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Synthesis of $M^0(\eta^2\text{-dppf})_2$ (M = Pd, Pt; dppf = $Fe(C_5H_4PPh_2)_2$) and their reactions with $Fe_3(\mu_3\text{-S})_2(CO)_9$ and elemental sulfur

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Abstract

Reduction of $MCl_2(\eta^2\text{-dppf})$ with $NaBH_4$ gives $M(\eta^2\text{-dppf})_2$ (M = Pt, **1**, Pd, **2**). Oxidation of **1** or **2** with S_8 gives the tetrasulfido complex $M(\eta^2\text{-}S_4)(\eta^2\text{-dppf})$. Addition of **1** or **2** to $Fe_3(\mu_3\text{-S})_2(CO)_9$ results in the heterometallic complex $(CO)_6Fe_2(\mu_3\text{-S})_2M(\eta^2\text{-dppf})$ (M = Pt, **5**; Pd, **6**) and two substitution side products $Fe_3(\mu_3\text{-S})_2(CO)_7(\mu\text{-dppf})$ (**7**) and $[Fe_3(\mu_3\text{-S})_2(CO)_8]_2(\mu\text{-dppf})$ (**8**).

Keywords: Palladium; Platinum; Diphosphine; Ferrocenyl phosphine; Sulfur; Cluster

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1. Introduction

Diphosphine complexes of zero-valent Pd and Pt are among the most useful substrates for the syntheses of various complexes of these metals [1]. Their synthetic utility is largely due to their facile synthesis, good shelf-life, and susceptibility to various oxidative and ligand replacement reactions. The synthetic value of these species is best exemplified by the abundant divalent complexes which have been prepared from them [2]. The most commonly used diphosphines are those with an alkyl-chain as backbone such as dppm [3], dppe [3c,3e,4], dppp [5] and dppb [6]. Our recent work in the chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) [7] suggests that the versatility of this ferrocenyl diphosphine as a ligand is greater than that of many common diphosphines. As part of our study of the dppf complexes of d^{10} metals, viz. Ag^I [8] and Au^I [9], we report the synthesis of other d^{10} complexes $M^0(\eta^2\text{-dppf})_2$ (M = Pd, Pt). The chemical reactivity of $MCl_2(\eta^2\text{-dppf})$ is rich and well-cited [10]. And Pd^{II} complex is a proven catalyst in many C–C coupling reactions [11]. On the contrary, and to our surprise, the isolation of these bis-chelated complexes has not been documented despite their possible participation (probably in the form of $[M(\eta^2\text{-dppf})]$) in the postulated catalytic cycles of some coupling reactions [12]. Also reported here are two representative reactions with S_8 and $Fe_3(\mu\text{-S})_2(CO)_9$ which characterize their liability to oxidation and substitution. This work is in the context of our continual interest in sulfide and polysulfide complexes [13].

2. Results and discussion

Borohydride reduction of $MCl_2(\eta^2\text{-dppf})$ in the presence of free dppf at r.t. rapidly gives orange and yellow $M(\eta^2\text{-dppf})_2$ (M = Pt, **1**, Pd, **2**) (Scheme 1) in 82% and 86% yields respectively. These solids can be briefly handled in air, but their solutions are air-sensitive. Both complexes gives a single ^{31}P-NMR resonance in solution. The high field shift of **1** and **2** in relation to $MCl_2(\eta^2\text{-dppf})$ is consistent with those observed for other diphosphines [1d,5b,14]. The characteristic 1 : 4 : 1 triplet in the ^{31}P-NMR spectrum of **1** with a Pt–P coupling of 3935 Hz gives the first indication of the formation of a Pt^0-phosphine complex [5b]. In C_6D_6 solution, complex **2** coexists with a species with very similar δ_p shifts (within ca. 1 ppm). Upon formation this species readily precipitates from the solution as a

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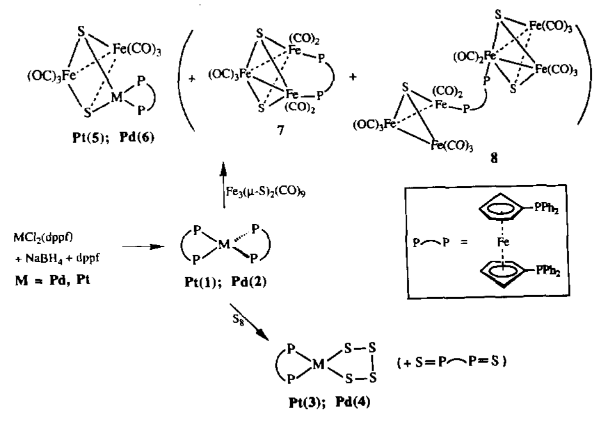

Scheme 1.

dark brown solid. We attribute this to a di- or polymerization process via chelate ring opening and bridge formation. This form of labilization of dppf chelate has been discussed in detail elsewhere [8b,15].

M^0 phosphine species characteristically undergo oxidation with elemental sulfur to give $M(\eta^2\text{-}S_4)(PP)$ ($PP = 2 \times PPh_3$ or dppe) which contains a $\{MS_4\}$ five-membered metallosulfur ring [16]. To prove the identity of **1** and **2**, similar reactions with sulfur were carried out (Scheme 1). This sulfuration also proceeds readily at room temperature (r.t.) to give $M(\eta^2\text{-}S_4)(\eta^2\text{-dppf})$ (M = Pt, **3**, Pd, **4**), giving $Fe(C_5H_4P(S)Ph_2)_2$ [17] as the by-product. Oxidation of Pt^0 to Pt^{II} is accompanied by a decrease of Pt–P coupling to 3015 Hz. This is comparable in magnitude with the J(P–P) of $Pt(\eta^2\text{-}S_4)(PPh_3)_2$ (2964 Hz) and $Pt(\eta^2\text{-}S_4)$(dppe) (2814 Hz) [16a].

The lability of PPh_3 in $Pt(PPh_3)_4$ allows its ready reaction with $Fe_3(\mu_3\text{-}S)_2(CO)_9$ to give the heterotrinuclear $(CO)_6Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2$ and $Fe_3(\mu\text{-}S)_2(CO)_{9-n}(PPh_3)_n$ ($n = 1$, 2) as by-products [18]. Reactions of **1** and **2** with $Fe_3(\mu_3\text{-}S)_2(CO)_9$ to give $(CO)_6Fe_2(\mu_3\text{-}S)_2M(\eta^2\text{-dppf})$ (M = Pt, **5**, Pd, **6**) proceed with similar ease despite the chelating effect of the bidentate dppf group (Scheme 1). This facile liberation of dppf would enable **1** and **2** to serve as a stable precursor for the unsaturated (14-e) fragment $[M(\eta^2\text{-dppf})]$ in other cluster reactions. Molecular weight (MW) measurement of both complexes also indicates ligand dissociation in solution with the Pd complex, as expected, more labile. A related [Ni(dbpm)] precursor has recently been reported [19]. Cluster complexes of dppf have attracted some recent attention regarding their structural, electrochemical and thermal properties [20].

Addition of **1** or **2** to $Fe_3(\mu_3\text{-}S)_2(CO)_9$ inevitably shifts the electron density of the capping sulfide to the M–S bonds. The weakened Fe–S bonds, prompted further by the weakness of the Fe–Fe bonds compared to their heavier congeners, lead to the rupture of a $[Fe(CO)_3]$ fragment. Such fragmentation is not observed in the reactions of $Os_3S_2(CO)_9$ with $Pt(PMePh_2)_4$ [21]. The adventitious ferrocenyl phosphine attacks the parent cluster to give the intramolecularly-bridged $Fe_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-dppf})$ (**7**) and intermolecularly-bridged $[Fe_3(\mu_3\text{-}S)_2(CO)_8]_2(\mu\text{-dppf})$ (**8**) clusters of dppf which have been reported [13e]. There is no evidence that $Fe(CO)_3(\eta^2\text{-dppf})$, from $[Fe(CO)_3]$ and dppf, is released.

To conclude, the isolation of $M(\eta^2\text{-dppf})_2$ provides a facile entry into the dppf complexes of Pd^{II} and Pt^{II}. It also serves as a convenient precursor for the release of the $[M(\eta^2\text{-dppf})]$ moieties in many transmetallation reactions for clusters. Current effort in our laboratory is directed towards these objectives.

3. Experimental section

3.1. General comments

All procedures were routinely performed under pure dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon. Analytical grade solvents could also be used as supplied when deoxygenated. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck. $MCl_2(\eta^2\text{-dppf})$ (Pt [22], Pd [11c]) and $Fe_3(\mu_3\text{-}S)_2(CO)_9$ [23] were prepared according to literature methods. Dppf was either prepared from ferrocene [17,24] or obtained commercially. All the other chemicals were used as received from commercial sources. Elemental analyses were performed by the microanalytical service of this department. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. Proton and $^{31}P\{^1H\}$ NMR spectra were obtained with a Bruker ACF 300 NMR spectrometer. ^{31}P-NMR chemical shifts relative to 85% phosphoric acid, are reported with positive values downfield from the reference. Presence of solvate in crystalline samples is supported by ^{1}H-NMR analysis.

3.2. Preparation of $Pt^0(\eta^2\text{-dppf})_2$ (1)

A suspension of $PtCl_2(\eta^2\text{-dppf})$ (0.532 g, 0.64 mmol) and dppf (0.353 g, 0.64 mmol) in a mixture of $EtOH/H_2O$ (2 : 1) (40 ml) was stirred at r.t. for 30 min, after which an aqueous solution (10 ml) of $NaBH_4$ (0.070 g, 1.83 mmol) was added dropwise. Stirring was continued for at least 10 h at r.t. before the mixture was filtered. The solid thus obtained was dried under vacuum and extracted by benzene (2 × 10 ml). The extract was filtered and to the filtrate was added pentane (20 ml). Upon slow cooling to −10°C, yellow microcrystalline deposits were collected and washed with pentane (2 × 5 ml) to give the desired Pt(η^2-dppf)$_2$ (0.684 g, 82%). Anal. calcd. for $C_{68}H_{56}Fe_2P_4Pt$: C, 62.52; H, 4.30; P, 9.52; Pt, 14.97. Found: C, 62.27; H, 4.25; P, 8.82; Pt, 15.57%. MW (C_6H_6) 1160 (calcd. 1303). δ_p(C_6D_6) 6.49 (t), $^1J(^{31}P-^{195}Pt)$ 3935 Hz.

3.3. Preparation of *Pd^0(η^2-dppf)$_2$ (2)*

The procedure, from PdCl$_2$(η^2-dppf), is similar to that of Pt(η^2-dppf)$_2$ but it was best carried out in THF at 50°C for 1 h. The solvent was removed in vacuo and the orange residue thus obtained was extracted with benzene. Precipitation with hexane, followed by filtration and washing with hexane gave the desired product. The freshly prepared product is yellowish orange but turns orange-brown upon prolonged storage. Yield: 86%. Anal. calcd. for $C_{68}H_{56}Fe_2P_4Pd$: C, 67.21; H, 4.64; P, 10.20; Pd, 8.76. Found: C, 67.77; H, 4.73; P, 10.32; Pd, 8.91%. MW (C_6H_6) 733 (calc. 1215). δ_H(C_6D_6): 7.78–7.71 (m, 10H, Ph), 7.06–6.93 (m, 10H, Ph), 4.76–4.74 (q, 4H, CpH$_\beta$), 4.34–4.32 (q, 4H, CpH$_\alpha$). δ_P(C_6D_6): 24.09 (s) (with minor resonances at 23.56 (s) and 25.58 (s)). Upon standing in C_6D_6, a dark-brown solution (δ_p 24.36 ppm) and a red-brown precipitate formed.

3.4. Reaction of *Pt(η^2-dppf)$_2$ (1) with elemental sulfur*

Solid S_8 (0.093 g, 0.36 mmol) was added to a solution of Pt(η^2-dppf)$_2$ (0.684 g, 0.52 mmol) in benzene (40 ml) at r.t. The resultant yellow solution was continuously stirred for 1 h, during which an orange-yellow solid was formed and precipitated gradually. The precipitate was separated by filtration and washed with toluene (2 × 5 ml) and hexane (2 × 5 ml). After recrystallization from CHCl$_3$/MeOH mixture, an orange-yellow microcrystalline solid of Pt(η^2-S$_4$)(η^2-dppf) (**3**) · 0.5CHCl$_3$ was obtained (0.147 g, 32%). Anal. calcd. for $C_{34.5}H_{28.5}Cl_{1.5}FeP_2PtS_4$: C, 44.20; H, 3.04; S, 13.66; P, 6.62. Found: C, 44.53; H, 3.25; S, 13.79; P, 6.76%. δ_H(CDCl$_3$): 7.77–7.70 (m, 10H, Ph), 7.44–7.33 (m, 10H, Ph), 4.36 (m, 4H, CpH$_\beta$), 4.15 (m, 4H, CpH$_\alpha$). δ_P(CDCl$_3$): 15.22 (t), $^1J(^{31}P-^{195}Pt)$: 3015 Hz. From the filtrate was isolated by TLC a by-product analyzed as Fe(C$_5$H$_4$P(S)Ph$_2$)$_2$. δ_H(CDCl$_3$): 7.64–7.34 (m, 20H, Ph), 4.64 (q, 4H, CpH$_\beta$), 4.28 (q, 4H, CpH$_\alpha$). δ_P(CDCl$_3$): 40.78 (s).

3.5. Reaction of *Pd(η^2-dppf)$_2$ (2) with elemental sulfur*

A similar procedure to that of Pt(η^2-S$_4$)(η^2-dppf) was adopted. A dark red-brown precipitate was collected, which was purified by recrystallization from CH$_2$Cl$_2$/hexane mixture to give a dark red crystalline solid of Pd(η^2-S$_4$)(η^2-dppf) (**4**) · CH$_2$Cl$_2$ (0.083 g, 27%). Anal. calcd. for $C_{35}H_{30}Cl_2FeP_2PdS_4$: C, 48.11; H, 3.43; S, 14.66 Found: C, 48.83; H, 3.00; S, 14.85% respectively. δ_H(CDCl$_3$): 7.62–7.26 (m, 20H, Ph), 5.30 (s, 2H, CH$_2$Cl$_2$), 4.64 (q, 4H, CpH$_\beta$), 4.29 (q, 4H, CpH$_\alpha$). δ_p(CDCl$_3$): 40.78 (s).

3.6. Reaction of *Pt(η^2-dppf)$_2$ (1) with Fe$_3$S$_2$(CO)$_9$*

A solution of Pt(η^2-dppf)$_2$ (0.090 g, 0.069 mmol) and Fe$_3$S$_2$(CO)$_9$ (0.035 g, 0.070 mmol) in benzene (40 ml) was stirred at r.t. for 23 h, during which the deep red colour turned to dark reddish brown. Solvent was removed under vacuum and the dark red-brown residue was extracted into a minimum amount of CH$_2$Cl$_2$ and chromatographed on silica TLC plates (CH$_2$Cl$_2$/hexane: 3 : 7). Three major bands were eluted, the first (i.e. with the highest R_f value) and second yielding on recrystallization from CH$_2$Cl$_2$/MeOH mixture [Fe$_3$(μ_3-S)$_2$(CO)$_8$]$_2$(μ-dppf) (**8**) (0.014 g, 26%) and Fe$_3$(μ_3-S)$_2$(CO)$_7$(μ-dppf) (**7**) (0.016 g, 22%) respectively. The third band was extracted with CH$_2$Cl$_2$ and, upon recrystallization from CH$_2$Cl$_2$/MeOH mixture, gave the reddish brown crystalline solid of Fe$_2$Pt(μ_3-S)$_2$(CO)$_6$(η^2-dppf) (**5**) · 0.5CH$_2$Cl$_2$ (0.021 g, 27%). Anal. calcd. for $C_{40.5}H_{29}ClFe_3O_6P_2PtS_2$: C, 42.80; H, 2.55; P, 5.46. Found: C, 42.70; H, 2.49; P, 5.36% respectively. ν_{max}(CO) (CH$_2$Cl$_2$): 2048s, 2007vs, 1969s, 1958m cm^{-1}. δ_H(CDCl$_3$): 7.78–7.72 (m, 10H, Ph), 7.46–7.39 (m, 10H, Ph), 5.30 (s, 1H, CH$_2$Cl$_2$), 4.32 (m, 4H, CpH$_\beta$), 4.18 (m, 4H, CpH$_\alpha$). δ_p(CDCl$_3$): 17.69 (t), $^1J(^{31}P-^{195}Pt)$: 2856 Hz.

3.7. Reaction of *Pd(η^2-dppf)$_2$ (2) with Fe$_3$(μ_3-S)$_2$(CO)$_9$*

A solution of Pd(η^2-dppf)$_2$ (0.061 g, 0.050 mmol) and Fe$_3$(μ_3-S)$_2$(CO)$_9$ (0.025 g, 0.052 mmol) in benzene (30 ml) was stirred at r.t. for 17 h. The resultant dark red-brown solution was evaporated to dryness and the residue was redissolved in minimum quantity of CH$_2$Cl$_2$ and chromatographed onto silica TLC plates. Elution with a mixture of CH$_2$Cl$_2$/acetone/hexane (3 : 1 : 6) yielded six bands. The second and sixth bands contained trace amounts of unidentified complexes. The first band gave a trace of unreacted Fe$_3$(μ_3-S)$_2$(CO)$_9$. The third and fourth bands gave, after recrystallization from CH$_2$Cl$_2$/CH$_3$OH mixture, [Fe$_3$(μ_3-S)$_2$(CO)$_8$]$_2$(μ-dppf) (0.004 g, 11%) and Fe$_2$Pd(μ_3-S)$_2$(CO)$_6$(η^2-dppf) (**6**) · 0.5CH$_2$Cl$_2$ (0.007 g, 13%). The latter was further purified by recrystallization from CH$_2$Cl$_2$/methanol mixture. Anal. calcd. for $C_{40.5}H_{29}ClFe_3O_6P_2PdS_2$: C, 46.44; H, 2.77; S, 6.11. Found: C, 46.47; H, 2.58; S, 6.19%. ν_{max}(CO) (CHCl$_3$): 2048s, 2006vs, 1971s, 1956m cm^{-1}. δ_H (CDCl$_3$): 7.73–7.70 (m, 10H, Ph), 7.47–7.39 (m, 10H, Ph), 5.30 (s, 1H, CH$_2$Cl$_2$), 4.33 (m, 4H, CpH$_\beta$), 4.17 (m, 4H, CpH$_\alpha$). δ_P (CDCl$_3$): 26.65 (s).

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