

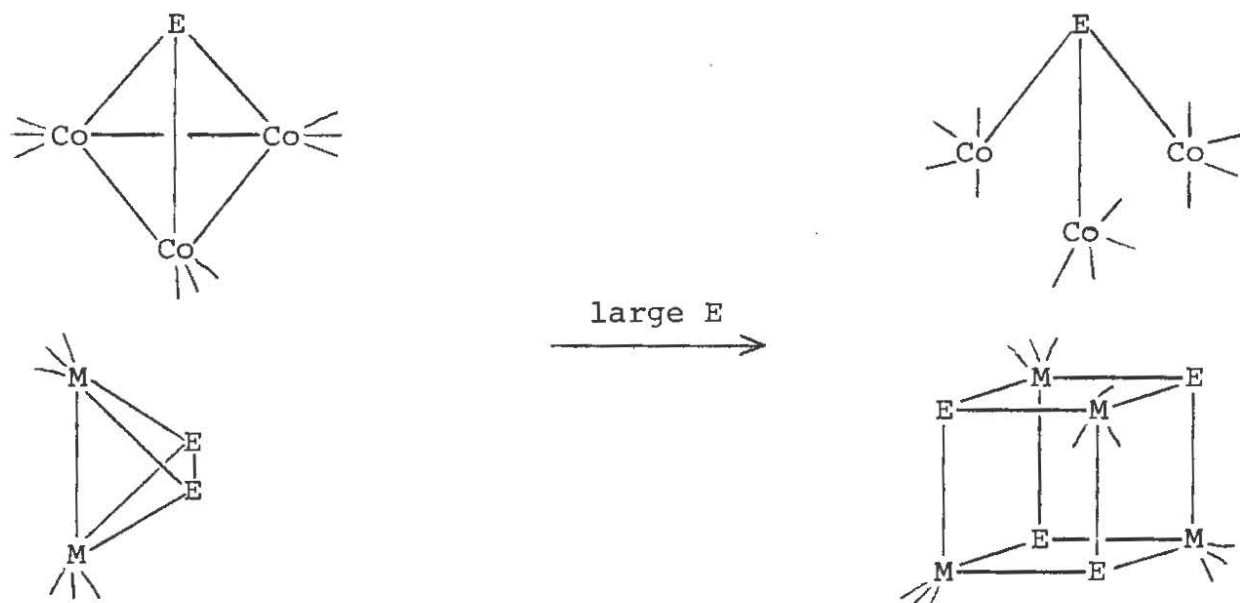
The Chemistry of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ 

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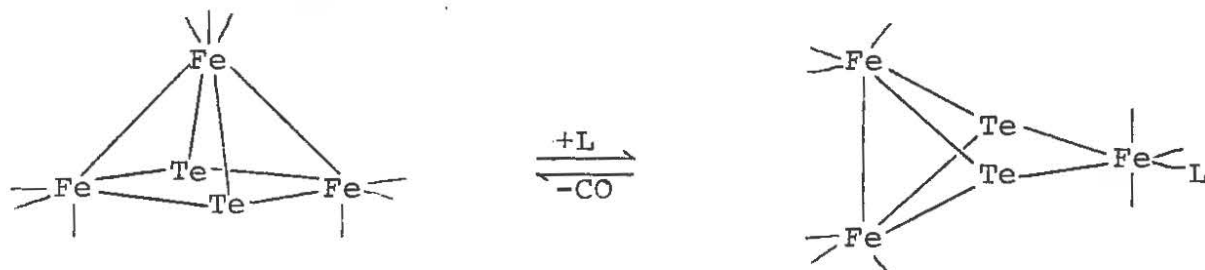
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The tellurium analogs of the two well-studied classes of transition-metal nonmetal clusters  $\text{Co}_3(\mu_3\text{-E})(\text{CO})_{9,12}$  ( $\text{E} = \text{CR}, \text{SiR}, \text{GeR}, \text{SnR}, \text{P}, \text{As}, \text{Sb}, \text{S}, \text{Se}$ ) [1] and  $[\text{M}(\mu\text{-E})(\text{CO})_3]_{2,4}$  ( $\text{M} = \text{Co}, \text{Fe}; \text{E} = \text{P}, \text{As}, \text{Sb}, \text{S}, \text{Se}$ ) [2] have not been reported. This fact plus the observation that when the covalent radius of E [ $r_{\text{COV}}(\text{E})$ ]  $\leq 1.22\text{\AA}$  the cluster is totally M-M bonded and when  $r_{\text{COV}}(\text{E}) \leq 1.40\text{\AA}$  the cluster is totally M-M nonbonded suggests that there might be unique properties associated with first row transition-metal clusters containing tellurium ( $r_{\text{COV}} = 1.36\text{\AA}$ ). Evidence for unusual reactivity has long been recognized for  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ , which, unlike  $\text{Fe}_3(\mu_3\text{-S})_2(\text{CO})_9$  or  $\text{Fe}_3(\mu_3\text{-Se})_2(\text{CO})_9$ , forms stable Lewis base adducts [3]. Previous workers suggested that this difference in reactivity was due to coordination of the Lewis base to tellurium [4].



The structure of the Lewis base adducts of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  was deduced by  $^{125}\text{Te}$  NMR spectroscopy while  $^{31}\text{P}$  NMR studies on the binding of bidentate ligands established the extreme facility of adduct formation [5]. The crystal structure of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9\text{PPh}_3$  confirmed our NMR results and demonstrated that the conversion of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  to its  $\text{PPh}_3$  adduct involved the scission of one Fe-Fe bond thus representing a nido to arachno conversion:

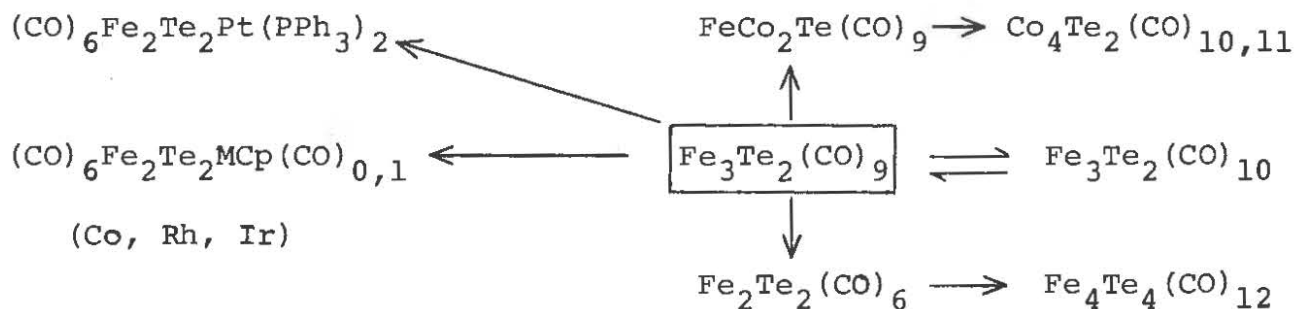


Thermal or chemical ( $\text{Me}_3\text{NO}$ ) decarbonylation of the characteristically orange adducts gives substituted products which are spectroscopically similar to the purple  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ . The maximum extent of substitution

is dominated by steric effects: ligands of large cone angle give disubstitution, those of intermediate cone angle give tri- or tetrasubstitution and lastly, very compact ligands (eg.  $P(OCH_2)_3CCH_3$ ) yield the hexasubstituted cluster.

$Fe_3(\mu_3-Te)_2(CO)_9$  can be obtained in ~90% yield from the thermal decarbonylation of  $Fe_3(\mu_3-Te)_2(CO)_{10}$  which in turn is prepared via the reduction of  $TeO_3^{2-}$  by  $HFe(CO)_4^-$ . A minor product (<10%) in this synthesis is  $Fe_2(\mu-Te_2)(CO)_6$  [6]. Although it is a useful precursor to mixed-metal clusters,  $Fe_2(\mu-Te_2)(CO)_6$  is relatively unstable with respect to its dimer,  $Fe_4(\mu_3-Te)_4(CO)_{12}$ , which in analogy to  $Co_4(\mu_3-Sb)_4(CO)_{12}$  has the cubane structure.  $Fe_2(\mu-Te_2)(CO)_6$  can also be generated in situ from  $Fe_3(\mu_3-Te)_2(CO)_9$  in MeCN and this process forms the basis for the reactions described below.

$Fe_3(\mu_3-Te)_2(CO)_9$  reacts with  $Pt(PPh_3)_2C_2H_4$  to give  $(CO)_6Fe_2(\mu_3-Te)_2Pt(PPh_3)_2$  whose structure, based on analogy with the crystallographically defined  $(CO)_6Fe_2(\mu_3-Se)_2Pt(PPh_3)_2$ , is similar to  $Fe_3(\mu_3-Te)_2(CO)_9(PPh_3)$  [7]. Its  $^{125}Te$  NMR chemical shift of -861 ppm is also similar to the adduct ( $\delta$ -887 and -938 ppm). The chemical shifts of these arachno clusters are in sharp contrast to those of the nido  $Fe_3(\mu_3-Te)_2(CO)_9-nLn$  ( $\delta$ +1100 ppm). This same chemical shift pattern was observed for the isoelectronic compounds  $(CO)_6Fe_2(\mu_3-Te)_2MCP(CO)_{0,1}$  ( $M = Co, Rh$ ) which were prepared from  $Fe_3(\mu_3-Te)_2(CO)_9$  and  $CpM(CO)_2$ . Reaction of excess  $Co_2(CO)_8$  with  $Fe_3(\mu_3-Te)_2(CO)_9$  results in sequential replacement of iron to ultimately give  $Co_4(\mu_4-Te)_2(CO)_{10,11}$ .



## References

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