CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF GEORGIA, ATHENS, GEORGIA

Reactions of Mixed Polydentate Ligands with Cobalt Tricarbonyl Nitrosyl

BY EARL P. ROSS AND GERARD R. DOBSON

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Hieber and Ellermann[1] have reported the preparation of the tetrahedral $Co(CO)(NO)(P(C_6H_5)_3)(As(C_6H_5)_3)$ *via* a two-step synthesis, but did not resolve the complex. We have investigated the possibility that "mixed" bi- and tridentate ligands containing phosphine and amine or phosphine and cyanide functional groups might in one step yield optically-active cobalt carbonyl nitrosyl derivatives which might easily be resolved. Thus, for example, taking advantage of the reluctance of $Co(CO)_3NO$ to undergo the displacement of more than two carbonyl groups,[2] the ligand $(C_2H_5)_2NC_2H_4P(C_6H_5)C_2H_4N(C_2H_5)_2$[3] (NPN) might be expected to yield a derivative of the type (NPN)Co(CO)NO in which the presence of a free amine group would facilitate resolution of the complex.

The reactions of an excess of $Co(CO)_3NO$[4] with each of five "mixed" ligands, NPN; $(C_2H_5)_2NC_2H_4P(C_6H_5)_2$[3] (NP); $(C_6H_5)_2PC_2H_4N(C_2H_5)C_2H_4P(C_6H_5)_2$[3] (PNP); $(C_2H_5)_2NCH_2CH(P(C_6H_5)_2)CH_2N(C_2H_5)_2$[5] (T–NPN); and $(C_6H_5)_2PC_2H_4CN$[6] (PCN), and purification of the products obtained were carried out under the conditions employed by Basolo, *et al.*,[7] for the reactions of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (diphos) with $Co(CO)_3NO$. The mode of attachment of ligand to metal for the derivatives of NP, NPN, T–NPN, and PNP was inferred from a comparison of their carbonyl and nitrosyl stretching frequencies to those of the "model" derivatives $Co(CO)_2(NO)P(C_6H_5)_3$ and $Co(CO)(NO)[P(C_6H_5)_3]_2$.[4] For the complexes of PCN, in addition, the cyanide stretching frequencies for the free and bonded ligand were compared. In every case these comparisons indicate that bonding of the ligands to cobalt is through phosphorus alone (see Table I). More vigorous reaction conditions failed to yield any evidence of the formation of complexes in which the ligands function as chelating groups. Heating pure $(NPN)Co(CO)_2NO$ in toluene at 90° for 1 week failed to induce attachment of the amine group to the metal, although disproportionation of the complex to give a small amount of the phosphorus-bonded $(NPN)_2Co(CO)NO$ was noted. Higher reaction temperatures (*ca.* 125°) resulted in destruction of the complex. The bulky NPN and T–NPN, unlike NP and PCN under similar reaction conditions, fail to yield disubstituted complexes, evidently due to steric factors, since such reactions proceed through a five-coordinate intermediate.[8] PNP gives a bridged binuclear complex analogous to a dimeric derivative of diphos reported by Basolo, *et al.*[7]

TABLE I

$Co(CO)_3NO$ DERIVATIVES OF "MIXED" POLYDENTATE LIGANDS

Compound	Color and form	Infrared spectra,[a] cm⁻¹			% C		% H		% N	
		ν CN	ν CO	ν NO	Calcd	Found	Calcd	Found	Calcd	Found
$(NP)Co(CO)_2NO$	Red-brown oil	...	2033, 1973	1758	55.81	55.71	5.63	5.95	6.51	6.29
$(NP)_2Co(CO)NO$	Red-brown crystals	...	1948	1715	64.62	64.93	6.89	7.01	6.11	5.34
$(NPN)Co(CO)_2NO$	Red-brown oil	...	2037, 1977	1763	52.97	53.05	7.35	7.42	...	...
$(PNP)[Co(CO)_2NO]_2$	Red-brown oil	...	2033, 1976	1958	53.79	54.69	4.38	4.65	...	...
$(T\text{–}NPN)Co(CO)_2NO$	Red-brown oil	...	2038, 1987	1758	58.24	59.30	6.86	6.81	...	...
$(NCP)Co(CO)_2NO$	Red-brown oil	2260	2040, 1984	1762	53.13	53.95	3.68	3.90	...	...
$(NCP)_2Co(CO)NO$	Red-brown crystals	2262	1952[b]	1707	62.52	62.22	4.75	4.87	...	...
PCN	...	2259[b]	...	...	...	...	...	...	...	...
$(C_6H_5)_3PCo(CO)NO$[4]	...	...	2035, 1981	1761	...	...	...	...	...	...
$[(C_6H_5)_3P]_2Co(CO)NO$[4]	...	...	1957	1717	...	...	...	...	...	...

[a] Cyclohexane solution unless noted. [b] Chloroform solution.

Very recently reported kinetic studies of the displacement of CO from $Co(CO)_3NO$ and $Co(CO)_2(NO)B$ by a variety of Lewis bases (B) showed that reaction rates varied soft base > hard base,[9] implying the preferential formation of bonds between cobalt and soft bases in such systems.[8,10] It is thus not too surprising that despite the favorable entropy effect only the soft base of the soft–hard pairs, phosphine and amine and phosphine and cyanide, should coordinate. The reactions of NP, NPN, and PNP with $Co(CO)_3NO$ and $Mo(CO)_6$ may be contrasted: the three ligands function as chelating groups in the substitution products of the latter.[3] The displacement of CO by sulfur-containing ligands from $Co(CO)_3NO$ also proceeds more slowly than in the corresponding reactions of

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(1) W. Hieber and J. Ellermann, *Chem. Ber.*, **96**, 1643 (1963).

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(3) G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Chem. Commun.*, 281 (1966).

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(5) T–NPN was prepared by the method of Mann and Millar (*J. Chem. Soc.*, 3039 (1952)) through reaction of $(C_6H_5)_2PMgBr$ and $(C_2H_5)_2NCH_2CHClCH_2N(C_2H_5)_2$ (obtained from Aldrich Chemical Co., Milwaukee, Wis.). The straw-colored oil was fractionally distilled (bp 146° (0.04 mm). *Anal.* Calcd for $C_{23}H_{35}N_2P$: C, 74.6; H, 9.5; N, 7.6; P, 8.4. Found: C, 74.8; H, 9.4; N, 7.6; P, 8.5. Further details of the preparative procedure will be given elsewhere.

(6) PCN, which had previously been prepared through reaction of acrylonitrile and diphenylphosphine in a sealed tube at 130° [F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 4453 (1952)] may be more easily obtained at room temperature from the same reactants *via* the base-catalyzed cyanoethylation method used to prepare bis(2-cyanoethyl)phenylphosphine, as described by M. M. Rauhut, *et al.*, *J. Am. Chem. Soc.*, **81**, 1103 (1959).

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ligands containing phosphorus, and it thus appears probable that "mixed" ligands containing both phosphorus and sulfur would yield much the same results as have been reported above.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139

Some Reactions of the Octahalodirhenate(III) Ions. V. Polarographic Reduction[1]

BY F. A. COTTON, W. R. ROBINSON, AND R. A. WALTON

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Relatively few studies of the redox reactions of metal atom cluster compounds have been published.[2,3] In those reported, the results (for M_6X_{12} species) have been remarkably consistent with the molecular orbital description of the bonding given by Cotton and Haas[4] for such systems. A comparable sort of MO analysis of the bonding[5,6] has been carried out for the $Re_2X_8^{2-}$ species (X = Cl, Br, and most recently,[7] NCS) which have D_{4h} symmetry. This treatment, which should also be applicable in its general features to any analogous technetium complexes, leads to the conclusion that there are two relatively low-lying, nonbonding σ orbitals which are directed outward along the fourfold axis of the molecule.

It would seem reasonable to suppose that at least one and perhaps two electrons could be added to these orbitals, thus forming $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ species, without interfering with any of the components, σ, π, or δ, of the Re–Re bond. Hence, the extremely short metal–metal distance and the eclipsed configuration should be maintained in the reduced species. Whether the $Re_2X_8^{4-}$ species should have zero or two unpaired electrons will depend on how nearly degenerate the two nonbonding σ orbitals are; this is difficult to predict with confidence.

The investigations described here were undertaken to test the foregoing ideas. The results are also relevant to the question of why the only known $Tc_2X_8^{n-}$ species[8,9] is $Tc_2Cl_8^{3-}$.

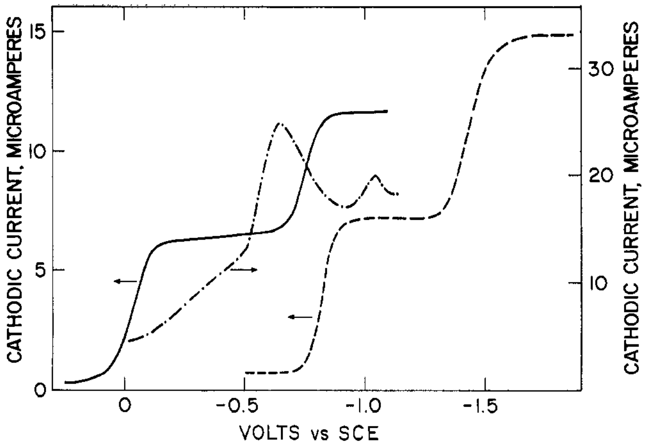

Figure 1.—Polarograms for the tetra-*n*-butylammonium salts of $Re_2Cl_8^{2-}$ (------), $Re_2(NCS)_8^{2-}$ (——), and $Re_2Br_8^{2-}$(–·–·–) in acetonitrile at 25°.

Experimental Section

The compounds $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$, X = Cl, Br, NCS, were prepared as described elsewhere.[7,10] Approximately 10^{-3} *M* solutions in acetonitrile containing 0.5 *M* tetra-*n*-butylammonium perchlorate as supporting electrolyte were used to record the polarograms. The results are displayed in Figure 1 and numerical results pertaining to the $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$ ions are summarized in Table I.

TABLE I

POLAROGRAPHIC DATA FOR $Re_2Cl_8^{2-}$ AND $Re_2(NCS)_8^{2-}$ IN ACETONITRILE[a] AT 25°

Step	$E_{1/2}$[b]	n	i_d[c]	I_d[d]	$E_{3/4} - E_{1/4}$, mv
		1.083 m*M* $[(C_4H_9)_4N]_2Re_2Cl_8$			
1	−0.82	1.1	6.54	2.80	65 ± 3
2	−1.44	~1.3	7.42	...	93 ± 3
		0.800 m*M* $[(C_4H_9)_4N]_2Re_2(NCS)_8$			
1	−0.04	1.1	5.5	2.7	65 ± 3
2	−0.71	1.1	4.6	2.6	59 ± 4

[a] 0.5 *M* $[(n\text{-}C_4H_9)_4N]ClO_4$ added as supporting electrolyte. [b] With respect to the standard calomel electrode, in volts. [c] Average limiting current in microamps. [d] $I_d = i_d/CM^{2/3}t^{1/6}$, where *C* = concentration, *M* = mercury flow rate, and *t* = time between drops.

Discussion

Both the $Re_2Cl_8^{2-}$ and the $Re_2(NCS)_8^{2-}$ salts gave conventional two-wave reduction polarograms. There are no simple reduction waves in the polarogram of $Re_2Br_8^{2-}$ although reduction obviously occurs. This polarogram will not be discussed further.

The number, *n*, of electrons involved in the reductions of the $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$ ions was estimated using the Ilkovic equation,[11] and these are recorded in Table I. The required values of *D*, the diffusion coef-

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(1) Research supported in part by the United States Atomic Energy Commission.

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(4) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

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