exchange with $Mn(CO)_5PPh_3^+$. This procedure affords a straightforward method for the production of these isotopically labeled complexes, and it should prove quite useful for the preparations of ^{17}O-labeled derivatives for nuclear resonance studies, i.e., either NMR or NQR measurements.

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 76-04494 is greatly appreciated.

Registry No. *cis*-$HMn(CO)_4PMe_2Ph$, 61477-64-3; *cis*-$HMn(CO)_4PPh_3$, 39796-96-8; *cis*-$HMn(CO)_4P(p\text{-}MeC_6H_4)_3$, 61477-65-4; *cis*-$HMn(CO)_4P(OCH_2)_3CEt$, 61477-66-5; *cis*-$HRe(CO)_4PPh_3$, 25838-69-1; $[Ph_3PMn(CO)_5][PF_6]$, 54039-57-5.

References and Notes

(1) D. J. Darensbourg and D. Drew, *J. Am. Chem. Soc.*, **98**, 275 (1976).

(2) ^{18}O incorporation into $Re(CO)_6^+$ was first reported by E. L. Muetterties, *Inorg. Chem.*, **4**, 1841 (1965).

(3) D. J. Darensbourg, M. Y. Darensbourg, D. Drew, and H. L. Conder, *J. Organomet. Chem.*, **74**, C33 (1975).

(4) D. Drew, D. J. Darensbourg, and M. Y. Darensbourg, *Inorg. Chem.*, **14**, 1579 (1975).

(5) D. Drew, M. Y. Darensbourg, and D. J. Darensbourg, *J. Organomet. Chem.*, **85**, 73 (1975).

(6) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 9, 1691 (1970).

(7) See review by F. Calderazzo on metal carbonyls in I. Wender and P. Pino, "Metal Carbonyls in Organic Synthesis", Interscience, New York, N.Y., 1968.

(8) H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 9, 1229 (1970).

(9) D. E. Hendriksen and R. Eisenberg, *J. Am. Chem. Soc.*, **98**, 4662 (1976).

(10) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 443 (1969).

(11) W. Hieber, G. Faulhaber, and F. Theubert, *Z. Anorg. Allg. Chem.*, **314**, 125 (1962).

(12) B. L. Booth and R. N. Haszeldine, *J. Chem. Soc. A*, 157 (1966).

(13) N. Flitcroft, J. M. Leach, and F. J. Hopton, *J. Inorg. Nucl. Chem.*, **32**, 137 (1970).

(14) C. R. Bailey and A. B. D. Cassie, *Proc. R. Soc. London, Ser. A*, **135**, 375 (1932).

(15) H. C. Allen, E. K. Plyler, and L. R. Blaine, *J. Chem. Phys.*, **26**, 400 (1957).

(16) H. J. Callomon, D. C. McKean, and H. W. Thompson, *Proc. R. London, Ser. A*, **208**, 341 (1951).

(17) Over a 3-day period oxygen exchange occurs between water and $Mn(CO)_5L^+$ with the production of $Mn(C^{16}O)_{5-x}(C^{18}O)_xL^+$ species (x = 1–5) with no measurable metal hydride formation (see ref 1).

(18) J. A. Froelich and D. J. Darensbourg, unpublished results.

(19) $HFe(CO)_4^-$ has been successfully prepared under anhydrous conditions by this procedure in tetrahydrofuran: M. Y. Darensbourg and A. McIntee, unpublished results.

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Coordination and Geometry of Gold in Chloro(α,β,γ,δ-tetraphenylporphinato)gold(III)

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Received September 20, 1976 AIC606829

In this note we report the geometry of the coordination of gold in chloro(α,β,γ,δ-tetraphenylporphinato)gold(III), (Cl)Au(TPP), and its relation to some recently determined porphyrin structures. The synthesis and spectroscopic properties of (mesoporphyrin IX dimethyl ester)gold(III) (1+)[1] and $[Au^{III}(TPP)^+](AuCl_4^-)$[2] have been discussed previously in context with gold phthalocyanine, Cu(TPP), and Ag^{II}(TPP). The single crystals of (Cl)Au(TPP) used in the present study were obtained by slow evaporation of a mixture of chloroform and petroleum ether (bp 60–110 °C).[3] X-ray diffraction measurements showed the crystals to be monoclinic, with a = 12.06 (1) Å, b = 22.35 (1) Å, c = 16.66 (1) Å, and β = 121.97 (5)° and of space group $P2_1/c$ with four molecules per unit cell. The crystal density (1.61 g cm^{-3}) indicated a chloroform of solvation giving a best fit formula unit of $(Cl)Au(TPP)(CHCl_3)_{0.7}$ for the asymmetric unit.

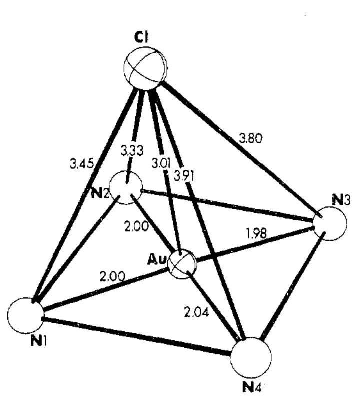

Figure 1. ORTEP drawing of the geometry of the gold coordination.

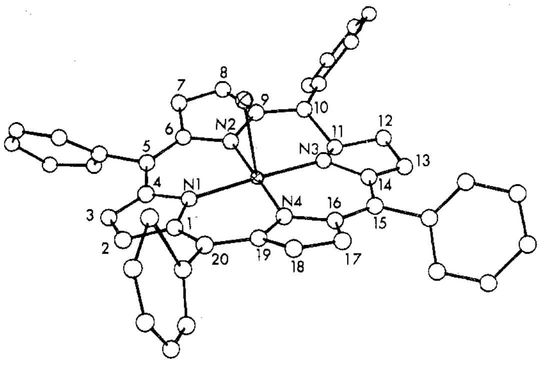

Figure 2. ORTEP drawing of (Cl)Au(TPP).

Table I. Bond Angles Involving the Gold Atom (deg)

N1-Au-Cl	84.4	N1-Au-N2	89.2
N2-Au-Cl	80.6	N2-Au-N3	89.4
N3-Au-Cl	97.0	N3-Au-N4	91.3
N4-Au-Cl	99.7	N4-Au-N1	91.2

The overwhelming electron content of the gold and the chlorine atoms in the unit cell, $(z_{Au}^2 + \sum z_{Cl}^2)/\sum z_{TPP}^2 = 4.2$, where z is the atomic number, precluded an accurate determination of the light-atom structure of (Cl)Au(TPP). This was emphasized when R was 0.27 ($R = \sum||F_o| - |F_c||/\sum|F_o|$) for a structure factor calculation based only on the position of the gold atom and when the ensuing electron density map using the gold atom phase angles revealed the complete structure. The trial structure obtained in this way was refined by the method of least squares using individual isotropic temperature factors for the atoms and for a disordered chloroform of solvation (R_{final} = 0.10).

The gold atom shows a distorted square-pyramidal geometry with the chloride ion coordinating in the apical position (Figure 1). The gold atom is located in the plane of the pyrrolic nitrogen atoms (±0.05 Å) giving unexpectedly short Au-N distances of about 2.00 (2) Å. On the other hand, the Au–Cl distance of 3.01 (1) Å is long compared to that of the terminal Au–Cl distance in Au_2Cl_6 (2.29 Å)[4] but compares favorably with the sum of ionic radii (3.18 Å).[5] The short Au–N and longer Au–Cl distances are consistent with an ionic structure for the gold coordination. This is in contrast to the structures of (Cl)Mn(TPP)[6] and (N_2)Mn(TPP)[7] which are both highly covalent.

The Au–Cl direction makes a 77° angle with respect to the least-squares plane of the molecule (Figures 1 and 2, Table I) in the direction of the partially disordered chloroform of solvation. This results from a strong interaction between the chloride ion and the carbon atom of the chloroform of solvation (3.21 Å); the latter also appears to be librating about its threefold axis. The chlorine of (Cl)Au(TPP) lies close to the threefold axis and makes a short van der Waals contact with

Table II. Deviations (Å) of Porphine Skeleton from Least-Squares Plane

Au	0.03	C7	0.54	C14	−0.27
N1	−0.05	C8	0.36	C15	0.21
C1	−0.28	C9	0.03	N4	0.05
C2	−0.41	C10	−0.17	C16	0.27
C3	−0.27	N3	0.04	C17	0.42
C4	−0.06	C11	−0.17	C18	0.35
C5	0.08	C12	−0.43	C19	0.05
N2	0.01	C13	−0.32	C20	−0.16
C6	0.16				

the chloroform carbon suggesting strongly that a weak hydrogen bond exists between the two atoms. The hydrogen of chloroform is highly acidic and is known to show such behavior in acetone solution.

Although the positions of the atoms of the porphine ring could not be determined with a high degree of certainty (±0.05 Å),[8] the standard deviation of the atoms from the least-squares plane was ±0.27 Å, with some atoms deviating up to 0.5 Å from the plane (Table II). Furthermore, the porphine ring shows a well-defined quasi S_4-$\bar{4}$ ruffling similar to that observed with (Cl)Mn(TPP),[6] (N_3)Mn(TPP),[7] and porphyrin diacids[9] where the pyrrole rings are tilted alternately up and down with respect to the $\bar{4}$ axis around the C_a–C_m bonds. Since the standard deviation from the plane is about 5 times the standard deviation in position, the ruffling and the symmetry of the porphine ring in (Cl)Au(TPP) are both highly significant. However, as with the Mn(TPP) structures, the underlying cause of the ruffling is not clear. The common feature of the central core region between the former covalent structures and the ionic (Cl)Au(TPP) is that both metals form strong interactions with the pyrrolic nitrogen atoms.

Acknowledgment. Acknowledgment is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. (Cl)Au(TPP), 61483-93-0.

Supplementary Material Available: Tables III and IV, listing the final atomic parameters of (Cl)Au(TPP) and chloroform of solvation (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 2496 (1965).
(2) E. B. Fleischer and A. Laszlo, *Inorg. Nucl. Chem. Lett.*, **5**, 373 (1969).
(3) We thank Dr. Henry E. Rosenberg for supplying us with a sample of the (Cl)Au(TPP).
(4) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 260.
(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966.
(6) B. M. L. Chen and A. Tulinsky, *J. Am. Chem. Soc.*, in press.
(7) V. W. Day, B. R. Stults, E. L. Tasset, R. S. Marianelli, and L. J. Boucher, *Inorg. Nucl. Chem. Lett.*, **11**, 505 (1975).
(8) See supplementary material for final atomic parameters.
(9) A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, **90**, 2735 (1968).

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Substituent Effects on the Electronic Structure of Aryl Isocyanide–Transition Metal Complexes

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Received October 5, 1976 AIC60730P

Hexakis(aryl isocyanide)manganese(I) compounds show a large variation in oxidation half-potential.[1,2] Members of the series $[Mn(CNC_6H_4R)_6]^+$ follow the sequence in $E_{1/2}$ values where R = p-OCH_3 < H ≈ o-, m-, p-CH_3 < p-NO_2. For a series of mixed methyl isocyanide–carbonyl complexes, we have previously shown a good correlation of $E_{1/2}$ value with the energy of the highest occupied molecular orbital (HOMO) of the complex which depends intimately on the nature of the π-bonded ligands.[3] The extent of π back-bonding will often be reflected in the stretching frequencies of the ligands,[3a,4] so one might expect to see variations in ν(CN) corresponding to the variations in $E_{1/2}$ for the series $[Mn(CNC_6H_4R)_6]^+$. Interestingly enough, ν(CN) is essentially invariant within the series, all having a strong CN stretch at 2089 ± 1 cm^{-1} (free-ligand values[1a] 2121 ± 4 cm^{-1}). In this note we reconcile the seemingly anomalous electrochemical and infrared data on the basis of nonempirical molecular calculations[5] on a series of aryl isocyanides, CNC_6H_4R (R = H, o-, m-, p-CH_3, p-OCH_3, p-NO_2).

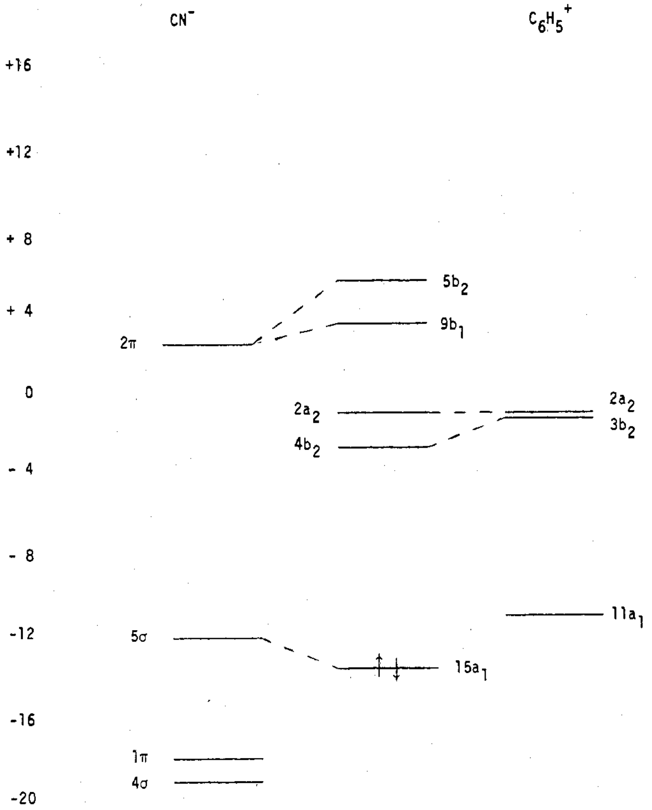

Figure 1. Bonding diagram of highest occupied and first four unoccupied molecular orbitals of CNC_6H_5. Contributions from the principal MO's of CN^- or $C_6H_5^+$ are shown. Energies are in eV.

The size of hexakis(aryl isocyanide) complexes has made their theoretical treatment difficult and studies to date have chiefly discussed the UV–visible spectra, on the basis of qualitative MO schemes for the complexes.[6] The theoretical treatment of the full complexes is further complicated by the lack of good structural data; the symmetry of such complexes is subject to much conjecture and spectral information does not provide an unambiguous answer.[6] Correlation of the UV–visible spectra also has been attempted on the basis of CNDO calculations on the free ligand.[7] The results of our calculations differ substantially from the CNDO results, particularly in the order of filled MO's. On the basis of what is reported by Fantucci et al., it is impossible to assess whether or not their calculations are consistent with the scheme presented here.

The MO scheme for CNC_6H_5 is representative of the entire series of substituted aryl isocyanides (Figure 1). Transformation into the canonical orbitals of CN^- and $C_6H_5^+$ was performed, which allows assessment of the bonding picture in terms of the molecular orbitals of the two fragments. In Table