reason for the nonlinearity in the present case is clear. As in the tungsten example,[20] the metal thereby acquires an 18-electron count, which would be exceeded if the lone pair on N(1) were to donate to Re also, to make the ReNN skeleton linear. By contrast, such a donation is required to *establish* the 18-electron count in the Mo, W, and Re complexes cited above possessing linear MNN skeletons.

It is instructive to compare the dimensions of the rhenium–hydrazido(2–) group in the two determined structures possessing linear and nonlinear geometries. In $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]Br$, the values observed for the linear Re–N–N system[29] are Re–N = 1.75 (1) Å, N–N = 1.28 (2) Å, and Re–N–N = 172 (1)°. Thus, the Re–N distance is considerably shorter than in the present case, consistent with this notion that the linearity is due to the nitrogen atom donating to Re the (otherwise) lone pair of electrons, thus increasing the multiple bonding to the Re atom. In both cases, however, the N–N bonds are not significantly different in length (and are slightly longer than a typical double-bond length). If the Re–N distance to the NH_3 ligand in ref 29 (2.200 (13) Å) can be taken as representative of a single bond, then it appears that a considerable degree of Re–N multiple bonding exists in the aryldiazenido complex and in both the linear and the bent hydrazido(2–) complexes.

Table VII lists the results of mean-plane calculations. The most striking features are as follows: (i) The geometry at N(2) is strictly planar (plane 3) due to the delocalization of the ReN(1)N(2) π system (the Re atom lies only 0.156 Å out of this plane). (ii) The phenyl ring (plane 2) is not coplanar with plane 3 but is twisted to make a dihedral angle of ca. 24°, probably to relieve intermolecular contacts between H(10) and the CH_3 group on N(2) (note that the H(10)–H(83) distance is only 1.85 Å); this may be compared with the nearly planar arrangement found in the tungsten compound,[20] where a N(2)H group is present instead of $N(2)CH_3$. (iii) Plane 3, that of the hydrazido(2–) ligand skeleton, does not bisect the angle at Re formed by the two carbonyl groups; rather, the hydrazido plane is twisted toward C(1)O(1) as can be seen from the smaller dihedral angle made with plane 5 (ca. 25°) compared to that with plane 4 (ca 61°). The reason for this twisted arrangement is not presently clear.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for support of this work through operating grants and the University of Concepcion, Concepcion, Chile, for a leave of absence (to C.F.B.-P).

Registry No. **1a**, 81028-25-3; **1b**, 81028-27-5; **1c**, 81028-29-7; **1d**, 81028-31-1; **1e**, 73838-58-1; **1f**, 81028-33-3; **1g**, 81028-35-5; **2a**, 81028-37-7; **2b**, 81028-39-9; **2c**, 81028-41-3; **2d**, 81028-43-5; **2e**, 81028-45-7; **3a**, 81045-30-9; **3b**, 81028-46-8; **3d**, 81028-47-9; **3g**, 81028-48-0; **4**, 36543-62-1; **5**, 73838-59-2; **6a**, 81028-49-1; **6b**, 81028-50-4; **6d**, 81028-51-5; **6e**, 81045-31-0; **7a**, 81028-52-6; **7b**, 81028-53-7; **7d**, 81028-54-8; **7e**, 81028-55-9; **8a**, 81028-57-1; **8b**, 81028-59-3; $MeCpMn(CO)_2(o\text{-}NHNC_6H_4CF_3)$, 81028-60-6; $MeCpMn(CO)_2(3,5\text{-}NHNC_6H_3Me_2)$, 81028-61-7; $CpRe(CO)(COPh)(p\text{-}N_2C_6H_4OMe)$, 81028-62-8; $(\eta^5\text{-}C_5H_5)Re(CO)(CO\text{-}n\text{-}Bu)(p\text{-}N_2C_6H_4NEt_2)$, 81028-63-9; $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$, 81028-64-0; $CpRe(CO)_2THF$, 59423-86-8; $(\eta^5\text{-}C_5H_5)Re(CO)_3$, 12079-73-1; $(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3$, 32628-49-2.

Supplementary Material Available: Thermal parameters (Table A), calculated hydrogen positions (Table B), intermolecular distances (Table C), and observed and calculated structure factors (Table D) (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department, Simon Fraser University,
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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. Low-Temperature (–100 °C) X-ray Structural Characterization of Nonlinear Tungsten–Arylhydrazido(2–) Coordination in $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ and a Comparison of the Reactions of Cp_2WH_2 and $CpRe(CO)_2H_2$ with Arenediazonium Ions

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Received November 5, 1981

The structure of $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ has been determined by single-crystal X-ray crystallography at –100 °C. The compound crystallizes in the space group $P2_1/c$ with a = 10.270 (3) Å, b = 10.591 (2) Å, c = 21.041 (5) Å, β = 107.35 (2)°, and Z = 4. The calculated and measured densities are 1.953 and 1.94 (1) g cm^{-3}, respectively. On the basis of 2479 observed, three-dimensional, X-ray counter-measured intensities with $I > 2.3\sigma(I)$ in the range $3° \le 2\theta \le 45°$ (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to R = 0.035 and R_w = 0.043. The environment of the tungsten atom in the cation is that of a very flattened tetrahedron, with the W atom displaced only 0.224 Å out of the plane defined by N(1) and the centroids of the two Cp rings, presumably toward the hydride ligand (which was not located). The p-fluorophenylhydrazido(2–) ligand is bound to W with a distinctly nonlinear W–N(1)–N(2) skeleton, with W–N(1) = 1.837 (7) Å, N(1)–N(2) = 1.315 (9) Å, and W–N(1)–N(2) = 146.4 (5)°. Unsuccessful attempts were made to synthesize other examples of metal–hydrazido(2–) complexes which might also contain nonlinear M–N–N skeletons by reacting p-fluorobenzenediazonium ion with related compounds $Cp_2W(Ph)H$ and $CpRe(CO)_2H_2$.

Introduction

Structural studies of aryldiazenido complexes have, by now, firmly established that this ligand may, in its coordination to transition metals, display a variety of skeletal geometries of which two, the "singly bent" (I) and "doubly bent" (II), modes are most common.[1] In simple terms, these geometries can

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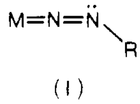
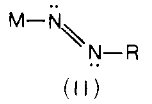
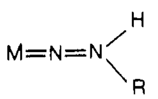
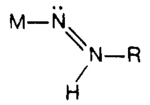
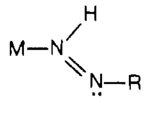

(I)


(II)

be thought to be determined by the electron requirements of the metal. That is to say, whether an electron pair on N(1) is a lone pair, as in II, or is involved in π donation to the metal, as in I. A similar situation might be expected to be found in arylhydrazido(2−) ligands, which can be viewed to arise formally (and, in some cases, in practice) by the protonation of the lone pair on N(2). Parallel structures would thus display linear (III) or nonlinear (bent) (IV) M−N−N frameworks.


(III)


(IV)


(V)

There are several known examples of aryl[2,3] and alkylhydrazido[4,5] complexes having the linear geometry III. Attempts to observe the bent geometry might be fruitless, in protonation reactions, if the N(1)-protonated aryldiazene ligand (V) is the kinetically and thermodynamically preferred product, and, indeed, there have been numerous such aryldiazene complexes prepared by the protonation of a doubly bent aryldiazenido ligand or by the insertion of an ArN_2^+ group into a metal−hydride bond.[1,6] Prior to this work, however, no example of a bent hydrazido(2−) ligand IV was known in either hydrazido, alkylhydrazido, or arylhydrazido compounds.

The hydride Cp_2WH_2 (Cp = η^5-C_5H_5) in toluene reacts with equimolar $[ArN_2][X]$ (Ar = Ph, p-FC_6H_4, p-MeC_6H_4, or p-$MeOC_6H_4$; X = BF_4 or PF_6) in methanol below ca. −20 °C to give yellow salts of composition $[Cp_2WH(NNHAr)][X]$. We previously deduced, on the basis of NMR and IR spectroscopic results, that these compounds were arylhydrazido(2−) complexes and not aryldiazene complexes. Although we could not be absolutely certain at that time, we believed them also probably to contain the bent M−N−N framework.[7] This conclusion has been shown to be correct by the results of a single-crystal X-ray structure determination carried out at −100 °C, reported in detail in this paper. A preliminary communication has appeared.[8] It was of interest also to examine an available related dihydride, namely, $CpRe(CO)_2H_2$, and a monosubstituted tungsten hydride such as $Cp_2W(Ph)H$ to see whether related products also having a bent M−N−N framework might be obtainable.

Experimental Section

All manipulations were carried out under nitrogen in Schlenk apparatus. Solvents were dried by usual methods and distilled under nitrogen. $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]$ was synthesized according to the published method.[7] $Cp_2W(Ph)H$ was synthesized by the method of Green et al.[9] $CpRe(CO)_2H_2$ was kindly donated by Professor W. A. G. Graham and Dr. J. K. Hoyano of the University of Alberta.[10]

Table I. Summary of Crystal and Intensity Collection Data

compd	$[(\eta^5\text{-}C_5H_5)_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot(CH_3)_2CO$
formula weight	573.21
formula	$W_1F_7P_1N_2O_1C_{18}H_{22}$
cell parameters	
a, Å	10.270 (3)
b, Å	10.591 (2)
c, Å	21.041 (5)
β, deg	107.35 (2)
V, Å^3	2184.5
Z	4
D_0(flotation), g cm^{-3}	1.94 (1)
D_c, g cm^{-3}	1.953
space group	$P2_1/c$
crystal dimens, mm	0.09 × 0.33 × 0.37
temp, °C	−100
radiation	Mo Kα (λ 0.709 26 Å) (graphite monochromator)
μ, cm^{-1}	57.47
range in transmission coefficients	0.200 → 0.605
takeoff angle, deg	3°
scan speed, deg/min (in θ)	2 (sym θ−2θ scan of 1.4° + 0.693 tan θ°)
bkgd count time, s	40% of total scan time; on both sides of reflctn
2θ limits, deg	3.0–45.0
diffractometer	Picker FACS-1
detector	scintillatn counter with pulse-height discriminatn
stds measd	2 every 70 reflctn
reflctn measd	2863
reflctn obsd	2479 ($I \geq 2.3\sigma(I)$)

^1H NMR spectra were measured on a Varian XL100-FT spectrometer operating at 100 MHz and are reported in ppm downfield relative to $SiMe_4$. IR spectra were measured with a Perkin-Elmer Model 599B instrument.

X-ray Structure Determination. Yellow crystals of $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ were grown from acetone–toluene at −35 °C. At this temperature, isomerism of the complex in solution to the η^2-arylhydrazido(1−) complex occurs very slowly, if at all.[7] However, the stability of these crystals to X-ray irradiation at ambient temperature was very poor. When crystals (mounted in capillaries) were cooled to ca. 0 °C in a stream of dry nitrogen, their lifetime under X-rays was prolonged sufficiently for preliminary photographic data to be obtained with a number of separate crystals. Weissenberg and precession methods gave systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$) which uniquely defined the space group as $P2_1/c$.

A crystal suitable for data collection was sealed under nitrogen in a Lindemann capillary. This was then attached to the copper tip of the cryogenic gonimeter head in an Air Products and Chemicals, Inc., Model AC-1-101A cryo-tip refrigeration unit, in such a way as to obtain maximum thermal contact of the crystal with the cold head. Accurate cell dimensions were determined at −100 °C by a least-squares refinement of 20 accurately centered reflections in the range 2θ = 27.3–33.7°. Crystal data and other parameters are listed in Table I. The data were corrected for absorption with use of the program of Gabe[11] and for Lorentz and polarization effects.

Structure Solution and Refinement. The position of the W atom was located by direct methods, while all other nonhydrogen atoms and some hydrogen atoms were located from subsequent Fourier and difference Fourier syntheses. All nonhydrogen atoms have been refined anisotropically with full-matrix least-squares methods. The hydrogen atoms associated with the C_5H_5 and aryl groups and the N(2)H hydrogen atom were included at idealized positions as fixed contributions (C−H = 0.95 Å; N−H = 0.87 Å; B = 3.00 Å^2)[12] during the later stages of refinement. The agreement factors for the absorption-corrected data settled at $R = 0.035$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$) and $R_w = 0.043$ ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) for 280 variables.

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Table II. Final Positional Coordinates for $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$[a]

atom	*x*	*y*	*z*
W	0.30299 (3)	0.81317 (3)	0.48028 (2)
P	0.2238 (2)	0.0990 (2)	0.1100 (1)
F(1)	0.3086 (9)	0.0085 (9)	0.0812 (4)
F(2)	0.2598 (9)	0.2068 (9)	0.0697 (5)
F(3)	0.3540 (7)	0.1203 (7)	0.1684 (4)
F(4)	0.1401 (8)	0.1960 (7)	0.1387 (4)
F(5)	0.0936 (7)	0.078 (1)	0.0509 (5)
F(6)	0.1860 (9)	−0.0050 (9)	0.1507 (7)
F(7)	1.0967 (5)	0.7451 (6)	0.7061 (3)
O	0.4752 (7)	1.0377 (6)	0.6883 (3)
N(1)	0.4753 (7)	0.8141 (5)	0.5412 (3)
N(2)	0.5513 (7)	0.8586 (6)	0.5983 (3)
C(1)	0.183 (1)	0.710 (1)	0.3776 (5)
C(2)	0.216 (1)	0.6233 (9)	0.4284 (6)
C(3)	0.350 (1)	0.6090 (8)	0.4527 (5)
C(4)	0.412 (1)	0.691 (1)	0.4191 (7)
C(5)	0.307 (2)	0.756 (1)	0.3722 (6)
C(6)	0.249 (1)	0.975 (1)	0.5433 (6)
C(7)	0.158 (1)	0.9830 (8)	0.4797 (5)
C(8)	0.0792 (8)	0.877 (1)	0.4686 (5)
C(9)	0.120 (1)	0.8012 (9)	0.5238 (7)
C(10)	0.227 (1)	0.861 (1)	0.5715 (5)
C(11)	0.6901 (8)	0.8253 (7)	0.6253 (4)
C(12)	0.7498 (8)	0.7351 (8)	0.5954 (4)
C(13)	0.8883 (9)	0.7080 (7)	0.6235 (5)
C(14)	0.9601 (8)	0.7709 (8)	0.6798 (4)
C(15)	0.9021 (9)	0.8589 (9)	0.7096 (4)
C(16)	0.7663 (8)	0.8852 (8)	0.6827 (4)
C(21)	0.529 (1)	1.1806 (9)	0.7778 (5)
C(22)	0.320 (1)	1.045 (1)	0.7493 (6)
C(23)	0.444 (1)	1.0835 (8)	0.7346 (5)

[a] Estimated standard deviations are given in parentheses. The coordinates are those of a connected set of atoms.

Table III. Important Distances (Å) and Angles (Deg) in $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$

W-Cp(1)[a]	2.043	N(1)-N(2)	1.315 (9)
W-Cp(2)[a]	2.014	N(2)-C(11)	1.41 (1)
W-N(1)	1.837 (7)	W-N(1)-N(2)	146.4 (5)
Cp(1)-W-Cp(2)[a]	135.5	N(1)-N(2)-C(11)	122.9 (6)
Cp(1)-W-N(1)	109.8	N(2)-C(11)-C(12)	121.3 (7)
Cp(2)-W-N(1)	110.8	N(2)-C(11)-C(16)	118.5 (7)

[a] Cp(1) and Cp(2) denote the centroids of the cyclopentadienyl rings.

The only significant residual peaks (of height 0.85 and 1.08 e/Å^3) observed in the final difference map were in the vicinity of the tungsten atom. Weights (w) were assigned to the F_o's on the basis of the standard deviations [$w = 1/\sigma(F_o^2)$]. Scattering factors, including anomalous dispersion factors for W and P atoms, were taken from ref 13. The computer programs have been cited elsewhere.[14]

Final positional coordinates are given in Table II. The calculated hydrogen atom positions (Table VII), a listing of observed and calculated structure amplitudes (Table VIII), and the anisotopic thermal parameters (Table IX) are available as supplementary material.

Results and Discussion

The crystal structure of $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ consists of four discrete cations and anions and four molecules of acetone of solvation per unit cell. Selected interatomic distances and interbond angles are listed in Table III. The PF_6 anion appears to be quite well-behaved and ordered. As Table IIIa, part B, shows, there are a number of relatively short nonbonded contacts between the fluorine atoms of the PF_6 group and hydrogens of the cyclopentadienyl ligands, which are close to the sum of the van der Waals radii (2.57 Å) of these two atoms. The most significant of these is between H(4) and F(2) at 2.37 Å.

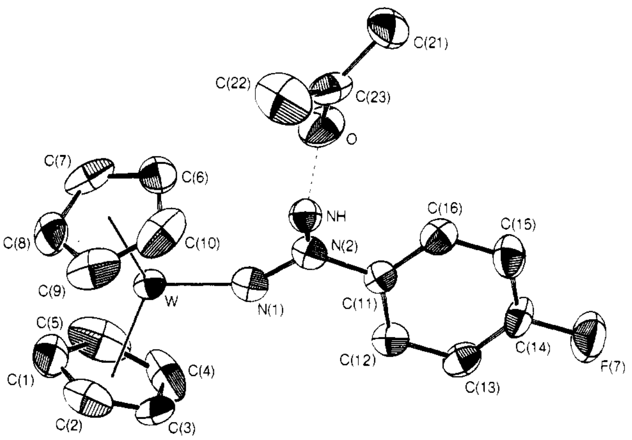

Figure 1. View of the geometry of the cation in $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$, showing the atom-numbering scheme and the acetone of solvation (ORTEP diagram, 50% probability contours for all atoms).

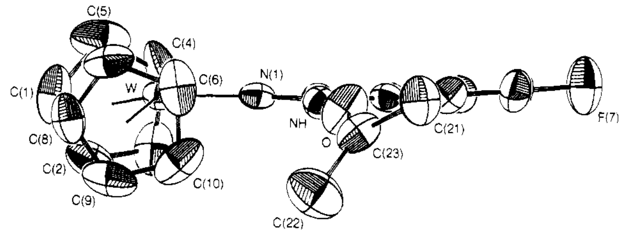

Figure 2. Side view of the cation in $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$, showing the near planarity of the tungsten–*p*-fluorophenylhydrazido(2−) moiety, the acetone of solvation, and the small displacement of the W atom out of the Cp(1)–Cp(2)–N(1) plane (Cp(1), Cp(2) = centroids of the Cp rings; ORTEP diagram, 50% probability contours for all atoms).

The structure of the $[Cp_2WH(p\text{-}NNHC_6H_4F)]^+$ cation is shown in two views in Figures 1 and 2. The hydride ligand, which is known to be present from NMR spectroscopic evidence,[7] was not located in this structure determination, but its most probable position can be inferred from the positions of the remaining ligands. The plane defined by the centroids Cp(1) and Cp(2) of the two Cp ligands and N(1) of the *p*-fluorophenylhydrazido(2−) ligand forms the base of a very flattened pyramid with the tungsten atom at the apex. The W atom is displaced only 0.2243 (3) Å from this plane and the sum of the angles at W is 356.1°. Presumably, the hydride ligand is located on the side of the W atom remote from this plane. The shallowness of the pyramid at tungsten in this cation (which can be seen in Figure 2) suggests that the stereochemical requirements of the small hydride ligand are rather overwhelmed by those of the heavier atoms and, in this respect, the geometry appeared to be unusual, considering the numerous structural determinations which have established a distinct and important stereochemical role for hydride ligands in transition-metal complexes.[15] A problem in determining

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Table IV. Comparison of the Coordination Spheres of Some Metal Hydride Systems

compd	ligand atoms in the plane[a]	dev (M),[c] Å	$\Sigma\angle_M$,[d] deg
(A) $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$[16c]	Cp(1), Cp(2), C(11)	0.287 (Nb)	351
(B) *trans*-$\{(\eta^5\text{-}C_5H_5)HW[\mu\text{-}(\sigma:\eta^5\text{-}C_5H_5)]_2WH(\eta^5\text{-}C_5H_5)\}$[16a]	Cp(1), Cp(2), C(2′)	0.265 (W(1))	356
(C) *trans*-$\{(\eta^5\text{-}C_5H_5)[CH_2SiMe_3]W[\mu\text{-}(\sigma:\eta^5\text{-}C_5H_4)]_2WH(\eta^5\text{-}C_5H_5)\}$[16a]	Cp(1), Cp(2), C(23)	0.299 (W(2))	351
(D) *cis*-$\{(\eta^5\text{-}C_5H_5)[CH_2SiMe_3]W[\mu\text{-}(\sigma:\eta^5\text{-}C_5H_4)]_2WH(\eta^5\text{-}C_5H_5)\}$[16a]	Cp(1), Cp(2), C(23)	0.230 (W(2))	354
$[(\eta^5\text{-}C_5H_5)_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot(CH_3)_2CO$[b]	Cp(1), Cp(2), N(1)	0.224 (W)	356

[a] All mean planes have been calculated in this laboratory as also have been the centroids of the Cp rings. The numbering of W and ligand atoms is as quoted in the original publications. [b] The present compound. [c] Deviation of M out of the plane. [d] Sum of the angles subtended at M.

whether this is a recurrent feature of the $Cp_2MH(L)$ type of system is that very few of these appear to have been structurally determined. In Table IV we compare data for four related hydridobis(cyclopentadienyl)tungsten or -niobium compounds[16] with the present one. In none of these determinations were the hydride ligands located either, but again their presence was inferred from NMR evidence, the requirement that the metal atom should attain an 18e configuration, or from geometrical considerations. We calculate that all of the compounds show displacements of the metal atom from the Cp(1)–Cp(2)–L plane in the range 0.230–0.299 Å, slightly larger but comparable with that found in our compound. Unfortunately, the structure of the niobium compound was determined from photographic data and is subject to large errors. From these limited examples it seems that a shallow Cp_2ML pyramid occurs regularly, and we think that it would be worthwhile to redetermine the structure of $Cp_2Nb(CO)H$ so as to locate the hydrogen. Similarly, it would be interesting to locate the hydride ligands in more compounds of this type so as to determine more exactly the stereochemical requirements of the hydride ligand in bis(cyclopentadienyl)(ligand)metal environments. A suitable example to compare more closely with the present one would be $Cp_2WH(OCOEt)$.[16b]

Previous reports of Cp_2ML_2-type structures have recognized an apparent interdependence between metal–Cp distances and the Cp–M–Cp inter-ring angles, which has been related to the steric requirements of the ligand L σ bonded to the metal. Bulkier ligands cause a contraction of the inter-ring angle, which is resisted by mutual repulsions of the approaching Cp ring hydrogen atoms, resulting in M–Cp lengthening.[16–18] The present structure exemplifies this effect and can be closely compared with the arylhydrazido(1−) compound $[Cp_2W(H_2NNPh)][BF_4]$ which has been structurally determined.[18] These arylhydrazido(1−) complexes result from isomerism[7] of the present hydrido(arylhydrazido)(2−) complexes above 0 °C. In the two compounds the Cp–W–Cp angles are large[18] and similar (135.5 and 136.8°, respectively), again suggesting that the steric requirement of the hydridoarylhydrazido(2−) moiety is (like that of the arylhydrazido(1−) ligand, with its small bite) rather small. In both compounds the Cp rings are well-centered above the W atoms as indicated by the closeness of the metal–ring-plane perpendicular distances (here: ring 1, 2.042 Å; ring 2, 2.013 Å) and the metal–ring-centroid distances (ring 1, 2.043 Å; ring 2, 2.014 Å). The small torsion angles in Table V show that the Cp rings in the present compound reasonably approximate to an eclipsed conformation (Figure 2).

The structure determination corroborates the presence of the monodentate arylhydrazido(2−) ligand (NNHAr) deduced on spectroscopic grounds and, furthermore, confirms the suggestion[7] that the metal–ligand skeleton is nonlinear (W–N(1)–N(2) = 146.3 (6)°). The N(2)-bound hydrogen atom, as well as being located on a difference Fourier map, is further substantiated by the location of the acetone molecule which is clearly placed in a suitable position for an O...H–N(2) hydrogen bond; the observed O...H–N(2) distance is 2.09 Å (Figures 1 and 2). The atoms N(1) and N(2) and those of the aryl group define, to a fair approximation, a plane (maximum deviation 0.061 (6) Å) which lies roughly normal to the mean planes of the two Cp rings (dihedral angles are 93.7° to ring 1 and 76.2° to ring 2). Furthermore, as can be seen from Figure 2, the N(2) H atom and acetone oxygen lie virtually in this plane. The two Cp groups are thus in nonequivalent environments, and we believe that this orientation, or one substantially like it, is the reason why two equal intensity ^1H NMR resonances are observed for the Cp groups in the low-temperature spectrum.[7,19] As the temperature is increased, these resonances broaden and coalesce and then sharpen to a single peak. What is the process by which these Cp groups are rendered equivalent? A rotation about the N–N bond (structure IV) would interconvert geometrical syn and anti isomers but would not of itself render the Cp groups equivalent. However, rotation about the W–N(1) bond would do so, and this provides the most plausible explanation. Rotation about N–N may possibly occur simultaneously. For there to be a substantial barrier (estimated to be $\Delta G^{\ddagger} = \sim 12$ kcal mol^{-1})[7] to rotation about the W–N(1) bond, this bond must have significant multiple character; in agreement, the W–N(1) bond length at 1.837 (7) Å is much shorter than expected for a W–N single bond, though noticeably it is not as short as the W–N bonds in hydrazido(2−) complexes which have linear W–N–N skeletons (1.73 (1)–1.768 (4) Å).[3,5,20,21] The N–N bond length of 1.315 (9) Å is clearly intermediate between a typical N–N double bond (1.23 Å)[22] and single bond (ca. 1.40 Å),[18,23,24] though it does not differ significantly from the values reported for the linear W–N–N hydrazido(2−) skeletons. Thus, rather than the formal valence structure IV which we described in the Introduction for bent hydrazido(2−)

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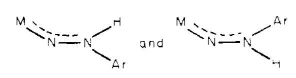
(16) (a) Couldwell, C.; Prout, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 335. (b) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950. (c) Kurillova, N. I.; Gusev, A. I.; Struchkov, Y. T. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 441; *Zh. Strukt. Khim.* **1972**, *13*, 473.

(17) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290.

(18) Cowie, M., Gauthier, M. D. *Inorg. Chem.* **1980**, *19*, 3142.

(19) Note that, of the two possible geometric isomers



only the former (syn) isomer is observed in the crystal structure and is presumably the isomer responsible for the low-temperature NMR spectrum.

(20) Heath, G. A.; Mason, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, *96*, 259.

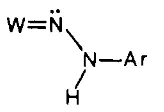
(21) Chatt, J.; Fakley, M. E.; Richards, R. L.: Hanson, I. R.; Hughes, D. L. *J. Organomet. Chem.* **1979**, *170*, C6.

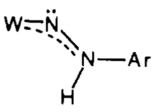
(22) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313 and references therein.

(23) Kita, W. G.; McCleverty, J. A.; Mann, B. E.; Seddon, D.; Sim, G. A.; Woodhouse, D. I. *J. Chem. Soc., Chem. Commun.* **1974**, 132.

(24) Bailey, N. A.; Frisch, P. D.; McCleverty, J. A.; Walker, N. W.; Williams, J. T. *J. Chem. Soc., Chem. Commun.* **1975**, 350.

ligands, the structural analysis suggests that, in this complex at least, structure VI makes an important contribution to the overall structure which may be described as VII.


(VI)


(VII)

It could indeed be argued that the stability of the bent arylhydrazido(2–) system with regard to the isomeric aryldiazene may be critically dependent on the ability of the metal to provide a pair of electrons for a metal–nitrogen double bond.

Reactions of $CpRe(CO)_2H_2$ and $Cp_2W(Ph)H$. As was pointed out previously, the common product of the insertion of an arenediazonium ion into a metal–hydride bond (where such products are stable enough to isolate) is the aryldiazene complex V (the 1,1-insertion product) rather than the arylhydrazido(2–) (or 1,2-insertion product) found for Cp_2WH_2. Therefore, we thought it worthwhile to see what the effect of (i) replacing one hydride ligand or (ii) replacing a Cp ligand by CO would have on the outcome of this reaction. In the first case we used $Cp_2W(Ph)H$ and, in the second, $CpRe(CO)_2H_2$. Unfortunately, the changes are drastic enough to completely alter the chemistry.

Addition of an equimolar amount of *p*-fluorobenzenediazonium hexafluorophosphate to $CpRe(CO)_2H_2$ in acetone–hexane at −35 °C produced no reaction. At room temperature, in acetone–methanol, reaction was complete within 2 days to yield the red complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4F)][PF_6]$, identified by a comparison of its IR spectrum (AgCl cells; $\nu(CO)$: 2070, 2010; $\nu(N_2)$: ca. 1750 cm^{-1}) and chemical properties (e.g., reaction with KI) with those reported for such complexes previously.[25,26] When the reaction was followed by IR (with AgCl cells), no IR absorptions other than those of either $CpRe(CO)_2H_2$ or the product could be seen, indicating that no intermediate "insertion" product was formed in an amount detectable in this way. We presume that direct reaction occurs with evolution of hydrogen, but we made no attempt to detect the hydrogen experimentally. The reaction thus appears to parallel the reactions of $CpRe(CO)_2HSiPh_3$ and $MeCpMn(CO)_2HSiPh_3$ in which elimination of $HSiPH_3$ occurs and the aryldiazenido complex is formed, without any detectable intermediate insertion product.[26]

The addition of *p*-fluorobenzenediazonium ion to $Cp_2W(Ph)H$ at −30 °C in acetone-d_6 produced an immediate color change to deep red and evolution of a gas which was presumably nitrogen. An immediate NMR spectrum at −30 °C showed complete loss of the original resonances of $Cp_2W(Ph)H$ [−11.3 (H), 4.6 (Cp), 6.6–7.7 ppm (Ph)], together with the formation of a sharp resonance at 7.36 ppm due to benzene and another at 5.6 ppm due to the Cp groups in a product; a multiplet near 7.3 ppm due to the FC_6H_4 moiety and/or C_6H_5 was also present. Removal of volatiles (consisting largely of acetone-d_6 and benzene by GC and NMR) left a red-brown oily residue which could not be successfully purified. A low-nitrogen content (microanalysis) showed it not to be an aryldiazenido or related derivative. Because of this, we have not pursued the reaction further, save to note that upon being warmed to room temperature before evacuation the solution turns deep blue, and evacuation yields a blue solid which we have not investigated. The gas evolution suggests that (i) any aryldiazenido-type intermediate, if formed, rapidly collapses by nitrogen extrusion or (ii) the diazonium ion itself is decomposed by the tungsten compound.

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Registry No. $[Cp_2WH(p\text{-}NNC_6H_4F)][PF_6]\cdot Me_2CO$, 76317-79-8.

Supplementary Material Available: Table IIIa, a more complete listing of bond lengths and angles, Table V, the torsion angles, Table VI, the mean-plane listing, Table VII, the calculated hydrogen atomic coordinates, Table VIII, a listing of observed and calculated structure amplitudes, and Table IX, the anisotropic thermal parameters (31 pages). Ordering information is given on any current masthead page.

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A Novel Series of Compounds Containing from One to Four Ruthenium(II) Bis(bipyridine) Units Bound to the Same Bridging Ligand[1]

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The synthesis and properties of a novel series of compounds containing one, two, three, and four ruthenium bis(bipyridine) units bound to the same bridging ligand are described. The formulations were verified by dilution conductivity studies. Both cyclic voltammograms and the visible spectra of the complexes suggest that the bridging ligand can be described as containing two equivalent subunits. The metal centers in the same subunit show the effects of metal–metal interaction in reduction potential data and in the apperance of intervalence electron-transfer bands (IT) for the mixed-valence ions. The metal centers in different subunits act independently of one another. Reduction of the binuclear and tetranuclear complexes results in electronic subunit–subunit interactions at sites closely associated with the pyrazine components.

Introduction

The behavior of multielectron-transfer agents is an area in inorganic chemistry which has received little attention, primarily for the lack of examples and model compounds. An understanding of the physical properties and reactivity patterns of such complexes is important, especially in light of the fact that multielectron-transfer processes in biochemical reactions are carried out with such ease.[2] Biochemical catalysts may

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[1] A preliminary account of this work was given at the Southeast/Southwest Regional Meeting of the American Chemical Society, New Orleans, LA, Dec 10–13, 1980.

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