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The Organic Chemistry of Dinitrogen

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Within the past decade, the ability of certain transition-metal systems to bind and activate molecular nitrogen (dinitrogen) has given access to a new and well-defined area of organic synthesis. This chemistry is based on the direct formation of carbon–nitrogen bonds by reaction of coordinated dinitrogen, or a protonated derivative, with a range of organic compounds including alkyl and acyl halides, carboxylic anhydrides, aldehydes, ketones, and activated aryl or vinyl halides.

The first reports of transition-metal-promoted incorporation of dinitrogen into organic compounds appeared[1] in the late 1960's. These studies however involved poorly defined systems in which reduction of a titanium complex, in the presence of dinitrogen and an organic compound, was followed by destructive hydrolysis to liberate the organonitrogen product. Although several titanium–dinitrogen complexes have been isolated and characterized since that time,[2] the reaction pathways by which carbon–nitrogen bond formation occurs in such systems have yet to be identified with any certainty.

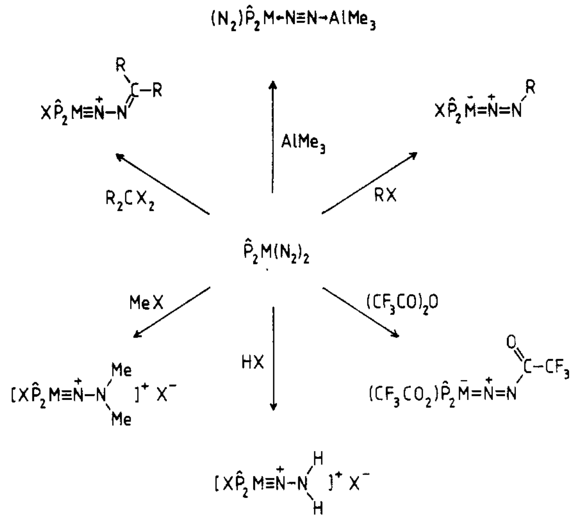
In 1972, Chatt and co-workers[3] reported experimental evidence for the formation of carbon–nitrogen bonds in reactions of the stable, well-defined dinitrogen complexes *trans*-[M$\hat{P}_2(N_2)_2$], where M = molybdenum or tungsten, and $\hat{P}$ = 1,2-bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$. The present Account is concerned with some recent developments in this type of chemistry, with particular emphasis on results from our own Laboratory.

Bonding and Reactivity of Dinitrogen Complexes

The bonding of dinitrogen to a low-valent transition-metal center is normally visualized (Figure 1) in terms of synergic σ-donor/π-acceptor interactions betwen dinitrogen and the metal.[4] This molecular orbital description is valuable in that it immediately accounts for the unique ability of *transition metals* to form stable dinitrogen complexes when other Lewis acids such as BF_3, which lack filled high-energy d orbitals, form only exceedingly weak van der Waals adducts with N_2.[5]

However, a complementary valence-bond model for complexation of dinitrogen (Figure 2) perhaps gives a more vivid impression of the *potential reactivity* of this most inert of diatomic molecules, by indicating the degree of weakening and polarization of the N–N bond that may in principle be achieved.

Scheme I



This picture moreover suggests strongly (and correctly) that the formation of metal–nitrogen multiple bonds is likely to be a key feature of many reactions involving ligating dinitrogen. Indeed, despite certain limitations, the valence-bond approach can provide a logical framework for a remarkably large part of organodinitrogen chemistry so that canonical structures, formal charges, and arrows to indicate shifts of electron density will feature prominently in this Account.

Although more than a hundred complexes of dinitrogen have been synthesized[4] since $[Ru(NH_3)_5(N_2)]^{2+}$ was first reported in 1965,[6] only a very limited number of these undergo well-defined reactions in which the dinitrogen ligand takes part. Sellmann and co-workers have shown, for example, that the dinitrogen ligand in certain cationic manganese carbonyl complexes may be attacked by powerful nucleophiles including methyl and phenyl carbanions.[7] The majority of N_2-reactive complexes, however, are of opposite type, containing transition metals in low oxidation states and strong σ-donor

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[1] M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayko, *J. Chem. Soc., Chem. Commun.*, 1038 (1968); M. E. Vol'pin, A. A. Belyi, N. A. Katkov, R. V. Kudryavtsev, and V. B. Shur, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 2858 (1969); E. E. Van Tamelen and H. Rudler, *J. Am. Chem. Soc.*, 92, 5253 (1970).

[2] J. H. Teuben and H. J. de Liefde Meyer, *J. Organomet. Chem.*, 46, 313 (1972); J. H. Teuben, *ibid.* 57, 159 (1973); R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 98, 8358 (1976).

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

[4] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 78, 589 (1978) and references therein.

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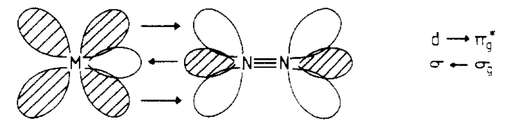


Figure 1. Molecular orbital description of the transition-metal–dinitrogen bond, involving donation of electrons from the filled σ_g (lone-pair) orbital of N_2 to a vacant metal d–p hybrid orbital with, more significantly, synergic back-donation from filled metal d–π orbitals to the vacant π_g^* orbitals of dinitrogen.

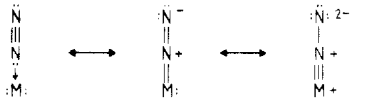
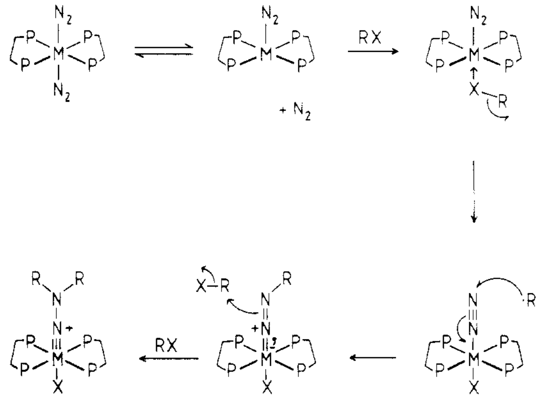


Figure 2. Valence-bond description of the transition-metal–dinitrogen interaction, indicating the degree of weakening and polarization of the N–N bond that may be achieved by formation of an M–N multiple bond.

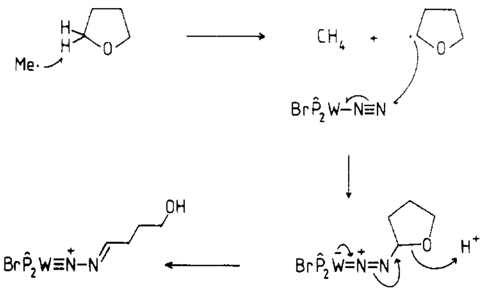
Scheme II



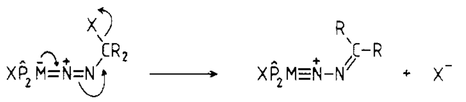
coligands such as tertiary phosphines. The buildup of electron density at the terminal nitrogen (Figure 2) thereby renders the N_2 ligand susceptible to attack by *electrophilic* reagents, though, as we shall see, this does not imply that reaction necessarily occurs by an electron-pair mechanism. Such "reactive" complexes include the zerovalent molybdenum and tungsten compounds $[MP_4(N_2)_2]$, where P is a tertiary monophosphine,[8] and in particular the readily prepared diphosphine derivatives $[M\hat{P}_2(N_2)_2]$ mentioned above.[8-11]

As shown in Scheme I, these complexes react with Lewis acids such as trimethylaluminum to form N-bonded adducts[12] and with protic acids[8,13] and organic electrophiles[3,14,15] to give complexes containing diazenido(1–), (RN_2–), hydrazido(2–) (R_2N_2–), or diazoalkane (R_2CN_2–) ligands. It should be noted that, with the exception of simple adduct formation, all these reactions require loss of one dinitrogen molecule from the complex and formation of a multiple bond between the metal and the reacting N_2 ligand.

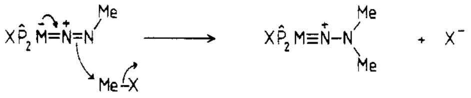
Scheme III



Scheme IV



Scheme V



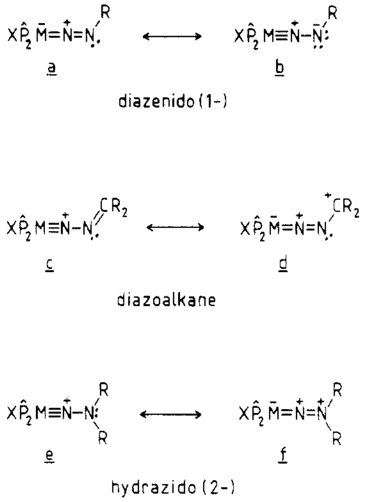


Figure 3. Canonical forms of organodinitrogen ligands, indicating the delocalized nature of the metal–ligand bond systems.

Protonation,[16] adduct formation,[12] and trifluoroacetylation[15] are all rapid processes (a few seconds to a few minutes), but many of the other reactions leading to carbon–nitrogen bond formation proceed via a free-radical mechanism (Scheme II)[17] and are very much slower, often requiring several hours at ambient temperature. For reactions that follow the pathway indicated in Scheme II, irradiation in the visible region is also necessary when M = W to promote initial dissociation of one of the dinitrogen ligands.

In agreement with this now well-established mechanism, and especially relevant to the work described later in this Account, is the observation that (as shown in Scheme III) organodinitrogen complexes derived from the 2-tetrahydrofuranyl radical are obtained[18,19] when

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(9) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *J. Chem. Soc., Chem. Commun.*, 1392 (1969); Y. Uchida, T. Uchida, M. Hidai, and T. Kodama, *Acta Crystallogr., Sect. B*, **31**, 1197 (1975).

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(15) H. M. Colquhoun, *Transition Met. Chem. (Weinheim, Ger.)* **6**, 57 (1981).

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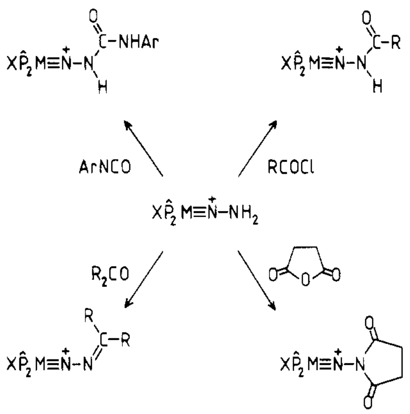
Scheme VI



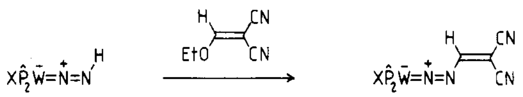
methylation is attempted in THF. Although the primary C–N bond formation often occurs by a radical pathway, subsequent reactions, including the conversion of an oxydiazenido(1–) complex to a diazoalkane derivative (Scheme III), and the ionization of a haloalkyldiazenido(1–) complex[20] (Scheme IV) may occur by electron-pair mechanisms, in this case intramolecular nucleophilic displacement. The final step in the formation of a dimethylhydrazido(2–) complex similarly involves nucleophilic attack (though now in an intermolecular sense) by the first-formed methyldiazenido(1–) complex on a second molecule of methyl halide[21,22] (Scheme V).

There is clearly a close relationship between the diazenido(1–), diazoalkane, and hydrazido(2–) ligands, and this can perhaps be clarified by reference to Figure 3. (For each type of complex two canonical forms can be considered to contribute to the actual structure). Form **3b**, for example, indicates that protonation or alkylation of a diazenido(1–) complex can occur at the terminal nitrogen and should give a hydrazido(2–) complex. Similarly, **3d** suggests that addition of an anion (halide, hydride, alkyl, etc.) to the formally positive diazoalkane carbon atom should give a neutral diazenido(1–) complex. These interconversions, and in some cases the reverse reactions, are, in fact, known and provide strong evidence for the bonding patterns shown in Figure 3.

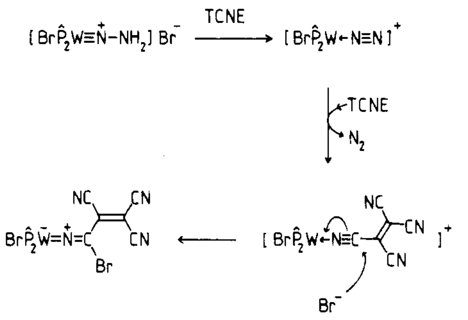
Complexes Containing Protonated Dinitrogen

The hydrazido(2–) complexes $[X\hat{P}_2M{\equiv}NNH_2]^+Y^-$ (M = Mo or W; X = F, Cl, Br, or CF_3CO_2; Y = BF_4, Cl, Br, or $(CF_3CO_2)_2H$), which are obtained in high yield on protonation of $[M\hat{P}_2(N_2)_2]$ by strong acids,[8,13,23] also play a significant role in organodinitrogen chemistry. Condensations with aldehydes and ketones, for example, yield diazoalkane complexes,[24,25] and reactions with acyl halides,[8] cyclic anhydrides, and aryl isocyanates[26] afford acyl-, diacyl-, and carbamoylhydrazido(2–) complexes, respectively (Scheme VI).

Scheme VII



Scheme VIII



Deprotonation of the parent hydrazido(2–) complexes by mild bases such as tertiary amines or aqueous carbonate generates a series of compounds containing the diazenido(1–) (HN_2–) ligand.[27,28] These neutral diazenido(1–) complexes $[X\hat{P}_2W{=}N{=}NH]$ (X = F, Cl, Br, CF_3CO_2) are substantially more nucleophilic than their cationic precursors. We have found, for example, that they readily attack electrophilic alkenes such as 1,1-dicyano-2-ethoxyethene to give compounds containing substituted vinyldiazenido(1–) ligands (SchemeVII).[29]

The reactions were carried out by addition of a tertiary amine to a solution containing the alkene and hydrazido(2–) complex, so generating the diazenido(1–) complex in situ. On one occasion, however, when tetracyanoethene (TCNE) was used as substrate, a reaction was observed even in the absence of base, though two molecular equivalents of TCNE were required for complete conversion of the hydrazido(2–) complex. The product, a deep red crystalline compound, contained only four nitrogen atoms per tungsten rather than the five expected for a tricyanovinyldiazenido(1–) complex, and it was evident that a completely different type of reaction had occurred. The product was finally identified crystallographically as a novel complex containing the previously unknown bromotricyanoprop-2-enylideneamino ligand (Scheme VIII).[29]

In order to account for this result, we have proposed[29] that one molecule of TCNE serves to oxidize the hydrazido(2–) ligand back to N_2 (a reaction known to occur with other oxidizing agents[8]) and that the second TCNE molecule displaces dinitrogen from the complex to give a cationic, 16-electron intermediate containing N-coordinated TCNE. Addition of bromide ion to the coordinated nitrile group then generates the observed, neutral, 18-electron structure (Scheme VIII).

Arylation Reactions

One of our long-term goals in organodinitrogen chemistry has been the synthesis of aromatic amines, and we have therefore investigated many reactions between dinitrogen, diazenido(1–), or hydrazido(2–)

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[20] R. Ben-Shoshan, J. Chatt, G. J. Leigh, and W. Hussain, *J. Chem. Soc., Dalton Trans.*, 771 (1980).

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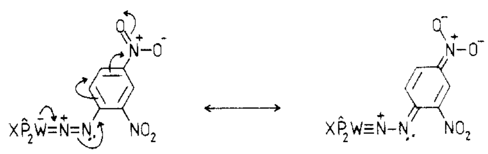
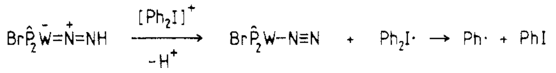


Figure 4. Delocalization of electron density from tungsten to the 2,4-dinitrophenyldiazenido(1−) ligand.

Scheme IX

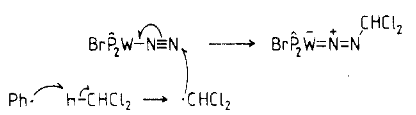


complexes and potential arylating agents. Unactivated aryl halides such as bromobenzene do not arylate such complexes, however, and only the very strongly electrophilic arene 2,4-dinitrofluorobenzene yields aryldiazenido(1−) complexes on reaction with $[\mathrm{X\hat{P}_2W{=}N{=}NH}]$ (X = F, Br, or CF_3CO_2).[23] The resulting 2,4-dinitrophenyldiazenido(1−) complexes are intensely colored, unlike their alkyldiazenido(1−) analogues, and their IR spectra have the curious feature that the symmetrical $\nu(NO_2)$ mode occurs at much lower frequency (1280 cm^{-1}) than is usual for aromatic nitro compounds. Both observations are, however, consistent with the presence of a highly conjugated system in which the metal atom behaves as a powerful source of π-electron density,[14] donating charge to the dinitrophenyl group via the N_2 linkage and thus lowering the effective N–O bond order of the nitro substituents (Figure 4).

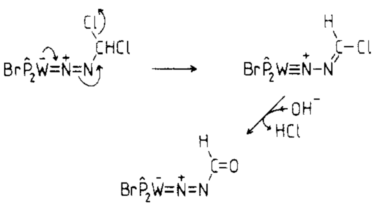
New Routes to Organodinitrogen Complexes

Attempts to phenylate the diazenido(1−) ligand in $[\mathrm{Br\hat{P}_2W{=}N{=}NH}]$ by reaction with diphenyliodonium salts $[Ph_2I]^+X^-$ were unsuccessful in their prime objective, but these experiments provided, quite unexpectedly, a new and potentially versatile route to other types of organodinitrogen ligand.[30] For example, the reaction between $[\mathrm{Br\hat{P}_2W{\equiv}NNH_2}]^+Br^-$ and $[Ph_2I]^+Br^-$, in the presence of aqueous carbonate and with use of dichloromethane as solvent, yielded not the anticipated phenyldiazenido(1−) derivative but the previously unknown *formyl*diazenido(1−) complex $[\mathrm{Br\hat{P}_2W{=}N{=}NCHO}]$. Although the formyl group seemed likely to have been derived from dichloromethane, the nature of this reaction remained obscure until a literature search revealed an analogous result in the chemistry of ferrocene. Attempts to arylate ferrocene in dichloromethane solution, using arenediazonium salts in aqueous acetate buffer, had instead given low yields of ferrocene monoaldehyde.[31] A free-radical pathway was invoked by the authors to account for this result, and an entirely analogous mechanism may be drawn for the formylation of dinitrogen, since free-radical attack on coordinated N_2 is already well-established. The diphenyliodonium ion $[Ph_2I]^+$ is known to behave as a one-electron oxidizing agent, being itself reduced to paramagnetic diphenyliodine, $Ph_2I\cdot$, which rapidly fragments to iodobenzene and a phenyl radical.[32] Oxidative deprotonation of the diazenido(1−) complex by $[Ph_2I]^+$ (Scheme IX) would thus generate Ph· and the known 17-electron complex $[\mathrm{Br\hat{P}_2W(N_2)}]$, which, as described earlier, is susceptible to radical attack at the terminal nitrogen atom.[17] The phenyl radical, however, abstracts hydrogen from the solvent more rapidly than it can diffuse to combine with the dinitrogen complex (Ph· is 3 or 4 orders of magnitude more reactive than Me· in hydrogen abstraction reactions[33]) so that it is a solvent-derived dichloromethyl radical that eventually reacts with $[\mathrm{Br\hat{P}_2W(N_2)}]$ (Scheme X). Hydrolysis of the resulting dichloromethyldiazenido(1−) ligand (probably via a cationic chlorodiazomethane derivative, see below) yields the observed formyldiazenido complex (Scheme XI).

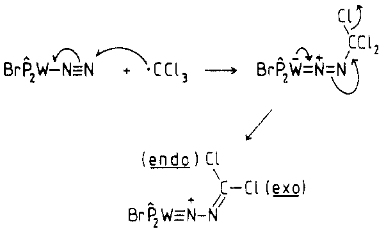
Scheme X



Scheme XI



Scheme XII



Since the phenyl radical will attack virtually *any* organic solvent,[33] either by atom abstraction or by addition to an unsaturated center, this type of reaction provides a potential route to a wide range of organodinitrogen complexes, merely by varying the nature of the solvent. Methyl acetate for example affords the complex $[\mathrm{Br\hat{P}_2W{=}N{=}NCH_2CO_2Me}]$,[30] while $CBrCl_3$ (an excellent source of trichloromethyl radicals due to ready homolysis of the C–Br bond) yields a complex containing ligating dichlorodiazomethane, $[Cl_2CN_2]$, a molecule unknown in the free state. In this case the first-formed trichloromethyldiazenido(1−) complex undergoes spontaneous ionization (Scheme XII), and the cationic dichlorodiazomethane complex that results may be isolated in >60% yield as its hexafluorophosphate salt.[34]

Despite its obvious resistance to hydrolysis (being prepared in the presence of aqueous base), ligating dichlorodiazomethane is relatively reactive, and has proved a versatile source of organodinitrogen ligands. It reacts rapidly at room temperature with a wide variety of nucleophiles including ammonia, primary and secondary amines, alkoxides, carbanions, and fluoride ion (Scheme XIII) to give complexes that often contain otherwise unknown ligands.[34]

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(30) H. M. Colquhoun, *J. Chem. Res., Synop.*, 275 (1981); *J. Chem. Res., Miniprint*, 3401 (1981).

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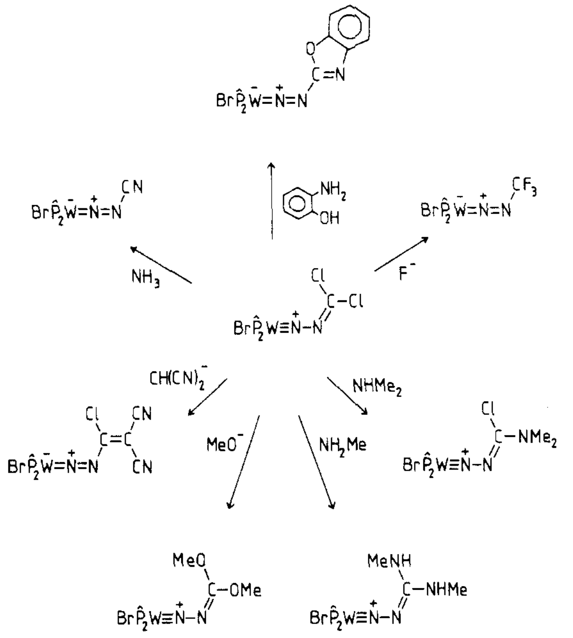
Scheme XIII



Scheme XIV

The type of product obtained is governed partly by steric factors, so that whereas alkoxides and primary amines yield disubstituted diazoalkane ligands, the somewhat bulkier secondary amines replace only the sterically unhindered exo chlorine. The dicyanomethyl anion also gives only monosubstitution in the exo position, but now deprotonation occurs at carbon to give a neutral vinyldiazenido(1−) complex (Scheme XIII). The same compound can be prepared[29] by reaction of 1,1-dichloro-2,2-dicyanoethene with $[\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{W{=}N{=}NH}]$, and its structure has been confirmed crystallographically.[34]

Although mono-secondary amines displace the exo but not the endo chlorine (which has been shown[34] to lie in a sterically hindered position between the phenyl rings of a phosphine ligand), di-secondary amines of the form $\mathrm{RNH(CH_2)}_n\mathrm{NHR}$ (R = Me or Et; n = 2 or 3) displace both chlorines from dichlorodiazomethane to form heterocyclic diaminodiazomethane ligands as shown in Scheme XIV.

Formation of a Dinuclear Complex

When the reaction of diphenyliodonium bromide with $[\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{W{\equiv}NNH_2}]^+\mathrm{Br}^-$ and aqueous base was carried out with use of $\mathrm{CHFBr_2}$ as solvent, small quantities (<10%) of the formyldiazenido(1−) complex $[\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{W{=}N{=}NCHO}]$ were again isolated, but the major product was now an intensely colored yellow-brown compound ($\lambda_{\max}$ 475 nm, ϵ 5.5 × 10^4), which crystallized in the form of "metallic" green-black plates.[35] This compound proved to be the bromide salt of a cationic complex that contained two nitrogen atoms per tungsten and, by $^{31}\mathrm{P}$ NMR of the derived $[\mathrm{PF_6}]^-$ salt, contained two $[\mathrm{W}\hat{\mathrm{P}}_2]$ units per anion. On this basis the complex was provisionally formulated as a monocationic, dinuclear species in which two $[\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{W(N_2)}]$ units are linked by a methylidyne (CH) group derived from the solvent. A single-crystal X-ray study of the Reineckate salt (Figure 5) has confirmed this formulation.[35]

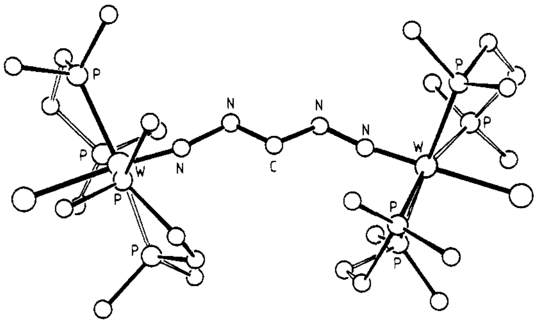


Figure 5. The structure of the $[(\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{WN_2})_2\mathrm{CH}]^+$ cation[36] (phenyl groups omitted for clarity).[2]

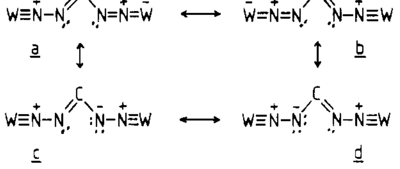
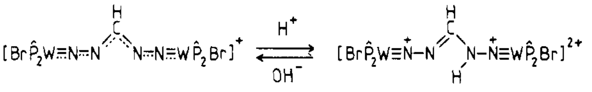
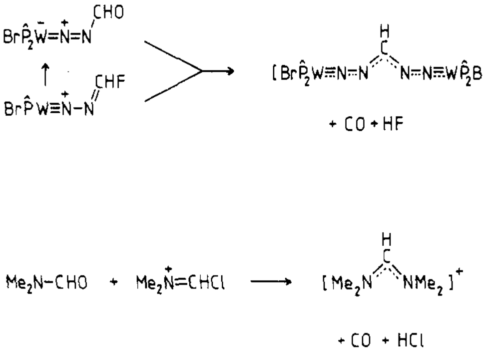


Figure 6. Canonical forms of the metal–ligand bridge system in the $[(\mathrm{Br}\hat{\mathrm{P}}_2\mathrm{WN_2})_2\mathrm{CH}]^+$ cation.

Scheme XV



Scheme XVI



The bridging ligand could be regarded formally (Figure 6) as a delocalized, triply deprotonated derivative of formazan ($\mathrm{H_2NN{=}CHN{=}NH}$) or, more exotically, as a quintuply deprotonated derivative of methane hydrazonic hydrazide ($\mathrm{H_2NN{=}CHNHNH_2}$).

Certainly the IR spectrum of the binuclear cation shows no evidence of a full C=N double bond, though strong bands at 1450 and 1325 $\mathrm{cm^{-1}}$ are assignable to ν(C⋯N) and ν(N⋯N), respectively. Reaction with trifluoroacetic acid, however, gives a dication whose IR spectrum contains a strong absorption at 1560 $\mathrm{cm^{-1}}$, assigned to ν(C=N). Protonation thus appears to "fix" the bond pattern in a more localized form, and in view of the relatively high electron density placed on nitrogen by canonical forms c and d (Figure 6), protonation probably occurs as shown in Scheme XV.

The mechanism described earlier for generation of the formyldiazenido complex (Schemes IX–XI) can be readily extended to account for the formation of a dinuclear complex. Since the observed formyldiazenido

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Acc. Chem. Res. **1984**, *17*, 28–34

derivative almost certainly arises from the hydrolysis of a fluorodiazomethane precursor complex, these two compounds can condense in a "tail-chasing" type of reaction to yield the final dinuclear product (Scheme XVI). Clear precedent for this latter condensation is found in the reaction of Me_2NCHO with $[Me_2N{=}CHCl]^+$, which gives the symmetrical, delocalized tetramethyl formamidinium ion by decarbonylation and loss of HCl.[36]

Conclusion

The organic chemistry of dinitrogen, in its molybdenum and tungsten complexes is clearly rich and varied. Sometimes it may resemble classical organonitrogen chemistry, as in the condensation of hydrazido(2–) complexes with carbonyl compounds, or in the facile dinitrophenylation of a diazenido(1–) (HN_2–) ligand. More often, however, the presence of the metal atom, with its ability to serve as an electron sink or as a center for redox processes, can generate novel mechanistic pathways, and as shown in this Account, the outcome of any new reaction is far from predictable. Nevertheless, once a mechanism has been identified, it often proves quite general and allows further extension of this fascinating and potentially valuable area of chemical synthesis.

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New Organoselenium Methodology

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Although the field of organoselenium chemistry dates back to the 19th century, it did not become a part of the mainstream of organic chemistry until the early 1970s. The apparent turning point came when Sharpless reported a mild method for the conversion of epoxides into allylic alcohols, which made use of the "first" organoselenium reagent, phenyl selenide anion.[1] Within months of this report, Reich disclosed his findings on reactions of various electrophilic selenium species.[2] What followed over the next 10 years was a worldwide explosion of interest in the development and use of new organoselenium methodology. In that period of time over 1000 publications utilizing some type of organoselenium methodology appeared in print.[3] In this Account some of the newer aspects of this renaissance in organoselenium chemistry are discussed.

What factors are responsible for the intense activity in this field? While there are a plethora of reasons that have contributed to the widespread interest, several factors clearly stand out as important. First, organoselenium anions are potent nucleophiles that exhibit a strong preference for reaction with soft acids.[4] On the other hand, when organoselenium species contain reasonable leaving groups (e.g., Cl, Br, O_2CCF_3, etc.), they can serve as extremely reactive, soft electrophiles.[5] Thus, in general, organoselenium moieties can be introduced into a variety of substrates in either a nucleophilic or an electrophilic sense. Moreover, these processes can almost always be accomplished in high yields and under very mild conditions.

Second, once selenium is incorporated into a substrate, a number of options become available for subsequent functional group manipulations. For example, since an arylseleno moiety is a relatively poor leaving group (its nucleofugality is comparable to phenoxide),[6]

Dennis Liotta was born in Brooklyn, NY, in 1949. He received his B.A. and Ph.D. degrees at the City University of New York (Queens College), where he worked with Robert Engel. After 2 years postdoctoral work with Leo A. Paquette at the Ohio State University, he joined the Emory University faculty, where he is now Associate Professor of Chemistry. He is the recipient of both an Alfred P. Sloan and a Camille and Henry Dreyfus Teacher–Scholar Fellowship. He has served as co-chairman of the NSF-sponsored Workshop on Reactive Intermediates from 1981 to 1983 and is currently one of the co-chairman of the Gulf Coast Chemistry Conference. Besides organoselenium chemistry, he is interested in synthetic methodology, total synthesis, photoelectron spectroscopy, and the application of molecular orbital concepts in understanding chemical reactivity. His older brother, Charles, is also a chemist and teaches at Georgia Institute of Technology.

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