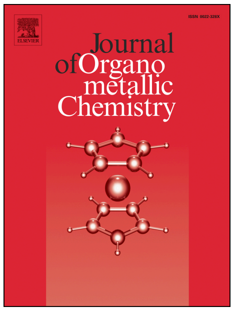

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Synthesis and molecular structures of the 52-electron triiron telluride clusters $[Fe_3(CO)_8(\mu_3\text{-}Te)_2(\kappa^2\text{-diphosphine})]$ - electrochemical properties and activity as proton reduction catalysts

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Dedicated to Prof. Irina P. Beletskaya on her 85th birthday, and in recognition of her outstanding contributions to organometallic chemistry.

Abstract – Heating the 50-electron cluster $[Fe_3(CO)_9(\mu_3\text{-}Te)_2]$ (**1**) with the diphosphines $Ph_2P\text{-}R\text{-}PPh_2$ [R = $-CH_2CH_2-$ (dppe), Z-CH=CH- (dppv), 1,2-C_6H_4 (dppb), $-CH_2CH_2CH_2-$ (dppp), ferrocenyl (dppf), naphthalenyl (dppbn)] in benzene affords the 52-electron diphosphine-containing tellurium-capped triiron clusters $[Fe_3(CO)_8(\mu_3\text{-}Te)_2(\kappa^2\text{-diphosphine})]$ (diphosphine = dppe, dppv, dppb, dppp, dppf, dppnd) (**2**-**7**) in moderate yields, resulting from both phosphine addition and carbonyl loss. With 1,2-bis(diphenylphosphino) benzene (dppb) a second product is the cubane cluster $[Fe_4(CO)_{10}(\mu_3\text{-}Te)_4(\kappa^2\text{-dppb})]$ (**8**). Cyclic voltammetry measurements on **2**-**7** reveals that all clusters show irreversible reductive behaviour at ca. -1.85 V with a series of associated small back oxidation waves, suggesting that reduction leads to significant structural change but that this can be reversed chemically. Oxidation occurs at relatively low potentials and is diphosphine-dependent. The first oxidation appears at ca. +0.35 V for **2**-**6** with a small degree of reversibility but is as low as +0.14 V for the bis(diphenylphosphino)naphthalene derivative **7** and in some cases is followed by further closely-spaced oxidation. Addition of $[Cp_2Fe][PF_6]$ to **2**-**7** results in the formation of new clusters formulated as $[Fe_3(CO)_8(\mu_3\text{-}Te)_2(\kappa^2\text{-diphosphine})]^+$, with their IR spectra suggesting oxidation at the diiron centre. This is supported by computational studies (DFT) of the bis(diphenylphosphino)propane cluster **5** showing that the HOMO is the Fe-Fe σ-bonding orbital, while the LUMO is centered on the diphosphine-substituted iron atom and has significant Fe-Te σ^*-anti-bonding character consistent with the irreversible nature of the reduction. Complexes **2**-**7** have been examined as proton reduction catalysts in the presence of *para*-toluenesulfonic acid (TsOH). All are active at their first reduction potential, with a second catalytic process being observed at slightly higher potentials. While their overall electrocatalytic behaviour is similar to that noted for the $[Fe_2(CO)_6\{\mu\text{-}E(CH_2)_3E\}]$ (E = S, Se, Te), the DFT results suggest that as the added electron is localised on the unique iron atom, the mechanistic aspects of hydrogen formation are likely to be quite different from the more widely studied diiron models.

Keywords: iron, tellurium, diphosphine, electrochemistry, proton reduction