(as subsequently confirmed by the X-ray structure) that N(2), binding solely an aryl substituent, would not also be bound to tungsten. The chelation of this arylhydrazido(1−) ligand then is essentially similar to that of the phenylhydrazine ligand observed in the complex $[CpMoI(NO)(H_2NNHPh)][BF_4]$.[35] The equivalence of the Cp resonances (and the two NH protons) requires, if the W coordination sphere is rigid, that the NN vector must lie in the Cp_2W midplane and that the N(2)–C bond is in the same plane, unless there is a low barrier to inversion at a pyramidal N(2) as expected for an aryl substituent.

In the IR spectra two strong bands were observed due to ν_{sym} and ν_{asym} of the NH_2 group, at 3240 and 3300 cm^{-1}, respectively (3260 and 3340 cm^{-1} for PF_6^- salts). The NH_2 bend occurred close to 1610 cm^{-1}, partly coincident with an aryl mode. With ^{15}N substitution at N(1), no band in the region 1600–800 cm^{-1} shifted significantly, so ν(NN) is apparently inactive in the infrared and could not be identified. A relatively intense band, not present in **1** and so characteristic of the coordinated arylhydrazido(1−) ligand in **2**, appeared near 1325 cm^{-1}. It is tentatively assigned to ν(N(2)-C(aryl)) since a band is commonly found in this region for arylamines. The frequency is higher than the usual single-bond C–N group frequency, which may be due to partial C–N multiple bonding and conjugation of the lone pair with the aryl ring. This same effect may also explain the tendency for the aryl protons in **2** to be at somewhat higher field than in the corresponding **1** complexes.

Continuing studies of this reaction, aimed at elucidating the mechanism of the formation of complexes **1** and **2**, will be reported subsequently.

Acknowledgment. The Natural Science and Engineering Research Council, Canada, is thanked for support through an operating grant and for the award of a postgraduate scholarship (to J.A.C.).

Registry No. **1a**, 73493-31-9; **1b**, 73493-24-0; **1b**-^{15}N(2), 74449-39-1; **1c**, 73493-29-5; **1c**-^{15}N(1), 74449-41-5; **1d**, 73493-26-2; **2a**, 73358-31-3; **2b**, 73358-24-4; **2b**-^{15}N(2), 74449-43-7; **2c**, 73358-28-8; **2c**-^{15}N(1), 74449-45-9; **2d**, 73358-26-6; Cp_2WH_2, 1271-33-6.

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The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Structure of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNC_6H_5)][BF_4]$: A Complex Containing the Unusual Side-On-Bonded Phenylhydrazido(1−) Ligand

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The structure of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNC_6H_5)][BF_4]$ has been determined by X-ray crystallography. The W atom has a pseudotetrahedral geometry with two of the coordination sites occupied by the cyclopentadienyl rings (Cp) and two by the novel side-on-bonded phenylhydrazido(1−) ligand. This unusual ligand has resulted from the insertion of $(C_6H_5)N_2^+$ into both W–H bonds of $(\eta^5\text{-}C_5H_5)_2WH_2$. The two W–N bond lengths are inequivalent (2.156 (9) and 2.034 (9) Å) with the shorter distance corresponding to the three-coordinate nitrogen atom, which is bonded to the phenyl group. This relatively short W–N distance may result from involvement of the free lone pair of electrons on this nitrogen atom in bonding with the W atom. The N–N distance of 1.43 (1) Å corresponds to a normal N–N single bond. The perpendicular distances from W to the Cp rings are 1.9839 (5) and 1.9695 (5) Å. The Cp–W–Cp angle is 136.8°, and the N–W–N angle is 39.7 (3)°. The phenyl ring is bent out of the W–N–N plane by 34.5 (8)°. This compound crystallizes in the space group $C_{2h}^5\text{–}P2_1/c$ with a = 8.5874 (6) Å, b = 10.4821 (8) Å, c = 19.5455 (14) Å, β = 107.176 (6)°, and Z = 4. On the basis of 1972 unique, observed reflections and 225 parameters varied, the structure was refined by full-matrix, least-squares techniques to R = 0.045 and R_w = 0.057. In this refinement all nonhydrogen atoms were refined anisotropically, the two hydrazido hydrogen atoms were refined isotropically, and all other hydrogen atoms were included as fixed contributions.

Introduction

The insertion reactions of aryldiazonium cations into transition-metal–hydride bonds have received much attention,[1-3] owing in part to the possible relevance of such studies to the biological reduction of dinitrogen, as initially suggested by Parshall.[4] Although several examples of monoinsertion reactions, in which an aryldiazonium cation inserts into one metal hydride bond, have been characterized and reported,[1-3] the isolation and characterization of stable products resulting from the double insertion of N_2Ph^+ into two metal–hydride bonds have not been reported until recently.[5,6] The hydrazido(1−) species resulting from this double-insertion reaction represents an important intermediate in model system studies of dinitrogen reduction.

The reaction of Cp_2WH_2 with N_2Ph^+ at low temperature initially yields[5,6] the monoinserted species $[Cp_2WH(NNHPh)]^+$. At room temperature this unstable intermediate rearranges to the diinserted product $[Cp_2W(H_2NNPh)]^+$, which on the basis of spectral measurements was believed to contain the novel side-on-bonded phenylhydrazido(1−) ligand.[5,6] Since the mode of coordination of the hydrazido(1−) ligand in such a complex is of interest in order to gain information related to the stereochemical processes occurring during dinitrogen reduction, the structure of the above hydrazido(1−) complex, as the BF_4^- salt, was undertaken in order to confirm this highly unusual bonding mode. A preliminary

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communication of this work has appeared.[5]

Experimental Section

Deep red crystals of the title compound were kindly supplied by Professor Sutton of Simon Fraser University. Preliminary film data showed Laue symmetry $2/m$, indicating a monoclinic system. The systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$) uniquely defined the space group as $P2_1/c$. Accurate cell parameters were obtained by a least-squares analysis of 12 accurately centered reflections, chosen from diverse regions of reciprocal space ($50° \leq 2\theta \leq 75°$, Cu K$\alpha$ X-radiation) and obtained by using a narrow X-ray source. Table I contains the pertinent crystal data.

Data were collected by the θ–2θ scan method on a Picker four-circle automated diffractometer, equipped with a scintillation counter and pulse-height analyzer tuned to accept 90° of the Cu Kα peak. Background counts were measured at both ends of the scan range with both crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections. The intensities of these standards decreased by approximately 4% over the duration of the data collection, and the observed intensities were corrected for this apparent decomposition.

The intensities of 2789 unique reflections ($3° \leq 2\theta \leq 120°$) were measured by using Cu Kα X-radiation. Data were processed in the usual manner by using a value of 0.05 for p.[7] A total of 1972 reflections had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in subsequent calculations. Absorption corrections were applied to the data by using Gaussian integration.[8]

Structure Solution and Refinement

A sharpened Patterson synthesis yielded the position of the W atom, and subsequent refinements and difference Fourier calculations led to the location of all other atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation[9] for all atoms except hydrogen, for which the values of Stewart et al.[10] were used. Anomalous dispersion terms[11] for W were included in F_c.

The carbon atoms of the phenyl group were refined as individual anisotropic atoms, while two refinement techniques were used for the cyclopentadienyl carbon atoms. In the first method, the Cp rings[12] were treated as hindered rotor groups[13] with D_{5h} symmetry. The positions, orientations, and the radii of these groups and their barriers to libration perpendicular to their group planes were refined. This refinement method has the important advantage over individual atom treatments that more chemically reasonable C–C distances for the Cp rings are obtained. Furthermore, significantly fewer parameters are refined by using this technique (see Table I). In the second method the cyclopentadienyl carbon atoms were refined as individual anisotropic atoms. The converged refinements for both models are briefly compared (vide infra); however, in spite of the advantages of the rigid-body refinement, only the individual atom refinement is reported in detail, owing to the better standard deviations in the parameters of interest obtained by using this model. In both refinement techniques, the phenyl and cyclopentadienyl hydrogen atoms were included as fixed contributions in the final few least-squares refinements. The idealized positions of the phenyl hydrogen atoms were calculated from the geometries about the attached carbon atom by using a C–H distance of 0.95 Å. These hydrogen atoms were given isotropic thermal parameters of 1 Å^2 greater than the equivalent isotropic B of their attached carbon atoms. The cyclopentadienyl hydrogen atoms were included as hindered rotor groups in both refinement methods using the group parameters obtained from the previous hindered rotor refinement of the Cp carbon atoms. The group thermal parameters were set at 1 Å^2 greater than those of the corresponding carbon atom group. The remaining nonhydrogen atoms were refined individually with anisotropic thermal parameters, while the two hydrogen atoms on N(1) were refined individually with isotropic thermal parameters. The final model, with individual anisotropic Cp carbon atoms, converged at $R = 0.045$ and $R_w = 0.057$[14] for 225 variables. In the final difference Fourier map, the highest 20 residuals (0.03–0.90 e/Å^3) were in the vicinity of the W atom and the BF_4^- anion. A typical carbon atom on earlier Fourier maps had an intensity of approximately 4.00 e/Å^3. Some difficulty was encountered in refining the BF_4^- anion owing to disorder of this group. More sophisticated models describing this disorder were not used, however, since the four fluorine positions used were clearly the most obvious from difference Fourier calculations (peaks from 2.5–5.4 e/Å^3). In addition, the added effort was not judged worthwhile as no change in the parameters of interest was

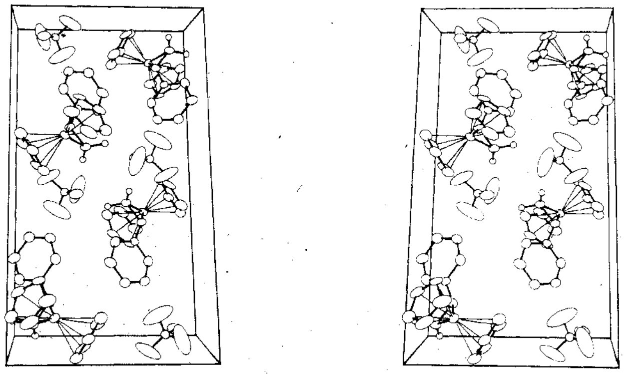

Figure 1. Stereoview of the unit cell of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$. The x axis is going into the page, the y axis is from left to right, and the z axis is from top to bottom. In this and all subsequent diagrams vibrational ellipsoids of 20% are shown for all atoms, except hydrogens which are shown artificially small.

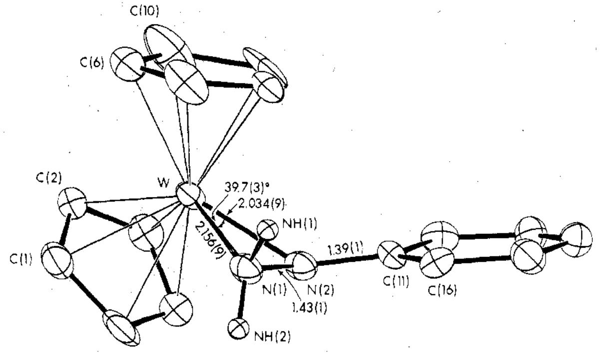

Figure 2. Perspective view of the $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)]^+$ cation showing the numbering scheme and some relevant parameters. Numbering of ring atoms is sequential around the rings.

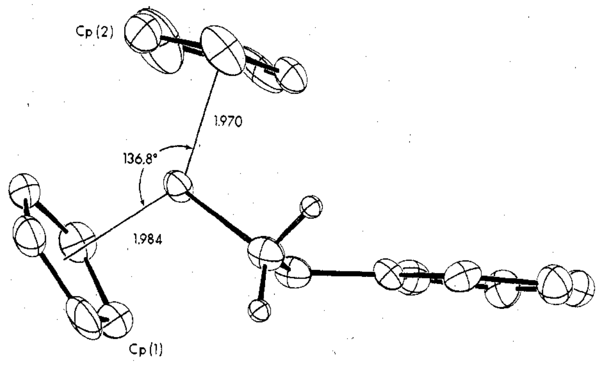

Figure 3. View of the $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)]^+$ cation in the plane of W–N(1)–N(2) showing the orientation of the phenyl group.

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(12) Abbreviations used: Cp = C_5H_5; Ph = C_6H_5; CR1 = center of Cp ring 1; CR2 = center of Cp ring 2; Me = CH_3; L = ligand.

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(14) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table I. Summary of Crystal Data, Intensity Collection, and Refinement Information

compd		$[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$
fw		507.98
formula		$W_1F_4B_1N_2C_{16}H_{17}$
cell parameters		
a, Å		8.5874 (6)
b, Å		10.4821 (8)
c, Å		19.5455 (14)
β, deg		107.176 (6)
V, Å^3		1680.9
Z		4
density, g/cm^3		2.007 (calcd), 2.01 (1) (exptl; flotation in aqueous $ZnBr_2$)
space group		C_{2h}^5-$P2_1/c$
cryst dimens, mm		0.231 × 0.158 × 0.180
cryst shape		monoclinic prism with major faces of the form {100}, {001}, {$\bar{1}$02}, {$\bar{1}$0$\bar{1}$}, {011}
cryst vol, mm^3		0.0359
temp, °C		22
radiatn		Cu Kα (λ 1.540 562 Å)
μ, cm^{-1}		132.74
range in abs corr factors (applied to F_o^2)		0.171–0.329
receiving aperture, mm		3.4 wide × 5.2 high (30 cm from crystal)
takeoff angle, deg		3.0
scan speed, deg/min		2 (in 2θ)
scan range, deg		0.80 below Kα_1 to 0.80 above Kα_2
bkgd counts, s		$2\theta \leqslant 99.00°$, 20; $2\theta > 99.00°$, 40
2θ limits, deg		3.0–120.0
unique data used ($F_o^2 \geqslant 3\sigma(F_o^2)$)		1972
model 1^a	final no. of parameters varied	149
	error in observn of unit wt, electrons	1.736
	R	0.048
	R_w	0.064
model 2^b	final no. of parameters varied	225
	error in observn of unit wt, electrons	1.640
	R	0.045
	R_w	0.057

[a] Cp rings treated as hindered rotors. [b] Cp rings treated as individual anisotropic atoms.

anticipated; certainly there was no significant change in these parameters between the refinements before and after inclusion of the anion.

The final positional and thermal parameters of the individual refined atoms and the group atoms are given in Table II. The idealized hydrogen positions and their thermal parameters and a listing of observed and calculated structure amplitudes used in the refinement are available.[15]

Description of the Structure

The structure of $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$ consists of four monomeric anions and cations per unit cell. Figure 1 shows a stereoview of the unit cell, while Figure 2 shows a perspective view of the cation, including the numbering scheme used (phenyl hydrogen atoms have the same number as their attached carbon atoms) and some relevant bond lengths. The representation of the cation, shown in Figure 3 and viewed in the W–N(1)–N(2) plane, shows the orientation of the phenyl ring in relation to the W–N(1)–N(2) plane and the Cp planes (vide infra).

The description of the tetrafluoroborate anion is somewhat inadequate owing to the disorder of this group. As a result, the thermal parameters for the four fluorine atoms are large (Table II) and much of the unassigned electron density in the final difference Fourier map lies in the region around the anion. In spite of the disorder, however, the anion clearly shows the expected tetrahedral configuration about the boron atom. The B–F distances, which range from 1.14 (2) to 1.38 (2) Å (Table III) are somewhat shorter than other reported values[16] but are not unreasonable considering the disorder. In addition, the F–B–F angles, ranging from 103 (2) to 114 (1)° (Table IV) are as expected. There are two significant nonbonded contacts between the fluorine atoms and the hydrogen atoms of the hydrazido ligand (F(1)–NH(2) = 2.1 (1) Å; F(2)–NH(1) = 2.0 (1) Å), both of which are much less than the sum of their van der Waals radii (2.57 Å). The corresponding N(1)–NH(1)–F(2) and N(1)–NH(2)–F(1) angles are 139 (8) and 154 (10)°, respectively.

The $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)]^+$ cation can be viewed as having pseudotetrahedral coordination about the tungsten atom, with the ($\eta^5\text{-}C_5H_5$) rings each occupying one coordination site and the two nitrogen atoms of the "side-on"-bonded phenylhydrazido(1–) ligand occupying the other sites. However, the coordination angles are significantly distorted from the ideal geometry owing to the large bulk of the Cp rings and the small bite angle of the hydrazido ligand; the CR1–W–CR2[12] angle is 136.8° while the N(1)–W–N(2) angle is 39.7 (3)°. There are no unusually short nonbonded interactions between the two cyclopentadienyl rings. The metal–carbon bond lengths are in the range 2.28 (1)–2.36 (1) Å for ring 1 (average 2.32 (3) Å) and 2.26 (1)–2.34 (1) Å for ring 2 (average 2.29 (3) Å). These M–C distances are quite typical for $CpML_n$[12] compounds.[17,18] The perpendicular distances between the metal and the ring planes are 1.9839 (5) Å (ring 1) and 1.9695 (5) Å (ring 2). They agree well with the metal–ring center distances (ring 1, 1.985 Å, and ring 2, 1.971 Å), indicating that each ring is well centered above the metal atom.

A comparison of Cp–M–Cp angles within a series of Cp_2ML_2 complexes containing staggered Cp groups indicates that the CR1–W–CR2 angle (136.8°) in the present compound, although comparable to other values (126.0–135.3°), is somewhat larger. An analysis of these angles[17] indicates that the larger angles tend to correspond to shorter Cp–M distances, implying that these angles are governed primarily by intramolecular repulsions. The small N(1)–W–N(2) angle (39.7 (3)°) in the present compound probably results in a less crowded environment for the Cp rings and consequently a larger CR1–W–CR2 angle. In $Cp_2Ti(\eta^2\text{-}C_6H_5CN)\text{-}2,6\text{-}(CH_3)_2C_6H_3$,[19] which also has a small ligand bite angle (35.1 (2)°), the Cp–Ti–Cp angle is again larger than that expected from the Cp–Ti distances.

The cyclopentadienyl rings assume a staggered conformation with C–CR1–CR2–C torsion angles averaging 32.9° (see Table IV). Other studies on similar systems have indicated that these ring conformations are governed primarily by crystal packing.[17] The carbon atoms in each of the rings are coplanar to within 0.01 Å (ring 1) and 0.02 Å (ring 2). Within each ring the C–C bond distances are in the range 1.38 (2)–1.43 (2) Å for ring 1 (average 1.41 (3) Å) and 1.32 (2)–1.49 (2) Å for ring 2 (average 1.37 (6) Å). These average values are shorter than the predicted value of 1.43 Å.[20] However, this

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Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$

atom	x^a	y	z	$U_{11}{}^b$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.04371 (5)	0.27650 (5)	0.38366 (2)	6.00 (3)	6.14 (3)	6.00 (3)	0.50 (2)	0.57 (2)	0.95 (2)
N(1)	0.266 (1)	0.385 (1)	0.4153 (5)	7.2 (6)	7.8 (7)	6.3 (5)	0.2 (5)	0.3 (4)	−0.4 (5)
N(2)	0.252 (1)	0.3023 (8)	0.3557 (4)	7.7 (5)	6.8 (6)	5.9 (5)	0.2 (4)	0.7 (4)	−0.4 (4)
C(1)	0.044 (2)	0.171 (1)	0.4859 (6)	11.1 (10)	9.4 (9)	7.3 (7)	−0.7 (8)	2.4 (7)	1.9 (7)
C(2)	−0.082 (2)	0.118 (1)	0.4293 (7)	9.4 (8)	7.0 (8)	10.0 (9)	−0.2 (6)	3.1 (7)	2.0 (7)
C(3)	−0.014 (2)	0.058 (2)	0.3810 (8)	11.4 (10)	9.3 (10)	9.8 (10)	0.6 (8)	3.4 (9)	1.3 (8)
C(4)	0.154 (2)	0.069 (1)	0.407 (1)	10.5 (11)	7.6 (10)	14.8 (13)	3.1 (8)	4.7 (10)	4.0 (9)
C(5)	0.192 (2)	0.138 (1)	0.4728 (8)	7.9 (8)	10.0 (11)	11.5 (11)	0.7 (7)	0.6 (8)	5.9 (9)
C(6)	−0.187 (2)	0.390 (2)	0.379 (1)	9.7 (12)	15.2 (18)	14.8 (16)	6.2 (12)	5.8 (11)	6.8 (14)
C(7)	−0.079 (2)	0.476 (1)	0.372 (1)	10.7 (11)	7.3 (10)	15.1 (16)	4.0 (8)	0.4 (11)	−0.9 (9)
C(8)	−0.039 (2)	0.446 (2)	0.311 (1)	9.7 (10)	8.9 (11)	11.8 (12)	3.3 (9)	2.4 (10)	4.7 (9)
C(9)	−0.123 (3)	0.348 (2)	0.2774 (7)	12.5 (14)	16.7 (19)	6.9 (8)	7.2 (13)	−2.7 (9)	−0.4 (10)
C(10)	−0.225 (2)	0.308 (2)	0.323 (2)	5.7 (8)	10.8 (16)	25 (3)	−0.7 (8)	−3.9 (12)	3.9 (15)
C(11)	0.302 (1)	0.345 (1)	0.2982 (5)	5.3 (5)	6.1 (7)	5.7 (5)	1.1 (4)	1.0 (4)	0.3 (5)
C(12)	0.260 (2)	0.270 (1)	0.2373 (7)	8.4 (8)	7.1 (7)	8.9 (8)	0.1 (6)	1.5 (6)	−0.0 (6)
C(13)	0.318 (2)	0.298 (1)	0.1805 (7)	11.8 (10)	7.6 (10)	7.8 (8)	0.6 (7)	3.8 (7)	−0.8 (6)
C(14)	0.405 (1)	0.407 (2)	0.1802 (7)	8.0 (8)	11.6 (12)	7.9 (8)	0.8 (8)	2.8 (6)	0.3 (8)
C(15)	0.446 (1)	0.483 (1)	0.2413 (7)	5.6 (5)	8.2 (9)	12.1 (10)	0.3 (5)	1.8 (6)	1.8 (8)
C(16)	0.394 (1)	0.454 (1)	0.2994 (6)	5.8 (5)	7.6 (8)	8.6 (7)	0.2 (5)	2.0 (5)	−0.9 (6)
B	−0.348 (2)	0.225 (1)	0.0503 (7)	6.4 (7)	6.4 (7)	7.0 (7)	1.8 (6)	0.0 (6)	−0.5 (6)
F(1)	−0.486 (1)	0.163 (1)	0.0555 (5)	10.6 (6)	18.0 (9)	12.2 (7)	−3.5 (6)	−0.4 (5)	4.6 (6)
F(2)	−0.250 (3)	0.152 (2)	0.043 (2)	36 (3)	19.4 (16)	62 (4)	14.7 (18)	36 (3)	17 (2)
F(3)	−0.290 (4)	0.264 (3)	0.106 (1)	44 (4)	66 (5)	19.9 (18)	−39 (4)	14 (2)	−17 (2)
F(4)	−0.375 (2)	0.310 (2)	0.004 (1)	17.5 (13)	25.5 (18)	34 (2)	1.4 (12)	4.4 (14)	18.9 (18)
NH(1)	0.25 (1)	0.49 (1)	0.404 (5)	7 (3)^c					
NH(2)	0.37 (2)	0.37 (1)	0.452 (6)	8 (3)^c					

[a] Estimated standard deviations in the least significant figure are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The quantities given for the U's are the thermal coefficients × 10^2. [c] Isotropic B (Å^2).

Table III. Selected Interatomic Distances (Å) in $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$

	Bonded Contacts		
W–N(1)	2.156 (9)	C(3)–C(4)	1.38 (2)
W–N(2)	2.034 (9)	C(4)–C(5)	1.43 (2)
W–C(1)	2.28 (1)	C(5)–C(1)	1.41 (2)
W–C(2)	2.29 (1)	C(6)–C(7)	1.34 (2)
W–C(3)	2.33 (2)	C(7)–C(8)	1.36 (2)
W–C(4)	2.36 (1)	C(8)–C(9)	1.32 (2)
W–C(5)	2.33 (1)	C(9)–C(10)	1.49 (3)
W–C(6)	2.29 (1)	C(10)–C(6)	1.35 (3)
W–C(7)	2.34 (1)	C(11)–C(12)	1.38 (2)
W–C(8)	2.26 (1)	C(12)–C(13)	1.37 (2)
W–C(9)	2.28 (1)	C(13)–C(14)	1.37 (2)
W–C(10)	2.29 (1)	C(14)–C(15)	1.39 (2)
N(1)–N(2)	1.43 (1)	C(15)–C(16)	1.37 (2)
N(1)–NH(1)	1.08 (11)	C(16)–C(11)	1.39 (1)
N(1)–NH(2)	0.97 (13)	B–F(1)	1.38 (2)
N(2)–C(11)	1.39 (1)	B–F(2)	1.18 (2)
C(1)–C(2)	1.41 (2)	B–F(3)	1.14 (2)
C(2)–C(3)	1.40 (2)	B–F(4)	1.24 (2)
	Nonbonded Contacts		
F(1)–NH(2)	2.1 (1)^a	H(2)–C(6)	2.90
F(2)–NH(1)	2.0 (1)^b	H(8)–C(11)	2.72
F(3)–H(9)	2.48	H(10)–C(2)	2.78
NH(1)–H(16)	2.19	H(12)–N(2)	2.52
NH(1)–H(8)	2.43	H(16)–N(1)	2.60
H(2)–H(10)	2.37	H(16)–N(2)	2.67
H(2)–C(10)	2.68		

Hindered Rotor Parameters

Cp(1)	Cp(2)
C–C = 1.421 (6) Bd = 1.82^c	C–C = 1.423 (6) Bd = 0.42

[a] NH(2) is associated with the molecule at the general equivalent position x, $^1/_2 - y$, $^1/_2 + z$. [b] NH(1) is associated with the molecule at the general equivalent position $\bar{x}$, $^1/_2 + y$, $^1/_2 - z$. [c] Bd is the barrier to libration in units of $2kT$, where k is the Boltzmann constant and T is the temperature.

Table IV. Selected Angles (Deg) in $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$

	Bond Angles		
N(1)–W–N(2)	39.7 (3)	C(1)–C(2)–C(3)	109 (1)
W–N(1)–NH(1)	115 (6)	C(2)–C(3)–C(4)	108 (1)
W–N(1)–NH(2)	133 (8)	C(3)–C(4)–C(5)	108 (1)
W–N(1)–N(2)	65.6 (5)	C(4)–C(5)–C(1)	108 (1)
W–N(2)–N(1)	74.8 (6)	C(5)–C(1)–C(2)	106 (1)
W–N(2)–C(11)	140.1 (6)	C(6)–C(7)–C(8)	108 (2)
N(2)–N(1)–NH(1)	117 (5)	C(7)–C(8)–C(9)	112 (2)
N(2)–N(1)–NH(2)	112 (7)	C(8)–C(9)–C(10)	105 (2)
NH(1)–N(1)–NH(2)	107 (10)	C(9)–C(10)–C(6)	105 (2)
N(1)–N(2)–C(11)	119.4 (9)	C(10)–C(6)–C(7)	111 (2)
N(2)–C(11)–C(12)	117 (1)	F(1)–B–F(2)	111 (2)
N(2)–C(11)–C(16)	124.2 (9)	F(1)–B–F(3)	104 (2)
C(11)–C(12)–C(13)	121 (1)	F(1)–B–F(4)	114 (1)
C(12)–C(13)–C(14)	120 (1)	F(2)–B–F(3)	103 (2)
C(13)–C(14)–C(15)	118 (1)	F(2)–B–F(4)	112 (2)
C(14)–C(15)–C(16)	121 (1)	F(3)–B–F(4)	112 (2)
C(15)–C(16)–C(11)	119 (1)	N(1)–NH(1)–F(2)	139 (8)^a
C(16)–C(11)–C(12)	119 (1)	N(1)–NH(2)–F(1)	154 (10)^b
CR1–W–CR2	136.8		
	Torsion Angles		
NH(1)–N(1)–N(2)–C(11)	32.3	C(3)–CR1–CR2–C(9)	33.5
C(1)–CR1–CR2–C(6)	31.2	C(4)–CR1–CR2–C(8)	34.7
C(2)–CR1–CR2–C(10)	32.1	C(5)–CR1–CR2–C(7)	33.2
	Vector/Plane Normal Angles		
N(2)–N(1)/NH(1)–N(1)–NH(2)	44 (7)^c		
N(2)–C(11)/W–N(1)–N(2)	55.5 (8)^c		

[a] F(2) is associated with the molecule at the general equivalent position $\bar{x}$, $^1/_2 + y$, $^1/_2 - z$. [b] F(1) is associated with the molecule at the general equivalent position x, $^1/_2 - y$, $^1/_2 + z$. [c] Angle between the vector defined by the first two atoms and the normal to the plane defined by the last three atoms.

apparent shortening is a consequence of thermal libration of the rings and is a general feature of η^5-C_5H_5 compounds where the Cp rings are refined as individual atoms. In this respect the hindered rotor refinement is useful since the ring radii are allowed to vary as the ring librates about the metal–CR axis. This model for the Cp groups minimizes the ring contraction that is so common when individual atom refinements are used.[17] From the hindered rotor refinement the C–C distances (1.421 (6) and 1.423 (6) Å for rings 1 and 2, respectively) agree very well with each other and with the predicted value.

Table V

Least-Squares Plane Calculations[a]

plane no.	equation	plane no.	equation
1	$-0.2728X + 0.7327Y - 0.6235Z + 1.8482 = 0$	4	$0.1702X - 0.4923Y - 0.8536Z + 7.8509 = 0$
2	$0.1126X + 0.8539Y - 0.5081Z + 3.3639 = 0$	5	$-0.7532X + 0.5300Y - 0.3897Z + 0.9023 = 0$
3	$-0.6073X + 0.6045Y - 0.5155Z - 1.1396 = 0$	6	$-0.8250X + 0.3563Y - 0.4387Z + 1.8727 = 0$

Deviations from the Planes (Å)

	plane no.					
atom	1	2	3	4	5	6
W	0.0	1.9839 (5)[b]	−1.9695 (5)[b]	0.0		
N(1)	0.0			−0.774 (10)[b]		0.0
N(2)	0.0			0.639 (8)[b]		0.0
C(1)		0.01 (1)				
C(2)		−0.01 (1)				
C(3)		0.01 (2)				
C(4)		0.00 (2)				
C(5)		−0.01 (2)				
C(6)			−0.02 (2)			
C(7)			0.02 (2)			
C(8)			−0.01 (2)			
C(9)			0.01 (2)			
C(10)			0.00 (2)			
C(11)	0.79 (1)[b]				−0.01 (1)	0.0
C(12)					0.03 (1)	
C(13)					−0.03 (2)	
C(14)					0.02 (1)	
C(15)					−0.01 (1)	
C(16)					0.00 (1)	
CR1				0.0		
CR2				0.0		

Dihedral Angles between Planes

plane A	plane B	angle, deg	plane A	plane B	angle, deg
1	2	24.3	1	6	40.6
1	3	21.6	2	3	44.8
1	4	82.8	5	6	11.9
1	5	33.2			

[a] *X, Y,* and *Z* are the orthogonal coordinates (Å) with *X* along the *a* axis, *Y* in the *a–b* plane, and *Z* along the *c** axis. [b] Not included in the least-squares plane calculation.

In the individual atom refinement of the Cp rings the group with the shorter average C–C distance (ring 2) also has the higher thermal parameters and corresponds to the group having the lower barrier to libration in the hindered rotor description (Table III).

The phenylhydrazido ligand is side-on bonded to the W atom through the two nitrogen atoms. The W–N(1)–N(2) plane essentially bisects the CR1–W–CR2 angle, and the dihedral angle between these planes is 82.8° (Table V). The two metal–nitrogen bonds are noticeably different, with W–N(1), involving the four-coordinate nitrogen atom (2.156 (9) Å), being significantly longer than W–N(2) (2.034 (9) Å), which involves the three-coordinate nitrogen atom. The shorter distance may result from donation of the available lone pair on N(2) to the metal, although the W atom formally has an 18-electron configuration already. Similar electron donation from the chloro ligands to the metal atoms is believed responsible for the short M–Cl bonds in Cp_2MCl_2 complexes.[17] The possible involvement of the free lone pair on N(2) may also explain the phenyl group orientation (see Figure 3) and the solution NMR characteristics[5,6] (vide infra). The W–N bonds can be compared to typical W–N single bonds in pyridine complexes which lie in the range 2.23–2.32 Å.[21,22] On the other hand, hydrazido(2−) complexes, with M–N bond orders greater than 1, typically have M–N bond lengths of ca. 1.75 Å.[23] While there are no other reported η^2 hydrazido(1−) metal compounds, a comparison can be made with the related compounds $[(\eta^5\text{-}C_5H_5)Mo(NO)I]_2(\mu\text{-}NNMe_2)$[24] and $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4]$.[25] In these species the Mo–N bonds involving the four-coordinate nitrogen atoms (2.133 (12)–2.184 (3) Å) are again significantly longer than that of the three-coordinate nitrogen atom (2.058 (12) Å), and both classes of W–N bonds compare well with the analogous distances in the present hydrazido(1−) complex. As a consequence of the above asymmetric bonding of the hydrazido(1−) ligand, the two nitrogen atoms are not equally spaced from the CR1–W–CR2 plane; instead N(1) is 0.774 (10) Å from the plane, and N (2) is displaced 0.639 (8) Å from this plane.

The N–N bond length in the title complex (1.43 (1) Å) compares well with the values for the two molydenum hydrazido compounds (1.400 (17)[24] and 1.430 (5) Å[25]) and is typical of an N–N single bond. By comparison, a characteristic N–N double bond is ca. 1.23 Å.[26] Both hydrogen atoms on N(1) were located and refined, resulting in normal N–H bond distances of 1.08 (11) Å for N(1)–NH(1) and 0.97

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(13) Å for N(1)–NH(2). The NH(1)–N(1)–NH(2) angle is 107 (10)°, close to that expected for a tetrahedral coordination about the nitrogen, and the angle of the N(2)–N(1) vector to the normal of the NH(1)–N(1)–NH(2) plane is 44 (7)°, comparable to the calculated value of ca. 35.3° for an idealized tetrahedral coordination. No electron density that would be consistent with a hydrogen atom is observed in the vicinity of N(2). This is consistent with the solution NMR studies[6] which show both protons on N(1) and none on N(2). It is somewhat surprising that both hydrazido hydrogen atoms are bonded to N(1) since in the initial monoinserted product the hydrogen atom and the phenyl ring are bonded to the same nitrogen atom,[6] indicating that in the second insertion process the transfer of a hydrogen atom from W to N(1) is accompanied by a hydrogen transfer from N(2) to N(1). The N(2)–C(11) bond (1.39 (1) Å) is somewhat shorter than a normal N–C single bond (1.43 Å) involving an sp^2 hybridized carbon atom but is not particularly unusual. The C–C lengths in the phenyl ring are all reasonable, and the carbon atoms of the ring are coplanar to within 0.03 Å (Table V). The phenyl ring is bent out of the W–N(1)–N(2) plane by 34.5 (8)° toward Cp ring 2 with C(11) being 0.79 (1) Å out of this plane (see Figure 3).

Although the phenyl group orientation on N(2) is characteristic of sp^3 hybridization of this atom, some distortion is evident. Instead of an eclipsed configuration about the N(1)–N(2) bond, the phenyl group is staggered with respect to the N(1) hydrogen atoms (the NH(1)–N(1)–N(2)–C(11) torsion angle is 32.3°). This twist about the N(1)–N(2) bond may result because of involvement of the lone pair of electrons on N(2) in bonding with the metal atom, as the twist is in the proper direction for such an interaction and the short W–N(2) bond is consistent with some multiple-bond character (vide supra). It is also possible that this distortion from eclipsed conformations about N(1) and N(2) may be steric in origin, resulting from nonbonded interactions between the cyclopentadienyl ring 2 and the phenyl ring pushing the phenyl ring toward the W–N(1)–N(2) plane. The only such contact which is significant (C(11)–H(8) = 2.72 Å) would favor this distortion. However, we have already noted that the CR1–W–CR2 angle is greater than generally observed, indicating that the cyclopentadienyl groups are not overly crowded. The staggered conformation may also result from steric interactions between NH(1) and H(16) since this contact (2.19 Å) is rather short.

Discussion

There is a notable lack of structural information on Cp_2ML complexes, in which L is a side-on-coordinated ligand, thereby limiting any comparision of structural parameters. Only the present structure and that of $Cp_2Ti(\eta^2\text{-}C_6H_5CN)\text{-}2,6\text{-}(CH_3)_2C_6H_3$[19] are known to us. At the first glance the structural differences between these complexes and the related Cp_2ML_2 species seem to result primarily from the reduced steric demands of the η^2 coordinated ligands as compared to the two σ-bonded ligands (vide supra). However, a more detailed analysis of the differences in the two types of systems must await further structural characterizations of Cp_2ML complexes containing side-on-coordinated ligands.

The structural determination of the present complex, besides providing some of this badly needed information has also proven useful in understanding the ^1H NMR data[6] which indicate that the two cyclopentadienyl rings are equivalent, even at low temperature. This equivalence could result from the complete planarity of the hydrazido(1–) ligand framework in the plane bisecting the angle between the two Cp rings or from a fluctional process which averages the Cp ring environments. The solid-state data indicate that the two cyclopentadienyl rings are inequivalent since the phenyl group is significantly displaced from the W–N(1)–N(2) plane toward Cp ring 2. As suggested earlier, this phenyl ring orientation may result from involvement of the free lone pair on atom N(2) in bonding with the W atom. This proposed bonding would account for the short W–N(2) bond length and, if the Cp equivalence results from "flipping" of the phenyl ring from one side of the W–N(1)–N(2) plane to the other, could also explain the facility of this process. The involvement of the N(2) lone pair in bonding with the W atom would allow the "flipping" mechanism to proceed by a concerted process with the simultaneous involvement of two N(2) electron pairs with the W atom. The involvement of the free lone pair on N(2) is not necessary to arguments regarding the flipping however, since N(2) can be viewed as an amino nitrogen atom, being bonded to W, N(1), and C(11), and the inversion of amines is known to occur readily.

The $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)]^+$ cation is believed to be the first structurally characterized complex containing a hydrazido(1–) ligand,[27] an important intermediate species in model systems for the reduction of dinitrogen. Although Hidai and co-workers[28] have reported the structure of a species which they claim is a hydrazido(1–) complex, $[WClBr_2(N_2H_3)(PMe_2Ph)_3]$, their crystallographic evidence does not support this claim, and even the authors admit doubt concerning its formulation. Certainly in solution their evidence for a species containing the $NHNH_2$ ligand is convincing, but their solid-state structure is more characteristic of a hydrazido(2–) ligand with a $W{=}N{=}NH_2$ moiety. All of their structural parameters, including the short W–N bond (1.80 (4) Å), the almost linear W–N–N fragment (177 (5)°), and the N–N distance (1.24 (6) Å) which is characteristic of an N=N double bond, support a terminally bonded hydrazido(2–) formulation. Furthermore, this structure bears a remarkable resemblance to the hydrazido(2–) complex $[W(\text{quinolin-8-olate})(NNH_2)(PMe_2Ph)_3]I$, recently reported by Chatt and coworkers.[23] The authors' suggestion[28] that the complex $[WClBr_2(N_2H_3)(PMe_2Ph)_3]$ may actually contain a $W\text{–}N\text{–}NH_3^+$ moiety is also not consistent with the observed structural parameters, in particular the short N–N distance. Our formulation of the title complex as a hydrazido(1–) species, on the other hand, is quite unambiguous with all parameters being consistent with this formulation; even the hydrazido hydrogen atom positions are well-defined.

The present structural determination is particularly relevant to our understanding of dinitrogen reduction. Insertion reactions of aryldiazo cations into metal–hydride bonds have long been considered as useful model systems for nitrogen fixation, and the complex $[Cp_2W(H_2NNPh)][BF_4]$ represents the first characterized species resulting from the "double insertion" of an aryldiazo cation into both metal–hydride bonds of a dihydrido species. This species is one step closer to a totally reduced N_2Ph^+ cation than the products obtained from the usual monoinsertion reactions. Furthermore the novel side-on coordination of this arylhydrazido(1–) ligand is relevant since both nitrogen atoms are activated by the W atom, suggesting the possibility of further reduction of this ligand.

Double-insertion reactions involving Cp_2MH_2 compounds (M = Mo, W) have been reported,[29] for example in the reactions with azobenzene and diazofluorene. However, the "double-insertion" products were not isolated, undergoing

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(27) A preliminary communication has appeared containing the report of an apparent hydrazido(1–) complex. However, the details are few and sketchy and some are apparently in error. See: McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Organomet. Chem.* **1979**, *168*, C1.

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instead loss of the reduced diazo molecule and subsequent attack of the "Cp_2M" species by excess ligand. Intermediates in hydride insertion reactions were obtained with diazodicarboxylate molecules,[29] but these reactions stopped at the monoinserted product. The title complex therefore represents an important intermediate in model system studies for the reduction of dinitrogen. Further studies are presently underway[30] in an attempt to structurally characterize the unstable first product $[Cp_2WH(NNHPh)][BF_4]$ in the above insertion reaction, in order to gain a better understanding of the factors favoring the unusual double-insertion reaction.

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Registry No. $[(\eta^5\text{-}C_5H_5)_2W(H_2NNC_6H_5)][BF_4]$, 73358-24-4.

Supplementary Material Available: Table VI showing the idealized hydrogen parameters and a listing of the observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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[30] Sutton, D., personal communication.

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Substituent Effects in the Control of the Oxidation–Reduction Properties of Metal Ions in Complexes with Macrocyclic Ligands

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The complexes $[Ni(Me_n[Z]tetraenatoN_4)]$ (Z = 14, 15 or 16) contain dianionic macrocyclic ligands having pairs of charged, unsaturated chelate rings which contain nucleophilic centers. These species have been used to produce a wide variety of substituted derivatives $[Ni(Me_nE_m[Z]tetraenatoN_4)]$ with the substituent ranging from electron-donating alkyl groups to electron-withdrawing nitro groups. The numbers of methyl substituents on the saturated chelate rings (n) have also been varied. The effects of the substituent (E) on the properties of the central metal atom are both large and systematic. Both the position of the d–d electronic band maximum (for the planar Ni^{II} ion) and half-wave potential for the Ni^{2+}/Ni^{3+} couple vary linearly with Hammett substituent constants. The correlations (R) are good and the sensitivities (ρ) large if the substituents are directly attached to the unsaturated chelate ring. Tests with various Hammett σ constants failed to indicate the mode of transmission of the electronic effects. Remote substituents (para-substituted benzoyl groups) gave relatively small effects. Significantly, the sensitivities (ρ values) to both direct and remote substituents were found to be essentially identical with those reported for porphyrin derivatives. Changes in the numbers of methyl groups on the saturated rings produce no effect, supporting the view that both the reduced and oxidized forms of the complexes contain planar nickel. This class of ligands facilitates close control over the electronic properties of the central metal atom.

Introduction

The design and synthesis of small molecules and ions that are capable of performing functions identified with metal-containing natural products are a multifaceted problem.[1,2] The natural products to be mimicked are complicated protein derivatives, and, most generally and somewhat simplistically, the protein provides two principal structural components to the coordination site.[1,2] It provides much of the primary ligand field, thereby determining the electronic properties of the metal ion, and it provides further aspects of the active-site environment. The work described here is concerned with the first set of relationships, the control of the electronic properties of the metal ion. Because heme proteins are involved in oxidation–reduction[3-5] processes, such studies are particularly germane to model heme protein studies. Complexes with synthetic macrocyclic ligands are uniquely convenient for the evaluation of the dependence of oxidation–reduction properties of metal chelates on the detailed structure of the ligand while a given metal ion is maintained in an essentially constant coordination geometry. A variety of kinds of process have been identified depending primarily on the metal ion, the ligand, and the solvent. These include oxidation and reduction of the central metal ion,[6-10] various oxidation and reduction reactions of the ligand,[7-14] and processes which involve both the central metal atom and the ligand.[8] The present study is concerned with the first kind of process, those centered on the metal ion. Complexes of neutral tetraaza macrocycles have dominated earlier studies of this kind. For a large number of such ligands it has been possible to identify electrode processes that are attributable to the same metal ion couple. Perhaps it is an indication of the ligating efficacy of tetraaza macrocycle that the previously rarely observed Ni^{2+}/Ni^{3+} couple has figured most heavily in these studies. The influences of various structural features[6] have been quantitated, including ring size,[6,15,17] degree and arrangement of unsaturation,[6,7,10,16] and alkyl substitution.[9,16]

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