

→ fluid triggering effect is, no doubt, the necessity of the two aromatic rings of the quencher ligand to assume a coplanar arrangement before quenching can occur. In the methyl substituted complex  $[(bpy)_2Os(CO)N,3,3'-trimethyl-4,4'-bipyridine]^{3+}$ , flattening can not occur because of steric repulsion; electrochemical measurements show that the pyridinium-based reduction is at  $-1.06$  V vs. SSCE, and intramolecular quenching of the  $^3MLCT(bpy)$  state in fluid solution is not observed.<sup>8b</sup> The analogous Re complex is currently under investigation.

The third novel feature in the figure is the appearance of clear evidence for a broad, higher energy luminescence at 400–525 nm. It seems clear that the higher energy emission must occur from a "singlet" analogue of the  $^3MLCT(bpy)$  state on the basis of the following evidence: vibrational progressions for both high- and low-energy emissions are nearly the same within experimental error and lifetime studies show that even at 80 K the lifetime of the higher energy emission is  $<20$  ns.

It has been suggested that a  $^1MLCT(bpy)$ -based emission does occur following excitation of  $Ru(bpy)_3^{2+}$  on the basis of the results of lifetime studies,<sup>14</sup> but the emission spectra shown here provide direct spectral evidence for such an emission for this type of chromophore. Our ability to observe the fluorescence so clearly in cold fluid solution is a direct consequence of intramolecular quenching of the relatively long-lived  $^3MLCT(bpy)$  state by bound  $BzQ^+$  or  $MeQ^+$ . At 80 K we estimate that  $\Phi_{em}(^1MLCT)/\Phi_{em}(^3MLCT) \approx 0.02$ . By 160 K, the intensities of the two emissions are comparable as shown in part B of the figure. It appears that at low temperature where intramolecular quenching by  $BzQ^+$  or  $MeQ^+$  is unimportant, the absolute radiative efficiency from the  $^1MLCT(bpy)$  state is low, suggesting that "fluorescence" competes unfavorably with "intersystem crossing",  $^1MLCT(bpy) \rightarrow ^3MLCT(bpy)$ , which is known to be the case for  $Ru(bpy)_3^{2+}$  at room temperature.<sup>15</sup>

**Acknowledgments** are made to the National Science Foundation under Grants CHE-8008922 and CHE-7920114 and to NATO and CNRS France for support of H.L.B.

**Registry No.**  $[(bpy)Re(CO)_3(MeQ)]^{2+}$ , 86695-84-3;  $[(bpy)Re(CO)_3(BzQ)]^{2+}$ , 86695-85-4.

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### Alkyl, Hydride, and Dinitrogen 1,2-Bis(dimethylphosphino)ethane Complexes of Chromium. Crystal Structures of $Cr(CH_3)_2(dmpe)_2$ , $CrH_4(dmpe)_2$ , and $Cr(N_2)_2(dmpe)_2$

Gregory S. Girolami, Julian E. Salt, and  
 Geoffrey Wilkinson\*

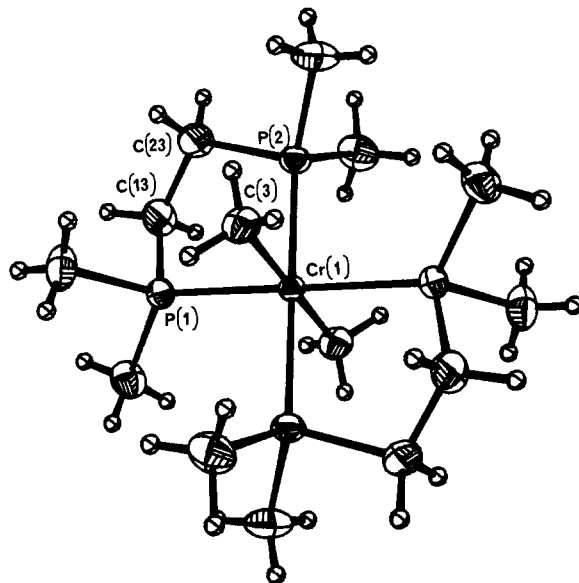
Department of Chemistry  
 Imperial College of Science and Technology  
 London SW7 2AY, England

Mark Thornton-Pett and Michael B. Hursthouse\*

Department of Chemistry, Queen Mary College  
 London E1 4NS, England

Received May 31, 1983

Inorganic and organometallic complexes of first row transition metals are more labile than their second and third row analogues,<sup>1</sup> and consequently they should exhibit relatively enhanced reactivity. Often, however, second and third row metal compounds have no first row counterparts, and in many instances this may be at-



**Figure 1.** Structure of  $CrMe_2(dmpe)_2$ . Important bond lengths (Å) and angles (deg): Cr(1)–C(3), 2.168 (4); Cr(1)–P(1), 2.342 (1); Cr(1)–P(2), 2.349 (1); Cr(1)–C(3)–H(31), 121 (2); Cr(1)–C(3)–H(32), 108 (3); Cr(1)–C(3)–H(33), 108 (2); P(2)–Cr(1)–P(1), 82.7 (1); C(3)–Cr(1)–P(1), 87.2 (2); C(3)–Cr(1)–P(2), 89.6 (2).

tributed to the increased labilities of the latter, which make decomposition pathways more accessible. In particular, apart from some carbonyl species, phosphine derivatives of the early first row metals are rare.<sup>2</sup> We now report some chromium complexes of the chelating phosphine ligand 1,2-bis(dimethylphosphino)ethane (dmpe), notably the first example of a mononuclear  $Cr^{II}$  alkyl, a  $Cr^{IV}$  hydride, and the first stable  $Cr^0$  dinitrogen complex to be fully structurally characterized, unlike previous examples that have been observed in solution.<sup>3</sup>

Evidence for the formation of adducts of divalent chromium halides with phosphine ligands is tenuous.<sup>2,4</sup> However, the interaction of  $CrCl_2(thf)_5$  with 2 equiv of dmpe in toluene rapidly yields a bright yellow-green solution, from which large prisms of  $CrCl_2(dmpe)_2$ <sup>6</sup> may be isolated. This complex is paramagnetic with a magnetic moment of  $2.76 \mu_B$  in solution at room temperature, indicating a low-spin  $d^4$  configuration.

The only two neutral  $Cr^{II}$  alkyls known are diamagnetic, quadruply bonded dimers.<sup>7</sup> By contrast, the alkylation of  $CrCl_2(dmpe)_2$  with methyllithium in diethyl ether gives mononuclear, red-orange  $CrMe_2(dmpe)_2$ <sup>8</sup> in high yield. This complex is also low spin ( $\mu = 2.7 \mu_B$ ). The infrared spectrum exhibits a rather low C–H stretching frequency of  $2780 \text{ cm}^{-1}$ , which can be assigned to the  $CrMe$  groups. It is likely that the lowering of these vibrations is associated with the electronic unsaturation (16e) of the metal center.

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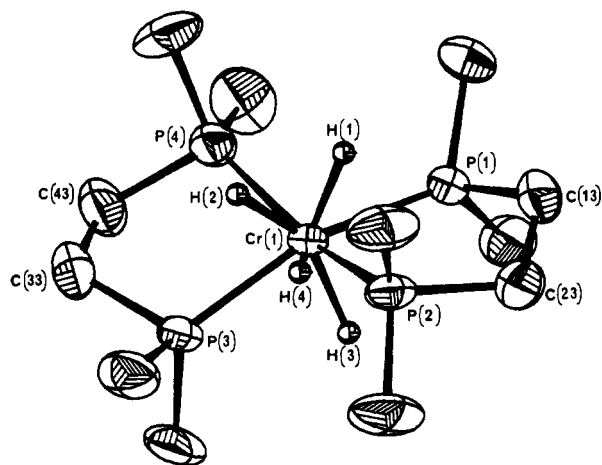
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(6) Anal. Calcd: C, 34.1; H, 7.66; Cl, 16.7; P, 29.3; Cr, 12.3. Found: C, 34.1; H, 7.55; Cl, 16.4; P, 29.2; Cr, 12.1. Mp  $270^\circ\text{C}$  dec;  $^1\text{H NMR}$  ( $\text{PhH}-d_6$ ,  $25^\circ\text{C}$ )  $\delta$   $-13.1$  ( $\text{PCH}_2$ , s,  $W_{1/2} = 240$  Hz),  $-33.5$  ( $\text{PMe}_2$ , s,  $W_{1/2} = 310$  Hz); MS,  $m/e$  422 ( $M^+$ , 1.5%).

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(8) Anal. Calcd: C, 44.0; H, 10.02; P, 32.4; Cl, 0. Found: C, 44.0; H, 10.18; P, 32.9; Cl,  $<0.4$ . Mp  $195^\circ\text{C}$  dec;  $^1\text{H NMR}$  ( $\text{PhH}-d_6$ ,  $25^\circ\text{C}$ )  $\delta$  0.9 ( $\text{PCH}_2$ , s,  $W_{1/2} = 260$  Hz),  $-28.6$  ( $\text{PMe}_2$ , s,  $W_{1/2} = 310$  Hz); MS,  $m/e$  387 ( $M^+$ , 1.7%).

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; Chapters 20, 28.

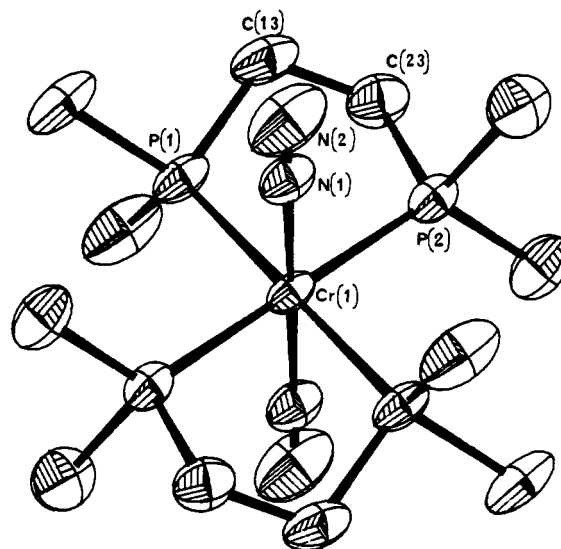


**Figure 2.** Structure of  $\text{CrH}_4(\text{dmpe})_2$ . Important bond lengths (Å) and angles (deg): Cr(1)–P(1), 2.258 (3); Cr(1)–P(2), 2.252 (3); Cr(1)–P(3), 2.258 (3); Cr(1)–P(4), 2.252 (3); Cr(1)–H(1), 1.60 (3); Cr(1)–H(2), 1.56 (3); Cr(1)–H(3), 1.53 (3); Cr(1)–H(4), 1.59 (3); P(2)–Cr(1)–P(1), 84.8 (1); P(3)–Cr(1)–P(4), 85.1 (1); P(3)–Cr(1)–P(1), 159.0 (1); P(2)–Cr(1)–P(4), 157.9 (1); P(3)–Cr(1)–P(2), 99.8 (1); P(4)–Cr(1)–P(1), 98.4 (1); H(1)–Cr(1)–H(2), 65 (2); H(3)–Cr(1)–H(4), 63 (2).

The X-ray structure<sup>9</sup> of  $\text{CrMe}_2(\text{dmpe})_2$  is given in Figure 1, along with some of the geometric parameters. The Cr–P distances of ca. 2.345 Å are rather shorter than those of 2.460 (1) Å in the dimer  $\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2$ .<sup>7a,b</sup> The metal bound methyl groups show no Cr···H interactions, such as those recently observed in  $\text{TiMeCl}_3(\text{dmpe})$ ,<sup>10</sup> despite the low electron count. The Cr–C–H angles of 108 (2)°, 108 (2)°, and 121 (2)° do show a small but statistically significant scatter. However, the distortion is probably not chemically significant; furthermore, it is not clear whether any distortion, if real, would be a reflection of electronic or steric effects.

Neutral hydrides of chromium are known only in the divalent oxidation state of chromium.<sup>11</sup> The reaction of  $\text{CrCl}_2(\text{dmpe})_2$  with *n*-butyllithium in hexane under a hydrogen atmosphere gives a dark-orange solution from which yellow  $\text{CrH}_4(\text{dmpe})_2$ <sup>12</sup> may be isolated. This complex is diamagnetic, and the hydride ligands appear as a binomial quintet in the <sup>1</sup>H NMR spectrum at room temperature. The proton-coupled <sup>31</sup>P NMR spectrum is also a binomial quintet with the same  $J_{\text{P-H}}$  coupling constant of 56.1 Hz, thus substantiating the tetrahydride formulation. Upon cooling to –80 °C, no change in the NMR line shapes is observed, except for broadening due to viscosity effects, indicating that the molecule remains fluxional at this temperature. Infrared bands at 1757 (m), 1725 (s), and 1701 (m)  $\text{cm}^{-1}$ , ascribable to Cr–H stretches, are rather low in frequency for terminally bound hydride ligands.

The X-ray crystal structure of  $\text{CrH}_4(\text{dmpe})_2$  is shown in Figure 2.<sup>12</sup> The hydride, which has approximate  $D_{2d}$  dodecahedral geometry, is the first example of eight-coordinate  $\text{Cr}^{\text{IV}}$ . The two interlocking trapezia are formed by P(1), P(3), H(1), H(2) and P(2), P(4), H(3), H(4), with the angle between the planes being



**Figure 3.** Structure of  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$ . Important bond lengths (Å) and angles (deg): Cr(1)–N(1), 1.957 (4); Cr(1)–P(1), 2.301 (1); Cr(1)–P(2), 2.307 (1); N(1)–N(2), 0.985 (4); P(2)–Cr(1)–P(1), 83.3 (1); P(1)–Cr(1)–N(1), 87.8 (1); P(2)–Cr(1)–N(1), 89.5 (1); Cr(1)–N(1)–N(2), 177.3 (2).

82.7°. The hydride ligands occupy the inner (A) sites of the trapezia, and the dmpe ligands occupy the outer (B) sites, bridging between the two trapezia.<sup>14</sup> Alternatively, the coordination geometry may be visualized as a trans octahedron, with the phosphine ligands showing a slight  $S_4$  warping out of the equatorial plane, and the hydride ligands occupying the axial sites in pairs. The H–Cr–H angles justify this view, the angle between corresponding pairs of hydrogen atoms being ca. 64°, giving H···H contacts of only 1.7 Å.

The reduction of  $\text{CrCl}_2(\text{dmpe})_2$  with sodium amalgam in tetrahydrofuran under a dinitrogen atmosphere gives the diamagnetic *trans*- $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$  as large red prisms in high yield.<sup>15</sup> All of the chromium dinitrogen complexes reported previously<sup>3</sup> decompose rapidly in solution at room temperature.<sup>15</sup> By contrast,  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$  solutions may be heated to 90 °C with no decomposition detectable by NMR spectroscopy.

The X-ray crystal structure of this complex is shown in Figure 3.<sup>16</sup> The molecules are centrosymmetric and crystallize in a fashion isomorphous with  $\text{CrMe}_2(\text{dmpe})_2$ . The dinitrogen ligands are bound in a linear configuration, Cr–N–N being 177.3°. The N–N distance at 0.985 (4) Å is significantly shorter than N–N distances in all other known transition-metal dinitrogen complexes<sup>17</sup> and is over 0.1 Å shorter than in  $\text{N}_2$  itself (1.0971 Å).<sup>18</sup> The origin of this shortening is unknown; part may be due to libration effects, although calculations show this to be no more than ca. 0.005 Å. The infrared spectrum in hexane solution, however, shows a single sharp absorption at 1932  $\text{cm}^{-1}$  (in  $\text{N}_2$ , 2331  $\text{cm}^{-1}$ ). Cr–P distances are shorter than those in  $\text{CrMe}_2(\text{dmpe})_2$ ; this is probably a result of poor  $\pi$ -bonding in the latter, which counteracts the usual decrease in metal radii as the oxidation state increases.

While the alkyl complex  $\text{CrMe}_2(\text{dmpe})_2$  has no analogue in molybdenum or tungsten chemistry, the corresponding analogues

(9) Triclinic, space group  $P\bar{1}$ , with  $a = 7.524$  (1),  $b = 8.751$  (1),  $c = 9.132$  (1) Å;  $\alpha = 103.91$  (1)°,  $\beta = 106.18$  (1)°,  $\gamma = 102.35$  (1)°;  $V = 534.5$  Å<sup>3</sup>,  $Z = 1$ . (Molecule has  $\bar{1}$  symmetry.)  $R = 0.030$  ( $R_w = 0.031$ ) for 2055/2574 observed data [ $F_0 > 3\sigma(F_0)$ ] measured on a diffractometer (CAD4, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\omega/2\theta$  scan mode).

(10) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410–1411.

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(12) Anal. Calcd: C, 40.4; H, 10.18; P, 34.8. Found: C, 40.7; H, 10.14; P, 34.0. Mp 130 °C dec; <sup>1</sup>H NMR (PhH-*d*<sub>6</sub>, 25 °C)  $\delta$  1.23 (PMe<sub>2</sub> and PCH<sub>2</sub>, s), –6.91 (CrH, quintet,  $J_{\text{P-H}} = 56.1$  Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (PhH-*d*<sub>6</sub>, 25 °C)  $\delta$  78.8.

(13) Monoclinic, space group  $P2_1/c$ , with  $a = 9.396$  (2),  $b = 18.004$  (2),  $c = 12.522$  (3) Å;  $\beta = 111.17$  (2)°;  $V = 1975.3$  Å<sup>3</sup>,  $Z = 4$ .  $R = 0.0355$ , ( $R_w = 0.0341$ ) for 3122/4283 observed data [ $F_0 > 3\sigma(F_0)$ ].

(14) For nomenclature see: Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179–249.

(15) Anal. Calcd: C, 35.3; H, 7.90; N, 13.7; P, 30.3. Found: C, 34.8; H, 7.88; N, 11.5; P, 29.0. Mp >350 °C. <sup>1</sup>H NMR (PhH-*d*<sub>6</sub>, 25 °C) 1.29 (PMe<sub>2</sub> and PCH<sub>2</sub>, s); <sup>31</sup>P{<sup>1</sup>H} NMR (PhH-*d*<sub>6</sub>, 25 °C)  $\delta$  69.3.

(16) Triclinic, space group  $P\bar{1}$ , with  $a = 7.556$  (3),  $b = 8.662$  (1),  $c = 9.094$  (1) Å;  $\alpha = 103.92$  (1)°,  $\beta = 106.09$  (2)°,  $\gamma = 103.34$  (2)°;  $V = 526.2$  Å<sup>3</sup>,  $Z = 1$ .  $R = 0.0315$ ,  $R_w = 0.0344$  for 2567/3067 observed data [ $F_0 > 3\sigma(F_0)$ ].

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of  $\text{CrH}_4(\text{dmpe})_2$  and  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$  have been known (for phosphines other than dmpe) for several years.<sup>19</sup> We are currently investigating the reaction chemistry of these chromium species in relation to that of their heavier congeners.

**Acknowledgment.** We thank the S.E.R.C. for a studentship (J.E.S.) and the National Science Foundation for a NATO Fellowship (G.S.G.).

**Registry No.**  $\text{CrCl}_2(\text{dmpe})_2$ , 86747-55-9;  $\text{CrMe}_2(\text{dmpe})_2$ , 86784-82-9;  $\text{CrH}_4(\text{dmpe})_2$ , 86747-56-0;  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$ , 86765-89-1;  $\text{CrCl}_2(\text{thf})$ , 36463-97-5; dmpe, 23936-60-9.

**Supplementary Material Available:** Synthesis of  $\text{CrCl}_2(\text{dmpe})_2$ ,  $\text{CrMe}_2(\text{dmpe})_2$ ,  $\text{CrH}_4(\text{dmpe})_2$ , and  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$  and tables of atom coordinates, temperature factors, and bond lengths and angles for  $\text{CrMe}_2(\text{dmpe})_2$ ,  $\text{CrH}_4(\text{dmpe})_2$ , and  $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$  (9 pages). Ordering information is given on any current masthead page.

(19) (a) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467-1474. (b) Uchida, T.; Uchida, Y.; Hidai, M.; Kodama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2883; *Acta Crystallogr., Sect. B* **1975**, *31*, 1197-1199. (c) Aresta, M.; Sacco, A. *Gazz. Chim. Ital.* **1972**, *102*, 755-780. (d) Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2492-2496.

## 18[(2,6)Pyridino<sub>6</sub>coronand-6]:<sup>1</sup> "Sexipyridine"

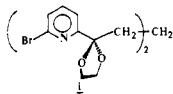
George R. Newkome\* and H.-W. Lee

Department of Chemistry, Louisiana State University  
Baton Rouge, Louisiana 70803-1804

Received June 3, 1983

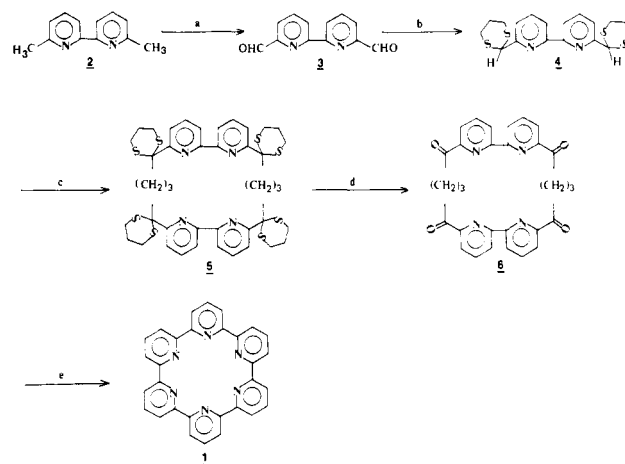
For over five decades, sexipyridine **1** has been the synthetic target of numerous research groups. Although *Chemical Abstracts* affords no information concerning **1**, many diverse procedures have been alleged and/or suggested.<sup>2</sup> The original and most obvious, albeit unsuccessful, route to **1** is via an Ullmann macrocyclization in which an appropriate dihalopyridine is heated in the presence of a metal surface. This procedure results in deleterious linear polymerization, probably due to the inability of the N-binding sites to wrap in an appropriate "metal template" to permit cy-

(1) Nomenclature: Weber, E.; Vögtle, F. *Inorg. Chim. Acta* **1980**, *45*, L65. (2) (a) Via an Ullmann cyclization: Burstall, F. H. *J. Chem. Soc.* **1938**, 1662. Morgan, G.; Burstall, F. H. *Ibid.* **1932**, 20. (b) Bloomfield, J. J., personal communication, see: Owsley, D. C.; Nelke, J. M.; Bloomfield, J. J. *J. Org. Chem.* **1973**, *38*, 901. (c) Nonnenmaker, E. Ph.D. Dissertation, University of Heidelberg, 1970 (Staab, H. A., personal communication, 1981). (d) Via an Ullmann coupling of **i** to give the bis(ketal) of **6**: Hager, D. C.,



unpublished results). (e) Via acalkylpyridinium salts, see: Kröhnke, F. *Synthesis* **1976**, 1. Also see: Constable, E. C.; Lewis, J. *Polyhedron* **1982**, *1*, 303. Professor Constable (personal communication, 1983) has attempted the synthesis of the *sym*-(4-phenyl)<sub>3</sub> analogue via this procedure. After the submission of this manuscript, Toner [Toner, J. L. *Tetrahedron Lett.* **1983**, *24*, 2707] reported the synthesis of a complex of a disubstituted cyclohexapyridine via the Kröhnke synthesis. The free hexaligand was, however, not accomplished. (f) Via reactions of the isobutylene dianion with 6,6'-dicyano-2,2'-bipyridine: Bates, R. B.; Hsu, H. F. 183rd American Chemical Society Meeting, Las Vegas, March 28-April 2, 1982, ORGN 225. Also see: Bates, R. B.; Gordon, B., III; Keller, P. C.; Rund, J. V.; Mills, N. S. *J. Org. Chem.* **1980**, *45*, 168. (g) Potts, K. T., personal communications, 1981, 1983. For methodology see: Potts, K. T.; Cipullo, M. J.; Ralli, P.; Theodoridis, G. *J. Org. Chem.* **1982**, *47*, 3027. Potts, K. T.; Cipullo, M. J. *Ibid.* **1982**, *47*, 3038. Professor Potts probably prepared a disubstituted derivative (SMe) or [N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O] of **1** by this procedure; however, due to sample size only mass spectral data were used to support this observation. (h) Cram et al. (Cram, et al. *J. Am. Chem. Soc.* **1977**, *99*, 6392) have predicted the free energy of association of *t*-BuNH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> with **1** as well as all other combinations of the 2,6-pyridino moiety melded with 18-crown-6; their prediction is that **1** will be the worst in the series!

Scheme I



<sup>a</sup>  $\text{SeO}_2$ , AcOH, 24 h, reflux. <sup>b</sup>  $\text{CH}_2(\text{CH}_2\text{SH})_2$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $p\text{-TsOH}$ , 5 h, reflux. <sup>c</sup>  $n\text{-BuLi}$ , THF,  $\text{CH}_2(\text{CH}_2\text{Br})_2$ , 3 days,  $-45^\circ\text{C}$ . <sup>d</sup> NBS, THF,  $\text{CH}_3\text{OH}$ . <sup>e</sup>  $\text{H}_2\text{NOH}\cdot\text{HCl}$ , AcOH.

clization.<sup>3</sup> To circumvent the necessity of this unfavored specific, rigid orientation prior to cyclization, we herein describe the first successful synthesis of the unsubstituted sexipyridine **1** (Scheme I) via an initial macrocyclization to give a flexible polyfunctional intermediate, from which the molecular rigidity is irreversibly introduced.

The  $\text{SeO}_2$  oxidation of **2**, prepared by coupling of 2-bromo-6-picoline with Pd/C under phase-transfer conditions,<sup>4</sup> gave dialdehyde **3**.<sup>5,6</sup> Treatment of **3** with 1,3-propanedithiol and *p*-toluenesulfonic acid in refluxing toluene afforded the bis(dithiane) **4**,<sup>5,8</sup> as colorless needles. Lithiation of **4** in THF with *n*-BuLi at  $-45^\circ\text{C}$  was followed by addition of 1,3-dibromopropane to give the tetrakis(dithiane) **5**, which was not fully characterized but lacks the singlet at  $\delta$  5.43 in the <sup>1</sup>H NMR. This macrocyclization proceeded best at  $-30$  to  $-40^\circ\text{C}$  over extended time (e.g., 3 days); shorter times and elevated temperatures gave rise to either side reactions or unchanged starting materials. Cleavage of the protecting group of **5** with NBS in aqueous THF at  $0^\circ\text{C}$  by a known procedure<sup>9</sup> gave **6**.<sup>5,10</sup> The convenient, one-step conversion of 1,5-diketones to a pyridine nucleus utilizes hydroxylamine<sup>11</sup> under acidic conditions; thus, treatment of **6** with  $\text{H}_2\text{NOH}$  in refluxing glacial acetic acid for 24 h generates sexipyridine **1**.<sup>5,12</sup> The upfield shift ( $\Delta\delta$  0.5 ppm) of the 3,5-H in **1** vs. the central ring in *anti*-terpyridine<sup>13</sup> further supports the syn configuration.

This general methodology has been successfully applied<sup>14</sup> to the construction of the remaining "pyridino" 18-crown-6 ethers<sup>2h</sup>

(3) Healy, M. d. S.; Rest, A. J. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 1 and ref cited therein.

(4) Newkome, G. R.; Puckett, W. E.; Kiefer, G. E.; Gupta, V. K.; Xia, Y.; Coreil, M.; Hackney, M. A. *J. Org. Chem.* **1982**, *47*, 4116.

(5) Analytical data were obtained for all new compounds and are within an acceptable range (C, H, N  $\pm$  0.3%).

(6) **3**: 64%; mp 234-235  $^\circ\text{C}$  (DMF); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.02-8.88 (m, py H), 10.65 (s, CHO); IR (KBr) 1697 (C=O)  $\text{cm}^{-1}$ .

(7) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53.

(8) **4**: 59%; mp 197-198  $^\circ\text{C}$  (toluene); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  2.14 (m,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ), 3.07 (m,  $\text{SCH}_2$ ), 5.43 (s, CHS), 7.48 (dd, 5-py H), 7.80 (dd, 4-py H), 8.44 (dd, 3-py H); MS,  $m/e$  392 ( $M^+$ , 3.6), 359 (100).

(9) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, *36*, 3553.

(10) **6**: 16% (from **4**); mp 206-208  $^\circ\text{C}$  ( $\text{CHCl}_3$ ); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  2.35 (5 lines,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 3.38 (t,  $\text{COCH}_2$ ), 7.77 (dd, 4-py H), 7.97 (d, 5-py H), 8.19 (d, 3-py H); IR (KBr) 1688 (C=O)  $\text{cm}^{-1}$ ; MS,  $m/e$  504 ( $M^+$ , 26), 155 (100).

(11) Brody, F.; Ruby, P. In "The Chemistry of Heterocyclic Compounds"; A. Weissberger, Ed.; Wiley-Interscience: New York, 1960; Part 1, Chapter 2.

(12) **1**: mp 292-295  $^\circ\text{C}$  dec; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.81 (t, 4-py H,  $J = 7.7$  Hz, 1 H), 8.13 (d, 3,5-py H,  $J = 7.7$  Hz, 2 H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  156.62 (C2,6), 137.76 (C4), 121.96 (C3,5); CI-MS ( $\text{CH}_4$ ) 388 ( $M^+ + 3\text{H} - 77$ ), 311 ( $M^+ + 3\text{H} - 154$ ), 154 ( $77 \times 2 + 3\text{H}$ , 100).

(13) The <sup>1</sup>H NMR data [ $\delta$  8.50 (d, 3,5-py H)] are indicative of a nonrigid, anti conformation analogous to terpyridine.

(14) H.-W. Lee, unpublished results.