ticular its diamagnetic character, suggest a structure in which either Cu–Cu interactions or antiferromagnetic coupling of spins results in a singlet ground state. The molecular weight of this complex, determined osmometrically in 0.02 M acetone and 1,2-dichloroethane solutions, was 1257 ± 20 and 2220 ± 40, respectively. Assuming complete ionic association, molecular weights of 2009 and 4018 are calculated for the monomer and dimer, respectively. The observed values can tentatively be ascribed to a dimeric hexaanion which shows different degrees of ionic associations depending on the dielectric constants of the solvents employed. The exact nature of III is still uncertain, however, and a complete description of its structure must await the results of further studies now in progress.

Attempts were made to replace the inert counterion of I with $(PPh_3)_2M^+$ [M = Cu(I) or Ag(I)]. The products obtained when aqueous solutions of I were extracted with CH_2Cl_2 solutions of $(PPh_3)_3MCl$ had the stoichiometry $(PPh_3)_2Cu^I(Dto)M(PPh_3)_2$ [M = Cu(I) or Ag(I)]. The same compounds as well as $(PPh_3)_2AgDtoAg(PPh_3)_2$ could also be obtained from K_2Dto and $M(PPh_3)_3Cl$ by a similar extraction procedure. The mode of coordination of the (presumed bridging) dithiooxalate ligand in these diamagnetic, X-ray-isomorphous complexes is at present uncertain.

Cyclic voltammetry on solutions of the Ph_4As^+ salts of I in CH_2Cl_2 (Table I) revealed the existence of a reversible one-electron oxidation at scan speeds $\leqslant 0.1$ V/sec. At scan speeds >0.2 V/sec a quasi-reversible wave[10] was observed, as evidenced by the separation between the anodic and cathodic portions of the wave ($E_p > 60$ mV). Chemical oxidation of solutions of the Ph_4As^+ or $BzPh_3P^+$ salts of I in DMF or CH_2Cl_2 by $CuCl_2 \cdot 2H_2O$ or anhydrous $FeCl_3$, respectively, gave rise to red, diamagnetic crystalline compounds of the composition $CatCu(Dto)_2$ (IV) (Cat = Ph_4As^+ or $BzPh_3P^+$). The infrared spectra of these light-sensitive compounds revealed the presence of coordinated dithiooxalate ligand[1] (Table I) and a new strong band at 2035 cm^{-1}. Addition of PPh_3 to dichloromethane solutions of IV led to a vigorous evolution of gas. The infrared and mass specta of this gas were found to be identical with those of gaseous COS.[11] The high C–O stretching frequencies observed at 2035 cm^{-1} in the ir spectra of IV suggest that the OCS molecule is coordinate "end-on" via the sulfur end of the molecule.[12] The electrochemical behavior of IV was examined by cyclic voltammetry and it was found that IV undergoes a reversible one-electron *reduction* at scan rates $\leqslant 0.1$ V/sec. At rates >0.2 V/sec a quasi-reversible wave was obtained. The potential at which IV undergoes reduction is approximately equal, and of opposite sign, to the potential at which oxidation of I is observed (Table I). Chemical reduction of IV in tetrahydrofuran (THF) with $NaBH_4$ occurs

readily, and the major product isolated was the "parent" copper dithiooxalate. The electrochemical properties of I and IV (Table I) suggest[14] that the electron-transfer rate in either the reduction of IV or the oxidation of I is slow, consistent with a redox scheme involving the breaking and forming of a C–C bond.[15]

$$[Cu^{II}(Dto)_2]^{2-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [Cu^I(COS)_2Dto]^- \qquad (1)$$
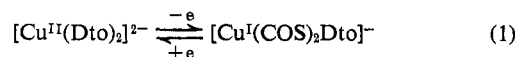
As a final comment, we would like to suggest that oxidation of the coordinated dithiooxalate ligand may provide a convenient general synthetic route to carbonyl sulfide complexes.

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(14) The mechanism of these redox processes is currently being investigated.

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Intramolecular Redox Equilibria of Cobalt–Nitrosyl Complexes

Sir:

The controversial nature of the nitrosyl ligand has been somewhat clarified by recent precise X-ray diffraction studies which in most cases illustrate either of two distinct NO bonding modes.[1] In the sense of formal oxidation states, this ligand behaves as $^+$NO in some complexes and as $^-$NO in others.[2] The former are characterized by linear metal–N–O bonds and rather short metal–N distances, whereas the latter exhibit metal–N–O angles approaching 120° and longer metal–N distances. Recently, we suggested[3] the possibility of conformational equilibria between the two forms of metal–nitrosyl bonding whereby the coordination geometry about the metal would change as the metal and the nitrosyl undergo a formal internal redox reaction. Experimental evidence consistent with such hybridization isomerism is presented below.

The most dramatic example of the dual nature of NO ligands is Eisenberg's report[4] of **1** wherein the two nitrosyl groups are found in the two limiting bonding modes. We have repeated the synthesis of **1** using isotopically labeled $RuCl(^{15}NO)(P(C_6H_5)_3)_2$ (**2**). During the 15 min required for isolation from methanol, four NO bands appear (Table I), indicating equilibration of the two forms in solution.

This interconversion is a restricted example of the hybridization tautomerism we had suggested earlier in that the two equilibrating forms are identical and

(10) R. S. Nicholson, *Anal. Chem.*, 37, 1351 (1965).
(11) The C–O stretching vibration in gaseous COS is found at 2064 cm^{-1}.
(12) A similar type of "end-on" coordination has been reported[13] to occur in a carbon disulfide complex of rhodium ($RhCl(CS_2)_2(PPh_3)_2$). The terminal C=S stretching frequency in this compound is found at 1510 cm^{-1}, and is 20 cm^{-1} smaller than the corresponding vibrational frequency in gaseous CS_2. The C–O stretch in COS which is σ bonded to platinum via carbon and sulfur atoms occurs at 1727 cm^{-1}.[13]
(13) M. C. Baird and G. Wilkinson, *J. Chem. Soc.*, 865 (1967).

(1) (a) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, 8, 1288 (1969); (b) J. H. Enemark and J. A. Ibers, *ibid.*, 7, 2339 (1968); (c) D. J. Hodgson and J. A. Ibers, *ibid.*, 7, 2345 (1968); (d) *ibid.*, 8, 1282 (1969).
(2) The use of the terms $^+$NO and $^-$NO is not intended to reflect the probable electron densities on the NO ligands in these complexes but rather to assign formal oxidation numbers to the central element.
(3) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).
(4) C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *ibid.*, 92, 4760 (1970).

Table I. Infrared Data

Compound	ν_{NO}, cm$^{-1\,a}$	Other selected bands
1, [RuCl(NO)$_2$(P(C$_6$H$_5$)$_3$)$_2$]$^+$PF$_6^-$	(1850), (1687)^b (1810)*, (1650)* ^{c}	
2, RuCl(NO)(P(C$_6$H$_5$)$_3$)$_2$	1762, 1730* ^{c}	
3a, CoCl$_2$(NO)(P(C$_2$H$_5$)$_3$)$_2$	1720 (w), 1650 (s)^c (1720) (m), (1640) (s)	
3b, CoCl$_2$(NO)(P(n-C$_4$H$_9$)$_3$)$_2$	1650 (s)^c (1720) (m), (1650) (s)	
3c, CoCl$_2$(NO)(P(CH$_3$)(C$_6$H$_5$)$_2$)$_2$	1750 (s), 1650 (s)^c 1725* (s), 1620* (s) (1735) (s), (1630) (m)	
3d, CoCl$_2$(NO)(P(p-CH$_3$C$_6$H$_4$)$_3$)$_2$	1712 (s), 1650 (w)^c (1710) (m) (1650) (s)	
3e, CoCl$_2$(NO)(P(C$_6$H$_5$)$_3$)$_2$	(1725) (m), (1640) (s)^c (1685)* (m), (1603)*(s)	(370), (342), (313) (309) $\nu_{Co-Cl}{}^d$
3f, CoCl$_2$(NO)(P(p-C$_6$H$_4$)$_3$)$_2$	(1750) (m), (1655) (s)^c	
4, IrCl$_2$(NO)(P(C$_6$H$_5$)$_3$)$_2$	(1560) (s)^e	
5, RhCl$_2$(NO)(P(C$_6$H$_5$)$_3$)$_2$	(1630) (s)^e	
6, RhCl$_2$(NO)(CO)(P(C$_6$H$_5$)$_3$)$_2$	(1630) (s)^c	(2080) (s) ν_{CO}
7, [CoCl(NO)(en)$_2$]$^+$ClO$_4^-$	(1611)^f	

^{a} All spectra were measured in CH$_2$Cl$_2$ solution except those in parentheses, which were determined in KBr pellets. ^{15}N peaks are indicated by an asterisk. Relative intensities are noted as w (weak), m (medium), and s (strong). ^{b} Reference 4. ^{c} This work. All compounds so indicated have yielded acceptable analyses for C, H, N, P, and Cl. ^{d} Corresponding iodides do not absorb at 300–400 cm^{-1}. ^{e} C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969). ^{f} Reference 8.

only the nitrosyl groups are undergoing a redox interexchange.
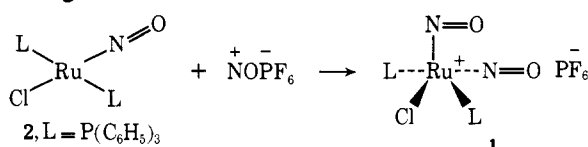
Compounds of the type CoX$_2$(NO)(PR$_3$)$_2$ were briefly described by Chatt,[5] who noted the presence of two ir bands in the NO stretching range. Chatt proposed that the additional band might be accounted for by free oxides of nitrogen or some equilibrium between different types of nitrosyl bonding. We have prepared a series of such compounds **3a–f** and found that most exhibit two distinct NO stretching modes in solution. In two cases, **3c** and **3e**, the assignment of ν_{NO} is confirmed by ^{15}N substitution (Table I). Throughout the series, the relative intensities of the two NO bands in solution are dependent upon the nature of the phosphine—the lower ($^-$NO) frequency growing in intensity as the phosphine becomes more basic. This is consistent with our hypothesis that two valence-bond isomers I and II are in equilibrium. More basic ligands would tend to stabilize the bent nitrosyl, square-pyramidal cobalt(III) form compared with the linear nitrosyl, trigonal-bipyramidal cobalt(I) form. The ν_{NO} band ratios measured in the solid state differ from those determined in solution (Table I). Crystal-packing energies undoubtedly impose isomer ratios in the solid. The solution-ir spectrum of the more soluble diphenylmethylphosphine complex **3c** was measured over the temperature range +30 to −70°. At room temperature, the 1650-cm^{-1} peak is slightly more intense but as the temperature is lowered, the 1750-cm^{-1} band increases and the 1650-cm^{-1} band diminishes in a smooth reversible manner. Within experimental error, the sum of NO absorbances remains constant over this temperature range.

That dimerization or dissociation of a ligand explains the presence of two NO bands was ruled out by the

(5) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

following experiments. The air-stable complexes **3a** and **3b** are monomeric in solution, but because of their air sensitivity, reliable molecular weight data could not be obtained for the other nitrosyls **3c–f**. The relative absorbances of the NO bands are independent of concentration over a fourfold dilution. The compounds are nonconductors in nitrobenzene. The proton magnetic resonance spectrum of the P(CH$_3$)(C$_6$H$_5$)$_2$ complex **3c** fails to show the presence of the uncoordinated ligand. Observation of a methyl triplet in the pmr spectrum of **3c** (unchanged from 25 to −60°) is consistent with the presence of *trans*-phosphine groups, ruling out cis–trans isomers.

Four ν_{Co-Cl} bands in the spectrum of **3e** suggest the presence of two different coordination geometries. The most attractive interpretation of these data is a rapid equilibrium between a trigonal-bypyramidal cobalt(I) complex with a linear nitrosyl (I) and a square-pyramidal cobalt(III) complex with a bent nitrosyl (II).
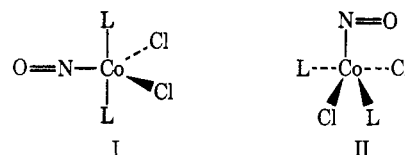
Iridium and rhodium analogs (**4** and **5**) of the cobalt complexes are known, but these exist only in the bent ($^-$NO) form and thus serve as models for II. An X-ray diffraction study[6] of the iridium complex **4** shows it to have a structure like II. The rhodium complex **5** forms a carbonyl derivative, **6**, without altering the ν_{NO} frequency (Table I). The stoichiometry of the carbonyl **6** requires assigning formal oxidation states of Rh(III) and $^-$NO.[7] The high Co frequency, 2080 cm^{-1}, is reasonable for a rhodium(III) system and is probably influenced by the strong, primarily σ-bonding trans effect of the presumed trans $^-$NO group. A

(6) Unpublished work of J. A. Ibers and D. P. M. Mingos described by G. R. Crooks and B. F. G. Johnson, *ibid.*, *A*, 1662 (1970).

(7) Otherwise the inert gas configuration would be exceeded, and we are not aware of any such instance among stable diamagnetic mononuclear transition metal complexes involving unidentate ligands.

very large trans effect of a bent $^-$NO group was reported[8] for the saturated cobalt(III) complex, [Co-Cl(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	+41	9.42	7.87	c	
(dimer)	−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

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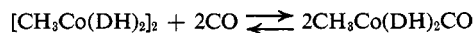
is evidenced by varying the CO pressure above solutions of the dimer in sealed nmr tubes. The resonances ascribed to the CO complex (Table I) increase in intensity with CO pressure in the expected manner. Purging of the solutions with N$_2$ or Ar causes disappearance of the absorptions due to the CO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