

## Reductive Nitrosylation of Group VIII<sub>B</sub> Metals

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

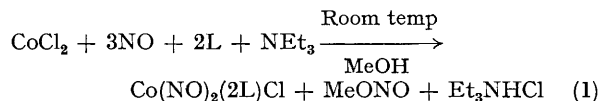
NITRIC OXIDE reacts with cobalt complexes of primary and secondary amines and ammonia to form mono-nitrosyl complexes.<sup>1</sup> We report a series of reactions in which NO functions unexpectedly. Passage of NO through a solution of CoCl<sub>2</sub> (1 mol) and *NNN'*N'-tetramethylethylenediamine (tmeda) (2 mol) in anhydrous methanol yields a solution of the cation Co(NO)<sub>2</sub>(tmeda)<sup>+</sup>, which can be precipitated as its PF<sub>6</sub><sup>-</sup> or BPh<sub>4</sub><sup>-</sup> salts. A molar ratio of tmeda:CoCl<sub>2</sub> less than 2:1 results in a reduction in yield; thus a molar ratio of 1:1 halves the yield of Co(NO)<sub>2</sub>(tmeda)<sup>+</sup>. However, other tertiary amines function equally well; 1:1:1 molar ratios of CoCl<sub>2</sub>:2L:NEt<sub>3</sub> produce the dinitrosyl complexes in yields of up to 90%, where 2L = tmeda, 2PPh<sub>3</sub>, and 1,2-bisdiphenylphosphinoethane (diphos) (Table).

TABLE

Compound <sup>a</sup>	Yield (%) <sup>b</sup>	$\nu_{\text{NO}}$ /cm <sup>-1</sup>	Ref.
Co(NO) <sub>2</sub> (tmeda)PF <sub>6</sub>	63	1876, 1818 <sup>c</sup>	e
Co(NO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> BPh <sub>4</sub>	32	1855, 1795 <sup>c</sup>	f
Co(NO) <sub>2</sub> (diphos)BPh <sub>4</sub>	58	1838, 1789 <sup>c</sup>	f
[Co(NO) <sub>2</sub> Cl] <sub>2</sub>	50	1866, 1792 <sup>d</sup>	g
Fe(NO) <sub>2</sub> Cl <sub>2</sub> HNet <sub>3</sub>	—	1773, 1697 <sup>d</sup>	h

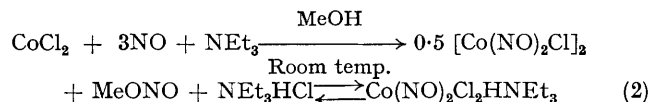
<sup>a</sup> All compounds reported here have been fully characterized by elemental analysis and/or comparison with authentic samples. <sup>b</sup> Based on yield from recrystallization or sublimation of crude products. <sup>c</sup> KBr disc. <sup>d</sup> Nujol mull. <sup>e</sup> W. Hieber and K. Kaiser, *Z. anorg. Chem.*, 1968, **362**, 169. <sup>f</sup> T. Bianco, M. Rossi, and L. Uva, *Inorg. Chim. Acta*, 1969, **3**, 443. <sup>g</sup> See ref. 2. <sup>h</sup> 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)<sub>2</sub>2L<sup>+</sup> 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)<sub>2</sub>2L<sup>+</sup> formed [equation (1)].



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

In the absence of potential ligands (2L), the reaction with CoCl<sub>2</sub> yields [Co(NO)<sub>2</sub>Cl]<sub>2</sub> or Co(NO)<sub>2</sub>Cl<sub>2</sub><sup>-</sup> [equation (2)].



FeCl<sub>2</sub> is likewise reduced by NO-amine-MeOH to yield Fe(NO)<sub>2</sub>Cl<sub>2</sub><sup>-</sup>; NiCl<sub>2</sub> 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 stoichiometric 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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<sup>1</sup> T. Jackson, M. Baker, J. Edwards, and D. Tutas, *Inorg. Chem.*, 1966, **5**, 2046; R. Feltham and R. Nyholm, *ibid.*, 1965, **4**, 1334; P. Gans, *J. Chem. Soc. (A)*, 1967, 943.

<sup>2</sup> A. Sacco, M. Rossi, and C. Nobile, *Ann. Chim. (Italy)*, 1967, **57**, 499.