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Synthesis, Reactivity, and Crystal Structure of [1,4-Bis(4-tolyl)tetraazabutadiene](η^5 -cyclopentadienyl)nickel

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The complex [1,4-bis(4-tolyl)tetraazabutadiene](η^5 -cyclopentadienyl)nickel has been prepared by reaction of bis(η^5 -cyclopentadienyl)nickel with 4-tolyl azide. The crystal and molecular structures have been determined by a single-crystal X-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 10.277$ (4) Å, $b = 15.139$ (6) Å, $c = 11.455$ (3) Å, and $\beta = 102.31$ (3)°. The final R value is 0.032 for 3150 reflections. The structure comprises mononuclear units with each central nickel atom coordinated to an η^5 -bonded cyclopentadienyl group and, via two nitrogen atoms at the 1- and 4-positions, to the tetraazabutadiene system. The resultant NiN_4 ring is planar with the aryl substituents twisted 45° out of this plane. The tetraazabutadiene moiety has a short central N(2)–N(3) distance (1.278 (2) Å) and two longer adjacent N–N bonds (1.345 (2) Å average). This complex can be reacted further either with aryl azides to produce bis(tetraazabutadiene)nickel complexes or with *tert*-butyl isocyanide to yield bis(*tert*-butyl isocyanide)[1,4-bis(4-tolyl)tetraazabutadiene]nickel. The title complex is paramagnetic. The ESR spectrum shows hyperfine coupling of the unpaired electron with two nitrogen atoms ($g_1 = 1.97$, $g_2 = 2.01$, $g_3 = 2.08$, $A_N(g_2) = 12$ G). XPS spectra of the Ni(2p) and N(1s) bands exhibit a shake-up satellite in the latter. The bonding in this compound is discussed on the basis of the crystal structure and the spectral data.

Introduction

In 1967 [Fe(R_2N_4)(CO) $_3$] $_2$ ($R = Me$) was first reported, but since then there have been relatively few publications concerning tetraazabutadiene–metal complexes.^{2a} To date four crystal structure determinations of such complexes have been reported.^{1,3–5} On the basis of the observed N–N bond lengths and various bond angles, a series of canonical forms has been considered in an attempt to describe the bonding of the tetraazabutadiene ligand to a metal center.² In the course of our studies into the chemistry of tetraazabutadiene complexes^{2b,3,6} we reported the first examples of bis(tetraazabutadiene)metal complexes, [Ni(Ar_2N_4) $_2$], which were prepared by the reactions of [Ni(COD) $_2$] with aryl azides. We report here the synthesis and characterization of [1,4-bis(4-tolyl)tetraazabutadiene](η^5 -cyclopentadienyl)nickel.⁷ This paramagnetic compound is a stable intermediate from the reaction of [Ni(Cp) $_2$] with 4-tolyl azide, which ultimately produces [Ni(1,4-(4-MeC $_6$ H $_4$) $_2$ N $_4$) $_2$].

[Ni(Ar_2N_4)(η^5 -C $_5$ H $_5$)] shows a striking structural similarity to the recently reported [Co(1,4-(C $_6$ F $_5$) $_2$ N $_4$)(η^5 -C $_5$ H $_5$)] complex.^{5,8} The bonding in the complex, which is important with respect to an understanding of the formal oxidation state of nickel and the (Ar_2N_4)–Ni interaction, has been studied with ESR and X-ray photoelectron spectroscopy (XPS or ESCA), and the data have been compared with those of other [Ni(η^5 -C $_5$ H $_5$)L $_2$] complexes.⁹

Experimental Section

All preparations were carried out in a dry deoxygenated N $_2$ atmosphere. All solvents were dried and freshly distilled prior to use. Silica-60 was dried for 5 h at 150 °C, 0.05 torr.

Bis(η^5 -cyclopentadienyl)nickel (Ni(Cp) $_2$),¹⁰ 4-tolyl azide,¹¹ *tert*-butyl isocyanide (*t*-BuNC),¹² 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (*t*-BuDAB-(H,H)),¹³ di-*tert*-butylsulfur diimide (DBSD),^{14a} and bis(4-chlorophenyl)sulfur diimide^{14b} were prepared according to literature procedures.

IR spectra were recorded on Beckman 4250 and Perkin-Elmer 283 spectrophotometers. ESR spectra were recorded on a Varian E 12 spectrometer at 4.2 K.

X-ray photoelectron spectra were collected with an AEI ES 200 spectrometer at a pressure of 10^{–10} torr obtained with turbomolecular and Ti sublimation pumps. As a source Mg K α radiation was used.

We have used the C(1s) line, set at 285.0 eV, as a reference.

Preparation of [1,4-Bis(4-tolyl)tetraazabutadiene](η^5 -cyclopentadienyl)nickel, [Ni(1,4-(4-MeC $_6$ H $_4$) $_2$ N $_4$)(η^5 -C $_5$ H $_5$)] (I). A mixture of [Ni(Cp) $_2$] (2 g, 10.6 mmol) and 4-MeC $_6$ H $_4$ N $_3$ (4 g, 30 mmol) was refluxed in 50 mL of toluene until the color of the solution changed from green to deep brown (ca. 35 min). The reaction mixture was refluxed for another 5 min, cooled, and concentrated in vacuo to 10 mL. The residue was then chromatographed over a silica column (10 \times 4 cm) with toluene (room temperature) as an eluent. The first fraction contained unreacted [Ni(Cp) $_2$] (40%) and unreacted azide. Then the deep purple fraction containing [Ni(1,4-(4-MeC $_6$ H $_4$) $_2$ N $_4$) $_2$] (5%) was collected. A brown band which remained on top of the column was eluted with hot (100 °C) toluene and this fraction concentrated in vacuo to 5 mL. Upon addition of 100 mL of pentane a black microcrystalline solid precipitated, which was washed with pentane (3 \times 5 mL) and dried at reduced pressure to yield 380 mg (10%) of I. (All yields are based on the total amount of nickel present.) Yields vary with concentration of the reactants, reaction time, and temperature. Prolonged heating of the reaction mixture eventually results in a vigorous, exothermic reaction with N $_2$ evolution and loss of I. In one experiment this happened after 55 min, and workup of the mixture yielded 15% of [Ni(1,4-(4-MeC $_6$ H $_4$) $_2$ N $_4$) $_2$].

Anal. Calcd for I (C $_{19}$ H $_{19}$ N $_4$ Ni): C, 63.02; H, 5.29; O, 0.0; N, 15.47; Ni, 16.21. Found: C, 62.8; H, 5.4; O, <0.2; N, 15.4; Ni, 15.8. IR spectrum (in KBr, cm $^{-1}$): 3100 vw, 2920 vw, 1500 vs, 1410 w, 1265 s, 1235 w, 1170 s, 1095 s, 1025 s, 825 s, 805 vs.

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Table I. Crystal Data and Details of the Structure Analysis

a. Crystal Data			
formula	C ₁₉ H ₁₉ N ₄ Ni	Z	4
<i>M_r</i>	362.1	<i>D</i> _{calcd} , g/cm ³	1.381
cryst syst	monoclinic	<i>F</i> (000), electrons	756
<i>a</i> , Å	10.277 (4)	μ (Mo K α), cm ⁻¹	11.20
<i>b</i> , Å	15.139 (6)	cryst size, mm	(010)→(010), 0.37; (001)→(001), 0.37; (012)→(012), 0.27; (100)→(100), 0.50
<i>c</i> , Å	11.455 (3)		
β , deg	102.31 (3)		
<i>V</i> , Å ³	1741 (1)		
space group	<i>P</i> 2 ₁ / <i>c</i>	cryst vol, mm ³	0.06
b. Data Collection			
θ_{\min} , θ_{\max} , deg		0.1, 27.5	
θ -2 θ scan with parameters <i>A</i> and <i>B</i> in width <i>A</i> + <i>B</i> tan θ		0.35, 0.35	
horiz and vert apertures, mm		1.3, 3.0	
std reflectns		214, 214	
total data		3998	
total unique data		3987	
obsd data <i>I</i> > 2.5 σ (<i>I</i>)		3150	
c. Refinement			
no. of parameters		275	
weighting scheme coefficient		0.04	
<i>g</i> in $w^{-1} = \sigma^2(F_o) + gF_o^2$			
final $R_F = \Sigma \Delta F / \Sigma F_o $		0.032	
$R_{wF} = [\Sigma w \Delta F ^2 / \Sigma F_o ^2]^{1/2}$		0.041	
shift/error av		0.14	
max		1.2	
goodness of fit, $[\Sigma (w(\Delta F)^2) / (n - m)]^{1/2}$		2.26	

Preparation of Bis(*tert*-butyl isocyanide)[1,4-bis(4-tolyl)tetraazabutadiene]nickel, [Ni((4-MeC₆H₄)₂N₄)(*t*-BuNC)₂] (II). To a stirred solution of I (150 mg, 0.41 mmol) in 10 mL of toluene was added *tert*-butyl isocyanide (0.06 mL, 0.9 mmol). The color of the reaction mixture changed immediately from brown to green. After the addition of 50 mL of pentane the mixture was stored at -20 °C for 18 h. The resulting green microcrystals were washed with pentane (4 × 5 mL) and dried in vacuo to yield 150 mg (79%) of known II.¹⁵

Reaction of I with 4-Tolyl Azide.¹⁶ A mixture of I (150 mg, 0.41 mmol) and 4-MeC₆H₄N₃ (2 g, 15 mmol) in 20 mL of toluene was refluxed for 2 h. The mixture was concentrated to 3 mL under reduced pressure and chromatographed on a silica-60 column (10 × 4 cm) with hexane/toluene (1:1) until the yellow band (unreacted azide) had been removed. Further elution with toluene provided a deep purple fraction, which was evaporated in vacuo to dryness, and the residue was washed with pentane (3 × 5 mL) to yield 115 mg (52%) of known microcrystalline [Ni(1,4-(4-MeC₆H₄)₂N₄)₂].¹⁵

Structure Determination and Refinement. Crystal data and other numerical details of the structure determination are given in Table I.

Accurate values of the unit cell and the crystal orientation matrix were determined at room temperature from a least-squares treatment of the angular settings of 20 reflections, carefully centered on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation ($\lambda = 0.71069$ Å).¹⁷ From the unit cell dimensions and systematic extinctions (*h*0*l*, *l* ≠ 2*n*; 0*k*0, *k* ≠ 2*n*) the space group was uniquely determined as *P*2₁/*c*. The standard deviations in the lattice parameters were derived from a comparison of the deviations from integer values of the indices, calculated with the orientational matrix for the angular settings of the orientation reflections as described by Duisenberg.¹⁸

Intensity data for 3998 reflections up to $\theta = 27.5^\circ$ were collected on Enraf-Nonius CAD4 PDP8-controlled diffractometer, equipped with a scintillation counter, in the ω -2 θ scan mode. The background was measured in an additional scan area of $\Delta\omega/4^\circ$ on both sides of the main scan with the same scan speed. The scan speed was selected such as to obtain $\sigma(I)/I = 0.02$ under the condition of a maximum

Table II. Positional Parameters and Their Esd's in Parentheses for C₁₉H₁₉N₄Ni

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.19339 (2)	0.41868 (2)	0.50750 (2)
N(1)	0.1353 (2)	0.3286 (1)	0.5934 (1)
N(2)	0.1577 (2)	0.3421 (1)	0.7120 (1)
N(3)	0.2226 (2)	0.4123 (1)	0.7484 (1)
N(4)	0.2422 (2)	0.4652 (1)	0.6593 (1)
C(1)	0.0455 (2)	0.2576 (1)	0.5560 (2)
C(2)	-0.0625 (2)	0.2429 (1)	0.6089 (2)
C(3)	-0.1476 (2)	0.1730 (2)	0.5723 (2)
C(4)	-0.1295 (2)	0.1162 (2)	0.4827 (2)
C(5)	-0.0207 (3)	0.1313 (2)	0.4317 (2)
C(6)	0.0655 (2)	0.2005 (2)	0.4677 (2)
C(7)	-0.2235 (3)	0.0404 (2)	0.4424 (3)
C(8)	0.3156 (2)	0.5429 (1)	0.7021 (2)
C(9)	0.4204 (2)	0.5404 (1)	0.8001 (2)
C(10)	0.4854 (2)	0.6172 (2)	0.8432 (2)
C(11)	0.4486 (2)	0.6978 (2)	0.7894 (2)
C(12)	0.3456 (3)	0.6993 (1)	0.6912 (2)
C(13)	0.2788 (2)	0.6230 (1)	0.6470 (2)
C(14)	0.5159 (3)	0.7827 (2)	0.8396 (4)
C(15)	0.0909 (3)	0.4225 (2)	0.3286 (2)
C(16)	0.1264 (3)	0.5054 (2)	0.3638 (2)
C(17)	0.2619 (3)	0.5085 (2)	0.3979 (2)
C(18)	0.3143 (3)	0.4267 (2)	0.3772 (2)
C(19)	0.2056 (4)	0.3722 (2)	0.3366 (2)
H(1)	-0.073 (2)	0.278 (1)	0.671 (2)
H(2)	-0.217 (2)	0.165 (1)	0.609 (2)
H(3)	-0.004 (2)	0.093 (2)	0.374 (2)
H(4)	0.138 (2)	0.209 (2)	0.429 (2)
H(5)	-0.248 (3)	0.014 (2)	0.506 (2)
H(6)	-0.179 (3)	-0.012 (2)	0.407 (2)
H(7)	-0.287 (3)	0.058 (2)	0.386 (2)
H(8)	0.445 (2)	0.485 (1)	0.842 (2)
H(9)	0.559 (2)	0.614 (2)	0.915 (2)
H(10)	0.320 (2)	0.753 (1)	0.661 (2)
H(11)	0.202 (2)	0.622 (1)	0.581 (2)
H(12)	0.467 (3)	0.832 (2)	0.816 (3)
H(13)	0.593 (3)	0.783 (2)	0.838 (3)
H(14)	0.566 (3)	0.773 (2)	0.926 (3)
H(15)	-0.006 (3)	0.399 (2)	0.295 (2)
H(16)	0.072 (3)	0.557 (2)	0.367 (2)
H(17)	0.317 (3)	0.554 (2)	0.427 (3)
H(18)	0.405 (3)	0.412 (2)	0.395 (3)
H(19)	0.209 (3)	0.322 (2)	0.321 (3)

of 2 min/reflection measurement time. The intensity of the standard reflections was measured every 0.5 h of X-ray exposure. The net intensities were calculated with $I_{\text{net}} = (\text{scale})(S - 2(L + R))/npi$, where *L* + *R* is the total background count, *S* the scan count, and *npi* the ratio of the maximum scan speed to the applied scan speed. The data were scaled to correct for short- and long-range fluctuations in the intensity. There was no indication for decay during the data collection.

The standard deviation in the net intensity was calculated with

$$\sigma(I) = (\text{scale}/npi)(S + 4(L + R))^{1/2}$$

Correction for absorption was made with a Gaussian integration technique by using a 9 × 10 × 11 grid; transmission factors ranged from 1.14 to 1.23. After averaging, a unique data set containing 3987 reflections, of which 3150 have *I* > 2.5 σ (*I*), was obtained. The data were corrected for Lorentz and polarization factors (*Lp*). The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by $\sigma(F) = [(I + \sigma(I)/Lp)^{1/2} - (I/Lp)^{1/2}]$.

With MULTAN78¹⁹ 14 of the 24 non-hydrogen atoms were located from an *E* map based on the best phase set. The remaining atoms were found by standard Fourier techniques. Subsequent refinement of positional and anisotropic parameters by block-diagonal least-squares converged to $R_F = 0.046$. The hydrogen positions were found in a difference Fourier map. Hydrogen temperature factors were given a value corresponding to the isotropic value of the atom they are attached to. Refinement of the non-hydrogen atom parameters and of the positional parameters of hydrogen was continued with weights

(15) IR and NMR data of this compound were identical with those of an authentic sample.

(16) Reactions of I with 4-MeOC₆H₄N₃ or [Ni(1,4-(4-MeOC₆H₄)₂N₄)₂] yielded mixtures of tetraazabutadiene-nickel complexes. These reactions will be discussed in a forthcoming paper.^{2c}

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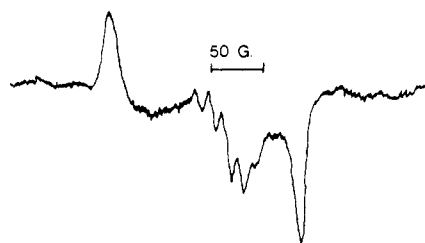
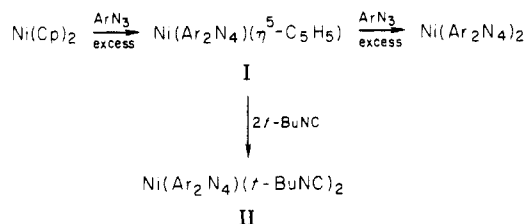


Figure 1. ESR spectrum of $[\text{Ni}(\text{1,4-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (I).

Scheme I



according to $w^{-1} = \sigma^2(F_0) + gF_0^2$, where the parameter g is chosen to give flat agreement analyses. Fractional atomic coordinates are given in Table II, and anisotropic thermal parameters are given in Table IIA (supplementary material). A final electron density difference Fourier synthesis showed no significant features higher than $0.3 \text{ e}/\text{\AA}^3$.

Scattering factors for nickel, nitrogen, and carbon are those of Cromer and Mann,²⁰ and the values for hydrogen were taken from Stewart, Davidson, and Simpson.²¹ All computer calculations were performed on a CDC CYBER-175 computer at the computer center of the University of Utrecht.

Programs used in this structure analysis included the programs CAD4TAPE (D. Kaas) for handling the raw diffractometer output, ASYM (A. L. Spek) for data averaging and ordering, PLUTO,²² PLATO (bonds, angles, planes, torsion angles, etc. with standard deviations), ORTEP,²³ OMEGA (tabulation) from the EUCLID Package by A. L. Spek, and the XRAY-76 system (Stewart²⁴) for most of the other calculations.

Results

Synthesis and Properties. In a previous paper we reported the synthesis of $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$, which may be obtained not only from the reaction of $[\text{Ni}(\text{COD})_2]$ with aryl azide (ArN_3) but also from the reaction of $[\text{Ni}(\text{Cp})_2]$ with aryl azides^{2b} (Scheme I). When the latter reaction is broken off after the color of the reaction mixture has changed from green to deep brown, an intermediate product, i.e., $[\text{Ni}(\text{1,4-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (I), can be isolated, albeit in low yield ($\pm 10\%$). This product may be separated from the starting products $[\text{Ni}(\text{Cp})_2]$ and $4\text{-MeC}_6\text{H}_4\text{N}_3$ as well as from some final product $[\text{Ni}(\text{1,4-(4-MeC}_6\text{H}_4)_2\text{N}_4)_2]$ by column chromatography.

The cyclopentadienyl ligand of I was easily displaced in the reaction with 2 equiv of $t\text{-BuNC}$, leading to $[\text{Ni}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ (II) in essentially quantitative yield. Furthermore, reaction of I with $4\text{-MeC}_6\text{H}_4\text{N}_3$ led to formation of $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$, which was isolated in 52% yield.¹⁶ Attempted reactions of I with PPh_3 , PET_3 , $t\text{-BuDAB}$, bis(4-nitrophenyl)sulfur diimide, AgSbF_6 , or MeI at room temperature were not successful. If more vigorous conditions were applied, some reaction took place but no identifiable nickel complexes could be isolated from the resultant mixtures.

I is a paramagnetic, slightly air sensitive, black crystalline solid. Solutions in toluene and THF are stable, but decom-

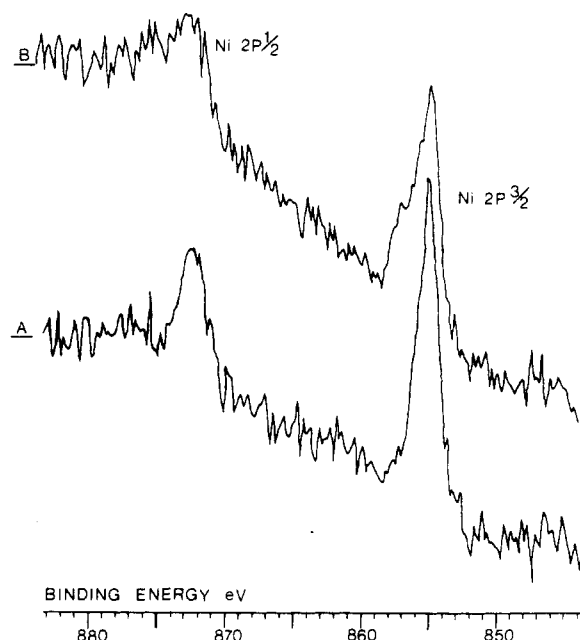


Figure 2. X-ray photoelectron spectra of the Ni(2p) region of $[\text{Ni}(\text{1,4-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (A) and $[\text{Ni}(\text{1,4-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$ (B).

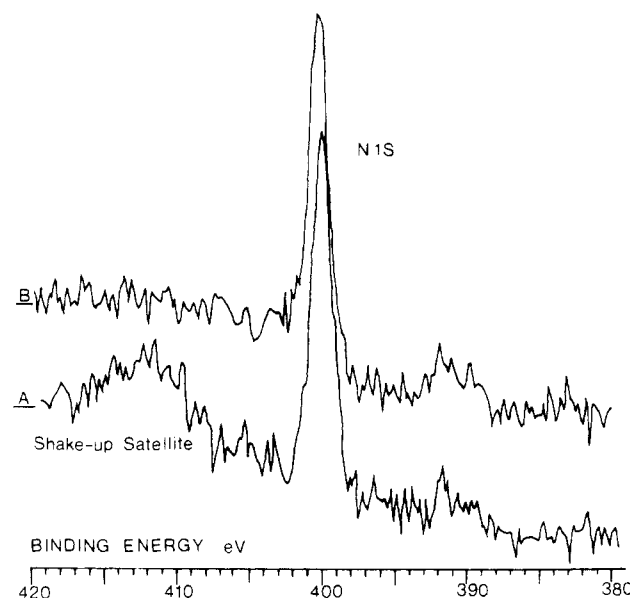


Figure 3. X-ray photoelectron spectra of the N(1s) region of $[\text{Ni}(\text{1,4-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (A) and $[\text{Ni}(\text{1,4-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$ (B).

position takes place in acetone, CCl_4 , CHCl_3 , CH_2Cl_2 , and hydrochloric acid. The stoichiometry of the compound was determined by elemental analysis.

The structural features as well as the bonding in I have been studied by using a variety of spectroscopic techniques. The ESR spectrum (X band in toluene at 4.2 K) of I (see Figure 1) shows an orthorhombic signal with nitrogen hyperfine coupling on g_2 .

X-ray photoelectron spectra showed a shake-up satellite in the N(1s) band, but no such phenomena were observed in the Ni(2p) band. These spectra, along with those of $[\text{Ni}(\text{1,4-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$ are shown in Figures 2 and 3.

No band could be attributed to the N_4 moiety in the IR spectra of I or II. However, the IR spectrum of II showed the stretching frequencies of the terminally bonded isocyanides.

Molecular Geometry. The molecular structure of the title compound along with the adopted numbering scheme are

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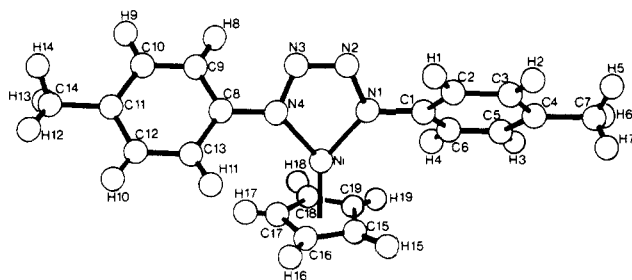


Figure 4. PLUTO drawing of the molecular structure of [Ni(1,4-(4-MeC₆H₄)₂N₄)(η^5 -C₅H₅)], showing the numbering scheme of the atoms.

Table III. Bond Distances (Å) and Angles (Deg) for C₁₉H₁₉N₄Ni

Ni-N(1)	1.853 (2)	C(4)-C(5)	1.387 (4)
Ni-N(4)	1.843 (2)	C(4)-C(7)	1.508 (4)
Ni-C(15)	2.096 (3)	C(5)-C(6)	1.377 (3)
Ni-C(16)	2.104 (3)	C(8)-C(9)	1.380 (3)
Ni-C(17)	2.073 (3)	C(8)-C(13)	1.383 (3)
Ni-C(18)	2.139 (3)	C(9)-C(10)	1.380 (3)
Ni-C(19)	2.109 (3)	C(10)-C(11)	1.382 (4)
N(1)-N(2)	1.344 (2)	C(11)-C(12)	1.370 (4)
N(1)-C(1)	1.422 (3)	C(11)-C(14)	1.515 (4)
N(2)-N(3)	1.278 (2)	C(12)-C(13)	1.383 (3)
N(3)-N(4)	1.346 (2)	C(15)-C(16)	1.345 (5)
N(4)-C(8)	1.427 (3)	C(15)-C(19)	1.390 (5)
C(1)-C(2)	1.392 (3)	C(16)-C(17)	1.364 (5)
C(1)-C(6)	1.379 (3)	C(17)-C(18)	1.390 (5)
C(2)-C(3)	1.380 (3)	C(18)-C(19)	1.387 (5)
C(3)-C(4)	1.381 (3)		
N(1)-Ni-N(4)	80.43 (7)	C(4)-C(5)-C(6)	121.6 (2)
Ni-N(1)-N(2)	114.9 (1)	C(1)-C(6)-C(5)	120.7 (2)
Ni-N(1)-C(1)	131.1 (1)	N(4)-C(8)-C(9)	121.4 (2)
N(2)-N(1)-C(1)	112.3 (2)	N(4)-C(8)-C(13)	119.6 (2)
N(1)-N(2)-N(3)	114.9 (2)	C(9)-C(8)-C(13)	119.0 (2)
N(2)-N(3)-N(4)	113.6 (2)	C(8)-C(9)-C(10)	120.2 (2)
Ni-N(4)-N(3)	115.7 (1)	C(9)-C(10)-C(11)	121.2 (2)
Ni-N(4)-C(8)	131.1 (1)	C(10)-C(11)-C(12)	118.1 (2)
N(3)-N(4)-C(8)	112.5 (2)	C(10)-C(11)-C(14)	121.4 (3)
N(1)-C(1)-C(2)	121.1 (2)	C(12)-C(11)-C(14)	120.5 (3)
N(1)-C(1)-C(6)	120.5 (2)	C(11)-C(12)-C(13)	121.5 (2)
C(2)-C(1)-C(6)	118.4 (2)	C(8)-C(13)-C(12)	120.0 (2)
C(1)-C(2)-C(3)	120.2 (2)	C(16)-C(15)-C(19)	108.6 (3)
C(2)-C(3)-C(4)	121.7 (2)	C(15)-C(16)-C(17)	108.2 (3)
C(3)-C(4)-C(5)	117.4 (2)	C(16)-C(17)-C(18)	109.3 (3)
C(3)-C(4)-C(7)	121.5 (2)	C(17)-C(18)-C(19)	105.9 (3)
C(5)-C(4)-C(7)	121.2 (2)	C(15)-C(19)-C(18)	107.9 (3)
N(1)-Ni-Cp ^a	140.7 (1)	N(4)-Ni-Cp ^a	139.0 (1)

^a Cp is the centroid of the Cp ring.

shown in a PLUTO drawing (Figure 4) and an ORTEP drawing (Figure 5, supplementary material). Bond distances and angles are given in Table III, torsion angles are given in Table IV, and least-square planes are given in Table V (supplementary material).

The crystal structure consists of discrete monomeric [1,4-bis(4-tolyl)tetraazabutadiene](η^5 -cyclopentadienyl)nickel units. Each central nickel atom is coordinated to an η^5 -bonded cyclopentadienyl group and, via two nitrogen atoms at the 1- and 4-positions, to the tetraazabutadiene system. The aryl rings are perpendicular to each other (89.5 (1)°) and make angles

Table IV. Some Relevant Torsion Angles (Deg) for C₁₉H₁₉N₄Ni^a

N(4)-Ni-N(1)-C(1)	163.2 (9)	N(1)-Ni-N(4)-C(8)	174.1 (2)
Ni-N(1)-C(1)-C(2)	-126.8 (2)	Ni-N(4)-C(8)-C(9)	-130.9 (2)
N(2)-N(1)-C(1)-C(2)	37.2 (2)	N(3)-N(4)-C(8)-C(9)	38.8 (2)
Ni-N(1)-C(1)-C(6)	54.6 (2)	Ni-N(4)-C(8)-C(13)	51.0 (2)
N(2)-N(1)-C(1)-C(6)	-141.5 (2)	N(3)-N(4)-C(8)-C(13)	-139.3 (2)
N(1)-N(2)-N(3)-N(4)	7.7 (2)		

^a The torsion angle A(1)-A(2)-A(3)-A(4) is viewed along A(2)-A(3), with a clockwise rotation of A(1) to A(4) taken to be positive (Klyne and Prelog convention).

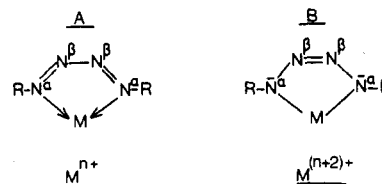


Figure 6. Two canonical forms for the formal valence structure of the coordinated tetraazabutadiene ligand.

of 45.0 (1) and 44.8 (1)°, respectively, with the NiN₄ plane, which is slightly puckered (rms deviation from the least-squares plane through NiN₄ is 0.028 Å; the maximum deviation is 0.043 (10) Å) (see Table V). The distances of the outer two N-N bonds, N(1)-N(2) = 1.344 (2) [1.346] Å and N(3)-N(4) = 1.346 (2) [1.348] Å are equal within their standard deviations, whereas the central N-N bond, N(2)-N(3) = 1.278 (2) [1.279] Å, is significantly shorter by 0.069 (3) Å. The numbers in brackets are values corrected for thermal motion. The cyclopentadienyl ring is flat with somewhat shorter bond lengths for C(15)-C(16) and C(16)-C(17) (1.345 (3) and 1.364 (5) Å, respectively). The dihedral angle between the planes through the cyclopentadienyl ring and the NiN₄ least-squares plane is 88.6 (6)° (see Table V).

Discussion

Reactivity of I. I is fairly stable to both decomposition and oxidation whereas most of the analogous [Ni(η^5 -C₅H₅)L₂] complexes are sensitive to air.⁹ In our experience the chemical reactivity of I is fairly limited. The reaction with *t*-BuNC, to yield II, is the only reaction we found to proceed under mild conditions. Under more vigorous conditions only the reactions with azides, yielding [Ni(Ar₂N₄)₂] products, provided identifiable nickel-containing products.^{2c} These observations point out that only with a restricted number of coligands can isolable tetraazabutadiene-nickel complexes be formed.

Molecular Structure and Bonding in [Ni(1,4-(4-MeC₆H₄)₂N₄)(η^5 -C₅H₅)] (I). In previous papers^{2b,3} we considered the bonding in tetraazabutadiene-metal complexes, which in most cases can be satisfactorily described by the limiting structures A and B (see Figure 6), representing the R₂N₄ moiety as either a neutral or a dianionic ligand, respectively. The N-N distances, the geometry around the metal, and the angles between the MN₄ ring and the aryl rings (if R is aromatic) are expected to be significantly different for either of the above-mentioned canonical forms and therefore can be used in determining which canonical form prevails in a given complex.

A clear example in which A dominates the bonding is the [Ni(Ar₂N₄)₂] complex,^{2b,3} which on the basis of all available evidence must be formulated as a Ni⁰ species. The assignment of [P(1,4-(4-NO₂C₆H₄)₂N₄)(CHC(PET₃)H(CH₂)₂CH=CHCH₂CH₂(PET₃))] as a platinum(II) complex according to form B is equally clear, not only because the complex possesses the observed reactivity and XPS spectra but also because the tetraazabutadiene ligand contains a N^β-N^β distance of 1.263 (8) Å and N^α-N^β distances of 1.385 (7) and 1.391 (7) Å, respectively.²⁵

The general trend in these complexes, as illustrated here by $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$, $[\text{Ni}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$, and the above-mentioned tetraazabutadiene-platinum complex, is a shortening of the $\text{N}^\beta\text{-N}^\beta$ bond and lengthening of the $\text{N}^\alpha\text{-N}^\beta$ bonds on increasing the net charge transfer from a filled metal d orbital to the LUMO of the ligand. This orbital is bonding between the N^β atoms but antibonding between N^α and N^β . A consequence of the accommodation of charge by the ligand is the breakup of the conjugated arrangement of the double bonds in the Ar_2N_4 system. Whereas in $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ this conjugation between the aryl rings and the N_4 π system keeps each $\text{Ni}(\text{Ar}_2\text{N}_4)$ fragment planar, in $[\text{Ir}(1,4\text{-FC}_6\text{H}_4)_2\text{N}_4\text{-(CO)(PPh}_3)_2\text{BF}_4]$, containing a dianionic Ar_2N_4 ligand, the aryl rings are twisted out of the IrN_4 plane.²⁶

The Ni-N distances in I and $[\text{Ni}(1,4\text{-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$ are equal within experimental error at 1.85 Å. As π back-donation is an important factor in these complexes, as in metal-olefin complexes, a short Ni-N distance in I was expected. However, since this distance apparently does not change upon population of the ligand LUMO, it seems correct to regard this orbital as located mainly on the tetraazabutadiene ligand.

The X-ray structure determination of $[\text{Ni}(1,4\text{-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (I) shows the complex to be almost isostructural with the recently reported $[\text{Co}(1,4\text{-(C}_6\text{F}_5)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$.⁵ Both complexes show appreciable contribution of form B to the bonding: (i) the short $\text{N}^\beta\text{-N}^\beta$ bonds are equal within experimental error at 1.278 Å, (ii) the $\text{N}^\alpha\text{-N}^\beta$ distances are significantly larger at around 1.35 Å, and (iii) the aryl rings are twisted out of the MN_4 plane and are mutually perpendicular. Although $\text{N}^\alpha\text{-N}^\beta$ distances in the cobalt complex are still somewhat smaller than the values reported for N-N single bonds in uncoordinated organic molecules,²⁷ this diamagnetic complex can be considered as a clear example of a Co^{III} complex. In contrast the formal oxidation state of Ni in the paramagnetic complex I is less obvious. When the structural features of I are taken into account, two possibilities can be envisaged: a Ni^{III} (17e) structure with the tetraazabutadiene ligand as a formally dianionic unit or a Ni^{II} (18e) structure in which the odd electron is accommodated by the Ar_2N_4 ligand and the metal is locally diamagnetic.

On the basis of the XPS results of I alone a choice between these two possibilities can not be made. The absolute value of the Ni(2p) BE (I, $\text{Ni}(2p_{3/2}) = 855.2$ eV; $[\text{Ni}(1,4\text{-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$, $\text{Ni}(2p_{3/2}) = 855.0$ eV) gives no reliable indication as to the formal metal oxidation state,²⁸⁻³⁰ in contrast to the unambiguous correlation found for the formal oxidation state of platinum and the Pt(4f) BE.³¹ However, the values observed for I fit very well with those reported for nickel

complexes containing a bidentate nitrogen-donor ligand.³²

It has been pointed out that a paramagnetic nickel complex should exhibit shake-up satellites in the XPS spectra of the Ni(2p) orbitals.³³ The applicability of this principle has been shown in studies differentiating between tetrahedral and square-planar nickel(II) complexes^{28,29a} and determining whether the odd electron resides mainly on the metal or on the ligand.^{29a} In I shake-up satellites are not observed in the XPS Ni(2p) band. Such satellites are to be expected if the complex contains a nickel(III) center, with the odd electron residing on the metal being coupled to the two N^α atoms.

The fact that a shake-up satellite does occur in the N(1s) band (see Figure 3) seems to suggest therefore that I is a nickel(II) species with the odd electron residing mainly on the tetraazabutadiene ligand. By comparison in the XPS spectra of $[\text{Ni}(1,4\text{-(3,5-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4)_2]$ (see Figure 3) shake-up satellites are absent in the N(1s) band, which is in line with our previous formulation of this compound as a 18e Ni^0 species. However, care must be taken when drawing conclusions from these XPS N(1s) spectra. Studies of azo compounds and their metal complexes, none of which are paramagnetic, have shown that shake-up phenomena can be observed in the N(1s) bands.^{29c,d} These observations warrant further investigation.

In contrast to these XPS results the ESR data seem to provide more straightforward information concerning the bonding pattern in I. If I was to be considered as a nitrogen-centered radical complex of nickel(II), all three g values would be expected to lie close to the spin-only value of 2.002³³ and the electron expected to be coupled with all four N atoms. The fact that coupling to only two, equivalent, N atoms is observed together with an appreciable orbital contribution to the g values strongly suggests that the unpaired electron is located primarily on the metal. This indicates that I should be considered as a 17e nickel(III) species containing the tetraazabutadiene ligand as a formally dianionic unit. Furthermore, comparison of these ESR data with those of $[\text{Ni}(2,2'\text{-bpy})(\eta^5\text{-C}_5\text{H}_5)]$ ($g_1 = 2.183$, $A_N = 7$ G; $g_2 = 2.080$, $A_N = 9$ G; $g_3 = 2.033$, $A_N = 11.5$ G)^{9,35} shows apart from the different g values a difference in coupling behavior. In the spectra of I, nitrogen coupling is only observed on g_2 , while in the bpy-nickel complex coupling on all three g factors is observed.

Conclusions

$[\text{Ni}(1,4\text{-(4-MeC}_6\text{H}_4)_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (I) is a stable intermediate in the reactions of aryl azides with $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$, which yield $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$. I is less inert than the $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ complexes, but the observed reactivity is still fairly limited, the only reactions to date being substitution of the cyclopentadienyl ring by two *tert*-butyl isocyanide ligands under mild conditions and ligand-exchange and -rearrangement reactions under more vigorous conditions.¹⁶

On the basis of its structural features and paramagnetic behavior, I can probably best be described as a formally 17e nickel(III) complex.

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assistance with the recording and interpretation of the XPS spectra. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation of Pure Research (ZWO).

Registry No. I, 73440-09-2; II, 73440-08-1; [Ni(1,4-(4-

MeC₆H₄)₂N₄)₂], 73432-46-9; [Ni(Cp)₂], 1271-28-9; 4-MeC₆H₄N₃, 2101-86-2.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters (Table IIA), and least-squares planes (Table V) and an ORTEP drawing (Figure 5) (25 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of [W(CH₂PMe₃)(CO)₂Cl(PMe₃)₃][CF₃SO₃], a Seven-Coordinate Tungsten(II) Complex Produced by Transfer of a PMe₃ Ligand to the W=CH₂ System

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The title complex, prepared by Schrock and co-workers from the reaction of [W(=CH₂)(PMe₃)₄Cl⁺][CF₃SO₃⁻] with CO, crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 9.249$ (2) Å, $b = 11.911$ (3) Å, $c = 13.573$ (3) Å, $\alpha = 81.49$ (2)°, $\beta = 78.63$ (2)°, $\gamma = 84.96$ (2)°, $V = 1447.2$ (6) Å³, $\rho(\text{calcd}) = 1.77$ g cm⁻³ for $Z = 2$, and mol wt 770.8. Diffraction data were collected with a Syntex P₂ automated four-circle diffractometer, and the structure was refined to $R_F = 4.3\%$ and $R_{wF} = 4.8\%$ for all 4048 independent reflections with $3.5^\circ < 2\theta < 46.0^\circ$ (Mo K α radiation). The coordination environment of the tungsten atom approximates to a monocapped trigonal-prismatic geometry. One triangular face is occupied by atom C(3) of an ordered CO ligand and by atoms P(1) and P(2) of PMe₃ ligands [W-C(3) = 1.957 (8) Å, W-P(1) = 2.548 (2) Å, and W-P(2) = 2.567 (2) Å], while the other triangular face contains P(3) of the third PMe₃ ligand [W-P(3) = 2.495 (2) Å] and disordered CO/Cl ligands, which were successfully resolved [W-C(1) = 1.968 (19) Å, W-Cl(1) = 2.557 (5) Å; W-C(2) = 1.940 (19) Å, W-Cl(2) = 2.527 (5) Å]. The CH₂PMe₃ ligand is linked to tungsten with W-C(4) = 2.305 (7) Å and occupies the capping position on the square face defined by P(1), P(2), C(1)/Cl(1), and C(2)/Cl(2).

Introduction

There are few examples of transition-metal complexes containing terminal methylene ligands, an observation that has, in some cases, been attributed to the high reactivity of the methylene complex under the conditions in which it is formed.¹ The first discovery of such a species, that of Ta(η^5 -C₅H₅)₂(=CH₂)(CH₃) by Schrock and co-workers,² has recently been followed by their synthesis of [W(=CH₂)(PMe₃)₄Cl⁺][CF₃SO₃⁻], a methylene complex of W(IV).³ Other examples of methylene ligands exist in tungsten chemistry, although none have been isolated as stable solids. Thus, [W(η^5 -C₅H₅)₂(=CH₂)(CH₃)⁺], which is isoelectronic with Ta(η^5 -C₅H₅)₂(=CH₂)(CH₃), was postulated as an intermediate in the formation of [W(η^5 -C₅H₅)₂(C₂H₄)H⁺] from [W(η^5 -C₅H₅)₂(CH₃)₂]⁺[PF₆⁻] upon treatment of the latter with the trityl radical.⁴ A similar species, [W(η^5 -C₅H₅)₂(=CH₂)H⁺], has also been proposed.⁵

Evidence supporting the structures of these intermediate methylene complexes was provided by the isolation of stable phosphonium ylide complexes with the formulas [W(η^5 -C₅H₅)₂(CH₂PMe₂Ph)CH₃]⁺[PF₆⁻] and [W(η^5 -C₅H₅)₂(CH₂PMe₂Ph)H⁺][PF₆⁻], respectively. Other examples of attack by a tertiary phosphine on an unsaturated carbon producing a phosphoylide are known. Thus the vinyl-bridged cluster (μ -H)Os₃(CO)₁₀(CH=CH₂) reacts with PMe₂Ph,

Table I. Experimental Data for the X-ray Diffraction Study of [W(CH₂PMe₃)(CO)₂Cl(PMe₃)₃][CF₃SO₃]

(A) Crystal Parameters ^a at 23 °C	
cryst syst: triclinic	space group: $P\bar{1}$
$a = 9.2494$ (20) Å	$\alpha = 81.487$ (18)°
$b = 11.9113$ (26) Å	$\beta = 78.626$ (18)°
$c = 13.5734$ (32) Å	$\gamma = 84.960$ (18)°
$V = 1447.2$ (6) Å ³	mol wt 770.8
$Z = 2$	$\rho(\text{calcd}) = 1.77$ g cm ⁻³
(B) Intensity Data	
radiation: Mo K α [$\lambda = 0.710730$ Å]	
monochromator: highly oriented graphite	
2θ range: 3.5–46.0°	
reflectns measd: $+h, \pm k, \pm l$	
scan type: $\theta(\text{cryst}) - 2\theta(\text{counter})$	
scan speed: 2.50° min ⁻¹	
scan range: [$2\theta(K\alpha_1 - 1.0)$]–[$2\theta(K\alpha_2 + 1.0)$]°	
reflectns collected: 4234 total yielding 4048 independent	
abs coeff: 46.5 cm ⁻¹	

^a Based on a least-squares fit to the setting angles of the unresolved Mo K α peaks of 25 reflections with $2\theta = 25$ –31°.

giving the 1,3-dipolar species (μ -H)Os₃(CO)₁₀(μ -C⁻-HCH₂P⁺Me₂Ph).⁶ The bridging formyl ligand in the complex [Ta(η^5 -C₅Me₄Et)₂Cl₂]₂(CHO)(H)⁷ undergoes a reaction with PMe₃, resulting in cleavage of the carbon-oxygen bond and formation of the ylide [Ta(η^5 -C₅Me₄Et)Cl₂]₂(C⁻HP⁺Me₃)(O)(H).⁸ The η^1 -alkynyl complex Fe(η^5 -C₅H₅)(CO)₂(η^1 -C \equiv CPh) reacts with PPh₃ in the presence of acid to yield [Fe(η^5 -C₅H₅)(CO)₂(η^1 -C(PPh₃) \equiv CHPh)⁺].⁹

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