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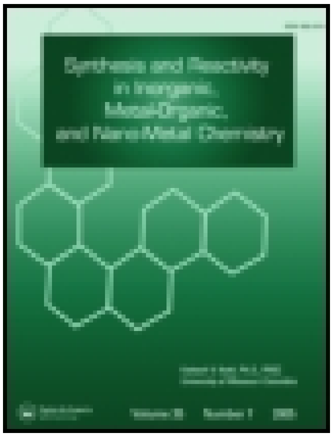

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Synthesis of Some Nickel(II) Diphosphine Complexes Having Coordinated Carboxylates

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Synthesis of Some Nickel(II) Diphosphine Complexes Having Coordinated Carboxylates

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Treatment of aminobis(methylphosphine) complexes of nickel (II) with carboxylic acids in the presence of silver(I) salts in dichloromethane gives the corresponding nickel(II) complexes of the type [NiA(P-P] where A = CO_3^- (carbonate), (2), 2-$^-OC_6H_4CO_2^-$ (salicylate, Sal), (3), $^-O_2CCH_2CH_2CH(NH_2)CO_2^-$ (glutamate, Glu), (4), $^-O_2CCH_2CH_2CO_2^-$ (succinicate, Suc), (5); P-P = $(Cy_2PCH_2)_2NMe$ (dcpam), $(Ph_2PCH_2)_2NMe$ (dppam). The complexes have been characterized by spectroscopic techniques such as ^{31}P-{^{1}H} NMR, FT-IR, UV-Vis, and mass spectrometry.

Keywords Phosphine, Nickel (II), Carboxylic Acids

INTRODUCTION

In view of the importance of phosphine complexes in medicine and in industry, we were interested in the synthesis of novel aminobis(methylphosphine) complexes of platinum group metals.[1−4] The phoshine metal carbonate and carboxylate complexes are useful starting compounds for the synthesis of M(0) and M(II) complexes.[5,6] Although there have been many reported studies on phosphine platinum or phospine palladium complexes, a relatively limited number of nickel-phosphine complexes and their chemistry have been reported that might be potentially useful in biomedicine and industry.[7] In addition to our previous work, this article presents the synthesis of nickel-phosphine complexes containing carbonate or carboxylate groups at one site. The preparation of the carbonate and carboxylate complexes provides the opportunity to develop further the chemistry of these systems.

RESULTS AND DISCUSSION

In order to investigate the reactivity of dichloro derivatives of nickel(II) aminomethylphosphine complexes, the reactions of nickel-phosphines with carbonate and carboxylic acids were carried out. [$NiCl_2$(dcpam)] (**1a**) or [$NiCl_2$(dppam)] (**1b**) were refluxed with Ag_2CO_3 in dichloromethane to give the carbonate compound only in the case of (1a), as shown in Scheme 1. The insoluble silver salt was filtered off and diethyl ether was added to give a brownish-red, powdery sample of [$Ni(CO_3)$(dcpam)] (**2**). The diphenyl derivative (**1b**) gave an uncharacterized white powder. Even with longer reaction times than cyclohexyl derivative (**1a**) the desired product was not obtained from (**1b**).

The carboxylate derivatives of the nickel-phosphines (**3**), (**4**), and (**5**) were synthesized by treating the dichloride derivatives of the Ni(II) phosphine complexes with the respective carboxylic acids in the presence of silver(I) oxide (Scheme 2). The desired products were obtained from the reaction of **1a** in good yield and characterized using spectroscopic techniques. Table 1 presents the ^{31}P-{^{1}H} NMR data, selected IR data, and melting points of these complexes (**2**)–(**5**). The reactions carried out with **1b** resulted in unreacted starting compound.

The ^{31}P-{^{1}H} NMR spectra of the complexes obtained showed more shielded signals as compared to the dichloride derivative (**1a**). Table 1 also shows the coordination shifts of the complexes (**2**)–(**5**) along with the chemical shift of the free ligand. The coordination shift values of the complexes (Δ), which is defined as $\Delta = \delta$ (complex-δ) (free ligand), vary depending on the metal and the ligand itself. The values of Δ have been correlated for many metal phosphine complexes.[8−11] Thus, depending on type of the phosphine ligand such as mono dentate or chelating ligand giving various ring size, the chemical shifts of the compound could be estimated for a certain metal complex.[12,13] In their solution ^{31}P-{^{1}H} NMR spectra, salicylate complex (**3**) exhibited the highest chemical shift with a broad peak at 19.72 ppm. In fact this singlet peak can be assumed as a doublet of doublets having two different phosphorus atoms with a distinctly different chemical environment.[4,8−11]

The prepared complexes (2)–(5) were further characterized by their IR spectra, which showed characteristic C=O symmetric streching bands in the range of 1640–1540 cm^{-1}, whereas the asymmetric ones assigned in the range of 1410–1380 cm^{-1} (Table 1). The frequence difference between symmetric and asymmetric vibration of carboxylate group is given as $\Delta\nu$, which indicates bonding to metal centre.

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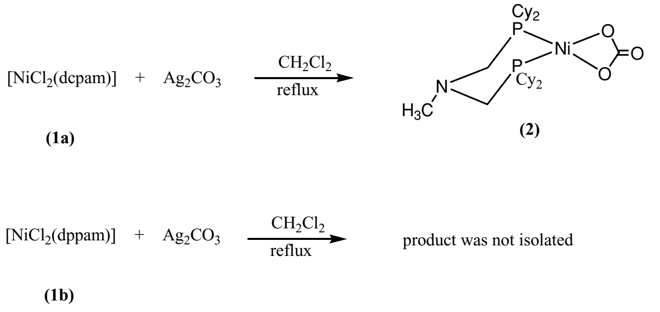
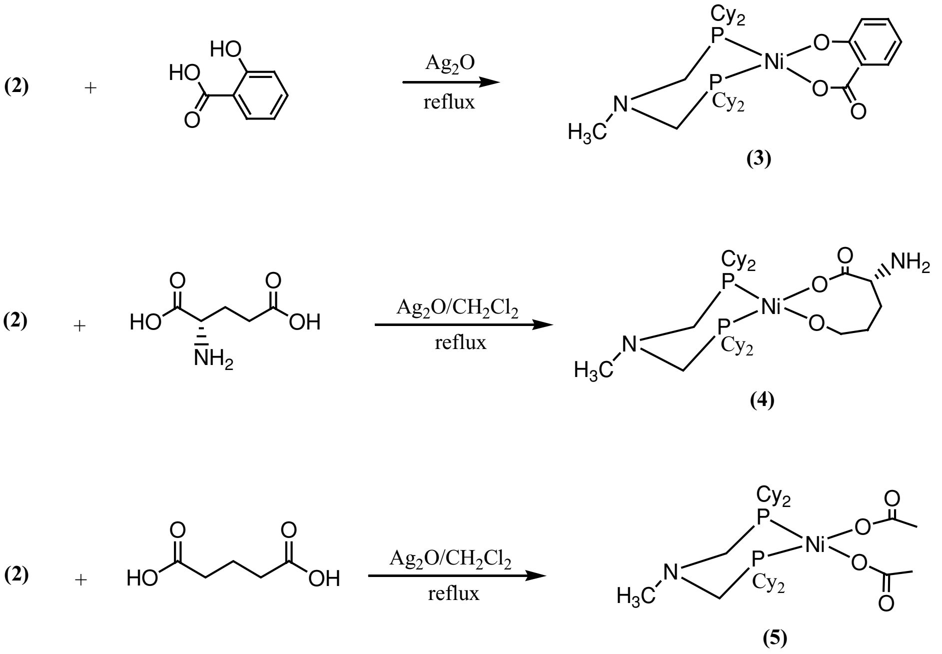


Scheme 1.

The relevant IR bands of the carboxylate complexes (**3**), (**4**), and (**5**) were compared with that of silver(I) acetate, Ag($OCOCH_3$), for which the asymmetric C=O vibration occurs at 1574 cm^{-1}, whereas the complexes (**3**), (**4**), and (**5**) exhibit this band at 1640, 1590, and 1585 cm^{-1}, respectively. The separation values of the asymmetric and the symmetric bands, $\Delta\nu$, are observed in the range of 185–230 cm^{-1}, which is in agreement with the values reported in the literature.[14,15] The separation value indicates the vibration mode of the coordinated carboxylate group and defined as $\Delta\nu = \nu_{asym} - \nu_{sym}$. The salyclate complex (**3**) presents an aromatic-H vibration at 3090 cm^{-1}. The mass spectra of the complexes showed a characteristic peak of the $Cy_2PCH_2^+$ ion at 211 due to the dcpam ligand and also a characteristic [M(dcpam)] peak for $Ni(dcpam)^{+2}$ at 510. Obtaining melting points distinct from the starting cyclohexyl substituted phosphine-nickel complex was also indicative of novel carboxylate derivative complexes.

The visible electronic spectra of the complexes in dichlomethane show only one absorption band in the range of 438–470 nm. On comparison with the starting compound, which



Scheme 2.

TABLE 1

$^{31}P\text{-}\{^1H\}$ NMR (in ppm), IR (in cm^{-1}), UV-Vis (in nm) spectra and melting points of the complexes (**2**)–(**5**)

	$^{31}P\text{-}\{^1H\}$ NMR		IR (C=O, cm^{-1})			UV-Vis	M.p.
Compound	δ (ppm)	Δ^a	asym	sym	$\Delta\nu^b$	λ_{max}	(°C)
dcpam	−16.15						60
[$NiCl_2$(dcpam)]	16.8	32.95				473	251
[Ni(CO_3)(dcpam)] (**2**)	17.8	33.65	1540	1355	185	470	213
[Ni(Sal)(dcpam)] (**3**)	19.7	35.85	1640	1410	230	438	225
[Ni(Glu)(dcpam)] (**4**)	16.4	32.55	1590	1380	210	468	250
[Ni(Suc)(dcpam)] (**5**)	9.08	25.23	1585	1380	205	458	212
Ag(OAc)			1574	1338	236		

has an absorption maximum, λ_{max}, at 473 nm. A distinct blue shift has been observed for each complex due to coordination of oxygen. These bands are consistent with those reported for nickel-diphosphine complexes and they correspond to square-planar geometry.[11] The broad bands observed almost at the same wavelength in the ultraviolet spectra of both complexes and the starting compound are assigned to the electronic transitions of n-π^* and to the π-π^*.

Magnetic susceptibility measurements of the complexes showed no paramagnetism, another indication of the square-planar geometry of the complexes.

Attempts to obtain and characterize phenyl-substituted phosphine-nickel complexes having chelated carboxylates at one site were unsuccessful. The spectroscopic investigations of the products showed starting dichloride derivative **1b**.

EXPERIMENTAL

Materials and Methods

The melting points of the prepared complexes were recorded on a Gallenkamp melting point apparatus. The mass spectra of the compounds were obtained by the FAB technique on a Kratos Concept Double Focusing Sector Mass Spectrometer. The ^{31}P NMR spectra were recorded in dichloromethane on a JEOL JMM-FX60 operating at 24.15 MHz with H_3PO_4 in D_2O as external reference The IR spectra were recorded on a Perkin-Elmer 580 FTIR spectrophotometer as KBr discs. Magnetic susceptibility measurements were carried out on a Sherwood Scientific Magnetic Susceptibility Balance at room temperature. The solvents dichloromethane and diethyl ether were dried prior to use by using sodiumwire/benzophenone.

Preparations were carried out under a dry, oxygen-free nitrogen atmosphere using standart Schlenk techniques. Ag_2O and Ag_2CO_3 were purchased from Aldrich Chemicals Inc. and used without further purification. [$NiCl_2$(dcpam)] and [$NiCl_2$(dppam)] were prepared by treating $NiCl_2{\cdot}6H_2O$ with the phosphines $(Cy_2PCH_2)_2NMe$, dcpam and $(Ph_2PCH_2)_2NMe$, dppam, respectively, which were obtained by treating phosphonium salts of the type $[R_2P(CH_2OH)_2]Cl$ (R=Cy, Ph) with methylamine in the presence of triethylamine as described in the literature.[5]

Synthesis of Compounds

[Ni(CO$_3$){(Cy$_2$PCH$_2$)$_2$NMe}] (2). Silver carbonate (0.066 g, 0.241 mmol) was added to a stirred solution of [$NiCl_2$(dcpam)] **(1a)** (0.08 g, 0.42 mmol) in dichloromethane (20 mL). The mixture was refluxed for 8 h. The solution was filtered through Celite. A red solute was obtained on addition of diethyl ether. Yield, 0.053 g (67.5% based on Ni). Anal. Calcd. for $[Ni(CO_3)\{(Cy_2PCH_2)_2NMe\}]$: C, 59.53; H, 9.42; N, 2.53. Found: C, 58.9; H, 9.01; N: 2.46. M.p. = 213°C decomp. ^{31}P-{^{1}H} NMR: $\delta = 17.5$ ppm. Mass spectrum: m/z 570; 570(1.5%) [M$^+$], 510 (4.9%) [Ni(dcpam)], 211 (89.6%) [Cy_2PCH_2]. IR: ν(C—H aliph.) 2940, 2789; ν(C=O) 1540 (asym), 1360 (sym); ν(CH_2) 1446; ν(C—C) 1206; ν(C—O) 1095; ν(Cyclohexyl) 1001, ν(N—CH_3) 847 cm^{-1}. Electronic spectrum: λ_{max} 470 nm.

[Ni(sal){(Cy$_2$PCH$_2$)$_2$NMe}] (3). Ag_2O (0.12 g, 0.72 mmol) was added to a stirred solution of [$NiCl_2$(dcpam)] (0.04 g, 0.068 mmol) in dichloromethane (20 mL). After addition of salicylic acid (0.026 g, 0.0144 mmol) the mixture was refluxed for 8 h and filtered through Celite. A yellow product was precipitated with diethyl ether, filtered, and dried. Yield: 0.026 g (58.5% based on Ni). Anal. Calcd. for [Ni(sal)(dcpam)]: C, 63.20; H, 8.56; N, 2.17. Found: C, 63.50; H, 8.76; N: 2.36. M.p = 225°C decomp. ^{31}P-{^{1}H} NMR: $\delta = 19.72$. Mass spectrum: m/z: 646; 646 (100%)[M$^+$]; 569 (1.5%) [M-Ph]; 510 (8.2%) [Ni(dcpam)]; 211 (61.9%) [Cy_2PCH_2]. IR: ν(ar-H) 3090; ν(C—H aliph.) 2990, 2850; ν(C=O) 1640 (asym), 1410 (sym); ν(CH_2) 1445; ν(C—C) 1212; ν(C—O) 1097; ν(Cyclohexyl) 1007, ν(N—CH_3) 852 cm^{-1}. Electronic spectrum: λ_{max} 438 nm.

[Ni(Glu){(Cy$_2$PCH$_2$)$_2$NMe}](4). Ag_2O (0.25 g, 1.13 mmol) was added to a stirred solution of [$NiCl_2$(dcpam)] (0.05 g, 0.086 mmol) in dichloromethane (20 mL). After addition of glutamic acid (0.015 g, 0.10 mmol) the mixture was refluxed for 8 h and then filtered through Celite. The solvent volume was reduced to 5 mL and the product was then precipitated with diethyl ether, filtered, and dried. Yield: 0.45 g (80.0% based on Ni). $[Ni(Glu)\{(Cy_2PCH_2)_2NMe\}]$: C, 58.60; H, 8.92; N, 2.14. Found: C, 58.20; H, 8.97; N: 2.41. M.p. = 250°C decomp. ^{31}P-{^{1}H} NMR: $\delta = 16.4$ ppm. Mass spectrum: m/z: 654; 654 (2.2%) [M$^+$]; 580 (3.2%) [M-$OCOCH_2NH_2$]; 510 (6.2%) [Ni(dcpam)]; 211 (100%) [Cy_2PCH_2]. IR: ν(N—H) 3450–3370 ν(C—H aliph.) 2931, 2854, 2782; ν(C=O) 1590 (asym), 1380 (sym); ν(CH_2) 1446; ν(C—C) 1211, 1174; ν(Cyclohexyl) 1009; ν(N—CH_3) 854 cm^{-1}. Electronic spectrum: λ_{max} 468 nm.

[Ni(Suc){(Cy$_2$PCH$_2$)$_2$NMe}] (5). Ag_2O (0.16 g, 1.07 mmol) was added to a stirred solution of [$NiCl_2$(dcpam)] (0.08 g, 0.14 mmol) in dichloromethane (20 mL). Following succinic acid addition (0.017 g, 0.143 mmol) the mixture was refluxed for 8 h. On cooling the mixture was filtered through Celite. The product was precipitated with diethyl ether to give a pale orange powder. Yield: 0.082 g (93.6%, based on Ni). $[Ni(suc)\{(Cy_2PCH_2)_2NMe\}]$: C, 53.40; H, 8.24; N, 2.01. Found: C, 53.8; H, 8.60; N: 2.35. M.p. = 212°C decomp. ^{31}P-{^{1}H} NMR: $\delta = 9.08$ ppm. IR: ν(C—H aliph.) 2929, 2850, 2788; ν(C=O) 1585 (asym), 1330 (sym); ν(CH_2) 1445; ν(C—C) 1212; ν(C—O) 1094; ν(Cyclohexyl) 1005; ν(N—CH_3) 850 cm^{-1}. Electronic spectrum: λ_{max} 458 nm.

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