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The reaction of cobalt powder with tetraiodo{1,2-bis(dibenzylphosphino)ethane} to form 1,2-bis(dibenzylphosphino)ethane cobalt diiodide, $Co(dBzP_2)I_2$; and the X-ray crystal structure of the diphosphinodioxide complex, $Co\{dBzP_2(O)_2\}I_2$

Peter T. Ndifon [a,*], Charles A. McAuliffe [b], Anthony G. Mackie [b], Robin G. Pritchard [b]

[a] *Department of Inorganic and Physical Chemistry, Faculty of Science, University of Yaoundé I, PO Box 812, Yaoundé, Cameroon*

[b] *Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, M60 1QD, UK*

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Abstract

The interaction of 1,2-bis(dibenzylphosphino)ethane, ($dBzP_2$) with diiodine in a 1:2 molar ratio leads to the isolation of tetraiodo-{1,2-bis(dibenzylphosphino)ethane}, ($dBzP_2I_4$) which readily reacts with coarse-grain cobalt powder to yield sky blue 1,2-bis(dibenzylphosphino)ethane cobalt diiodide, $Co(dBzP_2)I_2$. Exposure of a diethyl ether solution of $Co(dBzP_2)I_2$ to air yields crystals of 1,2-bis(dibenzylphosphinoyl)ethane cobalt diiodide, $Co\{dBzP_2(O)_2\}I_2$. The X-ray crystal structure of $Co\{dBzP_2(O)_2\}I_2$ reveals an infinite ribbon of the diphosphinedioxide-bridged cobalt(II) complex.

Keywords: Iodine complexes; Dibenzylphosphine; Diphosphorane complexes; Cobalt powder; Diphosphinodioxide complexes; Crystal structures; Cobalt complexes

1. Introduction

Tertiary phosphines have been known to react with dihalogens to form the 1:1 addition compounds, triorganophosphine dihalides [1–9]. The nature of these compounds has been studied mainly by electronic [2], vibrational [8,10], and ^{31}P NMR [5,11] spectroscopy and by conductimetry measurements [2,10], and recently some of these compounds have been characterised by single crystal X-ray techniques [5,8–11]. These studies have revealed some variety in the nature of these phosphoranes with some of the compounds having the ionic formulation, e.g. $[(PPh_3I)_2I_3]I_3$ [5], $[Bu_3^tPI]^+I^-$ [11], while others are molecular, examples of which include the five-coordinate bipyramidal configuration exemplified by Me_3PF_2 [6] and the four-coordinate arrangement involving the I–I (Ph_3PI–I) [8], or the Br–I (Ph_3PI–Br) [10] or the Br–Br (Ph_3PBr–Br) [9] interaction. More recent evidence from UV–Vis and FT-Raman spectra as well as conductimetry measurements show that these 1:1 addition compounds are charge-transfer adducts of the I^- donor with the Ph_3PI^+ acceptor, which dissociate on further addition of diiodine to give Ph_3PI^+ and I_3^- or I_5^- [12]. Although these phosphoranes, obtained from the interaction of monophosphines with dihalogens, are well documented, only a few diphosphoranes have been reported in the literature [11,13–15], e.g. Appel et al. [13] have reported the preparation of the tetrafluorophosphorane, $[(CH_3)_2F_2P$–$PF_2(CH_3)_2]$ from the reaction of hydrogen fluoride with bis(imidophosphorane).

We have recently reported the interaction of coarse-grain metal powders with triorganophosphorus dihalides, R_3PX_2 (X = I, Br), to form metal–tertiary phosphine complexes [16]. These reactions take place under very mild conditions and provide an alternative method for the preparation of metal–tertiary phosphine complexes. We have recently extended these studies to diphosphoranes derived from the interaction of dihalogens with diphosphines.

We wish to report here the synthesis of tetraiodo{1,2-bis(dibenzylphosphino)ethane} ($dBzP_2I_4$) and the subsequent reaction of this compound with cobalt powder to yield 1,2-bis(dibenzylphosphino)ethane cobalt diiodide, $Co(dBzP_2)I_2$. The X-ray crystal structure of the diphosphi-

* Corresponding author. E-mail: pndifon@uycdc.uninet.cm

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nedioxide complex $Co\{dBzP_2(O)_2\}I_2$, obtained from the oxidation of $Co(dBzP_2)I_2$, is also reported.

2. Results and discussion

The diphosphorane, $dBzP_2I_4$ was obtained in almost quantitative yield as a brown powder from a diethyl ether solution of 1,2-bis(dibenzylphosphine)ethane ($dBzP_2$) and diiodine in a 1:2 molar ratio. This compound is very sensitive to moisture and tends to decompose in air producing the phosphine oxide and other products. Once isolated, this adduct is very stable and can be stored indefinitely under dry inert conditions.

The $^{31}P\{H\}$ NMR spectrum of $dBzP_2I_4$ in $CDCl_3$ exhibits a single resonance at +59.9 ppm which represents a significant shift downfield (^{31}P NMR ($dBzP_2$) = −13.2 ppm). The electronic spectrum of this diphosphorane recorded as a 1,2-dichloroethane solution showed intense absorptions at $\lambda_{max} = 294$ and 362 nm (Fig. 1), suggesting the presence of the polyiodide ion, I_3^- in solution [2,17]. This and the observation of the single ^{31}P NMR peak at +59.9 ppm strongly suggest that $dBzP_2I_4$ in solution is a charge-transfer adduct formulated as $[(Bz_2)IP(CH_2)_2PI(Bz_2)]^{2+}2I_3^-$.

The observation of a strong Raman absorption in the solid state at 167 cm^{-1} assignable to the I–I bond [18] strongly suggests that this compound has a similar structure to that of the crystallographically characterised four-coordinate Ph_3PI–I, in which each phosphorus atom adopts a tetrahedral geometry, with diiodine bonded as a linear 'spoke' [8].

The reaction of $dBzP_2I_4$ with coarse-grain unactivated cobalt powder under strictly anhydrous conditions in diethyl ether in a sealed tube at 60°C produced 1,2-bis(dibenzylphosphino)ethane cobalt diiodide, $Co(dBzP_2)I_2$.

This reaction can be represented by

$$Co + dBzP_2I_4 \rightarrow Co(dBzP_2)I_2 + I_2 \quad (1)$$

The electronic spectrum of $Co(dBzP_2)I_2$ in 1,2-dichloroethane show a broad absorption at about 630 nm (Fig. 1), corresponding to the sky blue coloration of the cobalt(II) complex, (no peaks were observed at 294 and 362 nm).

We have recently shown that the reaction of coarse-grain metal powders with phosphoranes represents a new route to metal–tertiaryphosphine complexes. This reaction shows that unactivated cobalt powder can be oxidised by diphosphoranes under mild conditions in the same way as monophosphoranes, thus illustrating the high oxidising power of these phosphoranes.

After a diethyl ether solution of $Co(dBzP_2)I_2$ had been standing in air for 6 days, bright green crystals were observed. These crystals were analysed to be 1,2-bis(dibenzyphosphinoyl)ethane cobalt diiodide, $Co\{dBzP_2(O)_2\}I_2$. The IR spectrum of this compound showed absorptions at 1150 cm^{-1} assignable to the P=O stretch, indicating that the exposure of a solution of $Co(dBzP_2)I_2$ to air probably resulted in the oxidation of the phosphine ligands to yield $Co\{dBzP_2(O)_2\}I_2$ as reaction (2) illustrates:

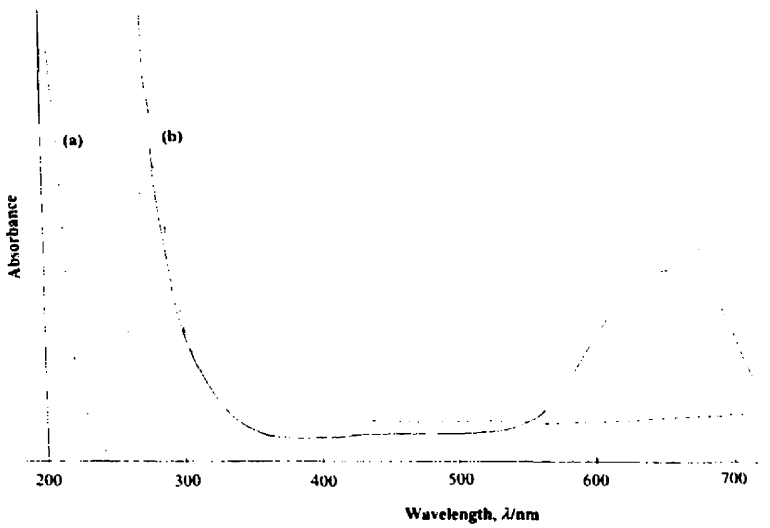

Fig. 1. Electronic spectra of (a) $dBzP_2I_4$ and (b) $Co(dBzP_2)I_2$.

We have recently shown that prolonged exposure of manganese(II)–tertiaryphosphine complexes to dioxygen results in the activation and splitting of dioxygen and the subsequent oxidation of the tertiaryphosphine ligand [19]. We think that the tertiaryphosphine in $Co(dBzP_2)I_2$ was probably oxidised in the same way as those in the manganese(II)–tertiaryphosphine complexes.

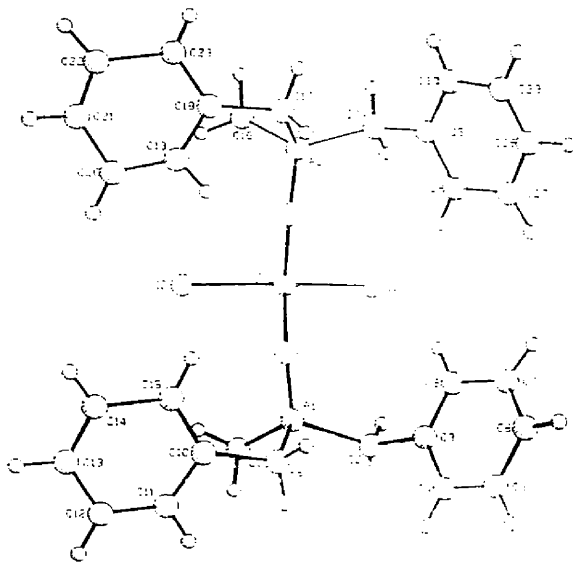

Fig. 2. The X-ray crystal structure of $Co\{dBzP_2(O)_2\}I_2$, including the labelling scheme. Hydrogen atoms are omitted for clarity.

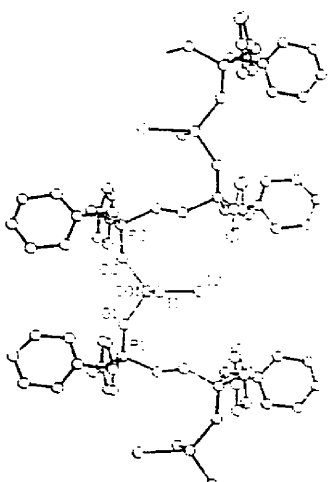

Fig. 3. Structure of $Co\{dBzP_2(O)_2\}I_2$, showing the polymeric arrangement of molecules. Hydrogen atoms omitted for clarity.

Table 1
Selected intramolecular and intermolecular bond distances (Å) and angles (°) involving the non-hydrogen atoms for $[Co\{dBzP_2(O)_2\}I_2]$

Intramolecular bond distances and angles			
I(1)–Co(1)	2.569(5)	C(4)–C(5)	1.39(4)
I(2)–Co(1)	2.618(5)	C(5)–C(6)	1.36(5)
Co(1)–O(1)	1.92(2)	C(6)–C(7)	1.34(5)
Co(1)–O(2)	1.96(2)	C(7)–C(8)	1.39(5)
P(1)–O(1)	1.49(2)	C(9)–C(10)	1.54(3)
P(1)–C(1)	1.76(3)	C(10)–C(11)	1.35(5)
P(1)–C(2)	1.82(3)	C(10)–C(15)	1.32(4)
P(1)–C(9)	1.82(3)	C(11)–C(12)	1.33(6)
P(2)–O(2)	1.53(2)	C(12)–C(13)	1.34(5)
P(2)–C(16)	1.79(3)	C(13)–C(14)	1.28(5)
P(2)–C(24)	1.78(3)	C(14)–C(15)	1.59(6)
C(1)–C(16)	1.54(3)		
C(2)–C(3)	1.49(3)		
C(3)–C(4)	1.36(4)		
C(3)–C(8)	1.33(8)		
I(1)–Co(1)–I(2)	109.0(2)	P(1)–C(1)–C(16)	116(2)
I(1)–Co(1)–O(1)	110.9(6)	P(1)–C(2)–C(3)	116(2)
I(1)–Co(1)–O(2)	111.9(7)	C(2)–C(3)–C(4)	117(3)
I(2)–Co(1)–O(1)	108.9(6)	C(2)–C(3)–C(8)	123(3)
I(2)–Co(1)–O(2)	111.7(7)	C(4)–C(3)–C(8)	120(3)
O(1)–Co(1)–O(2)	104.4(7)	C(4)–C(3)–C(5)	120(3)
O(1)–P(1)–C(1)	111(1)	C(4)–C(5)–C(6)	120(4)
O(1)–P(1)–C(2)	113(1)	C(5)–C(6)–C(7)	116(4)
O(1)–P(1)–C(9)	113(2)	C(6)–C(7)–C(8)	124(4)
C(1)–P(1)–C(2)	109(1)	C(3)–C(8)–C(7)	117(3)
C(1)–P(1)–C(9)	107(1)	P(1)–C(9)–C(10)	111(2)
C(2)–P(1)–C(9)	103(1)	C(9)–C(10)–C(11)	114(3)
O(2)–P(2)–C(16)	112(1)	C(9)–C(10)–C(15)	128(3)
O(2)–P(2)–C(17)	109(1)	C(11)–C(10)–C(15)	117(3)
O(2)–P(2)–C(24)	114(2)	C(10)–C(11)–C(12)	128(5)
C(16)–P(2)–C(17)	106(1)	C(11)–C(12)–C(13)	115(4)
C(16)–P(2)–C(24)	108(1)	C(12)–C(13)–C(14)	125(4)
C(17)–P(2)–C(24)	107(1)	C(13)–C(14)–C(15)	117(4)
Co(1)–O(1)–P(1)	143(1)	C(10)–C(15)–C(14)	116(3)
Co(1)–O(2)–P(2)	139(1)	P(2)–C(16)–C(1)	113(2)
Intermolecular bond distances			
P(2)–C(1)	2.78(3)		
O(2)–C(1)	3.45(4)		
C(3)–C(25)	3.55(4)		
C(6)–C(13)	3.60(5)		
C(7)–C(24)	3.54(5)		

3. The crystal structure of $Co\{dBzP_2(O)_2\}I_2$

The molecular structure of $Co\{(dBzP_2(O)_2\}I_2$ (with the following crystal data: molecular weight = 799.27; space group $P2_1/a$; crystal system = monoclinic; $a = 21.481(6)$, $b = 14.822(8)$, $c = 10.604(7)$ Å and $\beta = 103.98°$; (3); $V = 3276(5)$ Å^3; $Z = 4$; $D_{calc} = 1.602$ g cm^{-3}; $F(000) = 1564$, μ(Mo Kα) = 25.07 cm^{-1}, λ(Mo Kα) = 0.71069 Å) is shown in Fig. 2 together with the numbering scheme. Fig. 3 shows the arrangement of molecules in this compound. The structure has clearly been established as a polymeric cobalt(II) complex with the cobalt atoms linked together by bridging diphosphinedioxide ligands, $dBzP_2(O)_2$, forming a polymeric chain structure. Table 1 shows the intramolecular and intermolecular bond parameters. The bond angles at the

cobalt atom (I(1)–Co(1)–I(2) = 109.0(6), I(1)–Co(1)–O(1) = 110.9(6), I(2)–Co(1)–O(2) = 111.9(7), I(2)–Co(1)–O(1) = 108.9(6) and O(1)–Co(1)–O(2) = 104.4(7)°) are close to 109.5°, suggesting a tetrahedral arrangement of the ligands about each cobalt centre. The Co–I bond lengths of 2.569(5) and 2.618(5) Å, respectively, are identical to those found in other cobalt complexes containing terminal Co–I bonds [20]. The Co–O bond lengths (1.92(2) and 1.96(2) Å) are comparable with the value of 1.93(3) Å reported for other cobalt systems [21,22]. A similar diphosphine oxide-bridged cobalt(II) complex, $[(CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2)_2]$, has recently been reported by Nixons and co-workers [22], but in contrast with the ribbon-chain structure of $Co\{dBzP_2(O)_2\}I_2$, Nixon's bimetallic complex is bridged by two bis(phosphine oxide) ligands forming a 14-membered ring. The P–O bond lengths of 1.53(2) and 1.49(2) Å are slightly longer than those found for the above-mentioned bimetallic complex. These differences are probably caused by the different substituents on the bis(phosphine oxide) ligands. The carbon–carbon bond lengths in the phenyl rings range from 1.28(5) to 1.61(5) Å and these wide variations are probably due to some vibrations of these phenyl-ring carbon atoms. The benzyl substituents on each phosphorus atom have propeller conformations which tend to minimise steric effects.

4. Experimental

The diphosphorane $dBzP_2I_4$ is moisture sensitive, and strictly anhydrous conditions are employed for its syntheses; subsequent manipulations are carried out in an argon-filled glove box. Diethyl ether (BDH) was dried by standing over sodium wire overnight and subsequently refluxing over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. 1,2-Bis(dibenzylphosphino)ethane, ($dBzP_2$) was synthesised by standard Grignard techniques [23]. Iodine was used as obtained commercially (Aldrich Chemicals) without further purification. The diphosphorane $dBzP_2I_4$ was synthesised by dissolving 1,2-bis(dibenzylphosphino)-ethane (1.5 g, 3.30 mmol) in diethyl ether (ca. 90 ml), subsequently adding diiodine (1.68 g, 6.61 mmol) and stirring the mixture for about 6 days. The resulting brown solid was isolated by standard Schlenk techniques, dried in vacuo and stored in sealed argon-filled ampoules. *Anal.* Found: C, 37.1; H, 2.9; I, 53.2; P, 6.2. Calc.: C, 37.4; H, 3.3; I, 53.8; P, 6.4%.

1,2-Bis(dibenzylphospino)ethane cobalt diiodide, $Co(dBzP_2)I_2$, was synthesised by stirring a mixture of $dBzP_2I_4$ (1.0 g, 1.04 mmol) and cobalt powder (0.06 g, 1.02 mmol) in diethyl ether for about 10 days in a sealed tube at 60°C. The sky blue solid product was isolated by standard Schlenk techniques and dried in vacuo. *Anal.* Found: C, 46.5; H, 3.9; P, 7.9; Co, 7.4. Calc.: C, 46.9; H, 4.2; P, 8.1; Co, 7.7%.

The filtrate from $Co(dBzP_2)I_2$ was left to stand in air, and after 6 days blue crystals were observed to have formed on the sides of the flask. Analyses showed these crystals to be $Co\{dBzP_2(O)_2\}I_2$. *Anal.* Found: C, 44.4; H, 3.9; I, 30.8; P, 7.1; Co, 7.1. Calc.: C, 45.1; H, 4.0; I, 31.8; P, 7.7; Co, 7.4%.

Elemental analyses were performed by the Analytical Laboratory of the Department of Chemistry, University of Manchester, Institute of Science and Technology. Raman spectra were recorded by the University of Manchester, Raman Service. $^{31}P\{H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Brucker AC200 high resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard. Electronic spectra were recorded as 1,2-dichloroethane solutions on a Varian Cary 210 spectrophotometer.

5. X-ray crystal diffraction studies

A crystal of $Co\{(dBzP_2(O)_2\}I_2$, $I_2H_{32}P_2O_2CoC_{30}$, with approximate dimensions of $0.200 \times 0.200 \times 0.100$ mm, was mounted on glass fibre. All measurements were made on a Rigaku AFC6S diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The cell constants were obtained from full-matrix least-squares refinement using the setting angles of 19 carefully centred reflections in the range $15.42 < 2\theta < 25.38°$. The data were collected at 23°C using ω–2θ scan technique to a maximum 2θ value of 45.1°. Scans of (1.63 to 0.30 tan θ)° were made at a speed of 2.0° min^{-1}. Of the 4644 reflections measured, 4507 were unique ($R_{int} = 0.095$). The intensities of three representative reflections measured after every 150 reflections declined by 9.10% and this phenomenon was taken into account by applying a linear correction factor. The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods [24]. The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement based on 1471 observed reflections ($I > 4.00\sigma(I)$) and 174 variable parameters gave $R = 0.072$ ($R_w = 0.090$). All calculations were performed using the TEXSAN crystallographic software package [25].

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