

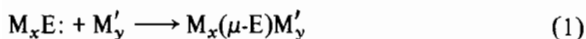
The Reactivity of $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ Towards $\text{Pt}(\text{PPh}_3)_4$

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The growing interest in the synthesis of mixed metal complexes has been attributed to their potential use as catalysts [1]. It is, however, only recently that non-serendipitous routes to complexes containing different metal fragments have started to appear in literature [2]. One convenient and well demonstrated strategy for building metal clusters is to use as starting blocks low nuclearity metal complexes having ligands which contain uncoordinated pairs of electrons as coupling agents [3]. The simplest types of such ligands are single atom ligands derived from elements of the main groups (e.g. P, As, S, Se, etc.). It is believed that the lone pairs of electrons on the ligands serve as the initial point of contact of the incoming metal unit to cluster through the formation of a donor–acceptor bond by using an empty metal orbital formed by the loss of a ligand (eqn. (1)). Often the bridging ligand influences



ligand elimination leading to new metal–metal bond formation.

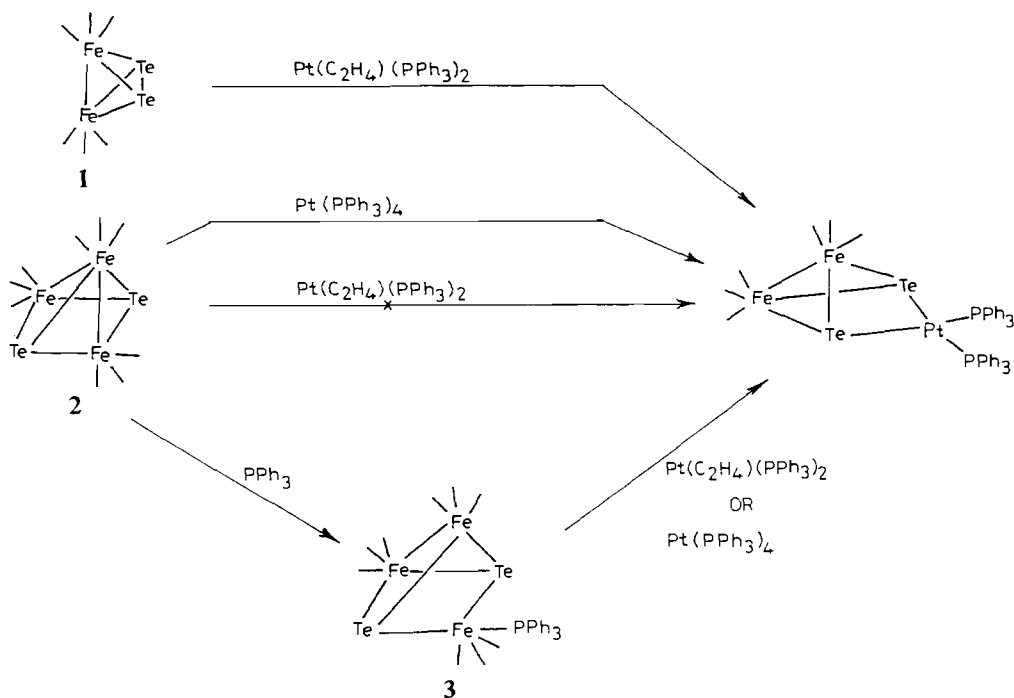
In contrast to the large number of sulfur and some selenium containing clusters, those containing tellurium have been little explored as potential starting blocks for cluster growth as they have been assumed to be chemically analogous to the sulfur and selenium derivatives. However, due to (a) the relatively large covalent radius (S 1.04 Å, Se 1.17 Å, Te 1.37 Å) and (b) the relative Lewis acidity of tellurium, certain geometrical and reactivity differences have been suggested for the tellurium bridged clusters, and therefore, the chemistry of tellurium containing transition metal complexes need not be identical to that of sulfur or selenium analogues. One of the few examples where tellurium acts as a bridge between different metal atoms is $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$ which has been prepared from $\text{Fe}_2(\mu\text{-Te})_2(\text{CO})_6$ (1) and $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ [4]. This method was originally used to separate trace amounts of 1 formed in the synthesis of $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ (2) which itself was found to be unreactive towards $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$. The addition of the $\text{Pt}(\text{PPh}_3)_2$ fragment across the Te–Te bond has been rationalized in terms of release

of a considerable amount of FeTeTeFe ring strain in 1. The potentiality of adding different metal fragments across the Te–Te bond has not been explored fully, probably due to the difficulties associated with obtaining even low yields of pure 1 [5].

Here, we wish to report our findings on the enhanced reactivity of the tellurium ligands in the easily accessible 2 towards platinum fragments. When equimolar amounts of 2 and $\text{Pt}(\text{PPh}_3)_4$ in benzene solvent were stirred at room temperature for 4 h, the red coloured $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$ was formed in yield of 84%, based on 2**, together with a trace amount of an as yet uncharacterised green coloured compound (Scheme 1). The mechanism of the formation of $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$ is difficult to predict with certainty. Overall, there is a loss of a $\text{Fe}(\text{CO})_3$ fragment and addition of a $\text{Pt}(\text{PPh}_3)_2$ fragment. The elimination of one of the basal $\text{Fe}(\text{CO})_3$ units of 2 seems more likely, as it would involve the cleavage of one Fe–Fe bond and two Fe–Te bonds, whereas the loss of the apical $\text{Fe}(\text{CO})_3$ unit would involve a total of four bond cleavages as well as the formation of a new Fe–Fe bond. Although both $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and $\text{Pt}(\text{PPh}_3)_4$ generate $\text{Pt}(\text{PPh}_3)_2$ fragments in solution, the free triphenylphosphine liberated in the case of the latter seems to influence the reactivity of 2 towards the platinum fragment. This is also suggested from our studies on the reactivity of the adduct $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9(\text{PPh}_3)$ (3) which is readily formed at room temperature by the addition of triphenylphosphine to a stirred benzene solution of 2 [6]. The phosphine is known to bond to the six coordinated basal iron atom and not the seven coordinated apical iron atom of 2, and the structure of 3 is remarkably similar to $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$. In fact, the description of 3 as $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Fe}(\text{CO})_3\text{PPh}_3$ suggests that if the $\text{Fe}(\text{CO})_3\text{PPh}_3$ fragment could be replaced by a $\text{Pt}(\text{PPh}_3)_2$ fragment, $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Pt}(\text{PPh}_3)_2$ would be obtained. We find that such a replacement does take place because when equimolar amounts of 3 and either $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ or $\text{Pt}(\text{PPh}_3)_4$ were stirred in benzene solvent for 2 h, $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$ was formed almost quantitatively. Thus, the free triphenyl phosphine present in solutions containing 2 and $\text{Pt}(\text{PPh}_3)_2$ fragments plays

** $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ (0.11 g, 0.2 mmol) and $\text{Pt}(\text{PPh}_3)_4$ (0.20 g, 0.2 mmol) were stirred in benzene solvent (20 ml) for 4 h. The solvent was removed *in vacuo* and the residue was chromatographed on alumina (grade 3). Elution with petroleum ether/dichloromethane (65:35) separated a trace amount of a green fraction from the major red coloured $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$. Yield, 84%. IR: ν_{CO} (CH_2Cl_2) 2031(s), 1988(s), 1955(s), 1948(wsh) cm^{-1} . Anal. Calc. for $\text{C}_{42}\text{H}_{30}\text{Fe}_2\text{O}_6\text{P}_2\text{Te}_2$: C, 40.21; H, 2.41. Found: C, 39.83; H, 2.40%.

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Scheme 1.

an important role in the mechanism of formation of $\text{PtFe}_2(\mu_3\text{-Te})_2(\text{CO})_6(\text{PPh}_3)_2$ by coordinating to the basal iron atom, which leads to cleavage of the Fe-Fe bond, facilitating the replacement of the $\text{Fe}(\text{CO})_3(\text{PPh}_3)$ unit by a $\text{Pt}(\text{PPh}_3)_2$ fragment.

We are currently exploring the generality of replacing the ' $\text{Fe}(\text{CO})_3 \text{L}$ ' fragment in $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9(\text{PR}_3)$ with various other metal fragments, and are investigating the complete mechanistic details of such reactions.

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