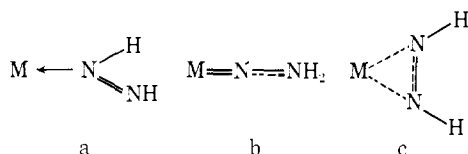


**Figure 1.**  $[W(N_2H_2)Cl(diphos)_2]^+$ , a perspective view of the coordination around the tungsten atom. Bond lengths are (Å) W-P(1) 2.517 (4), W-P(2) 2.515(4), W-P(3) 2.540 (4), W-P(4) 2.517 (4), W-Cl 2.421 (4), W-N(1) 1.73 (1), and N(1)-N(2) 1.37 (2); the bond angle W-N(1)-N(2) is 171 (1)°.

is carried out in the presence of sodium tetraphenylborate or if  $[W(N_2H_2)Cl_2(diphos)_2]$  (I) is treated with  $NaBPh_4$ , the 1:1 electrolyte  $[W(N_2H_2)Cl(diphos)_2]BPh_4$  (II) is obtained.

Spectroscopic data<sup>1</sup> were taken to suggest the monohapto diimine arrangement (a) for I but the apparent equivalence of the diimine protons (<sup>1</sup>H nmr) and the smaller separation of the  $\nu(N-H)$  bands suggested the monohapto hydrazido structure (b) or the dihapto diimine configuration (c) for II.

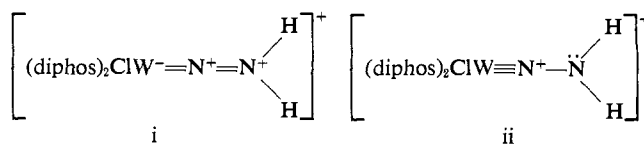


An X-ray diffraction analysis of  $[W(N_2H_2)Cl(diphos)_2]BPh_4$  has now been completed. Crystals (methanol) are monoclinic and  $a = 12.472$  (1),  $b = 19.658$  (2),  $c = 27.056$  (3) Å,  $\beta = 92.53$  (1)°,<sup>2</sup> space group  $P2_1/c$ , and  $Z = 4$ . Independent (5599) reflections with  $F_o^2 \geq 3\sigma(F_o^2)$  ( $4^\circ \leq 2\theta \leq 45^\circ$ ; Mo  $K\alpha$ , graphite monochromator) were observed by the  $\omega$ - $2\theta$  scan routine using an automatic four-circle diffractometer. The structure was solved by conventional heavy-atom techniques. Refinement of positional parameters of all nonhydrogen atoms, of anisotropic temperature factors for W, P, and Cl, and of isotropic Debye factors for the remainder has converged the discrepancy index,  $R_1$ , to 0.064. A general view of the structure of the cation and of important bond lengths and bond angles is shown in Figure 1.

Our principal concern here is with the geometry of the coordinated  $N_2H_2$  ligand. The essential linearity of W-N(1)-N(2) precludes protonation at N(1) and establishes the ligand as the monohapto hydrazido(2-) form (b). The N(1)-N(2) bond length indicates a bond order of approximately 1.5 and the W-N(1) bond distance is consistent with considerable multiple bond-

(2) Here, as elsewhere, the figure in parentheses refers to the esd of the accompanying observation and has been calculated by inversion of the appropriate least-squares matrix.

ing between the metal and ligand. The (linear) valence bond structures



must be considered as important and, in the absence of a precise W-N bond order-bond length relationship, would be distinguished by the stereochemistry of the nitrogen atom N(2), but difference electron density syntheses do not indicate clearly the hydrogen atom positions.

The metal-phosphorus bond lengths are similar ( $\pm 0.03$  Å) to those which have been established for tertiary phosphine complexes of metal tri- and tetrahalides<sup>3</sup> while the W-Cl bond length of 2.421 (1) Å suggests a trans influence ( $\sim 0.1$  Å) of the hydrazido ligand which is comparable with that of dimethylphenylphosphine.<sup>3</sup> The enhanced multiple bonding between the metal and hydrazido ligand, compared with that in the metal-dinitrogen complex, and the consequent weakening of the nitrogen-nitrogen bond follow simple expectations based on molecular orbital theory since protonation of dinitrogen must considerably stabilize its  $\pi^*$  levels. A comparison with the structural data for the protonated azo complex,  $[ReCl_2(NH_3)(N_2H-C_6H_5)(P(CH_3)_2C_6H_5)_2]Br$ ,<sup>4</sup> indicates that the canonical structure (ii) is of relatively little importance in the rhenium complex; we imagine that the substituent effect of the phenyl group and, more importantly, the effective Lewis basicity of  $W^{(n-1)+}$  compared with  $Re^{n+}$ , serve to reduce metal to ligand charge transfer in the rhenium species.

Recent speculations on the mode of action of the nitrogenase enzyme complex are based on the assertion<sup>5</sup> that monohapto dinitrogen complexes are nonreactive with respect to protonation, thus providing *prima facie* evidence that the enzyme binds dinitrogen as the dihapto  $\pi$  complex; this discussion<sup>5</sup> curiously overlooks the early synthetic results<sup>1</sup> which the present report confirms in detail. An X-ray analysis of  $[WCl_2(N_2H_2)(diphos)_2]$  is in hand to test the prediction<sup>1</sup> that, in this case, the diimine structure (a) will be adopted, but it is already obvious that the coordination number of the metal is an important factor in determining the geometry of the reduced  $N_2H_2$  species.<sup>6</sup>

(3) L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 30 (1970).

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### Reversible Protonation of a Phenylazo Complex of Rhenium(III)

Sir:

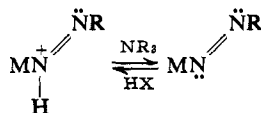
It is becoming obvious that the chemistries of metal-dinitrogen and metal-azo complexes have a number

Table I

|   | Bond lengths (Å) |           |          | Bond angles (deg) |             |
|---|------------------|-----------|----------|-------------------|-------------|
|   | Re–N(1)          | N(1)–N(2) | N(2)–C   | Re–N(1)–N(2)      | N(1)–N(2)–C |
| ReCl <sub>2</sub> (N <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <sup>a,b</sup>          | 1.77 (2)         | 1.23 (2)  | 1.43 (2) | 173 (2)           | 119 (2)     |
| ReCl <sub>2</sub> (N <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> )(P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <sup>b</sup>          | 1.74 (2)         | 1.22 (3)  | 1.42 (3) | 170 (2)           | 124 (2)     |
| [ReCl <sub>2</sub> (NH <sub>3</sub> )(N <sub>2</sub> HC <sub>6</sub> H <sub>5</sub> )(P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]Br | 1.75 (1)         | 1.28 (2)  | 1.42 (2) | 172 (1)           | 119 (2)     |

<sup>a</sup> V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970). <sup>b</sup> V. F. Duckworth, G. J. Gainsford, and R. Mason, manuscript in preparation.

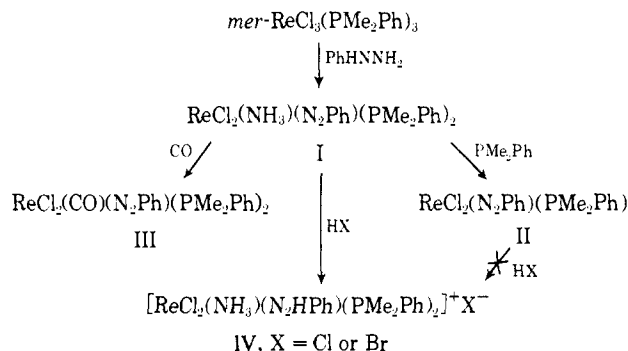
of common features. 1-η-Diimine metal complexes can be synthesized<sup>1,2</sup> from the reaction of metal hydrides with diazonium tetrafluoroborate; the coordinated diimine ligand is reversibly deprotonated forming the azo complex.



Tungsten and rhenium azo complexes can be prepared directly from the corresponding dinitrogen complexes,<sup>3,4</sup> but, hitherto, protonation of a metal-azo complex occurs on the first (metal-bonded) nitrogen, to give the corresponding diimine system. We now report the reactions of a coordinated azo ligand to provide protonation at its second nitrogen atom.

Scheme I shows that the reaction of *mer*-[ReCl<sub>3</sub>-

#### Scheme I



(PMe<sub>2</sub>Ph)<sub>3</sub>] with phenylhydrazine in ethanol provides ReCl<sub>2</sub>(NH<sub>3</sub>)(N<sub>2</sub>Ph)(PMe<sub>2</sub>Ph)<sub>2</sub> (I) as a major product together with a small amount of ReCl<sub>2</sub>(N<sub>2</sub>Ph)(PMe<sub>2</sub>Ph)<sub>3</sub> (II). Ammonia may be readily displaced from I with tertiary phosphine or carbon monoxide to give II and III but, more interestingly, I is protonated readily with aqueous hydrochloric or hydrobromic acids; we have not been able to protonate II even under such rigorous conditions as dry HCl or HBr in benzene.

IV has ν<sub>N-H</sub> at 2540 cm<sup>-1</sup> (X = Cl) and 2640 cm<sup>-1</sup> (X = Br), the N–H stretching frequencies of the coordinated NH<sub>3</sub> in I and IV being at >3130 cm<sup>-1</sup>.

Crystals of [ReCl<sub>2</sub>(NH<sub>3</sub>)(NNHC<sub>6</sub>H<sub>5</sub>)(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br (ethanol) are monoclinic with *a* = 9.561 (1), *b* = 31.802 (3), *c* = 11.004 (1) Å, β = 122.47 (1)°, and space group *P*2<sub>1</sub>/*n*. Independent reflections (2197) (Mo Kα, graphite monochromator, ω–2θ scan routine, four-circle

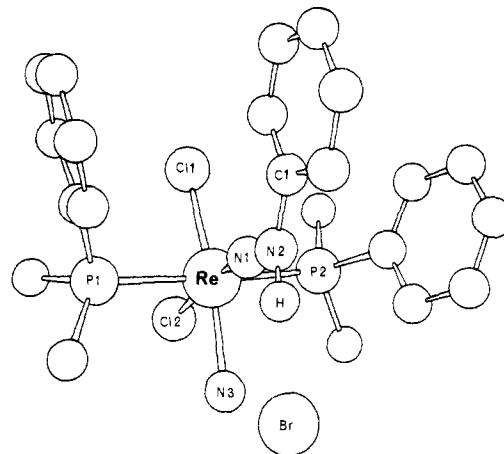


Figure 1. [ReCl<sub>2</sub>(NH<sub>3</sub>)(N<sub>2</sub>H.C<sub>6</sub>H<sub>5</sub>)(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br, a perspective view. Metal-ligand bond lengths (Å) are Re–P(1) 2.442 (8), Re–P(2) 2.448 (8), Re–Cl(1) 2.389 (5), Re–Cl(2) 2.422 (4), Re–N(1) 1.750 (12), and Re–N(3) 2.200 (13). N(1)–N(2) is 1.28 (2), N(2)–C(1) 1.42 (2), and N(2)–H···Br is 3.09 (1) Å. Bond angles (deg) are Re–N(1)–N(2) 172 (1), N(1)–N(2)–C(1) 119 (1), N(1)–N(2)–H 118 (5), and C(1)–N(2)–H 121 (5).

diffractometry) having  $F_o^2 \geq 3\sigma(F_o^2)$  and  $4^\circ \leq 2\theta \leq 46^\circ$  formed the basis of a straightforward structure analysis, which, on refinement of positional parameters for all nonhydrogen atoms, anisotropic temperature factors for Re, Br, Cl, and P, and isotropic motions for the C and N atoms, has converged to  $R_1 = 0.054$ ; a difference electron density synthesis, based on limited diffraction data ( $d_{\text{min}} = 1.4$  Å), demonstrates the positions of all hydrogen atoms in stereochemically acceptable positions.

Both the linearity of Re–N(1)–N(2) and the difference electron density synthesis confirm the site of protonation as N(2), its stereochemistry being essentially planar. The metal-ligand and intraligand bond lengths in several complexes are shown in Table I.

The Re–N(H<sub>3</sub>) bond length of 2.20 (1) Å establishes multiple bonding between the metal and coordinated arylazo ligands since differences of only 0.03 Å or so could be expected on the basis of hybridization alone at the nitrogen atom. The mean Re–P bond length of 2.445 (5) Å should be compared with that of 2.458 (6) Å in ReCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> and 2.505 (3) Å in ReCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>,<sup>5</sup> thus both the metal-phosphorus and N–N bond lengths suggest that the net charge distribution is that of a protonated azo complex of rhenium(III); an aminonitrene-rhenium(I) formulation is excluded by the observed planarity of N(2). In all three rhenium-azo complexes, the Re–N<sub>2</sub>R group is approximately planar, allowing of some electron delocalization, and hence stabilization of the protonated azo

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(3) J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1011 (1972).

(4) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 444 (1972).

ligand relative to the hydrazido(2-) form where the nitrogen-nitrogen bond length approaches 1.4 Å.<sup>6</sup>

The presently available structural data for azo complexes<sup>7-9</sup> all indicate linear bonding. The reactivity of the platinum(II) complex<sup>1</sup> argues for a nonlinear M-N-N bond which, one might anticipate by analogy with the nitrosyl ligand, would also be stabilized by low oxidation state metals in particular stereochemical configurations.<sup>10</sup>

(6) G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, **96**, 259 (1974).

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(9) J. A. Ibers and B. L. Haymore, unpublished results cited in ref 2; A. J. Schultz, J. V. McArdle, R. L. Henry, and R. Eisenberg, Proceedings of the American Crystallographic Association, Summer Meeting 1973, Abstract P.5.

(10) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1211 (1973), and references therein.

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## Stereochemistry of Some Electrophilic Reactions at Iron-Carbon $\sigma$ Bonds

Sir:

Stereochemical changes occurring at  $\alpha$  carbon in reactions of transition metal-alkyl complexes have been the subject of considerable interest.<sup>1-4</sup> By contrast, the stereochemistry at metal of these reactions has not been extensively explored.<sup>5,6</sup> Complementary data on changes in configuration at  $\alpha$  carbon and at metal are necessary for a complete understanding of mechanisms of transformations at metal-carbon bonds. Herein we report on the stereochemistry at metal of SO<sub>2</sub> insertion into and of the electrophilic cleavage by HI, I<sub>2</sub>, and HgI<sub>2</sub> of an iron-carbon  $\sigma$  bond (Scheme I). The SO<sub>2</sub> insertion is highly stereospecific whereas, for the first time, the cleavage processes are shown to involve a reaction intermediate.

The parent methyl complex **1** exists in the form of two diastereomerically related pairs of enantiomers, **1a** and **1b**,<sup>7</sup> owing to the presence of a chiral metal and an unsymmetrically substituted *h*<sup>5</sup>-cyclopentadienyl ring. **1a** and **1b** were prepared and isolated in varying degrees of isomeric purity (up to 100%) by the stereo-

(1) (a) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); (b) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, in press.

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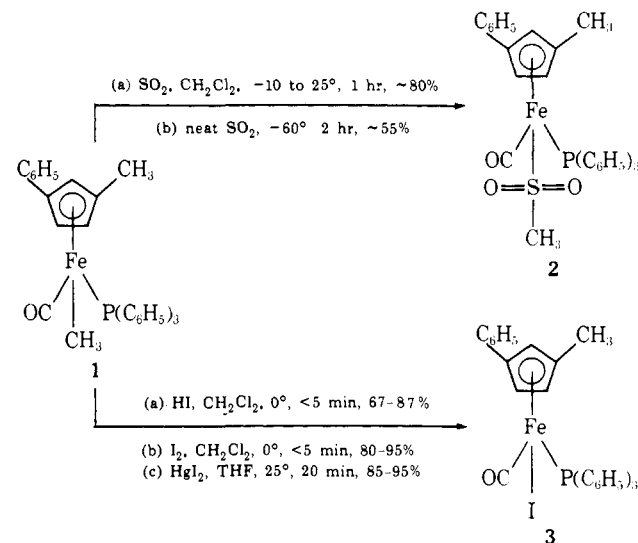
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(6) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

(7) **1a** and **1b** are derived, respectively, by the decarbonylation of the more and less soluble diastereomer of the acetyl. **2a** and **3a** are the dominant diastereomers obtained from **1a**, and **2b** and **3b**, from **1b**.

Scheme I



specific photochemical decarbonylation of the two diastereomers of the corresponding acetyl,<sup>8</sup> followed by fractional crystallization from benzene-pentane. The <sup>1</sup>H nmr spectrum of **1** showed that both the ring ( $\tau$  8.22 and 8.53) and the ligated ( $\tau$  9.91 d, 9.82 d;  $J = 6.4$  Hz) CH<sub>3</sub> groups are diastereotopic.

Reaction between **1a** or **1b** and SO<sub>2</sub> (50-fold excess, 0.4 M) in CH<sub>2</sub>Cl<sub>2</sub> yielded **2** (ir (CHCl<sub>3</sub>) 1958, (KBr) 1161, 1031 cm<sup>-1</sup>). The nmr spectra of **2** [diastereotopic CH<sub>3</sub> groups at  $\tau$  8.11 and 8.20 (ring) and  $\tau$  7.60 and 7.61 (sulfinate)] derived from **1a** and **1b** revealed that each conversion occurred with >95% stereoselectivity at iron. When this same reaction was carried out in liquid SO<sub>2</sub>, stereoselectivities of 76 and 82% were observed for the transformation of the two diastereomers of **1** into **2**. On the basis of a recent kinetic study<sup>9</sup> and the observation of inversion of configuration at  $\alpha$  carbon in the reaction of *h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CHDCHDC-(CH<sub>3</sub>)<sub>3</sub> with SO<sub>2</sub>,<sup>1</sup> a mechanism has been proposed for the SO<sub>2</sub> insertion which involves the intermediacy of a contact ion pair ([M]<sup>+</sup>SO<sub>2</sub>R<sup>-</sup>) and the *O*-sulfinate.<sup>9</sup> The stereochemical result of this study indicates that such an ion pair must possess high configurational stability. Partial epimerization (~20%) at iron in the reaction conducted in neat SO<sub>2</sub> likely resulted from a high concentration of the *O*-sulfinate which is present in equilibrium with the ion pair.<sup>10</sup> We cannot determine whether the high degree of stereospecificity corresponds to retention or inversion at iron;<sup>11</sup> however, the former appears much more likely on mechanistic grounds.

Reaction of **1** with HI, I<sub>2</sub>, or HgI<sub>2</sub> proceeded very rapidly to **3** (ir (CHCl<sub>3</sub>) 1949 cm<sup>-1</sup>). Iodine-containing

(8) T. G. Attig, P. Reich-Rohrwig, and A. Wojcicki, *J. Organometal. Chem.*, **51**, C21 (1973).

(9) S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **95**, 6962 (1973).

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(11) Studies have commenced to resolve this problem by X-ray crystallography. We have recently learned that T. C. Flood and D. L. Miles (*J. Amer. Chem. Soc.*, **95**, 6460 (1973)) studied the stereochemistry at iron of the insertion of SO<sub>2</sub> into the Fe-C bond of *h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)[P-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]CH<sub>2</sub>C(O)OC<sub>10</sub>H<sub>19</sub> [C<sub>10</sub>H<sub>19</sub>O = (-)-mentholate]. By using nmr and circular dichroism spectroscopy, they showed that the insertion in neat SO<sub>2</sub> occurs with >90% retention of configuration at iron. We thank Professor T. C. Flood for communicating this result to us prior to publication.