

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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(Received May 21, 1991; revised July 16, 1991)

Abstract

Bis(3-aminopropyl)phenylphosphine (bap) has been reacted with $fac\text{-}[\{PtMe_3I\}_4]$ in $CHCl_3$ solution to yield $fac\text{-}[PtMe_3(bap)]I$ which has the bap ligand tridentate NNP. Metathesis of $fac\text{-}[PtMe_3(bap)]I$ with $Na[BPh_4]$ in thf solution results in $fac\text{-}[PtMe_3(bap)][BPh_4]$. Bap is also NNP tridentate in the Group 6 metal(0) complexes $fac\text{-}[Mo(CO)_3(bap)]$ and $fac\text{-}[W(CO)_3(bap)]$, prepared from the reactions of bap with $cis\text{-}[M(CO)_4(pip)_2]$ ($M=Mo, W$). 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, $(NH_2CH_2CH_2)_3NH$ 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. $fac\text{-}[\{PtMe_3I\}_4]$ was prepared by a standard literature method [8]. $cis\text{-}[M(CO)_4(pip)_2]$ ($M=Mo, W$) 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 (δ) 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 $fac\text{-}[PtMe_3(bap)]I$ (1)

The trimethylplatinum iodide tetramer $fac\text{-}[\{PtMe_3I\}_4]$ (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(CH₂CH₂CH₂NH₂)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 C₁₅H₃₀IN₂PtP: C, 30.5; H, 5.1; N, 4.7. Found: C, 30.3; H, 5.3; N, 4.4%.

Preparation of fac-[PtMe₃(bap)][BPh₄] (2)

Na[BPh₄] (0.070 g, 0.2 mmol) was dissolved in dry thf (5 cm³) under a flow of N₂. The crude platinum complex *fac*-[PtMe₃(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 C₃₉H₅₀BN₂PtP: 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 cm³) with piperidine (10 cm³) 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 CH₂Cl₂ (20 cm³) and the bap ligand (0.30 g, 1.3 mmol) was added under a stream of N₂. 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 CH₂Cl₂/60–80 °C petroleum ether by leaving the layered solution at 5 °C overnight. *Anal.* Calc. for C₁₅H₂₁N₂O₃MoP: C, 44.5; H, 5.2; N, 6.9. Found: C, 44.5; H, 5.4; N, 6.8%. IR (cm⁻¹) ν (CO) at 2012 (sharp,m), 1892(s), 1837(m); ν (NH₂) 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*-[PtMe₃(bap)] [BPh₄] and *fac*-[M(CO)₃(bap)] (M=Mo, W)

bap ^a	(CDCl ₃ solution, 25 °C, ppm) δ (¹ H): 1.15s, 4H, (NH ₂), 1.47m, 4H, (CH ₂), 1.66m, 4H, (CH ₂ P), 2.66t, 4H, (CH ₂ N), 7.28m, 2H, 7.48m, 3H, (PhP) δ (³¹ P): -25.0 δ (¹³ C): 25.9, 30.3, 43.7, (3CH ₂), 128.9, 129.1, 132.9, 138.8, (C ₆ H ₅ P) (CD ₃ COCD ₃ solution, 25 °C, ppm) δ (¹ H): 1.59m, 4H, (CH ₂), 1.76m, 4H, (CH ₂ P), 3.13s, 4H, (NH ₂), 3.24t, 4H, (CH ₂ N), 7.39m, 3H, 7.59m, 2H, (PhP) δ (³¹ P): -25.3
<i>fac</i> -[PtMe ₃ (bap)] [BPh ₄]	(CD ₃ COCD ₃ solution, 50 °C, ppm) δ (¹ H): 0.47, dt, ² <i>J</i> (¹ H ¹⁹⁵ Pt) 51.9 Hz, ³ <i>J</i> (¹ H ³¹ P) 7.2 Hz, 3H, (Me–Pt <i>trans</i> P), 0.48, dt, ² <i>J</i> (¹ H ¹⁹⁵ Pt) 68.3 Hz, ³ <i>J</i> (¹ H ³¹ P) 7.3 Hz, 6H, (Me–Pt <i>trans</i> N); 1.75, m, 4H, 1.95, m, 4H, 2.55, m, 4H, (6CH ₂); 2.30, s, 4H, (NH ₂); 6.9–7.8, m, 25H, (PhP, 4PhB) δ (³¹ P): -30.9, ¹ <i>J</i> (³¹ P ¹⁹⁵ Pt) 1304 Hz δ (¹¹ B): -6.8
<i>fac</i> -[Mo(CO) ₃ (bap)]	(CDCl ₃ solution, 25 °C, ppm) δ (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) δ (³¹ P): +12.8
<i>fac</i> -[W(CO) ₃ (bap)]	(CDCl ₃ solution, 25 °C, ppm) δ (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) δ (³¹ P): -0.2, ¹ <i>J</i> (¹⁸³ W– ³¹ P) 233 Hz

^a Lit. values [1], (C₆D₆, r.t., ppm): δ (¹H): 1.01 (NH₂), 1.58, 2.50, 2.62 (3CH₂), 7.4(Ph); δ (³¹P): -25.6.

Preparation of *fac*-[W(CO)₃(bap)] (4)

Prepared in a similar manner to that described above for 3 (refluxed in CH₂Cl₂ for 2 h) as a pale yellow solid in 40% yield; m.p. 67 °C. *Anal.* Calc. for C₁₅H₂₁N₂O₃PW: C, 36.7; H, 4.5; N, 5.7. Found: C, 36.6; H, 4.8; N, 5.9%. IR (cm⁻¹): $\nu(\text{CO})$ at 2007(sharp,m), 1875(s), 1834(m); $\nu(\text{NH}_2)$ 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*-[PtMe₃I]₄ with Lewis bases usually lead to the cleavage of the iodide bridges of the tetramer, and either monometallic *fac*-[PtMe₃IL₂] complexes result in which an iodide ligand is retained within the coordination sphere of the platinum(IV) centre, or *fac*-[PtMe₃L₃]I complexes are formed in which the iodide ligand is also displaced [10]. Thus, for example, reactions of *fac*-[PtMe₃I]₄ with NH₃, bipy or NaCp result in the *fac* complexes [PtMe₃(NH₃)₃]I, [PtMe₃(bipy)]I and [PtMe₃Cp], 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*-[PtMe₃I]₄ tetramer.

A white coloured precipitate is formed, in excellent yield, after a few minutes warming of a CHCl₃ solution of *fac*-[PtMe₃I]₄ with 4 equiv. of bap (eqn. (1)). This white solid (compound 1), which gave satisfactory elemental analysis results for 'PtMe₃(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*-[PtMe₃(bap)]I or an ionic tridentate *fac*-[PtMe₃(bap)]I formulation. However, we tentatively formulate compound 1 as the latter on the basis of its subsequent metathesis reaction with Na[BPh₄] which produces the pale yellow anion-exchanged product *fac*-[PtMe₃(bap)][BPh₄] (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 ¹¹B spectra of 2 is consistent with its ionic formulation, *fac*-[PtMe₃(bap)][Ph₄B], 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.

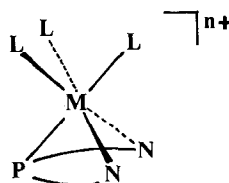
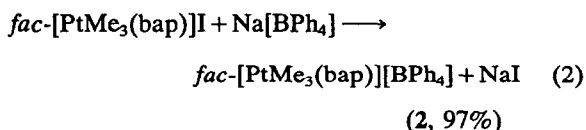
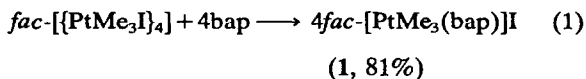


Fig. 1. Schematic drawing of the coordination sphere of the metal in the tridentate bis(3-aminopropyl)phenylphosphine (bap) complexes: M = Pt(IV), L = CH₃⁻, n = 1 (1, 2); M = Mo(0), L = CO, n = 0 (3); M = W(0), L = CO, n = 0 (4).



The tridentate nature of bap in 2 is clearly shown from multielement NMR studies. The ³¹P{¹H} spectrum of 2 shows one central signal (with associated ¹⁹⁵Pt satellites) at a chemical shift slightly upfield from that of the free ligand. The magnitude of ¹J(³¹P–¹⁹⁵Pt) coupling, 1304 Hz, is consistent with a P donor ligand coordinated to platinum(IV) *trans* to a methyl group [15]. The ¹H spectrum of 2 is also informative, with the Pt–Me region showing two signals of relative intensity 2:1, both coupled to ¹⁹⁵Pt, with the more intense resonance showing the largest ²J(¹H–¹⁹⁵Pt) coupling, consistent with these two methyl groups being *trans* to N [16, 17]. Further coupling of c. 7.2 Hz, ³J(³¹P–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 CH₂Cl₂ 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 ³¹P 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 ³¹P{¹H} NMR spectra of 3 and 4 each show one signal (with associated ¹⁸³W satellites for 4)

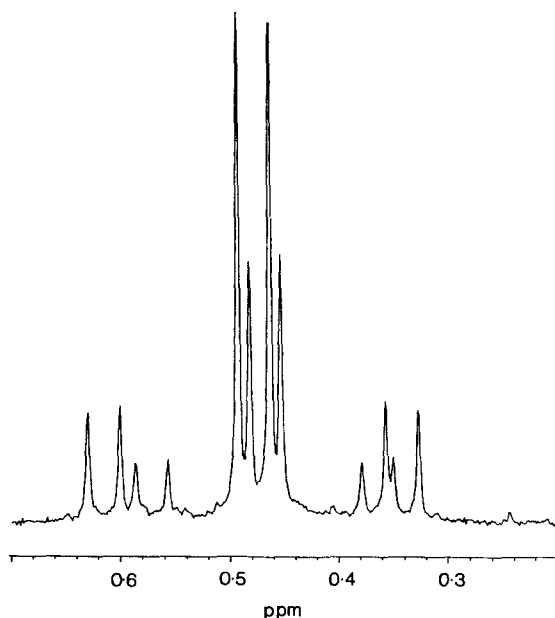
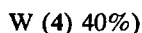
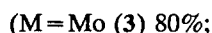
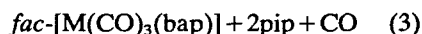


Fig. 2. Pt-methyl region of the 250 MHz ^1H spectrum of $\text{fac-}[\text{PtMe}_3(\text{bap})][\text{BPh}_4]$ (2) in CD_3COCD_3 solution at 50°C .

shifted downfield by *c.* 30 ppm from the free ligand value. These downfield shifts in the $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{W}(\text{CO})_4\text{-}\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}\}]$ 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.



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 $[\text{Mo}(\text{CO})_3\{(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}\}]$ and PPP $[\text{Mo}(\text{CO})_3\text{-}$

$\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}\}]$ 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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