

lattice site. The value of the effective 5s-electron density around the tin atom is in consonance with the characterization of the metal atom as being formally in the stannous state, which should not, however, be taken to imply the existence of Sn^{2+} ions in this structure.

From the above description of the bonding involving the tin atom in $\text{TaS}_2\text{-Sn}$, it will be clear that the oxidation state is simply a formality which has no real meaning in such compounds. Operationally, the ^{119}Sn isomer shift value suggests that the 5s-electron density at the tin nucleus is not very much different from what is observed in covalent "stannous" compounds. The trigonal-bipyramidal bonding to the five nearest-neighbor atoms, on the other hand, is similar to that encountered in organotin species, especially those in which a bridging ligand can give rise to a linear array of (planar) trialkyltin moieties. In such compounds, the tin atom is frequently considered to be formally in the "zerovalent" state. In the case of $\text{TaS}_2\text{-Sn}$, the formal oxidation state of the tin atom can only be described in purely phenomenological terms and has no fundamental significance in describing the elec-

tronic environment around the Sn atom.¹⁶

Acknowledgment. The authors are indebted to Dr. G. A. Wiegers for the sample of $\text{TaS}_2\text{-Sn}$ used in his crystallographic studies and to Professors J. San Filippo and H. Schugar for helpful discussions. This research was supported in part under Grant DMR 7808615A01 of the Division of Materials Research of the National Science Foundation and by a grant from the Center for Computer and Information Services, Rutgers University. This support is herewith gratefully acknowledged. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation.

Registry No. $\text{TaS}_2\text{-Sn}$, 52953-71-6; ^{119}Sn , 14314-35-3.

- (16) After this paper was submitted for publication Dr. G. A. Wiegers communicated to us the fact that a different interpretation describing the bonding in TaS_2 intercalates had been developed in the thesis work of R. Eppinga, Groningen, Feb 1980. In this description, the s orbital of the post transition metal is presumed to participate in the bonding with the TaS_2 sandwich, rather than involving sp^2 hybrid orbitals in the x-y plane. This work is to be published.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. NMR and IR Spectroscopic Characterization of "End-On"- and "Side-On"-Bound Arylhydrazido Ligands Formed by Insertion of the Arenediazonium Ion into a W-H Bond in $(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2$

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Received January 31, 1980

The hydride Cp_2WH_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) in toluene reacts with equimolar $[\text{ArN}_2][\text{X}]$ ($\text{Ar} = \text{Ph}$, $p\text{-FC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, or $p\text{-MeOC}_6\text{H}_4$; $\text{X} = \text{BF}_4$ or PF_6) in methanol below ca. -20°C to give yellow salts **1** of composition $[\text{Cp}_2\text{WH}(\text{NNHAr})][\text{X}]$. These have been fully characterized by IR and ^1H NMR (with ^{15}N isotopic substitution) to contain the formally arylhydrazido(2-) ligand bound to W through N(1). Temperature dependence of the ^1H NMR of the Cp groups shows the cation to be nonrigid, and this is interpreted to be due to a rotation of the plane of the hydrazido(2-) ligand molecular skeleton into the plane bisecting the angle subtended at the W atom by the Cp groups (the Cp_2W "midplane"). The stereochemistry of the arylhydrazido(2-) ligand and its orientation in the ground state are examined. Repeating the synthesis at ca. 0°C or stirring solutions of **1** near this temperature produces an isomeric product **2** of composition $[\text{Cp}_2\text{W}(\text{H}_2\text{NNAr})][\text{X}]$ which is an arylhydrazido(1-) complex in which the ligand is bound to W through both nitrogen atoms. The IR and ^1H NMR (with ^{15}N isotopic substitution) are discussed by comparison with the X-ray crystallographically determined structure reported elsewhere.

Introduction

It is now some 12 years since Parshall first demonstrated the ability of arenediazonium ions to apparently insert into the Pt-H bond in $\text{PtHCl}(\text{PEt}_3)_2$ and suggested that the resulting aryldiazene ligand might be an analogue of one hypothetical dinitrogen hydride intermediate in the mechanism of biological nitrogen fixation.¹ In the intervening years, considerable refinement has occurred in our understanding of the nitrogen-fixing enzyme nitrogenase² and, in particular, direct synthesis of molybdenum- and tungsten-bound dinitrogen hydrides by the protonation of coordinated dinitrogen in one or two specific complexes of Mo and W has been achieved.³ Despite this progress we have, as yet, only a primitive knowledge of the chemistry of dinitrogen hydride ligands, their electronic and geometrical features, the possible rearrangements they may undergo, their coordinating ability, their reactions, and their part in biological nitrogen fixation.

Until improved and more general methods for their synthesis become available, one alternative is to examine dinitrogen hydride ligands stabilized by the presence of an organic group, and some examples of these are conveniently synthesized from arenediazonium ions and suitable hydrido complexes as Parshall showed. Though the chemistry thus identified necessarily has diminished relevance to actual biological nitrogen fixation, it is an important foundation for the development of systems in which transition-metal complexes activate molecular nitrogen for the synthesis of organonitrogen compounds. Here, we report that the apparent insertion of an arenediazonium ion into one W-H bond in Cp_2WH_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) does not yield an aryldiazene ($\text{ArN}=\text{NH}$) complex but gives instead the complex ion $[\text{Cp}_2\text{WH}(\text{NNHAr})]^+$ (**1**) which formally contains an arylhydrazido(2-) ligand. This complex rearranges in solution and in the solid state to give $[\text{Cp}_2\text{W}(\text{H}_2\text{NNAr})]^+$ (**2**) in which now an arylhydrazido(1-) ligand is bound side-on to the tungsten through both nitrogen atoms. A preliminary report of this work has been published.⁴ In no instance have we been successful in duplicating, in these

(1) G. W. Parshall, *J. Am. Chem. Soc.*, **89**, 1822 (1967).
 (2) S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortensen, E. I. Stiefel, J. R. Chisnell, W. J. Brill, and V. K. Shah, *J. Am. Chem. Soc.*, **100**, 3814 (1978).
 (3) J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, **78**, 589 (1978).

(4) J. A. Carroll, D. Sutton, M. Cowie, and M. D. Gauthier, *J. Chem. Soc., Chem. Commun.*, 1059 (1979); M. Cowie and M. D. Gauthier, *Inorg. Chem.*, following paper in this issue.

reactions of Cp_2WH_2 with diazonium salts, the aryldiazenido complex $[Cp_2W(N_2Ar)][BF_4]$ referred to briefly by others.⁵

Experimental Section

The hydride Cp_2WH_2 was synthesized from WCl_6 (Alfa Inorganic Inc.) according to the published method and sublimed under vacuum from the crude product.⁶ Reactions were carried out in a standard Schlenk apparatus connected to a switchable nitrogen/vacuum system. Manipulations were conducted under nitrogen in the Schlenk apparatus or in a nitrogen-filled Vacuum Atmospheres Inc. drybox. Solvents were dried, purified, and distilled under nitrogen by using standard methods.⁷ Infrared spectra were obtained as KBr pressed disks prepared in the drybox and run on a Perkin-Elmer 457 instrument calibrated with polystyrene. ¹H NMR spectra were recorded at 100 MHz on a Varian XL-100 or at 60 MHz on a Varian A56/60 instrument. Temperatures were calibrated by using the chemical shifts of a methanol sample.⁸ ¹⁵N Fourier transform NMR spectra were obtained at 10.15 MHz on the XL-100 equipped with a multinuclear broad-band frequency synthesizer, using ca. 70 mg of ¹⁵N-enriched (96%) sample in a 12-mm diameter sample tube. Gated decoupled spectra were recorded with the decoupling off during acquisition. Typically, 1000–2000 scans were accumulated with 0.25-s acquisition time, 25- μ s pulse width, and 4-s delay. Microanalyses were performed by Mr. M. K. Yang of the Simon Fraser University Microanalytical Unit. Diazonium salts were synthesized by diazotization of the appropriate arylamine using $NaNO_2$. The ¹⁵N isotopic label was introduced at N(1) by using $Na^{15}NO_2$ (96% ¹⁵N) and at N(2) by using aniline-¹⁵N (99% ¹⁵N), purchased from Stohler Isotope Chemicals.

Reactions of Cp_2WH_2 with Diazonium Salts: (a) *p*-Fluorobenzenediazonium Hexafluorophosphate. **Procedure a.** The reaction was carried out in a 200-mL three-neck flask equipped with two pressure-equalizing addition funnels, connected to the N_2 /vacuum system. About 5–10 mL of the solution of Cp_2WH_2 (0.246 g, 0.778 mmol) in toluene (20 mL) contained in one funnel was run into the flask, which was immersed in a bath at $-30^\circ C$. The remaining hydride and a solution of $[p\text{-}FC_6H_4N_2][PF_6]$ (0.209 g, 0.777 mmol) in methanol (15 mL) were then added simultaneously, dropwise to the well-stirred solution over ca. 1 h. A transient orange color was observed where the solution of the diazonium salt contacted the bulk solution. A fine yellow solid (**1a**) quickly precipitated. A further 20 mL sample of toluene at $-30^\circ C$ was added to aid precipitation and the mixture stirred for a further 30 min. It was then filtered under nitrogen and the yellow solid **1a** washed with portions of 2:1 toluene-methanol, toluene, and finally diethyl ether (all at $-30^\circ C$) and then dried at room temperature under vacuum. The yield was 60%. This compound could be recrystallized from acetone-toluene below $-30^\circ C$. It was stored in a sealed ampule under nitrogen in a freezer at $-8^\circ C$ for 4 months without decomposition. This procedure gave the best yield of **1a** most conveniently, though the ease with which the product **1** could be precipitated with use of other arenediazonium salts varied greatly with the substituent. Yields of the isomerized product **2a** could be obtained from the filtrate by workup similar to that described in the following alternative method.

Procedure b. A similar apparatus was used. The solution of Cp_2WH_2 (91 mg, 0.29 mmol) in toluene (15 mL) was introduced to the flask and allowed to cool to $-25^\circ C$ with stirring. The solution of $[p\text{-}FC_6H_4N_2][PF_6]$ (76 mg, 0.28 mmol) in methanol (15 mL) was added dropwise over about 1 h. The yellow solid **1a** formed and was filtered off (53% yield) after the mixture was evaporated under vacuum to less than half volume. The filtrate was evaporated to dryness, redissolved in a minimum of acetone, and filtered to remove any black insoluble residue. Addition of excess toluene precipitated a dark oil which was solidified by repeated washing with portions of toluene and then recrystallized from acetone-toluene as a brown microcrystalline solid **2a**. Both analysis and ¹H NMR intensities indicated the presence of 0.7 $C_2H_3C_6H_5$ (see Table 1).

(b) **Benzenediazonium Tetrafluoroborate.** This reaction was carried out by using procedure b. The mixture became brownish yellow, and

Table 1. Analytical and Spectroscopic Data

compd	analysis ^a				¹ H NMR ^{b,c}				IR ^c			
	% C	% H	% N	NH or NH ₂	WH	Cp	aryl	other	temp., °C	solvent	NH	NH ₂
$[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]$ (1a)	34.4 (32.9)	3.01 (2.76)	4.71 (4.80)	10.8 br [1]	-2.05 [1] ^d	6.04 br s [10]	7.15–6.70 m [4]		-25	CD ₃ CN	3276 m	
$[Cp_2WH(NNHPh)][BF_4]$ (1b)	38.0 (37.8)	3.41 (3.37)	5.33 (5.51)	11.0 br [1]	e	6.13 br s [10]	7.66–6.74 m [5]		-19	CD ₃ CN	3240 s	
$[Cp_2WH(N^{15}NNHPh)][BF_4]$ (1b - ¹⁵ N/ 2)				11.8 d [1] ^f	-1.80 [1] ^g	6.31 s [5], 6.43 s [5]	7.38–6.81 m [5]		-55	(CD ₃) ₂ CO	3230 s	
$[Cp_2WH(p\text{-}NNHC_6H_4Me)][PF_6]$ (1c)	35.4 (35.2)	3.27 (3.30)	4.81 (4.83)	10.8 br [1]	-2.09 [1] ^h	6.05 s [10]	7.19 d, 6.73 d [4]	2.33 s [3] Me	-14	CD ₃ CN	3265 m	
$[Cp_2WH(p\text{-}^{15}NNHC_6H_4Me)][BF_4]$ (1c - ¹⁵ N/ 1)				10.9 br	e	6.11 s	7.22 d, 6.79 d	2.35 s Me	-24	CD ₃ CN	3240 m	
$[Cp_2WH(p\text{-}NNHC_6H_4OMe)][BF_4]$ (1d)	39.5 (37.9)	3.79 (3.56)	4.94 (5.21)	e	e	e	e				3236 m	
$[Cp_2W(p\text{-}H, NNC_6H_4F)][PF_6]$ (2a) ⁱ	38.8 (38.7)	3.31 (3.36)	4.34 (4.32)	3.90 br [2]		5.40 s [10]	7.02–6.52 m [4]	7.17 [3.5] ^j 2.32 [2] ^j	amb	CD ₃ CN	3336 m, 3261 m	
$[Cp_2W(H, NNHPh)][BF_4]$ (2b)	38.2 (37.8)	3.44 (3.37)	5.38 (5.51)	3.96 br [2]		5.52 s [10]	7.28–6.61 m [5]		amb	CD ₃ CN	3304 m, 3244 m ^k	
$[Cp_2W(p\text{-}H, NNC_6H_4Me)][BF_4]$ (2c)	38.9 (39.1)	3.85 (3.67)	5.26 (5.37)	3.92 br [2]		5.50 s [10]	7.04 d, 6.55 d [4]	2.22 s [3] Me	amb ^l	CD ₃ CN	3298 s, 3235 m ^m	
$[Cp_2W(p\text{-}H, ^{15}NNC_6H_4Me)][BF_4]$ (2c - ¹⁵ N/ 1)				3.97 d [2] ⁿ		5.49 s [10]	6.98 d, 6.53 d [4]	2.21 s [3] Me	-6	CD ₃ CN	3298 s, 3240 m	
$[Cp_2W(p\text{-}H, NNC_6H_4OMe)][BF_4]$ (2d)	37.9 (37.9)	3.61 (3.56)	5.33 (5.21)	3.92 br [2] ^o		5.49 s [10]	6.79 d, 6.57 d [4]	3.71 s [3] OMe	amb	CD ₃ CN	3303 m, 3237 m	

^a Calculated values in parentheses. ^b δ values downfield relative to internal Me₄Si. Relative integration in square brackets. ^c ν values in cm^{-1} . Abbreviations: amb, ambient; b, broad; d, doublet; m, multiplet (NMR), medium (IR); s, singlet (NMR), sharp (IR). ^d $J(^{15}N\text{-}^1H) = 106$ Hz. ^e Not investigated. ^f $J(^{15}N\text{-}^1H) = 99$ Hz. ^g $J(^{15}N\text{-}^1H) = 109$ Hz. ^h $J(^{15}N\text{-}^1H) = 109$ Hz. ⁱ 0.7 $C_2H_3C_6H_5$ solvent. ^j Ph and Me of $C_2H_3C_6H_5$ solvent. ^k 3310 m and 3250 m in $2b\text{-}^{15}N/2$. ^l The spectrum of the $[PF_6]$ salt at $-6^\circ C$ in CD_3CN shows 2.20 s [3] Me, 3.93 br [2] NH₂, 5.49 s [10] Cp, 6.52 d, 6.98 d [4] aryl. ^m 3340 s and 3270 s in $[PF_6]$ salt. ⁿ $J(^{15}N\text{-}^1H) = 88$ Hz. ^o Disappears on addition of D₂O.

(5) J. A. McCleverty and R. N. Whiteley, *J. Chem. Soc., Chem. Commun.*, 1159 (1971).

(6) M. L. H. Green and P. J. Knowles, *J. Chem. Soc., Perkin Trans. 1*, 989 (1973).

(7) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, Oxford, 1966.

(8) Varian Inc., Publication No. 87-202-001, p 28.

yellow **1b** precipitated. The filtrate gave **2b** as a brown solid which was recrystallized from acetone-toluene. The complex $[\text{Cp}_2\text{WH}(\text{}^{14}\text{N}^{15}\text{NHPH})][\text{BF}_4]$ (**1b**- $^{15}\text{N}(2)$) was synthesized similarly by using $[\text{}^{14}\text{N}^{15}\text{NPh}][\text{BF}_4]$. Solutions of **1b** in methanol or acetone became brown on stirring at room temperature, and evaporation gave the brown solid **2b**. The complex $[\text{Cp}_2\text{W}(\text{H}_2\text{}^{14}\text{N}^{15}\text{NPh})][\text{BF}_4]$ (**2b**- $^{15}\text{N}(2)$) was synthesized in this way from **1b**- $^{15}\text{N}(2)$ and recrystallized from acetone-ether-hexane as dark red crystals, used in the structure determination.⁴

(c) *p*-Tolyldiazonium Hexafluorophosphate. Procedure b gave the yellow complex **1c** in 71% yield, and the complex $[\text{Cp}_2\text{WH}(\text{}^{15}\text{N}^{14}\text{NHC}_6\text{H}_4\text{CH}_3)][\text{BF}_4]$ (**1c**- $^{15}\text{N}(1)$) was synthesized similarly by using $[\text{}^{15}\text{N}^{14}\text{NC}_6\text{H}_4\text{CH}_3][\text{BF}_4]$.

A synthesis carried out similarly at 0 °C using the diazonium tetrafluoroborate gave no yellow precipitate. Partial evaporation under vacuum gave a brown oil which subsequently solidified, was filtered off, and recrystallized from acetone-toluene to give $[\text{Cp}_2\text{W}(\text{}^{15}\text{N}^{14}\text{NHC}_6\text{H}_4\text{Me})][\text{BF}_4]$ (**2c**).

(d) *p*-Methoxybenzediazonium Tetrafluoroborate. This reaction could presumably be carried out with the usual procedures, but it was performed initially at lower temperature to determine if this would improve the yield or stabilize an intermediate adduct.⁹ Solid $[\text{}^{15}\text{N}^{14}\text{NHC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ (98 mg, 0.44 mmol) was added slowly over 1 h to Cp_2WH_2 (140 mg, 0.44 mmol) suspended in methanol (15 mL) at -75 °C. The solution became slowly orange, but 0.4 h after the final addition it became yellow again. Insoluble yellow solid was present throughout, which was shown to be largely a mixture of the reactants (IR). On warming of the solution slowly to 0 °C, an orange-brown solution formed, and the off-yellow solid **1d** precipitated and was filtered. A solution of **1d** in methanol, acetone, or acetonitrile stirred at room temperature readily turned brown. It was filtered from some insoluble black decomposition product and evaporated to dryness to yield the brown solid **2d** which could be recrystallized from acetone-toluene.

Results and Discussion

(a) $[\text{Cp}_2\text{WH}(\text{NNHAr})]^+$ (**1**). The careful, slow, addition of a solution of an arenediazonium tetrafluoroborate or hexafluorophosphate in methanol to a yellow solution of Cp_2WH_2 in toluene at -25 to -30 °C produced a transient orange color, which may be due to an electron donor-acceptor complex, by analogy with the ones suggested to be responsible for the colors of solutions of Cp_2WH_2 or Cp_2MoH_2 with some olefins possessing π -electron-withdrawing groups.⁹ A bright yellow solid formed in suspension upon further addition or upon partial removal of solvents under vacuum near this temperature. This has been characterized as the complex $[\text{Cp}_2\text{WH}(\text{NNHAr})][\text{X}]$ (**1**: Ar = (a) *p*-FC₆H₄, (b) Ph, (c) *p*-MeC₆H₄, or (d) *p*-MeOC₆H₄; X = BF₄ or PF₆). Because of its instability in solution at ambient temperature (see below), recrystallization could only be carried out near or below -20 °C and in some instances it was difficult to obtain recrystallized material free of contamination by decomposition products unless crystallization could be induced moderately quickly. Methanol-diethyl ether-hexane or acetone-toluene mixtures worked well, but until now we have not secured single crystals suitable for an X-ray diffraction study. This will be necessary in order to settle substantial questions which remain regarding the electronic structure, bond order, and geometry of the formally arylhydrazido(2-) ligand and its orientation in the limiting ground-state structure. Meanwhile, IR and NMR spectra have unambiguously established the composition of **1** and have revealed interesting features regarding its stereochemistry and nonrigidity.

The solubility of **1** is typical for an organometallic salt: very soluble in MeCN, soluble in acetone and MeOH, slightly soluble in CH₂Cl₂, and insoluble in ether, toluene, and hexane. It was not stable in well-degassed solvents above ca. -20 °C, as it underwent an isomerization to **2** as described below,

accompanied by some general, unidentified decomposition. The solid complex could be stored at room temperature in a nitrogen-filled drybox for several days, but evidently isomerization and decomposition still slowly occurred. However, samples were kept sealed under nitrogen in a freezer at -8 °C for some months without evident change.

Proton nuclear magnetic resonance spectra of **1** (Table I) allow a full structural picture to be drawn. The presence of the hydrido ligand is shown by a W-H resonance, integrating to a single proton, to high field of Me₃Si near δ -2. This resonance shifts somewhat with change in temperature, e.g., from δ -2.09 (-14 °C) to δ -2.18 (-43 °C) for **1c**. The weak satellites due to coupling with ¹⁸³W ($I = 1/2$, 14%) were observed ($J = 106$ -109 Hz). The NH resonance at low field, near δ 11.0, integrates for a single proton, and the slightly broad signal becomes possibly somewhat sharper with decrease in temperature (half-width ca. 5 Hz at -36 °C vs. ca 7 Hz at -14 °C for **1c**).

It has been possible to unambiguously demonstrate to which of the two nitrogen atoms, N(1) or N(2), is bound the proton through appropriate ¹⁵N labeling by separately synthesizing complexes $[\text{Cp}_2\text{WH}(\text{}^{15}\text{N}^{14}\text{NHC}_6\text{H}_4\text{CH}_3)][\text{BF}_4]$ (**1c**- $^{15}\text{N}(1)$) and $[\text{Cp}_2\text{WH}(\text{}^{14}\text{N}^{15}\text{NHC}_6\text{H}_5)][\text{BF}_4]$ (**1b**- $^{15}\text{N}(2)$). In the former case, the NH signal remained as a single, broad peak showing that the proton was not directly attached to N(1). The two-bond coupling to ¹⁵N(1) could not be resolved.¹⁰ A possibility remained that the proton was not coupled to ¹⁵N due to exchange. However, the latter complex (**1b**- $^{15}\text{N}(2)$) did indeed give the NH resonance as the expected sharp doublet at δ 11.8 with $^1J(^{15}\text{NH}) = 99$ Hz. The doublet collapsed to a singlet when the proton was decoupled from the ¹⁵N nucleus by irradiation at the ¹⁵N frequency of 10.141 06 MHz, thereby confirming the assignment. The ¹H NMR of an aqueous ¹⁵NH₄Cl standard decoupled at 10.139 17 MHz. This provides a value for the ¹⁵N(2) resonance frequency which is 1890 Hz (186 ppm) downfield from the aqueous ¹⁵NH₄Cl standard. Unfortunately, we were not able to obtain the ¹⁵N FT resonance spectrum directly, which may have been due to a low availability of the ¹⁵N(2)-enriched sample and difficulty in choosing the optimum instrumental parameters.

The nitrogen ligand is therefore unquestionably a formally arylhydrazido(2-) ligand (NNHAr),¹² but what is likely to be its geometry? The W-N(1)-N(2) group may be either linear, as in structure I, or bent at N(1), as in structure II. There is definite crystallographic precedent for structure I, but as far as we are aware there is none for the bent structure II. The linear structure I has been found, for example, in Mo, W, or Re complexes with hydrazido(2-),¹³ alkyldiazido(2-),¹⁴ and arylhydrazido(2-) ligands.^{13a,15} In most of these the multiple metal-nitrogen bond confers upon the metal an 18-electron configuration. But in the dicyclopentadienyltungsten complex **1** the corresponding linear structure I would, on the assumption that the Cp groups are 5-electron ligands,

(10) A typical value of $^2J(^{15}\text{N}-\text{H})$ in protonated diazo compounds is ca. 4 Hz.¹¹

(11) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 5369 (1975).

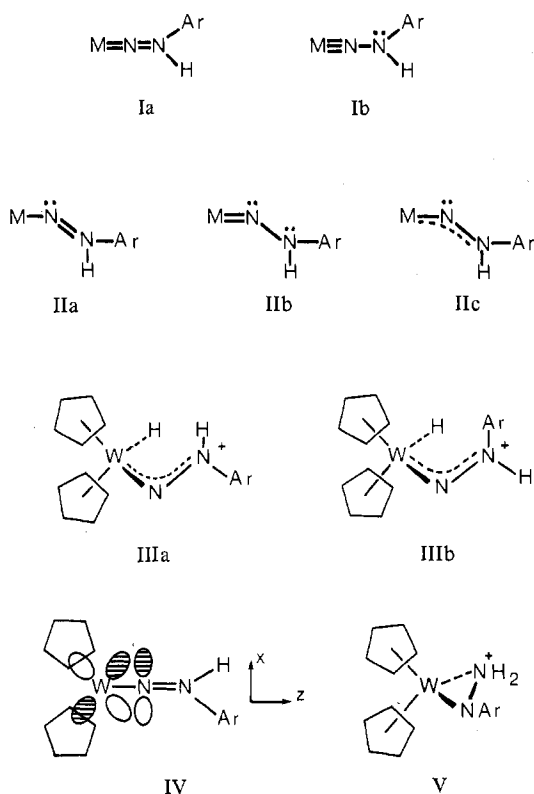
(12) In naming the ligands in **1** and **2** we follow the proposed recommendations of the IUPAC committee incorporated in the 1977 draft bulletin "The Nomenclature of Hydrides of Nitrogen and Derived Cations, Anions and Ligands", kindly communicated to us by Professor J. Chatt.

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involve a 20-electron configuration at the metal. However, it is not ruled out on this account since by binding the cyclopentadienyl group(s) asymmetrically the system may return to the more stable 18-electron configuration.¹⁶ This has been established crystallographically for the related "20-electron" systems $\text{Cp}_2\text{W}(\text{CO})_2$ ¹⁷ and $\text{Cp}_2\text{Mo}(\text{NO})\text{R}$ ($\text{R} = \text{alkyl}$).¹⁸ A similar distortion occurs in the "19-electron" complex¹⁹ $\text{Cp}_2\text{VNN}(\text{SiMe}_3)_2$. This complex is noteworthy in the present context since it is formed from Cp_2V and $\text{Me}_3\text{SiNNSiMe}_3$ through an unstable intermediate (which is probably the "17-electron" complex formed by η^2 -coordination of the bis(trimethylsilyldiazene))²⁰ and involves an isomerization of the silyldiazene ligand to the silyldiazido(2-) group, in the stable product.

Two limiting valence structures IIa and IIb can be written for the bent aryldiazido(2-) ligand.²¹ Each would give the tungsten atom in **1** an 18-electron configuration, as would the delocalized representation IIc. Although there is no definite precedent for an NNHAr group with this geometry, it has been previously proposed that structure IIb may occur as a tautomer of the diazene complex $\text{WCl}_2(\text{NHNCOR})(\text{dppe})_2$ ($\text{R} = \text{aryl or alkyl}$) and be present in equilibrium with it in solution;^{22a} a similar argument^{22b} has been made for $[\text{MoCl}(\text{NHNr})(\text{S}_2\text{CNR}_2)_3]$.

The spectroscopic evidence for **1** appears to be most readily interpreted in terms of structure II, as we shall now describe. The low-field resonance of the NH proton in **1** near δ 11 occurs in a region usually associated with the N(1)-bound proton of an aryldiazene ligand in $\text{M}(\text{NHNAr})$ complexes,^{1,11,23,24} presently ranging from 11.6 ppm in $[\text{RhCl}_3(p\text{-NHC}_6\text{H}_4\text{OMe})(\text{PPh}_3)_2]$ ^{23a} to 15.1 ppm in $[\text{PtCl}(\text{NHNPh})(\text{PET}_3)_2][\text{BF}_4]$.¹ Indeed, we were led initially by this observation to the expectation that **1** was a diazene complex. By contrast, in the only report of an NH resonance for a structurally determined, totally linear metal-aryldiazido(2-) group, $[\text{ReCl}_2(\text{NH}_3)(\text{NNHPh})(\text{PMe}_2\text{Ph})_2]\text{Br}$, $\delta(\text{NH})$ is at 4.92.^{27,28} In the more numerous, but not exactly comparable, cases of structurally determined (or indicated), totally linear metal-alkyldiazido(2-) complexes, reported values are as follows: $[\text{MoI}(\text{NNHC}_8\text{H}_{17})(\text{dppe})_2]\text{X}$, 3.76;^{14a} $[\text{MoBr}(\text{NNHtEt})(\text{dppe})_2]\text{Br}$, 5.9; $[\text{MoBr}(\text{NNHMe})(\text{dppe})_2]\text{Br}$, 8.5; $[\text{WBr}(\text{NNHMe})(\text{dppe})_2]\text{Br}$, 5.9; $[\text{WBr}(\text{NNH-}t\text{-Bu})(\text{dppe})_2]\text{Br}$, 2.4 ppm.^{22a} If these values can be taken as a guide, then the low-field NH resonance for **1** appears to contradict structure I, but then the question remains as to why the NH proton in structure II should resonate in an aryldiazene-like position.²⁹ This discussion must be deferred until the structure of the ligand has been determined unambiguously.

The 100-MHz ¹H NMR resonance due to the Cp groups occurs near δ 6, and its temperature dependence was monitored in the case of **1a** and **1b**.¹⁵ Below ca. -40 °C two Cp resonances are observed due to nonequivalent Cp groups in the limiting (ground-state) structure. As the temperature is raised, these resonances broaden, coalesce at about -40 °C, and then sharpen to a single peak at higher temperatures. The value of ΔG^\ddagger obtained from our analysis of the temperature dependence in the case of **1b**-¹⁵N(2) is $12.3 \pm 0.2 \text{ kcal mol}^{-1}$ ($T_c = 237 \text{ K}$, $\Delta\nu_\infty = 11.0 \text{ Hz}$).³⁰ The most reasonable explanation is that in the limiting structure the aryldiazido(2-) ligand is locked in a position which destroys the plane of symmetry defined by W, N(1), and the hydride ligand (which we shall call the Cp_2W midplane). Any orientation in which N(2) or the H and C(aryl) atoms bound to it lie out of the Cp_2W midplane is sufficient, but all such orientations are less favored sterically than the in-plane configuration. Therefore the actual orientation in the ground state is likely to be strongly influenced by electronic effects. The recent study of the

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 (24) The only apparent exceptions to this are $[\text{Pt}(p\text{-NHC}_6\text{H}_4\text{F})(\text{PPh}_3)_3][\text{BF}_4]$, $\delta(\text{NH})$ 2.85,²⁵ $[\text{IrH}(p\text{-NHC}_6\text{H}_3\text{OMe})(\text{PPh}_3)_3][\text{BF}_4]$, $\delta(\text{NH})$ 5.79, and $[\text{IrClH}(p\text{-NHC}_6\text{H}_3\text{OMe})(\text{PPh}_3)_2]$, δ 5.29 (see ref 26, and compare ref 23c). None of these resonances has been unambiguously identified as $\delta(\text{NH})$ by ¹⁵N-substitution.
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 (29) A series of protonated acyl- and aryldiazo complexes of general formula $[\text{MCl}_2(\text{N}_2\text{HCOR})(\text{dppe})_2]$ ($\text{M} = \text{Mo, W}$; $\text{R} = \text{acyl or aryl}$) are reported^{22a} to have $\delta(\text{NH})$ in the region 12.0–13.0. Because these have not been selectively ¹⁵N-substituted, which nitrogen atom is protonated is not known for certain. If these are hydrazido(2-) complexes (with protonation at N(2)), then the ligand in these and **1** may be structurally and electronically similar, though the CO group may influence the chemical shift in the former.
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orientation and dynamic properties of the alkylidene (CHR) or carbene (CH₂) ligands in [Cp₂Ta(alkyl)(CHR)] and [Cp₂Ta(alkyl)(CH₂)] provides an excellent precedent. In the former complex, the Cp resonances are also inequivalent, and in the ground state the alkylidene or carbene ligand is oriented almost perpendicular to the Cp₂Ta midplane.³¹ This has been determined to be the orientation which maximizes the interaction of the empty π -acceptor orbital of the carbene (which lies normal to the CH₂ plane) with the filled π -donor 1a₁ orbital on Ta, which lies in the midplane.¹⁶ Furthermore, rotation about this Ta=C bond in the case of the alkylidene complexes is believed to be responsible for the Cp resonances becoming equivalent as the temperature is increased, and the barrier to rotation, ΔG^\ddagger , was calculated to be in the range 15–19 kcal mol⁻¹, depending on the ligand.³¹

A similar effect readily explains the behavior of **1**. If the aryldiazido(2-) ligand adopts the bent structure II, then it must be oriented perpendicular to the Cp₂W midplane in order for the most effective delocalization of the tungsten electron pair (which populates the 1a₁ orbital¹⁶) into the π^* -acceptor orbital of the N=N bond (structures IIa–c). The ca. 12 kcal mol⁻¹ barrier to rotation is an indication that the tungsten–nitrogen bond is more than a single bond, though probably not a full double bond (cf. the alkylidene barrier). This view is supported by $\nu(\text{NN})$ (see below) and the NH chemical shift, which should be at higher field than observed if structure IIb were dominant; therefore, structure IIc appears to be the most suitable representation. There are two possible conformations of this limiting structure, which are the cis and trans isomers IIIa and IIIb, and each one should, in principle, give rise to two Cp resonances due to its own inequivalent Cp rings. Since we observe only one set of two Cp resonances in the limiting case, this could be explained in three ways: (i) the resonances for IIIa and IIIb happen to be coincident; (ii) only the preferred isomer is present, presumably IIIa; (iii) rapid equilibration of Ar and H positions is occurring, for example by a rotation about the NN bond. We believe case ii to be the most likely explanation.

If, instead, the aryldiazido(2-) ligand has the totally linear structure I, then again the low-temperature NMR requires that the plane of the WNN(H)C(aryl) skeleton must be noncoincident with the Cp₂W midplane in the ground state. The presence of just two low-temperature Cp resonances is then readily explained because no cis–trans isomerism is possible.³² However, the interaction between W and N(1) is considerably more difficult to describe than in the case of the bent structure. As mentioned previously, the “20-electron” totally linear structure II can be compared with [Cp₂Mo(NO)R], and for the latter a molecular orbital description has been given.¹⁶ The two electrons in the NO π^* orbitals are accommodated in a MO of a'' symmetry which is built from an a'' orbital on the Cp₂Mo fragment (a combination of metal d_{xz} and Cp orbitals) and one NO π^* orbital. This orbital is perpendicular to the midplane. To visualize the situation for the “linear” NN(H)R ligand, we shall consider that the nitrogen atom lone pair occupies a p orbital orthogonal to the NN π system (structure IV) and hence in the NN(H)C(aryl) plane. This p orbital, and therefore this plane, must be perpendicular to the Cp₂W midplane for most effective interaction with the a'' Cp₂W orbital (shown for simplicity as d_{xz} in IV) in the limiting structure. Thus it seems, in principle, that the dynamic NMR results can be accommodated with either proposed structure I or II. No matter which of the structures turns out to be correct, this orientation of the ligand is unusual

when compared with related structures. In Cp₂VNN(SiMe₃)₂ the VNN system is linear (structure I), but the nitrogen and silicon atoms lie in the Cp₂V midplane;¹⁹ in [Cp₂Mo(NH₃)(NH=CMe₂)]²⁺ the imine ligand lies in the midplane and the Cp groups are NMR equivalent.³³

In the infrared spectra of **1**, $\nu(\text{W-H})$ expected near 1850 cm⁻¹ could not be observed, and presumably this is due to a small dipole moment change in the normal mode. The $\nu(\text{NH})$ mode gives rise to a single, fairly strong, sharp band near 3240 cm⁻¹ (ca. 3270 cm⁻¹ for PF₆⁻ salts); the intensity of this band is higher than that of the aryldiazene complexes (i.e., with N(1)H groups) with which we have experience. Other absorptions are as expected for cyclopentadienyl, aryl, substituent, and counterion modes, but a band at 1360 cm⁻¹ shifted upon substitution with ¹⁵N at N(1) to become a mixed, broad peak at 1340 cm⁻¹, and on this basis we tentatively assign $\nu(\text{NN})$ at 1360 cm⁻¹. This position, if correct, is somewhat lower than the observed $\nu(\text{NN})$ values for coordinated aryldiazenes¹¹ but is still indicative of a degree of multiple bonding in the NN bond. It does not conclusively distinguish between the structural possibilities I or II.

(b) [Cp₂W(H₂NNAr)]⁺ (**2**). When addition of methanolic diazonium salt to Cp₂WH₂ in toluene was carried out at 0 °C, a brown product was obtained which analysis indicated to be an isomer of **1**. This is the aryldiazido(1-) complex [Cp₂W(H₂NNAr)]⁺[X]⁻ (**2**: Ar = (a) *p*-FC₆H₄, (b) Ph, (c) *p*-MeC₆H₄, or (d) *p*-MeOC₆H₄; X = BF₄⁻ or PF₆⁻). It could indeed be obtained by isomerization of **1** formed at a lower temperature, as described above, by letting solutions of **1** stir for at least 1 h at temperatures between 0 and ca. 20 °C. Solid **2** can be recrystallized from acetone–toluene or acetone–diethyl ether–hexane. Two unidentified materials have been observed from time to time to be deposited from solutions of **1** or **2**: a brown flocculent solid which is slightly soluble in MeCN and has $\nu(\text{NH})$ at 3340 cm⁻¹ and a black solid, being insoluble in the common organic solvents and having no infrared bands useful for characterization.

The proton magnetic resonance spectrum allows the cation in **2** to be assigned structure V, and this has been confirmed by a single-crystal X-ray structure determination⁴ carried out on **2b**. The NH₂ resonance is a single, broad peak at δ 3.9 integrating as two protons (Table I). It disappeared with addition of D₂O and occurred in the spectrum of the ¹⁵N-(1)-substituted analogue (**2c**-¹⁵N(I)) (i.e., synthesized with [¹⁵N¹⁴NC₆H₄CH₃][BF₄]) as a sharp doublet of separation ¹J(¹⁵N(1)H) = 88 Hz. The slow exchange necessary for the observation of coupling implies that N(1) has no lone pair for promoting ready proton transfer,³⁴ implying that N(1) is bound to the tungsten via this electron pair. We were successful in obtaining the ¹⁵N FT NMR spectrum of this enriched sample and observed the ¹⁵N(1) resonance at 68 ppm upfield from external ¹⁵NH₄Cl as a 1:2:1 triplet of separation 88 Hz, confirming the presence of the two protons bound to N(1). This resonance was examined carefully while simultaneously decoupling the protons in order to attempt to locate the weak satellites due to coupling with ¹⁸³W (14% natural abundance, *I* = 1/2). These are believed to have been observed, with ¹J(¹⁸³W¹⁵N) = 17 Hz. This, we believe, is the first observation of ¹⁸³W–¹⁵N coupling.

The resonance for all 10 cyclopentadienyl protons occurred as a sharp singlet, slightly upfield compared with the corresponding resonance in **1**; this showed no evidence of broadening down to a temperature of –80 °C. It was inconceivable to us

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(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 $[\text{CpMoI}(\text{NO})(\text{H}_2\text{NNHPh})][\text{BF}_4]$.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 $\nu(\text{NN})$ is apparently inactive in the infrared and could not be identified.

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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 $\nu(\text{N}(2)-\text{C}(\text{aryl}))$ 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**- $^{15}\text{N}(2)$, 74449-39-1; **1c**, 73493-29-5; **1c**- $^{15}\text{N}(1)$, 74449-41-5; **1d**, 73493-26-2; **2a**, 73358-31-3; **2b**, 73358-24-4; **2b**- $^{15}\text{N}(2)$, 74449-43-7; **2c**, 73358-28-8; **2c**- $^{15}\text{N}(1)$, 74449-45-9; **2d**, 73358-26-6; Cp_2WH_2 , 1271-33-6.

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Structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNC}_6\text{H}_5)][\text{BF}_4]$: A Complex Containing the Unusual Side-On-Bonded Phenylhydrazido(1-) Ligand

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Received February 21, 1980

The structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNC}_6\text{H}_5)][\text{BF}_4]$ 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 $(\text{C}_6\text{H}_5)\text{N}_2^+$ into both W-H bonds of $(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2$. 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 $\text{C}_{2h}^5\text{-P}2_1/c$ with $a = 8.5874$ (6) Å, $b = 10.4821$ (8) Å, $c = 19.5455$ (14) Å, $\beta = 107.176$ (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 $[\text{Cp}_2\text{WH}(\text{NNHPh})]^+$. At room temperature this unstable intermediate rearranges to the diinserted product $[\text{Cp}_2\text{W}(\text{H}_2\text{NNPh})]^+$, 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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