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Complexes of 1,2,4,5-tetrakis(diphenylphosphino)benzene. Synthesis and X-ray crystal structure of $[\{(CO)_3Fe\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$

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Abstract

Reaction of 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**) with excess iron nonacarbonyl yields the dimeric complex $[\{(CO)_3Fe\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(PH_2P)_2C_6H_2(PPh_2)_2\}]$ (**2**) in 61% yield, the X-ray crystal structure of which, as its bis-tetrahydrofuran solvate, has been determined. The radical catalysed reaction of **1** with ruthenium dodecacarbonyl gives initially the trinuclear complex $[(CO)_{10}Ru_3\{\eta^2\text{-}(Ph_2P)_2C_6H_2\text{-}(PPh_2)_2\}]$ (**3**), identified by IR spectroscopy. Work up, however, leads to cluster fragmentation and the formation of $[\{(CO)_3Ru\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ (**4**).

Introduction

The design and synthesis of new oligiomeric and polymeric materials anticipated to display novel physical properties is of considerable current concern, while the incorporation of transition metal atoms in such materials is especially promising since it permits the tailoring of both physical and geometrical properties of the material thus allowing for the simple modification of its optical, magnetic, and electronic properties.

Tertiary phosphine ligands are widely utilised towards the stabilisation of transition metal centres. Diphosphine ligands are especially useful since they can be adapted to either chelate a single metal centre or bridge two centres. Thus, the mode of binding of a diphosphine is highly dependant upon the nature of the backbone, that is those atom(s), n, which link the two phosphorus nuclei [1]. Thus when $n = 1$, there is a pronounced tendency to bridge two metal centres while when $n = 2$, metal chelation is preferred, effects attributable to the stability of five membered ring formation. In contrast to the wealth of diphosphine chemistry, complexes of multidentate phosphine ligands are relatively unexplored. A suitably designed tetraphosphine ligand should however be capable of incorporating both chelate and bridging properties of diphosphines. A simple, high yield synthesis of a tetraphosphine ligand which has this ability, namely 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**), has recently been described [2]. This ligand has the capacity to bind metal

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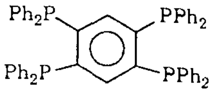
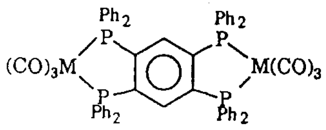
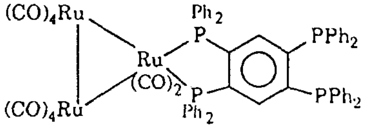


(1)



(2) M=Fe
(4) M=Ru



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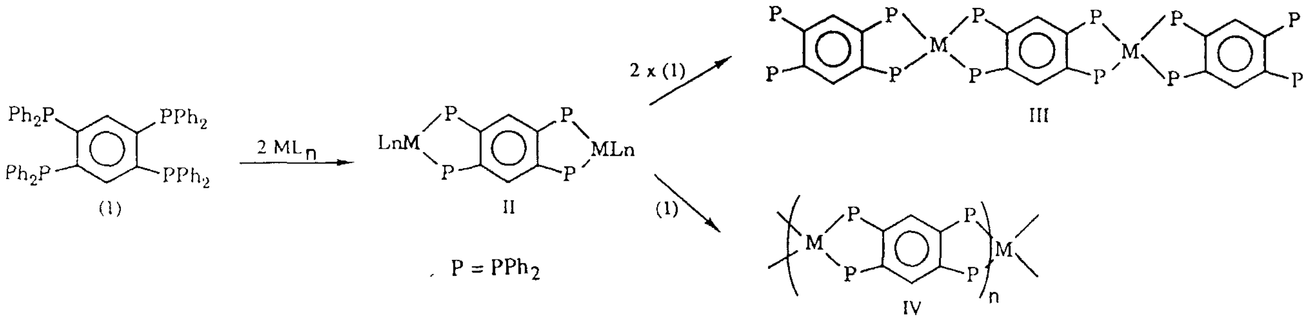

P = PPh_2

centres together while stabilising each centre via chelation, thus allowing for the synthesis of robust bimetallic complexes (II). These discreet molecular "dimers" can be considered as precursors towards the synthesis of new transition metal containing oligomers (III) and polymers (IV) as shown.

As previously stated, the geometrical nature of these new materials can be simply tailored via suitable choice of the transition metal centre(s) and multidentate phosphine ligand. With 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**), the aromaticity of the benzene ring forces the four phosphorus substituents to lie in the C_6 plane, allowing for a wealth of different types of new oligomers and polymers, the nature of which will be dependant upon the coordination geometry of the transition metal centre(s), e.g. linear sheet (square planar or octahedral), twisted chain (tetrahedral), or cyclic (trigonal bipyramidal or octahedral).

Since little is known of the chemistry of the 1,2,4,5-tetrakis(diphenylphosphino)benzene ligand we have begun our studies in this area by investigating the synthesis and structure of simple carbonyl stabilised discreet molecular "dimers". Herein we describe the synthesis of the new complexes $[\{(CO)_3M\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ (M = Fe or Ru).

Experimental

General comments. All reactions were carried out under an N_2 atmosphere using predried solvents. NMR spectra were recorded on a Varian VXR 400 spectrometer. IR spectra were recorded on a Perkin–Elmer 983 spectrometer. Column chromatography was carried out on columns of deactivated alumina (6% w/w water). Elemental analysis was performed within the chemistry department of University College. The ligand 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**) was prepared by the literature method [2].

Synthesis of $[\{(CO)_3Fe\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ *(2)*

A THF solution (50 cm^3) of **1** (0.97 g, 1.40 mmol) and $Fe_2(CO)_9$ (2.00 g, 5.58 mmol) was stirred at room temperature for 16 h resulting in the formation of a dark red solution and a bright orange precipitate. Removal of solvent under reduced pressure gave an orange solid which was repeatedly washed with 20 cm^3 portions of CH_2Cl_2 to give 0.8 g (61%) of **2** as a bright orange powder. Crystals suitable for X-ray diffraction were grown via slow mixing of a THF solution of **2** and light petroleum. Anal. Found; C, 65.15; H, 4.22; P, 11.47. $Fe_2C_{60}H_{42}O_6P_4$ calcd.: C, 65.81; H, 3.84; P, 11.33%. ^1H NMR ($CDCl_3$): δ 7.73 (2H, s, br, C_6H_2); 7.5–7.1 (40H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 92.8 (s). IR: ν(CO) (THF) 1985(s), 1923(s), 1906(s) cm^{-1}. The yellow washings which were air sensitive [ν(CO) 2047, 2019, 1992, 1947, 1934 cm^{-1}] were disguarded.

Synthesis of $[\{(CO)_3Ru\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ *(4)*

To a THF solution (30 cm^3) of $Ru_3(CO)_{12}$ (0.29 g, 0.45 mmol) and **1** (0.40 g, 0.49 mmol) was added a few drops of $PhCO_2^{\cdot}$ in THF. Stirring at room temperature for 3 h resulted in complete dissolution of ruthenium carbonyl to give a dark red solution. Removal of solvent under reduced pressure gave an orange solid which was extracted with hexane giving a dark red solution and bright orange solid.**4**. The dark red hexane extract has been tentatively identified as $[(CO)_{10}Ru_3\{\eta^2\text{-}(Ph_2P)_2C_6H_2\text{-}(PPh_2)_2\})$ (**3**). IR: (C_6H_{12}) 2097(w), 2046(m), 1992(m), 1963(m), 1945(m), 1924(w)

Table 1

Crystallographic data for **(2)**(THF)$_2$

Formula	$C_{68}H_{58}O_8P_4Fe_2$
FW	1238.84
a, Å	13.639(2)
b, Å	15.335(3)
c, Å	14.530(2)
α, deg	90.0
β, deg	97.03(1)
γ, deg	90.0
U, Å^3	3016.4
Z	2
$F(000)$	1284
d_{calc}, g/cm^3	1.37
cryst. size, mm	0.32×0.32×0.28
μ(Mo-K_α), cm^{-1}	6.40
Data collection instrument	Nicolet $R3mV$
Radiation	Mo-K_α ($\lambda = 0.71073$Å)
Orient. reflections: no.; range	30; $12 \leqslant 2\theta \leqslant 25$
Temp., °C	19
No. of unique data	5474
Total with $I \geqslant 3\sigma(I)$	3142
No. of parameters	370
R [a]	0.056
R_w [b]	0.059
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001742F^2$
largest shift/esd, final cycle	0.12
largest peak, e/Å^3	0.67

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = \Sigma[(|F_o - F_c|)\cdot w^{1/2}]/\Sigma[F_o \cdot w^{1/2}]$.

cm^{-1}. Attempted purification of **3** by column chromatography resulted in conversion to $Ru_3(CO)_{12}$ and (**4**). Thus, exposure of a CH_2Cl_2 solution of **3** onto an alumina column resulted in a rapid colour change from red to orange. Eluting with light petroleum/CH_2Cl_2 (1 : 1) gave an yellow band which afforded $Ru_3(CO)_{12}$. Further elution with CH_2Cl_2 gave an orange band which afforded **4** as a bright orange solid. Combined yield of **4** (0.46 g, 57%). Anal. Found: C, 60.16; H, 4.25; P, 9.97. $Ru_2C_{60}H_{42}O_6P_4$ calcd.: C, 60.81; H, 3.55; P, 10.47%. ^{1}H NMR ($CDCl_3$): δ 7.65 (2H, t, J 2, C_6H_2); 7.32–7.10 (40H, m). ^{31}P NMR (C_7D_8): δ 69.2 (s). IR: ν(CO) (CH_2Cl_2) 2004(s), 1935(s), 1910(s) cm^{-1}.

X-ray data collection

An orange crystal of approximate dimensions 0.32 × 0.32 × 0.28 mm was mounted on a glass fibre. All geometric and intensity data were taken from the crystal using an automated four-circle diffractometer (Nicolet $R3mV$) equipped with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Important crystallographic details are presented in Table 1. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. Axial photography was used to verify the Laue class and unit cell dimensions. The $\bar{\omega}$–2θ technique was used to measure 5703 reflections (5474 unique) in the range $5 \leqslant 2\theta \leqslant$

50°. Three standard reflections were measured every 97 reflections, and showed no sign of loss of intensity during the data collection. The data was corrected for Lorentz and polarisation effects and an empirical absorption correction applied. There are 3142 unique reflections with $I \geqslant 3\sigma(I)$. Structure determination and refinement was successfully accomplished in the space group $P2_1/n$.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$)

	x	y	z	U_{eq} [a]
Fe(1)	1955(1)	7291(1)	5633(1)	32(1)
P(1)	557(1)	7028(1)	4737(1)	30(1)
P(2)	1568(1)	6105(1)	6391(1)	29(1)
O(1)	3639(4)	6573(4)	4821(4)	74(2)
O(2)	2125(5)	8974(3)	4736(4)	93(3)
O(3)	2672(4)	8153(3)	7380(3)	67(2)
O(4)	7493(9)	525(11)	8960(6)	259(9)
C(1)	2950(5)	6805(4)	5136(4)	46(2)
C(2)	2034(5)	8307(4)	5085(5)	52(2)
C(3)	2359(4)	7804(4)	6706(4)	40(2)
C(4)	207(4)	5882(3)	4847(3)	26(2)
C(5)	691(4)	5442(3)	5628(3)	27(2)
C(6)	478(4)	4568(3)	5774(3)	31(2)
C(10)	554(4)	7122(3)	3477(4)	36(2)
C(11)	1191(7)	6586(5)	3060(5)	75(3)
C(12)	1207(8)	6633(6)	2117(6)	96(4)
C(13)	609(7)	7195(7)	1579(5)	83(4)
C(14)	−19(6)	7717(7)	1983(5)	84(4)
C(15)	−38(5)	7678(5)	2934(4)	59(3)
C(20)	−555(4)	7653(3)	4932(4)	36(2)
C(21)	−1509(5)	7394(4)	4619(5)	50(2)
C(22)	−2303(5)	7937(5)	4731(5)	58(3)
C(23)	−2159(6)	8718(5)	5161(5)	58(3)
C(24)	−1235(6)	8983(5)	5477(5)	72(3)
C(25)	−417(5)	8450(4)	5377(5)	57(3)
C(30)	939(4)	6190(4)	7436(4)	36(2)
C(31)	491(5)	6972(4)	7627(4)	48(2)
C(32)	−23(5)	7046(5)	8393(5)	65(3)
C(33)	−96(6)	6335(6)	8964(5)	68(3)
C(34)	338(6)	5553(5)	8778(4)	65(3)
C(35)	855(5)	5486(4)	8019(4)	50(2)
C(40)	2615(4)	5386(3)	6758(4)	33(2)
C(41)	3136(5)	5478(4)	7644(4)	48(2)
C(42)	3993(5)	5002(4)	7884(5)	58(3)
C(43)	4332(5)	4439(4)	7261(6)	59(3)
C(44)	3821(5)	435394)	6384(5)	56(3)
C(45)	2964(5)	4818(4)	6135(4)	46(2)
C(51)	8225(8)	438(9)	7694(9)	120(6)
C(50)	8396(9)	405(9)	8678(10)	138(6)
C(53)	6912(10)	961(10)	8332(9)	149(7)
C(52)	7366(9)	987(11)	7509(9)	141(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Structure solution and refinement

Complex **2** crystallises with two molecules of THF, the asymmetric unit containing half a molecule of **2** and a single THF molecule. The position of the iron atom was obtained by direct methods, with the remaining non-hydrogen atoms being found by iterative application of the least-squares refinement and difference-fourier analysis. All non-hydrogen atoms were refined anisotropically. The geometry of hydrogen atoms were idealised and a common temperature factor assigned [$U = 0.08$ Å^2]. The final least-squares refinement included 370 parameters for 3142 variables. The last cycle gave $R = 0.056$ and $R_w = 0.059$, quality of fit 1.27 and did not shift any parameter by more than 0.12 times its estimated standard deviation.

Atomic coordinates are listed in Table 2. Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors are available from the authors.

Results and discussion

Room temperature reaction of 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**) with excess di-iron nonacarbonyl gives the dimeric complex [$\{(CO)_3Fe\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}$] (**2**) in 61% yield. In the IR spectrum three absorptions characteristic of an iron tricarbonyl fragment are observed while in the ^{31}P NMR spectrum a singlet at δ 92.8 ppm indicates equivalent metal coordinated environments for all four phosphorus nuclei. The nature of **2** was confirmed via an X-ray crystallographic study the results of which are shown in Fig. 1 and Table 3.

The molecule consists of two iron tricarbonyl units linked via the 1,2,4,5-tetrakis(diphenylphosphino)benzene ligand such that each iron atom is chelated by a pair of adjacent phosphines. The tetraphosphine ligand is rigorously planar with iron atoms lying above and below the plane. The geometry at Fe(1) can be considered as intermediate between trigonal bipyramidal with P(1) occupying an equatorial and P(2) an axial site, and square pyramidal with C(1) at the apex [3].

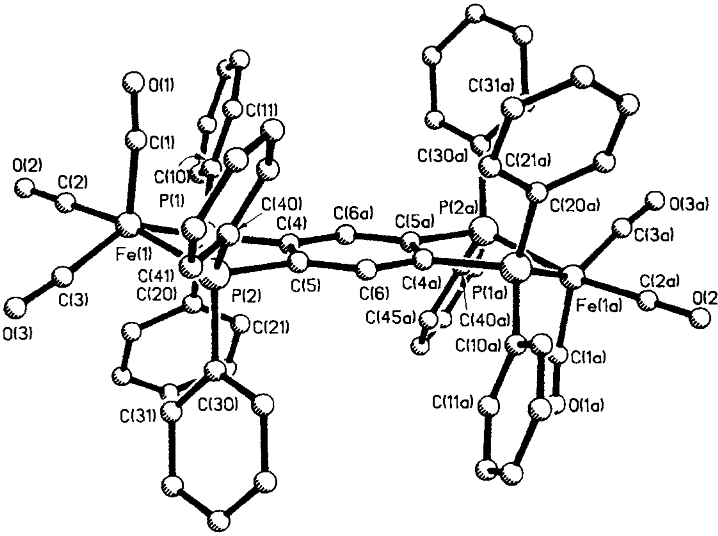

Fig. 1.

Table 3

Selected bond lengths (Å) and angles (°) in **2**

Fe(1)–P(1)	2.21092)	P(2)–C(5)	1.836(5)
Fe(1)–P(2)	2.223(2)	P(2)–C(30)	1.839(6)
Fe(1)–C(1)	1.776(7)	P(2)–C(40)	1.831(5)
Fe(1)–C(2)	1.759(7)	O(1)–C(1)	1.151(9)
Fe(1)–C(3)	1.774(6)	O(2)–C(2)	1.155(8)
P(1)–C(4)	1.833(5)	O(3)–C(3)	1.150(7)
P(1)–C(10)	1.837(6)	C(4)–C(5)	1.412(7)
P(1)–C(20)	1.845(6)	C(5)–C(6)	1.395(7)
P(1)–Fe(1)–P(2)	84.4(1)	Fe(1)–P(1)–C(4)	109.8(2)
P(1)–Fe(1)–C(1)	109.4(2)	Fe(1)–P(2)–C(5)	109.3(2)
P(2)–Fe(1)–C(1)	95.6(2)	P(1)–C(4)–C(5)	115.3(3)
P(1)–Fe(1)–C(2)	89.5(2)	P(2)–C(5)–C(4)	115.3(4)
P(2)–Fe(1)–C(2)	168.6(2)	P(1)–C(4)–C(6a)	119.5(4)
C(1)–Fe(1)–C(2)	95.593)	P(2)–C(5)–C(6)	125.0(4)
P(1)–Fe(1)–C(3)	138.7(2)	C(4)–C(5)–C(6)	119.7(4)
P(2)–Fe(1)–C(3)	89.7(2)	C(5)–C(6)–C(4a)	120.8(4)
C(1)–Fe(1)–C(3)	111.9(3)	C(5)–C(4)–C(6a)	119.5(4)
C(2)–Fe(1)–C(3)	88.6(3)		

This geometry is found for other small bite angle diphosphines bound to iron tricarbonyl units [3–5]. The P(1)–Fe(1)–P(2) bite angle in **2** of 84.5(1)° is similar to that found in the related complex $[Fe(CO)_3\{\eta^2\text{-}Ph_2PCH_2CH_2PPh_2\}]$ [3], as are the iron–phosphorus bond lengths [Fe(1)–P(1) 2.210(2); Fe(1)–P(2) 2.224(2) Å].

The free radical catalysed [6] reaction of ruthenium dodecacarbonyl with **1** initially gave a species identified as the trinuclear complex $[(CO)_{10}Ru_3\{\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ (**3**) on the basis of IR data. Thus, Deeming and co-workers have shown that for complexes of the type $[Os_3(CO)_{10}(\text{diphosphine})]$ in which the diphosphine may bridge two metal centres (1,2-isomer) or chelate a single metal (1,1-isomer), the nature of the diphosphine ligation can be easily ascertained from the infrared spectrum [7]. Significantly, the 1,1-isomers exhibit an absorption between 2060–2040 cm^{-1} which is absent in the 1,2-isomeric form. Similar detailed studies at the triruthenium centre are precluded due to the preference of diphosphines to adopt the 1,2-isomeric forms in which they span a metal–metal vector as exemplified by an X-ray crystallographic study of $[Ru_3(CO)_{10}(\mu\text{-}Ph_2CH_2CH_2PPh_2)]$ [8]. This latter molecule shows no absorptions between 2060–2040 cm^{-1} in its infrared spectrum. Thus, the observation of an absorption at 2046 cm^{-1} in **3** leads to our formulation of this complex as a bis-chelate (1,1-isomer).

Further attempts to characterise **3** were not successful since upon standing or chromatographic work up, cluster degradation led to the formation of $Ru_3(CO)_{12}$ and the new complex $[\{(CO)_3Ru\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-}(Ph_2P)_2C_6H_2(PPh_2)_2\}]$ (**4**) in 57% yield characterised by analytical and spectroscopic techniques. The facile degradation of the triruthenium framework in **3** is surprising since other $[Ru_3(CO)_{10}(\text{diphosphine})]$ complexes exhibit considerable stability. Thus for example, while both the bis(diphenylphosphino)ethane complexes $[Ru_3(CO)_{10}(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$ [8] and $[Ru(CO)_3(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)]$ [9] are both synthesised from ruthenium dodecarbonyl and the diphosphine, the formation of the latter via cluster degradation of the former has not been reported. Facile degradation of the trinuclear framework of **3** may be facilitated by the chelating nature of the tetraphosphine ligand.

These initial studies demonstrate the utility of the tetraphosphine ligand 1,2,4,5-tetrakis(diphenylphosphino)benzene (**1**) as a chelating ligand capable of bridging metal centres. We are currently investigating the application of complexes of this ligand towards the design of discrete transition metal "dimers" which may act as precursors towards new metal based oligomers and polymers.

Acknowledgements

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