Journal of Organometallic Chemistry, 65 (1974) C23—C26
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Preliminary communication

REACTION OF NITROGEN WITH TRIETHYLPHOSPHINE COMPLEXES OF ZERO-VALENT Ni, Pd, AND Pt: EVIDENCE FOR A NICKEL DINITROGEN COMPLEX

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(Received October 17th, 1973)

Dinitrogen complexes of the nickel triad are rare. Two compounds, $[(C_6H_{11})_3P]_2NiN_2Ni[P(C_6H_{11})_3]_2$ [1] and $HNi(N_2)[PEt_3]_2$ [2] are reported to have been isolated. The structure of the former has been determined by X-ray crystallography [1b]. Matrix isolation infrared and Raman spectroscopy have provided evidence for $(N_2)NiX_2$ [X = F, Cl] [3], $(N_2)Ni(O_2)$ [4], $(N_2)Ni(CO)_3$ [5], $Ni(N_2)_n$ [n = 1-4] [6], $Pd(N_2)_m$ [m = 1-3] [6] and $Pt(N_2)$ [7].

In this communication we wish to describe attempts to prepare dinitrogen complexes of zerovalent nickel, palladium, and platinum containing triethylphosphine and the spectroscopic characterization of a nickel dinitrogen complex in solution which we formulate as $(N_2)Ni[PEt_3]_3$*.

The pale-yellow crystalline complex $Ni[PEt_3]_4$ [9] dissociates in organic solvents under argon by reaction (1) to give permanganate-violet solutions showing an absorption maximum at 502 nm; $K_1 = 1.2 \times 10^{-2}\,M$ (benzene, 25°) [10]. The maximum at 502 nm is characteristic of the NiL_3 complex (ϵ 2.6×10^3 $cm^{-1} \cdot M^{-1}$), which can be isolated by heating the NiL_4 compound

$$NiL_4 \overset{K_1}{\rightleftharpoons} NiL_3 + L \tag{1}$$

in vacuo [11]. When N_2 and argon are alternately swept through the solutions, the color changes noticeably and rapidly, being more intensely violet under argon. The color changes are attributed to a rapid and reversible formation of $(N_2)Ni[PEt_3]_3$, with concomitant loss of absorbance at 502 nm. K_2 can be estimated as 0.8 atm^{-1} assuming that the nitrogen complex does not absorb at 502 nm.

$$N_2 + NiL_3 \overset{K_2}{\rightleftharpoons} (N_2)NiL_3 \tag{2}$$

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*Cundy independently noted the formation of a dinitrogen complex in solutions of $Ni(PEt_3)_4$, but was unable to determine its stoichiometry [8].

Formation of a nitrogen complex was also indicated by the presence of an infrared band of medium intensity at 2063 cm^{-1} (toluene) or 2074 cm^{-1} (cyclohexane) in N_2 saturated solutions of $Ni(PEt_3)_4$ or $Ni(PEt_3)_3$, assigned to $\nu(N_2)$ in $(N_2)Ni[PEt_3]_3$. Addition of PEt causes a reduction in the $\nu(N_2)$ band, as expected for equilibrium (3).

$$L + (N_2)NiL_3 \overset{K_3}{\rightleftharpoons} NiL_4 + N_2 \tag{3}$$

The ^{31}P NMR spectrum of $Ni(PEt_3)_3$ under argon in toluene at -13° showed a single sharp line at -2.2 ppm (85% H_3PO_4). Addition of increasing N_2 pressures caused a sharp new line to grow in at -8.4 ppm assigned to $(N_2)Ni(PEt_3)_3$. No other resonances were observed. Addition of PEt_3 to the solution reduced the intensity of the -8.4 ppm line and augmented the -2.2 ppm line; both remained sharp. A third broad resonance at high field sharpened and moved toward the position of free PEt_3 at +21 ppm as more ligand was added. Addition of PEt_3 to $Ni(PEt_3)_3$ under argon showed that the NiL_3 and NiL_4 complexes have accidentally similar chemical shifts and that exchange of free and coordinated phosphine is slow at -13°. The broad resonance at high field when PEt_3 was added to a solution of $Ni(PEt_3)_3$ under N_2 must arise from rapid exchange* between free PEt_3 and some fourth complex, possibly $L_2NiN_2NiL_2$ by analogy with L = P(cyclohexyl) [1]. The ^{31}P chemical shift of -8.4 ppm for $(N_2)Ni[PEt_3]_3$ can be compared with -15.3 ppm for the isoelectronic $(CO)Ni[PEt_3]_3$**. We have been unable to isolate $(N_2)Ni[PEt_3]_3$ as a pure compound. Exposing violet crystals of $Ni(PEt_3)_3$ to N_2 gives a brown solid showing $\nu(N_2)$ in the infrared, but analysis for nitrogen has been consistently low.

Attempts to obtain spectroscopic evidence for analogous palladium and platinum complexes have been unsuccessful. No color changes or changes in the ^{31}P NMR spectra of the ML_3 complexes [11] were observed when solutions were pressurized with 150 psig N_2. A reduced ability of Pd^0 and Pt^0 to back bond compared to Ni^0*** is reflected in the higher values of $\nu(N_2)$ in $(N_2)M$ or $\nu(CO)$ in $(CO)M(PEt_3)_3$ complexes, as shown in Table 1.

Reduction in $\nu(N_2)$ or $\nu(CO)$ in the nickel complexes on descending the Table indicates increasing ability of the nickel to back bond as the other ligands are changed. We conclude that the net flow of electron density is from the nickel atom in $Ni(CO)_3$ and to the nickel atom in $Ni(PEt_3)_3$.

Still lower values of $\nu(N_2)$ and $\nu(CO)$ in the $HCo(N_2)(PEt_3)_3$ and $HCo(CO)(PEt_3)_3$ complexes suggest an increased electron density on the formally cobalt (+1) hydrides* compared to the isoelectronic nickel(0) complexes.

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*Attempts to slow the exchange rate by cooling below -25° were unsuccessful because of the precipitation of $Ni(PEt_3)_4$.

**We have isolated the carbonyl complex as a yellow crystalline solid with the correct elemental analyses for Ni, P, C, and H.

***Increased back bonding in the sequence $Pd < Pt \ll Ni$ is shown by equilibrium constants (benzene, 25°) of $4.7 \pm 4 \times 10^{-1}$, $5.2 \pm 1.2 \times 10^{1}$, and $3.3 \pm 4 \times 10^{4}$ for the reaction $C_2H_4 + M(PEt_3)_3 \rightleftharpoons (C_2H_4)M(PEt_3)_2 + PEt_3$. The same sequence but with smaller *K*'s was reported earlier [12] for the aryl phosphine ethylene complexes.

*The composition of $HCo(N_2)(PEt_3)_3$ is shown unambiguously by the 1/3/3/1 quartet of the hydride in the proton NMR spectrum [13].

TABLE 1

INFRARED STRETCHING FREQUENCIES[a] IN $(N_2)ML_n$ OR $(CO)ML_n$ COMPOUNDS

ML_n	$\nu(N_2)$ (cm^{-1})	$\nu(CO)$ (cm^{-1})	Ref.
Pd	2213	2050	6,[f]
$Pd(PEt_3)_3$	—	1944	*b*
Pt	2206	2052	7 (ref. 15)
$Pt(PEt_3)_3$	—	1920	*b*
NiF_2	*c*	2200	3
$Ni(CO)_3$	2266	2050[d]	5
Ni	2169	2000	7
$Ni(PEt_3)_3$	2074	1908	*b*
$Ni[P(C_6H_{11})_3]_2$	2028[e]	—	1b
$CoH(PEt_3)_3$	2055	1881	*b*

[a] Literature frequencies are for low temperature matrices unless noted otherwise. [b] This work in cyclohexane at ambient temperature. [c] Formation of $(N_2)NiF_2$ was deduced from a band at 736 cm^{-1}. The $\nu(N_2)$ band must be very weak in the infrared. [d] Mean for split band observed in infrared for $Ni(CO)_4$ at 20 K. [e] In toluene at ambient temperature. [f] $\nu(CO)$ in argon matrix (see ref. 17).

Srivastava and Bigorgne [2] have reported the isolation of $HNi(N_2)[PEt_3]_2$. Their reported frequencies for $\nu(N_2)$ in a variety of solvents are remarkably similar to those we observe for $(N_2)Ni[PEt_3]_3$. Frequencies similar to theirs for ν(NiH) are found for $(CO)Ni[PEt_3]_3$ or for $Ni(PEt_3)_3$ treated with water. We suspect the formulation given by these authors [2], and suggest that they may have had a mixture of $(N_2)Ni[PEt_3]_3$ and other carbonyl or hydride containing complexes.

Formation of the 18 electron $(N_2)NiL_3$ as the principle N_2 containing species in our system rather than the 16 electron $L_2NiN_2NiL_2$ observed with tricyclohexylphosphine is understandable in terms of the much greater steric bulk of $P(C_6H_{11})_3$ (ligand cone angle 179° [14]) compared to PEt_3 (cone angle 132°). The smaller PMe_3 (cone angle 118°) forms such a stable NiL_4 complex that no N_2 complex can be detected in solution [10]. Bulky phosphites, like P(O-*o*-tolyl)$_3$ (cone angle 141°) [10], can give high concentrations of NiL_3 in solutions, but are too strongly electron withdrawing to form N_2 complexes. The isoelectronic nitrile complexes $(RCN)NiL_3$ are, however, quite stable [16].

Acknowledgments

We are indebted to Dr. P. Meakin for ^{31}P NMR spectra under N_2 pressure and to Dr. L.W. Gosser for a sample of $HCo(PEt_3)_4$ used to prepare $HCo(N_2)(PEt_3)_3$ and $HCo(CO)(PEt_3)_3$.

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