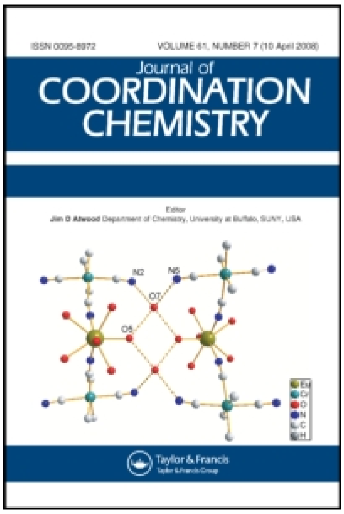

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Reactivity of Nickel(O) Nitrosyl Complexes with Mercury(II) Cyanide

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NOTE

REACTIVITY OF NICKEL(0) NITROSYL COMPLEXES WITH MERCURY(II) CYANIDE

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The ability[1] of zerovalent complexes of platinum and palladium to give heterobimetallic species with mercury(II) compounds has been widely described whereas zerovalent nickel complexes show a very low ability to give similar reactions.[2] We have reported the reactions of $Ni[P(OEt)_3]_4$ with mercury(II) halides or pseudohalides which readily proceed with formation of Ni(II) complexes and deposition of metallic mercury.[3] The nitrosyl complexes show interesting electronic features with respect to their interactions with Lewis acids such as HgX_2, and thus we now describe the formation of heterobimetallic complexes by reaction of $NiCl(NO)(L)_2$, L = PPh_3, $Ph_2PC_2H_4PPh_2/2$ (dppe/2), $P(CH_2CH_2CN)_3$, (t-cep) and $Hg(CN)_2$. Further investigations with related Ni(0) nitrosyls are currently been carried out to give a more complete interpretation of previous results.

Keywords: Heterobimetallic complexes, nitrosyls, nickel(0), mercury

RESULTS AND DISCUSSION

n the reactions of halonitrosyls with $Hg(CN)_2$ in THF or toluene different complexes are formed depending on the ligand phosphine and the solvent used Scheme 1).

Scheme I

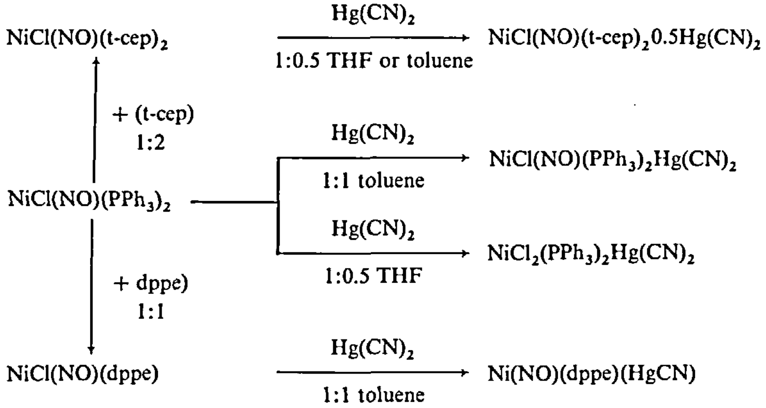

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TABLE I

Physical and analytical data for the new complexes.

	colour	reaction time (days)	analysis[a] (%) found (calc.)			IR(cm^{-1})[b]			μ_{eff} (B.M.)
			C	H	N	$\nu(CN)_{t\text{-}cep}$	$\nu(CN)_{HgCN}$	$\nu(NO)$[c]	
$NiCl(NO)(t\text{-}cep)_2$	blue violet		41.8 (42.3)	4.3 (4.7)	17.9 (18.6)	2245s		1765vs,br	
$NiCl(NO)(PPh_3)_2Hg(CN)_2$	pale blue	5	48.4 (50.6)	3.1 (3.3)	4.1 (4.6)		2153m	1755vs,br	
$NiCl_2(PPh_3)_2Hg(CN)_2$	greenish-white	8	49.2 (50.3)	2.9 (3.3)	2.9 (2.9)		2170m		3.11
$NiCl(NO)(t\text{-}cep)_2 0.5Hg(CN)_2$	blue violet	2	37.1 (35.8)	3.9 (3.8)	16.1 (17.6)	2242s	2140m	1783vs,br	
$Ni(NO)(dppe)(HgCN)$	gray violet	3	45.2 (45.4)	3.5 (3.3)	4.4 (3.9)		2158m	1760vs,br	

[a] Qualitative analysis of chlorine was carried out by X-ray fluorescence; [b] in KBr disks; [c] 1710 for $NiCl(NO)(PPh_3)_2$, ref. (7), 1734, 1713 for $NiCl(NO)(dppe)$, ref. (8).

Two reaction types are observed on the basis of the existence or not of the Ni(NO)-$(L)_2$ group in the complexes. The complexes $NiCl(NO)(PPh_3)_2.Hg(CN)_2$, NiCl(NO)$(t\text{-}cep)_2.0.5Hg(CN)_2$ and Ni(NO)(dppe).HgCN were isolated. IR spectra (Table I) show, as expected, v(CN) bands shifted to lower frequencies relative to that observed in uncoordinated $Hg(CN)_2$ (2195 cm^{-1}), as well as v(NO) bands shifted to higher frequencies in relation to the starting halonitrosyls. The new complexes show diffuse reflectance spectra with broad charge transfer absorptions in the 750–500 nm region involving the π*NO orbitals,[4] similar to those of the starting compounds. Thus, it is possible to consider a formally unchanged oxidation state for the bimetallilc compounds (Ni(0) complexes). Similar heterobimetallic interactions, as proposed in PPh_3 and t-cep complexes, have been found and interpreted as adduct formation, with other low oxidation state complexes such as ruthenium nitrosyls[5] and molybdenum carbonyls.[6]

The reaction of $NiCl(NO)(PPh_3)_2$ with $Hg(CN)_2$ in THF leads to a greenish-white solid. IR spectral data and magnetic behaviour are consistent with the formation of a six-coordinate Ni(II) compound which probably contains CN ligands as bridges. The interaction of NiCl(NO)(dppe) with $Hg(CN)_2$ can be considered in terms of halogen exchange to give a bimetallic complex with, probably, a Ni–HgCN bond.

EXPERIMENTAL

All procedures were carried out using standard Schlenck techniques under nitrogen atmosphere and freshly distilled, dried and degassed solvents. $NiCl(NO)(PPh_3)_2$ was prepared as previously described.[7] By substitution reactions, the NiCl(NO)(dppe) complex previously reported[8] and the new complex $NiCl(NO)(t\text{-}cep)_2$ were obtained.

IR spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. The magnetic susceptibilities were measured by the Faraday method, and electronic spectra were recorded using a Kontron Uvikon 820 spectrophotometer equipped with a reflectance attachment. Analysis (C,H,N) were carried out by Elemental Micro-Analysis Laboratories Ltd. (Devon), England.

Preparation of the heterometallic complexes

All the complexes were prepared by the same method here described.

To a solution of the halonitrosyl complex in the solvent indicated in the Scheme, mercury(II) cyanide in a 1:1 or 1:0.5 ratio was added and the mixture was stirred for several days (Table I) to give the products as solids which were filtered, washed with the used solvent and diethyl ether and dried under vacuum. The solids are unstable towards air and moisture.

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