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# Coordination chemistry of bis(3-aminopropyl)phenylphosphine (bap): reactions of bap with some $d^6$ metal complexes of molybdenum(0), tungsten(0) and platinum(IV)

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## Abstract

Bis(3-aminopropyl)phenylphosphine (bap) has been reacted with *fac*-[$\{PtMe_3I\}_4$] in $CHCl_3$ solution to yield *fac*-[$PtMe_3$(bap)]I which has the bap ligand tridentate NNP. Metathesis of *fac*-[$PtMe_3$(bap)]I with Na[$BPh_4$] in thf solution results in *fac*-[$PtMe_3$(bap)][$BPh_4$]. Bap is also NNP tridentate in the Group 6 metal(0) complexes *fac*-[$Mo(CO)_3$(bap)] and *fac*-[$W(CO)_3$(bap)], prepared from the reactions of bap with *cis*-[$M(CO)_4(pip)_2$] (M = Mo, W). The new complexes have been characterized by melting point, elemental analysis, and by IR and multielement ($^1H$, $^{11}B$, $^{31}P$) NMR spectroscopy.

## Introduction

The coordination chemistry of linear multidentate ligands containing PPP or NNN donor atoms such as bis(2-diphenylphosphinoethyl)phenylphosphine, $(Ph_2PCH_2CH_2)_2PPh$, or triethylenetriamine, $(NH_2CH_2CH_2)_2NH$ is thoroughly documented [1–4]. The ligand $(Ph_2PCH_2CH_2)_2PPh$ displays versatility in the way in which it coordinates to a metal centre and a number of possibilities have been encountered, e.g. bidentate in [$M(CO)_4\{(Ph_2PCH_2CH_2)_2PPh\}$] (M = Cr, Mo) and tridentate in [$M(CO)_3\{Ph_2PCH_2CH_2)_2PPh\}$] (M = Cr, Mo, W) [5, 6]. In contrast, the coordination chemistry of the related mixed NNP donor ligand, bis(3-aminopropyl)phenylphosphine ($(NH_2CH_2CH_2CH_2)_2PPh$, bap) has not been explored, and various coordination modes for this ligand can be envisaged. Thus bap could potentially act as (i) a monodentate P or N donor ligand, (ii) a bidentate NN or NP donor ligand, or (iii) as a tridentate NNP donor ligand. Bap has been prepared in a high yield synthesis by the photolytically induced free-radical reaction of phenylphosphine with two equivalents of allylamine [7] and is now commercially available. This paper investigates the reactions of bap with some $d^6$ metal complexes in attempts to determine which of the three coordination modes described above is the most favourable for this ligand.

## Experimental

### General

Reactions were carried out using standard Schlenk conditions under $N_2$ and all solvents were dried and distilled before use. Bis(3-aminopropyl)phenylphosphine (bap), $K_2[PtCl_6]$, [$W(CO)_6$], [$Mo(CO)_6$] and Na[$BPh_4$] were obtained from commercial sources and used without further purification. *fac*-[$\{PtMe_3I\}_4$] was prepared by a standard literature method [8]. *cis*-[$M(CO)_4(pip)_2$] (M = Mo, W) were prepared by a modification of a literature method [9] as detailed below. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrophotometer as nujol mulls, and elemental analyses (C, H and N) were determined using a Carlo Erba elemental analyser MOD 1106 (using He carrier gas). Multielement NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250 MHz for $^1H$, 62.8 MHz for $^{13}C$, 80.25 MHz for $^{11}B$ and 101.2 MHz for $^{31}P$. Chemical shifts ($\delta$) are given in ppm with positive values at high frequency (low field) from $SiMe_4$ for $^1H$ and $^{13}C$, from 85% $H_3PO_4$ for $^{31}P$, and from $BF_3\cdot OEt_2$ for $^{11}B$. NMR spectra were obtained on samples dissolved in $CDCl_3$ or $CD_3COCD_3$.

### Preparation of fac-[$PtMe_3$(bap)]I (1)

The trimethylplatinum iodide tetramer *fac*-[$\{PtMe_3I\}_4$] (0.367 g, 0.25 mmol) was dissolved in $CHCl_3$ (5 $cm^3$) under an $N_2$ atmosphere. To this

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solution was added dropwise, and with stirring, $PhP(CH_2CH_2CH_2NH_2)_2$ (bap) (0.224 g, 1.0 mmol). The reaction mixture was warmed to 50 °C for 5 min whereupon a thick white precipitate formed. The white solid was filtered and washed with 40–60 °C petroleum ether and dried *in vacuo* to yield analytically pure **1** (0.478 g, 81%); m.p. 210–213 °C. *Anal.* Calc. for $C_{15}H_{30}IN_2PPt$: C, 30.5; H, 5.1; N, 4.7. Found: C, 30.3; H, 5.3: N, 4.4%.

### *Preparation of fac-[PtMe$_3$(bap)][BPh$_4$] (2)*

Na[$BPh_4$] (0.070 g, 0.2 mmol) was dissolved in dry thf (5 $cm^3$) under a flow of $N_2$. The crude platinum complex *fac*-[$PtMe_3$(bap)]I (0.120 g, 0.2 mmol), used as prepared above, was added to this thf solution and the suspension was stirred for 24 h at room temperature. After this period the solution was filtered, to remove insoluble NaI (0.030 g, 0.2 mmol), and the filtrate was evaporated to dryness to yield a pale yellow solid (**2**, 0.150 g, 97%). The product was recrystallized from thf/40–60 °C petroleum ether as pale yellow plates; m.p. 185–190 °C (dec).). *Anal.* Calc. for $C_{39}H_{50}BN_2PPt$: C, 59.5; H, 6.9; N, 3.6. Found: C, 60.0; H, 6.7; N, 3.5%. NMR data are given in Table 1.

### *Preparation of cis-[Mo(CO)$_4$(pip)$_2$] and cis-[W(CO)$_4$(pip)$_2$].*

The reported method [9] was used, with minor changes for solvent. Thus, [$M(CO)_6$] (M=Mo, W; 1.0 g) was dissolved in benzene (50 $cm^3$) with piperidine (10 $cm^3$) and the reaction solution was refluxed under nitrogen. The product precipitated out of the refluxing solutions (after 2 h for Mo, after 48 h for W) as an analytically pure microcrystalline yellow solid which was separated by hot filtration, washed with cold benzene followed by cold petroleum ether, and then finally dried *in vacuo*. Yields of 71% and 90% were obtained for *cis*-[$Mo(CO)_4(pip)_2$] and *cis*-[$W(CO)_4(pip)_2$], respectively.

### *Preparation of fac-[Mo(CO)$_3$(bap)] (3)*

*cis*-[$Mo(CO)_4(pip)_2$] (0.50 g, 1.3 mmol) was dissolved in deoxygenated $CH_2Cl_2$ (20 $cm^3$) and the bap ligand (0.30 g, 1.3 mmol) was added under a stream of $N_2$. The reaction mixture was stirred for 2 h and the solvent was removed under vacuum to leave a yellow solid which was recrystallized as pale yellow crystals (0.42 g, 81%), m.p. 110 °C, from $CH_2Cl_2$/60–80 °C petroleum ether by leaving the layered solution at 5 °C overnight. *Anal.* Calc. for $C_{15}H_{21}N_2O_3MoP$: C, 44.5; H, 5.2; N, 6.9. Found: C, 44.5; H, 5.4; N, 6.8%. IR ($cm^{-1}$) $\nu$(CO) at 2012 (sharp,m), 1892(s), 1837(m); $\nu(NH_2)$ 3305(sharp,w); other bands (weak) 1582, 1073, 982, 890, 844, 747, 696. NMR data are given in Table 1.

TABLE 1. NMR data for bap, *fac*-[$PtMe_3$(bap)] [$BPh_4$] and *fac*-[$M(CO)_3$(bap)] (M=Mo, W)

| | |
|---|---|
| bap[a] | ($CDCl_3$ solution, 25 °C, ppm)<br>$\delta$ ($^1$H): 1.15s, 4H, ($NH_2$), 1.47m, 4H, ($CH_2$), 1.66m, 4H, ($CH_2P$), 2.66t, 4H, ($CH_2N$), 7.28m, 2H, 7.48m, 3H, (PhP)<br>$\delta$ ($^{31}$P): $-25.0$<br>$\delta$ ($^{13}$C): 25.9, 30.3.43.7, (3$CH_2$), 128.9, 129.1, 132.9, 138.8, ($C_6H_5P$) |
| | ($CD_3COCD_3$ solution, 25 °C, ppm)<br>$\delta$ ($^1$H): 1.59m, 4H, ($CH_2$), 1.76m, 4H, ($CH_2P$), 3.13s, 4H, ($NH_2$), 3.24t, 4H, ($CH_2N$), 7.39m, 3H, 7.59m, 2H, (PhP)<br>$\delta$ ($^{31}$P): $-25.3$ |
| *fac*-[$PtMe_3$(bap)] [$BPh_4$] | ($CD_3COCD_3$ solution, 50 °C, ppm)<br>$\delta$ ($^1$H): 0.47, dt, $^2J(^1H^{195}Pt)$ 51.9 Hz, $^3J(^1H^{31}P)$ 7.2 Hz, 3H, (Me–Pt *trans* P), 0.48, dt, $^2J(^1H^{195}Pt)$ 68.3 Hz, $^3J(^1H^{31}P)$ 7.3 Hz, 6H, (Me–Pt *trans* N); 1.75, m, 4H, 1.95, m, 4H, 2.55, m, 4H, (6$CH_2$); 2.30, s, 4H, ($NH_2$); 6.9–7.8, m, 25H, (PhP, 4PhB)<br>$\delta$ ($^{31}$P): $-30.9$, $^1J$ ($^{31}P^{195}Pt$) 1304 Hz<br>$\delta$ ($^{11}$B): $-6.8$ |
| *fac*-[$Mo(CO)_3$(bap)] | ($CDCl_3$ solution, 25 °C, ppm)<br>$\delta$ ($^1$H): 1.2s, 4H ($NH_2$), 1.64m, 4H, 2.05m, 4H, 2.75m, 4H, (6 $CH_2$), 7.26–7.81m, 5H, (PhP)<br>$\delta$ ($^{31}$P): $+12.8$ |
| *fac*-[$W(CO)_3$(bap)] | ($CDCl_3$ solution, 25 °C, ppm)<br>$\delta$ ($^1$H): 1.05s, 4H, ($NH_2$), 1.55m, 4H, 2.30m, 4H, 2.9m, 4H, (6 $CH_2$), 7.3–7.6m, 5H (PhP)<br>$\delta$ ($^{31}$P): $-0.2$, $^1J(^{183}W–^{31}P)$ 233 Hz |

[a] Lit. values [1], ($C_6D_6$, r.t., ppm): $\delta$ ($^1$H): 1.01 ($NH_2$), 1.58, 2.50, 2.62 (3$CH_2$), 7.4(Ph); $\delta$ ($^{31}$P): $-25.6$.

*Preparation of fac-[W(CO)$_3$(bap)] (4)*

Prepared in a similar manner to that described above for **3** (refluxed in $CH_2Cl_2$ for 2 h) as a pale yellow solid in 40% yield; m.p. 67 °C. *Anal.* Calc. for $C_{15}H_{21}N_2O_3PW$: C, 36.7; H, 4.5; N, 5.7. Found: C, 36.6; H, 4.8; N, 5.9%. IR (cm$^{-1}$): $\nu$(CO) at 2007(sharp,m), 1875(s), 1834(m); $\nu$($NH_2$) 3345(sharp,w); other bands (weak) 1579, 1157, 743, 697. NMR data are given in Table 1.

## Results and discussion

In order to gain an insight into the preferred coordination mode of bap, reactions of it with transition metal complexes which could accept the ligand in either a bidentate or tridentate fashion were tried.

Reactions of *fac*-[{$PtMe_3I$}$_4$] with Lewis bases usually lead to the cleavage of the iodide bridges of the tetramer, and either monometallic *fac*-[$PtMe_3IL_2$] complexes result in which an iodide ligand is retained within the coordination sphere of the platinum(IV) centre, or *fac*-[$PtMe_3L_3$]I complexes are formed in which the iodide ligand is also displaced [10]. Thus, for example, reactions of *fac*-[{$PtMe_3I$}$_4$] with $NH_3$, bipy or NaCp result in the *fac* complexes [$PtMe_3(NH_3)_3$]I, [$PtMe_3$(bipy)I] and [$PtMe_3$Cp], respectively [11–13]. The possibility that bap could act as a bidentate NN donor or as a tridentate NNP donor has lead us to react 4 equiv. of bap with the *fac*-[{$PtMe_3I$}$_4$] tetramer.

A white coloured precipitate is formed, in excellent yield, after a few minutes warming of a $CHCl_3$ solution of *fac*-[{$PtMe_3I$}$_4$] with 4 equiv. of bap (eqn. (1)). This white solid (compound **1**), which gave satisfactory elemental analysis results for '$PtMe_3$(bap)I', was found to be insoluble in water and in organic solvents. Solution NMR and conductivity data could not be obtained for **1** and in the absence of these data it is difficult to decide between a neutral bidentate *fac*-[$PtMe_3$(bap)I] or an ionic tridentate *fac*-[$PtMe_3$(bap)]I formulation. However, we tentatively formulate compound **1** as the latter on the basis of its subsequent metathesis reaction with Na[$BPh_4$] which produces the pale yellow anion-exchanged product *fac*-[$PtMe_3$(bap)][$BPh_4$] (**2**) in essentially quantitative yield (eqn. (2)). Fortunately, compound **2** is much more soluble than **1** in organic solvents and its identity has been determined from NMR studies and elemental analysis. The $^{11}$B spectra of **2** is consistent with its ionic formulation, *fac*-[$PtMe_3$(bap)][$Ph_4B$], and shows a signal at a chemical shift in the range characteristic of the tetraphenylborate anion [14]. The structures of the cations of **1** and **2** are shown schematically in Fig. 1.

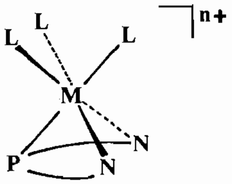

Fig. 1. Schematic drawing of the coordination sphere of the metal in the tridentate bis(3-aminopropyl)phenylphosphine (bap) complexes: M = Pt(IV), L+$CH_3^-$, n = 1 (**1**, **2**); M = Mo(0), L = CO, *n* = 0 (**3**); M = W(0), L = CO, *n* = 0 (**4**).

$$fac\text{-}[\{PtMe_3I\}_4] + 4bap \longrightarrow 4fac\text{-}[PtMe_3(bap)]I \qquad (1)$$

(**1**, 81%)

$$fac\text{-}[PtMe_3(bap)]I + Na[BPh_4] \longrightarrow fac\text{-}[PtMe_3(bap)][BPh_4] + NaI \qquad (2)$$

(**2**, 97%)

The tridentate nature of bap in **2** is clearly shown from multielement NMR studies. The $^{31}P\{^1H\}$ spectrum of **2** shows one central signal (with associated $^{195}$Pt satellites) at a chemical shift slightly upfield from that of the free ligand. The magnitude of $^1J(^{31}P–^{195}Pt)$ coupling, 1304 Hz, is consistent with a P donor ligand coordinated to platinum(IV) *trans* to a methyl group [15]. The $^1$H spectrum of **2** is also informative, with the Pt–*Me* region showing two signals of relative intensity 2:1, both coupled to $^{195}$Pt, with the more intense resonance showing the largest $^2J(^1H–^{195}Pt)$ coupling, consistent with these two methyl groups being *trans* to N [16, 17]. Further coupling of *c*. 7.2 Hz, $^3J(^{31}P–^1H)$, is also observed for both of the Pt–*Me* signals and 12 lines are clearly distinguished in this spectral region (Fig. 2).

The bap ligand was also reacted with one equivalent of *cis*-[M(CO)$_4$(pip)$_2$] (M = MO, W) to determine its preferred mode of coordination in this system. *cis*-[M(CO)$_4$(pip)$_2$] complexes have labile piperidine ligands which are easily displaced [9].

The reaction of bap with *cis*-[Mo(CO)$_4$(pip)$_2$] in $CH_2Cl_2$ solution proceeds rapidly and is complete within 2 h at room temperature (eqn. (3)). The reaction product, *fac*-[Mo(CO)$_3$(bap)] (**3**), in which a CO ligand and two piperidine ligands have been displaced from the coordination sphere of the metal by the bap ligand, was isolated in high yield (81%) and was characterized by $^{31}$P NMR, IR and elemental analysis. An analogous reaction was observed for *cis*-[W(CO)$_4$(pip)$_2$] but reflux conditions were necessary and the yield of the product, *fac*-[W(CO)$_3$(bap)] (**4**), was lower (40%).

The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** each show one signal (with associated $^{183}$W satellites for **4**)

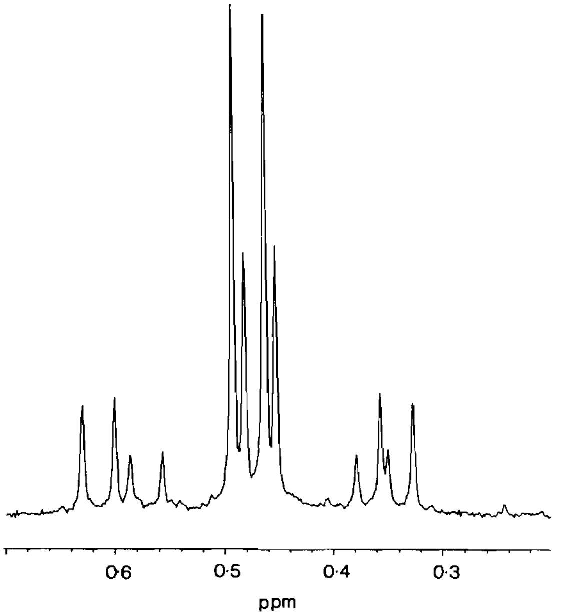

Fig. 2. Pt–methyl region of the 250 MHz $^1$H spectrum of *fac*-[PtMe$_3$(bap)][BPh$_4$] (2) in CD$_3$COCD$_3$ solution at 50 °C.

shifted downfield by *c.* 30 ppm from the free ligand value. These downfield shifts in the $^{31}$P{$^1$H} spectra of **3** and **4** indicate coordination to the metal centre of the phosphorus atom of the bap ligand since in the related bidentate compound [W(CO)$_4$-{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh}] the chemical shift of the uncoordinated phosphorus remains virtually unchanged whilst the coordinated phosphorus atoms are shifted downfield by a similar magnitude to those seen for **3** and **4** [6]. The structures of the neutral species **3** and **4** are shown schematically in Fig. 1.

$$\textit{cis}\text{-}[\mathrm{M(CO)_4(pip)_2}] + \mathrm{bap} \longrightarrow$$

$$\textit{fac}\text{-}[\mathrm{M(CO)_3(bap)}] + 2\mathrm{pip} + \mathrm{CO} \quad (3)$$

$$(\mathrm{M} = \mathrm{Mo}\ (\mathbf{3})\ 80\%;$$

$$\mathrm{W}\ (\mathbf{4})\ 40\%)$$

Tricarbonyl structures, rather than tetracarbonyl species, for compounds **3** and **4** are clearly indicated from the elemental analysis data and from their IR spectra which show three absorption bands of a general intensity and shape commonly found in tricarbonyl species of $C_s$ symmetry [18, 19]. For complex **3**, the carbonyl stretching frequencies (cm$^{-1}$) are between those reported for the related NNN [Mo(CO)$_3${(NH$_2$CH$_2$CH$_2$)$_2$NH]} and PPP [Mo(CO)$_3$-{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh}] complexes with the stretching frequencies being closer to those for the NNN complex [6, 20] indicating the overall electron donating nature of the tridentate NNP bap ligand. The formation of tricarbonyl containing products under these mild conditions, rather than the tetracarbonyl products, would indicate a strong preference for the bap ligand to be a tridentate NNP donor, as was also shown to be the case for the Pt(IV) reactions.

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