

to account for the observed high conductivity.<sup>45</sup>

Thus, the intermolecular back-bonding model is useful in describing the solid-state structures of various types of poorly conducting chain complexes. Intermolecular back-bonding provides a mechanism for stabilization of chain complexes and may contribute to the binding energy observed for Ni<sup>II</sup>-(HDMG)<sub>2</sub>; however, evaluation of the other contributing binding forces is necessary. Oxidation of a chain complex removes an electron either from an a<sub>1g</sub> band (and not altering the structure except for permitting a stronger a<sub>1g</sub> overlap and shorter M-M spacing) or from a ligand-centered MO (permitting POMO-POMO overlap and the possibility of a different relative rotation as well as shorter intermolecular spacings). Utilization of the model may reveal information about the electronic structure of chain complexes and may stimulate further study into the operative binding forces in chain complexes.

**Acknowledgment.** The author wishes to acknowledge the helpful and stimulating discussions with Drs. G. P. Ceasar, M. J. S. Dewar, C. B. Duke, R. Eisenberg, A. J. Epstein, J. E. Kuder, N. O. Lipari, W. A. Little, and G. D. Stucky.

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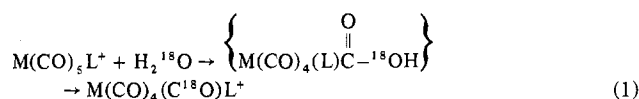
## Reaction of Cationic Group 7B Metal Carbonyl Derivatives with Sodium Hydrogen Sulfide. Production of Metal Hydrides

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Recently we reported on the stereospecific incorporation of oxygen-18 into manganese and rhenium pentacarbonyl derivatives via exchange reactions with H<sub>2</sub><sup>18</sup>O.<sup>1,2</sup> The equatorial CO sites were observed to be preferentially enriched in oxygen-18 over the axial CO group. This process was proposed to proceed through the intermediacy of a hydroxycarbonyl species, resulting from hydroxide attack at a carbonyl carbon site, which is in chemical equilibrium with the starting material and where proton exchange readily occurs between the two oxygens (eq 1). That these cationic species are susceptible



M = Mn, Re; L = phosphines, pyridine, CH<sub>3</sub>CN

to attack by nucleophiles at an equatorial carbonyl carbon atom is evident in that they have been found to react with the nucleophilic reagents  $\text{RLi}$ ,  $\text{RMgX}$ , and amines to yield  $\text{cis-RC(O)Mn(CO)}_4\text{L}$  and  $\text{cis-R}'_2\text{NC(O)Mn(CO)}_4\text{L}$  derivatives, respectively.<sup>3-5</sup> In addition, it has been noted that as L increases in electron-donating ability, thereby making the carbonyl groups more electron rich,<sup>6</sup> the relative rate of oxygen exchange was observed to decrease.

Similarly, the reaction of  $\text{Fe(CO)}_5$  with  $\text{OH}^-$  to afford  $\text{Fe(CO)}_4\text{H}^-$  and  $\text{CO}_2$  has been proposed to proceed through the intermediate  $[\text{Fe(CO)}_4\text{COOH}]^-$ .<sup>7</sup> Clark and Jacobs<sup>8</sup> have also implicated a hydroxycarbonyl intermediate in the reaction of  $[\text{PtCl(CO)(PEt}_3)_2]^+$  and water to yield the platinum(II) hydride species and  $\text{CO}_2$ , as have Hendriksen and Eisenberg<sup>9</sup> in the reaction of the anionic complex  $[\text{RhCl}_2(\text{CO})_2]^-$  with  $\text{H}_2\text{O}$  to yield Rh(I) and  $\text{CO}_2$ . On the other hand a stable iridium(III) hydroxycarbonyl,  $\text{IrCl}_2(\text{COOH})(\text{CO})(\text{PMe}_2\text{Ph})_2$ , has been prepared by Deeming and Shaw<sup>10</sup> from the reaction of the dicarbonyl cation with  $\text{H}_2\text{O}$ . Indeed this reaction was found to be reversible in that the dicarbonyl cation was reformed upon reaction of the hydroxycarbonyl species with dry HCl.

In order to obtain further information on the nature of this oxygen-exchange process between transition metal bound carbon monoxide and  $\text{H}_2\text{O}$  and possibly to observe related intermediates which are more stable, we have begun an investigation of the reactions of metal carbonyl derivatives with NaSH. In this communication we wish to report our findings on the reaction of group 7B  $\text{M(CO)}_5\text{L}^+$  derivatives with sodium hydrogen sulfide.

### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 521 and NMR spectra were obtained with a JEOL C60HL instrument.

The  $\text{M(CO)}_5\text{L}^+$  complexes were synthesized by methods described previously.<sup>3,4</sup> Acetonitrile was dried over  $\text{CaH}_2$  and distilled prior to use. Anhydrous sodium hydrogen sulfide was purchased from Ventron Corp. and  $\text{H}_2^{18}\text{O}$  was obtained from Mound Laboratory, Miamisburg, Ohio.

The details of a typical metal hydride preparation are given below.

**Preparation of  $\text{cis-HMn(CO)}_4\text{PPh}_3$ .** To a mixture of 1.01 g (1.7 mmol) of  $[\text{Ph}_3\text{PMn(CO)}_5][\text{PF}_6]$  and 0.12 g (2.0 mmol) of anhydrous sodium hydrogen sulfide under an inert atmosphere was added 30 mL of dry acetonitrile with stirring. The solution became somewhat lighter in color and gas evolution was noted. The reaction mixture was allowed to stir for an additional 10 min and the solvent was then removed in vacuo. The solid residue was extracted twice with hexane (60 and 10 mL, respectively) and filtered under nitrogen. Vacuum distillation of hexane afforded a yellow powder which was washed with water, was further purified by dissolving in hexane and filtering through Celite, and was recovered upon reducing the volume of solvent. The yield of purified material was 50%; mp 132–133 °C (in vacuo uncor) (lit.<sup>11</sup> mp 135.5 °C). Anal. Calcd for  $\text{HMn(CO)}_4\text{P(C}_6\text{H}_5)_3$ : C, 61.41; H, 3.75. Found: C, 61.2; H, 3.85.

### Results and Discussion

The reaction of  $\text{M(CO)}_5\text{L}^+$  derivatives ( $\text{M} = \text{Mn}$  and  $\text{L} = \text{PMe}_2\text{Ph}$ ,  $\text{PPh}_3$ ,  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ ,  $\text{P(OCH}_2)_3\text{CEt}$ ;  $\text{M} = \text{Re}$  and  $\text{L} = \text{PPh}_3$ ) with anhydrous sodium hydrogen sulfide has been studied in dry acetonitrile under nitrogen. Upon mixing stoichiometric quantities of the cationic carbonyls and NaSH in acetonitrile at room temperature an immediate reaction took place as noted by the evolution of a gas. The reaction mixture was stirred for an additional 10 min. An infrared spectrum taken of the reaction mixture indicated formation of a *cis*-disubstituted carbonyl species as evident by four strong  $\nu(\text{CO})$  absorptions of the required intensity pattern (e.g., for the  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$  derivative  $\nu(\text{CO})$  bands at 2056, 1974, 1963, and 1950  $\text{cm}^{-1}$  were observed). The solvent was removed under reduced pressure and the light yellow products were extracted into hexane and isolated. The  $\nu(\text{CO})$  frequencies observed for the products in hexane solution are listed in Table I. The

Table I. Infrared Spectra in the  $\nu(\text{CO})$  Region of *cis*- $\text{HM(CO)}_4\text{L}$  Derivatives

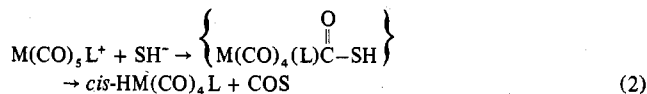
M	L	$\nu(\text{CO}),^a \text{ cm}^{-1}$			
		A <sub>1</sub>	A <sub>1</sub>	B <sub>1</sub>	B <sub>2</sub>
Mn	$\text{PMe}_2\text{Ph}$	2060	1987	1966	1953
Mn	$\text{PPh}_3$	2060	1985	1969	1958
Mn	$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	2059	1982	1969	1956
Mn	$\text{P(OCH}_2)_3\text{CEt}$	2079	2001	1990	1978
Re	$\text{PPh}_3$	2079	1992	1976	1963

<sup>a</sup> Frequencies determined in hexane solution. Band assignment based on intensity pattern.

$\nu(\text{CO})$  frequencies of the hexane-isolated products resulting from the reaction of  $\text{M(CO)}_5\text{PPh}_3^+$  ( $\text{M} = \text{Mn}$ ,  $\text{Re}$ ) with NaSH were identical with those previously reported for the *cis*- $\text{HM(CO)}_4\text{PPh}_3$  derivatives.<sup>11-13</sup> These complexes were previously prepared either by the reduction of  $[\text{Mn(CO)}_4\text{PR}_3]_2$  followed by reaction with acid<sup>11</sup> or by the thermal reaction of  $\text{HMn(CO)}_5$  ( $\text{M} = \text{Mn}$ ,  $\text{Re}$ ) with  $\text{PR}_3$ .<sup>12,13</sup> Further confirmation that the reaction of NaSH with these cationic carbonyls led to metal hydride formation comes from the observations of the Mn–H stretching vibration (a weak absorption at 1795  $\text{cm}^{-1}$  in KBr in the  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$  derivative) and the high-field proton NMR signal centered at a  $\tau$  value of 17.5 ppm in acetone-*d*<sub>6</sub> in the manganese derivatives. In addition, upon allowing these samples to stand in carbon tetrachloride overnight, complete conversion to the *cis*- $\text{ClMn(CO)}_4\text{PR}_3$  derivatives takes place. This transformation has previously been reported by Hieber and co-workers.<sup>11</sup>

The gas evolved from the reaction of NaSH with  $\text{M(CO)}_5\text{L}^+$  species was identified to be carbonyl sulfide by the strong gas-phase infrared absorption ( $\nu_3$ ) centered at 2062.5  $\text{cm}^{-1}$ .<sup>14-16</sup>

Therefore, the net reaction (eq 2) observed appears to result



from  $\text{SH}^-$  attack at a carbonyl carbon atom followed by rapid elimination of COS.

As indicated in eq 1 for the reaction of these substituted cationic carbonyls with  $\text{H}_2\text{O}$  (acetonitrile as solvent), elimination of  $\text{CO}_2$  must be slow relative to proton exchange and hydroxide or water elimination (the reverse reaction),<sup>17</sup> whereas COS elimination (eq 2) is rapid. We have shown that this is indeed the case in the reaction of  $\text{Mn(CO)}_6^+$  with  $\text{H}_2^{18}\text{O}$  where production of oxygen-18-enriched  $\text{Mn(CO)}_6^+$  species occurs more rapidly than  $\text{CO}_2$  elimination and metal hydride formation.<sup>18</sup> In fact, if the reaction between  $\text{Mn(CO)}_5\text{L}^+$  and excess water ( $\text{CH}_3\text{CN}$  as solvent) is allowed to proceed for extended periods of time, slow production of *cis*- $\text{HMn(CO)}_4\text{L}$  results (<10% conversion for an 80-fold excess of water over a 7-day reaction). However, this rate is much slower than the corresponding reaction between water and  $\text{Mn(CO)}_6^+$  in acetonitrile (reaction goes to completion in several hours). Similarly, the oxygen-18 water exchange with  $\text{Mn(CO)}_6^+$  is much faster than that with  $\text{Mn(CO)}_5\text{L}^+$ . On the other hand metal hydride production with  $\text{Mn(CO)}_5\text{L}^+$  can be enhanced in rate by using dibenzo-18-crown-6 solubilized NaOH in acetonitrile where an increase in the rate of formation of hydroxycarbonyl intermediate results with a concomitant rate enhancement for the production of metal hydride and  $\text{CO}_2$ .<sup>19</sup> Nevertheless, this reaction proceeds at a slower rate than the analogous reaction with NaSH where only elimination is observed.

Finally, we have prepared  $\text{C}^{18}\text{O}$ -enriched samples of *cis*- $\text{HMn(CO)}_4\text{PPh}_3$  and *cis*- $\text{ClMn(CO)}_4\text{PPh}_3$  employing the series of reactions described above coupled with prior  $\text{H}_2^{18}\text{O}$

exchange with  $\text{Mn}(\text{CO})_5\text{PPh}_3^+$ . This procedure affords a straightforward method for the production of these isotopically labeled complexes, and it should prove quite useful for the preparations of  $^{17}\text{O}$ -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*- $\text{HMn}(\text{CO})_4\text{PMe}_2\text{Ph}$ , 61477-64-3; *cis*- $\text{HMn}(\text{CO})_4\text{PPh}_3$ , 39796-96-8; *cis*- $\text{HMn}(\text{CO})_4\text{P}(\rho\text{-MeC}_6\text{H}_4)_3$ , 61477-65-4; *cis*- $\text{HMn}(\text{CO})_4\text{P}(\text{OCH}_3)_3\text{CEt}$ , 61477-66-5; *cis*- $\text{HRe}(\text{CO})_4\text{PPh}_3$ , 25838-69-1;  $[\text{Ph}_3\text{PMn}(\text{CO})_5][\text{PF}_6]$ , 54039-57-5.

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- (18) J. A. Froelich and D. J. Darensbourg, unpublished results.
- (19)  $\text{HFe}(\text{CO})_4^-$  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( $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato)gold(III)

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In this note we report the geometry of the coordination of gold in chloro( $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato)gold(III),  $(\text{Cl})\text{Au}(\text{TPP})$ , and its relation to some recently determined porphyrin structures. The synthesis and spectroscopic properties of (mesoporphyrin IX dimethyl ester)gold(III) ( $1+$ )<sup>1</sup> and  $[\text{Au}^{\text{III}}(\text{TPP})^+](\text{AuCl}_4^-)^2$  have been discussed previously in context with gold phthalocyanine,  $\text{Cu}(\text{TPP})$ , and  $\text{Ag}^{\text{II}}(\text{TPP})$ . The single crystals of  $(\text{Cl})\text{Au}(\text{TPP})$  used in the present study were obtained by slow evaporation of a mixture of chloroform and petroleum ether (bp 60–110 °C).<sup>3</sup> 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  $\beta = 121.97$  (5)° and of space group  $P2_1/c$  with four molecules per unit cell. The crystal density (1.61 g cm<sup>-3</sup>) indicated a chloroform of solvation giving a best fit formula unit of  $(\text{Cl})\text{Au}(\text{TPP})(\text{CHCl}_3)_{0.7}$  for the asymmetric unit.

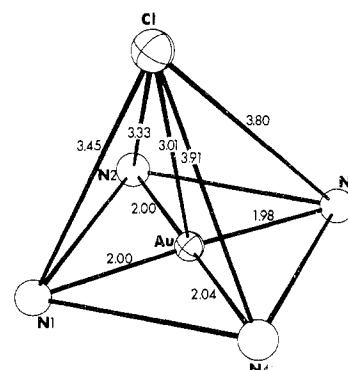


Figure 1. ORTEP drawing of the geometry of the gold coordination.

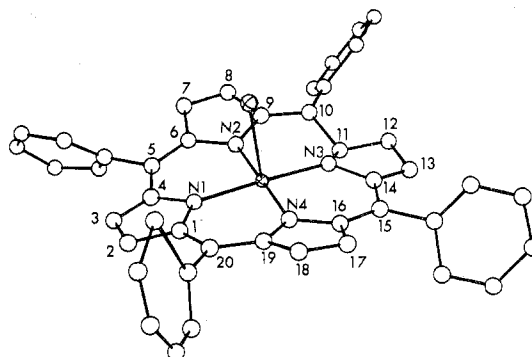


Figure 2. ORTEP drawing of  $(\text{Cl})\text{Au}(\text{TPP})$ .

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,  $(z_{\text{Au}}^2 + \sum z_{\text{Cl}}^2) / \sum z_{\text{TPP}}^2 = 4.2$ , where  $z$  is the atomic number, precluded an accurate determination of the light-atom structure of  $(\text{Cl})\text{Au}(\text{TPP})$ . 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 ( $R_{\text{final}} = 0.10$ ).

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 ( $\pm 0.05$  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  $\text{Au}_2\text{Cl}_6$  (2.29 Å)<sup>4</sup> but compares favorably with the sum of ionic radii (3.18 Å).<sup>5</sup> 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  $(\text{Cl})\text{Mn}(\text{TPP})$ <sup>6</sup> and  $(\text{N}_2)\text{Mn}(\text{TPP})$ <sup>7</sup> 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  $(\text{Cl})\text{Au}(\text{TPP})$  lies close to the threefold axis and makes a short van der Waals contact with