An Arylhydrazido(2−) Complex of Tungsten with a Distinctly Bent W–N–N Skeleton. *X*-Ray Crystal Structure of Biscyclopentadienylhydrido-*p*-fluorophenylhydrazido(2−)tungsten Hexafluorophosphate Acetone Solvate $[(\eta^5\text{-}C_5H_5)_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$

By TERRY JONES, A. J. LEE HANLAN, FREDERICK W. B. EINSTEIN, and DEREK SUTTON*
(Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6)

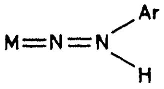
Summary. The title complex, synthesized by the insertion of *p*-fluorobenzenediazonium ion into one W–H bond in $(\eta^5\text{-}C_5H_5)_2WH_2$ below −20 °C, has been shown by a single-crystal *X*-ray structure determination at −100 °C to contain a formally *p*-fluorophenylhydrazido(2−) ligand co-ordinated with a distinctly bent W–N(1)–N(2) skeleton [angle at N(1) 146.3(6)°], this ligand is oriented such as to make the two $\eta^5\text{-}C_5H_5$ groups non-equivalent, consistent with the ground-state conformation in solution deduced from the low-temperature ^1H n.m.r. spectrum.

SINCE the first report by Parshall,[1] the migratory insertion of an arenediazonium ion $[RN_2]^+$ (R = aryl) into transition metal M–H bonds to give aryldiazene (HN=NR) complexes has been observed frequently.[2] However, as we have noted previously,[3,4] the low-temperature reaction of $[RN_2]^+$ with $(\eta^5\text{-}C_5H_5)_2WH_2$ yields compounds (**1a**—**e**) in which the hydrogen has apparently migrated to N(2) rather than N(1), to produce the ligand NNHR. Because this ligand [formally arylhydrazido(2−)], may also result from reactions of co-ordinated dinitrogen,[5–7] new results which extend our knowledge of its possible stereochemistry, electronic structure and conjugation with the metal are important in nitrogen fixation studies.

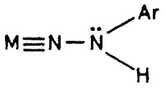
$$[(\eta^5\text{-}C_5H_5)_2W(H)\overset{1}{N}\overset{2}{N}HR]^+X^-$$

(1) **a**, R = Ph, X = BF_4
b, R = *p*-$MeOC_6H_4$, X = BF_4
c, R = *p*-MeC_6H_4, X = BF_4
d, R = *p*-MeC_6H_4, X = PF_6
e, R = *p*-FC_6H_4, X = PF_6

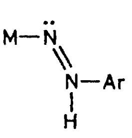
The W–N(1)–N(2) group may be linear (**2a**—**b**), or bent at N(1) (**3a**—**c**). The linear structure has been found in Mo, W, or Re complexes with hydrazido(2−) {NNH$_2$},[5] alkylhydrazido(2−),[6] and arylhydrazido(2−) ligands,[5d,7] but assuming the C$_5$H$_5$ groups to be η^5-bound, it results in a 20-electron count for (**1**), whereas the previously unobserved bent structure (**3a**—**c**) gives a more reasonable 18-electron count. The low field N(2)H resonance (*ca.* δ 10·8)[3] and the non-equivalence of the C$_5$H$_5$ rings in solution at low temperatures are both most readily interpreted in terms of (**3a**—**c**). Furthermore, the latter requires that, in the ground state, the ligand must be oriented in a sterically unfavourable manner, as shown in (**4**), so that the W···N···N plane is not coincident with the plane which equates the two cyclopentadienyl rings.[4]



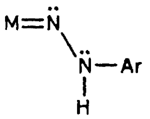
(2a)



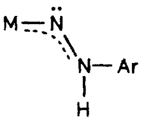
(2b)



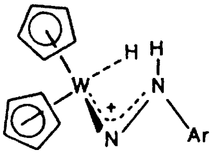
(3a)



(3b)



(3c)



(4)

These structures have been written to indicate bond orders and the localisation of lone-pairs of electrons involved in alternative representations; formal charges have been omitted

Yellow crystals of the title complex were grown from acetone–toluene at −35 °C to minimise isomerization.[3,4] Allowing for the Me$_2$CO, these exhibited i.r. and ^{1}H n.m.r. spectra identical with the original material.[4]

Crystal data: (at −100 °C) monoclinic, space group $P2_1/c$, a = 10·270(3), b = 10·591(2), c = 21·041(5) Å, β = 107·35(2)°, U = 2184·5 Å^3, Z = 4. Intensity data ($2\theta \leqslant 45°$) used for structure solution and refinement were collected on a Picker FACS-1 automatic four-circle diffractometer at −100 °C using Mo-K_α radiation (λ = 0·70926 Å); 2479 reflections were observed [$I \geqslant 2·3\ \sigma(I)$] out of a total of 2863 measured. The position of the tungsten atom was located using direct methods, and the non-hydrogen atoms were located from subsequent Fourier and difference Fourier maps. The structure has been refined using full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on the C$_5$H$_5$ and aryl groups, and the N(2)H hydrogen atom were included at calculated positions as fixed contributions in later cycles, and the current agreement for the absorption-corrected data is R = 0·034, R_W = 0·045.†

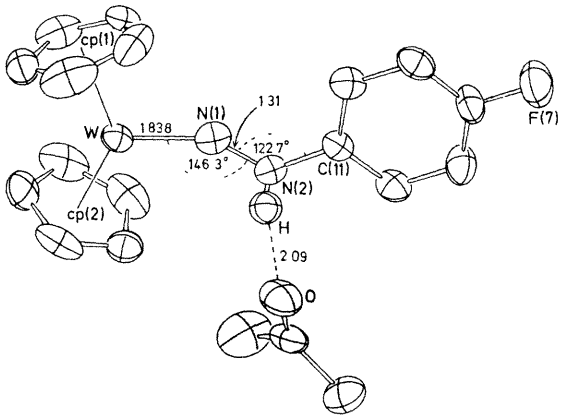


FIGURE. Structure of the [(η^5-C$_5$H$_5$)$_2$WH(p-NNHC$_6$H$_4$F)]$^+$ cation; distances in Å. Also, N(2)–C(11) = 1·42(1) Å, ∠cp(1)–W–N(1) = 110°, cp(2)–W–N(1) = 111°, cp(1)–W–cp(2) = 135°; dihedral angles between the planes of the arylhydrazido ligand and rings (1) and (2) are 94·7 and 77·1° respectively.

The structure of the cation is shown in the Figure. The tungsten atom is co-ordinated by two cyclopentadienyl groups and N(1) of a p-fluorophenylhydrazido(2−) ligand as suggested by the spectroscopic results. The hydride ligand has not been located. The observed ligand co-ordination at W is only slightly pyramidal, with W displaced by 0·23 Å from the N(1) . . . cp(1) . . . cp(2) plane (cp = centroid η^5-C$_5$H$_5$). The hydride ligand is presumably positioned so as to complete an irregular, flattened tetrahedron around the W atom. Its presence is unambiguously demonstrated by the ^{1}H n.m.r. spectrum which shows an upfield proton resonance at δ −2·09 of appropriate intensity, with observable ^{183}W satellites [$^1J(^{183}$WH) = 109 Hz]. The possibilities that the hydrogen is either bound instead to N(1) or is bridging W and N(1) can be discounted since the ^{1}H n.m.r. spectrum of the complex isotopically substituted with ^{15}N at N(1) exhibits only a small splitting (*ca.* 4 Hz) of this hydride resonance, which is quite consistent with a two-bond coupling of the hydride ligand to ^{15}N(1). One-bond ^{15}NH couplings are usually in the range 65—100 Hz.[8]

The WNNHC$_6$H$_4$F group was found, as suggested,[4] to have a non-linear W–N–N skeleton, with an angle of 146·3(6)° at N(1) and distances W–N(1) 1·838(6) Å, and N(1)–N(2) 1·31(1) Å, consistent with structure (**3c**), intermediate between idealized structures (**3a** and **b**).

The present W–N(1) bond is significantly longer than W–N bonds in linear hydrazido(2−) derivatives,[5–7] which are in the narrow range 1·73(1)—1·768(14) Å. This is consistent with increased metal–nitrogen multiple bonding in (**2a**, **b**), compared with (**3a**—**c**). The N–N bond lengths are not significantly different and are intermediate between typical single (1·43 Å) and double (1·23 Å) bonds. In support of the ^{1}H n.m.r. results on the ^{15}N-substituted derivatives which

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

suggested the presence of the N(2)H group, there is a molecule of acetone forming an O H–N hydrogen bond with this group at a distance of 2·09 Å, and significant electron density at the hydrogen atom position Atoms W, N(1), N(2) and those of the aryl substituent define to a good approximation a plane [max deviation 0 08(1) Å] which lies roughly normal to the least-squares planes of the two η^5-C_5H_5 rings This configuration may be rationalized as the one which allows for near optimum delocalization of the tungsten electron pair (which populates the $1a_1$ orbital[9]) into the π^*-acceptor orbital of the N=N bond Both the geometry and the temperature-dependent dynamic properties of this tungsten-arylhydrazido moiety may be compared with those of the metal–carbene and –alkylidene systems in [$(\eta^5$-$C_5H_5)_2$-Ta(alkyl)(CHR)] and [$(\eta^5$-$C_5H_5)_2$Ta(alkyl)(CH_2)] [10] In the present case, rotation of the ligand about the W–N bond is believed to be responsible for the η^5-C_5H_5 resonances becoming equivalent in the ^{1}H n m r as the temperature is increased [4]

This work was supported by N S E R C Canada through operating grants

(*Received, 28th May* 1980, *Com.* 558.)

[1] G W Parshall, *J Am Chem Soc*, 1967, **89**, 1822

[2] D Sutton, *Chem Soc Rev*, 1975, **4**, 443

[3] J A Carroll, D Sutton, M Cowie, and M D Gauthier, *J Chem Soc, Chem Commun*, 1979, 1058

[4] J A Carroll and D Sutton *Inorg Chem*, 1980 **19** 3137

[5] (a) G A Heath, R Mason, and K M Thomas, *J Am Chem Soc*, 1974, **96**, 259 (b) M Hidai, T Kodama, M Sato, M Harakawa, and Y Uchida, *Inorg Chem* 1976, **15**, 2694, (c) J Chatt M E Fakley R L Richards I R Hanson, and D L Hughes, *J Organomet Chem*, 1979, **170**, C6, (d) J Chatt, M E Fakley, P B Hitchcock, R L Richards, N Tuyet Luong-Thi, and D L Hughes, *ibid*, 1979, **172**, C55

[6] V W Day, T A George, S D A Iske and S D Wagner *J Organomet Chem* 1976, **112**, C55, F C March, R Mason, and K M Thomas, *ibid*, 1975, **96**, C43 and references therein M W Bishop, J Chatt, J R Dilworth, M B Hursthouse, and M Motevalli, *J Chem Soc, Dalton Trans*, 1979, 1600

[7] R Mason, K M Thomas, J A Zubieta, P G Douglas, A R Galbraith, and B L Shaw, *J Am Chem Soc*, 1974, **96**, 260, J Chatt, B A Crichton, J R Dilworth, P Dahlstrom, R Gutsoka, and J A Zubieta, *Transition Met Chem* (Weinheim, Ger), 1979, **4**, 271

[8] B L Haymore and J A Ibers, *J Am Chem Soc*, 1975, **97**, 5369

[9] J W Lauher and R Hoffmann, *J Am Chem Soc*, 1976, **98**, 1729

[10] R R Schrock, L W Messerle, C D Wood, and L J Guggenberger, *J Am Chem Soc*, 1978, **100**, 3793