Phosphino–Nitrosyl Complexes of Cobalt. A New Synthetic Route

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Summary. Cobalt–nitrosyl complexes of the type $Co(NO)(HPR_2)_3$ and $Co(NO)(PR_3)_3$ have been obtained by direct reaction of phosphines with $Co(NO_3)_2 \cdot 6H_2O$ in propan-2-ol.

THE complex $Co(NO)(PPh_3)_3$ is one of the few examples of well-characterized cobalt–nitrosyl complexes of the type $Co(NO)(L)_3$ (L = phosphine ligand).[1] It has been obtained by disproportionation on dissolving $[Co(NO)_2Cl]_2$ in molten PPh_3[2] or by reaction of dinitrosyl halides $[Co(NO)_2X]_2$ with excess of PPh_3 in the presence of reducing agents.[3]

We now find that the reaction between $Co(NO_3)_2 \cdot 6H_2O$ and phosphines in propan-2-ol offers new and wider possibilities for the preparation of nitrosyl complexes of the type $Co(NO)(L)_3$.

Secondary phosphines HPR_2 ($R_2 = Ph_2$, PhCy, Cy_2; Cy = cyclohexyl) react with $Co(NO_3)_2 \cdot 6H_2O$ (molar ratio 5:1) in propan-2-ol at room temperature under inert atmosphere, to give red solutions, from which red crystals of composition $Co(NO)(HPR_2)_3$ slowly precipitate. Reaction times are 2 h for $HPPh_2$, 4 h for HPPhCy and 3 days for $HPCy_2$. The compounds are diamagnetic and their i.r. spectra show an intense band in the 1640—1660 cm^{-1} region which may be assigned to a NO group bound to cobalt ($HPPh_2$: 1640 cm^{-1}; HPPhCy: 1655 cm^{-1}; $HPCy_2$: 1649 cm^{-1}). No bands attributable to NO_3^- groups are present. The ν_{NO} stretching frequency for the previously reported $Co(NO)(PPh_3)_3$,[3] is located at 1633 cm^{-1}.

Using the same experimental conditions, the secondary phosphines $HPEt_2$, HPMePh, and HPEtPh react immediately and exothermically with cobalt(II) nitrate to give dark-red solutions, from which no crystalline products can be isolated. However, the i.r. spectra in n-hexane of the red oils obtained after removal of the solvent, show a strong band in the 1655—1685 cm^{-1} region and suggest the presence of $Co(NO)(HPR_2)_3$ species in the solutions.

Also treatment of cobalt(II) nitrate in propan-2-ol with tertiary phosphines can yield $Co(NO)(PR_3)_3$ complexes, but refluxing conditions were necessary. Red crystalline compounds were isolated with the phosphines PMe_2Ph (ν_{NO} 1626 cm^{-1}) and $PMePh_2$ (ν_{NO} 1639 cm^{-1}, with a shoulder at 1649 cm^{-1}). ^1H n.m.r. spectra of $Co(NO)(PMe_2Ph)_3$ in CH_2Cl_2 exhibit a single resonance for methyl groups at τ 8·61, supporting a tetrahedral structure, which has also been suggested for $Co(NO)(PPh_3)_3$.[2] With PEt_3 and PEt_2Ph only red oils could be obtained, whose i.r. spectra in n-hexane solutions indicate the presence of $Co(NO)(PR_3)_3$ complexes (ν_{NO} at 1661 cm^{-1}).

Reaction times change from 4 h for PMe_2Ph to 2 days for $PMePh_2$. With larger tertiary phosphines, such as PPh_3 and PBu_3, the formation of nitrosyl complexes was not observed, probably owing to steric effects, even when these ligands were refluxed with $Co(NO_3)_2 \cdot 6H_2O$ in propan-2-ol for 4 days.

The stoicheiometry of the reaction has not yet been established, although phosphine oxides appear to be always present in the reaction mixtures.

We thank Prof. A. Turco for stimulating discussion and Mr. G. Gomiero for technical assistance.

(*Received*, 29*th April* 1974; *Com.* 486.)

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[1] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 1966, **7**, 272; N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.

[2] W. Hieber and K. Heinicke, *Z. Anorg. Chem.*, 1962, **316**, 305.

[3] T. Bianco, M. Rossi, and L. Uva, *Inorg. Chim. Acta*, 1969, **3**, 443.