Ruthenium Complexes of a Simple Tridentate Ligand Bearing Two "Distal" Pyridine Bases

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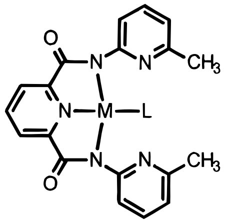
Treatment of *N,N′*-bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide (**1**) (H_2LMe_2) with $RuCl_2(PPh_3)_3$ in toluene yields the complex $RuCl_2(PPh_3)(LMe_2\{H\}_2)$ (**2**) in which the ruthenium atom is coordinated to the nitrogen atoms of the two deprotonated amides and the central pyridine of **1**. The two pendant pyridines in **2** are both protonated, and hydrogen bonds are formed to the coordinated chloride positioned in the molecular cleft between these two groups. Both of the chlorides in **2** can be replaced by other anions in simple metathesis reactions, and treatment of **2** with excess SCN^- or $CH_3CO_2^-$ yields the corresponding complexes $RuX_2(PPh_3)(LMe_2\{H\}_2)$ (X: SCN^-, **3**; $CH_3CO_2^-$, **4**). Treatment of **2** with NO_2^- also results in displacement of the chlorides, but in this case, the protons on the pendant pyridines are lost and the nitrosyl-containing complex $Ru(NO_2)(NO)(PPh_3)(LMe_2)$ (**5**) is formed. Single-crystal X-ray structure determinations have been carried out for the following compounds: **1**, space group *C*2/*c*, $a = 13.588(6)$ Å, $b = 11.518(2)$ Å, $c = 12.731(3)$ Å, $Z = 4$, $V = 1826.7$ Å^3; **2**, space group $P\bar{1}$, $a = 10.482(5)$ Å, $b = 11.349(8)$ Å, $c = 15.710(4)$ Å, $Z = 2$, $V = 1689(2)$ Å^3; **5**, space group $P\bar{1}$, $a = 12.204(2)$ Å, $b = 13.065(3)$ Å, $c = 14.722(6)$ Å, $Z = 2$, $V = 1973.9(10)$ Å^3.

Introduction

A feature that is common to a number of metalloenzymes is that the reactivity of bound substrates is modified through interactions involving both the metal center and nearby functional groups on the protein backbone.[1] In some instances important hydrogen-bonding interactions occur between the coordinated substrate and nearby acidic sites.[2] However, there have been relatively few reports of simple, synthetic coordination complexes that contain ligands with functional groups positioned to interact directly with coordinated substrates in the same or related ways. Reported complexes that embody interactions of this type often display unusual and interesting behavior.[3] We have therefore commenced a program to design and study new ligands that have the appropriate architectures in coordination compounds to interact directly with, and thereby influence the reactivity of, one or more of the other ligands also coordinated to the metal centers. In this paper we report the results of our preliminary studies of the coordination chemistry of a simple example of a ligand of this type, *N,N′*-bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide (H_2LMe_2) (**1**).[4] Molecules related to **1** have been utilized in the formation of receptors,[5] rotaxanes,[6] catenanes,[7] and supramolecular assemblies.[8]

As shown in the following conformation, doubly deprotonated H_2LMe_2 can coordinate to metals in a tridentate fashion through the two amidate nitrogen atoms and the central pyridine nitrogen:



Complexes containing amidato-*N* ligands ($L_nM{-}NRC(O)R$) have been much less studied than those containing amido ($L_nM{-}NR_2$) or amine ($L_nM{-}NR_3$) ligands. However, both early[9] and more recent[10] studies have shown that amidato-*N* ligands can readily form very stable complexes with a wide range of metals. Some important features of these ligands include the good σ-donor properties of the coordinated nitrogen, the ability to stabilize metals in high formal oxidation states, the relatively low chemical reactivity of the amide bond, and the ease of synthesis of the free carboxamides.

The two pendant pyridines in simple metal complexes of **1** are restrained from coordinating to the metal and are directed toward the donor atom of an ancillary ligand that occupies the

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(1) Lippard, S. J.; Berg, J. M. *Principles of bioinorganic chemistry*; University Science Books: Mill Valley, CA, 1994; pp 257−281.

(2) See, for example: (a) Everse, J., Everse, K. E., Grisham, M. B., Eds. *Peroxidases in chemistry and biology;* CRC Press: Boca Raton, FL, 1991; Vol. II, pp 2−16. (b) Kaim, W.; Schwederski, B. *Bioinorganic chemistry: Inorganic elements in the chemistry of life*; John Wiley and Sons: Chichester, England, 1994; pp 88−100.

(3) See, for example: (a) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (b) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (c) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (d) Collman, J. P.; Zhang, X.; Wong, K.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 6245. (e) Momenteau, M.; Reed, C. A. *Chem Rev.* **1994**, *94*, 659. (f) Tsao, B. L.; Pieters, R. J.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 2210. (g) Kimura, E.; Kodama, Y.; Koike, T.; Shiro, M. *J. Am. Chem. Soc.* **1995**, *117*, 8304.

(4) Copper complexes of related ligands were reported recently: (a) Hiratani, K.; Tagughi, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3331. (b) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. A.; Rheingold, A. L.; Borovic, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 285. (c) Kodama, M.; Koike, T.; Kimura, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1627.

(5) Chang, S.-K.; Van Engen, D.; Fan, E.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 7640.

(6) Vögtle, F.; Dünnwald, T.; Händel, M.; Jäger, R.; Meier, S.; Harder, G. *Chem. Eur. J.* **1996**, *2*, 640.

(7) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1209.

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(9) (a) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23. (b) Kimura, E. *J. Coord. Chem.* **1986**, *15*, 1.

(10) (a) Collins, T. J. *Acc. Chem. Res.* **1994**, *27*, 279. (b) Borovic, A. S.; Dewey, T. M.; Raymond, K. N. *Inorg. Chem.* **1993**, *32*, 413. (c) Campbell, C. J.; Castineiras, A.; Nolan, K. B. *J. Chem. Soc., Chem. Commun.* **1995**, 1939. (d) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Am. Chem. Soc.* **1993**, *115*, 5123. (e) Cantarero, A.; Amigo, J. M.; Faus, J.; Julve, M.; Dabaerdemaeker, T. *J. Chem. Soc., Dalton Trans.* **1988**, 2033. (f) Kimura, E.; Kurosaki, H.; Kurogi, Y.; Shionoya, M.; Shiro, M. *Inorg. Chem.* **1992**, *31*, 4314.

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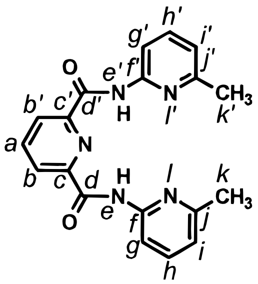

Figure 1. Atom-labeling scheme used for NMR assignments.

molecular cleft.[11] In this orientation the pendant pyridines can, in principle, assume a number of roles. For example, the nitrogen atoms can act as donor groups for (i) reversible protonation, (ii) the coordination of another metal, (iii) the interception of coordinated, reactive intermediates, or (iv) the stabilization of coordinated, electron-deficient species. In this paper ruthenium derivatives of H_2LMe_2 are described in which reversible protonation of the pendant pyridines plays an important role.

Experimental Section

General Procedures. Air-sensitive manipulations were carried out under dry nitrogen using standard Schlenk techniques. Dichloromethane and acetonitrile were dried over CaH_2 and distilled before use, benzene and hexane were dried over and distilled from sodium/benzophenone ketyl (under nitrogen) prior to use, and triethylamine was dried over activated A4 molecular sieves.

IR spectra (4000−400 cm^{-1}) were recorded on a Digilab FTS-7 spectrophotometer as Nujol mulls between KBr plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC200 or a Bruker AM400 spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm referenced to TMS, $\delta = 0.00$, and coupling constants (J) are given in hertz. X-ray intensity data for the crystal structures were collected on an Enraf-Nonius CAD-4 automatic diffractometer. Mass spectra were recorded on a VG 70-SE mass spectrometer. Analytical data were obtained by the Microanalytical Laboratory, University of Otago. Melting points (uncorrected) were recorded on a Reichert hot-stage microscope. $RuCl_2(PPh_3)_3$ was prepared by the literature method.[12]

Preparation of *N,N′*-Bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide (1) (H_2LMe_2). 2,6-Pyridinedicarbonyl chloride (3.00 g) was added to a stirred solution of 2-amino-6-methylpyridine (3.18 g, 0.0294 mol) and triethylamine (6.14 mL, 0.044 mol) in dry dichloromethane (50 mL). The mixture was stirred for 2 h, after which the solvent was removed under reduced pressure. The resulting solid was recrystallized from methanol to give pure H_2LMe_2 (4.73 g, 72%). Mp: 234−235 °C. Anal. Calcd for $C_{19}H_{17}N_5O_2{\cdot}H_2O$: C, 62.46; H, 5.24, N, 19.17. Found: C, 62.24; H, 5.21; N,19.15. IR: 3379 (m), 3264 (m), 1692 (s), 1601 (s), 1579 (s), 1533 (s), 1400 (m), 1301 (m), 1234 (m), 1143 (m), 1072 (m), 999 (w), 792 (m), 783 (m), 745 (m), 681 (m), 654 (w). ^{1}H and ^{13}C NMR assignments were made on the basis of $^{1}H-^{1}H$ and $^{13}C-^{1}H$ COSY spectra, DEPT 135 spectra, and proton integral values. ^{1}H NMR (the atom-labeling scheme used for this and the other new compounds is shown in Figure 1): δ 8.04 (t, 1H, H_{a}, $^{3}J_{HH} = 7.0$), 8.41 (d, 2H, $H_{b,b'}$ $^{3}J_{HH} = 7.2$), 11.1 (s, 2H, $H_{e,e'}$), 8.24 (d, 2H, $H_{g,g'}$ $^{3}J_{HH} = 8.1$), 7.61 (t, 2H, $H_{h,h'}$, $^{3}J_{HH} = 7.9$), 6.89 (d, 2H, $H_{i.,i'}$, $^{3}J_{HH} = 7.5$), 2.47 (s, 6H, $H_{k,k'}$), 5.30 (s, 2H, H_2O). ^{13}C NMR: δ 139.2 (s, C_{a}), 125.4 (s, C_{b}), 148.4 (s, C_{c}), 161.7 (s, C_{d}), 156.4 (s, C_{f}), 111.2 (s, C_{g}), 138.9 (s, C_{h}), 119.3 (s, C_{i}), 150.6 (s, C_{j}), 23.9 (s, C_{k}).

Preparation of $RuCl_2(PPh_3)(LMe_2\{H\}_2)$ (2). (Note: "$LMe_2\{H\}_2$" is used here to represent the ligand derived from *N,N′*-bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide in which the two amide nitrogens are deprotonated and the two pendant pyridine nitrogens are protonated.) $RuCl_2(PPh_3)_3$ (1.00 g) and H_2LMe_2 (0.38 g) were added to dry, deoxygenated toluene (100 mL), and the mixture was heated under reflux with stirring for 24 h. The mixture was allowed to cool, and the dark purple crystals of pure **1** were removed by filtration and washed with hexane (0.558 g, 68%). Mp: >350 °C. Anal. Calcd for $C_{37}H_{32}Cl_2N_5O_2PRu$: C, 56.86; H, 4.13; N, 8.96; Cl, 9.07. Found: C, 56.97; H, 4.16; N, 8.87; Cl, 9.44. IR: 3452 (w), 3052 (w), 1638 (s), 1619 (s), 1594 (s), 1524 (s), 1404 (w), 1343 (s), 1274 (s), 1174 (m), 1148 (s), 1091 (m), 1042 (w), 1005 (w), 798 (m), 762 (w), 750 (w), 700 (s), 531 (s). ^{1}H NMR: δ 7.43 (dd, 1H, H_{a}, $^{3}J_{HH} = 8.7, 6.8$), 8.62 (d, 2H, $H_{b,b'}$, $^{3}J_{HH} = 8.2$), 7.64 (m, 4H, $H_{g,g',h,h'}$), 6.78 (d, 2H, $H_{i,i'}$, $^{3}J_{HH} = 7.2$), 2.63 (s, 6H, $H_{k,k'}$), 13.69 (s, 2H, $H_{l,l'}$), 6.85−7.20 (m, 15H, PPh_3). ^{13}C NMR: δ 130.9 (s, C_{a}), 127.2 (s, $C_{b,b'}$), 147.7 (s, $C_{c,c'}$), 172.6 (s, $C_{d,d'}$), 160.2 (s, $C_{f,f'}$), 115.2 (s, $C_{g,g'}$), 141.9 (s, $C_{h,h'}$), 120.5 (s, $C_{i,i'}$), 156.8 (s, $C_{j,j'}$), 19.0 (s, $C_{k,k'}$), 128.8 (s, *para*-C PPh_3), 127.5 (d, *ortho*-C PPh_3, $^{2}J_{CP} = 9.2$), 133.0 (d, *meta*-C PPh_3, $^{3}J_{CP} = 9.4$), 133.2 (d, *ipso*-C PPh_3, $^{1}J_{CP} = 42.2$).[13]

Preparation of $Ru(SCN)_2(PPh_3)(LMe_2\{H\}_2)$ (3). $RuCl_2(PPh_3)(LMe_2\{H\}_2)$ (0.100 g) and KSCN (0.100 g) were added to deoxygenated methanol (40 mL), and the mixture was heated under reflux with stirring for 24 h. The solution was allowed to cool, and the solvent was removed under reduced pressure. The red-brown solid was dissolved in dichloromethane (40 mL), and the solution was washed with water (40 mL). The organic phase was removed and methanol (20 mL) was added. The solvent volume was then reduced under low pressure to give red-brown crystals, which were collected and recrystallized from chloroform/hexane to give pure **2** (0.088 g, 83%). Mp: 236−240 °C dec. Anal. Calcd for $C_{39}H_{32}N_7O_2PRuS_2{\cdot}CHCl_3$: C, 50.77; H, 3.52; N, 10.36. Found: C, 50.67; H, 3.60; N, 10.68. IR: 2085 (s), 2077 (s), 1647 (s), 1626 (s), 1605 (s), 1591 (s), 1526 (s), 1406 (w), 1337 (s), 1271 (s), 1173 (m), 1155 (m), 1146 (m), 1093 (w), 816 (m), 799 (m), 696 (m), 530 (s). ^{1}H NMR: δ 7.55 (dd, 1H, H_{a}, $^{3}J_{HH} = 8.9, 6.3$), 8.60 (d, 2H, $H_{b,b'}$, $^{3}J_{HH} = 8.9$), 7.64 (m, 2H, $H_{g,g'}$), 7.87 (dd, 2H, $H_{h,h'}$, $^{3}J_{HH} = 7.4, 8.8$), 7.17 (m, 2H, $H_{i,i'}$), 2.86 (s, 6H, $H_{k,k'}$), 12.89 (s, 2H, $H_{l,l'}$), 6.85−7.25 (m, 15H, PPh_3). ^{13}C NMR: δ 127.4 (s, $C_{b,b'}$), 147.9 (s, $C_{c,c'}$), 172.2 (s, $C_{d,d'}$), 159.5 (s, $C_{f,f'}$), 116.7 (s, $C_{g,g'}$), 143.3 (s, $C_{h,h'}$), 120.2 (s, $C_{i,i'}$), 155.6 (s, $C_{j,j'}$), 20.9 (s, $C_{k,k'}$), 129.3 (s, *para*-C PPh_3), 127.9 (d, *ortho*-C PPh_3, $^{2}J_{CP} = 9.1$), 132.7 (d, *meta*-C PPh_3, $^{3}J_{CP} = 9.5$), 131.7 (d, *ipso*-C PPh_3, $^{1}J_{CP} = 43.1$) (C_{a} resonance not observed).

Preparation of $Ru(O_2CCH_3)_2(PPh_3)(LMe_2\{H\}_2)$ (4). $RuCl_2(PPh_3)(LMe_2\{H\}_2)$ (0.098 g) and $Tl(O_2CCH_3)$ (0.070 g, 2.1 equiv) (*Caution*! *Toxic*) were placed in a Schlenk tube under nitrogen. Dry acetonitrile (20 mL) was added, and the suspension was heated under reflux for 16 h. During this time, a fine white solid precipitated and the solution became orange. The heating was stopped, and the solution was allowed to cool. The TlCl was removed by filtering the solution twice through Whatman No. 4 filter paper, and the solvent was then removed from the filtrate under reduced pressure. The resulting brown solid was recrystallized from CH_2Cl_2/hexane to give pure **4** as a brown microcrystalline solid (0.90 g, 87%) Mp: 170−180 °C. Anal. Calcd for $C_{41}H_{38}N_5O_6PRu{\cdot}0.5C_6H_{14}$: C, 60.61; H, 5.20; N, 8.03. Found: C, 60.65; H, 4.73; N, 7.92. IR: 1616 (s), 1591 (s), 1560 (s), 1400 (m), 1346 (s), 1279 (m), 1236 (m), 1153 (m), 1092 (m), 1041 (w), 1001 (w), 795 (m), 747 (m), 698 (s), 532 (m), 519 (m). ^{1}H NMR: δ 6.9−7.6 (m, *ca*. 20H, $H_{a,g,g'h,h'}$ and PPh_3), 8.39 (d, 2H, $H_{b,b'}$, $^{3}J_{HH} = 8.7$), 6.64 (d, 2H, $H_{i,i'}$, $^{3}J_{HH} = 7.3$), 2.51 (s, 6H, $H_{k,k'}$), 1.70 (s, 3H, CH_3CO_2), 1.99 (s, 3H, CH_3CO_2) ($H_{l,l'}$ resonances not observed). ^{13}C NMR: δ 133.3 (s, C_{a}), 125.8 (s, $C_{b,b'}$), 150.4 (s, $C_{c,c'}$), 172.5 (or 172.9) (s, $C_{d,d'}$), 162.8 (s, $C_{f,f'}$), 115.7 (s, $C_{g,g'}$), 139.6 (s, $C_{h,h'}$), 118.4 (s, $C_{i,i'}$), 158.5 (s, $C_{j,j'}$), 22.4 (s, $C_{k,k'}$), 128.5 (s, *para*-C PPh_3), 127.4 (d, *ortho*-C

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(11) Pendant arm ligands are usually designed so that in metal complexes the pendant arm coordinates to the metal center. See, for example: (a) Bernhardt, P. V.; Lawrance, G. A. *Cood. Chem. Rev.* **1990**, *104*, 297. (b) Collman, J. P.; Groh, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 1391. (c) Adams, H.; Bailey, N. A.; Dwyer, M. J. S.; Fenton, D. E.; Hellier, P. C.; Hempstead, P. D.; Latour, J. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1207. (d) Bu, X. H.; An, D. L.; Chen, Y. T.; Shionoya, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1995**, 2289.

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Table 1. Crystallographic Data

	$H_2LMe_2 \cdot H_2O$	$RuCl_2(PPh_3)(LMe_2\{H\}_2)$	$Ru(NO_2)(NO)(PPh_3)(LMe_2) \cdot C_6H_6$
empirical formula	$C_{19}H_{19}N_5O_3$	$C_{37}H_{32}Cl_2N_5O_2PRu$	$C_{43}H_{36}N_7O_5PRu$
fw	365.39	781.62	862.83
T, K	293	193	293
a, Å	13.588(6)	10.482(5)	12.204(2)
b, Å	11.518(2)	11.349(8)	13.065(3)
c, Å	12.731(3)	15.710(4)	14.722(6)
α, deg	90.0	92.55(3)	108.62(2)
β, deg	113.54(2)	90.06(3)	112.20(2)
γ, deg	90.0	115.22(3)	68.22(2)
V, Å^3	1826.7(10)	1689(2)	1973.9(10)
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
ρ_{calc}, g cm^{-3}	1.329	1.537	1.452
μ, mm^{-1}	0.093	0.712	0.493
λ, Å	0.710 69	0.710 69	0.710 69
R(F)[a]	0.0556	0.0395	0.0412
R_w (F^2)[b]	0.1224	0.0890	0.1085

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

PPh$_3$ $^2J_{CP} = 8.7$), 132.4 (d, *meta*-C PPh$_3$ $^3J_{CP} = 9.8$), 131.4 (d, *ipso*-C PPh$_3$ $^1J_{CP} = 43.9$), 184.2, 172.9 (or 172.5) (s, CH$_3$*C*OO), 20.7 (s, *C*H$_3$-COO).

Preparation of Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$) (5). RuCl$_2$(PPh$_3$)(LMe$_2$\{H\}$_2$) (0.150 g) and NaNO$_2$ (0.150 g) were placed in a Schlenk tube, and methanol (30 mL) was added. The mixture was degassed, placed under an atmosphere of nitrogen, and then heated under reflux for 24 h. The resulting light brown solution was evaporated to dryness under reduced pressure, the residue was dissolved in dichloromethane (20 mL), and this solution was shaken with water (20 mL). The dichloromethane solution was separated from the water and dried over anhydrous magnesium sulfate. Hexane was added, and the solvent volume was lowered under reduced pressure to effect crystallization of crude **5**. This was collected and recrystallized from dichloromethane/hexane to give pure **5** (0.130 g, 86%). Mp: 230 °C. Anal. Calcd for $C_{37}H_{30}N_7O_5PRu \cdot CH_2Cl_2$: C, 52.48; H, 3.71; N, 11.27. Found: C, 52.34; H, 3.45; N, 11.17. IR: 1898 (s), 1634 (s), 1603 (s), 1574 (s), 1406 (s), 1356 (s), 1317 (s), 1298 (m), 1229 (m), 1157 (m), 1094 (s), 816 (m), 791 (m), 743 (m), 696 (s), 646 (m), 525 (s). ^{1}H NMR: δ 8.13 (t, 1H, H$_a$, $^3J_{HH} = 7.8$), 8.08 (d, 2H, H$_{gg'}$, $^3J_{HH} = 8.3$), 7.99 (d, 2H, H$_{bb'}$, $^3J_{HH} = 7.7$), 7.48 (dd, 2H, H$_{hh'}$, $^3J_{HH} = 7.4$, 8.2), 6.82 (d, 2H, H$_{ii'}$, $^3J_{HH} = 7.3$), 7.15−7.43 (m, 15H, PPh$_3$). ^{13}C NMR: δ 142.7 (s, C$_a$), 126.8 (s, C$_b$), 156.8 (s, C$_{c,f \text{ or } j}$), 166.1 (s, C$_d$), 156.44 (s, C$_{f,c \text{ or } j}$), 117.6 (s, C$_g$), 138.0 (s, C$_h$), 119.2 (s, C$_i$), 155.5 (s, C$_{j,c \text{ or } f}$), 23.5 (s, C$_k$), 131.8 (s, *para*-C PPh$_3$), 129.1 (d, *ortho*-C PPh$_3$, $^2J_{CP} = 10.1$), 133.8 (d, *meta*-C PPh$_3$, $^3J_{CP} = 10.1$) (*ipso*-C PPh$_3$ not observed).

X-ray Crystallography. Unit cell parameters for all compounds were obtained by least-squares fits to the setting angles of 25 well-distributed reflections. Data collection was performed at room temperature for H$_2$LMe$_2$ (**1**) and Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$) (**5**) and at −80 °C for RuCl$_2$(PPh$_3$)(LMe$_2$\{H\}$_2$) (**2**). Data collection with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) employed $\omega/2\theta$ scans, and reflections were scanned until $I/\sigma(I)$ was 2500 or until the scanning time had reached a maximum of 60 s. Three reflections were monitored throughout data collection as a check on crystal movement or decomposition, no evidence of either being found. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections, using ψ scans, were applied to **2** and **5**, locally written software being used for this purpose.

Structure solution was accomplished by direct methods for **1** and Patterson and difference Fourier methods for **2** and **5**. The structures were refined by full-matrix least-squares procedures using scattering curves taken from the *International Tables for Crystallography*. All non-hydrogen atoms were allowed to assume anisotropic motion. Hydrogen atoms for **1** and pyridinium hydrogens for **2** were located from difference maps and allowed to refine with a common thermal parameter. For **2** and **5** the remaining hydrogen atoms were located in calculated positions and allowed to ride at a fixed distance from the parent atom with a 20% greater thermal parameter. For **5** there were no peaks in the difference electron density map which could be interpreted as protons on the pyridine nitrogen atoms. There is one molecule of benzene present in the lattice for each molecule of **5**, the benzene molecules being distributed on centers of symmetry. There is some evidence for disorder in the methyl carbon C(19) in **5**, as indicated by the larger thermal parameter for this atom. Programs used were SHELXS-86 for structure solution and SHELXL-93 for refinement. Diagrams were produced by the SHELXTL set of programs.

Results and Discussion

The molecule *N,N′*-bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide (H$_2$LMe$_2$) is conveniently prepared by reaction of 2,6-pyridinedicarbonylchloride with 2-amino-6-methylpyridine. Spectral data for this compound are collected in the Experimental Section. The X-ray crystal structure determination of H$_2$LMe$_2$ (*vide infra*) shows that in the solid state a water molecule is associated with H$_2$LMe$_2$ through hydrogen bonds to the amide protons and the pendant pyridines. In the IR spectrum (Nujol mull) a broad band centered at 3379 cm^{-1} is assigned to ν(OH) of the guest water molecule and a broad band at 3264 cm^{-1} is assigned to ν(NH) of the amide groups. Water appears to remain associated with H$_2$LMe$_2$ in solution, and in the ^{1}H NMR spectrum a broad resonance at δ 5.30 ppm, which integrates for two protons, is assigned to hydrogen-bonded water. Only a single set of signals is seen for the two pendant groups of H$_2$LMe$_2$ in both the ^{1}H and ^{13}C NMR spectra. This indicates that the two “arms” of the ligand are magnetically equivalent in solution on the corresponding NMR time scales.

Molecular Structure of H$_2$LMe$_2$·H$_2$O. The structure of H$_2$LMe$_2$ (**1**) was determined by a single-crystal X-ray diffraction study (see Table 1 for crystallographic data for compounds **1**, **2**, and **5**). The molecular structure is shown in Figure 2 and selected bond distances and angles are given in Table 2.

The amide and pyridine nitrogen atoms are all directed toward the center of the molecular cavity, and there is a 2-fold axis passing through atoms C(3) and N(1). The molecule is essentially planar, and the rms deviation from the plane of best fit through all the atoms is 0.04 Å. A water molecule that is associated with the molecular cavity lies 0.485(6) Å above the molecular plane and is thus disordered about the 2-fold axis. The distances of N(3)−O(2) (2.789(6) Å) and N(2)−O(2) (2.965(6) Å) indicate the water molecule forms relatively weak hydrogen bonds to the amide hydrogens and the pendant pyridine nitrogens. These distances come at the longer ends of the ranges reported for the corresponding classes of hydrogen bonds, i.e. O−H···N (2.68−2.79 Å) and N−H···O (2.81−3.04

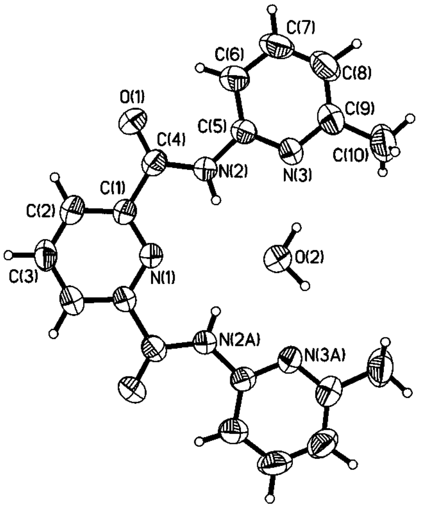
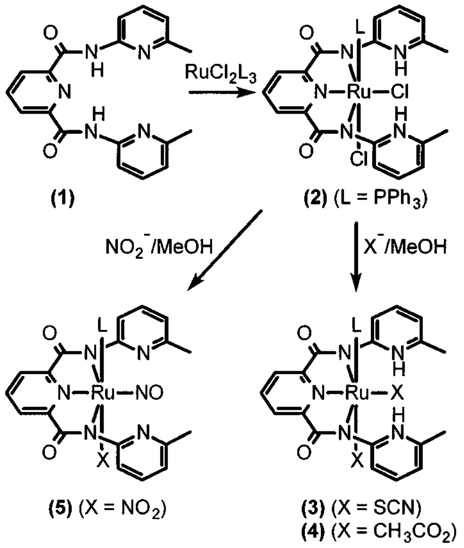


Figure 2. Molecular structure of H$_2$LMe$_2$·H$_2$O. Atoms are depicted as 50% ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for H$_2$LMe$_2$·H$_2$O

N(2)−C(4)	1.352(4)	O(1)−C(4)	1.222(3)
N(2)−C(5)	1.402(4)	C(1)−C(4)	1.506(4)
C(4)−N(2)−C(5)	129.2(2)	N(2)−C(4)−C(1)	114.3(2)
N(1)−C(1)−C(4)	117.5(2)	N(3)−C(5)−N(2)	113.5(2)

Scheme 1



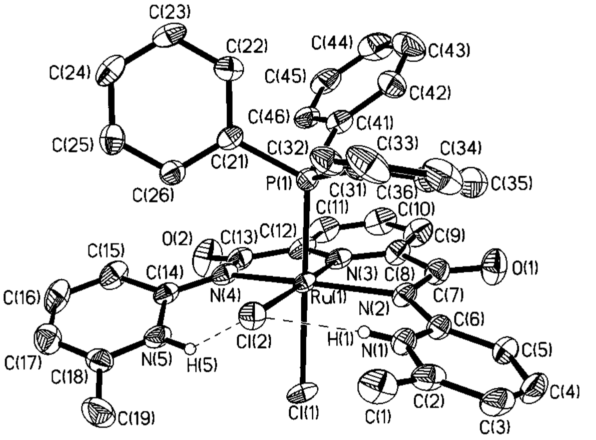


Figure 3. Molecular structure of RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$). Atoms are depicted as 50% ellipsoids.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$)

Ru(1)−N(3)	1.947(4)	O(2)−C(13)	1.242(6)
Ru(1)−N(2)	2.140(4)	N(2)−C(7)	1.378(6)
Ru(1)−N(4)	2.155(4)	N(2)−C(6)	1.380(6)
Ru(1)−P(1)	2.279(2)	N(4)−C(14)	1.367(6)
Ru(1)−Cl(1)	2.465(2)	N(4)−C(13)	1.370(6)
Ru(1)−Cl(2)	2.5165(14)	C(7)−C(8)	1.488(7)
O(1)−C(7)	1.234(6)	C(12)−C(13)	1.482(7)
N(2)−Ru(1)−N(4)	155.26(14)	N(1)−C(6)−N(2)	115.0(4)
N(3)−Ru(1)−Cl(1)	91.39(11)	N(2)−C(7)−C(8)	113.5(4)
N(4)−Ru(1)−Cl(1)	84.54(11)	N(3)−C(8)−C(7)	114.4(4)
P(1)−Ru(1)−Cl(1)	175.27(4)	N(3)−C(12)−C(13)	114.9(4)
N(3)−Ru(1)−Cl(2)	178.68(11)	N(4)−C(13)−C(12)	113.4(4)
C(7)−N(2)−C(6)	118.3(4)	N(5)−C(14)−N(4)	115.1(4)
C(14)−N(4)−C(13)	117.8(4)		

Å).[14] There are no significant intermolecular hydrogen bonds. The separation between the two amide nitrogens is 4.537(5) Å, and the pendant pyridine nitrogens are 5.457(5) Å apart.

Synthesis of RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$) (2). The complex RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$) (**2**) is formed in good yield as dark purple crystals upon treatment of RuCl$_2$(PPh$_3$)$_3$ with H$_2$LMe$_2$ in refluxing toluene for 16 h (see Scheme 1). The yield of **2** is not significantly improved if bases such as triethylamine are present in the reaction mixture. Spectral data for **2** are collected in the Experimental Section. In the IR ν(NH) of the protonated pendant pyridines is observed at 3452 cm^{-1}, and the amide I band[15] of the free ligand at 1692 cm^{-1} is replaced by a lower frequency band at 1638 cm^{-1}. This type of behavior is typically observed for amidato-*N* complexes.[10,11,16] The signal from the two pyridinium protons is observed at δ 13.69 ppm in the ^{1}H NMR spectrum. Only one set of signals is observed for the two pendant arms in the ^{1}H and ^{13}C NMR spectra, indicating that in solution these pendant groups are magnetically equivalent on the corresponding NMR time scales.

Molecular Structure of RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$) (2). The molecular structure of RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$) was determined by X-ray crystallography, and the molecular structure is shown in Figure 3.

Selected bond distances and angles are given in Table 3. The geometry about ruthenium can be viewed in terms of a distorted octahedron. The atoms Ru(1), Cl(2), N(2), N(3), and N(4) are nearly coplanar, with the mean deviation from the plane of best fit through these atoms being 0.08 Å. The angles Cl(1)−Ru(1)−P(1) and Cl(2)−Ru(1)−N(3) are close to linear, but the bonds to the two amidate nitrogens are not, and the angle N(2)−Ru(1)−N(4) is 155.26(14)°. The distance between the two nitrogen atoms, N(2) and N(4), is 4.196(6) Å. This is considerably shorter than the corresponding distance in the free ligand, H$_2$LMe$_2$, where N(2)---N(2A) is 4.537(5) Å. The two Ru−N(amidato) bond lengths (Ru(1)−N(2) = 2.140(4), Ru(1)−N(4) = 2.155(4) Å) are both considerably longer than the mean value of other reported Ru−N(amidato) distances (2.042 Å).[17] However, the Ru−N(pyridine) bond length of 1.947(4) Å is one of

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(15) Bellamy, L. J. *The infra-red spectra of complex molecules*, 3rd ed.; Chapman and Hall: London, 1975.

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(17) The mean value of Ru−N(amidato) distances (Å) was obtained from a search of the Cambridge Structural Database (Nobs, 21; Mean, 2.042; SDsample, 0.050).

the shortest that has been reported.[18] The distances and angles associated with the bonds between Ru and N(2), N(3), and N(4) indicate that there is a minor mismatch between the arrangement of the constrained nitrogen donor atoms and the preferred coordination geometry for the ruthenium atom.

The two nitrogen atoms of the pendant pyridines are both protonated and oriented toward the molecular cavity. Close approaches are made by both nitrogens to the chloro ligand, Cl(2), that is projected into the cavity. The distances N(1)$\cdots$Cl(2) = 3.028(5) Å and N(5)$\cdots$Cl(2) = 3.019(4) Å are toward the short end of the range of lengths reported for N−H$\cdots$Cl hydrogen bonds (3.00−3.20 Å),[14] indicating that the protonated pyridine groups form relatively strong hydrogen bonds to Cl(2). In contrast, the distances N(1)$\cdots$Cl(1) = 3.931(4) Å and N(5)$\cdots$Cl(1) = 3.388(5) Å are too long for significant hydrogen-bonding interactions. The two pendant pyridines are both twisted somewhat out of the plane through the remainder of the bis(amidato-*N*) ligand and the torsion angles C(13)−N(4)−C(14)−C(15) and C(7)−N(2)−C(6)−C(5) are −32.8(7) and −13.4(7)°, respectively. Deviations from planarity for metalated amide groups can be described using the parameters originally defined by Dunitz and Winkler[19] and subsequently modified by Collins.[20] The parameter τ can be interpreted as the angle between the idealized positions of the pπ orbitals on the C and N atoms of the amide group and reaches maximum values at ±90°. The parameters χ_N and χ_C describe the degree of pyramidalization at the amide nitrogen and carbon atoms, respectively, and the pyramidalization terms equal ±60° for idealized sp^3 hybridized atoms.[20] In compound **2** the parameter τ has very low values for the two amide groups (−8.9(6), N(2) amide; 0.0(6), N(4) amide), and the values for the pyramidalization terms, χ_C (0.2(8) for C(7) and 5.0(8) for C(13)) and χ_N (3.5(8) for N(2) and −11.4(8) for N(4)) are also very small. Thus, N-metalation of the two amides in this compound causes very little deviation from planarity to occur for these groups.

Substitution Reactions of RuCl$_2$(PPh$_3$)(LMe$_2${H}$_2$) (2). The chloride ligands in **2** can be substituted if moderately forcing conditions are employed. For example, if a mixture of **2** and excess potassium thiocyanate is heated under reflux in methanol for 16 h, both chlorides are substituted and the complex Ru(SCN)$_2$(PPh$_3$)(LMe$_2${H}$_2$) (**3**) can be isolated from solution (see Scheme 1). Bands associated with ν(CN) of the the thiocyanate groups appear in the IR spectrum at 2085 and 2077 cm^{-1}. It is difficult to determine by IR spectroscopy whether the thiocyanate ion is coordinated through N or S. Usually ν(CN) of S-bound thiocyanate appears closer to 2100 cm^{-1} and that of N-bound thiocyanate closer to 2050 cm^{-1}.[21] Using this criterion, it appears that the thiocyanate ions are most probably S-bound in **3**. The ^{1}H and ^{13}C NMR spectra of **3** are similar to the corresponding spectra observed for **2** (see Experimental Section). Therefore, it is likely that the structure of **3** is similar to that found for **2**.

The chloride ligands in **2** can also be replaced by acetate. On treatment of **2** with thallium(I) acetate in acetonitrile, thallium chloride is precipitated and the complex Ru(O$_2$CCH$_3$)$_2$(PPh$_3$)(LMe$_2${H}$_2$) (**4**) is formed. The ν(CO) bands of the acetate groups are obscured by the strong amide absorptions in the IR spectrum of **4**. The resonances of the two acetate groups are observed in the ^{1}H NMR spectrum at 1.70 and 1.99 ppm. Other spectral data for **4** are collected in the Experimental Section.

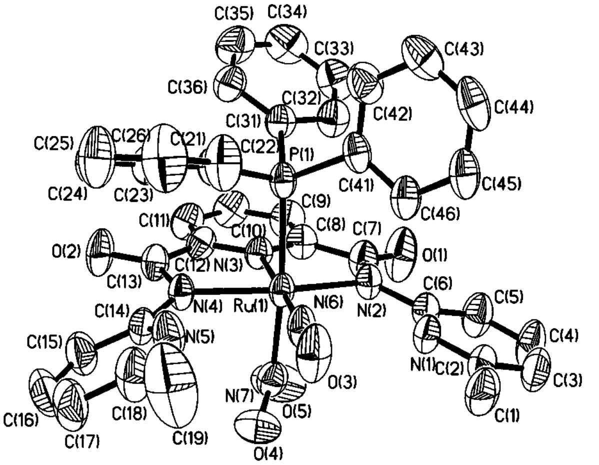

Figure 4. Molecular structure of Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$)$\cdot$C$_6$H$_6$. Atoms are depicted as 50% ellipsoids.

Reaction of **2** with sodium nitrite in methanol also results in substitution of both chloride ligands, but the ultimate product formed in this instance is the nitrito-*N*/ nitrosyl complex Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$) (**5**) (see Scheme 1). Complexes containing nitrosyl ligands have been synthesized by a number of different routes,[22] and one of these involves reaction of coordinated nitrite with acid.[23] It is reasonable to expect that the protonated pyridine groups in **2** act as an internal proton source for the conversion of nitrite to nitrosyl. In the IR spectrum of **5**, ν(NO) appears as an intense band at 1898 cm^{-1}.

Molecular Structure of Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$) (5). A single-crystal X-ray structure determination has been obtained for Ru(NO$_2$)(NO)(PPh$_3$)(LMe$_2$) (**5**), and the molecular structure is shown in Figure 4.

Selected bond distances and angles are collected in Table 4. The spatial arrangement of ligands about ruthenium is similar to that found for **2**. The triphenylphosphine and nitrito-*N* ligands are mutually *trans* (the angle N(7)−Ru(1)−P(1) is 174.35(8)°), and the equatorial plane is occupied by the three nitrogen donor atoms of the bis(amidato-*N*) ligand and the nitrogen of the coordinated nitrosyl. This latter ligand occupies the molecular cleft formed by the two pendant pyridines. The Ru(1)−N(6) distance (1.745(3) Å) is very close to the mean value of other reported Ru−NO distances.[24] The nitrogen atom of the pyridine coordinated *trans* to the nitrosyl group approaches the ruthenium atom closely (Ru(1)−N(3) = 2.016(3) Å), although this distance is not as short as the corresponding distance in **2**. The two Ru−N(amidato) bond lengths (2.106(3) and 2.124(3) Å) are slightly shorter than those found in **2.** Accordingly, the distance

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(18) A search of the Cambridge Structural Database reveals that only five Ru−N(pyridine) distances less than 1.950 Å have been reported (Nobs, 1164; Mean, 2.088; SDsample, 0.055).

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(24) A search of the Cambridge Structural Database revealed a mean value of 1.753 Å for reported Ru−NO distances (Nobs, 88; SDsample, 0.036).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ru(NO_2)(NO)(PPh_3)(LMe_2)\cdot C_6H_6$

Ru(1)−N(6)	1.745(3)	N(4)−C(14)	1.413(4)
Ru(1)−N(3)	2.016(3)	N(6)−O(3)	1.141(4)
Ru(1)−N(4)	2.106(3)	N(7)−O(5)	1.180(4)
Ru(1)−N(2)	2.124(3)	N(7)−O(4)	1.230(4)
Ru(1)−N(7)	2.144(3)	O(1)−C(7)	1.223(4)
Ru(1)−P(1)	2.4374(10)	O(2)−C(13)	1.233(4)
N(2)−C(7)	1.359(4)	C(7)−C(8)	1.490(5)
N(2)−C(6)	1.426(4)	C(12)−C(13)	1.489(5)
N(4)−C(13)	1.348(4)		
N(6)−Ru(1)−N(3)	178.39(12)	O(5)−N(7)−Ru(1)	122.4(3)
N(4)−Ru(1)−N(2)	153.24(11)	O(4)−N(7)−Ru(1)	115.9(2)
N(3)−Ru(1)−N(7)	86.35(11)	N(1)−C(6)−N(2)	114.4(3)
N(4)−Ru(1)−N(7)	84.05(11)	N(2)−C(7)−C(8)	112.6(3)
N(7)−Ru(1)−P(1)	174.35(8)	N(3)−C(8)−C(7)	115.3(3)
C(7)−N(2)−C(6)	120.0(3)	N(3)−C(12)−C(13)	114.6(3)
C(13)−N(4)−C(14)	121.0(3)	N(4)−C(13)−C(12)	112.9(3)
O(3)−N(6)−Ru(1)	178.3(3)	N(5)−C(14)−N(4)	114.9(3)

N(4)---N(2) (4.116(4) Å) is also slightly less than the corresponding distance in **2**.

Unlike **2**, the pendant pyridines in this molecule are not protonated. However, the nitrogen atoms of these groups are still oriented toward the nitrosyl ligand, even though this brings the pyridine nitrogen lone pairs into close proximity of the π orbitals associated with the nitrosyl ligand. The distances between the nitrosyl nitrogen and the two pendant pyridine nitrogen atoms are very similar (N(5)---N(6) = 2.695(4) Å, N(1)---N(6) = 2.712(4) Å) and both values are shorter than the van der Waals contact distance of 3.00 Å for two nitrogen atoms. As yet, we have not observed any chemical reactions in which interactions between the pendant pyridines and the nitrosyl group appear to play an important role. The torsion angles C(7)−N(2)−C(6)−C(5) (1.2(5)°) and C(13)−N(4)−C(14)−C(15) (27.0(5)°) are slightly smaller than the corresponding angles found in **2** (−13.4(7) and −32.8(7)°). Examination of the parameters τ, χ_C, and χ_N shows that there is little deviation from planarity for the two amide groups, as was the case in **2**. The values of these parameters for **5** are $\tau = -1.8(5)$, $\chi_C = -1.1(8)$, and $\chi_N = 12.4(8)$ for the N(2) amide and $\tau = 9.2(4)$, $\chi_C = 0.9(7)$, and $\chi_N = -2.6(7)$ for the N(4) amide.

Conclusions

In its doubly deprotonated form, H_2LMe_2 can coordinate to metals in a tridentate fashion through the two amidate nitrogen atoms and the central pyridine nitrogen. The two pendant pyridines form a molecular cleft with the nitrogen atoms of these groups directed toward one of the coordination sites of the metal. In the neutral ruthenium derivative $RuCl_2(PPh_3)(LMe_2\{H\}_2)$ (**2**), the two pendant pyridines are protonated and hydrogen bonds are formed to the metal-bound chloride that is held within the cleft of the ligand. The chloride ligands in **2** are readily replaced by other anionic ligands such as thiocyanate or acetate in simple metathesis reactions. Replacement also occurs with nitrite, but in this instance the nitrito-*N*/nitrosyl-containing complex $Ru(NO_2)(NO)(PPh_3)(LMe_2)$ (**5**) is formed where the coordinated nitrosyl occupies the ligand cleft. During the formation of **5**, the protonated pyridines appear to act as sources of internal acid that facilitate the nitrosyl ligand formation.

The pendant pyridines in these complexes can be viewed as providing sites for reversible protonation. Other complexes in which these pendant groups act as donor groups for the interception of coordinated, reactive intermediates or for the coordination of other metals have been obtained, and these results will be reported separately. More elaborate analogues of H_2LMe_2 have also been prepared, and the chemistry of metal derivatives of these species is currently under investigation.

Acknowledgment. We thank the University of Auckland Research Committee for partial support of this work through grants-in-aid.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**, **2**, and **5** are available on the Internet only. Access information is given on any current masthead page.

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