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Studies of Chelation. V.[a] Ditertiary Phosphine Complexes of Nickel(II) Nitrate

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Whereas $(R_2PCH_2)_2$ *(R = Me, Ph) reacts with* $Ni(NO_3)_2\cdot 6H_2O$ *in ethanol solution to form diamagnetic, square planar* $[NiL_2](NO_3)_2$*, the sterically more hindered ligand (R = Cy) forms a diamagnetic square pyramidal complex* $[NiL(NO_3)_2(H_2O)]$ *containing unidentate coordinated nitrate in the solid state and in solution in solvents of low dielectric constant. An isomeric square planar complex* $[NiL(NO_3)(H_2O)]NO_3$ *is present in more polar solvents.*

Introduction

Tertiary phosphine complexes of nickel(II) halides have been the focus of much interest aroused by the subtle variations in structure which are observed. More recently these studies have been extended to complexes formed by polytertiary phosphines. It has been shown that in ditertiary phosphines, both the steric effects within, and the length of the chelate chain have an important influence on the type of complex formed from the reaction with nickel(II) halides and pseudohalides.[1]

The reaction between $Co(NO_3)_2\cdot 6H_2O$ and various secondary and tertiary phosphines, L, in alcohol solvent produces nitrosyl complexes of the type $[Co(NO)L_3]$ in a process which is apparently sensitive to steric effects at phosphorus.[2] The profound influence of steric effects in phosphorus donor ligands upon the formation and reactions of nickel complexes is now well documented.[3]

We have made a systematic investigation of the reaction between certain ditertiary phosphines $R_2PCH_2CH_2PR_2$ (R = Me, dmpe; R = Ph, dppe; R = Cy, dcpe) and $Ni(NO_3)_2\cdot 6H_2O$ in ethanol solution. This was done in order to determine whether nitrosyl complexes of the type $[Ni(NO)(R_2PCH_2CH_2PR_2)]_2$ could be prepared and to examine the potential denticity of the weakly coordinating nitrate ion. At the same time it was expected that the increasing steric constraint in the ditertiary phosphine ligand[4] might be apparent in the type of product obtained. An orange complex $[Ni(dppe)_2](NO_3)_2$ was prepared in very low yield and characterised by conductivity measurements some years ago.[5] The complexes $[Ni(o\text{-}C_6H_4(PEt_2)_2)_2](NO_3)_2$[5] and $[Ni(Ph_2PCH_2PPh_2)_2](NO_3)_2$[6] have also been described.

Results and Discussion

The reaction between $Ni(NO_3)_2\cdot 6H_2O$ (1 mol) and the ditertiary phosphine ligand $R_2PCH_2CH_2PR_2$ (2 mol) proceeds rapidly on stirring the reagents in ethanol solution at ambient temperature (290 K). For both dmpe and dppe as ligands, the product was of the type $[NiL_2](NO_3)_2$, but in the case of dcpe the product is $[Ni(dcpe)(NO_3)_2(H_2O)]$.

The complexes $[Ni(dmpe)_2](NO_3)_2$ (orange yellow) and $[Ni(dppe)_2](NO_3)_2$ (bright yellow) were obtained in high yield (70–80%). The identity of both compounds as square planar nickel(II) complexes was established by their diamagnetism and conductivity (1:2 electrolytes in nitromethane). Infrared and Raman spectra of the solids (Table I) showed the presence of ionic nitrate only. Neither of the complexes gave a mass spectrum. The electronic spectra (Table II) are also consistent with a square planar coordination at nickel.

The diamagnetic solid complex of molecular formula $[Ni(dcpe)(NO_3)_2(H_2O)]$ is remarkable for its reddish rust-brown colour. Dichloromethane solutions ($10^{-3}M$) of the complex in CH_2Cl_2 are non-conducting, but in nitromethane solution ($10^{-3}M$) the conductivity indicates the presence of a 1:1 electrolyte.[7] Raman and infrared spectra of the solid complex show the presence of coordinated nitrate only. The separation of the two highest frequency nitrate vibrations in the infrared, together with the sequence of relative intensities of the three highest frequency Raman shifts attributable to nitrate fundamentals,[8] are both consistent with the presence of unidentate coordinated nitrate. It was not possible to observe all the nitrate fundamentals of the complex in either nitromethane or acetonitrile solution.

The electronic spectrum of the complex $[Ni(dcpe)(NO_3)_2(H_2O)]$ both in the solid state and in solvents

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[a] Part IV: ref. 11.

TABLE I. Vibrational Spectra in the Region of Fundamental Absorptions of the Nitrate Ion (cm^{-1}).

$[Ni(dppe)_2](NO_3)_2$	1370s	1045m	815m	720m
$[Ni(dmpe)_2](NO_3)_2$	1380s	1040s	830m	724m
$[Ni(dcpe)(NO_3)_2(H_2O)]$	1490s, 1285s	1050m	805m	750m, 735m
$[Ni(dcpe)(NO_3)(H_2O)]BPh_4$	1480s, 1270s	1030s	810m	745m[a]

[a] Band obscured by BPh_4 vibration.

TABLE II. Electronic Spectra of Nickel(II) Complexes.

Complex	Solvent	λ_{max}/kK (ε_{max})		
$[Ni(dppe)_2](NO_3)_2$	EtOH	24.1 (50)	30.3 (186)	36.6 (7400)
$[Ni(dmpe)_2](NO_3)_2$	EtOH	27.0 (580)	32.0 (3200)	41.7 (43500)
$[Ni(dcpe)(NO_3)_2(H_2O)]$	EtOH	22.4 (240)	33.9 (2000)	38.3 (9100)
	$CHCl_3$	22.1 (586)	34.5 (8000)	39.2 (32000)
	–	22.5		
	MeCN	24.2 (960)	34.4 (5000)	
$[Ni(dcpe)(NO_3)(H_2O)]BPh_4$	CH_2Cl_2	24.1 (800)		

of low ($CHCl_3$) to medium (MeOH) dielectric constant, shows a ligand field band at *ca.* 22.2 kK which is consistent with a square pyramidal geometry at five coordinate nickel(II).[9] In more polar solvents (MeCN, Me NO_2) the ligand field band shifts to higher energy (*ca.* 24 kK), suggesting that in these solvents the nickel is square planar.[1] Recovery of the solid from acetonitrile solution and redissolving it in dichloromethane confirms the reversibility of the process indicated by the equilibrium,

$$[Ni(dcpe)(NO_3)_2(H_2O)] \rightleftharpoons [Ni(dcpe)(NO_3)(H_2O)]NO_3$$

There is no evidence for the incorporation of a donor polar solvent molecule in the cation.

Further evidence to support the equilibrium is provided by the observation that, whereas the addition of $NaBPh_4$ to $[Ni(dcpe)(NO_3)_2(H_2O)]$ in CH_2Cl_2 solution causes only slow precipitation of an uncharacterised material over a period of several days, in MeCN solution a precipitate of $NaNO_3$ forms immediately and $[Ni(dcpe)(NO_3)(H_2O)]BPh_4$ is subsequently isolated.

A mass spectrum of the complex $[Ni(dcpe)(NO_3)_2(H_2O)]$ showed the presence of an ion m/e 560 (68%) assigned as $[Ni(dcpe)(NO_3)(H_2O)]^+$, and a much weaker ion m/e 602 which may be assigned to $[Ni(dcpe)(NO_3)_2]^+$. Attempts to achieve dehydration of the solid complex on a preparative scale by heating at 400–420 K/10^{-3} mmHg for 8–20 hr were unsuccessful as judged by infrared spectra. At higher temperature up to the normal decomposition point, decomposition of the complex in vacuum gave black, uncharacterised materials.

It would be reasonable that the greater steric requirements of dcpe (for which the ligand cone angle[4] is 147°) is responsible for the contrast in behaviour which is observed. Further evidence is provided by the fact that, whereas nickelocene reacts with dppe to form $[Ni(dppe)_2]$ which is pale yellow,[10] with dcpe the product $[Ni(dcpe)_2]$ is deep violet in colour. Such an observation is consistent with those made on other NiL_4 (L = phosphine, phosphite) compounds[4] and indicates that in $[Ni(dcpe)_2]$ the nickel atom is effectively three coordinate. Solutions of $[Ni(dcpe)_2]$ in donor solvents such as acetone are much more stable to oxidation and to reaction with CO than are solutions in toluene. When CO is passed through $[Ni(dcpe)_2]$ in toluene $[Ni(dcpe)(CO)_2]$ (ν_{max} 2018s, 1994s cm^{-1}) is formed.

The non-bonding steric interference between vicinal Cy_2P groups is clearly important in these and other[3] nickel compounds and also in complexes of other transition metals,[11] and exerts a decisive influence upon substitution reactions by ligands containing this group. It is nonetheless remarkable that although the four coordinate square planar ion, $[Ni(dcpe)_2]^{2+}$, cannot apparently be formed, the arguably more constrained five coordinate complex $[Ni(dcpe)NO_3)_2(H_2O)]$, which lacks the unfavourable non-bonding interaction, is formed under mild conditions.

Experimental

All experiments were carried out in an atmosphere of purified nitrogen. Solvents and liquid reagents were purged with nitrogen before use. The ligands dmpe, dppe and dcpe were prepared by standard methods.[11]

Nickel(II) nitrate was reagent grade. Conductivity in solution was determined with a Phillips PR 9500/01 bridge in nitromethane solution. Infrared spectra were measured on a Perkin-Elmer 521 grating instrument and Raman spectra on a Cary 82 with red and green lasers. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer in solution and a Beckman DK-2A (solid reflectance, nujol mull and MgO disc). Magnetic measurements were made by the n.m.r. method. Mass spectra were recorded on an AEI MS12 instrument.

Preparation of $[Ni(dcpe)(NO_3)_2(H_2O)]$

The ligand dcpe (1.5 g, 3.6 mmol) was added to a stirred solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.52 g, 1.8 mmol) in ethanol (20 cm^3). After stirring for two hours the precipitated product was isolated by filtration and washed with cold ethanol. The rust-brown solid (65% yield) was dried under high vacuum. Dec. pt. 442° K. Found: C, 50.2; H, 8.0; N, 4.5; P, 10.0; Ni, 9.3; O (by difference), 18.0. Calc'd for $C_{26}H_{50}NiN_2O_7P_2$: C, 50.5; H, 8.1; N, 3.6; P, 9.8; Ni, 9.6; O, 18.1%. Λ ($10^{-3}M$ in $MeNO_2$) 60 S cm^2 mol^{-1}. ν (O–H) 3400 s, br cm^{-1}.

Preparation of $[Ni(dcpe)(NO_3)(H_2O)]BPh_4$

Addition of $NaBPh_4$ (0.20 g, 0.6 mmol) to $[Ni(dcpe)(NO_3)_2(H_2O)]$ (0.37 gm, 0.6 mmol) in acetonitrile (10 cm^3) resulted in immediate precipitation of a white solid which was isolated and shown to be $NaNO_3$. The resulting clear yellow solution was isolated by decantation. Evaporation of the solvent under reduced pressure left an oily solid which was dissolved in CH_2Cl_2. Addition of ethanol to the CH_2Cl_2 solution precipitated a yellow solid. This solid was purified by repeated precipitation (CH_2Cl_2/EtOH) and then dried under vacuum (50% yield). Dec. pt. 390° K. Found: C, 71.2; H, 8.4; N, 1.0. Calc'd for $C_{50}H_{70}BNiNO_4P_2$: C, 69.6; H, 7.9; N, 1.6%. ν (O–H) 3350 m, br cm^{-1}.

Preparation of $[Ni(dcpe)_2]$

The ligand dcpe (0.5 g, 1.19 mmol) was added to a stirred solution of nickelocene (0.11 g, 0.59 mmol) in toluene (30 cm^3). The mixture was heated at reflux (24 hr), filtered and the complex isolated as a purple solid by concentration. Found: C, 65.2; H, 10.2; P, 10.7; Ni, 6.4. Calc'd for $C_{52}H_{96}NiP_4$: C, 69.3; H, 10.6; P, 10.7; N, 6.5%. The purple solid is *very* sensitive to oxidation. ν_{max} (Nujol/HCB) 2940 s, 1540 m, 1260 m, 1160 s, 890 m, 850 m, 810 s cm^{-1}.

The other complexes were obtained by adding $(R_2PCH_2)_2$ (R = Me, Ph) (2 mol proportion) to $Ni(NO_3)_2 \cdot 6H_2O$ (1 mol proportion) in EtOH (20 cm^3). $[Ni(dppe)_2](NO_3)_2$ (70% yield), dec. pt. 479° K. Found: C, 63.1; H, 5.0; N, 2.5; P, 12.9; Ni, 6.2; O (by difference), 10.3. Calc'd for $C_{52}H_{48}NiN_2O_6P_4$: C, 63.7; H, 4.9; N, 2.9; P, 13.7; Ni, 6.0; O, 9.8%. Λ ($10^{-3}M$ in $MeNO_2$) 150 S cm^2 mol^{-1}. $[Ni(dmpe)_2](NO_3)_2$ (75% yield), dec. pt. 563° K. Found: C, 30.3; H, 6.6; N, 5.6; P, 24.8; Ni, 12.1; O (by difference), 20.6. Calc'd for $C_{12}H_{32}NiN_2O_6P_4$: C, 29.8; H, 6.6; N, 5.8; P, 25.7; Ni, 12.2; O, 19.9%. Λ ($10^{-3}M$ in $MeNO_2$) 124 S cm^2 mol^{-1}.

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