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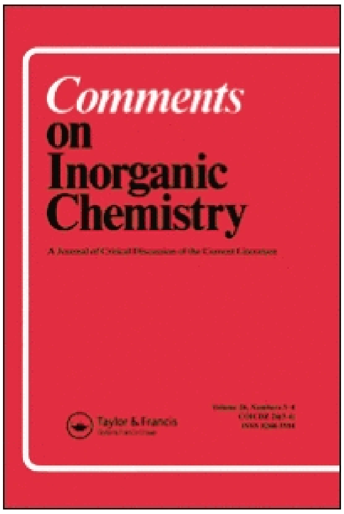

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Reactions of Coordinated Azido Groups

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Reactions of Coordinated Azido Groups

Coordinated azido groups undergo a great variety of reactions and therefore exhibit an interesting synthetic potential. In most cases the azido group decomposes and transforms partially or completely to molecular nitrogen yielding new compounds with metal–nitrogen bonds or complexes with a reduced metal. The products can be nitrido, nitrene, or phosphoraniminato complexes with metal–nitrogen multiple bonds as well as nitrosyl, cyanato, chlorineamine, and dinitrogen complexes. In other cases the complete azido group is involved in a cycloaddition reaction or a nitrene is inserted in a metal–metal or metal–ligand bond. Typical examples of the different types of reactions are discussed.

1. INTRODUCTION

In the past few years azido complexes of the transition metals have been found to be useful educts for the synthesis of interesting new compounds. Among those are, for example, nitrido, nitrene, phosphoraniminato, chlorineamine and dinitrogen complexes as products of a decomposition of the azido group. Moreover, many cycloaddition reactions of the coordinated azido group with double bonds are known. The different reactions which have been observed so far can be classified into four types:

(a) Cleavage of the $N_\alpha{-}N_\beta$ bond of a coordinated azido group $M{-}N_\alpha{-}N_\beta{=}N_\gamma$ to form molecular nitrogen and a nitrene $M{-}\underline{\overline{N}}$, which needs to be stabilized.

(b) Complete elimination of the azido group in the form of molecular nitrogen and reduction of the central metal atom

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by one electron per azido group. This type of reaction may also include the formation of N_2 complexes.

(c) Cycloaddition reactions with multiple bonds as C≡C, C=C, C≡N or C=S.

(d) Insertion of a nitrene $R-\underline{N}$ into a M–CO, M–H or M–M bond.

This comment will mainly focus on reactions of type (a). Reactions of organic azides RN_3 with metal complexes are discussed only briefly, as they have been reviewed elsewhere.[1,2] Other review articles describe some aspects of the decomposition of azido complexes.[3–5]

2. CLEAVAGE OF COORDINATED AZIDO GROUPS

A count of the electrons of a coordinated azido group shows that cleavage of the N_α–N_β bond to form molecular nitrogen produces a nitrene M–N that needs to be stabilized by two additional electrons (Eq. (1)).

$$\left.\begin{array}{l} L_nM-\overline{N}=N=\underline{\overline{N}}| \\ \\ L_nM-\underline{\overline{N}}-N\equiv N| \end{array}\right\} \longrightarrow L_nM-\underline{N} + N\equiv N \qquad (1)$$

L_nM represents the central atom with additional ligands.

Four main possibilities for the stabilization of the nitrene have so far been found:

—a two-electron oxidation of the central metal atom,
—the reductive elimination of two ligands,
—formation of a diimine complex,
—the reaction with a Lewis base such as PR_3, R^-, Cl^-, CO.

Besides the well-studied Staudinger reaction[6,7] of an azide RN_3 with a phosphane PR_3 yielding a phosphoranimine (Eq. (2)), the mechanisms of these reactions are mostly unknown.

$$RN_3 + PPh_3 \longrightarrow R{-}N{=}PPh_3 + N_2 \qquad (2)$$

However it can be assumed that in cases where the reaction occurs at relatively low temperatures a nitrene intermediate need not necessarily be formed. Instead, a concerted mechanism seems more likely. On the other hand, an intermediate nitrene may be produced if a photochemical reaction is carried out.

The most simple way of stabilizing a nitrene $L_nM{-}\underline{\overline{N}}$ is the formation of a nitrido group $M{\equiv}N$ or of a metal nitride. It obviously depends on the oxidation state of the metal atom in the azido complex whether the metal or the ligands will be oxidized.

2.1. Formation of Nitrido Complexes by Cleavage of the Coordinated Azido Group and Simultaneous Oxidation of the Central Metal Atom

If the central metal atom possesses an intermediate oxidation state it will usually be oxidized in two steps during the formation of the nitrido complex. Some typical examples are given in Eqs. (3)–(8)

$$Mo^{IV}Br_3N_3 \longrightarrow Mo^{VI}NBr_3 + N_2\,^{8} \qquad (3)$$

$$Mo(N_3)_4L \longrightarrow MoN(N_3)_3L + N_2 \qquad (4)$$

where L is pyridine,[9] 2,2′-bipyridine.[10]

$$MoCl_4(NCMe)_2 + Me_3SiN_3 + 2L \longrightarrow MoNCl_3L_2 + N_2 + 2MeCN + Me_3SiCl\,^{11} \qquad (5)$$

where L_2 is 2,2′-bipyridine, L is $OPPh_3$.

$$MoCl_4(terpy) + 3Me_3SiN_3 \longrightarrow MoN(N_3)_2Cl(terpy) + N_2 + 3Me_3SiCl\,^{12} \qquad (6)$$

$$(TMP)MnN_3 \longrightarrow (TMP)MnN + N_2\,^{13} \qquad (7)$$

where $TMPH_2$ is Tetramesitylporphine.

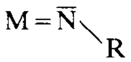
$$(\text{salen})\text{CrN}_3\,\text{H}_2\text{O} \xrightarrow{h\nu} (\text{salen})\text{CrN}\,\text{H}_2\text{O} + \text{N}_2 \;[14] \tag{8}$$

where salenH_2 is N,N'-bis(salicylidene)ethylene-diimine.

In the nitrido complexes $\text{MoN(N}_3)_3\text{L}$,[9,10] MoNCl_3L [11] and $\text{MoN(N}_3)_2\text{Cl(terpy)}$ [12] the molybdenum atom exhibits coordination numbers five, six, or seven. The fivefold coordination in $\text{MoN(N}_3)_3\text{py}$ is in the form of a square pyramid with the nitrido ligand at the apex. In $\text{MoN(N}_3)_2\text{Cl(terpy)}$ a pentagonal bipyramid is observed, the nitrido and chloro ligands being in axial positions (see Fig. 1).

It is also possible that a metal complex reacts with an organic azide RN_3 to give a nitrene complex $L_nM{\equiv}NR$ with an oxidized metal M (Eqs. (9)–(14)).

The M=N–R arrangement is usually linear, whereby the N atom is sp-hybridized forming a metal–nitrogen triple bond. A few examples with a bent



group are also known. In these cases the nitrene ligand NR^{2-} functions only as a four-electron donor; otherwise the metal atom

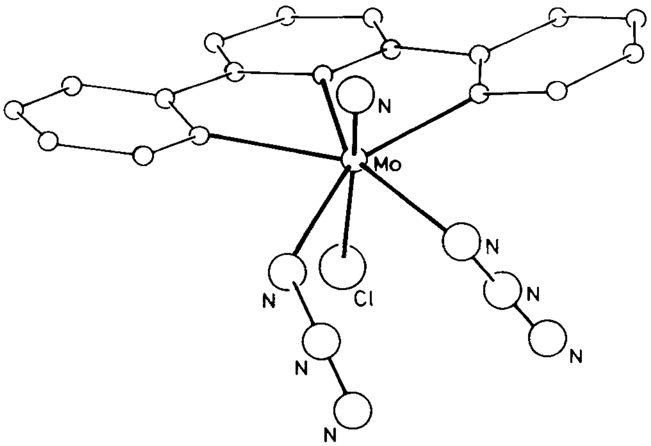


FIGURE 1 Structure of the nitrido complex $\text{MoN(N}_3)_2\text{Cl(terpy)}$ with a terminal M≡N group (Ref. 12).

would reach more than 18 electrons. One example is *cis*-$Mo(NPh)_2(S_2CNEt_2)_2$ [18] (Eq. (13)) with one bent and one linear MNPh arrangement.

$$(Ph_3P)_2Ir(CO)Cl + RN_3 \longrightarrow (Ph_3P)_2Ir(CO)(Cl)(NR) + N_2\ ^{15} \qquad (9)$$

$$(Ph_2MeP)_4M + RN_3 \longrightarrow (Ph_2MeP)_2MNR + N_2 + 2Ph_2MeP \qquad (10)$$

where M is Pd, Pt; R is CF_3CHFCF_2.[15]

$$Ta(CHCMe_3)(PMe_3)_4Cl + Me_3SiN_3 \longrightarrow Cl(PMe_3)_2(CHCMe_3)Ta(NSiMe_3) + N_2 + 2PMe_3\ ^{16} \qquad (11)$$

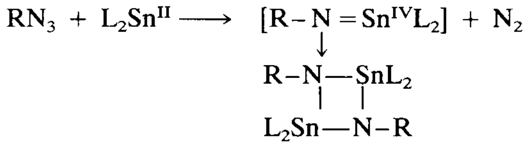
$$W(CO)_2(S_2CNEt_2)_2(PPh_3) + 2RN_3 \longrightarrow W(CO)(NR)(S_2CNEt_2)_2 + CO + 2N_2 + RNPPh_3\ ^{17} \qquad (12)$$

$$Mo(CO)_2(S_2CNEt_2)_2 + 2PhN_3 \longrightarrow cis\text{-}Mo(NPh)_2(S_2CNEt_2)_2 + 2N_2 + 2CO\ ^{18} \qquad (13)$$

$$Mo(CO)_3(S_2PPh_2)_2 + 2ArN_3 \longrightarrow (ArN)_2Mo(S_2PPh_2)_2 + 2N_2 + 3CO\ ^{19} \qquad (14)$$

where Ar is p-tolyl or 2,4,6-mesityl.

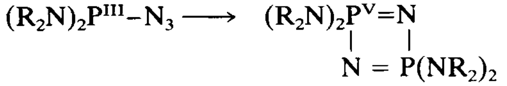
Main group metals may react analogously with an organic azide, but as they prefer single bonds, oligomeric or polymeric compounds are obtained (Eq. (15)).[20]



$$RN_3 + L_2Sn^{II} \longrightarrow \begin{array}{c}[R{-}N{=}Sn^{IV}L_2] + N_2\\ \downarrow \\ \begin{array}{ccc} R{-}N & — & SnL_2 \\ | & & | \\ L_2Sn & — & N{-}R \end{array}\end{array} \qquad (15)$$

(Ref. 20) where L is $(Me_3Si)_2N$; R is phenyl or p-tolyl.

Recent results show that azido compounds of nonmetals such as phosphorus can also decompose by oxidizing the central atom (Eq. (16)).[21]



$$(R_2N)_2P^{III}{-}N_3 \longrightarrow \begin{array}{l}(R_2N)_2P^{V}{=}N\\ \quad\;\; | \qquad\;\; |\\ \quad\;\; N = P(NR_2)_2\end{array} \qquad (16)$$

(Ref. 21) where R is i-C_3H_7. Probably a nitridophosphorane $(R_2N)_2P{\equiv}N$ is formed as an intermediate which subsequently dimerizes.

2.2. Formation of Nitrido Complexes by Cleavage of the Coordinated Azido Group and Simultaneous Reductive Elimination of Ligands

An azido complex as $MoCl_5N_3$ or WCl_5N_3 with the metal being already in the highest possible oxidation state splits off Cl_2 besides N_2 to form a nitrido complex (Eq. (17))

$$MCl_5N_3 \longrightarrow MNCl_3 + N_2 + Cl_2 \qquad (17)$$

where M is Mo, W.[22]

It is interesting that the analogous pentafluoroazidotungsten(VI) [23] does not yield a nitrido complex. The oxidizing ability of the nitrene is probably not high enough for the elimination of F_2.

In nitrido trichloro molybdenum(VI), $MoNCl_3$, an asymmetric nitrido bridge $Mo{\equiv}N{-}Mo$ is formed, resulting in an eight-membered, planar Mo–N ring [24] (Fig. 2). This type of ring structure is frequently observed. Additional examples are $[WNCl_3]_4\,2HN_3$ [25] and $[MNCl_3\,POCl_3]_4$ (M = Mo,[26] W,[27] Re [28]). The structures of $WNCl_3$ and $ReNCl_3$ are not yet known, but probably the same cyclic arrangement is present.

The metal nitrides TiNCl and VON which are obtained from the azides $TiCl_3N_3$ and $VOCl_2N_3$ [29] (Eqs. (18) and (19)) are polymeric compounds, not containing metal–nitrogen π-bonds.

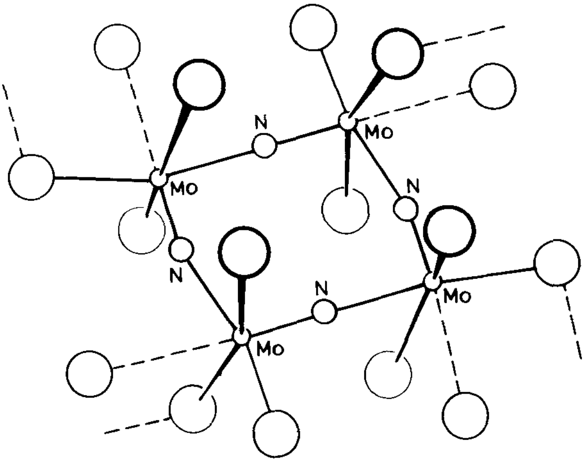


FIGURE 2 Structure of the **nitrido complex $MoNCl_3$ with asymmetrical nitrido** bridges Mo≡N–Mo (Ref. 24).

$$TiCl_3N_3 \longrightarrow TiNCl + N_2 + Cl_2 \qquad (18)$$

$$VOCl_2N_3 \longrightarrow VON + N_2 + Cl_2 \qquad (19)$$

The decomposition of $ReCl_4N_3$ [30] is an example of the involvement of both the oxidation of the metal atom and the reductive elimination of chlorine (Eq. (20)).

$$ReCl_4N_3 \longrightarrow ReNCl_3 + N_2 + 1/2\ Cl_2 \qquad (20)$$

The formation of chlorine is certainly due to the thermal lability of the possible intermediate $ReNCl_4$. This nitrido complex can be obtained at 0 °C from $ReCl_5$ and NCl_3.[31] It easily decomposes to $ReNCl_3$ and 1/2 Cl_2.

Another interesting example is the decomposition of tetraphenylporphyrinato-(azido)iron(III) (TPP)FeN_3 [32,33] (Eq. (21)). It yields a dinuclear complex

$$2(TPP)FeN_3 \longrightarrow (TPP)Fe{=}N{=}Fe(TPP) + 5/2\ N_2 \qquad (21)$$

with a symmetrical nitrido bridge and iron in the oxidation state +3.5 by simultaneous oxidation of the metal atoms and one of the azido groups.

The reductive elimination of an azido group is also observed, when $[Co(NH_3)_6](N_3)_3$ is decomposed to the nitride CoN (Eq. (22)).[34]

$$[Co(NH_3)_6](N_3)_3 \longrightarrow CoN + 6NH_3 + 4N_2 \qquad (22)$$

Equation (23) shows that azides of nonmetals may behave similarly. $PCl_5N_3^-$ evolves N_2 and Cl_2 forming $(PNCl_2)_n$.[35]

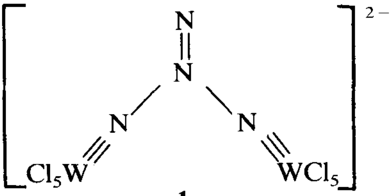
$$PCl_5N_3^- \longrightarrow 1/n(PNCl_2)_n + N_2 + Cl_2 + Cl^- \qquad (23)$$

2.3. Formation of a Diimine Complex

In 1979 Liebelt and Dehnicke[36] reported a reaction of $MoCl_5$ with IN_3 yielding $MoNCl_4$ (Eq. (24)).

$$MoCl_5 + IN_3 \longrightarrow MoNCl_4 + N_2 + ICl \qquad (24)$$

On the basis of the paramagnetic behavior of $MoNCl_4$ with $\mu = 1.63$ B.M. and of the IR and mass spectrum as well they proposed a dimeric structure $Cl_4Mo{=}N{=}N{=}MoCl_4$ with a N=N double bond. Therefore $[MoNCl_4]_2$ can be interpreted as a diimine complex. Although Liebelt and Dehnicke assume a mechanism via an intermediate $MoCl_5IN_3$ adduct, which splits off N_2 and ICl to form $MoNCl_4$, an azido complex $MoCl_4N_3$ may also be likely as a preliminary step. In this connection it is of interest that Dehnicke and co-workers[37] also obtained in the case of tungsten as central atom an isotetrazene complex $Cl_5WN_4WCl_5^{2-}$ (**1**) (Fig. 3) as result of the decomposition of an azido complex.



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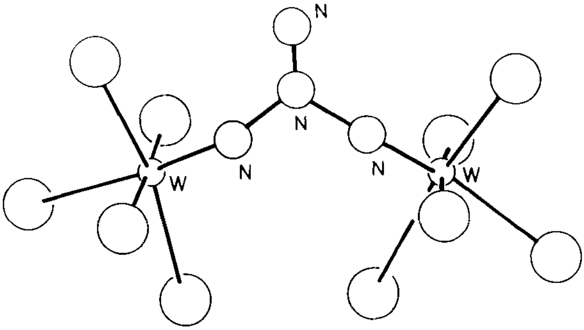


FIGURE 3 Structure of the isotetrazene complex $Cl_5WN_4WCl_5^{2-}$ (Ref. 37).

It seems to be possible that such a species functions as an intermediate during the formation of a diimine complex (Eq. (25)).

$$2\ MoCl_4N_3 \xrightarrow{-N_2} Cl_4MoN_4MoCl_4 \xrightarrow{-N_2} Cl_4MoN_2MoCl_4 \qquad (25)$$

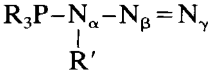
In this regard the diimine complex could be considered as a linkage of two nitrene species.

2.4. Reactions of Azido Complexes with Lewis Bases

2.4.1. The Staudinger reaction

The azido complexes $NbCl_4N_3$ and $TaCl_4N_3$ are stable compounds at room temperature.[38] $TaCl_4N_3$ may be irradiated with UV in boiling CCl_4 as solvent without decomposition. However, by adding PPh_3 at room temperature, the azides eliminate N_2 spontaneously and the phosphoraniminato complexes $Cl_4M{=}N{=}PPh_3$ (M is Nb, Ta) (see Fig. 4) are obtained.[39,40] If the reaction is carried out below 0 °C the red-colored intermediate Staudinger adduct $Cl_4MN_3PPh_3$ remains stable.

Two possibilities for the structure of the Staudinger adduct have been discussed:[6,7,41]



$$R_3P-\underset{\substack{|\\ R'}}{N_\alpha}-N_\beta=N_\gamma$$

A

$$R'-N_\alpha=N_\beta-N_\gamma=PR_3$$

B

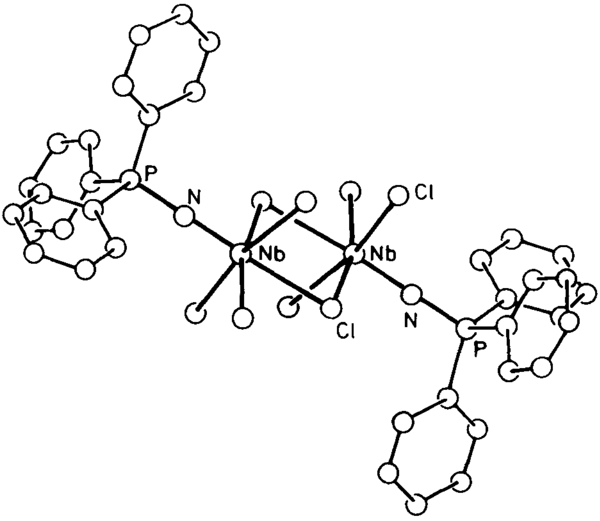


FIGURE 4 Structure of the phosphoraniminato complex $[Cl_4Nb=N=PPh_3]_2$ (Ref. 39).

Since with special substituents R′ such as $p-SO_2-C_6H_4-CH_3$, the Staudinger adducts are stable at room temperature their structure could be determined by spectroscopic methods, and it was shown that form B is present.[6,7] For the decomposition of the adduct B, which Staudinger named phosphazide,[42] Leffler and Temple[6] proposed a four-membered ring intermediate that splits off $(\beta-\gamma)N_2$ to form the phosphoranimine (Eq. (26)):

$$\begin{array}{lllll} R_3P=N_\gamma-N_\beta=N_\alpha-R' \longrightarrow & R_3P & - \; N_\alpha-R' & \longrightarrow R_3P=N_\alpha-R' & \\ & \;\;| & \;\;| & \qquad\quad + & (26) \\ & N_\gamma & = N_\beta & \qquad N_\gamma\equiv N_\beta & \end{array}$$

This mechanism was confirmed by Bock and Schnöller by studying the decomposition of $^{15}N_\beta$- and $^{15}N_\gamma$-labeled phosphazides.[7]

Hillhouse, Goeden and Haymore stabilized the phosphazide $p-CH_3C_6H_4N_3PPh_3$ by coordination to a metal atom in the complexes $MBr_2(CO)_3(R'N_3PPh_3)$ (M is Mo, W) and solved the crystal structure.[43] It exhibits the phosphazide ligand as bound to the metal in a chelating fashion through the α and γ nitrogen atoms.

It is reasonable to suggest that the reaction of metal azido complexes with phosphanes occurs via the same mechanism. Therefore the Staudinger adduct $Cl_4MN_3PPh_3$ primarily formed probably adopts a phosphazide structure B.

In this connection it is of interest that the reaction of Cl_4TaN_3 with the amine NPh_3 yields a phosphazide-analogous red compound $Cl_4TaN_3NPh_3$, which is stable at room temperature, since a four-membered ring intermediate (Eq. (26)) is not likely, because the nitrogen atom cannot form five bonds like phosphorus. Staudinger reactions with metal azido complexes have also been studied by Müller, Dehnicke *et al.* They synthesized the phosphoraniminato complexes $[Cl_5M{=}N{=}PPh_3]^-$ [44] and $[Br_5M{=}N{=}PPh_3]^-$ [45] (M is Nb, Ta) from the corresponding azides. Whereas $[NbCl_5N_3]^-$ and $[NbBr_5N_3]^-$ react with PPh_3 at room temperature, for the formation of the Ta compounds photochemical activation was necessary. In the same way the complex $[Cl_5Nb{=}N{=}AsPh_3]^-$ can be obtained from the azide and $AsPh_3$.[45]

Additional examples are given in Eqs. (27) and (28)

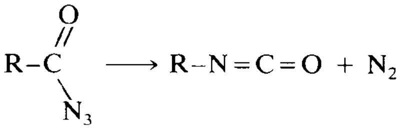
$$\eta^5\text{-}C_5H_5TiCl_2N_3 + PR_3 \longrightarrow \eta^5\text{-}C_5H_5TiCl_2(NPR_3) + N_2{}^{46} \qquad (27)$$

$$R_3SnN_3 + PR_3 \longrightarrow R_3Sn{-}N{=}PR_3 + N_2{}^{47,48,49} \qquad (28)$$

For the tin compound R_3SnNPR_3 a Sn–N single bond with an sp^2-hybridized N atom has to be formulated. On the other hand, the transition metals, being in a high oxidation state, from a double bond and a linear M=N=P arrangement (see Fig. 4).

2.4.2. *The Curtius acid azide decomposition*

Since Curtius found in 1894 that organic acid azides decompose with a simultaneous rearrangement to an isocyanate and N_2 [50] (Eq. (29)),



$$R{-}C({=}O)N_3 \longrightarrow R{-}N{=}C{=}O + N_2 \qquad (29)$$

reactions of this type have been studied extensively.[51] Paetzold[5] then observed that boron azides show a similar behavior, for instance the thermolysis of the trimetric azidodichloroboron leads to hexachloroborazine by migration of Cl ligands from the boron to the nitrogen atoms (Eq. (30)),

$$(BCl_2N_3)_3 \longrightarrow (ClBNCl)_3 + 3N_2 \qquad (30)$$

Reichle[52] reported analogous reactions of Ph_3SiN_3 and Ph_3GeN_3. A transition-metal azido complex for which the same mechanism of decomposition may possibly occur is VCl_4N_3. It can be assumed that one chlorine atom migrates to the nitrogen forming the nitrene complex $Cl_3V{\equiv}N{-}Cl$ [53] (Eq. (31)),

$$VCl_4N_3 \longrightarrow Cl_3V{\equiv}N{-}Cl + N_2 \qquad (31)$$

In the crystal structure[54] and in the gas state as well,[55] Cl_3VNCl exhibits an almost linear $V{\equiv}N{-}Cl$ arrangement with a $V{\equiv}N$ triple bond and a very short $N{-}Cl$ single bond. The same is true for the isotypic Cl_3VNI [56] (Fig. 5).

2.4.3. Reaction of azides with HCl

A few examples of metal azido complexes, which can be transformed to chlorineamine complexes by reaction with HCl (Eqs. (32) and (33)), are known.

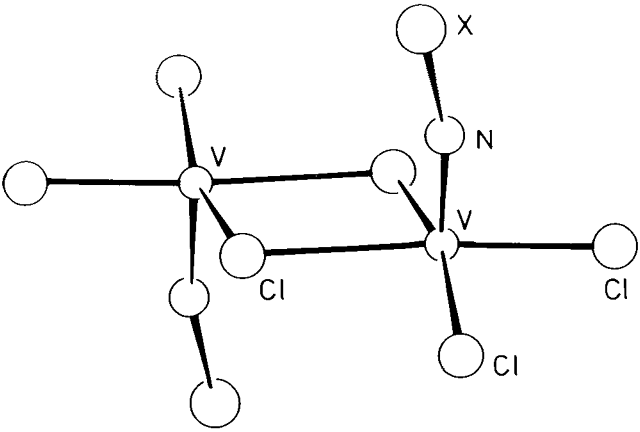


FIGURE 5 Structure of the chlorinenitrene complex $Cl_3V{\equiv}N{-}Cl$ (Ref. 54).

$$[M(NH_3)_5N_3]^{2+} + HCl + H^+ \longrightarrow [M(NH_3)_5NH_2Cl]^{3+} + N_2 \quad (32)$$

where M is Rh,[57] Ir,[58]

$$trans[Ir(N_3)_2(en)_2]^+ + 2HCl + 2H^+ \longrightarrow [Ir(NH_2Cl)_2(en)_2]^{3+} + 2N_2\ ^{59} \quad (33)$$

In the case of $[Ir(NH_3)_5N_3]^{2+}$ irradiation with UV light was used and a coordinated nitrene was proposed as an intermediate.

2.4.4. *Reaction of azido complexes with CO*

It was first found by Beck and co-workers that coordinated azido groups react with carbon monoxide to yield the corresponding isocyanato complexes.[60,61] Isocyanato complexes are also obtained by the reaction of metal carbonyls with the azido anion[60] (Eq. (34)),

$$M(CO)_6 + N_3^- \longrightarrow M(CO)_5(NCO)^- + N_2 \quad (34)$$

where M is Cr, Mo, W.

The reaction with CO can occur under very mild conditions at ambient temperature and pressure as the examples of $(Ph_3P)_2M(N_3)_2$ (M is Pd, Pt), $(Ph_3P)_2Ir(CO)N_3$ and $(Ph_3P)_3RhN_3$ [61] prove (Eqs. (35)–(37)):

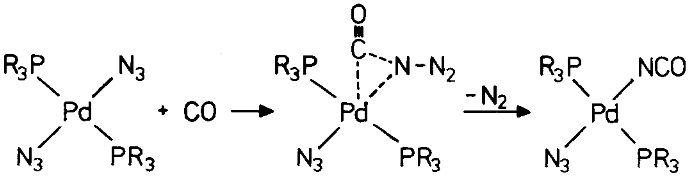
$$(Ph_3P)_2M(N_3)_2 + 2CO \longrightarrow (Ph_3P)_2M(NCO)_2 + 2N_2 \quad (35)$$

where M is Pd, Pt.

$$(Ph_3P)_2Ir(CO)N_3 + CO \longrightarrow (Ph_3P)_2Ir(CO)(NCO) + N_2 \quad (36)$$

$$(Ph_3P)_3RhN_3 + CO \longrightarrow (Ph_3P)_3RhNCO + N_2 \quad (37)$$

For these square-planar complexes Beck *et al.*[61] proposed a mechanism based on kinetic studies (Eq. (38)). The first step in this mechanism is the addition of CO by the central metal atom thereby increasing its coordination number. Then a three-membered ring intermediate is formed and N_2 is split off:



(38)

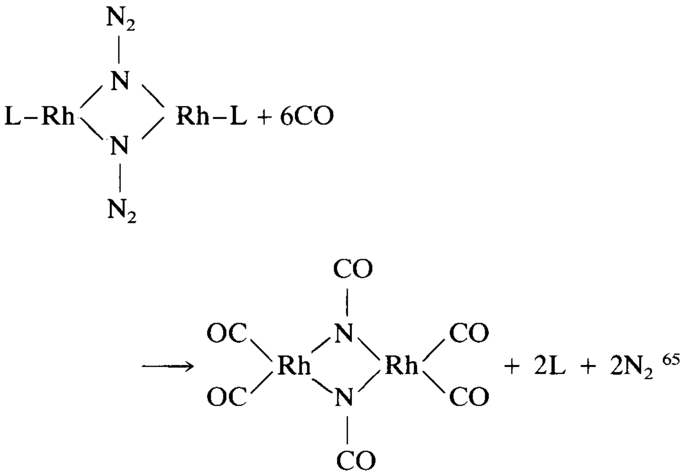
This mechanism is especially favored for the low coordinated square-planar complexes of the d^8 metals and by the linear complex Ph_3PAuN_3. Complexes with a sixfold coordination such as $Sn(N_3)_6^{2-}$ or with bridging azido ligands by contrast usually require higher temperature and high CO pressure to form the isocyanate group, as the addition of CO and the formation of the three-membered ring intermediate are hindered. The mechanism shown in Eq. (38) is supported by the observation that in the sequence $(C_6H_{11})_3P < (C_4H_9)_3P < (C_6H_5)_3P$ the reactivity of the complexes $(R_3P)_2M(N_3)_2$ increases as the decreasing basic character of the phosphane ligands facilitates the nucleophilic attack of CO.

For the reaction of the metal hexacarbonyls with N_3^- (Eq. (34)) a similar mechanism was formulated.[62,63] The initial step is the nucleophilic attack of the N_3^- ion at the C atom of one CO group and then the identical three-membered ring intermediate is formed.

Busetto *et al.* showed that thiocarbonyl ligands undergo an analogous reaction with the azide ion[64] (Eq. (39)).

$$[(C_5H_5)Fe(CO)_2CS]^+ + N_3^- \longrightarrow [(C_5H_5)Fe(CO)_2NCS] + N_2 \quad (39)$$

In the past few years several additional examples of the reaction of CO with coordinated azido ligands have been reported. They are summarized in Eqs. (40)–(43).



(40)

where L is a diolefine.

$$Re_2(CO)_{10} + 2IN_3 \longrightarrow [(OC)_4Re(NCO)]_2 + 2N_2 + I_2{}^{66} \qquad (41)$$

$$Os_3(CO)_{12} + 3IN_3 \longrightarrow 3Os(CO)_2(NCO) + 3CO + 3/2\, I_2 + 3N_2{}^{66} \qquad (42)$$

$$[(\pi\text{-}C_3H_5)PdN_3]_2 + 2CO \longrightarrow [(\pi\text{-}C_3H_5)Pd(NCO)]_2 + 2N_2{}^{67} \qquad (43)$$

2.4.5. Reaction of azido complexes with a peroxo group

Only one example is known of a coordinated azido ligand reacting with a peroxo group to yield a nitrosyl complex[68] (Eq. (44)):

$$[Cr(NH_3)_5N_3]^{2+} + HSO_5^- \longrightarrow [Cr(NH_3)_5(NO)]^{2+} + HSO_4^- + N_2 \qquad (44)$$

Experiments with ^{18}O labeling show that the terminal O atom of the peroxo group S–O–O was transferred to the azido ligand.

3. REDUCTIVE ELIMINATION OF AZIDO LIGANDS AND THE FORMATION OF N_2-COMPLEXES

The reductive elimination of azido groups in form of molecular nitrogen is frequently known. The ionic metal azides MN_3 (M is an alkalimetal,[69] Tl [70]) and $Pb(N_3)_2$ [71] decompose to give the metal itself. In addition a variety of reductive elimination reactions of azido complexes have been observed (Eqs. (45)–(48)).

$$[Pt(N_3)_6]^{2-} \longrightarrow [Pt(N_3)_4]^{2-} + 3N_2 \,^{72} \tag{45}$$

$$[Pt(CN)_4(N_3)_2]^{2-} \longrightarrow [Pt(CN)_4]^{2-} + 3N_2 \,^{73} \tag{46}$$

$$[Co(NH_3)_6](N_3)_3 \longrightarrow [Co(NH_3)_2(N_3)_2] + 4NH_3 + 1.5\,N_2 \,^{74} \tag{47}$$

$$[Ru(bpy)_2(N_3)_2]^+ + MeCN \longrightarrow [Ru(bpy)_2(MeCN)(N_3)]^+ + 1.5\,N_2 \,^{75} \tag{48}$$

An interesting example is the formation of an As(II) compound with an As–As bond via the reductive elimination of an azido ligand.

$$2R_2AsN_3 \longrightarrow R_2As{-}AsR_2 + 3N_2 \,^{76} \tag{49}$$

where R is Me, Et, Ph.

The decomposition of azido compounds may also yield complexes of molecular nitrogen. The first example of this type of reaction was found by Allen *et al.*[77] (Eq. (50)).

$$2[Ru(NH_3)_5N_3]^{2+} \longrightarrow 2[Ru(NH_3)_5N_2]^{2+} + N_2 \tag{50}$$

Kane-Maguire *et al.*[78] then showed that the decomposition of $[Ru(NH_3)_5N_3]^{2+}$ also produces the N_2 bridged dinuclear species $[(NH_3)_5Ru{-}N{\equiv}N{-}Ru(NH_3)_5]^{4+}$. Another Ru(III) complex undergoing a reductive elimination of N_2 is *cis*-$[Ru(en)_2(N_3)_2]^+$ [78] (Eq. (51)).

$$2cis[Ru(en)_2(N_3)_2]^+ \longrightarrow 2cis[Ru(en)_2(N_3)(N_2)]^+ + N_2 \quad (51)$$

Ruthenium (II) o-phenylene-bis(dimethylarsine)azide chloride $Ru(das)_2(N_3)Cl$ decomposes to $[Ru(das)_2Cl(N_2)]^+$ and $[Ru(das)_2Cl(NH_3)]^+$ upon treatment with acid.[79] In this connection it is of interest that $[Ru(das)_2Cl(N_2)]^+$ is also obtained, if the azido complex $[Ru(das)_2Cl(N_3)]$ is allowed to react with NO^+ or NO_2^+ [79] (Eqs. (52)–(53)).

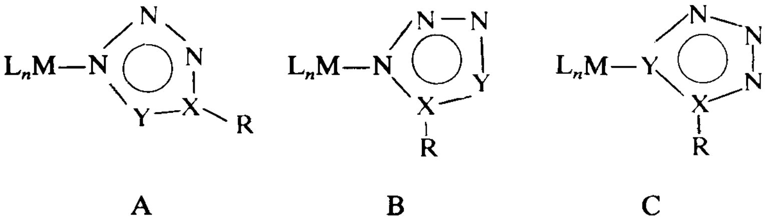
$$Ru(das)_2Cl(N_3) + NO^+ \longrightarrow [Ru(das)_2Cl(N_2)]^+ + N_2O \quad (52)$$

$$Ru(das)_2Cl(N_3) + NO_2^+ \longrightarrow [Ru(das)_2Cl(N_2)]^+ + 2NO \quad (53)$$

These examples exhibit additional possibilities for reactions of coordinated azido ligands.

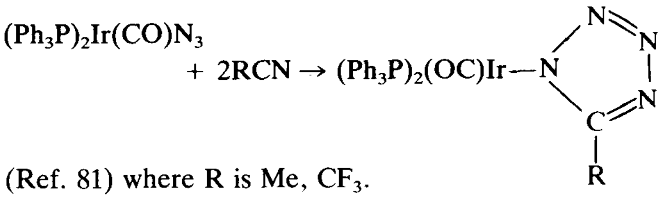
4. CYCLOADDITION REACTIONS OF COORDINATED AZIDO LIGANDS WITH COMPOUNDS CONTAINING MULTIPLE BONDS

Coordinated azido ligands undergo a number of cycloaddition reactions with compounds containing multiple bonds. Nitriles, isonitriles, isocyanates, thiocyanates, isothiocyanates, carbon disulfide, alkanes, and alkines can be added to form a five-membered heterocycle. Several of these reactions have been studied by Beck and coworkers [80] and Ziolo and Dori as well.[2] With compounds R–X=Y usually a heterocycle of type A or B is formed.[81]



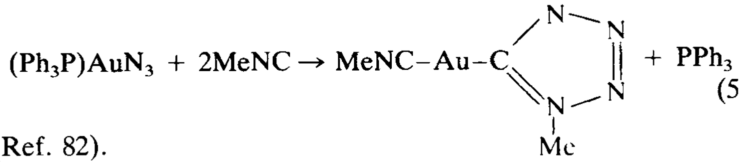
where R–X=Y is R–C≡N, R–N≡C, R'S–C≡N, R'N=C=S, S=C=S.

In addition a rearrangement forming type C may also occur. Some typical examples are given in Eqs. (54)–(60).



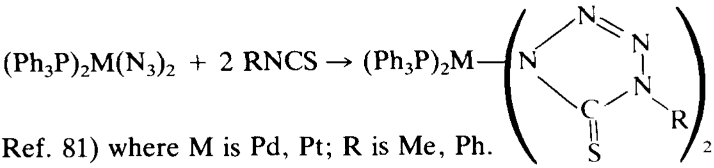
(54)

(Ref. 81) where R is Me, CF_3.



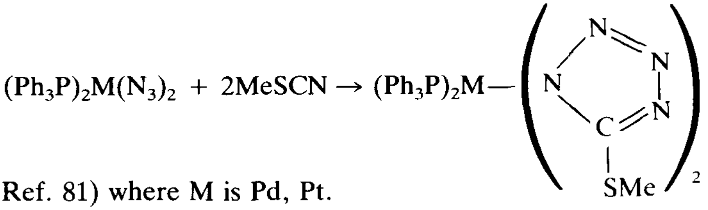
(55)

(Ref. 82).



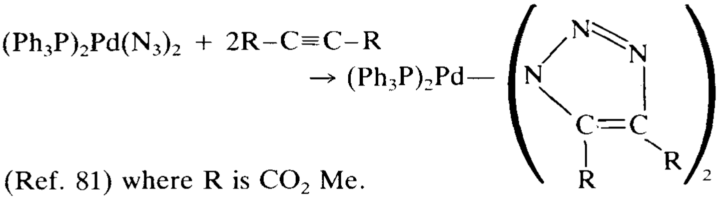
(56)

(Ref. 81) where M is Pd, Pt; R is Me, Ph.



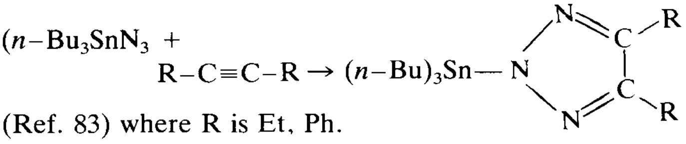
(57)

(Ref. 81) where M is Pd, Pt.



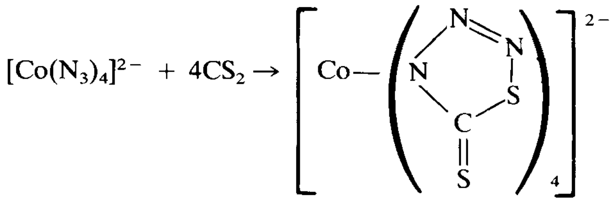
(58)

(Ref. 81) where R is CO_2 Me.



(59)

(Ref. 83) where R is Et, Ph.



(60)

(Ref. 84).

In a few cases the cycloaddition products have been investigated by crystal structure determinations.[85,86]

5. INSERTION REACTIONS

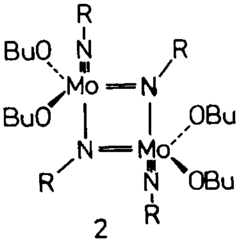
Organic azides RN_3 may react with metal complexes by insertion of a nitrene RN into a metal–metal, metal–hydrogen, or metal–carbonyl bond. These reactions demonstrate once more the manifold possibilities and the high synthetic potential of the azide group as a useful educt for interesting new compounds. In this section only a few examples are given. More details are discussed in a review article.[1]

5.1. Insertion Reactions with Metal–Metal Bonds

Organic azides react with metal–metal single bonds as well as with multiple bonds. From hexabutyldistannane and an organic azide, a bis(tributylstannane) imide $RN(SnBu_3)_2$ is obtained[87] (Eq. (61)).

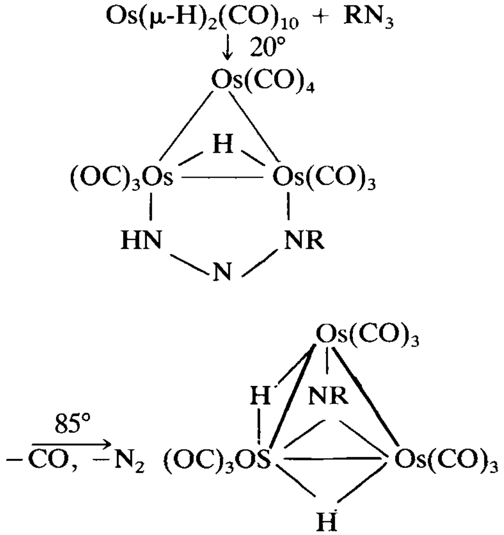
$$RN_3 + Bu_3Sn{-}SnBu_3 \longrightarrow RN(SnBu_3)_2 + N_2 \qquad (61)$$

The first example for the oxidative cleavage of a metal–metal triple bond was reported by Chisholm *et al.*[88] Addition of phenyl or p-tolyl azide to $Mo_2(O\text{-}t\text{-}Bu)_6$ leads to the formation of $[Mo(O\text{-}t\text{-}Bu)_2(NR)_2]_2$ and N_2. The crystal structure of the resulting imido compound exhibits two bridging and two terminal imido ligands in a planar $Mo_2(NR)_2(\mu\text{-}NR)_2$ arrangement as shown in **2**. Each Mo atom is in a five-coordinate environment.



2

with the two BuO ligands and the shorter Mo–N bond of the asymmetrical nitrido bridge being in the equatorial plane of a trigonal bypyramid. The imido ligand may also function as a μ_3-bridge as in $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)$ [89,90] or in $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)$.[91] The latter is obtained from $Os_3(\mu\text{-}H)_2(CO)_{10}$ and RN_3. It is of special interest, as an intermediate of this reaction was isolated and its structure determined. Thereafter the first step of the reaction is the insertion of the azide in one of the Os–H–Os bridges (Eq. (62)) (Figs. 6 and 7).



(62)

5.2. Insertion Reaction with Metal–Carbonyl Bonds

A great variety of reactions of azides with metal carbonyls is observed.[1] Besides the reactions not involving the M–CO bond as

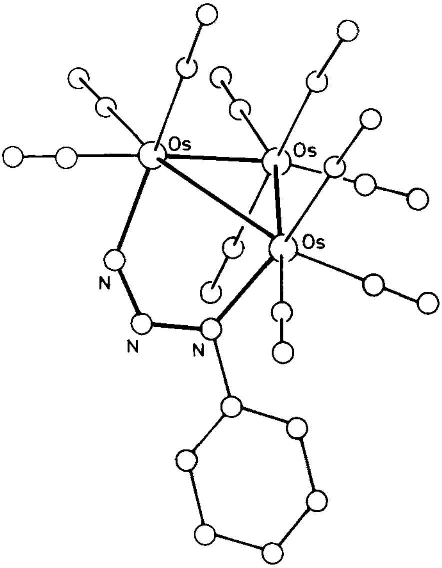


FIGURE 6 Structure of the PhN_3 insertion product $Os_3(CO)_{10}$ (μ-HN_3Ph) (Ref. 91).

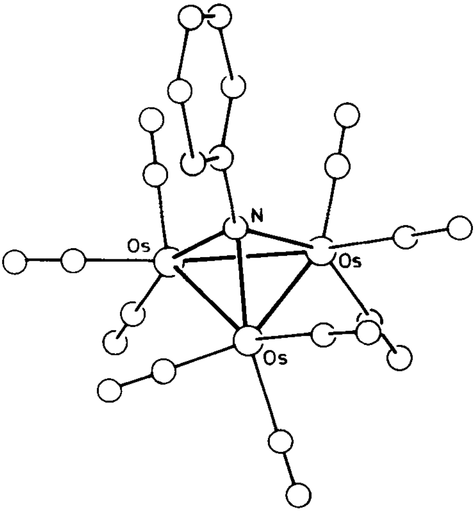
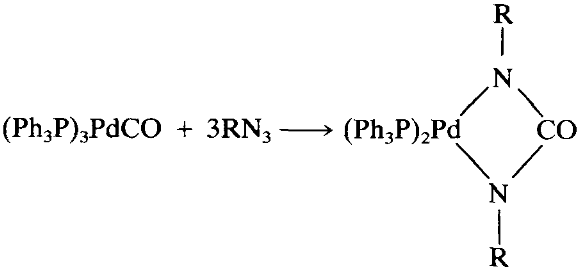
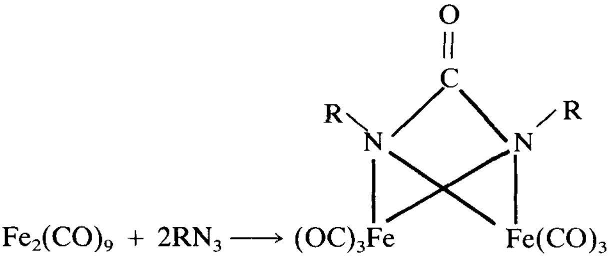


FIGURE 7 Structure of the complex $Os_3(CO)_9(\mu_3NR)$ with a triply bridging nitrene ligand (Ref. 91).

discussed in Section 5.1, the formation of isocyanate complexes with a M–OCNR group or of ureylene derivatives is possible. The ureylene ligand –N(R)CO(R)N– may act in a chelating or bridging fashion (Eqs. (63) and (64)).

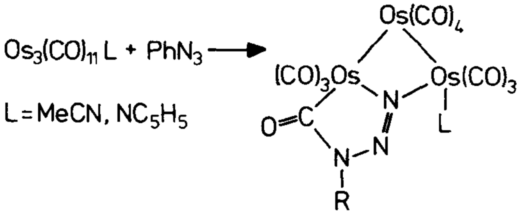


$+ 3N_2 + RN{=}PPh_3$ [92] (63)



$+ 2CO + 2N_2$ [1] (64)

A recent crystal structure determination of $Os_3(CO)_{10}L(CON_3Ph)$ shows that a nucleophilic attack of the α-N atom of the azide RN_3 at the carbonyl C atom is possible[93] (Eq. (65)).



(65)

Furthermore, organic azides may produce tetrazadiene ligands R–N_4–R by reacting with carbonyl complexes.[1]

5.3. Insertion Reactions with Metal–Hydrogen Bonds

In addition to the possibilities discussed in Section 2 nitrenes RN can also be stabilized by an H^- anion forming an amido ligand RHN^-. This occurs when an azide reacts with a M–H function and the nitrene is inserted. Some of these reactions are summarized in the Eqs. (66)–(68).

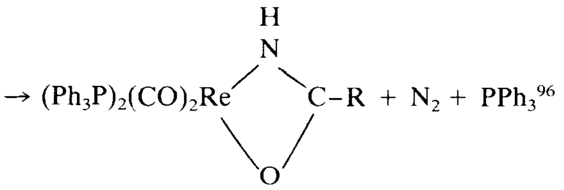
$$Me_3SnH + RN_3 \longrightarrow Me_3Sn{-}NH{-}R + N_2 \qquad (66)$$

where R is Ph,[93] R′–C_6H_4–SO_2.[94]

$$R_3P(Cl)_2PtH + O_2N(C_5H_3N)N_3$$

$$\longrightarrow R_3P(Cl_2)Pt{-}NH{-}C_5H_3N{-}NO_2 + N_2{}^{95} \qquad (67)$$

$$ReH(CO)_2(PPh_3)_3 + RCON_3$$



(68)

5.4. Insertion Reaction with a Germanium–Phosphorus Bond

One example of the insertion of a nitrene into a Ge–P bond was reported in 1975.[97] At ambient temperature $Me_3GeP(Me)R$ reacts with $R'N_3$ to form $Me_3GeNR'P(Me)R$ (Eq. (69)). At higher temperature another mole of azide oxidizes the P atom to a phosphoranimine.

$$\begin{aligned}&Me_3Ge{-}P(Me)R\\ &\qquad + R'N_3 \longrightarrow Me_3Ge{-}NR'{-}P(Me)R + N_2 \qquad (69)\end{aligned}$$

6. CONCLUDING REMARKS

The aim of this Comment was to show that azido groups undergo a great variety of reactions yielding many very interesting compounds. It seems to be clear that in the future more types of reactions will be discovered. Although some of the compounds need special care because of their explosive characters, safe handling is possible and an extension of this chemistry is promising.

Acknowledgments

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