Reductive Nitrosylation of Group VIIIB Metals

By DOUGLAS GWOST and KENNETH G. CAULTON*
(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary Nitric oxide, in the presence of an amine and alcohol, functions as a one-electron reductant towards Fe^{II} and Co^{II}, yielding bis(nitrosyl) complexes and the solvent-derived alkyl nitrite.

NITRIC OXIDE reacts with cobalt complexes of primary and secondary amines and ammonia to form mono-nitrosyl complexes.[1] We report a series of reactions in which NO functions unexpectedly. Passage of NO through a solution of $CoCl_2$ (1 mol) and *NNN'N'*-tetramethylethylenediamine (tmeda) (2 mol) in anhydrous methanol yields a solution of the cation $Co(NO)_2(tmeda)^+$, which can be precipitated as its PF_6^- or BPh_4^- salts. A molar ratio of tmeda : $CoCl_2$ less than 2 : 1 results in a reduction in yield; thus a molar ratio of 1 : 1 halves the yield of $Co(NO)_2(tmeda)^+$. However, other tertiary amines function equally well; 1 : 1 : 1 molar ratios of $CoCl_2$: 2L : NEt_3 produce the dinitrosyl complexes in yields of up to 90%, where 2L = tmeda, $2PPh_3$, and 1,2-bisdiphenylphosphinoethane (diphos) (Table).

TABLE

Compound[a]	Yield (%)[b]	ν_{NO}/cm^{-1}	Ref.
$Co(NO)_2(tmeda)PF_6$ ..	63	1876, 1818[c]	e
$Co(NO)_2(PPh_3)_2BPh_4$ ..	32	1855, 1795[c]	f
$Co(NO)_2(diphos)BPh_4$ ..	58	1838, 1789[c]	f
$[Co(NO)_2Cl]_2$	50	1866, 1792[d]	g
$Fe(NO)_2Cl_2HNEt_3$	—	1773, 1697[d]	h

[a] All compounds reported here have been fully characterized by elemental analysis and/or comparison with authentic samples. [b] Based on yield from recrystallization or sublimation of crude products. [c] KBr disc. [d] Nujol mull. [e] W. Hieber and K. Kaiser, *Z. anorg. Chem.*, 1968, **362**, 169. [f] T. Bianco, M. Rossi, and L. Uva, *Inorg. Chim. Acta*, 1969, **3**, 443. [g] See ref. 2. [h] W. Hieber and H. Führling, *Z. anorg. Chem.*, 1970, **373**, 48.

Trap-to-trap fractionation of the volatile products after the reaction is complete yields 1 mol. equiv. of methyl nitrite (i.r., g.l.c., and high-resolution mass spectral characterization) for each mol. of $Co(NO)_2 2L^+$ produced. Thus in contrast to all known reactions of NO, the system NO–amine–MeOH functions as a reducing agent; this is confirmed by our finding that 3 mol. equiv. of NO are consumed for every mol. of $Co(NO)_2 2L^+$ formed [equation (1)].

$$CoCl_2 + 3NO + 2L + NEt_3 \xrightarrow[MeOH]{\text{Room temp}} Co(NO)_2(2L)Cl + MeONO + Et_3NHCl \quad (1)$$

Solid triethylammonium salt is also isolated in agreement with this stoicheiometry.

In the absence of potential ligands (2L), the reaction with $CoCl_2$ yields $[Co(NO)_2Cl]_2$ or $Co(NO)_2Cl_2^-$ [equation (2)].

$$CoCl_2 + 3NO + NEt_3 \xrightarrow[\text{Room temp.}]{MeOH} 0{\cdot}5\,[Co(NO)_2Cl]_2 + MeONO + NEt_3HCl \rightleftarrows Co(NO)_2Cl_2HNEt_3 \quad (2)$$

$FeCl_2$ is likewise reduced by NO–amine–MeOH to yield $Fe(NO)_2Cl_2^-$; $NiCl_2$ is unreactive under the same conditions.

Regardless of the arbitrary assignment of the oxidation state of co-ordinated NO, it is clear that there has been an oxidation of NO to RONO; we view this as the first example of a stoicheiometric reduction of a metal complex by NO followed by dissociation of the oxidized form of NO and concomitant co-ordination of free NO.

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