Synthesis and structure of a terminal dinitrogen complex of nickel¹

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Abstract: Reaction of petroleum ether solutions of $[(dtbpe)Ni]_2(\eta^2\mu-C_6H_6)$ (1, dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) with triphenylphosphine under a dinitrogen atmosphere gives the Ni(0) dinitrogen adduct (dtbpe)Ni(N₂)(PPh₃) (2), which can be isolated as dark red crystals in 87% yield. The X-ray crystal structure of 2 reveals pseudotetrahedral geometry about Ni and a terminal dinitrogen ligand with Ni—N(1) = 1.830(2) Å, N(1)—N(2) = 1.112(2) Å, and Ni-N(1)-N(2) = 177.5(2)°.

Key words: dinitrogen, nickel, X-ray.

Résumé : La réaction du $[(dtbpe)Ni]_2(\eta^2,\mu-C_6H_6)$ (1, dtbpe = 1,2-bis(di-*tert*-butylphosphino)éthane) en solution dans l'éther de pétrole avec de la triphénylphosphine, sous une atmosphère de diazote, conduit à la formation de l'adduit Ni(0) diazote (dtbpe)Ni(N₂)(PPh₃) (2) que l'on peut isoler sous la forme de cristaux rouges avec un rendement de 87 %. Une étude du composé 2 par diffraction des rayons X révèle une géométrie pseudotétraédrique autour du Ni et la présence d'un ligand diazote terminal avec des distances Ni—N(1) = 1,830(2) Å, N(1)—N(2) = 1,112(2) Å et un angle Ni-N(1)-N(2) = 177,5(2)°.

Mots clés : diazote, nickel, rayons X.

[Traduit par la Rédaction]

Introduction

The 1965 report from University of Toronto chemistry professor Bert Allen and his graduate student Caesar Senoff of the isolation of stable dinitrogen complex salts of the formulation $[(NH_3)_5Ru(N_2)^{2+}][X^-]_2$ from the reaction of ruthenium trichloride with hydrazine hydrate in aqueous solution rocked the scientific community (1, 2). The crystallographic determination of the solid-state structure of the Allen and Senoff complex definitively corroborated the proposed binding mode of the N₂ ligand as end-on bound to Ru in an approximately linear fashion (3). In the intervening 40 years since that landmark discovery, nearly every transition metal has been reported to utilize dinitrogen as a ligand, and many binding modes, including bridging and side-bound, have been observed for N2 ligands (4). Because the dinitrogen ligand is often quite labile, N₂ complexes can serve as useful starting materials for a variety of synthetic purposes. Over the years much research effort has focused on designing systems containing ligated N₂ in which coordination to a metal sufficiently activates the N-N triple bond that it can be subsequently functionalized (or "fixed"), such as in processes that cleave the N-N triple bond (5) or model enzymatic systems that perform catalytic N_2 reduction (6).

Only a few examples of isolated nickel complexes possessing a dinitrogen ligand have appeared in the literature. Most Ni–N₂ species have been dimeric or polynuclear (7–9). The dinitrogen-bridged complex $[(PCy_3)_2Ni]_2(\mu-N_2)$ has been reported and structurally characterized (9), and an unusual side-bound N₂ complex, $[(C_6H_5Li)_6Ni_2(N_2)(Et_2O)_2]_2$, has been reported (7). Surprisingly, no structural data exist for simple end-on N₂ complexes of nickel, even though this is by far its most common coordination mode. Herein we report the preparation and structural characterization of the first example of an isolable nickel complex containing a terminal, end-on bound N₂ ligand.

Experimental

General considerations

Unless otherwise stated, all operations were performed in a M. Braun Lab Master dry box under an atmosphere of purified nitrogen. Petroleum ether was dried by passage through activated alumina and Q-5 columns. C_6D_6 was purchased form Cambridge Isotope Laboratory (CIL), degassed, and dried over CaH₂ or activated 4 Å molecular sieves. Celite[®], alumina, and 4 Å molecular sieves were activated under vacuum overnight at a temperature above 180 °C. Anhydrous solvents such as benzene and diethylether were purchased from Acros or Fischer, stirred over sodium metal, and filtered through activated alumina. [(dtbpe)Ni]₂(η^2 , μ -C₆H₆) (1, dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) was

Received 9 September 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 22 March 2005.

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¹This article is part of a Special Issue dedicated to Dinitrogen Chemistry.

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prepared according to the literature procedure (10). All other chemicals were used as received. IR data (Fluorolube S-20 mulls, CaF₂ plates) were measured with a Nicolet 670 FT-IR instrument. Elemental analyses were performed by Desert Analytics (Tucson, Arizona). ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker 500 and 400 MHz NMR spectrometers. ¹H and ¹³C NMR data are reported with reference to solvent resonances (residual C₆D₅H in C₆D₆, 7.16 ppm; C₆D₆, 128.0 ppm). ³¹P NMR spectra are reported with respect to external 85% H₃PO₄ (0 ppm).

Preparation of (dtbpe)Ni(N₂)(PPh₃) (2)

In a nitrogen-filled, inert-atmosphere glovebox, a 25 mL round-bottomed flask was charged with 72 mg (0.087 mmol) of $[(dtbpe)Ni]_2(\eta^2,\mu-C_6H_6)$ (1) and 45 mg (0.174 mmol) of PPh₃ followed by 14 mL of petroleum ether. The solution immediately became blood red in color and was filtered after stirring for 90 min. The volume of the solution was reduced to ca. 5 mL, and upon cooling to -35 °C, dark red crystals were deposited, which were collected by filtration and dried to give 2 (100 mg, 0.149 mmol, 87% yield). IR (Fluorolube mull, CaF₂, cm⁻¹): 3050–2850 (vs br), 2072 (v_{NN}, vs), 1585 (m), 1479 (s), 1434 (s), 1392 (m), 1360 (m). ¹H NMR (22 °C, 500 MHz, C_6D_6) & 7.94 (t, C_6H_5 , 6H), 7.15 (d, C_6H_5 , 6H), 7.07 (t, C_6H_5 , 3H), 1.55 (m, CH_2 , 4H), 1.17 (mult, CH₃, 36H). ¹³C NMR (22 °C, 125.8 MHz, C₆D₆) δ : 133.8 (d, J_{PC} = 14.5 Hz, C_6H_5), 129.8 (s, C_6H_5), 127.9 (s, C_6H_5), 127.7 (s, C_6H_5), 34.6 (m, $J_{PC} = 4.4$ Hz, $C(CH_3)_3$), 30.7 (br t, J_{PC} = 3.6 Hz, CH_3), 23.4 (m, CH_2). ³¹P NMR (22 °C, 202.4 MHz, C_6D_6) &: 73.5 (d, $J_{PP} = 95.7$ Hz, $PtBu_2$), 28.7 (t, $J_{PP} = 95.7$ Hz, PPh_3). Anal. calcd for $C_{36}H_{55}N_2NiP_3$: C 64.78, H 8.31, N 4.20; found: C 65.11, H 8.28, N 3.31.

Crystallographic data collection, structure solution, and refinement

A dark red block of 2 was selected under a stereomicroscope while immersed in mineral oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection, and mounted and centered on a Bruker SMART APEX system in a nitrogen cold stream. Rotation and still images showed diffractions to be sharp, while frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set. A "hemisphere" data set was obtained, which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using 10 s integration times for each frame. The space group was determined as P-1 based on systematic absences and intensity statistics. Direct methods were used to locate non-hydrogen atoms from the electron difference map. All heavy atoms were converted to and refined anisotropically. Hydrogen atoms were refined isotropically and fixed at calculated positions. A semiempirical absorption correction was applied from ψ -scans. All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, Wisconsin). Details of the data set and the refinement are given in Table 1. Table 2 lists selected metrical parameters of the structure of 2.⁴

Results and discussion

Reaction of petroleum ether solutions of the benzene complex $[(dtbpe)Ni]_2(\eta^2,\mu-C_6H_6)$ (1) with PPh₃ under a nitrogen atmosphere gives a dark red solution from which the dinitrogen complex (dtbpe)Ni(N₂)(PPh₃) (2) can be isolated as analytically pure dark red crystals in 87% yield (eq. [1]).



Even in the presence of excess PPh₃, only **2** is formed and no tetrakisphosphine species is observed. Characterization of **2** followed from its NMR (¹H, ¹³C, and ³¹P) and IR spectra, and a single crystal X-ray diffraction study. The ³¹P NMR spectrum of **2** exhibits a single resonance for the dtbpe ligand (δ 73.5, doublet) and a single resonance for the PPh₃ ligand (δ 28.7, triplet) with ²J_{PP} = 95.7 Hz for both, indicating pseudotetrahedral geometry about nickel. The solid-state IR spectrum of **2** shows a strong v_{NN} at 2072 cm⁻¹.

Single crystals of **2** were grown by slowly cooling concentrated hexane solutions of the complex. A perspective view of the molecular structure of **2** is shown in Fig. 1 with select metrical parameters given in Table 2. The complex features a pseudotetrahedral nickel center with a terminal N₂ ligand with a short N—N bond of 1.112(2) Å. The nitrogen ligand is approximately linear with Ni-N(1)-N(2) = 177.5(2)° and Ni—N(1) = 1.830(2) Å. These values can be compared with those found in the structure of the bridged dinitrogen complex [(PCy₃)₂Ni]₂(μ -N₂) (9) which exhibits Ni—N bond lengths of 1.77 and 1.79 Å, and N—N = 1.12 Å (standard errors were not given in the report).

Complex 2 is, to the best of our knowledge, the only example of an *isolated* nickel complex with a terminal N₂ ligand. It is noteworthy that a family of nickel(II) complexes of the formula L_2NiX_2 (X = Cl or Br; L = PEt₃, PEt₂Ph, or P-*n*-Bu₃) can be reduced in the presence of phosphine to generate $L_3Ni(N_2)$ species that have not been isolated, but lose N₂ to give tetrakisphosphine nickel(0) complexes L_4Ni upon precipitation (11). Solution IR, ³¹P NMR, and electronic spectra for these $L_3Ni(N_2)$ complexes led to their formulation as pseudotetrahedral at Ni with terminal N₂ ligands

⁴Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml for information on ordering electronically). CCDC 261287 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via ww.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Empirical formula	C ₃₆ H ₅₅ N ₂ NiP ₃
Formula weight	667.44
Temperature (K)	100
Wavelength (Å)	0.710 73
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	9.7911(7)
<i>b</i> (Å)	13.7423(10)
<i>c</i> (Å)	13.8687(10)
α (°)	81.6860(10)
β (°)	76.5680(10)
γ (°)	80.1250(10)
Volume (Å ³)	1777.4(2)
Ζ	2
Density (calculated) (Mg/m ³)	1.247
Absorption coefficient (mm ⁻¹)	0.707
F(000)	716
Crystal size, description	210 μm × 200 μm × 200 μm, dark red cube
θ Range for data collection	2.02-28.30
Index ranges	$-12 \le h \le 12, -18 \le k \le 18, -18 \le l \le 18$
Reflections collected	19 902
Independent reflections	8 305 ($R_{\rm int} = 0.0336$)
Completeness to $\theta = 28.30$	94.0%
Absorption correction	Semiempirical from ψ scans
Max and min transmission	0.8714 and 0.8656
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8 305/0/379
Goodness-of-fit on F^2	1.058
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0403, \ wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0461, wR_2 = 0.0999$
Largest diff. peak and hole (e $Å^{-3}$)	1.188 and -0.365

Table 1. Crystal and structure refinement for $(dtbpe)Ni(N_2)(PPh_3)$ (2).

Table 2. Selected bond lengths and angles for $(dtbpe)Ni(N_2)(PPh_3)$ (2).

Bond lengths (Å)	
Ni—N(1)	1.830(2)
Ni—P(3)	2.2048(6)
Ni-P(1)	2.2302(6)
Ni—P(2)	2.2328(5)
N(1)—N(2)	1.112(2)
Bond angles (°)	
N(2)-N(1)-Ni	177.5(2)
N(1)-Ni-P(3)	96.12(5)
N(1)-Ni-P(1)	112.07(5)
P(3)-Ni-P(1)	123.66(2)
N(1)-Ni-P(2)	109.03(5)
P(3)-Ni-P(2)	122.60(2)
P(1)-Ni-P(2)	93.62(2)

(11*a*). These transient complexes have N–N stretching frequencies in the range of 2050–2100 cm⁻¹, which can be compared to the corresponding stretch at 2072 cm⁻¹ in **2** and 2028 cm⁻¹ in $[(PCy_3)_2Ni]_2(\mu-N_2)$, although the latter value, recorded in solution, has been suggested to be for monoFig. 1. A perspective view of the structure of $(dtbpe)Ni(N_2)(PPh_3)$ (2). Hydrogen atoms have been omitted for clarity.



meric (PCy₃)₂Ni(N₂) that results from dissociation of the dimer in toluene (9). In the light of these previous reports, the stability of **2** is undoubtedly the result of the steric bulk of the dtbpe ligand, which prevents expulsion of N₂ and coordination of a second PPh₃ ligand to give the hypothetical (dtbpe)Ni(PPh₃)₂. Finally, an unusual "Ni(I)" complex, (PEt₃)₂Ni(H)(N₂), has been formulated on the basis of UV–vis and IR data (12), but the absence of magnetic susceptibility or ¹H NMR information and the similarity of the IR and UV–vis spectra to (PEt₃)₃Ni(N₂) (vide supra) casts doubts on the identity of this compound (11*a*).

Acknowledgments

We are grateful to the National Science Foundation for financial support of this research through Grant CHE-0244239 to G.L.H., and to the Department of Education for a GAANN Fellowship to R.W.

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