparison of observed and calculated isotope patterns for the ion $[Fe_2Os_3Te_2]^+$.

Scheme II. Proposed Mechanism of Formation of $Fe_2Os_3Te_2(CO)_{17}$



UV irradiation of **3** in benzene solvent for 0.5 h or reflux in the same solvent for 6 h gave **1** quantitatively. However, there is no evidence that the formation of **1** from **3** occurred via the maroon intermediate as observed when **1** was obtained from $Os_3(CO)_{10}(CH_3CN)_2$ and **4**. Similarly, compound **2** was obtained in very good yield by photolysis or thermolysis of $Fe_2Ru_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$.

Experimental Section

All operations were carried out under an atmosphere of pure argon with use of standard Schlenk techniques. All solvents were thoroughly purified, dried, and distilled under argon immediately before use. The compounds $Os_3(CO)_{11}(CH_3CN)$, $Os_3(CO)_{10}(CH_3CN)_2$, $Ru_3(CO)_{10}(CH_3CN)_2$,[21,22] and $Fe_2Te_2(CO)_6$[23] were prepared by established procedures. $Ru_3Fe_2Te_2(CO)_{17}$ was prepared as reported previously.[19]

Photochemical reactions were carried out by irradiating hexane solutions of the compounds through a water-cooled double-walled quartz vessel. A 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. was used. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in hexane in NaCl cells.

Preparation of $Os_3Te_2(CO)_9$. To a solution of $Os_3(CO)_{10}(CH_3CN)_2$ (466 mg, 0.5 mmol) in benzene (100 mL) was added a 2-fold excess of $Fe_2Te_2(CO)_6$ (534 mg, 1 mmol) in a 1:1 mixture of benzene and hexane

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(100 mL). The mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo; the reddish brown residue was dissolved in 100 mL of CH_2Cl_2 and filtered through a 10 cm thick Celite plug. Chromatography of the residue on a silica gel column with hexane as the eluant gave a yellow band of $Os_3Te_2(CO)_9$. Further elution with a 20:80 mixture of CH_2Cl_2 and hexane gave a maroon compound that in solution slowly converted to $Os_3Te_2(CO)_9$. UV irradiation of a benzene solution of the maroon compound for 30 min gave a total conversion to $Os_3Te_2(CO)_9$ (overall yield of $Os_3Te_2(CO)_9$ 180 mg, 34%). Reflux of a benzene solution of the maroon compound also resulted in complete conversion to $Os_3Te_2(CO)_9$ after 3 h (total yield of $Os_3Te_2(CO)_9$ 150 mg, 28%). IR (hexane; ν(CO), cm^{-1}): 2069 (vs), 2049 (vs), 2036 (m), 2027 (s), 2009 (vs).

The ruthenium analogue, $Ru_3Te_2(CO)_9$, was similarly prepared, in 45% yield, from $Ru_3(CO)_{10}(CH_3CN)_2$ and $Fe_2Te_2(CO)_6$. IR (hexane; ν(CO), cm^{-1}): 2069 (vs), 2047 (vs), 2017 (vs).

Preparation of $Fe_2Ru_3(CO)_{17}(\mu_4\text{-Te})(\mu_3\text{-Te})$. A benzene solution (50 mL) of $Fe_2Te_2(CO)_6$ (3-fold excess) was stirred with $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) at room temperature for 8 h. The solvent was removed under vacuum, the residue was dissolved in 100 mL of CH_2Cl_2, and the solution was filtered through a Celite pad and chromatographed on a silica gel column. Hexane eluted the trace amount of $Ru_3Te_2(CO)_9$ and the unreacted $Ru_3(CO)_{12}$, and further elution with a 10:90 CH_2Cl_2–hexane mixture gave the maroon $Fe_2Ru_3Te_2(CO)_{17}$ (66 mg, 74%). Recrystallization from hexane–dichloromethane at −4 °C afforded dark red, air-stable crystals of the product. Anal. Calcd for $C_{17}Fe_2O_{17}Ru_3Te_2$: C, 17.70%. Found: C, 17.40. IR (hexane; ν(CO), cm^{-1}): 2122 (w), 2093 (s), 2053 (vs), 2040 (m), 2028 (w), 2020 (m), 1994 (m), 1985 (m).

Preparation of $Fe_2Os_3(CO)_{17}(\mu_4\text{-Te})(\mu_3\text{-Te})$. To a solution of $Os_3(CO)_{11}(CH_3CN)$ (225 mg, 0.25 mmol) in benzene (100 mL) was added a 2-fold excess of $Fe_2Te_2(CO)_6$ (267 mg, 0.5 mmol) in a 1:1 mixture of benzene and hexane, and the mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo, the residue was dissolved in 100 mL of CH_2Cl_2, and the solution was filtered through a 10-cm Celite pad to remove the decomposition products and chromatographed on a silica gel column. Hexane eluted trace amounts of $Os_3Te_2(CO)_9$ (10 mg, 4%), and further elution with 20:80 CH_2Cl_2–hexane gave the reddish orange compound $Fe_2Os_3Te_2(CO)_{17}$ (245 mg, 70%). Anal. Calcd for $C_{17}Fe_2O_{17}Os_3Te_2$: C, 14.37. Found: C, 14.40. IR (hexane; ν(CO), cm^{-1}): 2127 (w), 2099 (s), 2069 (m), 2053 (vs), 2044 (s), 2038 (m), 2022 (m), 2015 (m), 2005 (w), 1995 (m), 1989 (sh), 1974 (w).

Thermolysis of $Fe_2Os_3Te_2(CO)_{17}$. A benzene solution (50 mL) of $Os_3Fe_2Te_2(CO)_{17}$ (50 mg, 0.036 mmol) was refluxed for 6 h. The solvent was removed in vacuo, and the residue was transferred to silica gel TLC plates in a minimum quantity of CH_2Cl_2. Hexane eluted $Fe_3Te_2(CO)_9$ (4.8 mg, 20%) followed by $Os_3Te_2(CO)_9$ (18 mg, 50%).

Thermolysis of $Fe_2Ru_3Te_2(CO)_{17}$. A solution of $Ru_3Fe_2Te_2(CO)_{17}$ (57 mg, 0.05 mmol) in benzene (50 mL) was refluxed for 2 h. Removal of the solvent and chromatography of the mixture on silica gel TLC plates with hexane as the eluant separated $Fe_3Te_2(CO)_9$ (3.4 mg, 10%) from $Ru_3Te_2(CO)_9$ (22 mg, 55%).

Photolysis of $Fe_2Os_3Te_2(CO)_{17}$. A benzene solution (90 mL) of $Fe_2Os_3Te_2(CO)_{17}$ (50 mg, 0.036 mmol) was irradiated by UV light under a constant argon purge for 30 min, during which time the solution changed color from reddish orange to light brown. The solvent was removed in vacuo, the residue was dissolved in the minimum amount of CH_2Cl_2, and the solution was chromatographed on silica gel TLC plates. Elution with hexane afforded $Os_3Te_2(CO)_9$ (24 mg, 60%). Further elution with a 20:80 CH_2Cl_2–hexane mixture separated traces of several other compounds, which could not be characterized.

Photolysis of $Fe_2Ru_3Te_2(CO)_{17}$. A benzene solution (90 mL) of $Fe_2Ru_3Te_2(CO)_{17}$ (57 mg, 0.05 mmol) was irradiated with UV light for 10 min under a constant purge of argon at room temperature. The color of the solution changed from reddish orange to light brown. The solvent was removed in vacuo, and the residue was placed on an alumina column. Elution with hexane separated $Ru_3Te_2(CO)_9$ (24 mg, 60%) from small amounts of other products, which could not be characterized.

Acknowledgment. We are grateful to the Department of Atomic Energy, Government of India, for financial assistance.

Additions and Corrections

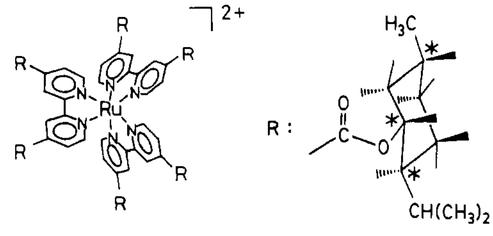
1989, Volume 28

J. David Walker and Rinaldo Poli*: $FeCl_3$–Phosphine Adducts with Trigonal-Bipyramidal Geometry. Influence of the Phosphine on the Spin State.

Pages 1796 (Figure 1) and 1798 (Figure 4) and related text. Due to miscalibration of the EPR instrument frequency, all the reported experimental *g* values are low by 3%. The new values can be obtained by multiplying the old numbers by 1.033.—Rinaldo Poli

Katsutoshi Ohkubo,* Taisuke Hamada, Tohru Inaoka, and Hitoshi Ishida: Photoinduced Enantioselective and Catalytic Reduction of $Co(acac)_3$ with a Chiral Ruthenium Photosensitizer.

Page 2021. The structure of the (1*R*,2*S*,5*R*)-(−)-menthylcarboxy group was incorrectly drawn. The text name for the compound was correct. The revised structure is printed below:



$[\,Ru((-)\text{-}mncb)_3]^{2+}$

—Katsutoshi Ohkubo