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Generation of σ,π-furyl and thienyl ligands at di-iron centers *via* facile phosphorus–carbon bond cleavage: Synthesis and molecular structures of $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C_4H_3E)\{\mu\text{-}P(C_4H_3E)_2\}]$ (E = O, S)☆

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ABSTRACT

Treatment of $[Fe_3(CO)_{12}]$ with tri(2-furyl)phosphine (PFu_3) or tri(2-thienyl)phosphine (PTh_3) in dichloromethane at 40 °C leads to facile phosphorus–carbon bond scission affording di-iron furyl- and thienyl-bridged complexes $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C_4H_3E)\{\mu\text{-}P(C_4H_3E)_2\}]$ (**1** E = O, Fu; **3** E = S, Th) in good yields, together with smaller amounts of the phosphine-substituted $[Fe_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-}C_4H_3E)\{\mu\text{-}P(C_4H_3E)_2\}\{P(C_4H_3E)_3\}]$ (**2** E = O, **4** E = S). When the same reactions were carried out at room temperature, small amounts of the tri-iron clusters $[Fe_3(CO)_{11}\{P(C_4H_3E)_3\}]$ (**5** E = O, **6** E = S) were isolated in which the coordinated phosphine(s) remain intact. Thermolysis of $[Fe_3(CO)_{11}\{P(C_4H_3E)_3\}]$ at 40 °C in dichloromethane gave $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C_4H_3E)\{\mu\text{-}P(C_4H_3E)_2\}]$, which also undergo phosphine substitution under similar conditions. However, both of these processes are too slow to account for the reaction product ratios and yields observed in the room temperature reactions. In contrast, addition of catalytic amounts of $Na^+[Ph_2CO]^{\bullet}$ to **5** resulted in the rapid formation of **1**. We therefore propose that these reactions may occur *via* a radical-initiated mechanism proceeding through the initial formation of the 49-electron radical anions $[Fe_3(CO)_{11}\{P(C_4H_3E)_3\}]^{\bullet}$. The crystal structures of $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}Fu)(\mu\text{-}PFu_2)]$ (**1**), $[Fe_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-}Fu)(\mu\text{-}PFu_2)(PFu_3)]$ (**2**), $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}Th)(\mu\text{-}PTh_2)]$ (**3**) and $[Fe_3(CO)_{11}(PFu_3)]$ (**5**) have been determined. The di-iron complexes all show the expected *cis* arrangement of three-electron donor ligands, short iron–iron distances consistent with a 34-valence electron count, and, in **2**, the phosphine is coordinated to the π-bound iron atom and lies *trans* to the metal–metal bond. Close inspection of the bonding parameters within the Fe_2C_2E core reveals that these alkenyl species are quite different to those without electron-withdrawing substituents. The tri-iron cluster **5** has two independent molecules in the asymmetric unit. Each contains two bridging carbonyls and the molecules differ in the relative positions of these carbonyls and the coordinated phosphine ligand, the latter lying in the equatorial plane in both molecules.

1. Introduction

The organometallic chemistry of tri(2-furyl)phosphine (PFu_3) [1–18] and tri(2-thienyl)phosphine (PTh_3) [19–29] has been extensively developed over the past decade. Sterically they are somewhat similar to triphenylphosphine; however, the electron-withdrawing nature of the 2-heteroaryl rings is greater than that of the phenyl ring, which makes PFu_3 and PTh_3 poorer σ-donors than PPh_3 [30]. This has been exploited in certain catalytic reactions, with PFu_3-containing catalysts often being more active than traditional PPh_3-based catalysts [3–9].

While in the majority of instances PFu_3 and PTh_3 act simply as two-electron donor ligands, a second reactivity pattern is the relatively facile carbon–phosphorus bond cleavage leading to phosphido and furyl/thienyl moieties [1,11–16,20,23,27,29] (Scheme 1). Thus Wong and co-workers prepared dinuclear

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☆ In memory of Professor F.G.A. Stone FRS, a leading protagonist of low-valent transition metal cluster chemistry and an inspiration to us all.

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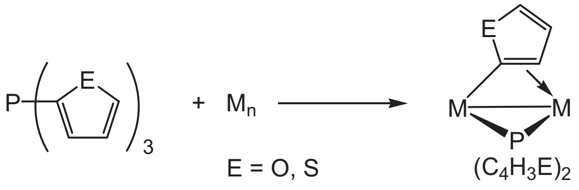


Scheme 1.

$[Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)]$ from the reaction of $[Ru_3(CO)_{12}]$ with PFu_3 at 67 °C in which the heteroaromatic group is bound to the bimetallic framework in a σ,π-alkenyl fashion [15]. In developing the use of PFu_3 as a source of a furyl ligand, we have recently shown that this transformation occurs *via* initial coordination of PFu_3 to the triruthenium center, as heating $[Ru_3(CO)_{12-n}(PFu_3)_n]$ ($n = 2, 3$) affords the same complex [16], while a similar thermolysis of $[Ru_3(CO)_9(PFu_3)_3]$ in the presence of Me_3NO affords $[Ru_2(CO)_5(PFu_3)(\mu\text{-PFu}_2)(\mu\text{-}\eta^1,\eta^2\text{-Fu})]$ [16]. In seeking to further utilise this facile carbon–phosphorus bond scission to prepare related di-iron furyl and thienyl complexes, we herein report reaction of $[Fe_3(CO)_{12}]$ with PFu_3 and PTh_3, and show that phosphorus–carbon bond cleavage is very facile at the tri-iron center, leading to the facile formation of di-iron furyl- and thienyl-bridged complexes, which is proposed to occur *via* a radical-initiated mechanism.

2. Results and discussion

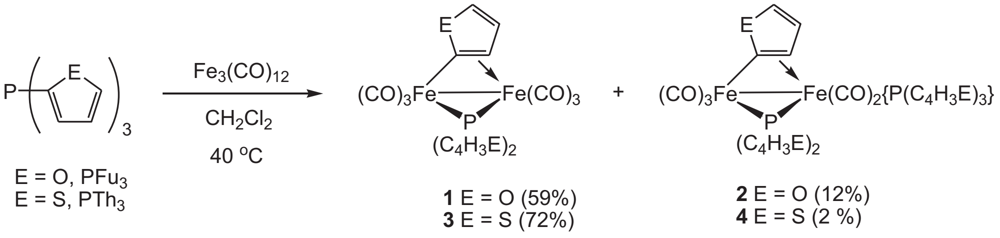
2.1. Thermolysis of $[Fe_3(CO)_{12}]$ with PFu_3 and PTh_3 – synthesis of σ,π-alkenyl complexes via carbon–phosphorus bond scission

Refluxing a dichloromethane solution of $[Fe_3(CO)_{12}]$ and PFu_3 for 12 h led to the isolation of the di-iron complexes $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)]$ (**1**) and $[Fe_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)(PFu_3)]$ (**2**) after chromatography, in yields of 59 and 12%, respectively. The same reaction with PTh_3 gave primarily $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-Th})(\mu\text{-PTh}_2)]$ (**3**) (72%) together with small amounts of phosphine-substituted $[Fe_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-Th})(\mu\text{-PTh}_2)(PTh_3)]$ (**4**) (2%) (Scheme 2).

Characterisation of these new complexes was straightforward. The IR spectra of **1** and **2** show four terminal carbonyl bands, the patterns being characteristic of an $Fe_2(CO)_6(\mu\text{-X})(\mu\text{-Y})$ core (where X and Y are different three-electron donor ligands). Cleavage of a carbon–phosphorus bond leading to the generation of a phosphido-bridge could be established from the $^{31}P\{^1H\}$ NMR spectrum. Thus **1** displays a low-field singlet at 91.7 ppm as compared to −75.8 ppm for the free phosphine ligand, while in **3** the phosphido signal is shifted to even lower field, appearing at 113.0 ppm. For **2** and **4** the IR spectra are consistent with a di-iron pentacarbonyl core and the $^{31}P\{^1H\}$NMR spectra did again provide the most useful characterizing data. Thus the spectrum of **2** consists of doublets at 80.9 and 21.3 ppm, assigned to the phosphido and coordinated intact phosphine ligands, respectively, the phosphorus–phosphorus coupling constant of 29.1 Hz suggesting a relative *cis* disposition of the two ligands. A similar spectrum is observed for **4**, consisting of doublets at 75.9 and 23.2 ppm ($J_{PP} = 26.2$ Hz).

In order to confirm the nature of the phosphorus–carbon bond cleavage process and also determine the relative positions of the phosphido and coordinated phosphine ligands, the crystal structures of **1**–**3** were determined. The molecular structures are shown in Figs. 1 and 2; relevant bond distances and angles are summarized in Table 1. The latter also contains some key metric data for related diphenylphosphido-bridged complexes and the parameters ΔC_α and ΔFe_π, defined as $\{(Fe_\pi–C_\alpha)–(Fe_\sigma–C_\alpha)\}$ and $\{(Fe_\pi–C_\alpha)–(Fe_\pi–C_\beta)\}$, respectively [31], with ΔC_α being a measure of how symmetrically the α-carbon bridges the di-iron centre and ΔFe_π differentiating between metallaolefin and metallacyclic binding modes [31]. For **2** there are two independent molecules in the asymmetric unit (Fig. 2). They differ primarily in the relative positions of the furyl groups on the phosphido-bridge. Otherwise the structures are very similar with only minor variations in bond lengths and angles.

All three complexes contain the same di-iron-phosphido-furyl/thienyl framework, with the two three-electron donor phosphido and furyl/thienyl ligands lying *cis* to one another, as expected. The metric parameters within the three complexes are similar to those in related σ,π-alkenyl complexes (Table 1). The iron–iron bond lengths vary only slightly within this series, as has been previously noted in a large number of alkenyl-bridged di-iron complexes [31–44]. Likewise, there is little variation in the carbon–carbon bond length in the alkenyl moiety, those in **1**–**3** of 1.405(7)–1.409(4) Å being typical. More interesting are the bond lengths between the alkenyl and di-iron centre. In all three structures, the α-carbon atom bridges the di-iron centre in a highly unsymmetrical fashion that arises as a result of both the relatively short $Fe_\sigma–C_\alpha$ and long $Fe_\pi–C_\alpha$ distances. The ΔC_α values thus vary between 0.172(4) and 0.223(4) Å, as compared to more typical values of around 0.1 Å. Bonds to the β-carbon are also long, with $Fe_\pi–C_\beta$ varying between 2.269(3) and 2.370(4) Å, some 0.1 Å longer than in related alkenyl complexes. The lengthening of both of the Fe_π–C bonds results in ΔFe_π values of 0.094(4)–0.173(7) Å, being similar to those seen previously. As observed in related complexes, the binding of the phosphido-bridge is slightly unsymmetrical, with the bonds to Fe_σ being consistently shorter than those to Fe_π. The most significant feature of **2** is the position of the phosphine ligand which is bound to the π-bound iron centre and lies approximately *trans* to the iron–iron bond [P(1)–Fe(2)–P(2) 156.22(3)–156.51(3)°]. It sits at approximately right angle to the phosphido-bridge and the angles subtended between the two phosphorus atoms [P(1)–Fe(2)–P(2) 105.89(3), P(3)–Fe(4)–P(4) 104.55(3)°] are in accord with the relatively small phosphorus–phosphorus coupling constants observed in solution. The structural features seen for **2** are very similar to those found in the analogous ruthenium complex $[Ru_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)(PFu_3)]$ (**2-Ru**, cf. Table 1) [16]. Table 1 also presents metric parameters for $[Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)]$ (**1-Ru**) [15,16] and $[Ru_2(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-Fu})(\mu\text{-PFu}_2)(PFu_3)]$ (**2-Ru**) [16]. In general, the structures differ only slightly upon exchange of iron for ruthenium, but there are some important subtle differences that are



Scheme 2.