of $CrH_4(dmpe)_2$ and $Cr(N_2)_2(dmpe)_2$ 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.

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. $CrCl_2(dmpe)_2$, 86747-55-9; $CrMe_2(dmpe)_2$, 86784-82-9; $CrH_4(dmpe)_2$, 86747-56-0; $Cr(N_2)_2(dmpe)_2$, 86765-89-1; $CrCl_2(thf)$, 36463-97-5; dmpe, 23936-60-9.

Supplementary Material Available: Synthesis of $CrCl_2(dmpe)_2$, $CrMe_2(dmpe)_2$, $CrH_4(dmpe)_2$, and $Cr(N_2)_2(dmpe)_2$ and tables of atom coordinates, temperature factors, and bond lengths and angles for $CrMe_2(dmpe)_2$, $CrH_4(dmpe)_2$, and $Cr(N_2)_2(dmpe)_2$ (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$_6$coronand-6]:[1] "Sexipyridine"

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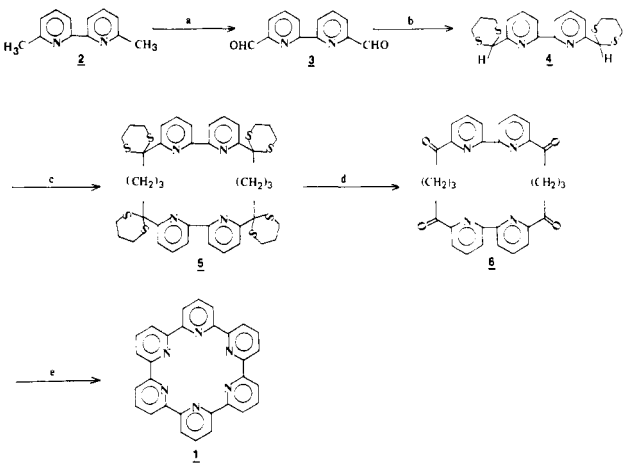
For over five decades, sexipyridine **1** has been the synthetic target of numerous research groups. Although *Chemical Abstracts* affords no information concerning **1**, many diverse procedures have been alleged and/or suggested.[2] The original and most obvious, albeit unsuccessful, route to **1** 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 cyclization.[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.

Scheme I



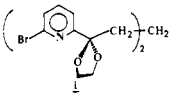
[a] SeO_2, AcOH, 24 h, reflux. [b] $CH_2(CH_2SH)_2$, $C_6H_5CH_3$, *p*-TsOH, 5 h, reflux. [c] *n*-BuLi, THF, $CH_2(CH_2Br)_2$, 3 days, −45 °C. [d] NBS, THF, CH_3OH. [e] $H_2NOH{\cdot}HCl$, AcOH.

The SeO_2 oxidation of **2**, prepared by coupling of 2-bromo-6-picoline with Pd/C under phase-transfer conditions,[4] gave dialdehyde **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 procedure[9] gave **6**.[5,10] The convenient, one-step conversion of 1,5-diketones to a pyridine nucleus utilizes hydroxylamine[11] under acidic conditions; thus, treatment of **6** with H_2NOH in refluxing glacial acetic acid for 24 h generates sexipyridine **1**.[5,12] The upfield shift ($\Delta\delta$ 0.5 ppm) of the 3,5-H in **1** vs. the central ring in *anti*-terpyridine[13] further supports the syn configuration.

This general methodology has been successfully applied[14] to the construction of the remaining "pyridino" 18-crown-6 ethers[2h]

(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 cyclosexipyridine 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 $[N(CH_2CH_2)_2O]$ 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*-$BuNH_3^+Cl^-$ 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!

(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 ($CDCl_3$) 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 ($CDCl_3$) δ 2.14 (m, $SCH_2CH_2CH_2S$), 3.07 (m, 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 °C ($CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.35 (5 lines, $CH_2CH_2CH_2$), 3.38 (t, $COCH_2$), 7.77 (dd, 4-py H), 7.97 (d, 5-py H), 8.19 (d, 3-py H); IR (KBr) 1688 (C=O) 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 156.62 (C2,6), 137.76 (C4), 121.96 (C3,5); CI-MS (CH_4) 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.

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as well as is currently being adapted to the synthesis of other macrocycles possessing electron-rich cavities, such as: 15-[(2,6)pyridino$_5$coronand-5], as well as the pyridine analogues to "spherands".[15]

Acknowledgment. We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for partial support of the initial phases of this project. Special thanks are given to Mrs. Kröhnke for the contribution of numerous dissertations from her husband's archives and to Professor Roger Laine for the special mass spectral data.

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 $Au(NO_3)PPh_3$ with Cationic Polyhydride Cluster Complexes of Iridium(III). Structures of $[AuIr_3H_6(NO_3)(dppe)_3]BF_4$ and $[Au_3Ir(NO_3)(PPh_3)_5]PF_6$

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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 $[AuCl(PR_3)]$ or $[Au(PR_3)]^+$ and reactions between neutral metal hydrido clusters and $[Au(CH_3)(PR_3)]$, although several other synthetic routes have also been reported.[6,7] A very recent report[8] describes the preparation and structure of a μ-H iridium–gold complex $[(PPh_3)Au(\mu\text{-}H)Ir(H)_2(PPh_3)_3]BF_4$. The above studies clearly demonstrate a structural similarity between certain hydrido–metal complexes and $AuPR_3$ derivatives. Indeed, many of the synthetic schemes for mixed-metal gold clusters have involved the replacement of a μ-H ligand and $AuPR_3$.

We report here the reactions of $Au(NO_3)PPh_3$ with $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3H_3(dppe)_3](BF_4)_2$ (**1**)[9] and $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$ (**2**)[10] in acetone solution which yield respectively the new cationic iridium–gold clusters $[AuIr_3H_6(NO_3)(dppe)_3]BF_4$ (**3**) [dppe = $Ph_2P(CH_2)_2PPh_2$] and $[Au_3Ir(NO_3)(PPh_3)_5]PF_6$ (**4**).[11] These reactions are the first examples where *cationic* hydrido–metal complexes are converted into mixed-metal gold clusters by reaction with $AuX(PR_3)$ and illustrate that the replacement of a metallo hydrogen ligand by $AuPR_3$ 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 "$Au_3M(PPH_3)_3$" structural unit has not been previously reported.[12]

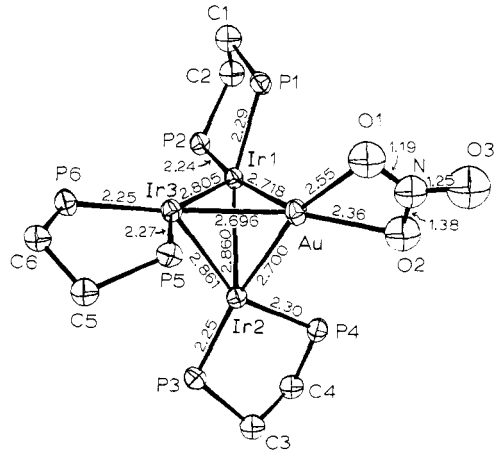
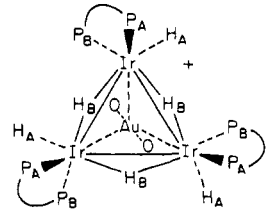


Figure 1. ORTEP drawing of the core of cation **3**. Selected angles (deg) where the numbers refer to respective Ir atoms are: 1–2–3, 58.71 (2); 1–2–Au, 58.44 (2); 3–2–Au, 57.90 (2); 2–1–3, 60.67 (2); 2–1–Au, 57.83 (2); 3–1–Au, 58.41 (2); 1–3–2, 60.62 (2); 1–3–Au, 59.18 (2); 2–3–Au, 58.05 (2); 1–Au–2, 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.



3

The ^1H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of **3** in the hdyride 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 μ_3-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 $AuNO_3$ has replaced the μ_3-hydride. The $^{31}P\{^1H\}$ NMR (120 MHz, CH_2Cl_2, 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 PPh_3 to a $CHCl_3$ solution of **3** results in the rapid and complete replacement of the nitrate ligand giving $[AuIr_3H_6(PPh_3)(dppe)_3]^{2+}$

(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.

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

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

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

(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 $AuNO_3(PPh_3)$ 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 $CHCl_3/Et_2O$. Complex **4** was prepared in ca. 30% isolated yield by the addition of 4 equiv of $AuNO_3(PPh_3)$ 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 $[Au_3(PPh_3)_3Mn(CO)_4]$ (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 "$Au_3M(PPh_3)_3$" structural unit.

0002-7863/83/1505-5957$01.50/0