# 'Side-on' Co-ordination of a Phenylhydrazido Ligand: Synthesis and *X*-Ray Structure Determination of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$

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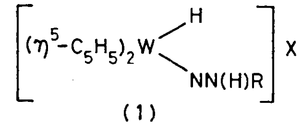
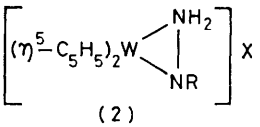
*Summary* The low-temperature product, $[(\eta^5\text{-}C_5H_5)_2WH(NNHR)][X]$ (R = aryl, X = $BF_4$ or $PF_6$), from the reaction of $[RN_2][X]$ with $(\eta^5\text{-}C_5H_5)_2WH_2$ rearranges in solution above −20 °C to yield $[(\eta^5\text{-}C_5H_5)_2W(H_2NNR)][X]$ in which the arylhydrazido ligand is bound to W in a 'side-on' or dihapto manner.

THE stereochemistry and rearrangement processes adopted by nitrogen hydrides bound to transition metals are of considerable importance in understanding nitrogen-fixation intermediates and in designing syntheses for organonitrogen compounds from nitrogen or ammonia. The hydrazido(1−) ligand $N_2H_3$ has been synthesized by protonation of co-ordinated dinitrogen,[1] but there is a lack of direct structural evidence as to the stereochemistry of this ligand or its organic derivatives in complexes.

We now report the preparation and structure of a 'side-on' or $\eta^2$-arylhydrazido(1−) ligand bound to tungsten, and its ready formation by rearrangement of an 'end-on' [formally arylhydrazido(2−)] NN(H)R ligand in a precursor.



(1)



(2)

**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 = $PF_6$

$(\eta^5\text{-}C_5H_5)_2WH_2$ reacts with an equimolar amount of an arenediazonium tetrafluoroborate or hexafluorophosphate in methanol–toluene below −20 °C to give the yellow crystalline solids (**1a**—**e**).† The $^1H$ n.m.r. spectrum [$CD_3CN$ or $(CD_3)_2CO$] of (**1d**) at 259 K exhibits $\delta$ (downfield from internal $Me_4Si$) −2·09 (s, 1H, WH, with $^{183}W$H satellites $J$ = 109 Hz), 2·33 (s, 3H, Me), 6·05 (s, 10H, $C_5H_5$) 6·73 (d, 2H, 2,6-aryl), 7·10 (d, 2H, 3,5-aryl), and 10·8 (br s, 1H, NH). The NH proton was shown unequivocally to be bound to $N^2$‡ by selectively isotopically substituting each nitrogen atom with $^{15}N$. Thus, the $^1H$ n.m.r. spectrum of [$^{15}N^1$]-(**1c**) was virtually unchanged, but the spectrum of [$^{15}N^2$]-(**1a**) showed the NH resonance as a sharp doublet with $^1J(^{15}NH)$ = 99 Hz. This is, to our knowledge, the first example of 'insertion' of an arenediazonium ion into a M–H bond not producing an aryldiazene (HNNR) ligand. In the i.r. spectrum ν(NH) is at 3240 cm$^{-1}$ (X = $BF_4$) and a very weak band at 1950 cm$^{-1}$ is assigned as ν(WH).

Repeating the synthesis at 0 °C, or stirring solutions of (**1**) above −20 °C produces complexes (**2a**—**e**) [ν(NH) 3300 and 3240 cm$^{-1}$ (X = $BF_4$)] as brown solids which recrystallize from acetone–diethyl ether–hexane as dark red rhombic crystals. The $^1H$ n.m.r. spectrum of (**2c**) exhibits $\delta$ 2·22 (s, 3H, Me), 3·92 (br s, 2H, $NH_2$), 5·50 (s, 10H, $C_5H_5$), 6·55 (d, 2H, 2,6-aryl), and 7·04 (d, 2H, 3,5-aryl). The location of both NH protons on $N^1$ was identified from the $^1H$ n.m.r. spectrum of (**2c**) (synthesized using [*p*-$MeC_6H_4N{\equiv}^{15}N$][$BF_4$]) for which the NH resonance occurred as a sharp doublet of intensity 2H with $^1J(^{15}NH)$ = 88 Hz. This was confirmed by observing the same coupling constant for a 1 : 2 : 1 triplet in the proton-coupled $^{15}N$ n.m.r. spectrum at 10·14 MHz ($\delta$ 68 p.p.m. upfield from external $^{15}NH_4Cl$).

$[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$, (**2a**) crystallizes in the space group $P2_1/c\text{-}C^5_{2h}$ with $a$ = 8·5874(6), $b$ = 10·4821(8), $c$ = 19·546(1) Å, $\beta$ = 107·175(6)°, $U$ = 1680·9 Å$^3$, $Z$ = 4. Intensity data were collected (for $2\theta \leqslant 120°$) on an automated Picker four-circle diffractometer using Ni-filtered Cu-$K_\alpha$ radiation. Of the 2794 unique reflections measured, 1963 had $F_0{}^2 \geqslant 3\,\sigma(F_0{}^2)$ and were used in the solution and refinement of the structure (using conventional Patterson, Fourier, and full-matrix, least-squares methods) which has converged for the absorption-corrected data at $R$ = 0·048, $R_W$ = 0·064. The $C_5H_5$ rings were refined as hindered rotor groups[2] and all other non-hydrogen atoms were

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† Satisfactory C, H, and N analyses have been obtained.

‡ Nitrogen atoms are numbered with respect to the parent arenediazonium ion $[R\text{–}N^2{\equiv}N^1]^+$.

refined anisotropically. All hydrogen atoms were located in Fourier maps and were included in the least-squares calculations as fixed contributions.§

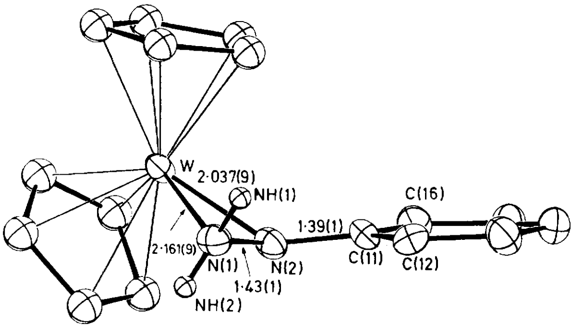

FIGURE. The structure of the $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)]^+$ cation; distances in Å. In addition N(1)–W–N(2) = 40·0(3) and N(1)–N(2)–C(11) = 119·7(9)°.

The cation (Figure) has a quasi-tetrahedral geometry with the four co-ordination sites occupied by the two $(\eta^5\text{-}C_5H_5)$ rings and the nitrogen atoms of the phenylhydrazido(1−) ligand which is 'side-on' bound to the tungsten. Each cyclopentadienyl group is symmetrically located with respect to the metal, and the angle between them is essentially bisected by the W–N(1)–N(2) plane. Notably, the W–N distances are not equivalent, the distances to the three-co-ordinate nitrogen atom N(2) [2·037(9) Å] being much shorter than that involving the four-co-ordinate atom N(1) [2·161(9) Å]. Whilst there are no other documented examples of dihapto hydrazido(1−) ligands for comparison, we note that the single example containing a dihapto phenylhydrazine, $[(\eta^5\text{-}C_5H_5)Mo(NO)I(H_2NNHPh)][BF_4]$, has metal–nitrogen bond distances of 2·134(3) and 2·184(3) Å which are similar to the W–N(1) length observed here.[3] Significantly, the $NH_2$ and NHPh groups are eclipsed in the molybdenum compound,[3] but we find that the N(2)–C(11) bond is not eclipsed by the N(1)–NH(1) bond but rather is staggered by *ca.* 32°, with the twist occurring such that the N(2) lone pair could be more accessible for possible overlap with metal d-orbitals. Whilst such a contribution may account for the shorter W–N(2) bond, it should be noted that the tungsten already has an 18-electron configuration. A somewhat comparable complex $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2\text{-}NNMe_2]$ also shows unequal Mo–N distances to the dihapto $NNMe_2$ ligand with values of 2·133(12) Å to the 4-co-ordinate ($NMe_2$) atom and 2·054(12) Å to the 3-co-ordinate nitrogen atom.[4]

The N(1)–N(2) bond length [1·43(1) Å] corresponds to a typical N–N single bond and compares well with values of 1·430(5) and 1·40(2) Å respectively in the above molybdenum complexes. By contrast, a typical N–N double bond[5] is *ca.* 1·23 Å.

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§ 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.

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