very large trans effect of a bent $^-$NO group was reported[8] for the saturated cobalt(III) complex, [CoCl(en)$_2$NO]$^+$ClO$_4^-$ (7). Many bent NO complexes lack a ligand trans to that group.

Organic chemistry has many examples of isolable structurally distinct valence-bond isomers, but organotransition metal chemistry exhibits very few instances in which two such hybridization isomers can be detected.[9] On the other hand, fluxional isomerism[10] is very common among transition metal compounds. The fact that such inorganic hybridization or fluxional isomers are not isolable is probably due to low intervening energy barriers. Qualitatively, such energy barriers are explained by orbital correlation arguments.[11] Such high energy barriers rarely arise between systems having low-lying excited states such as those derived from incompletely filled d shells.[12] In the present case, distinct hybridization isomers accidentally having nearly the same free energies are apparently in rapid equilibrium, although thus far we have not been able to assess the interconversion rates. An X-ray diffraction study in progress is required to establish unequivocally our hypothesis regarding these equilibrating nitrosyl complexes.

(8) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 9, 2760 (1970).

(9) Organic valence-bond isomers are the closest analogy to the hybridization isomers discussed here, but the former differ in that the connectivity of the carbon framework is usually changed. We are excluding cis–trans geometric isomers of four- and six-coordinate complexes as well as systems which undergo a spin change.

(10) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

(11) R. Hoffmann and R. B. Woodward, *ibid.*, 1, 17 (1968).

(12) T. H. Whitesides, *J. Amer. Chem Soc.*, 91, 2395 (1969).

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Carbon Monoxide and Methyl Isocyanide Complexes of Methylatobis(dimethylglyoximato)cobalt(III)

Sir:

Despite considerable interest in the reaction of CO with vitamin B_{12a},[1] bis(dimethylglyoximato)cobalt(III),[2] and other planar tetradentate cobalt(III) complexes,[3] no simple CO adducts of these species have been observed. However, a CO adduct of cobaloxime (I) has been reported.[4] Attempts to form CO or CH$_3$NC complexes of methylcobinamide have met with no success.[5]

(1) G. N. Schrauzer and L. P. Lee, *Arch. Biochem. Biophys.*, 138, 16 (1970).

(2) L. P. Lee and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 90, 5274 (1968).

(3) (a) G. Costa, G. Mestroni, G. Pellizer, G. Tauzher, and T. Licari, *Inorg. Nucl. Chem. Lett.* 5, 515 (1969); (b) G. Costa, G. Mestroni, and G. Pellizer, *J. Organometal. Chem.*, 15, 187 (1968).

(4) G. N. Schrauzer, J. H. Weber, and T. M. Beckham, *J. Amer. Chem. Soc.*, 92, 7078 (1970).

The absence of a CO complex in this case has been suggested[5] as evidence for a lack of significant π bonding from cobalt to the axial ligand in these systems. By contrast, the ligand-exchange results for methylatobis(dimethylglyoximato)cobalt(III) (methylcobaloxime) complexes, CH$_3$Co(DH)$_2$B, indicate that π bonding is an important factor in the binding of ligands with π-acceptor character.[6] We report here the formation and some properties of the CO and CH$_3$NC complexes of methylcobaloxime in methylene chloride solution.

The dimeric association[6] of CH$_3$Co(DH)$_2$ is readily disrupted by addition of CH$_3$NC to form a stable six-coordinate cobalt(III) species, which has been characterized by isolation and elemental analysis and by its pmr spectrum (Table I). When dried CO is bubbled

Table I. Chemical Shifts as a Function of Temperature for Several Methylcobaloximes, CH$_3$Co(DH)$_2$L

Ligand	Temp, °C[b]	Co–CH$_3$	DH–CH$_3$	O–H–O	Coord ligand
None (dimer)	+41	9.42	7.87	c	
	−70	9.43	8.13	−3.46	
			7.88	−9.13	
			7.69		
			7.67		
CH$_3$CN[d]	+40	9.30	7.86	−8.42	7.99
	−52	9.33	7.80	−8.59	7.95
CH$_3$·NC	+41	9.08	7.83	−8.28	6.65
	−60	9.14	7.81	−8.50	6.64
CO	+41	8.57[e]	7.87[f]	c	
		9.39[e,g]	7.87[f]		
	−60	8.55	7.79	−8.13	
		9.43[g]	8.13[g]	−3.46[g]	
			7.89[g]	−9.10[g]	
			7.68[g]		

[a] Spectra recorded at 60 MHz in dichloromethane and referenced to TMS as an internal standard. [b] Temperature measurements were made using a methanol standard and checked against an iron-constantan thermocouple. [c] Resonance too broad to measure or unobserved. [d] Values taken from ref 8. [e] Resonance shows exchange broadening. [f] Single sharp resonance attributable to two species in equilibrium and undergoing fast exchange. [g] Resonance assigned to ligand-free [CH$_3$Co(CH)$_2$]$_2$.

through a CH$_2$Cl$_2$ solution of [CH$_3$Co(DH)$_2$]$_2$ an appreciable concentration of the six-coordinate CO complex is formed, as observed in the low-temperature pmr spectrum (Figure 1). The existence of a mobile equilibrium

$$[CH_3Co(DH)_2]_2 + 2CO \rightleftharpoons 2CH_3Co(DH)_2CO$$
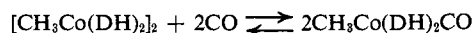
is evidenced by varying the CO pressure above solutions of the dimer in sealed nmr tubes. The resonances ascribed to the CO complex (Table I) increase in intensity with CO pressure in the expected manner. Purging of the solutions with N$_2$ or Ar causes disappearance of the absorptions due to the CO complex and reappearance of the nmr spectrum of the pure dimer solution.[7] Addition of water to a CO-contain-

(5) R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. A*, 381 (1969).

(6) L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, 91, 5188 (1969).

(7) Bubbling of CO through a CH$_2$Cl$_2$ solution of the dimer for several hours leads to the appearance in the ir spectrum of a pair of absorptions at 2024 and 1998 cm^{-1}. Aside from the appearance of a low-intensity band at 1167 cm^{-1}, no other changes are seen in the ir spectrum. There is no detectable change in the nmr spectra of such solutions as compared with those obtained from addition of CO over

ing solution results in formation of the pure aquo complex, $CH_3Co(DH)_2 \cdot H_2O$. The incompleteness of equilibrium with respect to formation of the CO complex is suggestive of the results obtained with diphenyl sulfoxide,[8] in which case the equilibrium is also incomplete.

A single, sharp intense absorption centered at 2115 cm^{-1} appears in the infrared spectrum of CH_3Co-$(DH)_2CO$ in CH_2Cl_2 solution.[9] The fact that this frequency is substantially below that for free CO (and, incidentally, lower than the CO stretching frequencies for cationic platinum complexes of CO)[10] suggests that the Co–CO bond contains a substantial π-bond component.[11] Molecular orbital calculations of metal–CO interactions indicate that the σ interactions alone should result in an increase in the CO bond stretching force constant.[12] This, added to the increase in CO stretching frequency expected simply from coupling with the M–C bond stretch, would require an increase in CO stretching frequency upon adduct formation. Lowering of the CO stretching frequency with respect to free CO is thus indicative of an important contribution to the bonding from the π-acceptor character of CO. The C≡N stretching mode in the isocyanide complex in CH_2Cl_2 solution occurs at 2231 cm^{-1} as compared with 2169 cm^{-1} for the free ligand.

Although it was not possible to carry out quantitative exchange studies, pmr spectra exemplified by those depicted in Figure 1 provide information on the lability of the CO complex toward exchange, presumably by a dissociative pathway, as observed for other CH_3Co-$(DH)_2B$ species.[6,8] The lines due to the dimethylglyoximato methyl groups of the dimer collapse to a broad singlet at a temperature $(+22°)$ at which there is still no appreciable broadening of the single dimethylglyoximato methyl resonance due to the CO adduct (Figure 1A). At 41° these methyl resonances, which differ at 220 MHz by only 14.0 Hz, have coalesced to a singlet. The two axial methyl resonances are, however, still distinguishable, although the onset of exchange is evident in the broadening.

Further insight into the nature of the cobalt–ligand interaction can be obtained from the comparative chemical shifts of the axial methyl groups in the series of complexes listed in Table I. In contrast to the chemical shifts of the methyl groups in the dimethylglyoximato ligands, the axial methyl chemical shift is sensitive to the nature of the trans ligand. As a general rule it appears about 0.4 ppm to lower field for "soft" donor groups such as S or P, as compared with O or N. The three ligands listed in Table I are alike in that they all involve a triple bond in the same geometrical relationship to the axial methyl group. The great variance in the methyl chemical shifts cannot therefore be ascribed to magnetic anisotropy effects arising in the ligand itself. Neither is the ordering of chemical shifts $CH_3CN > CH_3NC > CO$ in the order of stability of

Figure 1. Pmr spectra (220 MHz) of some methylcobaloximes at various temperatures in dichloromethane referenced to TMS as an internal standard: (A) $CH_3Co(DH)_2CO$ at $+22°$, (B) CH_3Co-$(DH)_2CO$ at $-17°$, (C) $CH_3Co(DH)_2$ at $-17°$.

the adducts, $CH_3NC > CO \approx CH_3CN$. The shift to lower field is, however, in the order of expected π-acceptor character of the ligands, $CO > CH_3NC > CH_3CN$. The CO complex appears to exchange at rates roughly comparable to those for the diphenyl sulfoxide or acetonitrile complexes, as deduced from the pmr spectra at various temperatures. The CH_3NC adduct, on the other hand, shows no evidence of exchange with excess ligand at the highest temperature examined, 41°.

Aside from the inherent interest in the formation of a CO adduct with cobalt formally in the (III) state, the present results are of interest because of their possible relevance to the chemistry of B_{12} coenzyme and related compounds.[13] It has been established that the reactivity of the Co–alkyl bond in alkylcobinamides is strongly dependent on the nature of the trans ligand.[14] The possibility of CO adduct formation with methylcobalamin and the chemical properties of the prospective species are under investigation.

several minutes. The ir bands are probably due to formation of a small amount of a cobalt–carbonyl compound, as yet unidentified. There is no evidence for CO insertion into the Co–CH$_3$ bond.

(8) L. M. Ludwick, Ph.D. Thesis, University of Illinois, 1969.

(9) The ir spectrometer was frequency calibrated to within ±1 cm^{-1} using gaseous CO.

(10) A. R. Brause, M. Rycheck, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 6500 (1967).

(11) T. L. Brown and D. Y. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967).

(12) (a) R. F. Fenske and R. L. DeKock, *ibid.*, **9**, 1053 (1970); (b) K. F. Purcell, *J. Amer. Chem. Soc.*, **91**, 3487 (1969).
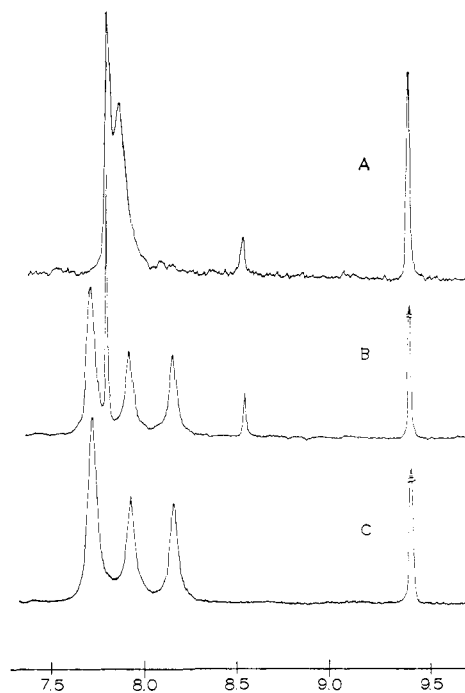
(13) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

(14) (a) W. H. Pailes and H. P. C., Hogencamp, *Biochemistry*, **7**, 4160 (1968); (b) H. P. C. Hogencamp and S. Holmes, *ibid.*, **9**, 1886 (1970).

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