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Organometallic Diazo Compounds

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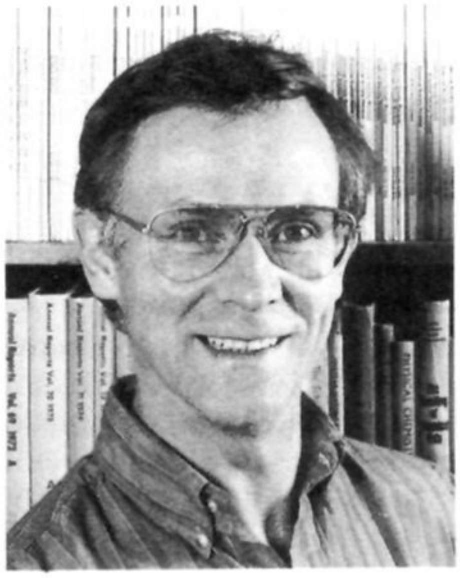

Derek Sutton was born in London, England in 1937. He received his B.Sc. (Hons) from the University of Nottingham in 1958 and, after teaching for two years, returned in 1960 to study under Prof. C. C. Addison for his Ph.D. which was obtained in 1963. He was appointed Lecturer in Inorganic Chemistry and continued to work in close association with Prof. Addison at Nottingham on the nonaqueous synthesis and IR–Raman spectra of anhydrous metal nitrates and nitrato complexes until 1967. He then joined the faculty at Simon Fraser University, where he is currently Professor of Chemistry. His research interests have centered on the complexation of arenediazonium ions by transition metals, and the versatile nature of the aryldiazenido ligand and its derivatives. This has led the research to expand to include C–H activation involving dinitrogen complexes, hetero- and homobimetallic compounds and the organometallic chemistry of rhenium and iridium.

I. Introduction

Organometallic chemistry has traditionally, by definition, been concerned with the chemistry of metal–carbon-bonded compounds. Nevertheless, there is growing interest in metal–heteroatom bonds such as M–N, M–O, M–S, etc., in organometallic compounds.

The present article systematically summarizes the literature dealing with transition-metal organometallic compounds having some kind of M–N–N skeleton, here broadly classified under the generalized name organometallic "diazo" compounds. This area has not been reviewed previously as a topic, but mention can be made of some earlier reviews that have discussed some of the types of compounds to be covered here. The most recent general review of inorganic complexes with miscellaneous nitrogen ligands was published in 1987.[1] Others have dealt with organometallic compounds with nitrogen ligands,[2,3] ligands related to reduced dinitrogen,[4] aryldiazenido complexes,[5] the N═N group,[6a] diazoalkanes,[6b] trimethylsilyldiazenes,[6c] and substituted hydrazines.[6d,e] There are useful theoretical papers discussing diazo ligands.[6f–h]

In order to focus the review and to keep it to a reasonable length the discussion will be limited for the most part to the following types of ligands (where R signifies an organic group or H): diazenide (NNR), diazene (RNNR), hydrazide(1–) ($NRNR_2$), hydrazide(2–) (NNR_2), and hydrazine (R_2NNR_2). That is to say, the article is concerned with the MNN skeleton in all conceivable permutations of bond orders, stereochemistry, and degrees of substitution in organotransition metal compounds. The simplest "diazo" ligand, dinitrogen, will not, however, be discussed, except in instances where a direct relation to subject of the review is evident, for example in the case of some of the Schrock "hydrazide(4–)" formulations. Dinitrogen complexes, including organometallics, have been extensively reviewed elsewhere.[4,7] There are also numerous classical inorganic coordination complexes containing the ligands under review; for the most part, these types of compounds will not be detailed here, and the reader is referred to the earlier reviews.[1,4,6d] Finally, this review will normally exclude compounds in which the NN fragment is part of a heterocyclic organic molecule (e.g., pyrazole), and the coverage of simple metal carbonyl derivatives (including clusters) will be selective.

II. Titanium, Zirconium, Hafnium

In a series of papers Leigh and co-workers have described the synthesis and structures of diazenide and hydrazide derivatives of $CpTiCl_3$ that are notable for the tendency of these ligands to adopt side-on (η^2) bonding. $CpTiCl_2(N_2Ph)$ (**1**) was synthesized as an orange solid by reacting $CpTiCl_3$ and $Me_3SiNNPh$.[8,9] This and the *t*-Bu analog were also synthesized by an interesting dehydrogenation reaction from the hydrazido complex, a reaction which has promise for the

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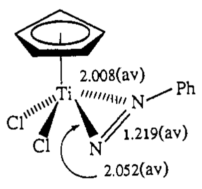
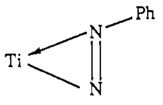


(1)

synthesis of other *alkyl*diazenido complexes (alkyldiazonium ions are not normally available reagents) (eq 1).

$$\mathrm{CpTiCl_2(NHNHBu^t) + EtO_2CNNCO_2Et \rightarrow CpTiCl_2(NNBu^t) + EtO_2CNHNHCO_2Et} \quad (1)$$

The structure of 1 shows the side-bonded phenyldiazenide group. The Ti, N, and phenyl C atoms are essentially coplanar, and the N–N bond length 1.219 Å (av) indicates a double bond. These features suggest that the structure may be approximated as the metallacycle 2, and the adoption of side-on bonding is a further example of the oxo-philic and azo-philic nature of the titanium group that gives rise to η^2-acyls[10] and η^2-imines.[11,12] This complex is, at the time of writing, the only structurally identified example of side-on bonding of a diazenide ligand in a mononuclear complex.

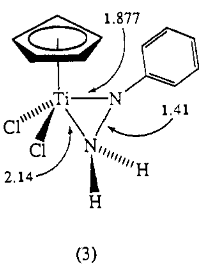


(2)

The reaction of CpTiCl$_3$ with a variety of trimethylsilylhydrazines, Me$_3$SiN(R)NR$_2$, produces organohydrazide(1−) derivatives in excellent yield (eq 2).

$$\mathrm{CpTiCl_3 + Me_3SiN(R)NR_2 \rightarrow Me_3SiCl + CpTiCl_2(NRNR_2)} \quad (2)$$

The lithium hydrazides may also be used.[13] In the case of Me$_3$SiNHNHPh the product was CpTiCl$_2$(η^2-NPhNH$_2$) resulting from a 1,2-hydrogen shift. Such migrations are not unexpected in view of the similar observation in the synthesis of [Cp$_2$W(η^2-NPhNH$_2$)]$^+$ and the proton exchange observed in Schrock's tungsten hydrazido complexes (vide infra). The structures of CpTiCl$_2$(η^2-NPhNH$_2$) (3) and CpTiCl$_2$(η^2-NHNMe$_2$) (4) may be compared with that of the phenyldiazenide 1.



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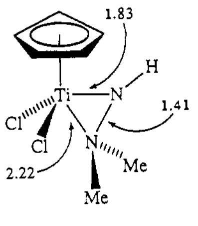


(4)

In 3 and 4 the hydrazide(1−) ligand has its NN axis in the CpTiCl$_2$ mirror plane with the monosubstituted nitrogen nearest the Cp ring in both cases; in 1 the NN axis is perpendicular to the CpTiCl$_2$ mirror plane, i.e., the diazenide group is rotated by ca. 90°. The geometry at the monosubstituted nitrogen in 3 and 4 is trigonal planar, suggesting that the nitrogen lone pair is located in a p orbital that is involved in overlap with a Ti d$_\pi$ orbital, giving rise to relatively short Ti–N distances of 1.8–1.9 Å compared with ca. 2.2 Å for the other Ti–N bond. The structures of CpTiCl$_2$(η^2-NMeNMe$_2$) and CpTiCl$_2${η^2-NMeN(Me)SiMe$_3$} are similar.[14] Bidentate bonding of the hydrazide(1−) ligand is also observed in the structure of TiCl$_2$(NMeNMe$_2$)$_2$.[14]

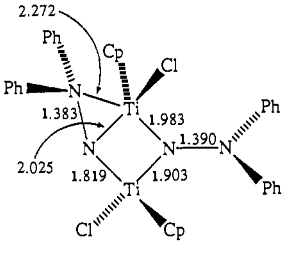
Proton abstraction from 3 by using t-BuNH$_2$ yields a product formulated as the binuclear 1,1-hydrazido(2−) complex {CpTiCl(NNHPh)}$_2$ rather than the 1,2-hydrazido(2−) complex "CpTiCl(NHNPh)" that might be expected without a 1,2 H-shift.[15]

Related hydrazido(2−) complexes were synthesized according to eqs 3 and 4.[15]

$$\mathrm{Ph_2NNH_3{}^+Cl^- + 3LiBu^n + CpTiCl_3 \rightarrow \underset{\mathbf{5}}{\{CpTiCl(NNPh_2)\}_2}} \quad (3)$$

$$\mathrm{\underset{\mathbf{4}}{CpTiCl_2(NHNMe_2)} + LiBu^n \rightarrow \{CpTiCl(NNMe_2)\}_2} \quad (4)$$

The structure of {CpTiCl(NNPh$_2$)}$_2$ (5), typifying these binuclear complexes, is not symmetrical. It involves one side-bonded η^2-NNPh$_2$ group that is bound to the second Ti atom through the unsubstituted nitrogen atom, whereas the other NNPh$_2$ group is η^1-bonded and uses this nitrogen atom to bridge the titanium atoms. As will be evident from structures elsewhere in this review, this turns out to be a common motif in several binuclear bishydrazido(2−) and bisdiazoalkane complexes.

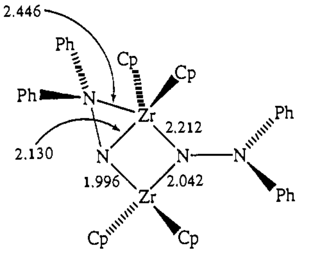


(5)

The reaction of CpTiCl$_3$ with Me$_3$SiN(Me)NHMe or LiN(Ph)NPhLi in 2:1 ratio results in compounds tentatively formulated as the 1,2-hydrazido(2−) complexes CpCl$_2$Ti(NRNR)TiCl$_2$Cp (R = Me, Ph).[15] However, CpTiCl$_3$ reacted with Me$_3$SiNHNHSiMe$_3$ or LiNHNH$_2$ to evolve N$_2$ and NH$_3$. It was postulated that the unobservable analogs, e.g., CpCl$_2$TiNHNHTiCl$_2$Cp were formed and that reductive disproportionation of bound NHNH^{2-} and NHNH$_2{}^-$ was occurring.[16] The related systems where Cp is replaced by tris(pyrazolyl)borate have been investigated.[17,18] No analog of the phenyldiazenido complex (1) has been reported, but the hydrazido(1−) complexes (HBpz$_3$)TiCl$_2$(η^2-NMeNMe$_2$) and (HBpz$_3$)TiCl$_2$(η^2-NPhNH$_2$) (cf. 3) were prepared and have structures similar to the cyclopentadienyl homologs.[17]

The hydrazido(1−) complex Cp$_2$Zr(NHNPh$_2$)(CH$_2$CH$_2$CMe$_3$) has been synthesized from LiNHNPh$_2$ and the chloro complex.[19] Thermolysis of this at 110 °C for

12 h results in loss of 2,2-dimethylbutane and generation of the mononuclear η^1-bonded hydrazido(2–) transient $Cp_2Zr{=}NNPh_2$ which dimerizes in the absence of a trapping agent to give **6**, the X-ray structure of which is very reminiscent of **5**. However, the transient is trapped by 4-(*N*,*N*-dimethylamino)pyridine (DMAP) to give the X-ray structurally determined mononuclear complex $Cp_2Zr(\eta^1\text{-}NNPh_2)(DMAP)$. The transient undergoes cleavage of the N–N bond in reactions with alkynes or CO.[19]



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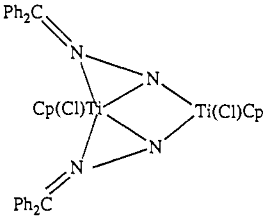

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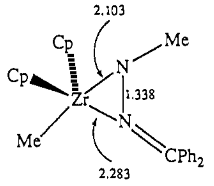

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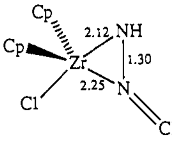
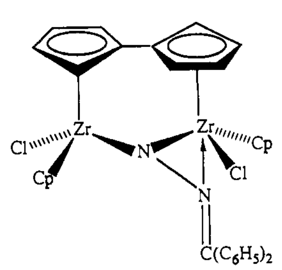


(9)

Diphenyldiazomethane reacts with $\{CpTiCl_2\}_n$ to give a complex formulated as **7**. This is supported by a partial X-ray analysis.[20] Note the similarity between the Ph_2CN_2 binding in **7** and the hydrazido(2–) bridging in **5** and **6**. In the case of Cp_2ZrMe_2 there is a 1,1-insertion into one Zr–Me bond to give **8**, and structurally similar **9** is formed from Cp_2ZrHCl.[21,22] The η^2-Ph_2CN_2R (R = Me, H) ligand is more delocalized than the related hydrazido(1–) ligand in the above titanium complexes, with a rather shorter N–N bond, and while the Zr–N(Me) or Zr–N(H) bond is shorter than the Zr–N(CPh_2) bond the differences are somewhat less pronounced than in the titanium hydrazido(1–) complexes. Note that this Zr–H insertion product contrasts with the 1,3-insertion of R_2CN_2 into the metal–hydride bond in $CpM(CO)_3H$ (M = Mo, W) (vide infra). Cp_2ZrCl_2 reacts with $Li_2NNC(H)Ph$ or with $LiNHNC(H)Ph$ and base in a stepwise reaction to form a dimeric complex that has a structure similar to that illustrated for the Cp′ analog **10**; this is also accessible by reaction of $Cp_2Zr(DMPE)$ (DMPE = $Me_2PCH_2CH_2PMe_2$) with $PhCHN_2$.[23a] The X-ray structure of **10** confirmed the presence of the two types of bridging $[PhCHNN]^{2-}$ ligands, and the similarity with complexes **5** and **6** is quite evident. The structure of the binuclear fulvalene complex **10a** exhibits a similar diphenyldiazomethane bridge.[23b] $Cp_2Ti(CO)_2$ reacts with Ph_2CN_2 to give the complicated trinuclear product **11** whose X-ray structure was determined.[24] With diethyl diazomalonate (DEDM) and $Cp_2Ti(CO)_2$ the complex $Cp_2Ti(DEDM)$ is formed, which has the structure **12** in which the diazo ligand is bonded through both nitrogens and one oxygen of an ester group. By contrast, Cp_2V gives a simple η^2-complex (vide infra).[24] Contrasting with the dicarbonyl, $Cp_2Ti(PMe_3)_2$ or $Cp_2Ti(CO)(PMe_3)$ react with Ph_2CN_2 to give the η^1-bonded diazoalkane complex **13**. The orientation of the ligand and the short Ti–N (1.83 Å), N–N (1.26 Å), and N–C (1.31 Å) distances indicate Ti–N multiple bonding and an extensively delocalized system.[25] Cp_2TiCl_2 reacts with $Me_3SiN{=}NSiMe_3$ to give $Cp_2TiNN(SiMe_3)_2$ which is assigned a structure similar to that of the vanadium compound $Cp_2VNN(SiMe_3)_2$ (vide infra).[26]



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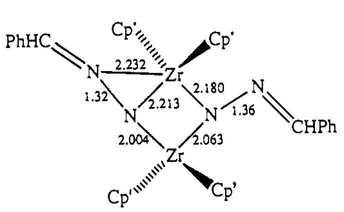
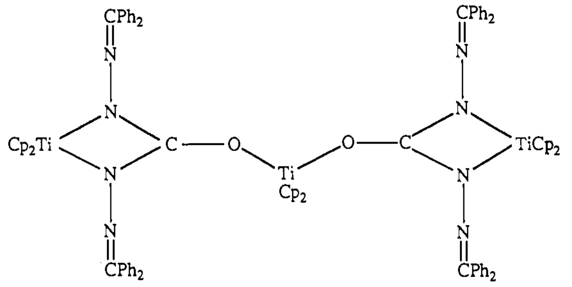


Cp′= C_5H_4Me

(10)



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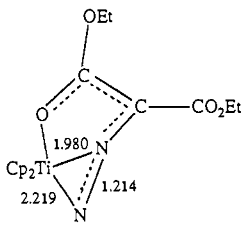

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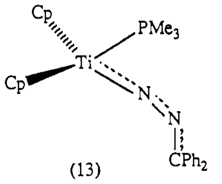
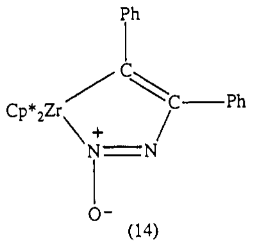


The insertion of N_2O into the Zr–C bond of $Cp^*_2Zr(\eta^2\text{-}PhC{\equiv}CPh)$ occurs without N_2 extrusion to give the metallacyclic complex **14** which is thermally unstable and extrudes N_2 to give the diphenyloxametallacyclobutene product **15**. Ph_2CN_2 also inserts into the Zr–C bond of $Cp^*_2Zr(\eta^2\text{-}PhC{\equiv}CPh)$ to give **16**, and into that of **15** to give **17**.[27] The X-ray structure of the titanium analog of **14** has been determined.[28]

Volpin[29] has invoked the formation of various cyclometalated aryldiazenido complexes of Cp_2Ti and subsequent NN bond cleavage to account for the formation of small amounts of anilines and ammonia when Cp_2TiPh_2 and the related tolyls are heated under a pressure of N_2. Direct evidence for NN bond cleavage occurs in the reaction of $\{CpTiCl_2\}_n$ with azobenzene to



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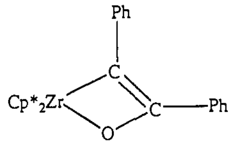

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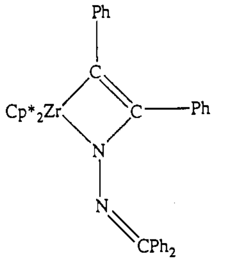
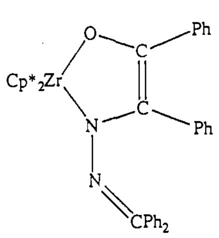
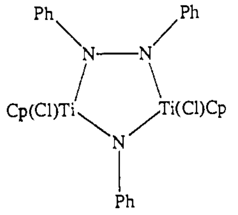


(16)



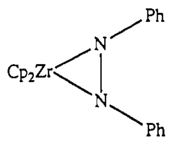
(17)

give **18**, incorporating a bridging phenylnitrene ligand.[20] In other cases the cleavage of the NN bond in azobenzene or benzo[*c*]cinnoline by organotitanium complexes such as the alkoxide $(ArO)_2Ti(C_4Et_4)$ gives terminal nitrene complexes.[30,31]



(18)

There are, however, several examples of the formation of η^2-azobenzene (or 1,2-diphenylhydrazido(2−)) complexes with Ti, Zr, or Hf.[12,31-34] $Cp_2Ti(CO)_2$ reacted with azobenzene, azotoluene or benzo[*c*]cinnoline to lose CO and give $Cp_2Ti(\eta^2\text{-RNNR})$.[34] $Cp_2Zr(CO)_2$ was found not to behave similarly.[33] However, $Cp_2Zr(\eta^2\text{-PhNNPh})$ (**19**) could be generated either by the reaction of $Cp_2ZrMeCl$ with the potassium salt of 1,2-diphenylhydrazine to give the η^2-bonded hydrazido(1−) complex $Cp_2Zr(Me)(\eta^2\text{-NPhNHPh})$ followed by thermolysis at 65 °C in THF, or by adding 1-lithio-1,2-diphenylhydrazine to $[Cp_2ZrHCl]_n$ in THF, or by the reaction of Cp_2ZrCl_2 with 1,2-dilithio-1,2-diphenylhydrazide. The free $Cp_2Zr(\eta^2\text{-PhNNPh})$ is highly reactive and has not been isolated; it readily adds a further donor ligand to form isolable pyridine, nitrile, THF or PMe_3 adducts. On the basis of the crystal structure of the pyridine adduct the metallacycle is preferably viewed as Zr^{IV} bonded to a bidentate 1,2-diphenylhydrazido(2−) ligand rather than a Zr^{II}–azobenzene complex.[33] The structure of $Cp_2Ti(\eta^2\text{-PhNNPh})$ is comparable, and probably should be viewed in the same way.[34] Both structures are notable for relatively acute CNNC torsional angles of 72° and 91° suggestive of the absence of a π-bond between the two nitrogens. This may be compared with torsion angles of 137° in $CpRe(CO)_2(PhNNPh)$[35] and 153–156° in the π-azobenzene complexes $Ni(CNCMe_3)_2(N_2Ph_2)$[36] and $Ni\{P(tolyl)_3\}_2(N_2Ph_2)$.[37] The structure of $Ti(OAr)_2(py)_2(\eta^2\text{-PhNNPh})$ has been reported (Ar = 2,6-isopropylphenyl) in which the ligand is again viewed as $[PhNNPh]^{2-}$ but no detailed analysis of the $Ti(N_2Ph_2)$ fragment was provided for a comparison with the above.[12] In contrast to early metal amides, the strained 3-membered metallacycle in $Cp_2Zr(\eta^2\text{-PhNNPh})$ results in facile insertion of internal alkynes into the Zr–N bond to give 2,3-diazametallacyclopentenes such as **20** (eq 5).[33]



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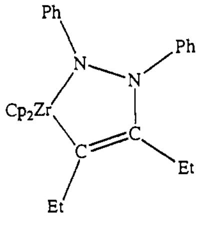
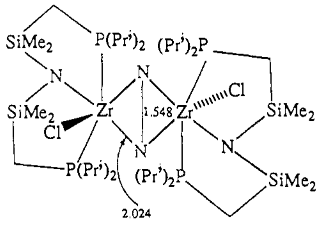


(20)

$$\underset{\mathbf{19}}{Cp_2Zr(\eta^2\text{-PhNNPh})} + EtC\equiv CEt \rightarrow \mathbf{20} \qquad (5)$$

Related structures have been proposed as intermediates in the titanium-mediated NN bond cleavage of azobenzene.[32]

Finally, as an extreme example of the propensity for η^2-coordination of diazo ligands to Ti or Zr that has been well documented in this section, mention should be made of the structure of the dinitrogen complex **21** synthesized by Fryzuk.[38] Here, the N–N bond length is 1.548(7) Å, the current world record, and longer than the bond length in hydrazine (1.47 Å) and the Zr–N bond length, 2.024(4) Å, is shorter than a typical single bond. The N_2 can be viewed as reduced to hydrazido(4−) and engaging in both σ and delocalized π bonding to Zr.

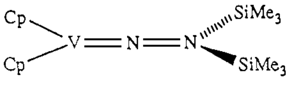


(21)

III. Vanadium, Niobium, Tantalum

The hydrazido(1−) complexes $CpVCl_2(NRNR_2)$ and $CpNbCl_3(NRNR_2)$ ($NRNR_2 = NMeNMe_2$ or $NPhNH_2$) have been synthesized from $CpVCl_3$ or $CpNbCl_4$ by using either the lithium- or trimethylsilyl-substituted hydrazine.[39] These compounds are anticipated to have structures analogous to the related titanium ones, and therefore involve η^2-coordination of the hydrazide group, but neither X-ray structures nor other details have been published. Vanadocene, Cp_2V, reacts with

Ph_2CN_2 or diethyl diazomalonate (DEDM) to give $Cp_2V(N_2CPh_2)$ and $Cp_2V(DEDM)$ in which the diazo ligand is proposed to be side-on bonded to the metal on the basis of an incomplete X-ray structure of the latter.[24] With $Me_3SiN{=}NSiMe_3$ migration of a $SiMe_3$ group occurs and the resulting hydrazido(2–) complex $Cp_2V\{NN(SiMe_3)_2\}$ (**21a**) has been structurally determined.[40] Few other vanadium or niobium diazo complexes have been synthesized, and these generally are not organometallic compounds. Mention can be made of $[V(\eta^1\text{-}NH_2NHPh)_2(salen)]^+$ (in which the phenylhydrazines are bound to V through the NH_2 group), $VI(NMeNMe_2)(salen)$, $V(OC_6H_4CHNNH_2)_3$, and $[VCl_2(\eta^2\text{-}NH_2NMePh)_2(\eta^1\text{-}NNMePh)]^+$ (which has both side-on hydrazine and end-on hydrazido(2–) groups).[41–44]



(21a)

While no derivatives of Nb or Ta with hydrazine, diazene, or their organo-substituted analogs appear to have been synthesized, mention must be made of Schrock's niobium and tantalum dinitrogen complexes of the form $Nb(\mu\text{-}N_2)Nb$ and $Ta(\mu\text{-}N_2)Ta$.[45–49] These have metal–nitrogen and N–N distances and reactivity that are consistent with the view that they formally involve the hydrazido(4–) ligand $[N_2]^{4-}$ rather than dinitrogen, and indeed syntheses have not only utilized sodium amalgam reductions in the presence of N_2 but effectively the "substitution" of two $=CHPh$ groups in $PhCH{=}NN{=}CHPh$ by the metal fragment, e.g., eq 6.

$$2Ta(CHCMe_3)(THF)_2Cl_3 \xrightarrow[-2PhCH=CHCMe_3]{PhCH=NN=CHPh} (THF)_2Cl_3Ta{=}NN{=}TaCl_3(THF)_2 \quad (6)$$

In the case of $Ta(CHCMe_3)(DIPP)_3(THF)$ (DIPP = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) the reaction results in substitution of only one CHPh group, to give the resulting phenyldiazomethane derivative (eq 7).[49]

$$Ta(CHCMe_3)(DIPP)_3(THF) \xrightarrow[-PhCH=CHCMe_3]{PhCH=NN=CHPh} Ta(NN{=}CHPh)(DIPP)_3(THF) \quad (7)$$

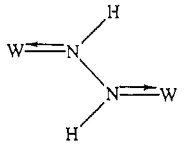
IV. Chromium, Molybdenum, Tungsten

In his pioneering studies, Sellmann[50] obtained the first complexes of *trans*-HN=NH by oxidation of the corresponding binuclear hydrazine complexes of chromium, molybdenum, or tungsten carbonyl (eq 8).

$$Mo(CO)_5(THF) \xrightarrow{N_2H_4} (CO)_5MoNH_2NH_2Mo(CO)_5 \xrightarrow{Cu^{2+}/H_2O_2} (CO)_5MoNH{=}NHMo(CO)_5 \quad (8)$$

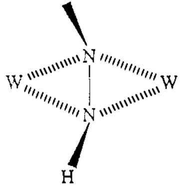
The X-ray structure of $(CO)_5CrNH{=}NHCr(CO)_5$ is consistent with the view that the N_2H_2 group is behaving as the neutral *trans*-diazene and forming dative bonds to the $Cr(CO)_5$ fragments with Cr—N = 2.076(1) Å and N=N = 1.25 Å.[51] The diazene protons undergo rapid exchange with $^2H^+$ and a mechanism for base-catalyzed disproportionation into the corresponding binuclear dinitrogen and hydrazine complexes has been proposed.[52]

An alternative formulation of an N_2H_2 ligand that might be considered is 1,2-hydrazido(2–) $[HNNH]^{2-}$ where the N–N bond is formally single, and each nitrogen carries a further electron pair. The reaction of the alkylidyne $(\eta^5\text{-}C_5Me_4Bu^t)WI_2(CCMe_3)$ with N_2H_4 in the presence of NEt_3 yields $[(\eta^5\text{-}C_5Me_4Bu^t)WI(CCMe_3)]_2(\mu\text{-}N_2H_2)$ **22**. The X-ray structure of **22** has two significant features.[53] First, the N–N distance (1.410(9) Å) corresponds to a single bond, supporting the view that N_2H_2 is a 1,2-hydrazido(2–) ligand. Second, the W, N, and H atoms are coplanar, and the W–N distance (1.932(7) Å) is *shorter* than the above Cr–N bond length. These features can be reconciled with σ, π donation of the nitrogen lone pairs to the tungsten atoms to form partial double bonds, **23**.



(23)

The 1,2-hydrazido(2–) ligand bridges two tungsten atoms in an entirely different fashion (**24**) as a $\mu\text{-}\eta^2,\eta^2\text{-}NHNH^{2-}$ group in **25** which, in addition, contains a $\mu\text{-}\eta^1,\eta^1$ hydrazine ligand.[54] Now the W–N bond lengths to the $N_2H_2^{2-}$ group range from 2.106(12) to 2.170(12) Å and are single bonds; the N–N bond length is 1.391(15) Å. The W–N bonds to the hydrazine ligand are somewhat longer (2.320(11)–2.353(11) Å) and N–N = 1.434(14) Å, is close to the value for free hydrazine. The ^1H NMR of **25** exhibits NH and NH_2 resonances at δ 5.70 and δ 4.26 in 1:2 ratio and each occurs as a doublet ($J(^{15}NH)$ = 68 Hz) in ^{15}N-labeled **25** synthesized from $^{15}NH_2{}^{15}NH_2$. The ^{15}N resonances appear as a doublet at δ ~57.0 and a triplet at δ ~54.9 relative to NH_3(l). The protons of only the hydrazido(2–) group exchange with CD_3OD alone, and additionally those of the hydrazine ligand do so in CD_3OD/Et_3N.



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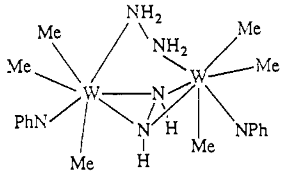

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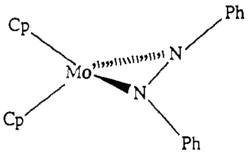
Many years ago, Otsuka and co-workers[55a] synthesized **26**, the first example of a mononuclear chromium group organometallic complex of a diazene ligand, and one in which the *trans*-diphenyldiazene (azobenzene) group was assigned, from spectroscopy, to be coordinated side-on (η^2) in a π-complex and acts as a 2-electron donor. (The coordination of azobenzene and other substituted diazenes and hydrazines to carbonyls of Cr, Mo, and W has been extensively studied by Ackermann and will not be discussed further here.[55b]) In sharp contrast with this is the recent report by Schrock et al.[56] of the complex $Cp^*WMe_3(\eta^2\text{-}MeNNMe)$ (**27**) where the η^2-



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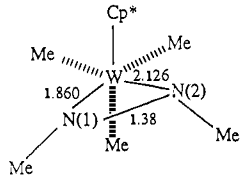
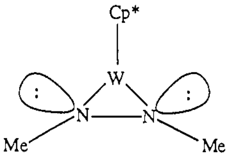


(27)

MeNNMe ligand is described as either a 4-electron donor η^2-dimethyldiazene or a 6-electron donor η^2-1,2-dimethylhydrazido(2−) group (eq 9).

$$[\mathrm{Cp^*WMe_4}][\mathrm{PF_6}] \xrightarrow{\mathrm{MeHNNHMe}} [\mathrm{Cp^*WMe_4}(\eta^2\text{-NHMeNHMe})][\mathrm{PF_6}] \xrightarrow{-\mathrm{CH_4}} \underset{\mathbf{29}}{[\mathrm{Cp^*WMe_3}(\eta^2\text{-NHMeNMe})][\mathrm{PF_6}]} \xrightarrow{-\mathrm{H^+}} \mathbf{27} \quad (9)$$

The W–N(1) bond length (1.860(8) Å) is much shorter than W–N(2) (2.126(7) Å), and N(1)–N(2) = 1.38(1) Å is in the range of other η^2-azobenzene complexes. The geometry at N(2) is pyramidal (sp^3), but that at N(1) is nearly planar and this nitrogen can be described as sp^2 hybridized and using the $p\pi$ electron pair to form a partial multiple bond to W. The ^{1}H and ^{13}C NMR in solution at −80 °C are consistent with this model, with the *N*-methyl groups inequivalent. A fluxional process interconverts the NMe groups at room temperature via a proposed symmetrical intermediate structure **28** having no W–ligand π-bond ($\Delta G^{\ddagger}_{278}$ = 13.6 kcal mol^{-1}). The structure of the intermediate [Cp*WMe$_3$(η^2-NHMeNMe)]$^+$ ion (**29**) is presumed to be similar to that determined for the pseudooctahedral unsubstituted hydrazido(1−) analog (**30**) (see below).[57]



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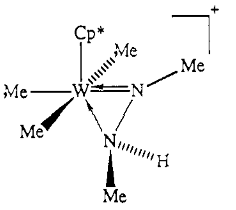

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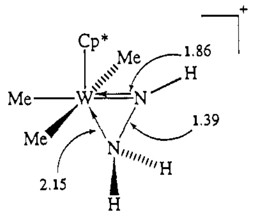

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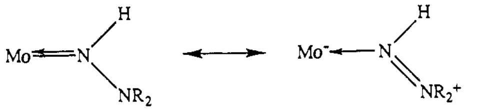
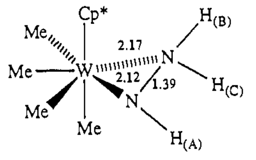
Complexes containing the unsubstituted hydrazido(1−) ligand [N$_2$H$_3$]$^-$ were probably first synthesized by McCleverty and co-workers[58,59a] in 1983, although no X-ray structure was available and only two of the three NH protons could be found in the ^{1}H NMR spectrum in support of the formulations Mo{HB(Me$_2$pz)$_3$}(NO)(I)(NHNH$_2$) and W{HB(Me$_2$pz)$_2$(3,5-Me$_2$-4-BrC$_3$N$_2$)}(NO)(Br)(NHNH$_2$). The reaction involved treating the diiodo complex with hydrazine. The structures of two similar complexes with substituted hydrazido(1−) ligands were determined, however, and revealed that the organohydrazido(1−) ligands in Mo{HB(Me$_2$pz)$_3$}(NO)(I)(NHNMePh) (**31**) and its NHNMe$_2$ analog are monohapto (η^1). The short Mo–N bond length (1.88 Å), coupled with N–N = 1.37 Å and Mo–N–N = 144° in **31** suggested a delocalized formulation **32** for the η^1-hydrazido(1−) ligand.



(32)

Protonation of these complexes caused loss of the hydrazido(1−) ligand as hydrazinium ion [N$_2$H$_5$]$^+$, and there was no evidence for ammonia or amine formation. The structures of the Mo and W nitrosyl (hydrazido-(1−)) complexes M(NO)(MPTE)(η^2-NHNH$_2$) and M-(NO)(MPTE)(η^2-NHNMe$_2$) have been determined by ^{1}H NMR and an X-ray structure on the latter (M = Mo) which shows the side-bound ligand with Mo–N(H) = 2.099(11) Å, Mo–NMe$_2$ = 2.172(12) Å (both indicative of single bonds), and N–N = 1.403(16) Å. The NH proton was not located in the structure. In the ^{1}H NMR the NH$_2$ protons of the former were assigned to a broad resonance near δ 2.9 (although they are diastereotopic) and the NH resonances for the two Mo compounds were assigned to signals observable below −20 °C at δ 3.8 and δ 4.8 respectively.[59b]

Further examples of the rare unsubstituted hydrazido(1−) ligand were reported by Schrock and co-workers.[57,60] The reaction of [Cp*WMe$_4$][PF$_6$] with excess hydrazine gave Cp*WMe$_4$(η^2-NHNH$_2$) (**33**) presumably by deprotonation of an initially formed cationic hydrazine complex. The structure of a low-temperature stable THF solvate was determined and revealed **33** to have a distorted pentagonal bipyramidal structure with two coordinated nitrogen atoms located in the pseudoequatorial plane although the N$_2$H$_3$ group had previously been tentatively formulated as η^1.[60] The N$_2$H$_3$ hydrogens were not located, but their positions were inferred from hydrogen-bonding contacts to the THF molecule. A combination of ^{1}H and ^{15}N NMR spectroscopy shows that in the fluxional behavior of **33** two of the three protons (H$_A$ and H$_C$) equilibrate first, probably by a 1,2-shift (Scheme Ia) of one NH$_2$ proton (H$_B$, endo to the Cp* ring) to the neighboring NH lone pair. A higher temperature process (b), that when coupled with the first one causes interchange of all protons, is proposed to involve exchange of H$_B$ and H$_C$ via a η^1 intermediate and rotation about the N–N bond with inversion. The presence of the lone pair on one nitrogen is supported by reaction with HBF$_4$ to give the η^2-hydrazine complex [Cp*WMe$_4$(η^2-NH$_2$NH$_2$)]-[BF$_4$] (**34**) notable for the single ^{15}N resonance at δ 29.7



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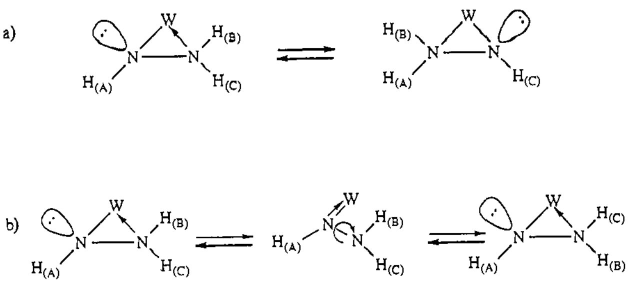
Scheme I



(rel NH_3(l)) with J(NH) = 80 and 83 Hz for the inequivalent NH_2 protons. Compound **33** is thermally labile by loss of CH_4, giving the hydrazido(2−) complex $Cp^*WMe_3(NNH_2)$ (**35**, see below) which can be protonated by triflic acid to give a second η^2-hydrazido(1−) complex $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)][OTf]$ (**30**). The protons of the $NHNH_2$ ligand were located and refined in the X-ray structure of **30**, which shows the hydrazido(1−) ligand to be oriented with its axis in the pseudo-mirror plane of the Cp^*WMe_3 fragment, with the NH group nearest the Cp* ring.

The ^{15}N and ^1H NMR spectra show that the hydrazido(1−) ligand protons in **30** are not exchanging at a significant rate in the absence of added base.[57] The NH nitrogen atom has nearly planar geometry and is essentially sp^2 hybridized and engaging in a significant degree of π-bonding with the W atom, accounting for the short W–N bond length (1.86(1) Å). The structure compares directly with those of $CpTiCl_2(NPhNH_2)$ (**3**) and $CpTiCl_2(NHNMe_2)$ (**4**) discussed above. In all three, the hydrazido(1−) ligand has a similar orientation, geometry, and dimensions. This can be contrasted with the structure of $[Cp_2W(\eta^2\text{-}NPhNH_2)]^+$, discussed below,[61-63] where the ipso carbon atom of the phenyl ring does not lie in the plane of the tungsten and nitrogen atoms, and the electron count for W is 18 without the participation of the lone pair on the (pyramidal) NPh nitrogen atom.

It would be simplistic to view the formation of **30** from $Cp^*WMe_3(NNH_2)$ (**35**) as merely the addition of H^+ to N_α. First, while the structure has not been established with certainty, the ^{15}N NMR shifts and ^{15}NW coupling constants support a linear η^1 W≡N—NH_2 arrangement in **35** similar to low oxidation state tungsten systems,[57] rather than an η^2-NNH_2 group.

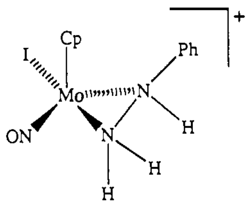
$$Cp^*Me_3W{=}NNH_2$$

(35)

(Note that η^2-NNH_2 has, so far, never been structurally identified.) Second, by using CF_3SO_3D at −78 °C the resulting $[Cp^*WMe_3(N_2H_2D)]^+$ (**30**-d_1) contained deuterium that was statistically distributed between the two nitrogen atoms, whereas the expected lifetime of **30** in regard to proton scrambling at this temperature is estimated from room-temperature ^{15}N and ^1H NMR data to be of the order of 10^3 s. A mechanism such as protonation at N_β to give $[Cp^*WMe_3(NNH_3)]^+$ followed by proton migration would seem to account for the deuterium distribution pattern. The (NNH_3) ligand has been identified crystallographically in one reported example, that of $[W(PMe_3)_4(Cl)(NNH_3)]Cl_2$,[64] and $Cp^*WMe_3(NNMe_2)$ the dimethylhydrazido analog of **30** is reported to give $[Cp^*WMe_3(NNMe_3)]^+$ upon methylation.[65]

A number of other structures of chromium group organohydrazido(1−) complexes have been completed. In two of these[66,67] the ligand is also side-on coordinated, i.e., $[Mo(NHNMePh)(NNMePh)(S_2CNMe_2)_2]^+$ (notably also formed by protonation of a linear hydrazido(2−) ligand) and $Mo(NHNHCO_2Me)(N_2CO_2Me)(S_2CNMe_2)_2$; however, it is end-on (η^1) in Mo{$N_2C(O)Ph$}{NHNHC(O)Ph}{PhC(S)N(Me)O}$_2$.[68] The factors that control the hapticity of the hydrazido(1−) ligand (and for that matter also hydrazine etc.,) are far from well understood at present. Clearly the electron demand of the metal is a factor: i.e., if the $NRNR_2^-$ group is only required to act as a 2-electron donor it will be end bound. But in cases where $NRNR_2^-$ is a 4-electron donor both steric and orbital considerations can influence whether the ligand uses two electron pairs from the NR nitrogen and is η^1 as in **31**, or a pair from each nitrogen and is η^2, as in **30** or **33**.

A few hydrazine or organohydrazine complexes have also been synthesized in this group. $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)][BF_4]$ (**34**) formed by protonation of **33** has been mentioned above.[57] In the published crystallographically determined structure of $[CpMo(NO)(I)(\eta^2\text{-}NH_2NHPh)][BF_4]$ (**36**), the side-on phenylhydrazine is bound with Mo–N distances of 2.184(3) and 2.134(3) Å and N–N = 1.430(5) Å.[69] The related compounds



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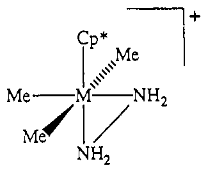
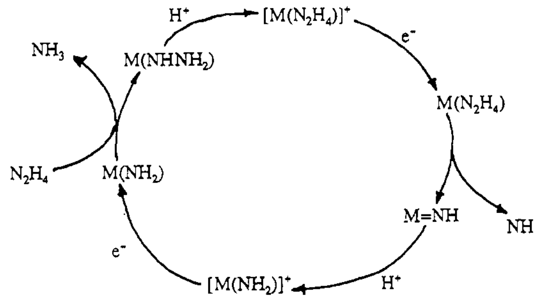


(37)

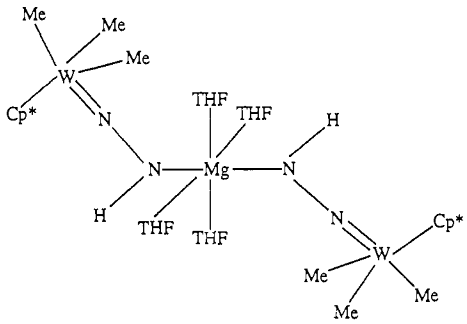
$CpMo(NO)I_2(NH_2NMe_2)$ and $CpMo(NO)I_2(NHMeNHMe_2)$ have also been described.[59a,70] Hydrazine reacts with the d^1 Mo^V or W^V complexes $Cp^*MMe_3(OTf)$ to give the hydrazine complexes $[Cp^*MMe_3(\eta^2\text{-}NH_2NH_2)][OTf]$ (**37**) that are presumed to contain bidentate hydrazine bonded in a structure and orientation similar to the related hydrazido(1−) complex **30**; this has now been verified by a crystal structure for **37** (M = W).[71] Interest in these high oxidation state complexes centers on the reductive cleavage of the hydrazine ligand with the formation of ammonia. In the absence of a proton source, sodium amalgam reduction of **37** gave the imido complex $Cp^*WMe_3({=}NH)$ and NH_3 (70%) presumably involving a 1,2-shift of a proton from N_α to N_β; in the presence of the proton source 2,6-lutidine hydrochloride 90% conversion of both nitrogens to NH_3 resulted. Furthermore, hydrazine could be reduced catalytically by **37** to ammonia in high yield under similar conditions. The catalytic sequence in Scheme II was proposed.[71]

Recently, the Schrock group has reported further details of the hydrazido(2−) complex $Cp^*WMe_3(NNH_2)$ (**35**). It can be successively lithiated by Bu^nLi to yield $[Cp^*Me_3WNNH(Li)]_x$ and $[Cp^*Me_3W(NNLi_2)]_x$ and correspondingly silylated when these are in turn reacted with Me_3SiCl. $MgNp_2(TMEDA)$ (TMEDA = $Me_2NCH_2CH_2NMe_2$; Np = neopentyl) reacts to yield

Scheme II



the X-ray structurally characterized [Cp*Me$_3$W(NNH)]$_2$[μ-Mg(THF)$_4$] (**38**) following crystallization from THF.[65]



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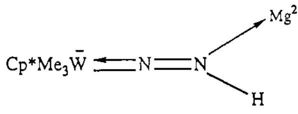
The ^{15}N NMR spectrum of **38** shows a resonance at δ 425.9 assigned to N$_\alpha$ and at δ 192.2 assigned to N$_\beta$, (relative to liquid NH$_3$, $\delta = 0$). The chemical shifts for the lithio, SiMe$_3$, and related derivatives are also reported.[65] Adjusting the scale relative to δ(MeNO$_2$) = 0 (δ(NH$_3$) = −380) that is advocated[72] and frequently used by others[73,74] gives $\delta(\mathrm{N}_\alpha) \approx +45.9$ and $\delta(\mathrm{N}_\beta) \approx -187.8$ for **38**. These compounds can be formally viewed in two extreme ways: (i) as tungsten diazenido complex anions coordinated to Mg^{2+}, Li$^+$, SiMe$_3$$^+$ etc., **39**, or (ii) as derivatives of the hydrazido(3−) ligand **40**. Structure **39** is of the form described to approximate the bonding in the reported X-ray structures of CpMo(CO)$_2$(μ_2,η^2-NNC$_6$H$_4$CH$_3$)Re(CO)$_2$Cp (**41**) and CpW(CO)$_2$(μ_2,η^2-N$_2$Me)Cr(CO)$_5$ (**42**).[75,76] The observed near-linearity of the W–N–N skeleton in **38** (Note: the structure did not refine satisfactorily, and no metrical details are reported[65]) means that in representation (**40**) the N$_\alpha$ lone pair is delocalized; the question of whether the lone pair on N$_\beta$ is also, must await more detailed X-ray structures to define the geometry at N$_\beta$. At this point, the ^{15}N chemical shifts for N$_\alpha$ and N$_\beta$ in these compounds alone are not sufficient to distinguish unambiguously between the diazenido and hydrazido(3−) formalisms in view of the relatively large chemical shift range for the presently known diazenido complexes, a paucity of data on bridging aryldiazenido ligands, and uncertainties in the theoretical interpretation of nitrogen chemical shifts. However, the separation between N$_\alpha$ and N$_\beta$ is rather larger than usually seen in typical singly bent diazenido complexes.[1] The dilithio and bis(trimethylsilyl) derivatives are formally hydrazido(4−) species. Completing the picture, synthetic methods have been developed for substituting one or both NH hydrogens in **35** by suitable metal fragments in rational syntheses of the hydrazido(4−) (or dinitrogen) complexes **43**–**45** and the hydrazido(3−) (or diazenido) complexes **46** and **47**.[65] Other dinitrogen complexes of Mo and W that can best be described as containing the hydrazido(4−) moiety have been reported.[77-79] These variously protonate to give high yields of either hydrazine[77] or upon reduction, ammonia.[78,79]



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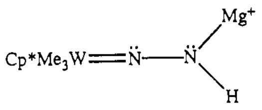

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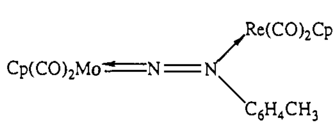

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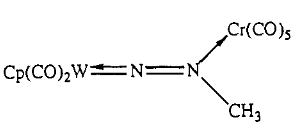


(42)

$\mathrm{Cp^*Me_3W{=}N{-}N{=}WMe_3Cp^*}$

(43)

$\mathrm{Cp^*Me_3W{=}N{-}N{=}MoMe_3Cp^*}$

(44)

$\mathrm{Cp^*Me_3W{=}N{-}N{=}TaMe_2Cp^*}$

(45)

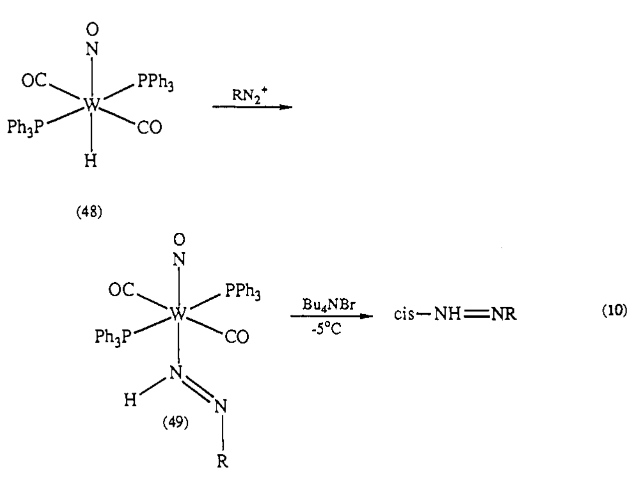
$\mathrm{Cp^*Me_3W{=}N{-}N(H)ZrMeCp_2}$

(46)

$\mathrm{\{Cp^*Me_3W{=}N{-}N(H)\}_2\,ZrCp_2}$

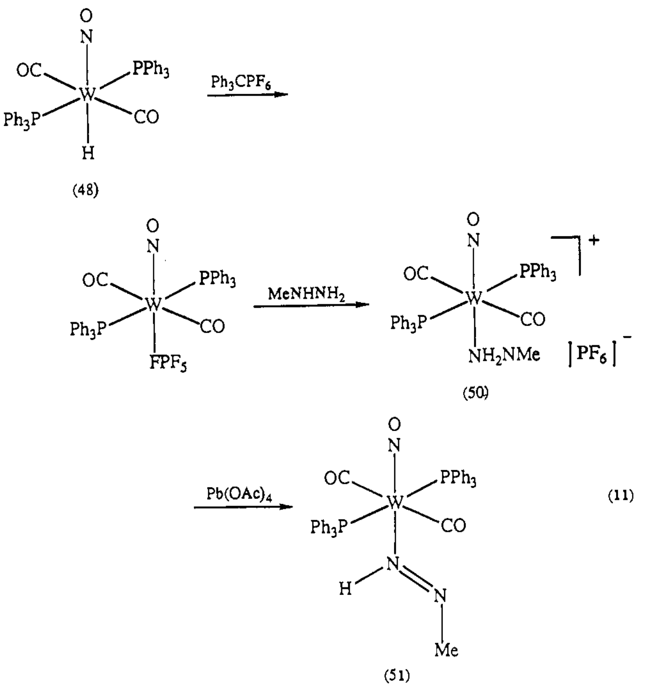
(47)

Complexes that contain the unstable molecule phenyldiazene (PhN=NH) stabilized by coordination to a transition metal have long been known to be accessible in favorable instances by "insertion" of arenediazonium ions into M–H bonds or by protonation of suitable aryldiazenido complexes at N$_\alpha$.[1,5] Several examples will be described in other sections of this review. In a notable case, the hydrido complex **48** reacts with a variety of arenediazonium salts [RN$_2$][PF$_6$] to afford the air-stable *cis*-aryldiazene complexes **49** in high yield (eq 10).[80]



(10)

Treatment of **49** with Bu_4NBr at −40 °C and warming to −5 °C displaces the free *cis*-aryldiazene, identified as such on the basis of $\delta(NH) = 15.45$ in the ^1H NMR and low values of $|^2J(^{15}NH)| = 2.0$ Hz and $|^1J(^{15}NH)| = 49.4$ Hz for R = Ph. The free *cis*-PhNNH reacts regiospecifically and stereoselectively with 1-hexyne-d_1 to give only the *E* isomer of $Ph(D)C{=}C(H)C_4H_9$, i.e., with formal cis addition of $Ph^{\bullet}$ and $H^{\bullet}$ to the alkyne. However, in the case of 1-phenylethyne, both *cis*- and *trans*-stilbene-d_1 are formed, and additional deuteration studies support the initial addition of $Ph^{\bullet}$ to give a stilbenyl radical that then undergoes rapid isomerization followed by H abstraction.[81] The corresponding alkyldiazene complexes (**49**; R = alkyl) are not accessible by a route similar to eq 10, because alkyldiazonium ions are unstable. Instead, the *cis*-methyldiazene complex **51** was synthesized by an alternate strategy, the selective oxidation of the methylhydrazine complex **50** by $Pb(OAc)_4$ at −20 °C (eq 11).



(48)

(50)

(51)

(11)

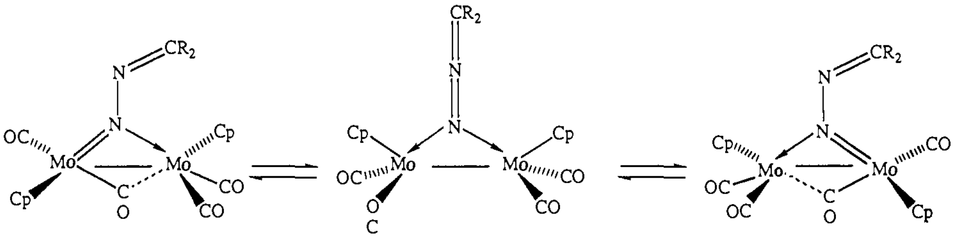
The structure of **51** is supported by ^1H NMR data and an X-ray structure determination, and the unstable free *cis*-$MeNH{=}NH$ may be released by treatment with Bu_4NBr as in the case of phenyldiazene.[82]

Some time ago, the insertion of diazomethane into the Mo–H or W–H bond of $CpM(CO)_3H$ (M = Mo, W) was employed to synthesize rare examples of methyldiazenide complexes $Cp(CO)_2M(N_2Me)$; the tungsten compound was crystallographically characterized.[83,84] The products obtained from other diazomethane derivatives were dependent on the substituents.[83,85] It is interesting to note that the corresponding aryldiazenido complexes $CpMo(CO)_2(N_2R)$, made by King and Bisnette as far back as 1964, and the first diazo complexes to be synthesized, were, of course, also the first organometallic diazo compounds.[86] The phenyldiazenido complex was later synthesized by Green[87] from $CpMo(CO)_2H$ and $PhNHNH_2$, and the tungsten and chromium analogs have also been made.[87,88] Since that time, numerous other aryl and alkyl diazenido complexes of Mo or W have been synthesized, as well as examples with the parent protio group (N_2H). Many of these have resulted (along with hydrazido(2−) and diazoalkane analogs) from investigations into the protonation and alkylation of molybdenum and tungsten dinitrogen complexes in studies of the binding and activation of N_2 at a transition-metal center, some of which may model possible mechanisms for the activity of the biological nitrogen-fixing molybdoenzyme nitrogenase. For the most part, these compounds only have phosphorus or sulfur coligands, or are oxo clusters,[89] so do not fall into the category of organometallic diazo compounds. These will not be considered further here, but have been reviewed elsewhere.[1,4,90,91]

The chemistry of chromium with diazo ligands is much less well developed than that of Mo or W. Stable diazo complexes have only been obtained in a few cases such as $CpCr(CO)_2(N_2R)$[88] and $[(C_6Me_6)Cr(CO)(L)(N_2R)]^+$ (L = CO, $P(OMe)_3$, $P(OPh)_3$), whereas for L = PPh_3, PMe_2Ph_2 or PMe_2Ph oxidation by the diazonium ion occurs.[92] The stable chromium aryl(methyl)diazene complex $CpCr(NO)_2(CH_3NNC_6H_5NO_2)$ will be discussed later.[93] The reaction of $CpCrCl_2$ with $Me_3SiNNSiMe_3$ gave[94] the N=N bond cleavage product $[CpCr(NSiMe_3)_2]_2$ although $(CO)_5Cr\{NNC(SiMe_3)_2\}$ exits (vide infra).[95] The chemistry of $CpMo(CO)_2(N_2R)$ and $(HBpz_3)Mo(CO)_2(N_2R)$, originally synthesized by King[86] and Trofimenko,[96] respectively, has been greatly expanded by Lalor and co-workers,[97-106] and related compounds with a bidentate bis(aryldiazenido) ligand have been described.[107] The bis(aryldiazenido)triphenylphosphine complexes $[CpMo(N_2R)(N_2R')(PPh_3)][PF_6]$ are accessible from the reaction of $CpMo(N_2R)(CO)(PPh_3)$ with further aryldiazonium ion $[N_2R']^+$ and are precursors for a variety of other bis(aryldiazenido)molybdenum complexes.[97,105] The crystal structures of $CpMo(CO)(p\text{-}N_2C_6H_4Me)(PPh_3)$ and $[CpMo(p\text{-}N_2C_6H_4Me)(p\text{-}N_2C_6H_4F)(PPh_3)][PF_6]$ have been determined and both contain typical singly bent aryldiazenide groups, as expected.[105] Bis(aryldiazenido) complexes are not common, but a further series of such molybdenum compounds, synthesized by condensation of *cis*-dioxomolybdenum complexes and arylhydrazines, has been characterized by Zubieta and co-workers for various coligands, as well as for high nuclearity polyoxomolybdates.[89,108,109]

Both $CpMo(CO)_2(N_2R)$ and the tungsten analog react with I_2 to give *trans*-$CpMI_2(CO)(N_2R)$ (M = Mo, W) and $\{CpMI_2(N_2R)\}_2$ (M = Mo), and in the case of Mo with SnI_4 to give $CpMo(I)(SnI_3)(CO)(N_2R)$.[101] Substitution reactions of these derivatives have been described,[103] including formation of the anionic aryldiazenido complex $[CpMoI_3(N_2R)]^-$. There is a 1:2 adduct of $CpMo(CO)(PPh_3)(p\text{-}N_2C_6H_4Me)$ with $HgBr_2$ of uncertain structure.[101] The reaction of the bis(aryldiazenido)triphenylphosphine complex $[CpMo(N_2R)_2(PPh_3)][BF_4]$ with $Tl(HBpz_3)$ yielded examples of bis(aryldiazenido) tris(pyrazolyl)borate complexes, i.e., $(HBpz_3)MoF(N_2R)_2$; these, unlike the Cp analogs, are not accessible by more direct routes from $(HBpz_3)Mo(CO)_2(N_2R)$.[102] Several complexes with mixed NO and N_2R ligands related to the above bis(aryldiazenido) complexes have been described,[106] for Mo and W, e.g., $CpM(NO)(N_2R)Cl$, $(HBpz_3)M(NO)(N_2R)Cl$, $[(HCpz_3)M(NO)(N_2R)Cl]^+$, and $[CpM(NO)(N_2R)(PPh_3)]^+$ which are formed by reactions such as shown in eqs 12 and 13. The crystal structures of $(HBpz_3)Mo(NO)(p$-

Scheme III



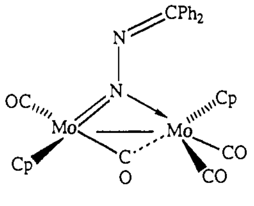
$N_2C_6H_4F)Cl$ and $[CpMo(NO)(p\text{-}N_2C_6H_4F)(PPh_3)][PF_6]$ show them both to contain the typical singly bent aryldiazenide ligands as expected.[106]

$$CpMo(CO)_2(N_2R) \xrightarrow{NOCl} CpMo(NO)(N_2R)Cl \quad (12)$$

$$CpMo(CO)(N_2R)(PPh_3) \xrightarrow{NO^+} [CpMo(NO)(N_2R)(PPh_3)]^+ \quad (13)$$

It is surprising that there has been little attempt to explore the reactivity of unsaturated metal–carbon centers such as alkylidynes or alkylidenes with unsaturated N–N groups. In one example, it was found that the arenediazonium ion did not react at the alkylidyne ligand in $CpMo\{P(OMe)_3\}_2(\equiv CCH_2Bu^t)$, but displaced a $P(OMe)_3$ ligand and a proton to give the vinylalkylidene complex $CpMo\{P(OMe)_3\}(N_2R)(=C=CHBu^t)$.[110a] Very recently, the synthesis and chemistry of a zwitterionic intermediate formed by the insertion of *cis*-azobenzene into the W=C bond of the Fischer carbene $(CO)_5W=C(OMe)Ph$ has been described.[110b]

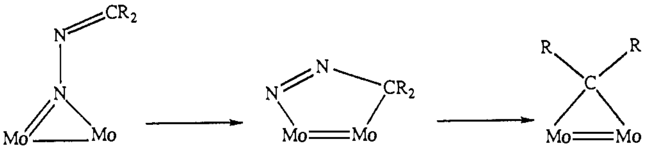
There have been several studies of reactions between diazo compounds and the Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ and its C_5H_4Me or C_5Me_5 relatives. The products show a remarkable diversity of structures, depending on the nature of the diazoalkane and the degree of methyl substitution of the Cp groups.[111a,112] Diphenyldiazomethane (Ph_2CN_2) reacts with $Cp_2Mo_2(CO)_4$ to give **52**.[113] The X-ray structure of **52** shows that the Mo centers are inequivalent, one CO group is semibridging, and the diazo group forms an asymmetric bridge with Mo–N distances of 1.914(8) Å for the formal Mo=N bond and 2.083(8) Å for the Mo–N bond. The plane of the $NNC(C_{ipso})_2$ skeleton lies perpendicular to the Mo–Mo vector. The low-temperature ^{13}C and ^1H NMR spectra are consistent with this structure, but at room temperature the Cp groups are equivalent as are the CO groups and phenyl carbons, and the fluxional process in Scheme III involving a symmetrical intermediate has been proposed to account for this.

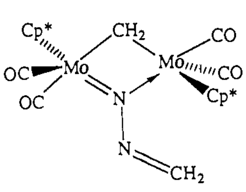


(52)

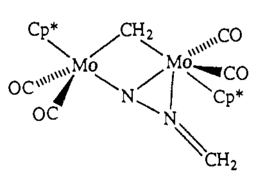
Above 60 °C, intramolecular nitrogen extrusion occurs to give the bridging diarylalkylidene complex, by way of a postulated cyclic intermediate (Scheme IV). In the structure of the resulting μ-alkylidene complex, determined for R = *p*-tolyl, one *p*-tolyl substituent is π-bonded to its neighboring Mo atom to form an η^3-allyl type interaction. Structures similar to **52** are proposed for the products from $(C_5H_4Me)_2Mo_2(CO)_4$ and $(C_5Me_5)_2Mo_2(CO)_4$ on the basis of the NMR and IR spectra, but in the latter case the molecule is not fluxional on the NMR time scale at room temperature. With diazomethane itself and employing $(C_5Me_5)_2Mo_2(CO)_4$, Herrmann obtained a product with bridging methylene and diazomethane groups which was assigned structure **53a** or **53b** on the basis of spectroscopy.[111b] No identifiable product could be obtained for $Cp_2Mo_2(CO)_4$.[113] $(C_5Me_5)_2Mo_2(CO)_4$ gives yet a further different product **54** in the case of Me_2CN_2, which was structurally determined by X-ray crystallography and has the η^1:η^2 bridging diazoalkane group that is suggested for **53b**.[114] This configuration for the diazo group is very reminiscent of the structure of the molybdenum dimethylhydrazido complex **55** obtained by McCleverty and co-workers from the reaction of $\{CpMo(NO)X_2\}_2$ or $Cp_2Mo(NO)I$ with 1,1-dimethylhydrazine,[70,115] and both are similar to compounds **5**, **6**, **7**, and **10** described earlier. The products in the case of $Cp_2Mo_2(CO)_4$ and $(C_5H_4Me)_2Mo_2(CO)_4$ are believed to have a structure similar to **54** on the basis of a partly completed X-ray structure of the former.[113] A second isomer in solution is believed to have the Me_2CN_2 ligand bridging in a manner similar to **52**.

Scheme IV

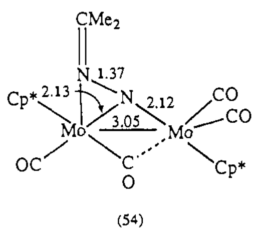




(53a)



(53b)



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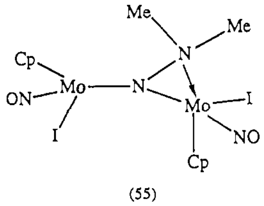
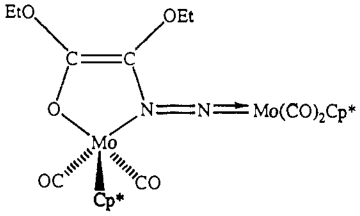


(55)

Ethyl diazoacetate forms a complex with $(C_5Me_5)_2Mo_2(CO)_4$ that also has a structure similar to **54**, whereas diethyl diazomalonate or α-ketodiazoalkanes react to give products with the Mo≡Mo bond cleaved, such as **56** and **57**.[113,116] In **56** and **57** the two Mo–N bond lengths are unequal, reflecting the multiple bond to the unchelated Mo atom. In these, the bridging diazo group has a structure and function very similar to that of bridging aryldiazenide in **41** or the bridging methyldiazenide in **42**.[75,76] In other instances, such as diazofluorene or diazocyclopentadiene, nitrogen extrusion occurs and complexes with bridging carbene or cyclopentadienyl groups result.[117,118] $Cp^*_2W_2(CO)_4$ reacts differently again with Me_2CN_2 or diazacyclopentadiene to result in scission of the N=N bond and incorporation of the fragments as bridging alkylidene amido and terminal isocyanate ligands.[119]



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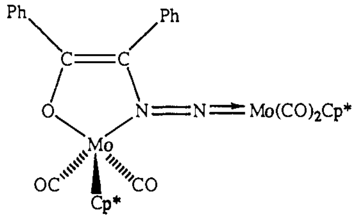
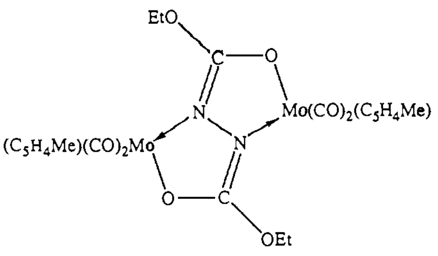


(57)

Diethyl azodicarboxylate ($EtO_2CN_2CO_2Et$) reacts with $(C_5H_4Me)_2Mo_2(CO)_4$ to give **58** with a N–N single bond length of 1.423(7) Å.[120] The diaryl diazomethane ligand and the alkylidene ligand are both terminal in the product **59** of reaction of Ar_2CN_2 (Ar = p-tolyl) with $Cp_2Mo_2(CO)_4(\mu\text{-}CAr_2)$. The Mo–N bond length of 1.74(1) Å is consistent with a Mo≡N triple bond and N–N = 1.323(12) Å. This compound has a complex temperature-dependent NMR behavior.[112] The Ph_2CN_2 groups are also terminal and bent at N_β in the products formed from the Mo≡Mo binuclear alkoxides $Mo_2(OR)_6$[121] (but are bridging in the tungsten compounds), as well as in various Mo or W dithiocarbamate complexes.[122]

Mononuclear Mo or W complexes with terminal N-bonded diazoalkanes cannot normally be accessed from the free diazoalkanes, owing to N_2 extrusion to give alkylidene compounds,[6b,111a] and are commonly obtained by elaboration of dinitrogen or hydrazido(2–) ligands.[4] However, the mononuclear bis(trimethylsilyl)diazomethane complexes of W (**60**) and Cr have been synthesized from the reaction between $M(CO)_5(PPh_3)$ and $Me_3Si(Li)CN_2$ followed by addition of Me_3SiCl. Contrasting with the above bent 4e⁻ donor diazoalkane in **59** the X-ray structure of **60** exhibits a near-linear W–N–N–C skeleton with a W–N single bond (W–N = 2.161(11) Å), plus N–N and N–C bond lengths (1.165(15) and 1.34(1) Å) that are intermediate between double and triple, and single and double bonds respectively.[95]



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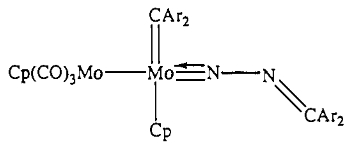

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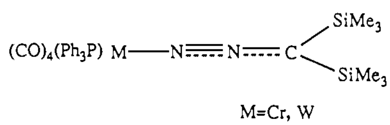


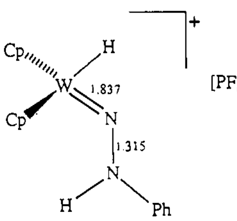
(60)

Cp_2MoH_2 reacts with azobenzene in aprotic solvents to give $Cp_2Mo(\eta^2\text{-}PhNNPh)$ (**26**) and hydrazobenzene, but in protic solvents such as MeOH reductive cleavage of the N=N bond occurs to give aniline.[55,123] Cp_2WH_2 reacts with aryldiazonium salts below −20 °C to formally insert the diazonium ion into one W–H bond (eq 14).

$$Cp_2WH_2 + [PhN_2][PF_6] \rightarrow \underset{\textbf{61}}{[Cp_2W(H)(NN(H)Ph)][PF_6]} \quad (14)$$

The reaction is interesting in that the product **61** is not the phenyldiazene complex W(NHNPh) (that would result from a 1,1-insertion into the W–H bond as noted above for compound **49**) but is the 1,2-insertion product, a phenylhydrazido(2–) complex.[62] This was demonstrated by the effect of ^{15}N-substitution on the ^1H NMR spectrum and by an X-ray structure determination[62,124] of the p-fluorophenylhydrazido complex, which confirmed that the linkage is bent at N_α with an interbond angle of 146°. This can be rationalized by noting that the W atom achieves an 18e configuration and does not require donation of the remaining electron pair on N_α. The W=N distance of 1.837(7) Å is consistent with a double bond, and the N–N distance is 1.315(9) Å which is intermediate between typical N–N single and double bond lengths. The molecule is fluxional on the NMR time scale by restricted rotation about the W=N bond. Spectroscopic evidence is also consistent with a bent hydrazido(2–) ligand in $(CO)_5W{=}NNMe_2$, synthesized by the photochemical metathesis of the carbene $(CO)_5W{=}C(p\text{-tolyl})Ph$ with the triazene $PhN{=}NNMe_2$.[125a] This is borne out by the crystal structure of a phosphine derivative.[125b]

An isomer, **62**, of compound **61** is obtained if the reaction is carried out at 0 °C or by isomerization of **61** at this temperature in solution. The metal hydride and NH protons of **61** have both migrated to N_α, and the resulting phenylhydrazido(1–) ligand is bonded side on to the tungsten.[61–63] It is interesting to compare the metrical details of the η^2-phenylhydrazido(1–) ligand in **62** with those of the comparable ligands $NHNH_2$ in **30**, $NHNMe_2$ in $CpTiCl_2(NHNMe_2)$ (**4**), and $NPhNH_2$



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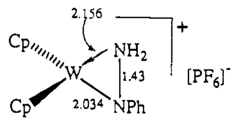
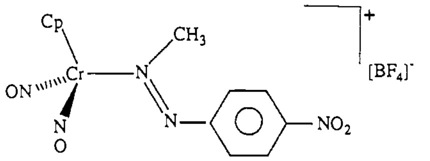


(62)

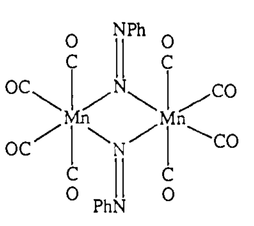
in $CpTiCl_2(NPhNH_2)$ (**3**). In **62** the ipso carbon of the phenyl group does not lie in the WNN plane and the W-NPh bond length is 2.034(9) Å, indicating a single bond. Thus the lone pair on this nitrogen is not strongly donated to the tungsten atom, and such an interaction is not mandatory since the electron count on tungsten is 18 without it. Compounds **3**, **4**, and **30** have, as discussed earlier, strict planar geometry at the three-coordinate nitrogen atom and short metal–nitrogen bonds indicative of involvement of the nitrogen lone pair in a required π-interaction with the metal. The other dimensions for **62**, $W-NH_2$ = 2.156(9) Å and N–N = 1.43(1) Å, are normal.

While the insertion of aryldiazonium ions into metal hydrogen bonds are well known and reasonably common, the corresponding insertion into a metal–carbon bond was, until quite recently, unknown, and several attempts to execute such a reaction in the author's laboratory had proved unsuccessful. Now, Legzdins has demonstrated that the chromium compounds $CpCr(NO)_2(R)$ (R = Me, CH_2SiMe_3, or Ph) undergo unprecedented insertions of electrophiles NO^+, NS^+, and $[p\text{-}N_2C_6H_4NO_2]^+$ into the Cr–C bond. The crystal structure of product **63** from the insertion of the diazonium ion into the $Cr-CH_3$ bond was determined.[93] The *cis*-methyl(aryl)diazene ligand that results is η^1-bonded with normal bond lengths Cr—N = 2.057(4) Å and N=N = 1.225(6) Å.



(63)

V. Manganese, Technetium, Rhenium



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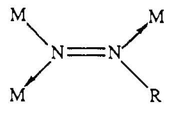

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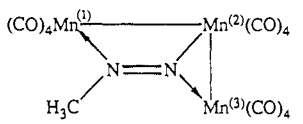

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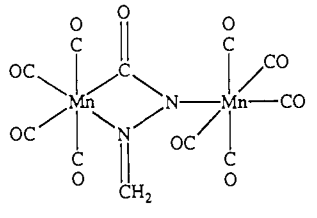
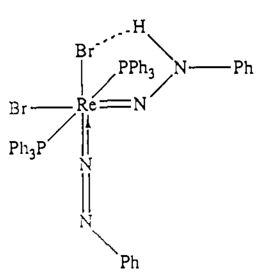


(67)

It is remarkable that after nearly 30 years and the synthesis of numerous organodiazenido complexes,[1] manganese still provides the only example of simple metal carbonyl diazenido complexes. The binuclear complex $[Mn(CO)_4(N_2Ph)]_2$ (**64**) was obtained from the reaction of $Mn(CO)_5Br$ and $PhN{=}NSiMe_3$ and its crystal structure determined.[126,127] The μ_2-η^1 phenyldiazenido bridging ligands act as 3-electron donors; a terminal singly bent phenyldiazenido ligand is also a 3-electron donor, yet no mononuclear complex $Mn(CO)_4(N_2Ph)$ could be detected or prepared. However, the phenyldiazenido bridges in **64** were cleaved by PPh_3 to give the mononuclear derivatives $Mn(CO)_3(N_2Ph)(PPh_3)$ and $Mn(CO)_2(N_2Ph)(PPh_3)_2$. The C-bonded nitrogen atom in the μ_2-η^1-bridging organodiazenido ligand carries an unshared electron pair that is theoretically capable of donation to a third metal center to give the triply bridging arrangement **65**. This occurs in a second manganese carbonyl derivative $[Mn(CO)_4]_3N_2CH_3$ (**66**) which is formed in about 10% yield along with other products (vide infra) in the reaction of $Mn(CO)_5H$ with CH_2N_2 at low temperature.[6b,128–130] In the crystal structure of **66** the N=N bond length is 1.224(11) Å, typical of a double bond, and the manganese nitrogen distances are 2.061(8), 1.964(8), and 1.879(8) Å, respectively, to Mn(1), Mn(2), and Mn(3).[129,130] Other products from this reaction are $Mn_2(CO)_{10}(N_2CH_2)$ (**67**) and $Mn_2(CO)_{10}(H_2N_2CH_2COCH_3)$.[128,130] The structure of **67** is also unusual since the diazomethane forms part of a diazametallacyclobutanone ring.[130] The N–N distance (1.390 Å) is between that of single (1.45 Å) and double (1.24 Å) bonds, and the $NNCH_2$ angle is 124.3°. An analogous product is formed from $Re(CO)_5H$ and CH_2N_2. The reaction of $Mn_2(CO)_5(DPPM)_2$ with CH_2N_2 gives the adduct $Mn_2(CO)_5(N_2CH_2)(DPPM)_2$. Although the definitive structure was not deduced, the inequivalence of the phosphorus atoms in the ^{31}P NMR excluded symmetrical structures, and the absence of phosphorus coupling to the CH_2N_2 protons taken with the stability of the complex toward nitrogen extrusion led the author to reject a $Mn-CH_2N_2-Mn$ bridge (like the intermediate in Scheme IV). The author opted for terminal bonding of the CH_2N_2 to one Mn atom as the most likely structure, but it seems the data could equally well accommodate structures with the CH_2N_2 ligand bridging as represented in **53a** or **53b** analogous to known modes for dialkyl- or diphenyldiazomethane.[131] $Mn_2(CO)_5(DPPM)_2$ was also reported to react with $[PhN_2][BF_4]$ to give the complex $[Mn_2(CO)_5(DPPM)_2(N_2Ph)][BF_4]$, but it was not determined whether the N_2Ph group was terminal or bridging. Reversible protonation of the above CH_2N_2 adduct with HBF_4 gave a product formulated as the methyldiazenido complex $[Mn_2(CO)_5(DPPM)_2(N_2Me)][BF_4]$ with a reported $\nu(NN)$ = 1762 cm^{-1} which would, if correct (no ^{15}N isotopic substitution was reported), indicate a terminal N_2Me ligand. These compounds deserve fuller characterization. It was noted that neither Ph_2CN_2 nor $PhMeCN_2$ reacted with $Mn_2(CO)_5(DPPM)_2$, but 1:1 adducts were formed with the activated diazoalkanes $N_2C(CO_2Et)_2$ and $N_2C_5Cl_4$.[131]

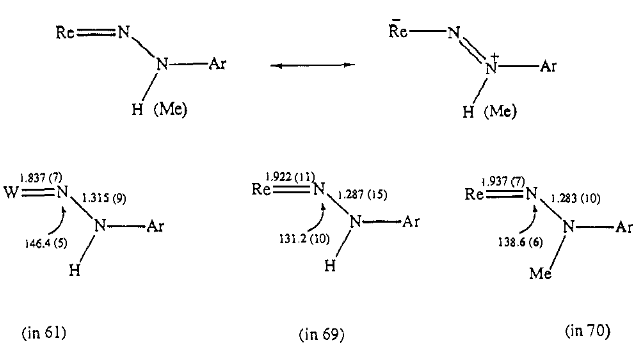
Shaw and co-workers have treated the bis-chelating DPPM complex *trans*-$ReCl(CO)(DPPM)_2$ and the related *trans*-ReCl(CO)(VDPP)$_2$ (VDPP = Ph$_2$PC(=CH$_2$)PPh$_2$) with aryldiazonium salts [RN$_2$][X] (X = PF$_6$ or BF$_4$) whereupon one of the chelate rings opened up to become monodentate to accommodate the singly bent aryldiazenide ligand in [ReCl(CO)(N$_2$R)(η^2-DPPM)(η^1-DPPM)]$^+$ and the corresponding VDPP salt.[132] These react with *trans*-PtHCl(PPh$_3$)$_2$, Rh$_2$Cl$_2$(CO)$_4$, or CuCl to give heterobimetallic compounds (RN$_2$)ClRe(μ-DPPM)$_2$(μ-CO)PtCl (**68**), [(RN$_2$)(CO)ClRe(μ-VDPP)$_2$(μ-Cl)Rh(CO)][BF$_4$], and [(RN$_2$)(CO)Re(μ-VDPP)$_2$(μ-Cl)CuCl][PF$_6$]. The structure of **68** (R = *p*-tolyl) was determined by X-ray crystallography. The VDPP analog of **68** was capable of protonation and methylation at N$_\beta$ to give hydrazido(2–) complexes in the usual fashion.[133] The structure of a homobinuclear rhenium complex anion [Re$_2$(NNPh)$_2$(SPh)$_7$]$^-$ prepared from ReCl(N$_2$Ph)$_2$(PPh$_3$)$_2$ and thiophenol/Et$_3$N has been reported.[134] ReCl(N$_2$Ph)$_2$(PPh$_3$)$_2$ was prepared from ReOCl$_3$(PPh$_3$)$_2$ and PhNHNH$_2$. The structures of the (*p*-bromophenyl)diazenido analog ReCl(*p*-N$_2$C$_6$H$_4$Br)$_2$(PPh$_3$)$_2$ and some other rhenium diazenido or hydrazido(2–) complexes with aromatic thiolate coligands have also been reported,[135] as has the structure of the mixed hydrazido(1–)/hydrazido(2–) complex ReCl$_2$(PPh$_3$)$_2$[NN(H)COPh](NHNHCOPh).[136] ReX(N$_2$Ph)$_2$(PPh$_3$)$_2$ (X = Cl, Br) can alternatively be prepared from ReOX$_3$(PPh$_3$)$_2$ and 4 equiv of Me$_3$SiN$_2$Ph in 70–80% yield. Protonation with HCl or HBr occurs on the β-nitrogen of one phenyldiazenido ligand and the crystal structure of the bromo complex **69** shows it to contain one singly bent phenyldiazenido ligand and one bent phenylhydrazido(2–) ligand.[137] The position of the hydrogen was located. The angle Re=N—N in the hydrazido(2–) group is 131.2(10)° and the nitrogen bonded to Re essentially carries an unshared electron pair that is not involved in bonding to the metal. The bent hydrazido(2–) ligand is then formally a 2e$^-$ donor (neutral) or 4e$^-$ donor dianion and the Re atom thereby achieves an 18-electron configuration. The Re=N bond length to the hydrazido(2–) group is 1.922(11) Å and N–N is 1.287(15) Å. These dimensions are very similar to those in the other structurally characterized rhenium hydrazido(2–) complex CpRe(CO)$_2${*p*-NN(CH$_3$)C$_6$H$_4$OMe} (**70**), discussed below. The shortening of N–N from the single-bond value (1.45 Å) and planar geometry at the β(carbon-bound) nitrogen atom indicate delocalization of the lone pair at this nitrogen into the N–N bond (Scheme V). In the third structurally characterized bent hydrazido(2–) complex, the tungsten compound **61** described above, the longer N–N bond and shorter W=N bond are consistent with a smaller contribution from the zwitterionic structure in this case.



(69)

Haymore[138] has synthesized the Mn and Re complexes M(CO)$_2$(N$_2$Ph)(PPh$_3$)$_2$ as illustrated in eq 15 for Mn.

Scheme V



$$\mathrm{MnH(CO)_3(PPh_3)_2} \xrightarrow{\mathrm{PhN_2^+}} [\mathrm{Mn(NHNPh)(CO)_3(PPh_3)_2}]^+ \xrightarrow{\mathrm{NaOMe}} \mathrm{Mn(CO)_2(N_2Ph)(PPh_3)_2} \quad (15)$$

The starting material in the case of Re was ReH(CO)$_2$(PPh$_3$)$_3$ since CO substitution by N$_2$Ph$^+$ is more difficult in the tricarbonyl compound. The reaction of Mn(CO)$_2$(N$_2$Ph)(PPh$_3$)$_2$ with further diazonium ion provides [Mn(CO)(N$_2$Ph)$_2$(PPh$_3$)$_2$]$^+$ and MnX(N$_2$Ph)$_2$(PPh$_3$)$_2$ (eq 16). The mixed nitrosyl(phenyldiazenido) complexes [Mn(CO)(NO)(N$_2$Ph)(PPh$_3$)$_2$]$^+$ and MnX(NO)(N$_2$Ph)(PPh$_3$)$_2$ were also synthesized.

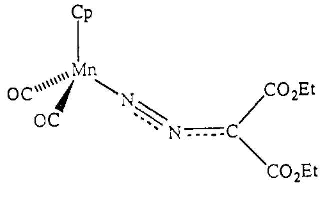
$$\mathrm{Mn(CO)_2(N_2Ph)(PPh_3)_2} \xrightarrow{\mathrm{PhN_2^+}} [\mathrm{Mn(CO)(N_2Ph)_2(PPh_3)_2}]^+ \xrightarrow[\mathrm{X=Cl,Br,NCO}]{\mathrm{PPN^+X^-}} \mathrm{MnX(N_2Ph)_2(PPh_3)_2} \quad (16)$$

The CpM(CO)$_2$ fragment and its methylated analogs have figured prominently in the organometallic diazo chemistry of Mn and Re. CpMn(CO)$_2$THF reacts with N$_2$H$_4$ to give CpMn(CO)$_2$(N$_2$H$_4$).[139] Controlled oxidation of the coordinated hydrazine gives the dinitrogen complex CpMn(CO)$_2$(N$_2$) and a low yield of the binuclear complex of *trans*-diazene Cp(CO)$_2$MnNH=NHMn(CO)$_2$Cp.[140,141] This reaction is proposed to proceed by oxidation of CpMn(CO)$_2$(N$_2$H$_4$) to give CpMn(CO)$_2$(N$_2$H$_3$). This disproportionates to CpMn(CO)$_2$(N$_2$H$_2$) which captures a second CpMn(CO)$_2$ moiety.[142] CpRe(CO)$_2$THF exhibits essentially similar chemistry with formation of CpRe(CO)$_2$(N$_2$H$_4$) and controlled oxidation of this to give CpRe(CO)$_2$(N$_2$) and Cp(CO)$_2$ReNH=NHRe(CO)$_2$Cp. However, the rhenium hydrazine complex easily disproportionates to the N$_2$ complex and CpRe(CO)$_2$NH$_3$ at room temperature.[143] Mixed chromium–manganese hydrazine and diazene complexes can also be synthesized (eq 17).[144,145]

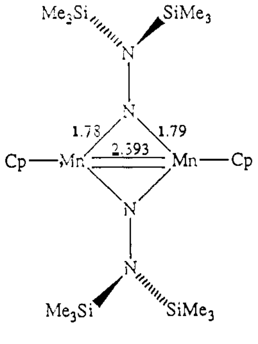
$$\mathrm{CpMn(CO)_2(N_2H_4)} \xrightarrow{\mathrm{Cr(CO)_5THF}} \mathrm{Cp(CO)_2MnNH_2NH_2Cr(CO)_5} \xrightarrow{\mathrm{O_2\ or\ H_2O_2}} \mathrm{Cp(CO)_2MnNH{=}NHCr(CO)_5} \quad (17)$$

Related to these binuclear diazene complexes are corresponding binuclear dinitrogen complexes, accessible from the reaction of (RC$_5$H$_4$)Mn(CO)$_2$THF (R =

H, Me) and 1,1,1-trifluorodiazoethane.[146] Diazoalkane reactions with $(RC_5H_4)Mn(CO)_2THF$ have been thoroughly studied and commonly give nitrogen-loss products such as terminal or bridged alkylidene species.[6b,111a] Complex **71** is an example where a direct η^1-diazoalkane complex is formed.[147] Wiberg has reported the structure of the diamagnetic, centrosymmetric $Cp_2Mn_2\{NN(SiMe_3)_2\}_2$ (**72**) synthesized from $Me_3SiNNSiMe_3$ and Cp_2Mn. The bis(trimethylsilyl)hydrazido(2–) ligands that are formed by rearrangement of the diazene bridge the Mn–Mn bond symmetrically [compare the structure of the monomeric vanadium complex $Cp_2V\{NN(SiMe_3)_2\}$ (**21a**)].[26,94]



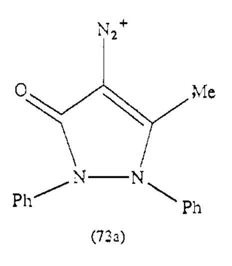
(71)



(72)

The terminal N_2 ligand in $CpMn(CO)_2(N_2)$ has been described to be capable of successive nucleophilic and electrophilic attack by LiPh and H^+, and the product has been formulated as $CpMn(CO)_2(PhNNH)$ where the phenyl is located on N_α adjacent to the manganese.[148] In view of the possibility of the η^1-η^2-η^1 rearrangement pathway as described below for the PhNNPh ligand in $CpRe(CO)_2(PhNNPh)$ (which could give rise to either an η^2-NHNPh or a Mn-NHNPh arrangement), or the possibility of H migration to give a hydrazido(2–) ligand, this product deserves a complete and unambiguous characterization. A MeNNMe analog has been synthesized by successive Me^- and Me^+ attack.[148]

The manganese aryldiazenido complexes $[(C_5H_4Me)Mn(CO)_2(N_2R)][BF_4]$ (**73**) are accessible from the reaction of the arenediazonium ion with $(C_5H_4Me)Mn(CO)_2(H)(SiPh_3)$, whereas THF or phosphine complexes are simply oxidized.[149,150] The X-ray structure of the o-$CF_3C_6H_4N_2$ complex confirms the expectation that the aryldiazenido ligand is a normal, singly bent, $3e^-$ donor.[149,150a] The less oxidizing antipyrene-4-diazonium cation (**73a**) does, however, give an isolable aryldiazenido complex when reacted at –50 °C with the manganese THF complex.[104] A product of $NaBH_4$ reduction of **73** (together with $(C_5H_4Me)Mn(CO)_2(N_2)$, vide infra) is a compound with $\delta(NH) = 13.7$ formulated as the "normal" aryldiazene complex $(C_5H_4Me)Mn(CO)_2(o\text{-}NHNC_6H_4CF_3)$ by analogy with the completely characterized rhenium analogs to be discussed now.[151]



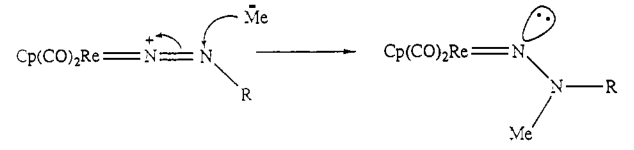
(73a)

The rhenium series of aryldiazenido complexes $[CpRe(CO)_2(N_2R)][BF_4]$ (**74**) and $[Cp^*Re(CO)_2(N_2R)][BF_4]$ (**75**) are synthesized directly from $CpRe(CO)_2(THF)$ or $Cp^*Re(CO)_2(THF)$ and the arenediazonium salt.[151,152] The reaction of $NaBH_4$ with **74** delivers H^- at N_α as demonstrated unambiguously in the ^1H NMR spectrum by ^{15}N-labeling at this position (δ(NH) near 15 with $^1J(^{15}NH)$ near 70 Hz) (eq 18). While

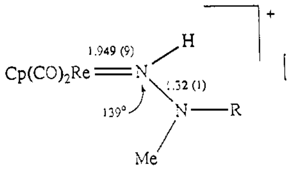
$$[Cp(CO)_2Re{=}^{15}N{=}NR]^+ \xrightarrow{H^-} Cp(CO)_2Re{-}^{15}NH{=}NR \quad (18)$$

no crystal structure has been determined, the equivalence of the CO groups in the ^{13}C NMR spectrum at room temperature precludes a rigid side-on bound *trans*-aryldiazene (but not a fluxional one) and is consistent with the η^1-bound ligand illustrated.[153] When the nucleophile is MeLi, Me^- is delivered at N_β, with the result that a bent metal–hydrazido(2–) linkage is formed (Scheme VI). This was confirmed by the crystal structure for R = p-C_6H_4OMe (**70**) which has been discussed earlier in the context of related bent hydrazido(2–) compounds **61** and **69**; each of the latter was synthesized by a very different method, i.e., RN_2^+ insertion into a W–H bond, and *protonation* of an aryldiazenide group, respectively. The resulting electron-pair on N_α is able to be protonated by HBF_4 to give the η^1-hydrazido(1–) complex **76** where the mode of attachment of the ligand was confirmed by the crystal structure for R = p-tolyl.[154]

Scheme VI



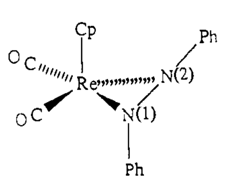
(74) (70)



(76)

It is interesting to note that the bond distances and angles in the hydrazido(2–) and hydrazido(1–) ligands in the two structures are very similar and, in both cases, support a degree of delocalization of the electron pair on N_β into the NN bond.

The diphenyldiazene (azobenzene) complex $CpRe(CO)_2(PhNNPh)$ (**77**) has also been prepared.[35] The



(77)

crystal structure shows that the azobenzene is side on

Scheme VII

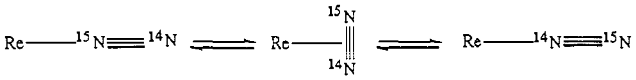
$$[CpRe(CO)_2(N_2R)]^+ \xrightarrow{e^-} CpRe(CO)_2(N_2R) \xrightarrow{-R^\cdot} CpRe(CO)_2(N_2)$$

bonded (η^2) and adopts a pseudo-trans arrangement of the phenyl groups with torsional angle of 137° between the NNC(phenyl) planes. As a result the two Re–N bonds are not equivalent by symmetry and do have different lengths: Re–N(1) = 2.048(12) Å and Re–N(2) = 2.136(11) Å; the phenyl group on N(2) is angled toward the Cp ring. The N–N bond length is 1.415(17) Å, comparable with the length in $Cp_2Zr(py)(\eta^2\text{-}PhNNPh)$ (1.410(6) Å)[33b] and $(ArO)_2(py)_2Ti(\eta^2\text{-}PhNNPh)$ (1.416(8) Å)[12] and marginally longer than in $Cp^*WMe_3(\eta^2\text{-}MeNNMe)$ (1.38(1) Å),[56] $Ni\{P(tolyl)_3\}_2(\eta^2\text{-}PhNNPh)$ (1.371(6) Å),[37] $Ni(Bu^tNC)_2(\eta^2\text{-}PhNNPh)$ (1.385(5) Å),[36] and $Cp_2Ti(\eta^2\text{-}PhNNPh)$ (1.339(8) Å).[34] The N–N bond length is probably not a reliable guide to whether the ligand is best described as π-bound azobenzene or as a 1,2-diphenylhydrazido(2–) ligand in complexes of this type. The torsional angle may be a better guide as discussed earlier in connection with the structure of $Cp_2Zr(py)(\eta^2\text{-}PhNNPh)$. In solution, **77** is in equilibrium with a second isomer in which the azobenzene is η^1 or a σ-complex. The relative proportion of the η^2-form increases as the para substituent is changed in the order Me < H < F. Furthermore, NMR spectra indicate that the η^1-isomer is fluxional, and that the rhenium–nitrogen σ-bond shuttles from one nitrogen atom to the other through the intermediacy of the side-on bonded form.

In addition to the reactions described above in which the N_2R ligand in $[CpRe(CO)_2(N_2R)]^+$ is elaborated, both this and the Cp* analog give rise to numerous aryldiazenido complexes as a result of substitution or transformation of a CO group and there are parallels with the chemistry of $[CpRe(CO)_2(NO)]^+$.[155,156] As examples, aqueous NaOH yields stable hydroxycarbonyl complexes $CpRe(CO)(N_2R)(COOH)$ which can be deprotonated to give the carboxylato (or CO_2) complexes $[CpRe(CO)(N_2R)(CO_2)]^-$ or decarboxylated to give the hydrido complexes $CpReH(CO)(N_2R)$;[157] other nucleophiles generate $CpReX(CO)(N_2R)$ (X = Cl, Br, I, NCO, CO_2R, C(O)R, $CONH_2$, CONHMe, and $CONMe_2$).[151,152] Some of these can also be synthesized for the (methylcyclopentadienyl)manganese system.[151,152] The heterobimetallic rhenium–gold compound $Cp(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$ has also been synthesized and its crystal structure determined.[158]

One transformation which is, as far as can be ascertained, currently unique to the cyclopentadienylmanganese or -rhenium systems is the reduction of the aryldiazenide ligand to dinitrogen. This was initially observed in the reaction of $[(C_5H_4Me)Mn(CO)_2(N_2R)]^+$ or $[CpRe(CO)_2(N_2R)]^+$ with I^-, Cl^-, Br^-, CN^-, SCN^-, or PPh_3 and was attributed at that time to either nucleophilic attack at the ipso carbon atom of the aryl group[149] or a radical mechanism.[150] (Note, however, that the manganese derivative of the heterocyclic diazonium ion **73a** was reported not to transform to the dinitrogen complex in the presence of bromide ion.[104]) Other reagents such as $NaBH_4$ or MeLi also are effective.[151,152,159] The transformations can be conducted cleanly electrochemically or by using cobaltocene and the results are best accommodated by Scheme VII.[153,159] Because it is easy to introduce the ^{15}N label at the unsubstituted nitrogen atom in aryldiazonium ions by using nitrite-^{15}N in the diazotization of the appropriate aromatic amine, this means that the rhenium or manganese dinitrogen compounds can be prepared uniquely labeled at N_α, e.g., $Cp^*(CO)_2Re\text{-}^{15}N^{14}N$. ^{15}N NMR spectroscopy shows that at ambient temperature linkage isomerization of the dinitrogen ligand occurs and the ^{15}N label is incorporated into both of the inequivalent N_α and N_β sites.[159,160] A crossover experiment indicates that this isomerization is intramolecular and nondissociative so that the N_2 ligand undergoes end-to-end rotation via the η^2-N_2 structure, with $\Delta G^{\ddagger}_{287}$ = 90 kJ mol^{-1} (Scheme VIII).[159]

Scheme VIII

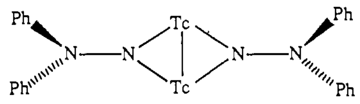


In an extension to rhenium of the novel molybdenum and tungsten hydrazine and hydrazido chemistry discussed earlier, Schrock has recently reported related derivatives of the Cp^*ReMe_3 fragment (eq 19).[161] It is

$$Cp^*ReMe_3(OTf) \xrightarrow{N_2H_4} \underset{\mathbf{78}}{[Cp^*ReMe_3(NH_2NH_2)][OTf]} \underset{HOTf}{\overset{DBU}{\rightleftharpoons}} \underset{\mathbf{79}}{Cp^*ReMe_3(NHNH_2)} \quad (19)$$

not yet established whether **78** contains an η^1-NH_2NH_2 ligand, or whether it is η^2 and possibly analogous to the structurally determined tungsten analog $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)][OTf]$ (**37**, M = W).[71] Reduction of compound **78** by zinc amalgam or sodium amalgam yields ammonia both in the absence and the presence of the proton source 2,6-lutidine hydrochloride.

There has been, by comparison, little investigation of the diazo chemistry of technetium.[162-164] Of note is the structure of the binuclear catecholate anion $[Tc_2(NNPh_2)_2(C_6Cl_4O_2)]^-$ in which the diphenylhydrazido(2–) ligands adopt the symmetrical μ_2-η^1 bridging mode (**80**).[162] A related bridging mode has been observed in three previous cases $Cp_2Mo_2(NO)_2I_2(NNMe_2)$ (**55**),[70,115] $Cp_2Ti_2Cl_2(NNPh_2)_2$ (**5**),[15] and $Cp_2Zr(NNPh_2)_2$ (**6**)[19] as described earlier, but in each of these the bridge is unsymmetrical with unequal metal–nitrogen distances. Here, the Tc–N bond lengths are essentially equal at ca. 1.94 Å and this indicates some multiple-bond character. The N–N bond lengths (1.297(13) Å and 1.311(13) Å) approach that of a double bond and are shorter than in the other examples.[162] The technetium bis(aryldiazenido) complexes $TcCl(NNAr)_2(PPh_3)_2$, analogous to the manganese and rhenium complexes discussed above, have been synthesized from the reaction of arylhydrazines with $[TcOCl_4]^-$ and PPh_3[163] or with $TcCl_4(PPh_3)_2$.[164] The X-ray structure of $TcCl(p\text{-}NNC_6H_4Br)_2(PPh_3)_2$ was



(80)

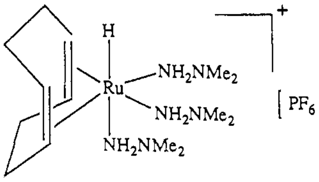
determined[164] and is essentially similar to that of the rhenium analog.[135] Addition of excess HCl(g) protonated one aryldiazenide ligand at N_β to give the aryldiazenido(arylhydrazido(2−)) complex $TcCl_2(NNR)(NNHR)(PPh_3)_2$ that is formulated as such by a comparison of the spectroscopic data with that of the structurally characterized rhenium analog. A second protonation of this ligand occurs with HBr(g) in benzene to give the dibromo(arylhydrazido(1−)) complex $TcBr_2(p\text{-}NNC_6H_4Br)(p\text{-}NHNHC_6H_4Br)(PPh_3)_2$, formulated as such on the basis of two separate doublets for the NH protons at 12.7 and 14.95 ppm in the ^1H NMR spectrum with $J_{H\text{-}H} = 14.5$ Hz. These are assigned to the N_β and N_α protons, respectively, and the latter exchanges more rapidly with H_2O than does the former.[164]

$TcCl(N_2R)_2(PPh_3)_2$ reacts with DMPE or DPPE to give the monoaryldiazenido complexes $[TcCl(N_2R)(DPPE)_2]^+$ or $[TcCl(N_2R)(DMPE)_2]^+$, and various hydrazido(2−) complexes of technetium derived from substituted hydrazines and $[TcOCl_4]^-$ have been reported.[163]

VI. Iron, Ruthenium, Osmium

The complexes $[(arene)RuCl_2]_2$ (arene = C_6H_6 or $p\text{-}MeC_6H_4CHMe_2$) react with hydrazine hydrate or 1,1-dimethylhydrazine to give the cations $[(arene)Ru(N_2H_4)_3]^{2+}$ and $[(arene)Ru(NH_2NMe_2)_3]^{2+}$, isolated as BPh_4^- or PF_6^- salts.[165] The N_2H_4 complexes have δ(NH) near 5.7 and 3.4 in the ^1H NMR, assigned to the bound and unbound NH_2 protons, respectively, in the $\eta^1\text{-}N_2H_4$ ligands. The NH_2NMe_2 ligands show δ(NH) at around 6.5, indicating them to be bound to the metal by the less hindered NH_2 group. By comparison, the reaction of $CpRu(CO)_2L$ (L = CO, PR_3, etc.,) with N_2H_4 or NH_2NMe_2 involved only nucleophilic attack at CO to give the resulting isocyanate ligand.[166a] N_2H_4 derivatives of related iron compounds, i.e., $[CpFe(CO)_2(N_2H_4)]^+$ and $[CpFe(DPPE)(N_2H_4)]^+$ have been described.[166b]

In an extensive series of papers[167–176] Singleton and co-workers have described the synthesis and structures of related cationic hydrazine and substituted hydrazine salts of the type $[Ru(COD)(N_2H_4)_4]^{2+}$ or $[RuH(COD)(N_2H_4)_3]^+$ and their synthetic utility. Treatment of a suspension of $\{Ru(diene)Cl_2\}_n$ (diene = COD or NBD) in MeOH with the appropriate hydrazine was used to prepare $[Ru(diene)(N_2H_4)_4]^{2+}$, $[Ru(COD)(NH_2NHMe)_4]^{2+}$, and $[RuH(COD)(NH_2NMe_2)_3]^+$. Using the latter, ligand exchange with other hydrazines afforded $[RuH(COD)(NH_2NH_2)_3]^+$ and $[RuH(COD)(NH_2NHMe)]^+$. For the hydrazine complexes resonances near δ 5 or 6 were assigned to the coordinated NH_2 protons and at δ 3.7 to the free NH_2 group; resonances for the NH protons in the substituted hydrazines were also assigned.[171] The X-ray structure of the hydrido complex $[RuH(COD)(NH_2NMe_2)_3][PF_6]$ (**81**) shows that a pseudooctahedral structure is adopted with $\eta^1\text{-}NH_2NMe_2$ ligands in a facial arrangement bound to Ru by the NH_2 groups, and interconnected by hydrogen bonds between the NH_2 protons and the β-nitrogen of a neighboring group.[172,174] Treatment of $[Ru(diene)(N_2H_4)_4]^{2+}$ with an excess of phosphites or phosphonites (e.g., $P(OMe)_3$) in boiling acetone caused loss of the diene and the production of bishydrazone salts,[171] e.g., $[Ru(NH_2NCMe_2)_2\{P(OMe)_3\}_4][BPh_4]_2$ (**82**). The X-ray structure of **82** shows it is the trans isomer and that the hydrazone ligands are η^1-bonded through the NH_2 groups, with no unusual features.[168] Addition of LiCl or LiBr to a boiling methanol–acetone solution of $[RuH(COD)(NH_2NMe_2)_3][BPh_4]$ gave the insoluble crystalline binuclear complexes $\{RuHX(COD)\}_2(\mu\text{-}NH_2NMe_2)$ (**83**; X = Cl, Br). The crystal structure of **83** (X = Cl) showed that the molecule was unsymmetrical with a $\mu_2\text{-}\eta^2\text{-}NH_2NMe_2$ group and both a terminal and a bridging Cl ligand. Correspondingly, the hydride ligands, for which there was some evidence in electron-density difference maps, were also assumed to be both terminal and bridging.[169,173,175] Compound **83** underwent bridge-splitting reactions with phosphines, arsines, stibines, and pyridine accompanied by loss of the hydrazine to give, for example, $RuHX(COD)L_2$ (L = $PMePh_2$) or $[RuH(COD)L_3]^+$ (L = MeCN or 4-methylpyridine).[173] A series of hydrazone–isonitrile complexes of formula $[Ru(CNR)_4(NH_2NCMe_2)_2][BPh_4]$ have been prepared from $[Ru(COD)(N_2H_4)_4]^{2+}$ and the appropriate isonitrile in boiling acetone; however, $CNBu^t$ and ethanol solvent gave the hydrazine complex $[Ru(CNBu^t)_3(N_2H_4)_3][BPh_4]_2$, which converted to *trans*-$[Ru(CNBu^t)_4(N_2H_4)_2][BPh_4]_2$ in cold acetone and to *mer*-$[Ru(CNBu^t)_3(NH_2NCMe_2)_3][BPh_4]_2$ in boiling acetone. For methylhydrazine the compounds *trans*-$[Ru(CNR)_4(NH_2NHMe)_2][PF_6]_2$ were obtained.[176]



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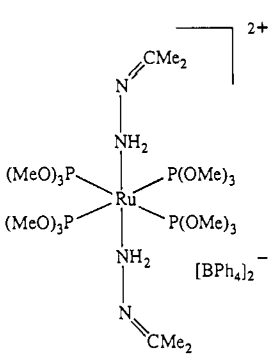

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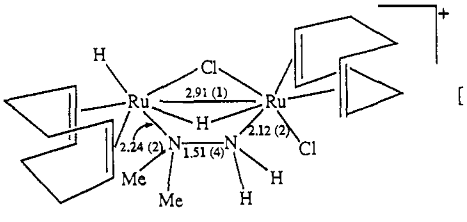


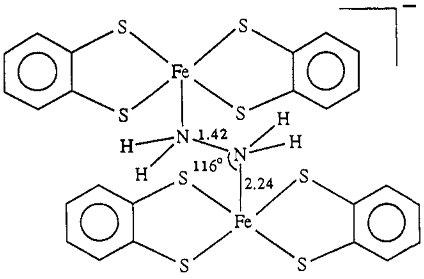
(83)

More recently, this methodology has been extended to osmium. $[Os(COD)Cl_2]_n$ reacted with N_2H_4 or NH_2NMe_2 to give $[OsCl(COD)(N_2H_4)_3][BPh_4]$, $[OsCl(COD)(NH_2NMe_2)_3][PF_6]$ and $[Os(COD)(N_2H_4)_4][BPh_4]_2$. Unlike the ruthenium case, no hydrido complex was formed when using dimethylhydrazine.[177,178]

$[Os(COD)(N_2H_4)_4][BPh_4]_2$ reacted with $CNBu^t$ to give *mer*-$[Os(CNBu^t)_3(N_2H_4)_3][BPh_4]_2$ and *trans*-$[Os(CNBu^t)_4(N_2H_4)_2][BPh_4]_2$ by using refluxing ethanol, and the hydrazone complex $[Os(COD)(CNBu^t)_2(NH_2NCMe_2)_2][BPh_4]_2$ (**84**) in refluxing acetone (cf. ruthenium, above). Hydrazone complexes with other nitrile or phosphine ligands were also obtained.

The structure of **84** showed that the hydrazone ligands are mutually trans, and are bound to the metal through the NH_2 groups (as in the case of **82**) with no unusual features.[177,178]

In an extension to iron and ruthenium of the kinds of bridging hydrazine (i.e., $M(\mu\text{-}NH_2NH_2)M$) and diazene (i.e., $M(\mu\text{-}NH{=}NH)M$) moieties identified for Cr, Mo, W, Mn, and Re (vide supra), Sellmann has synthesized and characterized several compounds of this type with sulfur coligands. These may be important structural models for the stabilization of diazene as a possible intermediate in biological reduction of nitrogen if it occurs at iron rather than uniquely at molybdenum or vanadium, as now seems possible in the light of recent developments.[179a] The reaction of $N_2H_4{\cdot}H_2O$ with $[Bu_4N][Fe(S_2C_6H_4)_2]$ gave the binuclear centrosymmetric complex anion **85** in which two $Fe(S_2C_6H_4)_2$ centers are bridged by N_2H_4.[179b] The oxidation of an iron hydrazine complex $Fe(N_2H_4)L$ (where L is the pentadentate NS_4 ligand derived from H_2L = *o*-$HS(C_6H_4)S(CH_2)_2NH(CH_2)_2S(C_6H_4)SH$-*o*) gave the binuclear centrosymmetric complex $LFe(\mu\text{-}NHNH)FeL$ (**86**) in which the iron atoms are bridged by *trans*-diazene.[179a] A closely related ruthenium *trans*-diazene complex $\{Ru(PPh_3)(DTTD)\}_2(\mu\text{-}NHNH)$ (where DTTD = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2−)) was formed by oxidation of the mononuclear hydrazine complex $Ru(N_2H_4)(PPh_3)(DTTD)$ and was also structurally determined by X-rays.[180] This may be compared with the binuclear ruthenium complexes of a cofacial diporphyrin prepared by Collman and co-workers, where bridging hydrazine was oxidized to bridging *trans*-diazene, and, furthermore, the bridging dinitrogen and bis(terminal) NH_3 analogs could also be synthesized.[181]



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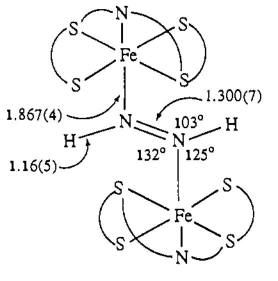
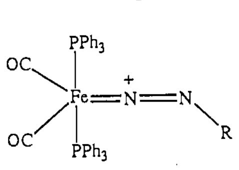


(86)

Aryldiazenido complexes of Fe, Ru, and Os have been known for many years and their synthesis and properties have been reviewed before.[1,5] The coverage here will therefore be brief and focus on the more recent developments. For iron, there are currently two principal structural types: the pentacoordinate trigonal bipyramidal ones, exemplified by $[Fe(CO)_2(N_2R)(PPh_3)_2]^+$, where the singly bent N_2R ligand is equatorial (**87**);[104,182-189] and the pseudotetrahedral type exemplified by $Fe(CO)(NO)(N_2R)(PPh_3)$ (**88**).[182,187,190] A convenient route to **88** is the reaction of **87** with nitrite ion (eq 20).[190]

$$\underset{\mathbf{87}}{[Fe(CO)_2(N_2R)(PPh_3)_2]^+} + NO_2^- \rightarrow \underset{\mathbf{88}}{Fe(CO)(NO)(N_2R)(PPh_3)} + CO_2 + PPh_3 \quad (20)$$

Ligand substitution reactions for **87** giving rise to $FeX(CO)(N_2R)(PPh_3)_2$ have been described,[189] but LiOEt and PPh_3 or some other donor ligands[191] effect loss of the aryldiazenide ligand and the formation of e.g. $Fe(CO)_2(PPh_3)_3$. It would be interesting to reinvestigate this reaction in the light of the reductions of $[CpM(CO)_2(N_2R)]^+$ (M = Mn, Re) described earlier, to determine whether a transient iron dinitrogen complex is involved. The iron center in **88** is, of course, chiral, and analogs of **88** where PR_3 is a chiral diphenyl(amino)phosphine have been synthesized as diastereomers which were separated by chromatography.[192]



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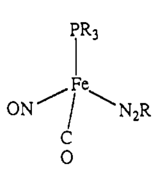
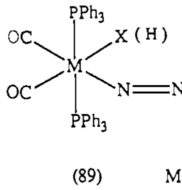


(88)

For M = Ru or Os the currently known mononuclear organometallic aryldiazenido complexes are of the types (a) $[M(CO)_2(N_2R)(PR_3)]^+$, (b) $MX(CO)(N_2R)(PR_3)_2$, (c) $MH(CO)(N_2R)(PR_3)_2$, (d) $MX(CO)_2(N_2R)(PR_3)_2$, and (e) $MH(CO)_2(N_2R)(PR_3)_2$. References to other simple aryldiazenido complexes of Ru or Os can be located in the reviews.[1,5] Types a–c are trigonal bipyramidal with apical phosphine ligands and equatorial, singly bent aryldiazenide ligands, whereas types d and e are octahedral with cis carbonyl ligands and doubly bent 1e⁻ donor aryldiazenide ligands **89**.[186,193-196]



(89) M = Ru, Os

The hydrido complexes c and e were obtained by deprotonation of aryldiazene intermediates formed by insertion of RN_2^+ into one M–H bond in $MH_2(CO)(PPh_3)_3$ or $OsH_2(CO)_2(PPh_3)_2$, see for example eq 21.

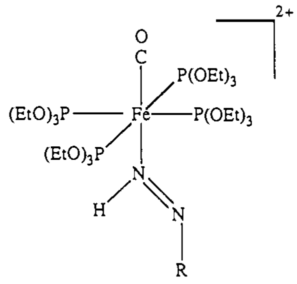
$$OsH_2(CO)_2(PPh_3)_2 \xrightarrow{RN_2^+} OsH(HNNR)(CO)_2(PPh_3)_2 \xrightarrow{OH^-} OsH(NNR)(CO)_2(PPh_3)_2 \quad (21)$$

In a series of papers, Bordignon and co-workers have described a number of new aryldiazene and aryldiazenido complexes of Fe, Ru and Os incorporating phosphite[197] coligands; these include the first examples of bis(aryldiazene) complexes.[198-206] The cationic hydride *trans*-$[FeH(CO)\{P(OEt)_3\}_4]^+$ reacted slowly with $[pXC_6H_4N_2][BF_4]$ (X = Me, F, Cl) in CH_2Cl_2 to give the aryldiazene complex *trans*-$[Fe(CO)(HNNR)\{P(OEt)_3\}_4]^{2+}$ (**90**) (eq 22). This was identified as such by

$$[FeH(CO)\{P(OEt)_3\}_4]^+ \xrightarrow[CH_2Cl_2]{RN_2^+} \textit{trans}\text{-}[Fe(CO)(HN{=}NR)\{P(OEt)_3\}_4]^{2+} \quad (22)$$

90

analysis and spectroscopy; there was a single resonance in the ^{31}P NMR and in the ^1H NMR a broad resonance for δ(NH) at 13.3 which was split into a sharp doublet upon $^{15}N_\alpha$ labeling, with $J(^{15}NH)$ = 67 Hz.[198] The corresponding reaction conducted in acetone gave only the acetone complex $[Fe(OCMe_2)(CO)\{P(OEt)_3\}_4]^{2+}$, which was also formed by reacting **90** with acetone in CH_2Cl_2. This facile replacement of the aryldiazene ligand occurred with other ketones, nitriles, isonitriles, CO, azide, imidazole, pyridine, and sulfides.[198,199] Of particular relevance to this review, arylhydrazines yielded $[Fe(NH_2NHR)(CO)\{P(OEt)_3\}_4]^{2+}$ (**91**). The latter are assigned the cis geometry illustrated on the basis of the ^{31}P NMR spectra. The ^1H NMR spectra included resonances at δ 4.7–5.2 and δ 6.16–7.82 attributed to the NH_2 and NH protons respectively.[199]



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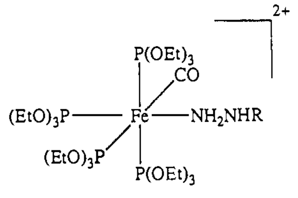
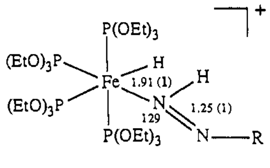
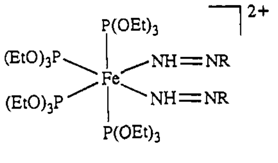


(91)

In previously described reactions of aryldiazonium ions with dihydrides such as $MH_2(CO)(PPh_3)_3$ (M = Ru, Os) and Cp_2WH_2, it will have been noted that the insertion of only one $[RN_2]^+$ group has been observed, despite the presence of two metal–hydride bonds. However, the dihydride $FeH_2\{P(OEt)_3\}_4$ reacts sequentially with an excess of aryldiazonium ions in CH_2Cl_2 at −80 °C to give first *cis*-$[FeH(HNNR)\{P(OEt)_3\}_4]^+$ (**92**) and subsequently the bis(aryldiazene) complex ion *cis*-$[Fe(HNNR)_2\{P(OEt)_3\}_4]^{2+}$ (**93**), which can be separated by fractional crystallization (eq 23).[200]



(92; R = p-MeC$_6$H$_4$)



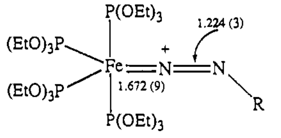
(93)

$$FeH_2\{P(OEt)_3\}_4 \xrightarrow{RN_2^+} \underset{\mathbf{92}}{[FeH(HNNR)\{P(OEt)_3\}_4]^+} \xrightarrow{RN_2^+} \underset{\mathbf{93}}{[Fe(HNNR)_2\{P(OEt)_3\}_4]^{2+}} \quad (23)$$

The structures of **92** and **93** have been established by ^{31}P and ^1H NMR spectra including $^{15}N_\alpha$ labeling. Now the aryldiazene ligands are rather inert to substitution by CO, nitriles, isonitriles, and phosphite. The configuration of **92** (R = p-MeC_6H_4) was confirmed by a crystal structure determination.[200] The bis(aryldiazene) complexes **93** react with 1 equiv of Et_3N to give the pentacoordinate mono aryldiazenido complexes **94** (eq 24).[200]

$$\underset{\mathbf{93}}{[Fe(HNNR)_2\{P(OEt)_3\}_4]^{2+}} \xrightarrow{Et_3N} \underset{\mathbf{94}}{[Fe(N_2R)\{P(OEt)_3\}_4]^+} + Et_3NH^+ + N_2 + RH \quad (24)$$

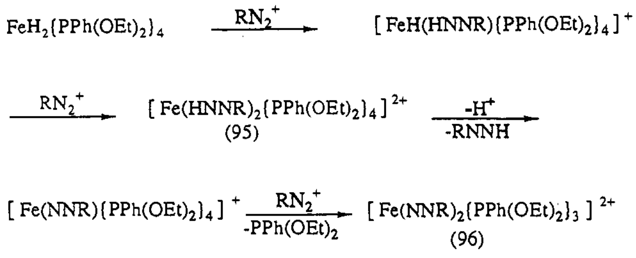
These are trigonal bipyramidal with an equatorial singly bent aryldiazenide ligand, as shown by the crystal structure of **94** (R = p-C_6H_4Me) and are analogous to the complexes $Fe(CO)_2(N_2R)(PPh_3)_2$ (**87**) described earlier. The Fe–N–N angle is 166.6(9)°, which is rather small for the singly bent N_2R ligand; the corresponding angle is 179.2(5) in $[Fe(CO)_2(N_2Ph)(PPh_3)_2]^+$.[185]



(94; R = p-C$_6$H$_4$Me)

It now appears that the chemistry of these iron phosphite diazo compounds may be critically dependent on the particular phosphite ligand employed. In the case of the dihydride $FeH_2\{PPh(OEt)_2\}_4$, the reaction with excess diazonium salt yielded a mixture of the bis(aryldiazene) complex **95** and the bis(aryldiazenido) complex **96**; the mono(aryldiazenido) complex analogous to **94** could not be detected.[201] The reaction is proposed to proceed as shown in Scheme IX. The hydrido mono(aryldiazene) complex $[FeH(HNNR)\{PPh(OEt)_2\}_4]^+$ can be isolated almost quantitatively if 1 equiv of RN_2^+ is used, and this reacts with further RN_2^+ to give initially **95**. Furthermore, **95** can be easily deprotonated by base to give $[Fe(NNR)\{PPh(OEt)_2\}_4]^+$

Scheme IX



$$FeH_2\{PPh(OEt)_2\}_4 \xrightarrow{RN_2^+} [FeH(HNNR)\{PPh(OEt)_2\}_4]^+ \xrightarrow{RN_2^+} \underset{(95)}{[Fe(HNNR)_2\{PPh(OEt)_2\}_4]^{2+}} \xrightarrow[-RNNH]{-H^+} [Fe(NNR)\{PPh(OEt)_2\}_4]^+ \xrightarrow[-PPh(OEt)_2]{RN_2^+} \underset{(96)}{[Fe(NNR)_2\{PPh(OEt)_2\}_3]^{2+}}$$

and this is known to react reversibly with further RN_2^+ to give **96**. It is presumed that traces of water effect the deprotonation reaction in the synthetic procedure in Scheme IX.[201]

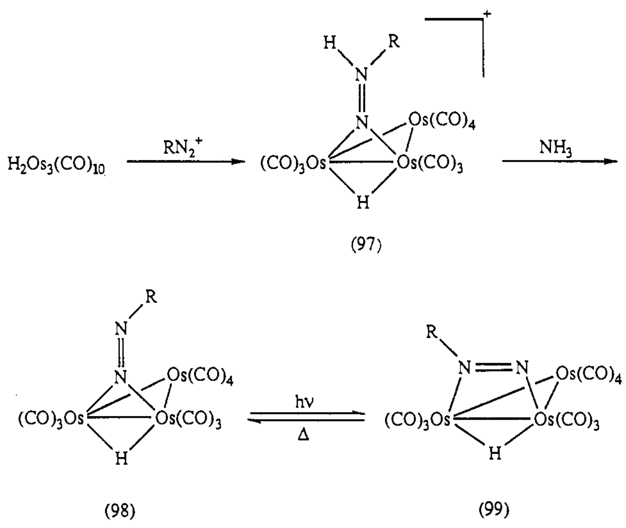
More recently, the behavior of corresponding ruthenium and osmium phosphite dihydrides toward aryldiazonium ions has been reported. $RuH_2\{P(OEt)_3\}_4$ gave the mono and bis(aryldiazene) complexes *cis*-$[RuH(HNNR)\{P(OEt)_3\}_4]^+$ and *cis*-$[Ru(HNNR)_2\{P(OEt)_3\}_4]^{2+}$, respectively, with stoichiometric and excess RN_2^+, analogous to iron. The X-ray structure of the latter was determined.[202] The bis(aryldiazene) complexes were deprotonated by Et_3N to give $[Ru(N_2R)\{P(OEt)_3\}_4]^+$, indicated by ^{31}P NMR to be trigonal bipyramidal with an equatorial singly bent aryldiazenide ligand. These can be protonated by HBF_4 or CF_3CO_2H, and ^1H NMR with ^{15}N labeling shows unambiguously that protonation occurs at N_α to give the aryldiazene complexes $[Ru(HNNR)\{P(OEt)_3\}_4]^{2+}$ or $[Ru(HNNR)(CF_3CO_2)\{P(OEt)_3\}_4]^+$. While protonation at the lone pair on N_β might have been anticipated, the N_α protonation actually observed is in keeping with the site of protonation of the singly bent RN_2 ligand in certain other trigonal-bipyramidal d^8 complexes such as $Re(N_2R)(CO)_2(PPh_3)_2$.[1] Substitution of one diazene ligand in *cis*-$[Ru(HNNR)_2\{P(OEt)_3\}_4]^{2+}$ occurs to give a variety of derivatives including *trans*-$[Ru(CO)(HNNR)\{P(OEt)_3\}_4]^{2+}$, $[Ru(HNNR)\{P(OEt)_3\}_5]^{2+}$, and $[Ru(HNNR)(CNR)\{P(OEt)_3\}_4]^{2+}$ for which the X-ray structure was determined.[203]

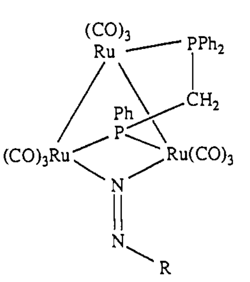
In the case of osmium, both $OsH_2\{P(OEt)_3\}_4$ and $OsH_2\{PPh(OEt)_2\}$ were investigated and reacted essentially similarly to $RuH_2\{P(OEt)_3\}_4$ to give the mono and bis(aryldiazene) complexes $[OsH(HNNR)L_4]^+$ and $[Os(HNNR)_2L_4]^{2+}$ (L = phosphite).[204] The latter also underwent a similar deprotonation to give the aryldiazenides $[Os(NNR)L_4]^+$ with structures essentially similar to the Fe and Ru analogs. These in turn could be protonated at N_α, as were the above Ru complexes, to give $[Os(HNNR)L_4]^{2+}$.

Reflecting current interest in η^2-dihydrogen complexes, the Fe, Ru, and Os complexes $[MH(\eta^2\text{-}H_2)L_4]^+$ have been synthesized for the phosphites L = $PPh(OEt)_2$, $P(OEt)_3$, and (for Ru, Os) $P(OMe)_3$ by protonation of the dihydrides MH_2L_4. The iron and ruthenium complexes (but not the osmium ones) react with arenediazonium ions to lose H_2 and form aryldiazene and aryldiazenido complexes such as $[Fe(N_2R)_2L_3]^{2+}$, $[Fe(HNNR)(NCR)L_4]^{2+}$, $[Ru(N_2R)L_4]^+$, $[Ru(HNNR)L_4]^{2+}$, $[Ru(HNNR)_2L_4]^{2+}$ and $RuH(HNNR)L_4]^+$; some of these have been obtained previously by the reactions described above involving the hydrido complexes, but several are new or have been obtained for the first time for a particular phosphite by this route.[205,206]

These elements are well known for the formation of $M_3(CO)_{12}$ clusters and their derivatives and for numerous clusters of higher nuclearity. Yet, the diazo derivatives of these clusters have been scarcely explored. A notable example is the reaction of $H_2Os_3(CO)_{10}$ with RN_2^+. This first produces a green complex presumed to be the μ_2-η^1-arylhydrazido(2–) cation **97** which is converted by neutralization with NH_3 to the yellow μ_2-η^1-aryldiazenido complex **98**. UV irradiation isomerizes **98** to the μ_2-η^2-aryldiazenido complex **99** and this isomerization is reversed thermally (Scheme X). The X-ray structures of both isomers **98** (R = *p*-tolyl) and **99** (R = phenyl) have been determined.[207] Complex **98** can alternatively be synthesized by reacting $Os_3(CO)_{10}(MeCN)_2$ with phenylhydrazine. The μ_2-η^1-aryldiazenide bridging mode is still not common, and the μ_2-η^2 mode has been observed in only two published structures to date; so the relative parameters for each isomer are of considerable interest. The ν(N=N) IR stretching frequencies for the two isomers, corrected for coupling with aromatic modes, were observed to be near 1525 cm^{-1} for **98** and near 1480 cm^{-1} for **99**. In **98** the Os–N distances are 2.036(11) and 2.056(11) Å and N=N = 1.238(18) Å. In **99** the Os–N distances are, within experimental error, similar at 2.14(2) and 2.11(3) Å and N=N = 1.20(4) Å. The $^{15}N_\alpha$ resonances obtained using $RN^{15}N^+$ (recalculated relative to $MeNO_2$) are isomer **98** δ +68.6 [$^2J(NH)$ = 2Hz] and isomer **99** δ +313.5. This latter low-field chemical shift is characteristic of a coordinated aryldiazenide nitrogen atom carrying an unshared electron pair.[1] Isomer **99** is protonated by $HBF_4\cdot Et_2O$ in CH_2Cl_2, and the ^1H NMR exhibits δ 15.4 for the NH proton, with $^1J(^{15}NH)$ = 81 Hz; the ^{15}N resonance occurs at δ –60.5 as an expected doublet with the same coupling constant. Isomer **98** is not protonated on ^1H NMR evidence, even by excess $HBF_4\cdot Et_2O$.[207] The X-ray structure of a ruthenium cluster **100** containing a μ_2-η^1-bridging aryldiazenide ligand has also been reported.[208] On heating the phenyldiazenido complex, this ligand undergoes cyclometallation to give **101**.

Scheme X





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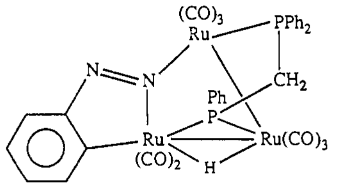
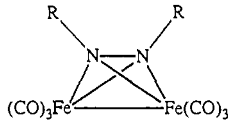


(101)

Interest in diazo derivatives of the binary carbonyls of Fe, Ru, and Os dates back to 1967 when Dekker and Knox reported the formation of $Fe_2(CO)_6(PhNNPh)$

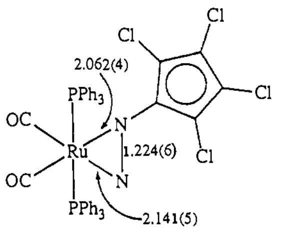
from $Fe_2(CO)_9$ and phenylazide.[209] The "tetrahedrane" bridging μ_2-η^2-RNNR framework **102** has been structurally verified for several examples, e.g., R_2N_2 = Me_2N_2,[210] benzo[c]cinnoline,[211] or 2,3-diazanorbornene.[212]



(102)

Rearrangement with scission of N=N to give *o*-semidine derivatives occurs readily in the case of azobenzene itself, and cyclometalated derivatives can also result.[213] Complexation with iron carbonyls can be a useful method for characterizing new organic diazo compounds.[214] A normal μ_2-η^1,η^1 bridge rather than the "tetrahedrane" unit occurs in $Cp_2Fe_2(CO)_2$(2,3-diazanorbornene).[215] The review by Kisch[6a] should be consulted for additional examples. Interest is increasing in the formation of RNNR derivatives of $M_3(CO)_{12}$ and higher clusters for Fe, Ru, and Os, and in particular the facile N=N cleavage to give cluster organonitrene complexes.[216-220] Cyclometalated mono- and triosmium azobenzene derivatives are among the products of the reaction of $Os_3(CO)_{12}$ with azobenzene.[221] Hydrazines and hydrazones were found to react thermally with $Ru_3(CO)_{12}$ to bind the intact N-N unit as a μ_3-bridging ligand to the triangular Ru_3 framework. The X-ray structure of the N_2H_4 product shows it to be $HRu_3(CO)_9(\mu_3\text{-}NHNH_2)$.[219b]

While diazoalkanes frequently react with N_2 loss to produce alkylidene compounds,[6b] some instances can be cited where diazoalkane derivatives have been obtained for this group. The $C_5Cl_4N_2$ ligand was observed to be side-on bonded in **103**.[222] Structurally characterized **104** and **105** were obtained from diaryldiazomethanes and $Fe(CO)_5$ or $Fe_3(CO)_{12}$.[223] $Ru_3(CO)_{12}$ reacts with CH_2N_2 with N_2 loss to give $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$[224] and $H_2Os_3(CO)_{10}$ also only gives N_2-loss products with CH_2N_2, N_2CHMe, and N_2CHCO_2Et.[225] However, structurally characterized compounds **106** (R = Me, Ph) are among the products obtained[226] from reactions of $H_2Os_3(CO)_{10}$ and Ph_2CN_2, $PhCHN_2$, $PhMeCN_2$, and Me_2CN_2. Diazomethane reacts cleanly with the coordinatively unsaturated $Os_3(CO)_9(C_2Ph_2)$ to give a thermally stable diazomethane adduct for which structure **107** is proposed; this loses N_2 upon photolysis to give $Os_3(CO)_9(C_2Ph_2)(CH_2)$.[227] Dimethyl azodicarboxylate reacts with $Os_3(CO)_{11}(CH_3CN)$ or $Os_3(CO)_{10}(CH_3CN)_2$ to give products **108** and **109** and the latter takes up CO to give **110**. In all three an Os–Os bond has been broken and the ligand acts as a bridging hydrazide with a single N-N bond.[228]



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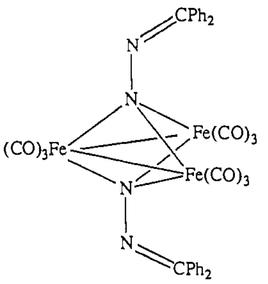

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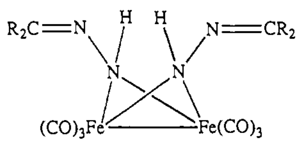

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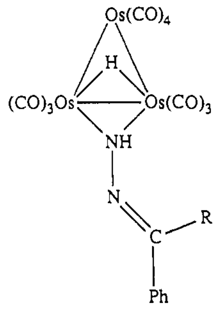

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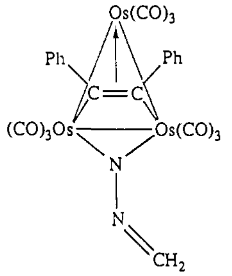

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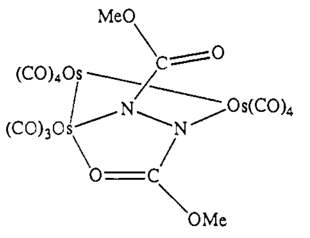

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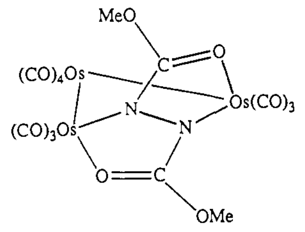

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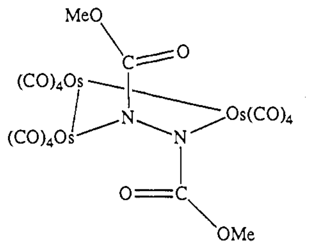


(110)

VII. Cobalt, Rhodium, Iridium

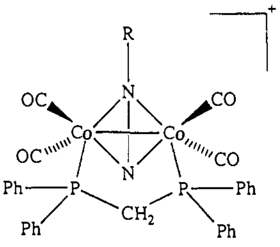
The complexes formed by these elements, in particular rhodium and iridium, with arenediazonium ions, have mostly been reviewed before,[1,5] therefore the treatment here will be selective and emphasize recent developments.

Only a few aryldiazenido compounds of cobalt are known. An unstable red oil was isolated from the reaction of $[(Ph_3P)_2N][Co(CO)_4]$ with PhN_2^+ and PPh_3 at −70 °C and formulated as $Co(N_2Ph)(PPh_3)(CO)_2$ on the basis of IR spectroscopy; ν(NN) at 1689 cm^{-1} was substantiated by ^{15}N isotopic substitution and indicates a 3e⁻ donor singly bent N_2Ph ligand.[182,187] Despite the extensive chemistry of arenediazonium ion insertions into Fe–H bonds in phosphite complexes described in the previous section, the corresponding attempts for $CoH\{P(OEt)_2Ph\}_4$ led only to oxidation of the cobalt complex. The cationic dihydride $[CoH_2\{P(OEt_2)Ph\}_4]^+$ did, however, yield the previously reported cationic aryldiazenido complex $[Co(N_2R)\{P(OEt)_2Ph\}_4]^{2+}$ and H_2.[229,230] This and related complexes were obtained initially by displacement of coordinated CO from the cobalt(I) phosphite complexes $[Co(CO)L_4]^+$ (L = $P(OEt)_2Ph$ or $P(OEt)_3$) by arenediazonium ion (eq 25).

$$[Co(CO)L_4]^+ + RN_2^+ \rightleftharpoons [Co(N_2R)L_4]^{2+} + CO \quad (25)$$

This reaction was ineffective for L = $P(OMe)_3$, but the aryldiazenido complex could be obtained by starting with $[Co\{P(OMe)_3\}_5]^+$. These green diamagnetic solids have two IR bands for ν(NN) near 1780 and 1760 cm^{-1} both in the solid state and in CH_2Cl_2, but it is not clear whether this arises from vibrational coupling or the presence of isomers. The ^{31}P NMR spectrum at low temperature is consistent with a trigonal-bipyramidal configuration with an equatorial singly bent N_2R group, similar to that of the iron complex **94**. The N_2R group is easily substituted by Cl^-, phosphite, CO, NO, and CNR. No formation of analogous aryldiazene complexes was observed.

One of the most exciting developments has undoubtedly been the synthesis of the complexes $[Co_2(CO)_4(\mu\text{-DPPM})(\mu\text{-}N_2R)]^+$ (**111**). These are the first examples of complexes where the RN_2^+ group is bridging normal to a metal–metal bond, in a manner reminiscent of an alkyne or the RN=NR ligand in **102** to give the aryldiazadimetalla tetrahedrane configuration **112**.[231] The X-ray structure of **111** was determined for R = *p*-tolyl. The N–N distance of 1.342(12) Å is considerably longer than the N–N double bond in the "diazadimetallacyclobutene" bridging mode in $H\text{-}Os_3(CO)_{10}(NNPh)$ (**99**), and in $[Cp_2{}^*Ir_2(CO)_2(NNR)]^+$ (see below), but is not a full single bond length (1.45 Å); the Co–Co distance of 2.440(2) Å is unusually short.



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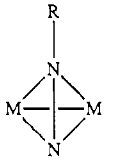
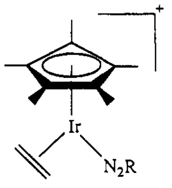


(112)

The reaction of arenediazonium ions with the bis(ethylene) complex $Cp^*Ir(C_2H_4)_2$ gives the (ethylene)(aryldiazenido)iridium cation $[Cp^*Ir(C_2H_4)(N_2R)]^+$ (**113**) which has been structurally characterized by X-ray crystallography for R = *p*-C_6H_4OMe. This 18e$^-$ complex has a typical 3e$^-$ donor singly bent N_2R ligand with ν(NN) 1710 cm^{-1} and bond lengths Ir—N = 1.811(7) Å and N=N = 1.205(9) Å.[232] This cation reacts with the metal-centered Lewis base $Cp^*Ir(CO)_2$ with displacement of the C_2H_4 and CO migration to give the binuclear cation **114**. This is only the second example of the aryldiazenide ligand bridging in this fashion and has distances N=N = 1.29(2), Ir—N(R) = 2.02(2), and Ir—N = 2.06(2) Å, which may be compared with those of the corresponding osmium example (**99**).



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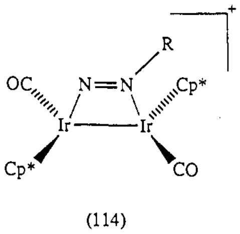
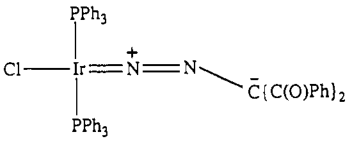


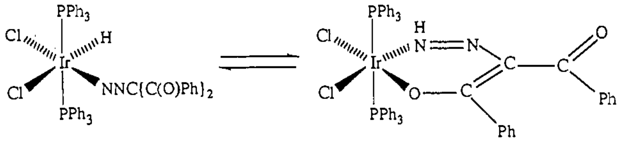
(114)

There have been several reports of the interaction of diazoalkanes with these elements other than the ubiquitous[233] formation of alkylidene compounds. The iridium complexes $IrCl(N_2C_5X_4)(PR_3)_2$ (X = Cl, Br) and their reactions were described by Schramm and Ibers,[234] and the diazo ligand shown to be end on bonded (compare the ruthenium complex **103**).[235] Dibenzoyldiazomethane, $\{PhC(O)\}_2CN_2$, forms an analogous complex **115**, and this reacts with HCl to give an equilibrium mixture of a hydride **116** and an N_α-protonated derivative **117** where the diazo ligand now forms a chelate through a benzoyl oxygen (Scheme XI).[236] The nitrogen-loss products from **115** have also



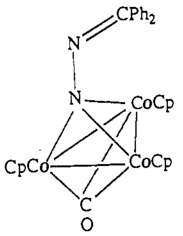
(115)

Scheme XI



(116) (117)

been described and involve hydrogen transfers and unusual rearrangements.[237] Diphenyldiazomethane reacted with $CpCo(CO)_2$ under low-temperature photolysis to give $Cp_2Co_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ and the diphenyldiazomethane bridged cluster **118**.[238] Dickson and coworkers have obtained a wide variety of products from the reactions of substituted diazoalkanes with $Cp_2Rh_2(\mu\text{-CO})(\mu\text{-CF}_3C_2CF_3)$ that show a strong dependence on the nature of the diazoalkane. Observed compounds where the diazo function is retained include **119** and **120**.[239] A particularly stable bridging diazoalkane complex, that does not eliminate N_2 either thermally or photochemically, is the rhodium "A-frame" complex **121** formed by the reaction of ethyl diazoacetate or diethyl diazomalonate with $Rh_2(\mu\text{-H})_2(CO)_2(DPPM)_2$. The arenediazonium salt $[p\text{-}NO_2C_6H_4N_2][PF_6]$ yields a similar cationic "A-frame" complex with a bridging aryldiazenide ligand.[240]



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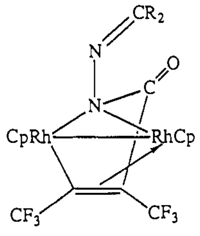

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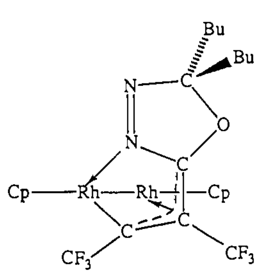

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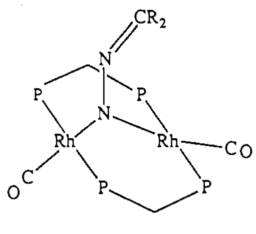
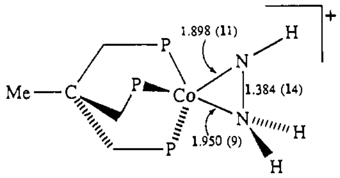


(121)

There has been very little in the way of hydrazine chemistry of these elements. Huttner and co-workers[241] have briefly reported the formation of a cobalt(II) hydrazido(1−) complex cation $[(\text{tripod})\text{Co}(\eta^2\text{-N}_2\text{H}_3)]^+$ (**122**) that is formed by reacting cobalt(II) tetrafluoroborate with N_2H_4 in the presence of the tripod phosphine $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$. The formulation was based upon the observation of three ν(NH) stretching frequencies in the IR spectrum and the inequivalent Co–N distances in the X-ray structure (hydrogens of N_2H_3 were not located). A similar structure was observed for $[(\text{tripod})\text{Co}(\eta^2\text{-NHNMe}_2)]^+$. The CoNN triangle is coplanar with one of the Co–P bonds. Protonation converts **122** to the dicationic hydrazine complex $[(\text{tripod})\text{Co}(\eta^2\text{-N}_2\text{H}_4)]^{2+}$ (**123**). In the structure of **123** the Co–N distances are now equal at 1.941(10) and 1.949(10) Å and the N–N bond is rotated by 90° compared with **122** so that the CoNN plane is now normal to the plane containing a Co–P bond and bisecting the angle between the other two phosphorus atoms. The hydrazine hydrogens were not located, but the N–N bond length 1.446(7) Å, and the IR ν(NH) absorptions and the equal Co–N lengths all support the presence of hydrazine.



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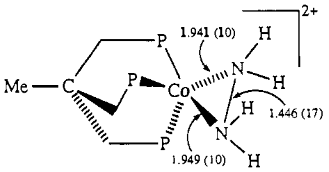
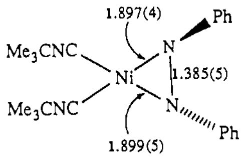


(123)

VIII. Nickel, Palladium, Platinum

Most of the diazo compounds formed by these elements have been described in the earlier reviews,[1,5] and few of these are in fact, derivatives of organometallic compounds.

Nickel diazo complexes are rather scarce, and attempts to prepare examples of aryldiazenido complexes in the author's laboratory have so far been unsuccessful. There are diazoalkane complexes $\text{NiL}_2(\eta^2\text{-diazoalkane})$ (L = Bu^tNC or PPh_3; diazoalkane = $N_2C_5Cl_4$, $N_2C_5Br_4$, diazofluorene),[222,242] and the azobenzene complexes $\text{Ni}(\text{Bu}^t\text{NC})_2(\eta^2\text{-PhN=NPh})$ (**124**)[36,243] and $\text{Ni}\{\text{P(tolyl)}_3\}_2(\eta^2\text{-PhN=NPh})$ (**125**).[37] X-ray structure determinations have shown that the nickel binds side on to the NN bond in these complexes, as illustrated for **124**, **125**, and $\text{Ni}(\text{Bu}^t\text{NC})_2$(diazofluorene) (**126**). Ab initio calculations[244] also show a preference for Ni to bond side-on with diazomethane and diazene in model complexes. Related palladium complexes are known for these ligands.[222] Cyclometalation reactions can often occur with azobenzene, as illustrated by the nickel and palladium complexes **127**[245] and **128**.[246] The reaction of **128** with NaCo(CO)_4, and NaM(CO)_5 (M = Mn, Re) has been employed to synthesize cyclometalated azobenzene chelates of Co(CO)_3 and M(CO)_4 fragments.[245b] Stone and co-workers[247] have observed the coupling of bis(trifluoromethyl)diazomethane molecules to give the ligand $(CF_3)_2C{=}NN{=}C(CF_3)_2$ which is bound to Ni, Pd, or Pt through a C=N double bond. Recently, the structure was published[248] of an unusual orthometalated platinum compound **128a** that was derived from the coupling of diphenyldiazomethane molecules in reacting with *cis*-$(C_6F_5)_2\text{Pt(THF)}_2$.



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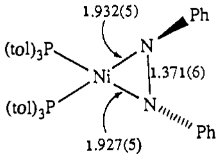

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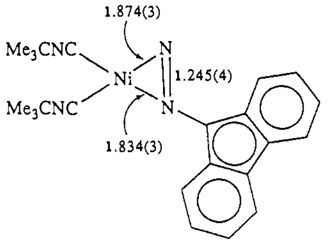

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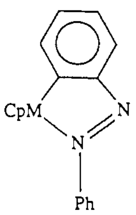
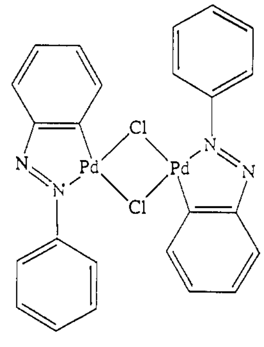


(M = Ni, Pd)
(127)



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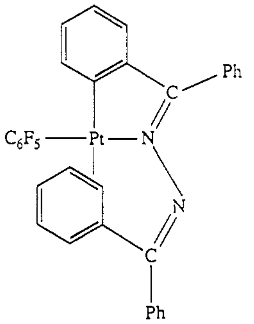
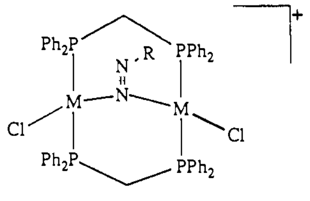


(128a)

Among the older work, a notable reaction is the conversion of the arenediazonium ion to aryldiazene, doubly bent aryldiazenide, and arylhydrazine ligands bound to Pt as shown in Scheme XII. The crystal structures of each derivative have been obtained[249–251] and a mechanism proposed for the arenediazonium "insertion" into the metal hydride bond.[252] Binuclear Pt complexes with diazenido (N_2H) bridging ligands e.g., $[\text{Pt}_2(\text{PPh}_3)_4(\text{N}_2\text{H})_2]^{2+}$ have been proposed[253] to be formed in the hydrazine reduction of *cis*-$\text{Pt}(\text{PR}_3)_2\text{Cl}_2$.

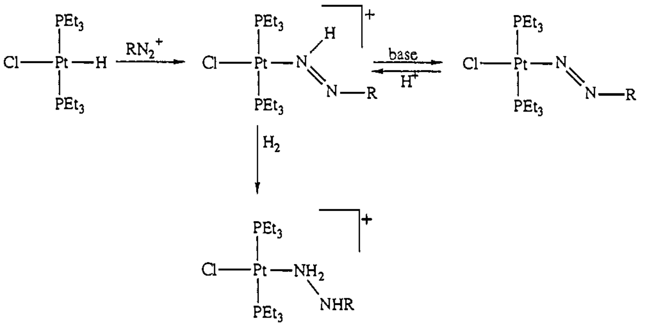
Insertion of arenediazonium ions into the metal–metal bond of the Pd and Pt dimers $M_2Cl_2(DPPM)_2$ gives the A-frame complexes **129** possessing a bridging aryldiazenido ligand[254,255a] (compare **121**); the structure of the platinum compound has been determined for R = *p*-C_6H_4OMe.[255a] There is a closely related analog of **129** with C_6F_5 substituting for one of the Cl ligands.[255b] Mononuclear $[Pd(PPh_3)_3(N_2R)][PF_6]$ can be obtained from $Pd(PPh_3)_4$ and $[RN_2][PF_6]$ for R = *p*-C_6H_4OMe, but nitrogen extrusion to give arylpalladium compounds accompanies the aryldiazenido complexes for other R groups studied.[256] Regioselective addition of N_2H_4 to the σ-allenyl group in *trans*-$PtBr(PPh_3)_2(CH{=}C{=}CH_2)$ yields the platinapyrazoline derivative **131** via the proposed intermediate **130** (Scheme XIII).[257]



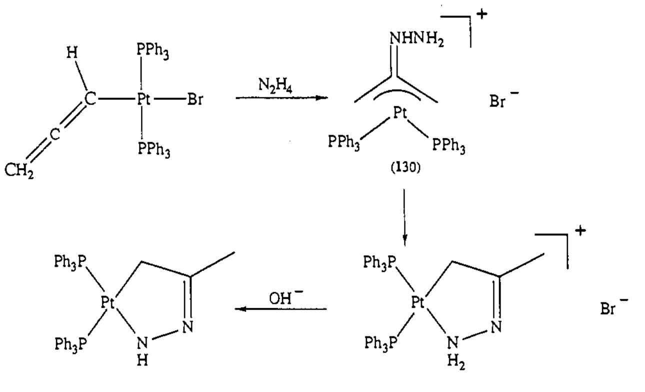
M = Pd , Pt

(129)

Scheme XII



Scheme XIII



(131)

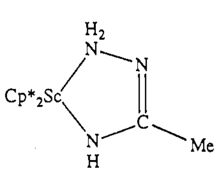
IX. Copper, Silver, Gold

There at present appear to be no organometallic diazo compounds of these elements. The copper complexes of phenyldiazene, $Cu_4Cl_4(NH{=}NPh)$, and azomethane, Cu_4Cl_4 (NMe=NMe), are known and the structure of the latter has been determined.[258]

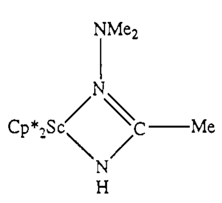
X. Scandium, Lanthanides, Actinides

The reaction of N_2H_4 or Me_2NNH_2 with $Cp^*{}_2ScCH_3$ produces the hydrazido(1−) complexes $Cp^*{}_2Sc(\eta^2\text{-}NHNH_2)$ and $Cp^*{}_2Sc(\eta^2\text{-}NHNMe_2)$ (eq 26).[259] The mode of coordination of the hydrazido(1−) groups is believed to be η^2 by a comparison with other d° systems (see, for example **3**, **4**, **30**, and **33**), but at present no concrete structural evidence is available. These hydrazido(1−) complexes react with CH_3CN to give the metallacyclic compounds **132** and **133**. The crystal structures of these were determined. Note the formation of 5- and 4-membered rings, respectively. By means of ^{15}N labeling studies using $CH_3C^{15}N$, the NH group nitrogen atom has been shown to originate from CH_3CN, and mechanisms for the formation of these products have been discussed. This incorporation of CH_3CN can be compared with a related example observed previously.[83c]

$$Cp^*ScCH_3 + R_2NNH_2 \rightarrow Cp_2^*Sc(NHNR_2) + CH_4 \quad (26)$$



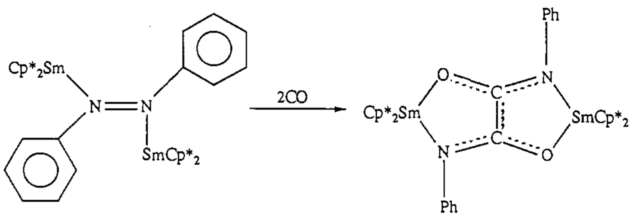
(132)



(133)

An azobenzene complex $\{Cp^*{}_2Sm\}_2(N_2Ph_2)$ (**134**) of unusual structure is formed when azobenzene is reacted with $Cp^*{}_2Sm(THF)_2$. This has been shown by X-ray crystallography to have each nitrogen of *trans*-azobenzene separately σ-bonded to a $Cp^*{}_2Sm$ group; however, the structure is very unsymmetrical and the two Sm atoms are closer to one phenyl ring than the other and interact with it through agostic bonds to ortho C–H positions.[260] The N=N bond length (1.25(1) Å) is the same as that in free azobenzene (1.247(3) Å), whereas the N–C bonds are significantly longer. This complex reacts with CO to undergo a double insertion of CO into the N=N bond (Scheme XIV).[261] The monomeric species $[Cp_2M\{N_2(tolyl)_2\}]^+$ (M = Th, U) have been identified in the mass spectral fragmentation of Cp_2ML_2 (where L = *N,N'*-di-*p*-tolyltriazenide).[262]

Scheme XIV



(134)

Very recently, the reaction of $Cp^*{}_2Sm$ with hydrazine has been reported.[263] The yellow crystalline product was shown by an X-ray structure (Figure 1) to be a tetranuclear complex of composition $[Cp^*Sm]_4(NH\text{-}NH)_2(NHNH_2)_4(NH_3)_2$. It consists of a distorted tetrahedron of Sm atoms bridged by two hydrazido(2−) ($NHNH^{2-}$) anions along opposite edges of the tetrahedron. Each Sm is bonded side on to one $NHNH^{2-}$ group and end on to one nitrogen of the other. Four hydrazido(1−) ($NHNH_2$) anions are located in bridging

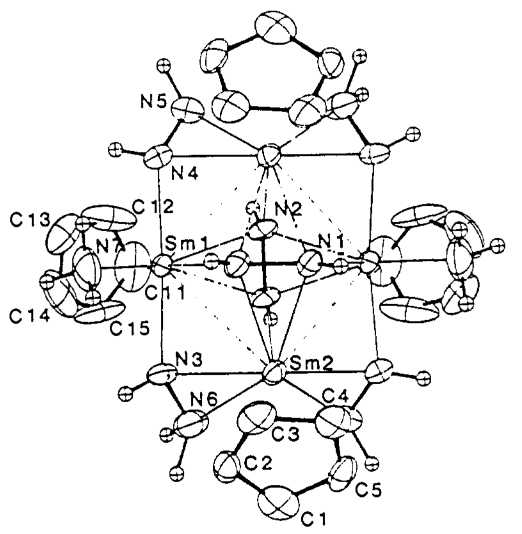
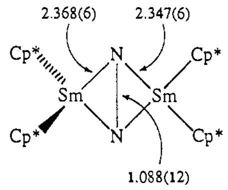


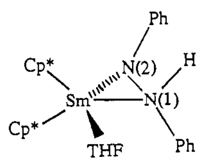
Figure 1. Molecular structure of $[Cp^*Sm]_4(NHNH)_2(NHNH_2)_4(NH_3)_2$ viewed parallel to the 2-fold axis, with probability ellipsoids drawn at the 50% level. Cp* methyl groups have been omitted for clarity. (Reprinted from ref 263. Copyright 1992 American Chemical Society.)

positions on the remaining four edges of the tetrahedron. Each of two Sm atoms is coordinated by a NH_3 ligand. In view of the existence of the side-on bonded dinitrogen complex $Cp^*_2Sm(\mu_2\text{-}\eta^2\text{-}N_2)SmCp^*_2$ (**135**) obtained by Evans and co-workers,[264] the Cp^*_2Sm binuclear system



(135)

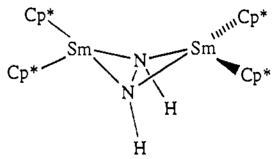
promises to give rise to interesting and significant structural and chemical relationships between dinitrogen and its reduction products. This expectation has been vindicated in the most recent reports from this group.[265-266] While 1,2-diphenylhydrazine reacts with $Cp^*_2Sm(THF)_2$ to undergo NN bond cleavage and form $Cp^*_2Sm(NHPh)(THF)$, Cp^*_2Sm itself reacts to give a yellow-green complex formulated as $Cp^*_2Sm(PhNHNPh)$ (**136**) which can be isolated as the THF adduct $Cp^*_2Sm(\eta^2\text{-}PhNHNPh)(THF)$ (**137**).[265] The



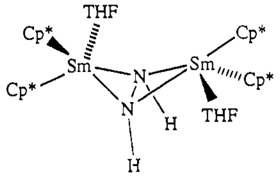
(137)

X-ray crystal structure of **137** demonstrated the presence of the side-on coordinated diphenylhydrazide(1−) ligand; the Sm–N(1) distance to the protonated nitrogen atom is 2.610(5) Å, longer than the Sm–N(2) distance (2.330(5) Å) to the 3 coordinate nitrogen atom. The N–N distance is 1.443(7) Å, typical of a single bond. The orientation of the phenyl group on N(2) indicates essentially sp^3 hybridization at this nitrogen atom and no significant π-bond to Sm (this compares with complex **62** and contrasts with complexes **3**, **4**, and **30**). The complex **136** is also obtainable from the reactions of $[Cp^*_2Sm(\mu\text{-}H)]_2$ with PhNHNHPh or PhN=NPh and from reactions of PhNHNHPh with **134** or $Cp^*_2Sm(PhNNPh)(THF)$.

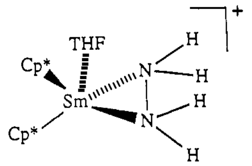
Hydrazine reacts with either Cp^*_2Sm or $[Cp^*_2Sm(\mu\text{-}H)]_2$ to produce the bridging *cis*-diazene complex $[Cp^*_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}HNNH)$ (**138**). This may be compared with the tungsten compound **25**. The N–N distance in **138** is 1.473(6) Å, indicative of a N–N single bond and a formal $[NHNH]^{2-}$ ligand. The butterfly arrangement of the Sm_2N_2 unit contrasts with the more symmetrical arrangement previously observed in bridging units encapsulated by the tetrahedral "$Cp^*_2Sm\cdots SmCp^*_2$" cavity.[265] The crystal structure of **139**, the THF adduct of **138**, has also been solved and shows that the side-on bridging HNNH ligand has been retained.[266] The N–N distance is 1.484(6) Å. The reaction of **139** with 2 equiv of $[Et_3NH][BPh_4]$ in THF forms the mononuclear η^2-hydrazine complex $[Cp^*_2Sm(THF)(\eta^2\text{-}NH_2NH_2)][BPh_4]$ (**140**). The structure of **140** was also determined (with the N_2H_4 hydrogens being located) and it also has a N–N single bond distance of 1.471(3) Å which may be compared with the N–N distance of 1.446(17) in **123**.



(138)



(139)



(140)

XI. Conclusion

It is quite apparent from this review that diazo ligands can, and do, exhibit great variety and novelty in the structures, electronic configurations, hapticity, and degree of multiple bond formation when they bind to metals in organometallic systems. Yet, we can be sure that others still await discovery; for much less attention has been paid, thus far, to these nitrogen-based ligands in organometallic compounds by comparison with carbon ligands. In particular, current work has emphasized structure determination and spectroscopy; the transformations of these ligands have hardly been investigated.

There are clearly enormous opportunities for research in this area. The activation and reduction of molecular N_2 in organometallic systems is just one of several broad areas of investigation that will continue to stimulate activity in diazo chemistry. For example, much of the research into high oxidation state organometallic dinitrogen, diazene, and hydrazide chemistry that is revolutionizing the traditional approaches to this problem is of very recent origin indeed.

It is hoped that this review will provide a further stimulus for activity in this fascinating area of chemistry.

XII. Acknowledgement

I would here like to thank and acknowledge those graduate students, postdoctoral fellows and research assistants, past and present, whose hard work and creativity have been responsible for the research accomplished in my laboratory. The Natural Sciences and Engineering Research Council of Canada have generously supported this work through operating and equipment grants. I wish also to express my sincere thanks to Ms. Sharon Beever for expert and dedicated preparation of the manuscript, and to YingXia He, Carmen Leiva-Paredes, and Antonio Cusanelli for preparing the numerous diagrams.

XIII. Abbreviations

Bu	butyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DEDM	diethyl diazomalonate
DIPP	2,6-diisopropylphenoxide
DMAP	4-(*N*,*N*-dimethylamino)pyridine
DMPE	1,2-bis(dimethylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DTTD	2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2−)
Et	ethyl
$HBpz_3$	tris(1-pyrazolyl)borate
$HB(Me_2pz)_3$	tris(3,5-dimethyl-1-pyrazolyl)borate
Me	methyl
MPTE	1,2-bis[(2-mercaptophenyl)thio]ethane(2−)
NBD	norbornadiene
Np	neopentyl
OTf	trifluoromethanesulfonate
Ph	phenyl
Pr	propyl
salen	*N*,*N*′-bis(salicylidene)ethylenediaminate
THF	tetrahydrofuran
TMEDA	1,2-bis(dimethylamino)ethane
VDPP	1,1-bis(diphenylphosphino)ethene

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