

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.¹⁹ We are currently investigating the reaction chemistry of these chromium species in relation to that of their heavier congeners.

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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)Pyridino₆coronand-6]:¹ "Sexipyridine"

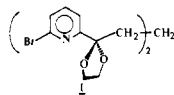
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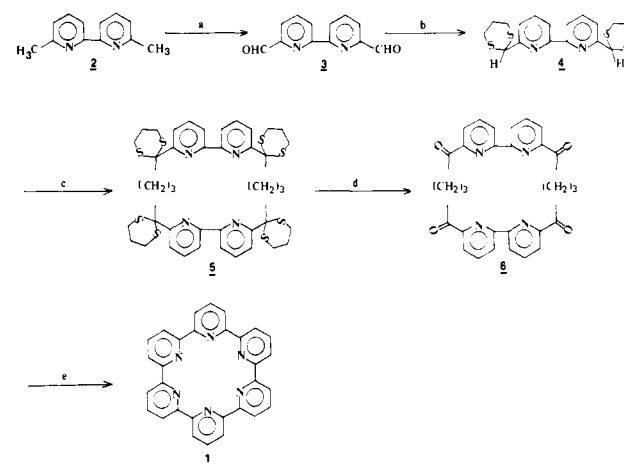
For over five decades, sexipyridine **1** has been the synthetic target of numerous research groups. Although *Chemical Abstracts* affords no information concerning **1**, many diverse procedures have been alleged and/or suggested.² The original and most obvious, albeit unsuccessful, route to **1** is 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)₃ 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(CH₂CH₂)₂O] 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*-BuNH₃⁺Cl⁻ 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



^a SeO₂, AcOH, 24 h, reflux. ^b CH₂(CH₂SH)₂, C₆H₅CH₃, *p*-TsOH, 5 h, reflux. ^c *n*-BuLi, THF, CH₂(CH₂Br)₂, 3 days, -45 °C. ^d NBS, THF, CH₃OH. ^e H₂NOH·HCl, AcOH.

clization.³ 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 SeO₂ oxidation of **2**, prepared by coupling of 2-bromo-6-picoline with Pd/C under phase-transfer conditions,⁴ gave di-aldehyde **3**.^{5,6} Treatment of **3** with 1,3-propanedithiol and *p*-toluenesulfonic acid in refluxing toluene afforded the bis(dithiane) **4**,^{5,8} as colorless needles. Lithiation of **4** in THF with *n*-BuLi at -45 °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 δ 5.43 in the ¹H NMR. This macrocyclization proceeded best at -30 to -40 °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 °C by a known procedure⁹ gave **6**.^{5,10} The convenient, one-step conversion of 1,5-diketones to a pyridine nucleus utilizes hydroxylamine¹¹ under acidic conditions; thus, treatment of **6** with H₂NOH in refluxing glacial acetic acid for 24 h generates sexipyridine **1**.^{5,12} The upfield shift (Δδ 0.5 ppm) of the 3,5-H in **1** vs. the central ring in *anti*-terpyridine¹³ further supports the syn configuration.

This general methodology has been successfully applied¹⁴ to the construction of the remaining "pyridino" 18-crown-6 ethers^{2h}

(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 ± 0.3%).

(6) **3**: 64%; mp 234-235 °C (DMF) (lit.⁷ mp 235 °C); ¹H NMR (CDCl₃) δ 8.02-8.88 (m, py H), 10.65 (s, CHO); IR (KBr) 1697 (C=O) cm⁻¹.

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

(8) **4**: 59%; mp 197-198 °C (toluene); ¹H NMR (CDCl₃) δ 2.14 (m, SCH₂CH₂CH₂S), 3.07 (m, SCH₂), 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 °C (CHCl₃); ¹H NMR (CDCl₃) δ 2.35 (5 lines, CH₂CH₂CH₂), 3.38 (t, COCH₂), 7.77 (dd, 4-py H), 7.97 (d, 5-py H), 8.19 (d, 3-py H); IR (KBr) 1688 (C=O) 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 °C dec; ¹H NMR (CDCl₃) δ 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); ¹³C NMR (CDCl₃) δ 156.62 (C2,6), 137.76 (C4), 121.96 (C3,5); CI-MS (CH₄) 388 (M⁺ + 3H - 77), 311 (M⁺ + 3H - 154), 154 (77 × 2 + 3 H, 100).

(13) The ¹H NMR data [δ 8.50 (d, 3,5-py H)] are indicative of a nonrigid, *anti* conformation analogous to terpyridine.

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

as well as is currently being adapted to the synthesis of other macrocycles possessing electron-rich cavities, such as: 15-[(2,6)pyridino₃coronand-5], as well as the pyridine analogues to "spherands".¹⁵

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Registry No. 1, 86712-08-5; 2, 4411-80-7; 3, 49669-26-3; 4, 86712-09-6; 5, 86712-10-9; 6, 86712-11-0; 1,3-dibromopropane, 109-64-8; 1,3-propanedithiol, 109-80-8.

(15) Cram, D. J.; Moran, J. R.; Maverick, E. F.; Trueblood, K. N. *J. Chem. Soc., Chem. Commun.* **1983**, 645 and ref cited therein.

Reaction of Au(NO₃)PPh₃ with Cationic Polyhydride Cluster Complexes of Iridium(III). Structures of [AuIr₃H₆(NO₃)(dppe)₃]BF₄ and [Au₃Ir(NO₃)(PPh₃)₅]PF₆

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There have been several recent reports on mixed-metal cluster compounds that contain gold atoms.¹⁻⁵ The majority of these clusters contain carbonyl ligands, and preparative methods have primarily involved reactions between anionic metal clusters and [AuCl(PR₃)] or [Au(PR₃)]⁺ and reactions between neutral metal hydrido clusters and [Au(CH₃)(PR₃)], although several other synthetic routes have also been reported.^{6,7} A very recent report⁸ describes the preparation and structure of a μ-H iridium-gold complex [(PPh₃)Au(μ-H)Ir(H)₂(PPh₃)₃]BF₄. The above studies clearly demonstrate a structural similarity between certain hydrido-metal complexes and AuPR₃ derivatives. Indeed, many of the synthetic schemes for mixed-metal gold clusters have involved the replacement of a μ-H ligand and AuPR₃.

We report here the reactions of Au(NO₃)PPh₃ with [Ir₃(μ₃-H)(μ-H)₃H₃(dppe)₃](BF₄)₂ (1)⁹ and [Ir₂(μ-H)₃H₃(PPh₃)₄]PF₆

(1) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 813. Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Ibid.* **1982**, 773. Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Ibid.* **1982**, 51.

(2) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. *J. Chem. Soc., Chem. Commun.* **1982**, 314; *Polyhedron* **1982**, 1, 105.

(3) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, 232, 171.

(4) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, 103, 7648.

(5) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, 101, 6106.

(6) Bruce, M. I.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1141.

(7) van der Velden, J. W. A.; Bour, J. J.; Otterloo, B. F.; Bosman, W. P.; Noordik, J. H. *J. Chem. Soc., Chem. Commun.* **1981**, 583.

(8) Lehner, H.; Matt, D.; Pregonis, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, 104, 6825.

(9) Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, 19, 1470. Wang, H. H. Ph.D. Thesis, University of Minnesota, 1980.

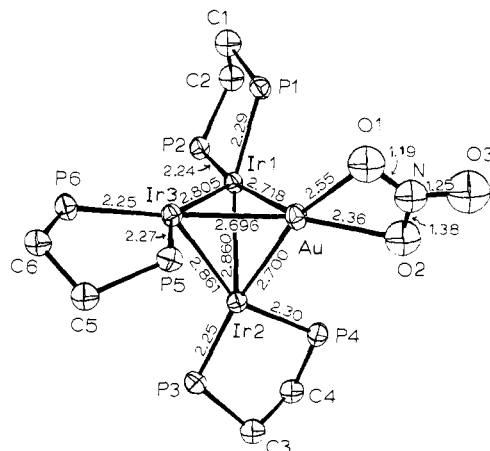
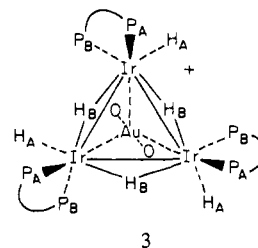


Figure 1. ORTEP drawing of the core of cation 3. Selected angles (deg) where the numbers refer to respective Ir atoms are: 1-2-3, 58.71 (2); 1-2-Au, 58.44 (2); 3-2-Au, 57.90 (2); 2-1-3, 60.67 (2); 2-1-Au, 57.83 (2); 3-1-Au, 58.41 (2); 1-3-2, 60.62 (2); 1-3-Au, 59.18 (2); 2-3-Au, 58.05 (2); 1-Au-2, 63.73 (2); 1-Au-3, 62.41 (2); 2-Au-3, 64.05 (2); P1-1-P2, 85.4 (2); P3-2-P4, 84.6 (2); P5-3-P6, 84.2 (2); O1-Au-O2, 53.7 (6); Au-1-P2, 170.4 (1); Au-2-P3, 164.1 (1); Au-3-P6, 173.2 (1). Phenyl carbon atoms have been omitted for clarity.

(2)¹⁰ in acetone solution which yield respectively the new cationic iridium-gold clusters [AuIr₃H₆(NO₃)(dppe)₃]BF₄ (3) [dppe =



Ph₂P(CH₂)₂PPh₂] and [Au₃Ir(NO₃)(PPh₃)₅]PF₆ (4).¹¹ These reactions are the first examples where cationic hydrido-metal complexes are converted into mixed-metal gold clusters by reaction with AuX(PR₃) and illustrate that the replacement of a metallo hydrogen ligand by AuPR₃ is very general. In addition, complexes 3 and 4 are very rare examples of mixed-metal gold clusters that do not contain carbonyl ligands. The structure of 4 (vide infra) also illustrates a new class of gold cluster compounds since this planar "Au₃M(PPh₃)₃" structural unit has not been previously reported.¹²

The ¹H NMR (300 MHz, CDCl₃, 25 °C) spectrum of 3 in the hydride region [δ -8.86, H_B (d, J(P_BH_B) = 72 Hz) intensity = 1; -15.04, H_A (mult), intensity = 1] is very similar to that of 1 except that the quartet resonance of the μ₃-hydride is missing, and small but significant shifts in the positions of the μ-H and terminal H resonances were observed. This spectrum is consistent with the structure shown in drawing 3 where AuNO₃ has replaced the μ₃-hydride. The ³¹P{¹H} NMR (120 MHz, CH₂Cl₂, 25 °C) spectrum of 3 shows two unassigned resonances: δ 44.3 ppm (br s) intensity = 1 and 32.1 (mult) intensity = 1. Addition of 1 equiv of PPh₃ to a CHCl₃ solution of 3 results in the rapid and complete replacement of the nitrate ligand giving [AuIr₃H₆(PPh₃)(dppe)₃]²⁺

(10) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, 141, 205.

(11) Complex 3 was prepared in ca. 35% isolated yield by the addition of 2 equiv of AuNO₃(PPh₃) to 1 equiv of 1 in an acetone/dichloromethane (1:1, v/v) solution at room temperature. The yellow solution became orange after stirring for 24 h in the dark, and orange crystals were obtained via evaporation and recrystallization from CHCl₃/Et₂O. Complex 4 was prepared in ca. 30% isolated yield by the addition of 4 equiv of AuNO₃(PPh₃) to 1 equiv of 2 in an acetone solution at room temperature. The yellow solution became dark red immediately, and crystals separated upon solvent removal.

(12) Professor J. E. Ellis has synthesized the compound [Au₃(PPh₃)₃Mn-(CO)₄] (Ellis, J. E.; Flatynek, R. A. *J. Am. Chem. Soc.* **1977**, 99, 1801) and preliminary X-ray diffraction results show the presence of a very similar planar "Au₃M(PPh₃)₃" structural unit.