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Research paper

Nickel(II) and nickel(0) complexes of bis(diisopropylphosphino)amine: Synthesis, structure, and electrochemical activity

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ABSTRACT

In its neutral state, bis(diisopropylphosphino)amine **HL** reacts in equimolar amounts with the nickel halides $NiCl_2{\cdot}6H_2O$, $NiBr_2$, and NiI_2 in ethanol solutions to give the air- and moisture-stable P,P-chelated complexes (**HL**)NiX_2 (X = Cl, Br, I). Under similar conditions, complexes of the form $[(\mathbf{HL})_2Ni]X_2$ (X = BF_4, NO_3, ClO_4) were prepared from 2:1 ligand-metal ratios of $Ni(BF_4)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, or $Ni(ClO_4)_2{\cdot}6H_2O$. Deprotonation of the ligand with $NaNH_2$ followed by reaction with NiI_2 gives $\mathbf{L}_2Ni$ when performed in Et_2O, but leads to the co-crystal $\mathbf{L}_2Ni{\cdot}2[NCCHC(Me)NH_2]$ when the solvent is acetonitrile. In addition to these Ni^{2+} compounds, the Ni^0 complex $(\mathbf{HL})_2Ni$ can be prepared from a toluene solution of $Ni(cod)_2$. Each complex has been characterized by a combination of IR and multi-nuclear NMR spectroscopies, as well as single-crystal X-ray diffraction. Electrochemical studies of the complexes revealed irreversible decomposition of the (**HL**)NiX_2 (X = Cl, Br, I) series, but electrocatalytic CO_2 reduction by the $[(\mathbf{HL})_2Ni]X_2$ (X = BF_4, NO_3, ClO_4) compounds.

1. Introduction

Nickel complexes in which the metal is bound to at least two phosphorus atoms are a very versatile class of molecules. They have been used as stoichiometric reagents for hydrosilation [1], to form nickelaoxetanes as models for catalytic oxidation processes [2], and to make mixed-metal compounds to model heterogeneous clusters [3]. They have been used as active catalysts, pre-catalysts, or catalytic model compounds for photoelectrochemical water splitting [4], ethylene oligomerization and polymerization [5], functionalization of unsaturated hydrocarbons [6], cross-coupling reactions [7], and other processes [8]. Of most interest to us, they are used for the activation and conversion of CO_2 [9], an area of growing concern both academically and industrially [10].

In many cases, the active nickel species is generated by combining the metal and phosphine ligand *in situ*, with little or no characterization of the resulting complex. Nevertheless, more than 2300 mononuclear NiP_2 complexes have been characterized by single-crystal X-ray diffraction [11]. Of these, approximately 100 contain bidentate ligands with a single-atom bridge between the phosphorus centers. With a few exceptions, the bridging atom is split roughly equally between N and C. A closer examination of these structures reveals a striking difference between these two groups. While most of the carbon bridges are simple methylene ($-CH_2-$) fragments, the vast majority of the nitrogen bridges are tertiary amines, with alkyl, aryl, or other groups as the third substituent. Only four complexes contain an unsubstituted nitrogen atom. Of those four complexes, three are based on the neutral ligands HN[P(*t*-Bu)$_2$PMe(*t*-Bu)] [12] or $HN(PPh_2)_2$ [13], while the fourth uses the latter in its anionic, deprotonated form $[N(PPh_2)_2]^-$. We have previously shown that Mg [14], Ca or Sr [15], or Zn [16] complexes of this anionic ligand will react with CO_2 in rather unexpected ways. When the phenyl groups are replaced by isopropyl groups, we have found that the reactivity is often more straightforward. The anion $\{N[P(i\text{-}Pr)_2]_2\}^-$ will chelate main group elements through the phosphorus atoms, and the resulting Zn [16], Sn [17], or In [18] complexes will insert CO_2 into the M—P bonds. Each of these complexes, however, is unstable in the presence of moisture, a serious drawback to any future, large-scale operation for CO_2 capture and recycle/conversion. We hypothesized that if the ligand were kept in its neutral form $HN[P(i\text{-}Pr)_2]_2$, the resulting complexes would be more likely to tolerate moisture and other protic environments. As well, with an eye towards a possible future capture and conversion process, Ni is fortunately an earth abundant metal, as are our previously-used Zn and Sn metals.

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Table 1
Crystallographic data for compounds **1**–**8**.

	1	2	3	4	5	6	7	7a	8
Chemical formula	$C_{12}H_{29}Cl_2NN\ iP_2$	$C_{12}H_{29}Br_2NN\ iP_2$	$C_{12}H_{29}I_2NNiP_2$	$C_{24}H_{58}B_2F_8N_2\ NiP_4$	$C_{24}H_{58}N_4NiO\ _6P_4$	$C_{24}H_{58}Cl_2N_2\ NiO_8P_4$	$C_{24}H_{56}N_2NiP_4$	$C_{32}H_{68}N_6NiP_4$	$C_{24}H_{58}N_2NiP_4$
Formula weight	378.91	467.83	561.81	730.93	681.33	756.21	555.29	719.51	557.31
Space group	*P21/c*	*P21/c*	*P21/n*	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*P-1*
a (Å)	14.2872(4)	14.760(3)	8.2480(2)	14.7820(5)	14.6971(3	14.8131(5)	14.9194(5)	11.1122(7)	9.8762(7)
b (Å)	9.8464(3)	9.7000(17)	21.7270(7)	15.0262(4)	14.9693(3)	13.7858(5)	11.5824(3)	18.8293(11)	10.4809(7)
c (Å)	14.2512(4)	14.658(3)	10.6538(3)	16.0322(5)	15.2423(3)	17.6853(7)	17.2569(5)	38.577(2)	17.0194(12)
α (°)									78.782(2)
β (°)	118.8760(10)	119.617(3)	92.537(2)						74.775(2)
γ (°)									64.898(2)
V (Å^3)	1755.56(9)	1824.4(6)	1907.34(9)	3561.03(19)	3353.39(12)	3611.5(2)	2982.03(15)	8071.7(8)	1532.34(19)
Z	4	4	4	4	4	4	4	8	2
Dcalcd (g cm^{-1})	1.434	1.703	1.956	1.363	1.350	1.391	1.237	1.184	1.208
μ (mm^{-1})	1.577	5.605	4.409	0.785	0.811	0.906	0.880	0.668	0.856
R (I > 2σI)	0.0286	0.0384	0.0266	0.0520	0.0283	0.0443	0.0264	0.0413	0.0294
Rw (I > 2σI)	0.0589	0.0613	0.0448	0.1325	0.0700	0.1015	0.0622	0.0826	0.0644

2. Experimental

2.1. General considerations

All manipulations were carried out in an argon-filled glovebox or by using standard Schlenk techniques unless otherwise noted. The ligand bis(diisopropylphosphino)amine **HL** was prepared according to literature procedures [19]. Anhydrous solvents were stored in the glovebox over 4 Å molecular sieves prior to use. ^{1}H and ^{13}C{^{1}H} spectra were referenced to residual solvent downfield of TMS. ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{19}F{^{1}H} spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and C_6F_6, respectively. Due to low solubility, ^{13}C{^{1}H} NMR was not obtained for most compounds. IR spectra were recorded as mineral oil mulls on KBr windows. Elemental analyses were performed by ALS Global (Tucson, AZ) or on a Perkin Elmer 2400 Series II CHNS/O Analyzer. Single-crystal X-ray diffraction studies were performed on a Bruker Kappa Apex II CCD diffractometer. Crystals were coated in Paratone-N oil and mounted on a MiTeGen MicroLoop™. The Bruker Apex3 software suite [20] was used for data collection, structure solution and refinement. Crystal data are summarized in Table 1.

Electrochemical measurements were carried out using an Autolab 302N potentiostat interfaced through Nova 2.0 software to a personal computer. Electrochemical measurements were performed using 0.1 M [Bu_4NPF_6]/THF electrolyte solutions from solvent that had been purified by passing through an alumina-based purification system. Diamond-polished glassy carbon electrodes of 3 mm diameter were employed for cyclic voltammetry (CV) scans. CV data were evaluated using standard diagnostic criteria for diffusion control and for chemical and electrochemical reversibility. The experimental reference electrode was a silver wire coated with anodically deposited silver chloride and separated from the working solution by a fine glass frit. The electrochemical potentials in this paper are referenced to ferrocene/ferrocenium couple, as recommended elsewhere [21]. The ferrocene potential was obtained by its addition to the analyte solution [22] at an appropriate time in the experiment.

2.2. Synthesis of (HL)$NiCl_2$ (**1**)

$NiCl_2{\cdot}6H_2O$ (1.0 mmol) was dissolved in 10 mL EtOH and warmed to 50 °C in air to get a yellow solution. A colorless solution of **HL** (0.25 g, 1.0 mmol) in 5 mL EtOH was then added, and the solution immediately turned bright red. The solution was allowed to cool slowly to room temperature and was then further cooled to 4 °C. After 24 h, the supernatant was decanted from red, X-ray quality single crystals. Yield = 0.23 g (61%), mp = >200 °C. IR *ν* 3202 (br, N—H) cm^{-1}. ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2): *δ* 1.33 (d, $^3J_{HH}$ = 7.2 Hz, 12H, C*H*$_3$), 1.57 (d, $^3J_{HH}$ = 7.2 Hz, 12H, C*H*$_3$), 2.41 (sept, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*), 3.07 (s, 1H, N*H*) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): *δ* 63.9 ppm. Anal Calcd. for $C_{12}H_{29}Cl_2NNiP_2$: C, 38.04; H, 7.71; N, 3.70. Found: C, 38.06; H, 8.31; N, 3.71.

2.3. Synthesis of (HL)$NiBr_2$ (**2**)

$NiBr_2$ (0.22 g, 1.0 mmol) was partially dissolved in 10 mL EtOH and warmed 50 °C in air to get a peach-colored suspension. A colorless solution of **HL** (0.25 g, 1.0 mmol) in 5 mL EtOH was then added, and the mixture immediately turned bright red. The heterogeneous mixture was held at 50 °C for two hours, and was then allowed to cool slowly to room temperature. After 24 h, the supernatant was decanted from the red-orange powder. Yield = 0.32 g (68%), mp = >200 °C. IR *ν* 3186 (br, N—H) cm^{-1}. ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2): *δ* 1.34 (d, $^3J_{HH}$ = 7 Hz, 12H, C*H*$_3$), 1.59 (d, $^3J_{HH}$ = 7 Hz, 12H, C*H*$_3$), 2.47 (sept, $^3J_{HH}$ = 7 Hz, 4H, C*H*), 3.11 (br s, 1H, N*H*) ppm.