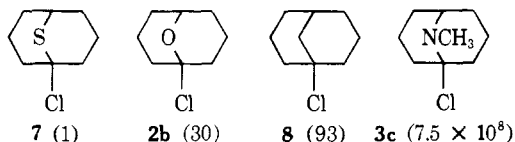


With normal enamines alkylation occurs primarily at carbon, and cyanogen bromide adds across the double bond¹⁴ rather than promoting a von Braun type reaction. Upon treatment of **1** with methyl acrylate in refluxing benzene only starting material was recovered. When olefin **1** was allowed to react with 1,3-diphenylisobenzofuran, the expected Diels–Alder adduct was obtained. Catalytic hydrogenation of **1** gave *N*-methylgranatinine (**3b**)¹⁵ which was also obtained by lithium aluminum hydride reduction of bridgehead chloride **3c**. The pK_a 's in 40% aqueous ethanol for the conjugate acids of **1** and **3b** are 9.09 and 10.19, respectively. The difference, 1.10 pK_a units, is in substantial agreement with the 1.13 unit difference found for quinuclidine and dehydroquinuclidine in water.¹⁶ Other reactions of **1** will be reported at another time.

Evidence relating to the geometric inhibition of resonance of nitrogen in satisfying electron demand by a bridgehead cation in the bicyclo[3.3.1]nonyl system has been gained by determining the kinetics of solvolysis of bridgehead chloride **3c** in 96% ethanol at 29°. The first-order rate constant calculated for **3c** under these conditions is $1.72 \pm 0.12 \text{ min}^{-1}$.¹⁷ The relative rates for a series of bridgehead chlorides are shown below in parentheses.¹⁷ In each case the products of solvolysis



are unrearranged alcohols and ethers. The tremendous rate enhancement of **3c** compared to **8** (nearly ten million times faster) is astounding and indicates that participation by nitrogen is much more effective than is the case for sulfur or oxygen. It should be noted that the majority of α -amino halides are ionic, existing as immonium halides.¹⁸ Indeed only five molecular α -amino chlorides have been reported previously,^{19–21} and these, like **3c**, owe their existence as covalent species to the fact that the immonium ion would introduce trans double bond character in a six-membered ring.^{22–24}

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(16) C. A. Grob, A. Kaiser, and E. Renk, *Chem. Ind. (London)*, 598 (1957).

(17) The rate constant was determined by measuring the half-life of **3c**. The values cited for **2b**, **7**, and **8** were adjusted from the previously reported values^{2,3a,7} for temperature differences and solvent composition using the Grunwald–Winstein equation: (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(18) H. Bohme and K. Osmers, *Chem. Ber.*, **105**, 2237 (1972), and previous papers.

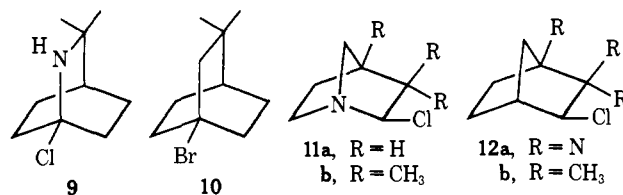
(19) H. Stetter, P. Tacke, and J. Gartner, *Chem. Ber.*, **97**, 3480 (1967).

(20) R. D. Fisher, T. D. Bogard, and P. Kovacic, *J. Amer. Chem. Soc.*, **94**, 7599 (1972); **95**, 3646 (1973).

(21) (a) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **90**, 1355 (1968); **91**, 2047 (1969); (b) P. G. Gassman, R. L. Cryberg, and K. Shudo, *ibid.*, **94**, 7600 (1972).

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However, in spite of this restriction, nitrogen must participate in the ionization of **3c** in order to account for the dramatic rate increase observed. Fisher, Bogard, and Kovacic have reported that bridgehead chloride **9** exhibits enhanced solvolytic reactivity compared to **10**,²⁰ and Gassman, Cryberg, and Shudo have presented evidence for participation by nitrogen in the 1-azabicyclo[2.2.1]heptyl chlorides (**11**).^{21b} The Gassman group found that the rates of solvolysis of **11** and **12** in anhydrous methanol are within 1 order of mag-



nitude of one another²⁵ and proposed that the bridgehead nitrogen provides an apparent rate acceleration of at least 10^3 and possibly 10^8 . In the bicyclo[3.3.1]nonyl system there is considerably less rigidity compared to the norbornyl framework, which might explain the real 10^7 increase in rate of **3c** over **8**.

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hedron, **21**, 2997 (1965); (d) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (e) R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) O. Lenoir, *Tetrahedron Lett.*, 4049 (1972); (g) D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972); (h) J. E. Gano and L. Eizenberg, *J. Amer. Chem. Soc.*, **95**, 972 (1973); (i) B. L. Adams and P. Kovacic, Abstracts of Papers, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26–31, 1973, ORGN 21; (j) H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973); (k) A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047 (1973); (l) N. Miyamoto, S. Isiyama, K. Utimoto, and K. Nozaki, *Tetrahedron*, **29**, 2365 (1973).

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(24) (a) For examples of amides with bridgehead nitrogen see H. Pracejus, *Chem. Ber.*, **92**, 988 (1959); **98**, 2897 (1965); (b) for ureas see H. K. Hall, Jr., and R. C. Johnson, *J. Org. Chem.*, **37**, 697 (1972).

(25) For an example in the quinuclidine system see C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967).

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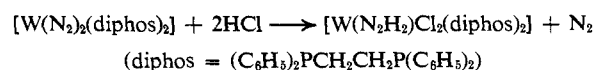
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Reduction of Coordinated Dinitrogen to the Coordinated Hydrazido Dianion. The Structural Characterization of the 1- η -Hydrazido(2-)-chlorobis-[1,2-bis(diphenylphosphino)ethane]tungsten(IV) Cation

Sir:

The reduction, under mild conditions, of dinitrogen complexes of molybdenum(0) and tungsten(0) by hydrogen chloride and hydrogen bromide has been described by Chatt, *et al.*¹ If, for example, the reaction



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

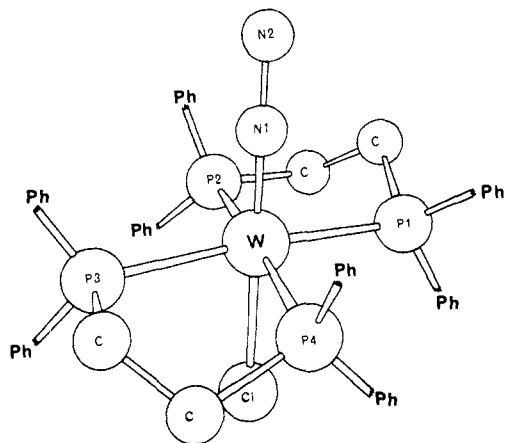
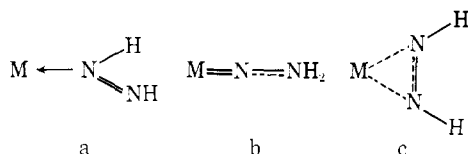


Figure 1. $[W(N_2H_2)Cl(diphos)_2]^+$, a perspective view of the coordination around the tungsten atom. Bond lengths are (Å) W-P(1) 2.517 (4), W-P(2) 2.515(4), W-P(3) 2.540 (4), W-P(4) 2.517 (4), W-Cl 2.421 (4), W-N(1) 1.73 (1), and N(1)-N(2) 1.37 (2); the bond angle W-N(1)-N(2) is $171 (1)^\circ$.

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 data¹ were taken to suggest the monohapto diimine arrangement (a) for I but the apparent equivalence of the diimine protons (¹H 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.

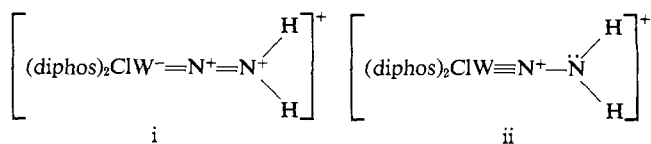


An X-ray diffraction analysis of $[W(N_2H_2)Cl(diphos)_2]BPh_4$ has now been completed. Crystals (methanol) are monoclinic and $a = 12.472 (1)$, $b = 19.658 (2)$, $c = 27.056 (3)$ Å, $\beta = 92.53 (1)^\circ$,² space group $P2_1/c$, and $Z = 4$. Independent (5599) reflections with $F_o^2 \geq 3\sigma(F_o^2)$ ($4^\circ \leq 2\theta \leq 45^\circ$; Mo $K\alpha$, graphite monochromator) were observed by the ω - 2θ 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 (± 0.03 Å) to those which have been established for tertiary phosphine complexes of metal tri- and tetrahalides³ while the W-Cl bond length of 2.421 (1) Å suggests a trans influence (~ 0.1 Å) of the hydrazido ligand which is comparable with that of dimethylphenylphosphine.³ 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 π^* levels. A comparison with the structural data for the protonated azo complex, $[ReCl_2(NH_3)(N_2H-C_6H_5)(P(CH_3)_2C_6H_5)_2]Br$,⁴ 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 assertion⁵ that monohapto dinitrogen complexes are nonreactive with respect to protonation, thus providing *prima facie* evidence that the enzyme binds dinitrogen as the dihapto π complex; this discussion⁵ curiously overlooks the early synthetic results¹ 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 prediction¹ 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.⁶

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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