The Effects of Main Group Atoms on Transition Metal Carbonyl Clusters

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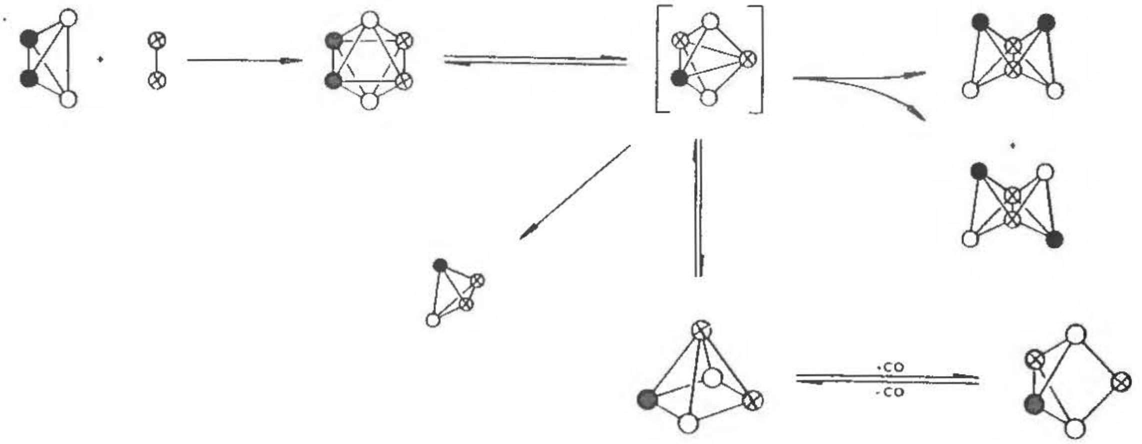
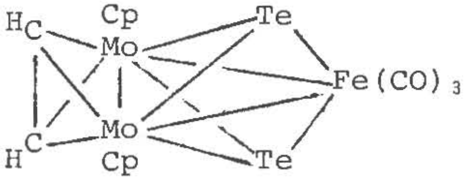
Transition metal carbonyl clusters (TMCCs) have been widely studied as soluble models for metal surfaces in heterogeneous catalysts and as homogeneous catalysts or catalyst precursors themselves [1]. Their rational use in the latter capacity is hampered by their inevitable fragmentation under the conditions of catalysis. Main group elements (MG) have been incorporated into the cluster core to tether the metal atoms together [2], since TM-MG bonds are generally stronger than TM-TM bonds [3]. Sulfur is one of the more commonly used main group elements for this purpose.

Central to control of metal vertex lability in transition metal main group element carbonyl clusters (TMMGCCs) is an understanding of the reaction pathways available to the clusters. Unfortunately, there have been very few such investigations [4]. The study of TMTeCCs is useful to such an understanding for three reasons. First, the chemistry of TMTeCCs complements that of the analogous sulfides; the heavier atom generally stabilizes intermediates which are not observable in TMSCC chemistry. Second, the compounds $Fe_3Te_2(CO)_9$ and $Co_4Te_2(CO)_{10}$ are anomalous in forming adducts with Lewis bases, a reaction the sulfide and selenide analogues do not undergo [4]. Third, ^{125}Te NMR spectroscopy is a useful probe of the cluster core structure, and as such it complements other methods which probe the ligands on the metal vertexes [5].

The reaction of $Fe_3Te_2(CO)_9$ with metal carbonyl dimers at 150-180° and under 1300-1750 psi of CO was found to be a convenient route to a variety of TMTeCCs. Comparison of the chemistry of similar Fe-Co-E and Fe-Mo-E (E = S, Te) systems led to the proposal that these reactions proceed by the pathway shown in the scheme below. The novel part of this mechanism is the rearrangement of a $(TM)_4E_2$ cluster by dissociation and recapture of a TM vertex. In the system $Fe_2(S_2)(CO)_6$ + $Cp_2Mo_2(CO)_4$ dissociated $Fe(CO)_x$ (x<5) fragments were trapped as $Fe_3S_2(CO)_9$. The formation of two isomers of $Cp_2Mo_2Fe_2S_2(CO)_8$ [6] is explained by this mechanism and a method was devised for isomerization of the <u>cis</u>- isomer to the <u>trans</u>- $Cp_2Mo_2Fe_2S_2(CO)_8$.



Heating $Cp_2Mo_2FeTe_2(CO)_7$ at 110° generated a reactive intermediate which was trapped with $Fe(CO)_5$, $CpCo(CO)_2$, and with RCCH (R = Ph, H). The product of the latter reaction has the formula $Cp_2Mo_2FeTe_2(CO)_3(RCCH)$, and its structure was established by a combination of ^1H and ^1H coupled ^{13}C NMR spectroscopy of three different derivatives.



Careful inspection of the crystal structure of $Cp_2Mo_2FeTe_2(CO)_7$ [7] revealed a short (3.14 Å) Te···Te contact. Subsequent inspection of the structures of the Lewis base adducts of $Fe_3Te_2(CO)_9$ and $Co_4Te_2(CO)_{10}$ revealed similar short Te···Te distances in those compounds. It is proposed that the anomalous Lewis acidity of $Fe_3Te_2(CO)_9$ and $Co_4Te_2(CO)_{10}$ is due to the stabilizing effect of those Te···Te interactions.

The two electron reduction of $Fe_3Te_2(CO)_9$ was found to be reversible, but attempts to isolate the stable dianion and compare its structure with that of the isoelectronic adduct $Fe_3Te_2(CO)_9(PPh_3)$ failed. Oxidation of $Cp_2Mo_2FeTe_2(CO)_7$ (which is isoelectronic with $Fe_3Te_2(CO)_9L$ and has a similar structure) with Br_2/CO gave a good yield of $CpMoFe(Te_2Br)(CO)_5$, which features a novel Te_2Br ligand. In solution the compound undergoes rapid exchange of Br making the Te atoms equivalent, but at −88° in toluene this exchange is slowed enough that ^1H NMR indicates a chiral compound.

Reaction of $AgSbF_6$ with $CpMoFe(Te_2Br)(CO)_5$ generates the cation $[CpMoFe(Te_2)(CO)_5]^+$. This compound reacts with a variety of nucleophiles to give products resulting from initial attack at Te. This behavior is novel in that the main group element is more reactive than the transition metals.

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