

Contribution from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia, and Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001

Ruthenium(II) Complexes of the C_{3v} Ligands Tris(2-pyridyl)amine, Tris(2-pyridyl)methane, and Tris(2-pyridyl)phosphine. 1. Synthesis and X-ray Structural Studies of the Bis(ligand) Complexes

F. Richard Keene,*¹ Michael R. Snow,² Philip J. Stephenson,¹ and Edward R. T. Tiekink²

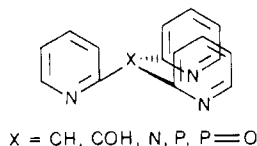
Received November 25, 1987

Bis(ligand)ruthenium(II) complexes [ligand = tris(2-pyridyl)amine, tris(2-pyridyl)methane, and tris(2-pyridyl)phosphine] were synthesized by the reaction of $[\text{Ru}(\text{DMF})_6]^{2+}$ (DMF = *N,N*-dimethylformamide) with excess of the respective ligands under anaerobic conditions in propan-1-ol solution. Crystals of $[\text{Ru}\{(\text{2-py})_3\text{CH}_2\}(\text{tosylate})_2 \cdot \text{H}_2\text{O}$ (**1**) crystallize in the monoclinic space group $C2/c$ with unit cell dimensions $a = 13.205$ (9) Å, $b = 13.437$ (6) Å, $c = 23.614$ (22) Å, $\beta = 96.57$ (6)°, $V = 4162.5$ Å³, and $Z = 4$; crystals of $[\text{Ru}\{(\text{2-py})_3\text{P}\}_2](\text{tosylate})_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**2**) are also monoclinic ($P2_1/c$) with $a = 10.065$ (7) Å, $b = 13.008$ (4) Å, $c = 34.772$ (22) Å, $\beta = 92.40$ (5)°, $V = 4548.6$ Å³, and $Z = 4$. $[\text{Ru}\{(\text{2-py})_3\text{N}\}_2](\text{S}_2\text{O}_8) \cdot 4\text{H}_2\text{O}$ (**3**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.914$ (3) Å, $b = 9.060$ (2) Å, $c = 11.243$ (2) Å, $\alpha = 95.52$ (1)°, $\beta = 104.19$ (2)°, $\gamma = 92.03$ (2)°, $V = 874.6$ Å³, and $Z = 1$. The structures were refined by a full-matrix least-squares procedure in each case. At convergence, final $R = 0.050$, $R_w = 0.055$ for 2931 reflections with $I \geq 2.5\sigma(I)$ for **1**, $R = 0.063$, $R_w = 0.065$ for 2017 reflections for **2**, $R = 0.039$, $R_w = 0.041$ for 2582 reflections for **3**. The cations show increasing distortion in the structure from ideal D_{3d} symmetry with an increase in the bridgehead (X)-C(py) bond distance.

Introduction

There has been considerable interest in the ruthenium^{3,4} and rhenium⁵⁻⁷ complexes containing polypyridyl ligands such as 2,2'-bipyridyl and 1,10-phenanthroline, primarily because of their potential as photosensitizers in significant processes such as water or carbon dioxide reduction.

Studies in these laboratories^{8,9} and by other workers^{10,11} involving complexes of tripodal ligands of the type



have drawn attention to the fact that such ligands stabilize the Co(I) (d^8) state, in the same manner as 2,2'-bipyridine and its congeners where such stabilization has generally been attributed¹² to the π -acceptor properties of the bidentate ligands. The synthetic versatility of the tripodal ligands¹³ commends their use in the study of a number of aspects relating to bonding in complexes of polypyridyl ligands, including the structural features and the physical properties of such complexes.

As part of our continuing interest in the complexes of tripodal π -acceptor ligands with transition metals of groups 6-11, we have undertaken studies of the synthesis, structure, and physical properties of the ruthenium(II) complexes of these ligands. We have previously reported¹⁴ investigations involving the tris(2-pyridyl)methanol ligand—we now report a new general synthetic method for this genre of RuL_2^{2+} complexes and the structural details of the bis(ligand)ruthenium(II) complexes of tris(2-pyridyl)amine, tris(2-pyridyl)methane, and tris(2-pyridyl)phos-

phine. Details of the spectroscopic and electrochemical behavior of these species will be published subsequently.¹⁵

Experimental Section

NMR spectra were recorded on a Bruker AM-300 spectrometer (CDCl_3 solvent; SiMe_4 internal reference). Elemental analysis were carried out by the Canadian Microanalytical Service (New Westminster, B.C.).

Syntheses. The ligand tris(2-pyridyl)amine¹⁶ was prepared by literature methods in 15% yield. The complexes $[\text{Ru}(\text{OH}_2)_6](\text{tos})_2$ (tos = 4-toluenesulfonate anion, $\text{H}_3\text{CC}_6\text{H}_4\text{SO}_3^-$) and $[\text{Ru}(\text{DMF})_6](\text{tos})_2$ (DMF = *N,N*-dimethylformamide) were prepared by methods of Bernhard et al.^{17,18}

Tris(2-pyridyl)methane. Bis(2-pyridyl)methane¹⁹ (6.40 g; 0.037 mol) in dry diethyl ether (70 mL) was added to *n*-butyllithium (23.8 mL of 1.55 M; 0.037 mol) at -60 °C and the mixture stirred for 15 min under an atmosphere of dry N_2 . Freshly distilled 2-bromopyridine (3.26 mL; 0.037 mol) in dry ether (70 mL) was added over 1.5 h with continuous stirring at -60 °C: the temperature was maintained in turn at that temperature for another 30 min, at -20 °C for 1 h, and at 0 °C for 30 min. Dry benzene (170 mL) was added, the ether removed by distillation, and the mixture refluxed overnight. After cooling, water (170 mL) was added and the benzene layer separated. The aqueous layer was reextracted with benzene (3×50 mL) and the combined organic extracts dried with MgSO_4 . The solvent was evaporated (rotary evaporator) and the (liquid) residue extracted with petroleum ether (300 mL). This solution was refluxed with activated charcoal, filtered hot, slowly evaporated to ca. 120 mL, and cooled, and the resultant solid was filtered, washed with cold petroleum ether, and air dried: yield 4.9 g, 53%; mp 100 °C (lit.²⁰ mp 99 – 100 °C). ^1H NMR (CDCl_3): singlet (methine proton), δ 5.98; ^{13}C NMR (CDCl_3): singlet (tertiary carbon), δ 64.1; five singlets (pyridine ring carbons), δ 121.6, 124.1, 136.4, 149.4, and 161.1.

Tris(2-pyridyl)phosphine was prepared by modification of a literature procedure.²¹ A solution of *n*-butyllithium in hexane (39 mL; 1.44 M) in dry diethyl ether (80 mL) was cooled to ca. -100 °C. Under an atmosphere of dry N_2 , freshly distilled 2-bromopyridine (5.4 mL) in dry diethyl ether (5 mL) was added dropwise with a gastight syringe, and the resultant dark red solution was stirred at -100 °C for 4 h. A solution of freshly distilled PCl_3 (1.60 mL) in diethyl ether (8 mL) was added dropwise over a period of 1 h, also with a gastight syringe. After further stirring for 2 h at -100 °C, the light tan suspension was warmed slowly to room temperature. The mixture was extracted three times with 2 M H_2SO_4 (1×40 mL, 2×20 mL), and the aqueous layer was neutralized

- (1) James Cook University of North Queensland.
- (2) University of Adelaide.
- (3) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717–2738.
- (4) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.
- (5) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161–2166.
- (6) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500–1502.
- (7) Hawecker, J.; Lehn, J.-M.; Zeissel, R. *Helv. Chim. Acta* **1986**, *69*, 1990–2012.
- (8) Szalda, D. J.; Keene, F. R. *Inorg. Chem.* **1986**, *25*, 2795–2799.
- (9) Hafeli, T. A.; Keene, F. R. *Aust. J. Chem.*, in press.
- (10) Boggess, R. K.; Zatzko, D. A. *Inorg. Chem.* **1976**, *15*, 626–630.
- (11) Boggess, R. K.; Zatzko, D. A. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 7–11.
- (12) Szalda, D. J.; Creutz, C.; Mahajan, D.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 2372–2379.
- (13) White, D. L.; Faller, J. W. *Inorg. Chem.* **1982**, *21*, 3119–3122.
- (14) Keene, F. R.; Szalda, D. J.; Wilson, T. A. *Inorg. Chem.* **1987**, *26*, 2211–2216.

- (15) Atkinson, I. M.; Keene, F. R.; Stephenson, P. J., unpublished work.
- (16) Wibaut, J. P.; La Bastide, G. L. C. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 493–498.
- (17) Bernhard, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1516–1518.
- (18) Bernhard, P., personal communication to F.R.K.
- (19) Cauty, A. J.; Minchin, N. J. *Aust. J. Chem.* **1986**, *39*, 1063–1069.
- (20) Osuch, C.; Levine, R. J. *Am. Chem. Soc.* **1956**, *78*, 1723–1725.
- (21) Kurtev, K.; Ribola, D.; Jones, R. A.; Cole-Hamilton, D. J.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1980**, 55–58.

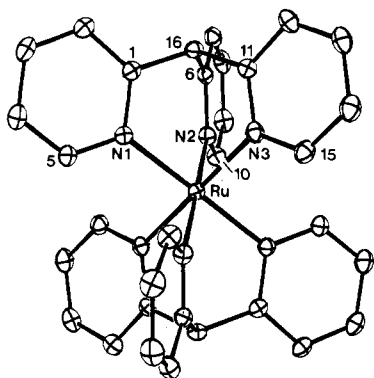


Figure 1. ORTEP drawing of $[\text{Ru}\{(2\text{-py})_3\text{CH}\}_2]^{2+}$ (1^{2+}) showing the atom-labeling scheme used. Note that the Ru atom is situated on a crystallographic 2-fold axis. Atoms not otherwise indicated are carbons, and hydrogen atoms have been omitted for clarity.

and adjusted to pH 10–11 by using a 30% NaOH solution (with cooling). The precipitated tris(2-pyridyl)phosphine was collected, washed with water (50 mL) and petroleum ether (4 × 5 mL), dried in vacuo, and stored under N₂; yield 3.3 g, 66%; mp 111–113 °C (lit.^{22,23} mp 115 °C). The product was recrystallized in 60% yield from deaerated acetone/petroleum ether.

Bis[tris(2-pyridyl)amine]ruthenium(II) Tosylate, $[\text{Ru}\{(2\text{-py})_3\text{N}\}_2](\text{tos})_2$. $[\text{Ru}(\text{DMF})_6](\text{tos})_2$ (0.1 g) was added to a degassed (Ar) solution of the ligand (0.08 g) in dry propan-1-ol (60 mL). The solution was refluxed overnight, during which time it changed from a light orange color to an intense yellow-orange. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol/ether. Yield: 0.09 g, 82%. Anal. Calcd for $[\text{Ru}(\text{C}_{15}\text{H}_{12}\text{N}_4)_2](\text{C}_7\text{H}_7\text{SO}_3)_2$: C, 56.2; H, 4.08; N, 11.9. Found: C, 56.3; H, 4.23; N, 11.8. The tosylate salt was converted (100%) to the PF₆⁻ form by adding solid NH₄PF₆ to an ethanolic solution; the resultant crystals were washed with cold ethanol and dried in vacuo. Orange-yellow crystals of the dithionate salt were grown for X-ray structural studies by layering an ethanolic solution of Li₂S₂O₆ above an aqueous solution of $[\text{Ru}\{(2\text{-py})_3\text{N}\}_2](\text{PF}_6)_2$.

Bis[tris(2-pyridyl)methane]ruthenium(II) tosylate hydrate, $[\text{Ru}\{(2\text{-py})_3\text{CH}\}_2](\text{tos})_2 \cdot \text{H}_2\text{O}$, was prepared in a manner similar to that used for the amine analogue. After evaporation of the propan-1-ol solvent, the residue was chromatographed on Sephadex LH-20 (methanol solvent) giving two incompletely separated species. The leading edge of the eluted band (yellow) was collected, the solvent removed under reduced pressure, and the residue recrystallized from methanol/diethyl ether. Yield: 44%. Anal. Calcd for $[\text{Ru}(\text{C}_{16}\text{H}_{13}\text{N}_3)_2](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot \text{H}_2\text{O}$: C, 57.7; H, 4.43; N, 8.8. Found: C, 57.5; H, 4.37; N, 8.6. Orange crystals of the tosylate salt for X-ray structural studies were grown by layering ether on top of a methanolic solution of the complex.

The tail of the band from the chromatography (orange) was treated in the same manner, giving a slightly lesser amount of an orange solid. The nature of this material will be addressed in a subsequent communication.¹⁵

Bis[tris(2-pyridyl)phosphine]ruthenium(II) tosylate ethanolate, $[\text{Ru}\{(2\text{-py})_3\text{P}\}_2](\text{tos})_2 \cdot \text{C}_2\text{H}_5\text{OH}$, was prepared in a manner similar to that used for the amine analogue, in 67% yield. Anal. Calcd for $[\text{Ru}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{P})_2](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$: C, 54.1; H, 4.35; N, 8.2. Found: C, 53.6; H, 4.38; N, 8.2. Orange-red crystals of the tosylate salt for the X-ray structural studies were grown by layering ether on top of an ethanolic solution of the complex.

Collection and Reduction of X-ray Data. Intensity data were measured at room temperature, 295 (2) K, with the use of Mo K α (graphite monochromator) radiation ($\lambda = 0.7107 \text{ \AA}$) on an Enraf-Nonius CAD4F diffractometer employing the ω - 2θ scan technique. Corrections were routinely applied for Lorentz and polarization effects and for absorption with an analytical procedure.²⁴ The net intensity values of three standard reflections (monitored after every 3600 s of X-ray exposure time) decreased to 80% of their original values for **1**, and hence the data were corrected for this variation; no such decomposition was detected during the data collection for **2** or **3**. All relevant data collection parameters and crystal data are listed in Table I.

Determination and Refinement of Structures. The structures of **1** and **2** were solved from the interpretation of the Patterson in both cases; for

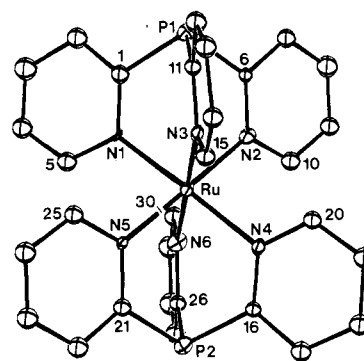


Figure 2. ORTEP drawing of $[\text{Ru}\{(2\text{-py})_3\text{P}\}_2]^{2+}$ (2^{2+}) showing the atom-labeling scheme used. Atoms not otherwise indicated are carbons, and hydrogen atoms have been omitted for clarity.

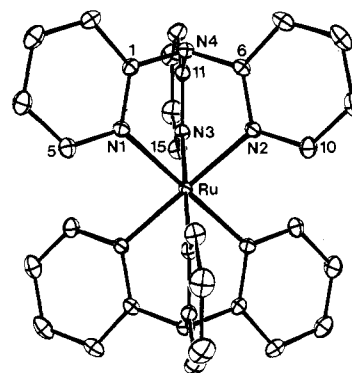


Figure 3. ORTEP drawing of $[\text{Ru}\{(2\text{-py})_3\text{N}\}_2]^{2+}$ (3^{2+}) showing the atom-labeling scheme used. Note that the Ru atom is situated on a crystallographic center of inversion. Atoms not otherwise indicated are carbons, and hydrogen atoms have been omitted for clarity.

3 the Ru atom was at a site of symmetry $\bar{1}$ at (0, 0, 0). The structures were each refined by a full-matrix least-squares procedure in which the function $\sum w\Delta^2$ was minimized, where w was the weight applied to each reflection, and $\Delta = |F_o| - |F_c|$.²⁴ The cation in **1** is situated about a crystallographic 2-fold axis as is a water molecule of crystallization. Anisotropic thermal parameters were introduced for all non-hydrogen atoms in **1** and **3**. However, due to the limited data set obtained for **2**, only Ru, N, O, P, and S atoms were refined anisotropically. Hydrogen atoms were included in each model at their calculated positions. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was introduced in the calculations, and the refinements were continued until convergence. The choice of C2/c as the space group for **1**, as opposed to Cc, was vindicated by the smooth and ready convergence of the refinement as well as the distribution of the E statistics.²⁴ Refinement details are given in Table I.

Fractional atomic coordinates are given in Tables II–IV, selected bond distances and angles for the compounds are listed in Tables V–VII, and the numbering schemes employed are shown in Figures 1–3 (drawn with ORTEP²⁵ at 15% probability ellipsoids). The scattering factors for C, H, N, O, P, and S were those incorporated in the SHELX program²⁴ and for central Ru were those (corrected for f' and f'') from ref 26.

Results and Discussion

Synthesis. There are a number of synthetic routes for polypyridyl complexes of ruthenium(II),²⁷ of which the most generally used is the reaction of $[\text{RuCl}_3(\text{OH}_2)]^{2-}$ (or similar chlororuthenate(III) species) with excess ligand either in a reducing solvent (e.g. methanol) or in aqueous solution in the presence of a reducing agent (e.g. sodium phosphinite, NaH₂PO₂). Although the former method was used satisfactorily in the preparation of the bis[tris(2-pyridyl)methanol]ruthenium(II) species,¹⁴ these methods generally were not satisfactory for the synthesis of the

(22) Mann, F. G.; Watson, J. *J. Org. Chem.* **1948**, *13*, 502–531.

(23) Boggess, R. K.; Zatzko, D. A. *J. Coord. Chem.* **1975**, *4*, 217–224.

(24) Sheldrick, G. M. "SHELX76, Program for Crystal Structure Determination"; University of Cambridge, England, 1976.

(25) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory; Oak Ridge, TN, 1971.

(26) Hamilton, W. C.; Ibers, J. A. *International Tables of X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(27) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, **1984**; pp 414–424 and references therein.

Table I. Crystal Data for 1-3

	[Ru{(py) ₃ CH ₂ }] ₂ (tos) ₂ ·H ₂ O	[Ru{(py) ₃ P}] ₂ (tos) ₂ ·C ₂ H ₅ OH	[Ru{(py) ₃ N}] ₂ (S ₂ O ₆)·4H ₂ O
formula	C ₄₆ H ₄₂ N ₆ O ₇ S ₂ Ru	C ₄₆ H ₄₄ N ₆ O ₇ P ₂ S ₂ Ru	C ₃₀ H ₃₂ N ₈ O ₁₀ S ₂ Ru
fw	956.1	1020.0	829.8
cryst syst	monoclinic	monoclinic	triclinic
space group	C2/c (C _{2h} ² , No. 15)	P2 ₁ /c (C _{2h} ² , No. 14)	P1̄ (C ₁ ¹ , No. 2)
a, Å	13.205 (9)	10.065 (7)	8.914 (3)
b, Å	13.437 (6)	13.008 (4)	9.060 (2)
c, Å	23.614 (22)	34.772 (22)	11.243 (2)
α, deg	90	90	95.52 (1)
β, deg	96.57 (6)	92.40 (5)	104.19 (2)
γ, deg	90	90	92.03 (2)
V, Å ³	4162.5	4548.6	874.6
D _{exptl} , mg m ⁻³	1.52	1.52	1.54
Z	4	4	1
D _{calcd} , mg m ⁻³	1.526	1.490	1.576
F(000)	1968	2096	424
μ, mm ⁻¹	0.490	0.514	0.584
cryst dimens, ^a mm	±(111) 0.18; ±(11̄1) 0.11; ±(001) 0.25	±(100) 0.25; ±(010) 0.06; ±(001) 0.06	±(011) 0.27; ±(021̄) 0.13; ±(110) 0.10; ±(101̄) 0.13
transmissn factors	0.9322; 0.8347	0.9422; 0.8931	0.8890; 0.7586
θ limits, deg	1-25	1-20	1-25
range	±h,k,l	±h,k,l	±h,±k,+l
no. of data colled	5306	5547	3611
no. of unique data	3662	4248	3081
R _{amalg} ^b	0.065	0.059	0.021
no. of unique data used with I ≥ 2.5σ(I)	2931	2017	2582
R	0.050	0.063	0.039
k	2.73	1.37	1.0
g	0.0007	0.0026	0.0130
R _w	0.055	0.065	0.041
r _{max} , e Å ⁻³	1.41	0.89	0.96

^a From centroid. ^b R_{amalg} = (Σ{N[w(F_{mean} - |F_o|²)]} / Σ{(N-1)Σ(w|F_o|²)})^{1/2}, where the inner summation is over N equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight, w, is taken as [σ(F_o)]⁻².

Table II. Fractional Atomic Coordinates for [Ru{(2-py)₃CH₂}]₂(tos)₂·H₂O (1) (×10⁴ for Ru; ×10⁴ for Remaining Atoms)

atom	x	y	z
Ru	0	24236 (3)	25000
N(1)	807 (3)	2427 (2)	1806 (2)
N(2)	999 (2)	1344 (2)	2851 (2)
N(3)	1031 (3)	3476 (2)	2859 (2)
C(1)	1834 (3)	2401 (3)	1895 (2)
C(2)	2421 (3)	2391 (3)	1449 (2)
C(3)	1966 (4)	2421 (3)	897 (2)
C(4)	917 (4)	2449 (3)	803 (2)
C(5)	373 (4)	2455 (3)	1263 (2)
C(6)	2000 (3)	1453 (3)	2812 (2)
C(7)	2715 (3)	778 (3)	3043 (2)
C(8)	2392 (3)	-50 (3)	3318 (2)
C(9)	1378 (4)	-188 (3)	3358 (2)
C(10)	704 (3)	529 (3)	3119 (2)
C(11)	2025 (3)	3305 (3)	2832 (2)
C(12)	2781 (3)	3928 (3)	3098 (2)
C(13)	2485 (4)	4739 (3)	3403 (2)
C(14)	1485 (4)	4919 (3)	3428 (2)
C(15)	765 (3)	4287 (3)	3147 (2)
C(16)	2302 (3)	2387 (3)	2506 (2)
S(1)	5092 (1)	2290 (1)	949 (1)
O(1)	4180 (3)	1996 (4)	596 (2)
O(2)	5078 (3)	1909 (3)	1527 (2)
O(3)	5341 (3)	3326 (3)	937 (2)
C(17)	6092 (3)	1633 (3)	676 (2)
C(18)	5923 (3)	680 (4)	469 (2)
C(19)	6703 (4)	151 (4)	255 (3)
C(20)	7666 (3)	566 (4)	251 (2)
C(21)	7821 (3)	1513 (4)	466 (2)
C(22)	7044 (3)	2062 (4)	675 (2)
C(23)	8534 (5)	5 (5)	34 (3)
O(4)	5000	6947 (5)	7500

title compounds, resulting in either very low yields or green products of uncertain composition. Similarly, the ligand substitution of [Ru(H)(OH)₂(CH₃OH)(PPh₃)₂]BF₄ in methanol solution, a method developed by Templeton for the preparation

of [Ru(py)₆]²⁺²⁸ and used subsequently in our laboratories in the synthesis of the [Ru(L)₂]ⁿ⁺ species [L = tris(2-pyridyl)-methanol],¹⁴ met with mixed success for the range of tripod ligands of the present study.

Accordingly, we have used as a general method for the synthesis of the bis(ligand)ruthenium(II) complexes the ligand substitution of a new precursor, [Ru(DMF)₆]²⁺ (DMF = N,N-dimethylformamide), developed by Bernhard and Sargeson.¹⁷ The reaction of this species with a 3 molar ratio of the respective ligand for 12 h in refluxing dry propan-1-ol under anaerobic conditions resulted in high yields of the respective [Ru(L)₂]²⁺ products.

The corresponding complex of tris(2-pyridyl)methanol was also prepared by this technique and yielded a product identical with that previously obtained by other methods.¹⁴

Description of Structures. Views of the cations [Ru{(2-py)₃CH₂}]₂²⁺ (1²⁺), [Ru{(2-py)₃P}]₂²⁺ (2²⁺), and [Ru{(2-py)₃N}]₂²⁺ (3²⁺) and the atom-labeling schemes used are shown in Figures 1-3, respectively. In all cases, the ligands are coordinated in a tripodal manner through the three py N atoms. Complex 1 has a crystallographic 2-fold axis, whereas there is only an approximate 2-fold axis in 2; on the other hand for 3, the molecule possesses a center of symmetry.

For the three cations of 1, 2, and 3, the average²⁹ Ru-N bond distances (see Tables V-VII) are 2.068 (2), 2.072 (4), and 2.066 (2) Å, respectively: the carbon- and phosphorus-bridged donors reveal significantly greater variations than the nitrogen-bridged donor in this distance. The average Ru-N(bpy) bond length reported in [Ru(bpy)₃]²⁺ is 2.056 Å.³⁰ the similar length of the

(28) Templeton, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4906-4917.

(29) A standard procedure for obtaining weighted averages was used:

$$\bar{x} = \frac{\sum_i (x_i / \sigma_i^2)}{\sum_i (1 / \sigma_i^2)} \quad \sigma^2(\bar{x}) = \sum_i (1 / \sigma_i^2)$$

(30) Rillema, D. P.; Jones, O. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849-851.

Table III. Fractional Atomic Coordinates for [Ru{(2-py)₃P}]₂(tos)₂·C₂H₅OH (**2**) (×10⁵ for Ru; ×10⁴ for Remaining Atoms)

atom	x	y	z
Ru	25985 (13)	22290 (12)	9226 (4)
P(1)	2813 (4)	4167 (4)	287 (2)
P(2)	2479 (5)	260 (4)	1555 (2)
N(1)	4284 (11)	3076 (9)	828 (4)
N(2)	1495 (12)	3560 (11)	933 (4)
N(3)	2175 (11)	2078 (11)	334 (3)
N(4)	906 (11)	1382 (10)	1033 (4)
N(5)	3711 (11)	900 (9)	897 (4)
N(6)	3017 (13)	2353 (12)	1515 (4)
C(1)	4293 (16)	3827 (14)	571 (5)
C(2)	5388 (17)	4436 (15)	514 (5)
C(3)	6617 (18)	4193 (15)	734 (6)
C(4)	6636 (17)	3435 (14)	988 (5)
C(5)	5462 (16)	2850 (15)	1031 (5)
C(6)	1595 (14)	4289 (12)	666 (5)
C(7)	814 (16)	5196 (13)	653 (5)
C(8)	-51 (18)	5351 (15)	940 (6)
C(9)	-171 (17)	4629 (13)	1211 (5)
C(10)	588 (16)	3715 (14)	1209 (6)
C(11)	2355 (14)	2913 (13)	101 (5)
C(12)	2152 (16)	2829 (15)	-290 (5)
C(13)	1739 (16)	1904 (13)	-449 (5)
C(14)	1516 (15)	1082 (13)	-217 (5)
C(15)	1776 (16)	1210 (15)	166 (5)
C(16)	941 (15)	596 (13)	1276 (5)
C(17)	-157 (17)	4 (14)	1352 (5)
C(18)	-1380 (17)	231 (14)	1145 (5)
C(19)	-1388 (17)	1045 (13)	890 (5)
C(20)	-235 (16)	1592 (13)	832 (5)
C(21)	3647 (15)	152 (13)	1167 (5)
C(22)	4376 (16)	-738 (14)	1151 (5)
C(23)	5265 (16)	-855 (14)	848 (5)
C(24)	5377 (16)	-134 (14)	591 (5)
C(25)	4591 (16)	772 (13)	614 (5)
C(26)	2908 (15)	1510 (14)	1747 (5)
C(27)	3106 (16)	1609 (15)	2133 (6)
C(28)	3468 (18)	2586 (15)	2297 (6)
C(29)	3568 (18)	3400 (17)	2055 (6)
C(30)	3325 (17)	3247 (16)	1669 (6)
S(1)	7399 (5)	7749 (5)	6571 (2)
O(1)	6202 (14)	7368 (11)	6724 (4)
O(2)	7203 (15)	8161 (11)	6191 (4)
O(3)	8452 (17)	7026 (13)	6608 (7)
C(31)	7878 (15)	8809 (12)	6859 (5)
C(32)	7089 (18)	9662 (14)	6877 (5)
C(33)	7516 (19)	10505 (15)	7097 (6)
C(34)	8722 (19)	10512 (17)	7295 (6)
C(35)	9482 (20)	9671 (16)	7268 (6)
C(36)	9091 (17)	8798 (14)	7065 (5)
C(37)	9152 (24)	11465 (20)	7514 (8)
S(2)	2461 (7)	7153 (6)	5078 (2)
O(4)	3762 (19)	7235 (14)	4920 (5)
O(5)	1521 (15)	7883 (12)	4900 (4)
O(6)	1981 (24)	6105 (14)	5090 (6)
C(38)	2619 (15)	7532 (12)	5566 (5)
C(39)	1686 (17)	7214 (15)	5828 (5)
C(40)	1819 (19)	7571 (14)	6211 (6)
C(41)	2821 (19)	8224 (15)	6330 (6)
C(42)	3719 (19)	8477 (15)	6078 (6)
C(43)	3689 (17)	8165 (13)	5694 (6)
C(44)	2910 (21)	8545 (18)	6739 (7)
O(7)	3246 (32)	8823 (28)	7985 (10)
C(45)	3681 (35)	9798 (28)	7962 (12)
C(46)	2509 (33)	10267 (25)	7850 (10)

metal-ligand bond in the title compounds provides some evidence for the presence of π -back-bonding, in comparison with [Ru(py)₆]²⁺ where the Ru-N bond length is 2.12 Å.²⁸

The average bridgehead (X)-C(py) bond distances are 1.518 (3) Å for X = CH, 1.823 (8) Å for X = P, and 1.440 (3) Å for X = N; the average bond angles about the bridgehead atoms for C(py)-X-C'(py') are 111.1 (2)° for X = C, 100.1 (3)° for X = P, and 112.4 (2)° for X = N. Again these data reveal increasing variation within the ligand as the bridgehead-C(py) bond distance

Table IV. Fractional Atomic Coordinates for [Ru{(2-py)₃N}]₂(S₂O₆)·4H₂O (**3**) (×10⁴)

atom	x	y	z
Ru	0	0	0
N(1)	1441 (3)	1299 (3)	-714 (3)
N(2)	-266 (3)	1899 (3)	1088 (3)
N(3)	1938 (3)	-294 (3)	1384 (3)
N(4)	2465 (3)	2290 (3)	1373 (3)
C(1)	2470 (4)	2256 (4)	101 (3)
C(2)	3504 (5)	3161 (4)	-246 (4)
C(3)	3508 (5)	3129 (5)	-1481 (5)
C(4)	2433 (5)	2156 (5)	-2327 (4)
C(5)	1431 (4)	1276 (4)	-1915 (3)
C(6)	1029 (4)	2767 (4)	1616 (3)
C(7)	1047 (5)	4022 (4)	2418 (4)
C(8)	-329 (6)	4419 (5)	2685 (4)
C(9)	-1651 (5)	3546 (5)	2142 (4)
C(10)	-1595 (4)	2315 (4)	1353 (4)
C(11)	2884 (4)	908 (4)	1871 (3)
C(12)	4216 (4)	889 (5)	2800 (3)
C(13)	4566 (4)	-449 (5)	3287 (4)
C(14)	3603 (5)	-1693 (5)	2806 (4)
C(15)	2289 (4)	-1587 (4)	1861 (3)
S(1)	5892 (1)	5135 (1)	4527 (1)
O(1)	5136 (3)	4756 (3)	3233 (3)
O(2)	6427 (3)	6691 (3)	4845 (3)
O(3)	7033 (3)	4114 (3)	5036 (3)
O(4)	1152 (3)	1118 (3)	4115 (3)
O(5)	8315 (5)	1367 (5)	4680 (6)

Table V. Selected Bond Distances (Å) and Angles (deg) for **1**

Ru-N(1)	2.055 (4)	N(3)-C(11)	1.341 (5)
Ru-N(2)	2.069 (3)	C(1)-C(16)	1.505 (6)
Ru-N(3)	2.075 (3)	C(6)-C(16)	1.524 (5)
N(1)-C(1)	1.349 (5)	C(11)-C(16)	1.521 (5)
N(2)-C(6)	1.344 (5)		
N(1)-Ru-N(2)	87.5 (1)	N(1)-Ru-N(3)	87.1 (1)
N(2)-Ru-N(3)	87.5 (1)	N(1)-Ru-N(1') ^a	179.7 (1)
N(2)-Ru-N(2')	91.0 (1)	N(2)-Ru-N(3')	178.4 (1)
N(3)-Ru-N(3')	94.1 (1)		
Ru-N(1)-C(1)	118.6 (3)	Ru-N(1)-C(5)	123.9 (3)
Ru-N(2)-C(6)	118.9 (3)	Ru-N(2)-C(10)	123.7 (3)
Ru-N(3)-C(11)	117.6 (3)	Ru-N(3)-C(15)	124.0 (3)
N(1)-C(1)-C(16)	116.5 (4)	N(2)-C(6)-C(16)	115.8 (3)
N(3)-C(11)-C(16)	117.2 (3)	C(1)-C(16)-C(6)	111.4 (3)
C(1)-C(16)-C(11)	112.2 (3)	C(6)-C(16)-C(11)	109.7 (3)

^a Where the primed atom is related by a 2-fold axis.

increases. Associated with the change in bond distances and angles at the bridgehead (X) is a contraction of the bite angle N(py)-Ru-N'(py') as the X-C(py) distance decreases, viz. 90.6 (2)° for X = P, 87.37 (6)° for X = CH, and 86.60 (6)° for X = N.

There are, as may be expected, substantial interionic interactions in the crystal lattices of **1** and **2**. These interactions occur between the electron-rich sulfonate moieties of the tosylate anions and the hydrogen atoms of the pyridyl rings. For **1**, the closest contact occurs between H(3) and O(1), 2.29 Å, and for **2** a contact of 2.25 Å occurs between H(15) and O(6') (where O(6') is related by the symmetry operation $x, 1/2 - y, 1/2 + z$). The closest interionic contact in **3** occurs between O(1) and H(3') of 2.30 Å (where H(3') is related by the symmetry operation $1 - x, 1 - y, z$).

Comparisons with Other Structures. There are very limited data on structural aspects of complexes containing the tris(2-pyridyl)methane ligand. In the species [AuMe₂(2-py)₃CH]-NO₃,³¹ the ligand coordinates in a bidentate mode with the Au(III) center having square-planar geometry. In addition, although no structures were reported, the ligand exhibits tripodal coordination, as claimed in the electrochemical studies of [Fe{(2-py)₃CH}]²⁺ by Boggess et al.³² and in the NMR studies of [Co{(2-py)₃CH}]³⁺

(31) Canty, A. J.; Minchin, N. J.; Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1795-1802.

Table VI. Selected Bond Distances (Å) and Angles (deg) for **2**

Ru-N(1)	2.06 (1)	Ru-N(2)	2.06 (1)
Ru-N(3)	2.08 (1)	Ru-N(4)	2.08 (1)
Ru-N(5)	2.06 (1)	Ru-N(6)	2.09 (1)
N(1)-C(1)	1.32 (2)	N(2)-C(6)	1.33 (2)
N(3)-C(11)	1.37 (2)	N(4)-C(16)	1.33 (2)
N(5)-C(21)	1.36 (2)	N(6)-C(26)	1.37 (2)
C(1)-P(1)	1.81 (2)	C(6)-P(1)	1.84 (2)
C(11)-P(2)	1.81 (2)	C(16)-P(2)	1.85 (2)
C(21)-P(2)	1.83 (2)	C(26)-P(2)	1.80 (2)
N(1)-Ru-N(2)	90.1 (5)	N(1)-Ru-N(3)	91.7 (5)
N(1)-Ru-N(4)	178.6 (5)	N(1)-Ru-N(5)	89.4 (5)
N(1)-Ru-N(6)	89.1 (5)	N(2)-Ru-N(3)	90.5 (5)
N(2)-Ru-N(4)	89.7 (5)	N(2)-Ru-N(5)	178.5 (5)
N(2)-Ru-N(6)	90.3 (6)	N(3)-Ru-N(4)	89.8 (5)
N(3)-Ru-N(5)	88.1 (5)	N(3)-Ru-N(6)	179.0 (6)
N(4)-Ru-N(5)	90.8 (5)	N(4)-Ru-N(6)	89.5 (5)
N(5)-Ru-N(6)	91.2 (5)		
Ru-N(1)-C(1)	122 (1)	Ru-N(2)-C(6)	122 (1)
Ru-N(1)-C(5)	120 (1)	Ru-N(2)-C(10)	121 (1)
Ru-N(3)-C(11)	119 (1)	Ru-N(4)-C(16)	122 (1)
Ru-N(3)-C(15)	124 (1)	Ru-N(4)-C(20)	119 (1)
Ru-N(5)-C(21)	122 (1)	Ru-N(6)-C(26)	120 (1)
Ru-N(5)-C(25)	120 (1)	Ru-N(6)-C(30)	120 (1)
N(1)-C(1)-P(1)	121 (1)	N(2)-C(6)-P(1)	121 (1)
N(3)-C(11)-P(1)	123 (1)	N(4)-C(16)-P(2)	121 (1)
N(5)-C(21)-P(2)	120 (1)	N(6)-C(26)-P(2)	122 (1)
C(1)-P(1)-C(6)	100.9 (8)	C(1)-P(1)-C(11)	99.6 (8)
C(6)-P(1)-C(11)	99.6 (7)	C(16)-P(2)-C(21)	100.5 (8)
C(16)-P(2)-C(26)	99.4 (8)	C(21)-P(2)-C(26)	101.0 (8)

Table VII. Selected Bond Distances (Å) and Angles (deg) for **3**

Ru-N(1)	2.064 (3)	Ru-N(2)	2.069 (3)
Ru-N(3)	2.066 (3)	N(1)-C(1)	1.346 (5)
N(2)-C(6)	1.346 (4)	N(3)-C(11)	1.339 (4)
N(4)-C(1)	1.428 (5)	N(4)-C(6)	1.445 (4)
N(4)-C(11)	1.444 (4)	O(1)-S(1)	1.447 (3)
O(2)-S(1)	1.454 (3)	O(3)-S(1)	1.449 (3)
S(1)-S(2)	2.139 (2)		
N(1)-Ru-N(2)	86.9 (1)	N(1)-Ru-N(3)	86.6 (1)
N(2)-Ru-N(3)	86.3 (1)	Ru-N(1)-C(1)	116.5 (2)
Ru-N(1)-C(5)	125.8 (3)	Ru-N(2)-C(6)	116.4 (2)
Ru-N(2)-C(10)	126.2 (3)	Ru-N(3)-C(11)	117.0 (2)
Ru-N(3)-C(15)	125.1 (2)	C(1)-N(4)-C(6)	112.8 (3)
C(1)-N(4)-C(11)	112.8 (3)	C(6)-N(4)-C(11)	111.6 (3)
N(1)-C(1)-N(4)	117.5 (3)	N(2)-C(6)-N(4)	117.4 (3)
N(3)-C(11)-N(4)	117.0 (3)	O(1)-S(1)-O(2)	113.8 (2)
O(1)-S(1)-O(3)	114.3 (2)	O(2)-S(1)-O(3)	113.8 (2)

and $[\text{Co}(\text{2-py})_3\text{CH}]^{2+}$ by White and Faller.¹³

Structural determinations have been made for ruthenium(II) complexes of the related C-bridgehead ligand, tris(2-pyridyl)methanol ($X = \text{COH}$).^{14,33} Two forms of $[\text{RuL}_2]^{n+}$ were identified:¹⁴ in both there is one (2-py)₃COH ligand coordinated through the three py N atoms (N, N', N''), with the other ligand having an N,N',O-coordination mode, but being either deprotonated or nondeprotonated. Since there is considerable distortion in the (py)₃COH-N,N',N'' ligand in $[\text{Ru}\{\text{(2-py)}_3\text{COH}\}_2]^{2+}$, the comparison of (py)₃COH-N,N',N'' in $[\text{Ru}\{\text{(2-py)}_3\text{COH}\}\{\text{(2-py)}_3\text{CO}\}]^+$ with (2-py)₃CH in the present instance seems more appropriate. The structural features are very similar for $X = \text{CH}$ and COH in these complexes: viz. the average bridgehead (X)-C(py) bond distance is 1.54 (1) Å for $X = \text{COH}$ (cf. 1.518 (3) Å for $X = \text{CH}$), the C(py)-X-C'(py') bond angle is 109.4 (3)° (cf. 111.1 (2)°), and the intraligand bite angle is 86.4° (cf. 87.37 (6)°). The (2-py)₃COH ligand in $[\text{Ru}(\text{NH}_3)_3\{\text{(2-py)}_3\text{COH}\}]^{2+}$ exhibits an N,N',O-coordination mode,³³ and is not relevant to the present discussion.

To our knowledge, the present structural study of $[\text{Ru}\{\text{(2-py)}_3\text{P}\}_2]^{2+}$ represents the first such determination of a complex

containing this ligand: the X-ray structure of the free ligand has been determined recently.³⁴ However, complexes containing this ligand have been reported previously: viz. $[\text{Co}\{\text{(2-py)}_3\text{P}\}_2]^{2+}$,^{10,23} and $[\text{Fe}\{\text{(2-py)}_3\text{P}\}_2]^{2+}$,³² in which the ligand was claimed to be tridentate via the py N atoms, and a series of ruthenium(II) and rhodium(I) species (e.g. $[\text{RuHCl}\{\text{(2-py)}_3\text{P}\}_3]$ and $[\text{RhCl}\{\text{(2-py)}_3\text{P}\}_2]$) in which ¹H and ³¹P NMR studies indicated tris(2-pyridyl)phosphine to be coordinated both as a monodentate ligand (via P) or as a bidentate ligand (via P and one py N).²¹

A number of structures involving the ligand tris(2-pyridyl)amine have been determined. Kucharski et al. reported the structures of $[\text{Fe}\{\text{(2-py)}_3\text{N}\}_2]^{2+}$ ³⁵ and $[\text{Co}\{\text{(2-py)}_3\text{N}\}_2]^{2+}$,³⁶ and in both cases the ligand adopted a tripodal coordination mode with the three py N atoms ligating. Ibers and co-workers³⁷ have also reported the structure of a cubane-like cluster $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2\{\text{(2-py)}_3\text{N}\}](\text{SO}_3\text{CF}_3)_2\cdot\text{C}_3\text{H}_6\text{O}$, in which the tris(2-pyridyl)amine behaves in a bidentate rather than a tridentate manner.

The only such comparison that may be made for any of the title ligands, for the same coordination mode of the ligand to different metal centers the intraligand bite angle observed for tris(2-pyridyl)amine seems related to the metal-N(py) bond length: viz. 85.6 (5)° for N-Co-N, where the Co-N bond length is 2.12 (2) Å,³⁶ 88.1 (3)° for N-Fe-N (Fe-N is 1.98 (1) Å),³⁵ and 86.60 (6)° for N-Ru-N (Ru-N is 2.066 (2) Å) in the present case.

By comparison of intraligand bond lengths in the $[\text{Co}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{bpy})_3]^+$ cations, Szalda et al.¹² were able to identify changes that were consistent with π -back-bonding from the Co(I) (d^8) metal center to the bpy ligand. In the present structures involving complexes of the tripodal ligands with the Ru(II) (d^6) center, the bond distances between the respective bridgehead atom (X) and the 2-carbon atom of the pyridine rings are very similar to those determined with other metal centers. The bond distance between the bridgehead atom P and the C(py) atoms in **2** averages 1.823 (8) Å; an X-ray structural determination reveals that this bond distance is essentially identical with that in the free ligand tris(2-pyridyl)phosphine (1.827 (2) Å).³⁴ In a similar manner, the average N-C(py) bond length in **3**—1.440 (3) Å—is indistinguishable from the equivalent bond lengths in other complexes of the same ligand (1.44 Å in $[\text{Fe}\{\text{(2-py)}_3\text{N}\}_2]^{2+}$ ³⁵ and $[\text{Co}\{\text{(2-py)}_3\text{N}\}_2]^{2+}$,³⁶ The C-C(py) bond length in **1**—1.518 (3) Å—is also the same as that found in tris(2-pyridyl)methane coordinated to Au(III),³¹ where the ligand is bidentate and the bond distances are identical for both the attached and free pyridine rings (1.52 (2) Å). The constancy of the bridgehead (X)-C(py) bond distances in all the title ligands regardless of the metal and the invariance of the bond lengths and angles in the P-C-N groupings in coordinated and uncoordinated tris(2-pyridyl)phosphine do not reveal any structural evidence of ring-to-ring delocalization through the σ -system or through d_{π} - p_{π} bonding between the bridgehead atom and the 2-carbon atom of the pyridyl ring as claimed by Boggess and Zatko^{10,11} in the stabilization of Co(I) by (2-py)₃P and its arsine analogue. We are currently undertaking molecular mechanics and MO calculations to rationalize the nature of the π -back-bonding in the ruthenium(II) and cobalt(I) species of these ligands; these results will be published shortly, together with details of the spectral (electronic, NMR, vibrational) and photochemical properties of the title complexes and their electrochemical behavior.¹⁵

The progressive distortion of the title molecules from ideal D_{3d} point group symmetry as the bridgehead (X)-C(py) bond distance is lengthened is not totally understood. Interestingly, for the least symmetrical of these complexes, $[\text{Ru}\{\text{(2-py)}_3\text{P}\}_2]^{2+}$, the asymmetric distortion is also seen in solution in ¹H/¹³C 2D NMR studies.¹⁵

(34) Keene, F. R.; Snow, M. R.; Tiekink, E. R. T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, in press.

(35) Kucharski, E. S.; McWhinnie, W. R.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 53-56.

(36) Kucharski, E. S.; McWhinnie, W. R.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 2647-2650.

(37) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3506-3517.

(32) Boggess, R. K.; Hughes, J. W.; Chew, C. W.; Kemper, J. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 939-945.

(33) Moritz, P. S.; Diamantis, A. A.; Keene, F. R.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.*, in press.

the N- and CH-bridged complexes show no such asymmetry in solution. This may well be a steric effect, and the molecular mechanics calculations¹⁵ will hopefully provide information on this unusual observation.

Acknowledgment. The assistance of Dr Paul Bernhard (Australian National University) in providing details of synthetic procedures for the precursors used in this study is gratefully acknowledged. This work was supported by the Australian Research Grants Scheme.

Registry No. 1, 114378-75-5; 2, 114378-78-8; 3, 114378-72-2; PCl_3 , 7719-12-2; $[\text{Ru}(\text{DMF})_6](\text{tos})_2$, 114378-79-9; tris(2-pyridyl)methane, 77429-58-4; bis(2-pyridyl)methane, 1132-37-2; 2-bromopyridine, 109-04-6; tris(2-pyridyl)phosphine, 26437-48-9; $[\text{Ru}\{(\text{2-py})_3\text{N}\}_2](\text{tos})_2$, 114466-50-1.

Supplementary Material Available: Tables S1-S12, listing thermal parameters, the derived hydrogen positions, and bond distances and angles for 1-3 (12 pages); Tables S13-S15, listing calculated and observed structure factors for 1-3 (44 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Unusual Bonding in the Secondary Aminophosphine $[\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$: X-ray Structures and NMR and IR Studies of the Main Group V Amino Compounds $\text{HE}(\text{NR}_2)_2$ (E = P, As, R = SiMe₃; E = P, R = Ph)

Marilyn M. Olmstead, Philip P. Power,* and Gary A. Sigel

Received December 17, 1987

Crystal structures of the secondary aminophosphines and -arsines $[\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (1), $\text{HAs}\{\text{N}(\text{SiMe}_3)_2\}_2$ (2), and $\text{HP}(\text{NPh}_2)_2$ (3) are described. In addition, the synthesis of $\text{HP}\{\text{N}(\text{C}_6\text{H}_{11})_2\}_2$ (4) is given, along with spectroscopic data for 2-4. The dimeric structure of 1 features a unique, planar, P_2H_2 core with hydrogen bridging of the P atoms. Each phosphorus atom has a distorted-tetrahedral geometry with P-H distances averaging 1.73 Å and P-N bond lengths averaging 1.818 Å. In contrast, compound 2, the arsenic analogue of 1, is monomeric. The As-N distances are 1.879 (3) and 1.874 (4) Å; N-As-N is 106.5 (1)°. Complex 3 is also monomeric, with no short intermolecular contacts. Crystallographic data with Mo K α radiation ($\lambda = 0.71069$ Å) at 130 K: (1) $a = 13.629$ (13) Å, $b = 18.210$ (7) Å, $c = 17.755$ (14) Å, $\beta = 91.84$ (7)°, monoclinic, space group $P2_1$, $Z = 4$, $R = 0.049$; (2) $a = 8.805$ (8) Å, $b = 11.252$ (10) Å, $c = 12.944$ (10) Å, $\alpha = 66.73$ (6)°, $\beta = 85.34$ (7)°, $\gamma = 69.63$ (6)°, $Z = 2$, triclinic, space group $P\bar{1}$, $R = 0.047$; (3) $a = 9.925$ (6) Å, $b = 38.632$ (18) Å, $c = 10.368$ (5) Å, orthorhombic, space group $F2dd$, $Z = 8$, $R = 0.036$.

Introduction

Primary and secondary aminophosphines are often unstable under ambient conditions due to amine elimination and formation of ill-characterized phosphorus polymeric species. However, kinetic stabilization of these compounds can be achieved by using bulky amino substituents.¹⁻⁶ Thus, the compounds $\text{HP}(\text{NR}_2)_2$, R = *i*-Pr, Ph, or SiMe₃, have been synthesized in relatively good yield by the reduction of the $\text{CIP}(\text{NR}_2)_2$ precursor by LiAlH_4 .²⁻⁶ Detailed structural information on transition-metal complexes of some aminophosphines has been provided by King and co-workers.^{7,8} However, no structures are currently available for the ligands themselves. Previously, we reported that $\text{HP}\{\text{CH}(\text{SiMe}_3)_2\}_2$ (isoelectronic with $\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2$) underwent an unusual rearrangement in its reaction with $\text{Rh}(\eta^4\text{-1,5-cyclooctadiene})(\eta^3\text{-2-Me-C}_3\text{H}_4)$.⁹ Similar work on $\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2$ (1) was in progress when large crystals were observed growing from the samples of the ligand as neat liquid. An X-ray structure determination of a crystal of 1 showed that it had a unique dimeric structure. This prompted us to investigate its arsenic analogue

2 and the aryl derivative $\text{HP}(\text{NPh}_2)_2$ (3). In this paper the first structural characterizations of secondary aminophosphine and -arsine complexes are described for 1-3. Also reported are spectroscopic data and additional information on a related compound $\text{HP}\{\text{N}(\text{C}_6\text{H}_{11})_2\}_2$ (4).

Experimental Section

General Procedures. All reactions were performed with modified Schlenk techniques under an inert atmosphere of N_2 . Solvents were freshly distilled from drying agents and degassed before use. The compound $\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2$ (4) and the precursors $\text{ClAs}\{\text{N}(\text{SiMe}_3)_2\}_2$ ¹⁰ and $\text{CIP}(\text{NPh}_2)_2$ ¹¹ were synthesized by published procedures.

Physical Methods. Infrared spectra were recorded on an IBM IR/32 spectrometer. ³¹P NMR spectra were obtained on an NT-200 FT NMR spectrometer operating at 81 MHz. All values are reported in ppm relative to an external standard of 85% H_3PO_4 or TMS.

$[\text{HP}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (1). After distillation of 1, slow cooling afforded colorless crystals suitable for X-ray diffraction studies. Spectroscopic data have been previously reported.^{2,4}

$\text{HAs}\{\text{N}(\text{SiMe}_3)_2\}_2$ (2). $\text{ClAs}\{\text{N}(\text{SiMe}_3)_2\}_2$ (27 g, 62.5 mmol) in Et_2O (200 mL) was added dropwise to a slurry of LiAlH_4 (1.18 g, 31.25 mmol) in Et_2O (10 mL) at -78 °C. The solution was allowed to warm to room temperature overnight and stirred for a further 24 h. Filtration to remove the brown precipitate, followed by removal of the solvent under reduced pressure, produced a yellow oil. The oil was extracted into *n*-hexane (50 mL) and filtered. Removal of the solvent, followed by distillation under reduced pressure (bp 74-84 °C/0.1 mm), afforded a colorless oil (13.1 g, 53% yield). Slow cooling of the oil to -20 °C gave colorless crystals suitable for X-ray diffraction studies. ¹H NMR (neat): δ 0.3 (36 H, SiMe₃), 7.2 (1 H). IR (As-H): 2041, 1928 cm^{-1} . Analogous to the

- Niecke, E.; Rüger, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 62.
- O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1983**, *22*, 814.
- King, R. B.; Sundaram, P. M. *J. Org. Chem.* **1984**, *49*, 1784.
- Cowley, A. H.; Kemp, R. A. *Inorg. Chem.* **1983**, *22*, 550.
- King, R. B.; Sandani, N. D.; Sundaram, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 477.
- King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 3094.
- King, R. B.; Sadanani, N. D. *Inorg. Chem.* **1983**, *22*, 814.
- King, R. B.; Sadanani, N. D. *J. Chem. Soc., Chem. Commun.* **1984**, 955.
- Murray, B. D.; Olmstead, M. M.; Power, P. P. *Organometallics* **1983**, *2*, 1700.

(10) Gynane, M. J.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(11) Falius, V. H.; Babin, M. Z. *Anorg. Allg. Chem.* **1976**, *420*, 65.