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Synthesis and characterisation of a bulky chelating bis(phosphine) ligand, 1,2-bis(diⁿbutylphosphino)ethane (DBPE), and its iron metal coordinated complexes, Fe(DBPE)₂Cl₂ and Fe(DBPE)₂(-C≡C-C₆H₅)₂

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Abstract

The synthesis of a bulky chelating bis(phosphine) ligand, 1,2-bis(diⁿbutylphosphino)ethane, ⁿBu₂PCH₂CH₂PⁿBu₂ (**1**) (Bu = Butyl = C₄H₉) (DBPE) is reported. This ligand was coordinated to iron by treatment with FeCl₂ to yield Fe(DBPE)₂Cl₂ (**2**) which is an important precursor of a variety of σ -acetylide complexes, e.g. Fe(DBPE)₂(-C≡C-C₆H₅)₂ (**3**). Complex **2** is paramagnetic in solution at room temperature and diamagnetic in the solid state. The optical absorption spectrum of **3** shows strong absorptions associated with $\pi-\pi^*$ transition of the acetylenic unit.

Introduction

Transition metal polyynes complexes of the type, [-M(PⁿBu₃)₂(-C≡C-R-C≡C-)]_n (M = Ni, Pd, Pt; R = *p*-C₆H₄; *p*-C₆H₄-C₆H₄-*p*), first developed by Hagihara [1], are of considerable interest because they exhibit novel physical properties [2–3] with potential applications in material science. The presence of bulky phosphine ligands makes these complexes soluble in common organic solvents [1], which helps in studies of their properties. During our investigations in this area, we devised [4–12] an alternative route to such metal σ -acetylide complexes. For the synthesis of soluble polyynes complexes of Group 8 metals (Fe, Ru, Os) with a rigid rod-like backbone we required a bulky chelating phosphine and we describe below the synthesis of the bidentate phosphine, 1,2-bis(diⁿbutylphosphino)ethane, (ⁿBu₂PCH₂CH₂PⁿBu₂, DBPE) (**1**) (Bu = Butyl =

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C_4H_9) (DBPE) and its iron complex, $Fe(DBPE)_2Cl_2$ (**2**). Complex **2** was used to prepare the model bis(σ -acetylide) complex, $Fe(DBPE)_2(-C\equiv C-C_6H_5)_2$ (**3**). The magnetic behaviour of **2** in solution and in the solid state, and the optical absorption spectra of **3** are reported.

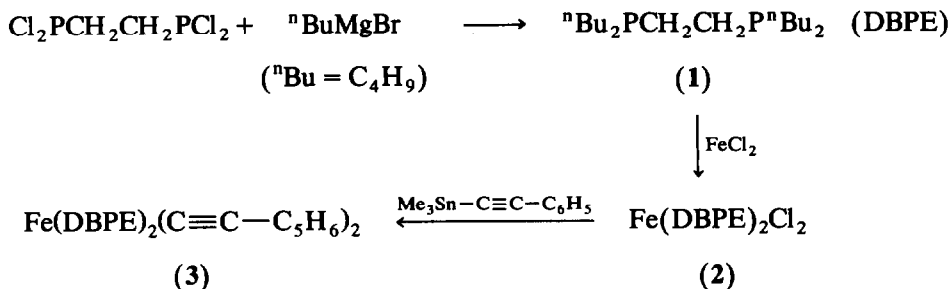
Results and discussion

The chelating bis(phosphine) (DBPE) (**1**) is a colourless liquid which is very sensitive to air and is produced in good yield by reaction of butylmagnesium bromide with 1,2-bis(dichlorophosphino)ethane. Attempts to prepare it by reaction of the latter with ⁿbutyllithium at low temperatures yielded a mixture of products difficult to separate. The identity of compound **1** was unambiguously established from its analysis and NMR spectra. The ³¹P{¹H} spectrum shows a single peak at 168.5 ppm whilst the ¹H NMR spectrum exhibits a complex coupling pattern.

The bidentate ligand **1** readily complexes with iron upon treatment with anhydrous iron(II)chloride in dry diethyl ether. The resulting green crystalline compound, $Fe(DBPE)_2Cl_2$ (**2**) is very soluble in common organic solvents giving clear green solutions. It is sensitive to air and moisture and turns brown on exposure. It was characterised from its analysis and mass spectrum. Its NMR spectra (³¹P{¹H} and ¹H) at room temperature show very broad peaks indicative of the formation of paramagnetic species. The magnetic behaviour of **2** in the solid state was examined by use of the Faraday balance [14] and this showed it to be diamagnetic in contrast to its paramagnetism in solution. This behaviour is in accord with a low spin configuration in the solid state and the low spin – high spin equilibrium in solution [15]. The magnetic properties of the analogous complexes $Fe(DMPE)_2Cl_2$ (**4**), $Fe(DEPE)_2Cl_2$ (**5**), and $Fe(DPrPE)_2Cl_2$ (**6**), (DMPE = 1,2-bis(dimethylphosphino)ethane; DEPE = 1,2-bis(diethylphosphino)ethane; DPrPE = 1,2-bis(dipropylphosphino)ethane) were studied previously [15]. Complex **4** was found to be diamagnetic in solution and in the solid state and to give rise to sharp resonances in the NMR spectra at room temperature; however, the complexes **5** and **6** containing bulkier phosphine, both show paramagnetic behaviour in solution under similar conditions [15] while being diamagnetic in the solid state.

The molecular structures of complexes **4–6** have been determined [15] and show the presence of chloride ligands in a *trans*-disposition at the metal centre. The crystals of the complexes with bulkier phosphines **5** and **6** were reported to suffer from a high degree of disorder. We have not yet obtained single crystals of complex **2**, those examined so far have all suffered from twinning and/or disorder. However, we would expect complex **2** to be isostructural with complexes **4–6**.

Treatment of complex **2** with an excess of $Me_3Sn-C\equiv C-C_6H_5$ gives the orange bis(σ -acetylide) complex, $Fe(DBPE)_2(-C\equiv C-C_6H_5)_2$ (**3**), which is very soluble in common organic solvents. In contrast to its precursor complex **2**, **3** is diamagnetic in solution at room temperature. It shows a single ³¹P{¹H} NMR resonance at ~ 73 ppm. Its IR spectrum has a single $\nu(C\equiv C)$ stretch at 2038 cm^{-1} for the σ -bound acetylenic units. These spectral features are consistent with a *trans*-disposition of the alkyne units at the metal centre, $(C_6H_5-C\equiv C-Fe(DBPE)_2(-C\equiv C-C_6H_5))_2$, which is in keeping [16] with the configuration of the structurally characterised iron-bis(acetylide) complexes $Fe(DMPE)_2(-C\equiv C-C_6H_5)_2$ and $Fe(DEPE)_2(-C\equiv C-C_6H_5)_2$.



Scheme 1.

The UV-visible spectra of the transition metal containing σ -acetylide complexes show strong absorptions that can be seen to be from π - π^* acetylenic transitions [2,7,10]. It has been demonstrated [10] that in such oligomeric and polymeric complexes of Group 10 metals there is extended π -conjugation through the metal sites on the chain, and the optical spectra of these complexes reflect the extent of $p\pi$ (acetylenic)- $d\pi$ (metal) hybridisation (monomeric to oligomeric/polymeric chain extension). The optical absorption spectrum for the bis-acetylide complex **3** was recorded with solutions of **3** in spectroscopically pure dichloromethane and shows strong absorptions at 3.32 eV (374 nm) and 4.84 eV (256 nm). These values agree well with those reported [15] for $\text{Fe}(\text{DMPE})_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2$ (THF solution, 364 and 259 nm) and $\text{Fe}(\text{DEPE})_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2$ (THF solution, 375 and 258 nm). A comparison of these values with those for the Pt-bis(acetylide) complex [17], *trans*- $\text{Pt}(\text{PR}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2$ (ether, 322 and 263 nm) reveals the effect of changing the metal from Pt (Group 10) to Fe (Group 8) which can be associated with increased $d\pi$ - $p\pi$ overlap in latter complexes.

In summary (Scheme 1) we have prepared a bulky chelating phosphine which complexes readily with iron to give an important precursor for a variety of soluble σ -acetylide complexes. The value of this complex in the preparation of rigid-rod like transition metal containing oligomeric and polymeric alkynyl complexes has been shown by the preparation of a model complex, $\text{Fe}(\text{DBPE})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2$. The syntheses of such monomeric, oligomeric and polymeric iron metal containing poly-yne complexes and their physical properties and redox behaviour are currently being studied.

Experimental

All reactions were carried out under nitrogen by glove box or high vacuum line techniques. Solvents were predried and distilled from appropriate drying agents. NMR spectra were recorded on a Bruker AM-400 spectrometer. $^{31}\text{P}\{^1\text{H}\}$ spectra were referenced to external trimethylphosphite and the ^1H spectra to solvent resonances. The IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform Spectrometer. The optical absorption spectra were recorded for dilute solutions in dichloromethane. $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ was prepared from phenylacetylene [8].

1,2-Bis(diⁿbutylphosphino)ethane (DBPE) (1)

The synthesis of chelating bis(phosphines) such as 1,2-bis(dimethylphosphino)ethane (DMPE), 1,2-bis(diethylphosphino)ethane (DEPE), 1,2-bis(diisopropylphosphino)ethane (DPrPE), have been reported [13]. The procedure described for the synthesis of **1** is an adaptation and modification of the method used for those [13].

To a suspension of magnesium turnings (1.9 g, 0.078 mol) in 100 ml of diethyl ether, a solution of bromobutane (11 g, 0.08 mol) in 50 ml of diethyl ether at 0°C was added dropwise under nitrogen during 1.5 h. When addition was complete the mixture was warmed to room temperature and stirred for 12 h. It was then cooled to -40°C and a solution of 1,2-bis(dichlorophosphino)ethane (3 g, 0.013 mol) in 50 ml of diethyl ether was added dropwise. The solution was warmed to 15°C and saturated aqueous ammonium chloride (50 ml) was added. The ethereal layer was separated, dried over anhydrous sodium sulphate overnight then filtered and the ether removed *in vacuo*. The residual liquid was distilled under reduced pressure to give compound **1** as a colourless liquid in 71% yield. Anal. Found: C, 67.68; H, 12.62. C₁₈H₄₀P₂ calcd.: C, 67.89; H, 12.66%. ³¹P{¹H} NMR (162 MHz, C₆D₆): 168.5 (s). ¹H NMR (400 MHz, C₆D₆): 0.91 (m, 12H), 1.41 (m, 24H), 1.56 (m, 4H).

Fe(DBPE)₂Cl₂ (2)

Compound **1** (0.85 g, 0.0027 mol) was added dropwise to a suspension of anhydrous FeCl₂ (0.17 g, 0.0013 mol) in 50 ml of dry diethyl ether. The mixture was stirred at room temperature for 14 h and the ether then removed *in vacuo*. The green residue was recrystallised from petroleum ether (30–40°C) to give complex **2** as green crystals (0.81 g, 79% yield). Anal. Found: C, 57.03; H, 10.75. C₃₆H₈₀P₄FeCl₂ calcd.: C, 56.62; H, 10.56%. Mass spectrum (+FAB) 762.8.

Fe(DBPE)₂(-C≡C-C₆H₅)₂ (3)

A green solution of **2** (50 mg, 0.065 mmol), Me₃SnC≡CC₆H₅ (50 mg, 0.189 mmol) and CuI (10 mg) in 25 ml of THF was refluxed for 4 h. THF was then removed *in vacuo* and the dark orange residue was dissolved in 5 ml of petroleum ether (30–40°C) and the solution cooled to -40°C to give complex **3** orange crystals in 58% yield. Anal. Found: C, 69.82; H, 10.18. C₅₂H₉₀P₄Fe calcd.: C, 69.78; H, 10.14%. Mass spectrum (+FAB) 894.5. IR (Nujol) ν(C≡C) stretch 2038 cm⁻¹. ³¹P{¹H} NMR (C₆D₆, 162 MHz) δ 72.8 ppm (s). ¹H NMR (C₆D₆, 400 MHz) 0.98 (m, 24H), 1.43 (m, 32H), 1.71 (m, 16H), 2.01 (m, 8H), 6.98, 7.59 (m, 10H).

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