Acetylenic Derivatives of $[Fe_2(CO)_6(\mu\text{-}Se_2)]$: Acetylenic Bond Reduction on a Selenium-stabilised Fe_2Pt Mixed-metal Complex

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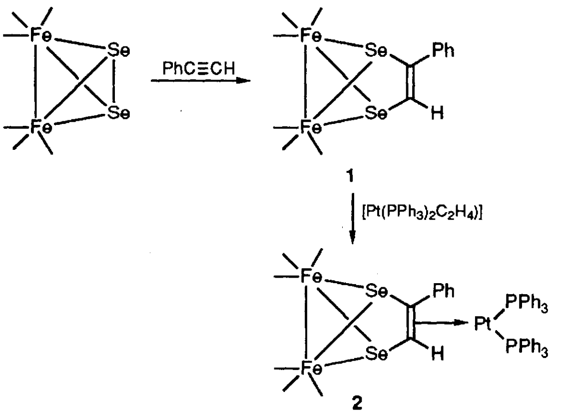
Stepwise addition of phenylacetylene and $Pt(PPh_3)_2$ across the Se–Se bond of $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ can be carried out at room temperature; X-ray analysis demonstrates the acetylenic carbon–carbon bond reduction in the mixed-metal complex $[(CO)_6Fe_2Pt(PPh_3)_2\{\mu\text{-}SeC(Ph)C(H)Se\}]$.

Interest in the chemistry of acetylene activation on transition metal complexes continues from two perspectives. First because the reduction of acetylenes to olefins is an important probe of the active metallic centre in the enzyme nitrogenase,[1] and secondly because of the potential of the coordinated alkynes to transform into useful carbon species.[2] In contrast to the large number of reports on the different types of acetylene bonding modes to transition metals, there is relatively little known on the activation of acetylenes on main group elements.[3] We have demonstrated the utility of the $[Fe_2(CO)_6(\mu\text{-}E_2)]$ (E = S or Te) as a starting material for the facile synthesis of mixed-metal clusters.[4] Recently, much



Scheme 1

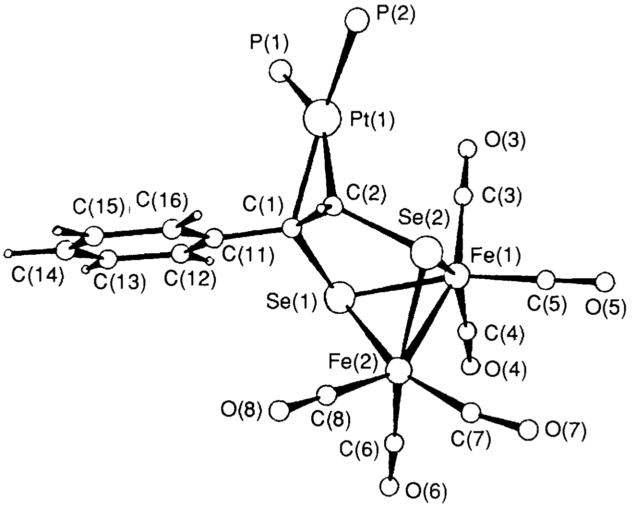


Fig. 1 Perspective view of a molecule of **2** with numbering scheme (the phenyl groups of the PPh_3 have been omitted). Selected interatomic distances (Å) and angles (°): Fe(1)–Fe(2) 2.534, Fe(1)–Se(1) 2.345(2), Fe(1)–Se(2) 2.369(2), Fe(2)–Se(1) 2.363(2), Fe(2)–Se(2) 2.383(2), Se(1)–C(1) 1.953(10), Se(2)–C(2) 1.94(1), Pt–C(1) 2.138(12), Pt–C(2) 2.069(13), C(1)–C(2) 1.423(15); Se(1)–Fe(1)–Se(2) 81.1(1), Se(1)–Fe(2)–Se(2) 80.4(1), Pt–C(1)–Se(1) 119.9(6), Pt–C(2)–Se(2) 119.6(6), Pt–C(1)–C(11) 113.6(6), C(1)–Pt–C(2) 39.5(4).

attention has been focused on the use of organoselenium compounds in organic and organometallic chemistry.[5] A convenient method for obtaining the reactive $[Fe_2(CO)_6(\mu\text{-}Se_2)]$[4] has given an opportunity to study the reactivity of the Se–Se bond towards acetylenes, and here we report the stepwise addition of phenylacetylene and '$Pt(PPh_3)_2$' to $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ to form a complex in which the phenylacetylene forms a bridge between two selenium and one platinum atom.

When phenylacetylene was added to an equimolar quantity of freshly prepared $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ in methanol, and the mixture was stirred at room temp. for 24 h, a red compound was isolated and identified as $[(CO)_6Fe_2\{(\mu\text{-}SeC(Ph)C(H)Se\}]$, **1**† (Scheme 1). Compound **1** and its Te analogue have previously been prepared by the thermal activation of $[Fe_3(CO)_9(\mu\text{-}E)_2]$ (E = Se or Te) and phenylacetylene and an X-ray structural analysis of the Te-containing compound has been reported.[6] These compounds belong to the general class of metal–alkyne complexes in which the alkyne formally serves as a two-electron donor, and there is a corresponding reduction of the acetylenic bond. The acetylene can also function as a four-electron donor and accordingly, the acetylenic bond can reduce beyond olefinic bond order. In order to investigate the possibility of converting the coordinated phenylacetylene in **1** from a two-electron donor to a four-electron donor, **1** was treated with $[Pt(PPh_3)_2(C_2H_4)]$ in benzene as solvent. After stirring at room temp. for 24 h, and chromatographic work-up on a silica-gel column using a 70 : 30 hexane–dichloromethane mixture as eluent, a deep-red compound, **2**† was isolated. Dark-red crystals of **2** were obtained from its hexane solution at −20 °C and an X-ray analysis was undertaken.‡

The molecular structure of **2** can be described as consisting of an Fe_2Se_2 butterfly and a $Pt(PPh_3)_2$ unit linked by a phenylacetylene, which formally can be considered as acting as a four-electron donor (Fig. 1). An important difference between the '$(CO)_6Fe_2Se_2$' unit in **2** and the structurally characterised $[Fe_2(CO)_6(\mu\text{-}Se_2)]$[7] is in the average Se–Fe–Se angles; in $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ it is 58°, whereas in **2** it is 81°, consistent with the opening of the Fe_2Se_2 butterfly-tetrahedron to accommodate the '$\{(PhCCH)Pt(PPh_3)_2\}$' unit between the wing-tip Se atoms. In $[(CO)_6Fe_2(\mu\text{-}Se)_2Pt(PPh_3)_2]$, which is obtained by addition of '$Pt(PPh_3)_2$' across the Se–Se bond of $[Fe_2(CO)_4(\mu\text{-}Se_2)]$, the Se–Fe–Se angle is increased to 78°.[8] The close to square planar environment around the platinum atom in **2** is similar to that observed in the reported $[Pt(PPh_3)_2(RC{=}CR)]$ complexes.[9] The acetylenic C–C bond distance [1.423(15) Å] in **2** is somewhat short for a four-electron acetylene donor. In $[Fe_3(CO)_9(PBu^t)_2(MeCCMe)]$, the acetylenic bond distance is 1.445(3) Å.[6] In $[Os_3(CO)_{10}(PhCCPh)]$, the acetylenic C–C bond [1.439(10) Å] is also reduced beyond olefinic bond order, consistent with its function as a four-electron donor.[10]

The attachment of the '$Pt(PPh_3)_2$' unit in **2** can be regarded as similar to the metal–olefin linkages observed in $[Pt(PPh_3)_2(RC{=}CR)]$ complexes. In such metal–olefin complexes, the preference of the metallacycle view or of the π-donor view of bonding depends on the extent to which the double bond of the ligand has been reduced to a single bond. In $[Pt(PPh_3)_2(HCCH)]$ the olefinic bond is reduced to 1.434(13) Å (in free ethylene, it is 1.335 Å),[11] whereas in $[Pt(PPh_3)_2\{(CN)_2CC(CN)_2\}]$, the double bond is reduced considerably more [from 1.31 Å in the free $(CN)_2C{=}C(CN)_2$ to 1.49(5) Å], reflecting a greater contribution of the metallacycle view of bonding.[12] In **2**, the relatively short C–C bond suggests that the bonding between PhCCH and platinum should be predominantly the $(PhCCH)\rightarrow Pt$ dative bond. In solution, **2** undergoes rapid loss of the '$Pt(PPh_3)_2$' group and $[Fe_2(CO)_6\{\mu\text{-}Se(Ph)CC(H)Se\}]$ is obtained in almost quantitative amounts.

Work is continuing on investigation of the reactivity of the acetylenic bond in **1** towards inorganic and organic molecules,

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† Compound **1**: air-stable red crystals: m.p. 105–107 °C. IR [ν(CO)/cm^{-1}, hexane]: 2073m, 2038s, 2001vs. Compound **2**: air-stable dark-red crystals: m.p. 132–133 °C. IR [ν(CO)/cm^{-1}, hexane]: 2057s, 2020vs, 1985s, 1980w, 1963m. Satisfactory elemental analyses were obtained for **1** and **2**.

‡ *Crystal data*: M = 1259.44, triclinic, $P\bar{1}$, a = 11.650(2), b = 14.368(2), c = 16.765(2) Å, α = 67.33(2), β = 89.33(2), γ = 65.89(2)°, V = 2560.5 Å^3, Z = 2, D_c = 1.635 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å^3, $F(000)$ = 1224, T = 290 K. The structure was obtained using Patterson and Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. Positions of hydrogen atoms were fixed geometrically. In final refinement, 697 independent parameters were refined in two blocks using 5403 observed reflections with $|F| > 3.0\sigma(F_o)$. Data were corrected for absorption, ψ scan (minimum and maximum transmission factors: 0.253 and 0.382, respectively). Final R = 0.059 and R_w = 0.06 [where $w = 1/\sigma^2(F) + 0.0018F^2$]. GDF = 1.166, $(\Delta/\sigma)_{max}$ = 0.782. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

as well as the effect of different substituents on the acetylene on its reactivity.

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