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# Cationic Nitrosyl Complexes of Nickel with Hybrid Bidentate Ligands containing Phosphorus and Nitrogen or Sulfur Donor Atoms

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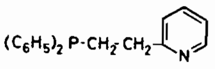
A number of nitrosyl complexes of nickel of the type $[Ni(NO)XL_2]$ and $[Ni(NO)L_3]^+$ are known in which L is a phosphorus ligand such as primary [1], secondary [1], tertiary [1–8], phosphines or phosphites [9, 10]. The compounds so far studied by X-ray analysis are pseudotetrahedral and exhibit 'linear' Ni–N–O groups with angles in the range 161–180° [4–7, 9].

In connection with an investigation concerning the syntheses and properties of phosphino–nitrosyl complexes of nickel [1] we have now prepared {NINO} [10] derivatives with hybrid bidentate ligands containing one phosphorus and one nitrogen or sulfur donor atom. Wtih the ligands used, 1-(2′-pyridyl)-2-(diphenylphosphino)ethane (P-Py) and 1-(thioethyl)-2-(diphenylphosphino)ethane (P-SEt), compounds of composition $[Ni(NO)(P–L)_2]BPh_4$ have been obtained:

$(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_3$

P-SEt



P-Py

An interesting feature of these complexes is that they are 'fluxional' in solution and we have conducted, and now report, a detailed study of their solution structure and dynamics by variable-temperature IR and NMR spectroscopies.

## Experimental

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Visible spectra were determined on an Optica CF4NI spectrophotometer. Conductance data were obtained using a LKB model 3216B conductance bridge. N.m.r. spectra were recorded on a Bruker WP-60 spectrometer operating at 14.09 kG in the FT mode ($^1H$ and $^{31}P$) and on a Bruker 90 MHz spectrometer ($^1H$). All materials were of reagent grade quality. The solvents were purified by standard methods.

The published procedures were used to prepare the ligands 1-(thioethyl)-2-(diphenylphosphino)ethane (P-SEt) [11] and 1-(2′-pyridyl)-2-(diphenylphosphino)ethane (P-Py) [12].

### *Preparation of the Complexes*

*$[Ni(NO)(P\text{-}L)_2]BPh_4$ (P-L = P-SEt, P-Py)*

A suspension of $[Ni(P\text{-}SEt)_2](ClO_4)_2$ [11] or $[Ni(P\text{-}Py)_2](ClO_4)_2$ [12] (2 mmol) in 25 ml of methanol was treated with $NaNO_2$ (0.14 g, 2 mmol). The mixture was refluxed under a carbon monoxide atmosphere for 30 min, and the resulting red-violet solution was cooled at room temperature. Sodium tetraphenylborate (1.37 g, 4 mmol) in 15 ml of methanol was added and the resulting violet precipitate was filtered off, washed with methanol, and then recrystallized from dichloromethane–methanol.

(a) $[Ni(NO)(P\text{-}SEt)_2]BPh_4$, m.p. 68–70 °C (decomp.) (Found: C, 70.71; H, 6.08; N, 1.48. $C_{56}H_{58}NOS_2P_2Ni$ requires C, 70.25; H, 6.11; N, 1.46%); conductivity 62 S cm$^2$ mol$^{-1}$ (*ca.* $10^{-3}$ *M* solution in nitromethane).

(b) $[Ni(NO)(P\text{-}Py)_2]BPh_4$, m.p. 163–164 °C (decomp.) (Found: C, 74.58; H, 5.65; N, 4.14. $C_{62}H_{56}N_3OP_2Ni$ requires C, 74.95; H, 5.68; N, 4.23%); conductivity 68 S cm$^2$ mol$^{-1}$ (*ca.* $10^{-3}$ *M* solution in nitromethane).

## Results and Discussion

The $[Ni(NO)(P\text{-}L)_2]BPh_4$ (P-L = P-Py, P-SEt) complexes were prepared according to the method of Booth and Chatt [13]. The compounds were characterized by elemental analysis and were found to be diamagnetic and 1:1 electrolytes in nitromethane. The ir spectra of both compounds exhibit a strong NO stretching vibration in the 1770–1820 cm$^{-1}$ region. The visible spectra are similar to each other and show two bands around 370 and 500 nm with a shoulder on the low-energy side at about 550 nm. Infrared and electronic spectral data (see Table I) are strictly related to those reported for the $[Ni(NO)L_3]^+$ complexes (L = phosphorous ligand) which have pseudotetrahedral geometry and contain linear Ni–N–O groups [1–10]. It seems likely that also the $[Ni(NO)(P\text{-}L)_2]^+$ cations could be formulated as nickel(0) derivatives and expected to be four coordinate and tetrahedral.

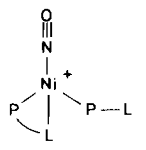
Tetracoordination is supported in the case of $[Ni(NO)(P\text{-}Py)_2]^+$ by ir spectrum which shows in the 1550–1650 cm$^{-1}$ region (pyridine ring deformation mode) absorptions attributable [14] both to coordinated (1604, 1577 cm$^{-1}$) and uncoordinated (1593, 1582, 1567 cm$^{-1}$) pyridyl groups. The data are

TABLE I. Spectroscopic Data of the Nickel Complexes.

| Complex | IR $\nu_{NO}{}^a$, cm$^{-1}$ | Electronic spectra $\lambda_{max}{}^a$, nm ($\epsilon_{max}$) | NMR$^c$ $^{31}P\{^1H\}$, ppm | | $^1H$, $\tau$ | |
|---|---|---|---|---|---|---|
| | | | 300 K$^b$ | 213 K$^b$ | 300 K$^b$ | 213 K$^b$ |
| [Ni(NO)(P-Py)$_2$]BPh$_4$ | 1778 | 365 (540)<br>500 (940)<br>550 (sh) | 32.2 | 32.1$^e$<br>34.6$^e$<br>($J_{PP}$ = 17.3 Hz) | 0.90$^f$ (bd)<br>2.50–3.35$^g$ (m)<br>7.90$^h$ (bs) | 0.29$^f$ (bd)<br>1.48$^f$ (bd)<br>2.50–3.35$^g$ (m)<br>7.47$^h$ (bs) |
| | | | 300 K$^a$ | 190 K$^a$ | 300 K$^d$ | |
| [Ni(NO)(P-SEt)$_2$]BPh$_4$ | 1802 | 370 (645)<br>510 (1180)<br>570 (sh) | 39.1 | 32.9 (d)<br>49.7 (d)<br>($J_{PP}$ = 10 Hz) | 2.50–3.20$^g$ (m)<br>7.22$^i$ (q) (J = 7.3 Hz)<br>7.79$^h$ (bs)<br>8.69$^l$ (t) (J = 7.3 Hz) | |

[a] In $CH_2Cl_2$. [b] In $CDCl_3$. [c] d = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [d] In $CD_2Cl_2$. [e] AB spin system. [f] α-ring proton of pyridyl group. [g] β- and γ-ring protons of pyridyl group or $C_6H_5$ protons. [h] $-CH_2-CH_2-$. [i] $-CH_3$. [l] $S-CH_2-$.

consistent with the structure I in which one P-Py molecule acts as monodentate ligand.



(I)

The $[Ni(NO)(P-L)_2]^+$ cations are stereochemically non rigid at ambient temperature on the nmr time scale but became stereochemically rigid at low temperature. The room temperature $^{31}P\{^1H\}$ nmr spectra of both complexes show a single sharp resonance. By lowering the temperature the singlet broadens and a resolved spectrum is obtained at 213 K for $[Ni(NO)(P-Py)_2]^+$ in $CDCl_3$ and at 190 K for $[Ni(NO)(P-SEt)_2]^+$ in $CH_2Cl_2$. The low temperature limiting $^{31}P\{^1H\}$ nmr spectrum of $[Ni(NO)(P-SEt)_2]$-$BPh_4$ is shown in Fig. 1a. The observed AX pattern is that expected for a structure in which only a P-SEt molecule behaves as chelate ligand. The phosphorus resonance at lowest field can be assigned to the phosphorus of a chelate P-SEt molecule, in agreement with the observation that phosphorus-containing five-membered ring systems show anomalous large down-field $^{31}P$ coordination chemical shift [15].

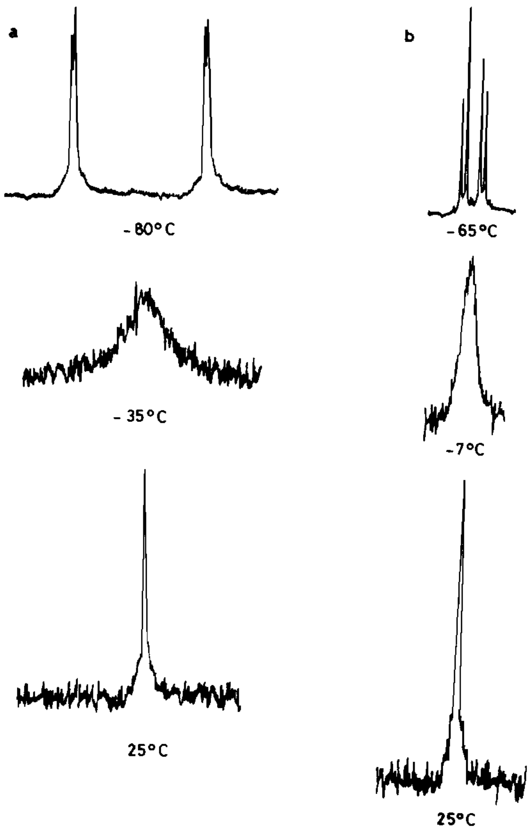


Fig. 1. Variable-temperature $^{31}P\{^1H\}$ nmr spectrum of (a) $[Ni(NO)(P-SEt)_2]BPh_4$ in $CH_2Cl_2$, and (b) $[Ni(NO)(P-Py)_2]BPh_4$ in $CDCl_3$.

The low temperature limiting spectrum of $[Ni(NO)(P-Py)_2]BPh_4$ (Fig. 1b) shows a pattern characteristic of an AB spin system. The $^{31}P$ coordination shifts for chelate (six-membered ring) and unchelated P-Py ligand are similar and cannot be used for structural assignments as in the case of P-SEt. However the coordination of pyridyl group can be verified from the chemical shift of the α-proton of the pyridine ring. In the room temperature $^1H$ nmr spectrum of the $[Ni(NO)(P-Py)]^+$ cation, the α-proton resonance appears as a broad doublet at τ 0.90. Lowering the sample temperature produces a complex sequence of changes and at –65 °C the $^1$H nmr spectrum shows two α-proton resonances as doublets at τ 0.29 and 1.48, which can be attributed to the presence of chelated and unchelated ligand. The position of resonance at τ 1.48 corresponds with that of the free ligand (τ = 1.42) while the signal at τ 0.29 can be attributed to the α-proton of a chelated P-Py molecule.

The downfield shift is due to coordination of pyridyl groups which causes the α-proton to be deshielded. The low temperature $^1$H and $^{31}$P nmr data for both $[Ni(NO(P\text{-}L)]^+$ cations are consistent with a tetracoordinate structure in which only a P-L molecule acts as chelating ligand. Since nmr data did not distinguish unambiguously between a pseudotetrahedral ($Ni^0$–$(NO^+)$) or a square planar ($Ni^{II}$–$(NO^-)$) structure we have examined the ir spectrum of the $[Ni(NO)(P\text{-}L)_2]BPh_4$ complexes in $CH_2Cl_2$ solution over the temperature range +20° to –80 °C. No substantial change was observed and no new bands in the NO stretching region appeared. Thus it is concluded that the nitrosyl compounds maintain also at low temperature the pseudotetrahedral structure I.

The observed variable temperature nmr behaviour is consistent with an intramolecular rearrangement which leads to interchange of the roles of the mono- and bidentate P-L ligands. A dissociative mechanism involving opening of chelate ring to give a three-coordinate intermediate appears to be reasonable in view of the saturated nature of $[Ni(NO)(P\text{-}L)_2]^+$ cations. However, if an intramolecular redox process $Ni^0(NO^+) \rightleftarrows Ni^{II}(NO^-)$ is energetically accessible exchange might well occur *via* an associative pathway, with formation of a five-coordinate intermediate.

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