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Journal of Organometallic Chemistry 500 (1995) 187–194

Journal of Organometallic Chemistry

Invited Review

Thirty years of organometallic aryldiazenido arylazo derivatives

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Received 10 January 1995

Abstract

The aryldiazenido ligands provide the fourth member of the isoelectronic series CO, NO^+, RNC, RN_2^+ of ligands for transition metal complexes. The first aryldiazenido metal complex was reported in 1964 when p-$CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$ was prepared by the reaction of $NaMo(CO)_3C_5H_5$ with p-$CH_3OC_6H_4N_2^+BF_4^-$. This review surveys the development of organometallic aryldiazenido chemistry since that time. Such organometallic aryldiazenido derivatives, including $RN_2M(CO)_2C_5H_5$, $RN_2M(CO)_2(Pz_3BH)$ (M = Cr, Mo, W), $[(\eta^6\text{-}Me_6C_6)Cr(CO)_2N_2Ar]^+$, $[(MeC_5H_4)M'(CO)_2N_2Ar]^+$ (M' = Mn, Re), $[trans\text{-}PhN_2Fe(CO)_2(PPh_3)_2]^+$, and $PhN_2M'(CO)_2(PPh_3)_2$ can be obtained by reactions of arenediazonium salts with suitably chosen transition metal nucleophiles. Analogous methods cannot be used to prepare alkyldiazenido transition metal complexes because of the instability of alkyldiazonium salts. However, the alkyldiazenido derivatives $RCH_2N_2M(CO)_2C_5H_5$ (R = H or Me_3Si) can be obtained from $HM(CO)_3C_5H_5$ and the corresponding diazoalkanes. Important aspects of the chemical reactivity of $RN_2M(CO)_2Q$ derivatives ($Q = C_5H_5$, Pz_3BH) include CO substitution reactions, coordination of the second nitrogen in the RN_2 ligand to give heterobimetallic complexes such as $C_5H_5Mo(CO)_2(\mu\text{-}NNC_6H_4Me)Re(CO)_2C_5H_5$, oxidative addition reactions with X_2 (X = Cl, Br, I), SnX_4, RSSR, and ClNO, and reactions with further RN_2^+ to give bis(aryldiazenido) derivatives $(RN_2)_2MQL^+$ ($L = CO$, X^-, etc.). Dearylation of an aryldiazenido ligand to a dinitrogen ligand can be effected by reaction of $[(MeC_5H_4)M'(CO)_2N_2Ar]^+$ with certain nucleophiles to give $(MeC_5H_4)M'(CO)_2N_2$.

Keywords: Aryldiazeno; Chromium; Molybdenum; Tungsten; Manganese; Carbonyl

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1. Introduction

Low formal oxidation states of transition metals were first encountered in the metal carbonyls [1] and metal nitrosyls [2] over a century ago. Since then transition metal derivatives containing these CO and NO^+ ligands have played an important role in the subsequent development of coordination and organometallic chemistry. A subsequent milestone in low oxidation state transition metal chemistry was the recognition of the analogy between the carbonyl group, CO, and the alkyl/aryl isocyanide groups, RNC, approximately a half century later [3], leading to the preparation of numerous RNC complexes analogous to well established metal carbonyls [4]. In this connection the aryl isocyanide ligands, RNC, may be considered as related to carbon monoxide, CO, by replacement of an oxygen atom with arylimino groups, RN. Analogous replacement of the oxygen atom in the NO^+ ligand with arylimino groups leads to the RNN^+ or RN_2^+ ligands. The free RN_2^+ ligands are, of course, the cations in the technically important arenediazonium salts [5], which have been known since the nineteenth century. Arenediazonium salts are readily prepared by the so-called ''diazotization'' of aromatic amines with nitrous acid generated from sodium nitrite and a strong mineral acid and can be isolated and handled safely as their BF_4^- or PF_6^- salts. Closely related covalent derivatives are azoarenes such as azobenzene, PhN=NPh.

These considerations suggested to the author in the early 1960s the possibility of preparing arylazo transition metal derivatives isoelectronic with the corresponding metal nitrosyls. In contemplating possible routes to arylazo compounds, relatively stable metal nitrosyls were considered which could be synthesized using NO^+ sources with the idea that analogous syntheses using arenediazonium salts would give analogous arylazo metal complexes. A particularly interesting possibility appeared to be an arenediazonium analog of the synthesis of the relatively stable cyclopentadienylmetal nitro-

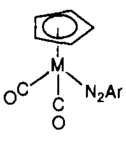
SSDI 0022-328X(95)00504-8

syl derivatives, $C_5H_5M(CO)_2NO$ (M = Cr, Mo or W), by the following reaction:

$$C_5H_5M(CO)_3^- + [NO^+] \rightarrow C_5H_5M(CO)_2NO + CO \qquad (1)$$

where the $[NO^+]$ source can be nitrous acid (HNO_2), "Diazald" (p-$CH_3C_6H_4SO_2N(NO)CH_3$) [6] or trifluoroacetyl nitrite ($CF_3C(O)ONO$) and the $C_5H_5M(CO)_3^-$ reagents are readily available from sodium cyclopentadienide and $M(CO)_6$ in a boiling ether solvent such as THF (M = Mo).

These considerations led to experiments in the 1960s by the author and his collaborator, M.B. Bisnette, at the Mellon Institute (now Carnegie–Mellon University), in which solid arenediazonium salts were added to $NaMo(CO)_3C_5H_5$ using the nonexplosive arenediazonium tetrafluoroborates for safety reasons. The initial experiments, using stoichiometric amounts of arenediazonium salts and $NaMo(CO)_3C_5H_5$ at ambient temperature, appeared to be unpromising giving red–purple solids insoluble in pentane, benzene, and diethyl ether but soluble in THF. These materials could not be purified by recrystallization. Furthermore, their IR spectra exhibited no ν(CO) frequencies indicating that they were not the desired $RN_2Mo(CO)_2C_5H_5$ derivatives analogous to $C_5H_5Mo(CO)_2NO$. However, when, owing to an accidental calculation error, only one-half of the stoichiometric amount of p-$CH_3OC_6H_4N_2^+BF_4^-$ was added to $NaMo(CO)_3C_5H_5$, the red-orange hexane-soluble arylazomolybdenum derivative p-CH_3O-$C_6H_4N_2Mo(CO)_2C_5H_5$ was obtained for the first time in 20%–25% yield [7,8]. This product was characterized by elemental analyses, IR ν(CO) frequencies at 1960 and 1900 cm^{-1} indicating a $C_5H_5Mo(CO)_2T$ unit (T = neutral three-electron donor ligand), the proton NMR spectrum expected for a η^5-C_5H_5 ligand and the p-$CH_3OC_6H_4$ group and also indicating diamagnetism, and the low conductivity of its acetone solution. All of these data are in accord with structure **I** (M = Mo) containing a covalently bonded p-$CH_3C_6H_4N{=}N$- group functioning as a neutral three-electron donor ligand like the nitrosyl group in $C_5H_5Mo(CO)_2NO$ (**II**: M = Mo). Subsequent experiments showed that the arylazo derivatives $RN_2Mo(CO)_2C_5H_5$ could be synthesized from stoichiometric amounts of $RN_2^+BF_4^-$ and $NaMo(CO)_3C_5H_5$ in THF if the solid arenediazonium salt is added gradually to the $NaMo(CO)_3C_5H_5$ solution at ambient temperatures or in one portion at low temperatures (e.g. −78°). Thus for the successful synthesis of $RN_2Mo(CO)_2C_5H_5$ from $NaMo(CO)_3C_5H_5$ and arenediazonium salts, local excesses of the arenediazonium salt at ambient conditions must be avoided since the initially formed $RN_2Mo(CO)_2C_5H_5$ is destroyed by excess RN_2^+ under these conditions.



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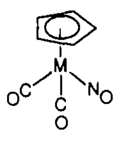


II

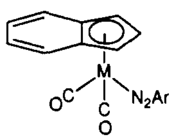
This article summarizes the highlights of the development of arylazo transition metal chemistry since our first report of $RN_2Mo(CO)_2C_5H_5$ derivatives more than 30 years ago [7]. This area of chemistry is of interest because of the analogy of the RN_2 ligand bonded to a transition metal center to intermediates in the protonation and alkylation of molybdenum and tungsten dinitrogen complexes which may model possible mechanisms for the activity of the biological nitrogen-fixing molybdoenzyme nitrogenase.

Arylazo transition metal complexes are discussed in two review articles by Sutton [9,10] to which the reader is referred for further details and more extensive literature citations. This article focuses on the chemistry of $RN_2M(CO)_2C_5H_5$ derivatives (M = Cr, Mo, and W) and related compounds. In the remainder of this article arylazo transition metal complexes containing the RN_2^+ ligand are called aryldiazenido complexes in accord with the terminology in Sutton's most recent review article [10].

2. Synthesis of organometallic aryldiazenido compounds

The synthesis of $RN_2Mo(CO)_2C_5H_5$ derivatives (**I**: M = Mo, R = aryl group) from $C_5H_5Mo(CO)_3^-$ and arenediazonium salts can be extended to the synthesis of the corresponding chromium [11] and tungsten [12] derivatives (**I**: M = Cr or W) by use of the corresponding $C_5H_5M(CO)_3^-$ anions (M = Cr or W). However, such reactions do not occur as readily as the corresponding reactions with $C_5H_5Mo(CO)_3^-$ since CO groups bonded to Cr and W are not as labile as those bonded to Mo, so that conversion of the original metal tricarbonyl to the metal dicarbonyl of **I** is more difficult. The reactions of $NaCr(CO)_3C_5H_5$ with arenediazonium salts are best carried out in glacial acetic acid at 25°C so that free $C_5H_5Cr(CO)_3H$ is the actual reactive intermediate. The compounds $PhN_2M(CO)_2C_5H_5$ (M = Mo or W) can also be obtained by reaction of the hydrides $C_5H_5M(CO)_3H$ with phenylhydrazine at 150°C [13].

The synthesis of aryldiazenido compounds from RN_2^+ and $C_5H_5Mo(CO)_3^-$ can also be extended to the synthesis of other $RN_2Mo(CO)_2Q$ derivatives (Q = a neutral five-electron donor ligand) from the corresponding $QMo(CO)_3^-$ anion and arenediazonium salts. Thus, reactions of the indenyl metal carbonyl anions $C_9H_7M(CO)_3^-$ (M = Cr or Mo, W) with $PhN_2^+BF_4^-$ give the corresponding dark red $PhN_2M(CO)_2C_9H_7$



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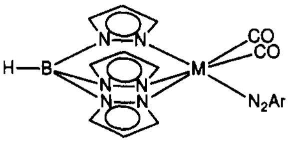


IV

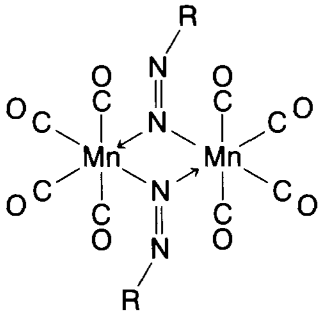
derivatives (**III**: R = Ph; M = Cr, Mo or W) in 25–35% yields [14]. Similarly, reactions of the tris(1-pyrazolyl)borate anions $HBPz_3M(CO)_3^-$ (Pz = pyrazolyl, M = Mo or W) with arenediazonium tetrafluoroborates give the corresponding tris(pyrazolyl)borate complexes $RN_2Mo(CO)_2(Pz_3BH)$ (**IV**: M = Mo, W) as red solids in up to ca. 85% yields; these appear to be the most thermally stable aryldiazenido complexes of the type $RN_2M(CO)_2Q$ with melting points above 200°C in some cases [15]. The structure of $PhN_2Mo(CO)_2(Pz_3BH)$ (**IV**: M = Mo, R = Ph) has been verified by X-ray diffraction confirming the presence and geometry of the aryldiazenido ligand [16]. Of particular interest is the essentially linear geometry of the aryldiazenido ligand with an Mo–N–N angle of 174.21(12)°.

Reactions of metal carbonyl anions other than those of the type $QM(CO)_3^-$ with arenediazonium salts in most cases fail to give any analogous aryldiazenido metal carbonyl derivatives. Thus aryldiazenido metal carbonyl derivatives could not be obtained from reactions of arenediazonium salts with the homoleptic metal carbonyl anions $V(CO)_6^-$, $Mn(CO)_5^-$, and $Co(CO)_4^-$, possibly owing to labilization of carbonyl groups by the presence of the good electron-withdrawing aryldiazenido group [8]. Carroll and Lalor [17] subsequently confirmed that reactions of these metal carbonyl anions with arenediazonium salts occur even at −70°C to give highly colored species, which do not survive warming to room temperature. However, IR spectroscopic evidence for an unstable aryldiazenido cobalt complex, assumed to be $PhN_2Co(CO)_2PPh_3$, was obtained from the reaction of $[(Ph_3P)_2N][Co(CO)_4]$ with PhN_2^+ and Ph_3P. Reaction of $Fe(CO)_3NO^-$ with PhN_2^+ at low temperatures in the presence of triphenylphosphine was found to give a more stable aryldiazenido complex $PhN_2Fe(CO)(NO)PPh_3$ [17].

A different method can be used to obtain a rather unusual binuclear aryldiazenido derivative of manganese carbonyl. Thus reaction of $PhN{=}NSiMe_3$ with $Mn(CO)_5Br$ in toluene at room temperature was found to give yellow binuclear $[PhN_2Mn(CO)_4]_2$ in ca. 20% isolated yield by the following reaction [18]:

$$2\ PhN_2SiMe_3 + 2Mn(CO)_5Br \rightarrow [PhN_2Mn(CO)_4]_2 + 2\ CO + 2\ Me_3SiBr \qquad (2)$$

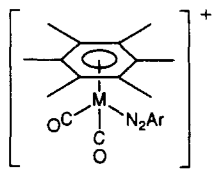
The structure of $[PhN_2Mn(CO)_4]_2$ has been shown by X-ray diffraction [19] to be **V** (R = Ph) in which one nitrogen atom of each aryldiazenido ligand bridges two manganese atoms.



V

The synthesis of the neutral aryldiazenido derivatives $RN_2M(CO)_2Q$ uses the arenediazonium cations as electrophiles for reactions with the corresponding metal carbonyl anions. Analogous reactions of sufficiently electron-rich neutral metal carbonyl derivatives with arenediazonium cations can lead to cationic aryldiazenido complexes. Thus, reaction of $Me_6C_6Cr(CO)_3$ with arenediazonium salts in dichloromethane solution gives maroon cationic derivatives $[(\eta^6\text{-}Me_6C_6)Cr(CO)_2N_2Ar]^+$ (**VI**: M = Cr), which can be converted to the neutral deep purple–brown cyclohexadienyl derivatives $(\eta^5\text{-}Me_6C_6H)Cr(CO)_2N_2Ar$ (**VII**: M = Cr) by hydride reduction using $NaBH_4$ [20]. Cationic cyclopentadienyl-manganese and -rhenium derivatives of the type $[(MeC_5H_4)M(CO)_2N_2Ar]^+$ (**VIII**: M = Mn, R = 2-$CF_3C_6H_4$, 2-FC_6H_4 or Ph; M = Re, R = 2-$FC_3C_6H_4$) closely related to **VI** have been obtained by reactions of the corresponding arenediazonium tetrafluoroborates with $C_5H_5MH(CO)_2SiPh_3$ in acetone at room temperature [21]. In addition, reaction of *trans*-$Fe(CO)_3(PPh_3)_2$ with $PhN_2^+BF_4^-$ in dichloromethane [17] gives orange [*trans*-$PhN_2Fe(CO)_2(PPh_3)_2]^+BF_4^-$, indicated by X-ray diffraction [22] to have structure **IX** (R = Ph, L = Ph_3P) containing a linear phenyldiazenido ligand (Fe–N–N angle = 179.2°).

Related chemistry can be used to prepare a series of aryldiazenido derivatives of manganese containing carbonyl but not cyclopentadienyl ligands [23]. Thus, the reaction of $HMn(CO)_3(PPh_3)_2$ with $PhN_2^+PF_6^-$ in acetone solution was found to result in addition of the Mn–H bond to the N_2 multiple bond of the diazonium



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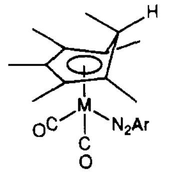

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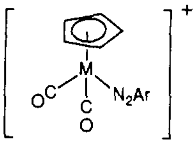

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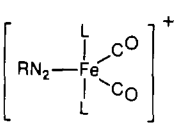


IX

cation to give a yellow phenyldiazene complex according to the following equation:

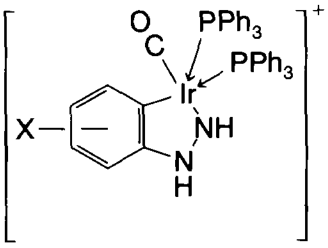
$$\mathrm{HMn(CO)_3(PPh_3)_2 + PhN_2^+PF_6^-} \rightarrow \mathrm{[Mn(CO)_3(HN_2Ph)(PPh_3)_2]^+PF_6^-} \qquad (3)$$

Deprotonation of $[\mathrm{Mn(CO)_3(HN_2Ph)(PPh_3)_2}]^+\mathrm{PF_6^-}$ with sodium methoxide in methanol also results in decarbonylation to give an orange aryldiazenido complex according to the following equation:

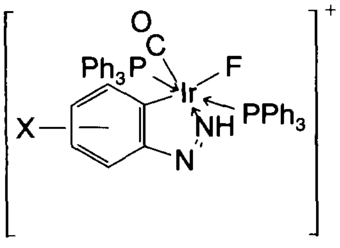
$$\mathrm{[Mn(CO)_3(HN_2Ph)(PPh_3)_2]^+PF_6^- + NaOMe} \rightarrow \mathrm{PhN_2Mn(CO)_2(PPh_3)_2 + MeOH + CO} \qquad (4)$$

A similar method using $\mathrm{HRe(CO)_2(PPh_3)_3}$ as the starting material can be used to prepare the orange–brown rhenium analog $\mathrm{PhN_2Re(CO)_2(PPh_3)_2}$.

The reactions of the hydride $\mathrm{HIr(CO)(PPh_3)_3}$ with arenediazonium tetrafluoroborates, $\mathrm{XC_6H_4N_2^+BF_4^-}$ (X = 2-$\mathrm{NO_2}$, 2-$\mathrm{CF_3}$, 2-F and 4-$\mathrm{NO_2}$) follow a different course [24]. The initial product **X** arises from addition of the hydride ligand to the diazonium salt followed by *ortho* metallation of the arene ring. These products can then undergo rather easy deprotonation to give the cyclic aryldiazene complexes, e.g. **XI**, with a fluoride ligand arising from the tetrafluoroborate anion. The structures of compounds of both types **X** (X = 2-$\mathrm{NO_2}$) and **XI** (X = 2-$\mathrm{CF_3}$) have been confirmed by X-ray diffraction [24].



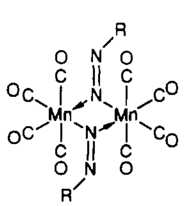
X



XI

The synthesis of alkyldiazenido metal carbonyl complexes by synthetic methods analogous to those used for the aryldiazenido metal carbonyl complexes discussed above is not feasible since the alkyldiazonium salts required as reagents for analogous syntheses cannot be isolated owing to rapid decomposition giving elemental nitrogen. However, Herrmann and Biersack [25,26] have shown that the aliphatic diazo compounds diazomethane, diazoethane and 2-diazopropane react with the hydrides $\mathrm{HM(CO)_3C_5H_5}$ (M = Mo or W) to give the corresponding alkyldiazo derivatives $\mathrm{RR'CHN_2M(CO)_2C_5H_5}$. For example, the reactions of $\mathrm{HM(CO)_3C_5H_5}$ (M = Mo or W) with diazomethane in diethylether/THF at −85 → 25°C give mixtures of the corresponding pale yellow σ-methyl derivatives $\mathrm{MeM(CO)_3C_5H_5}$ and the red methyldiazenido derivatives $\mathrm{MeN_2M(CO)_2C_5H_5}$ (**I**: R = Me), which can be separated by chromatography. Reaction conditions have been found which give > 60% yields of the methyldiazenido derivatives with < 3% yields of the corresponding σ-methyl derivatives. Reactions of $\mathrm{HM(CO)_3C_5H_5}$ (M = Mo or W) with $\mathrm{Me_3SiCHN_2}$ in diethyl ether at room temperature also give the corresponding alkyldiazenido derivatives $\mathrm{Me_3SiCH_2N_2M(CO)_2C_5H_5}$ [27]. However, reactions of $\mathrm{HM(CO)_3C_5H_5}$ (M = Mo or W) with phenyl-, 4-nitrophenyl-, 4-methoxyphenyl-diazomethane or 9-diazofluorene give only the corresponding alkyls $\mathrm{RR'CHM(CO)_3C_5H_5}$, which may be regarded as M–H insertion products of the carbene obtained by $\mathrm{N_2}$-elimination from the corresponding diazo compound [26].

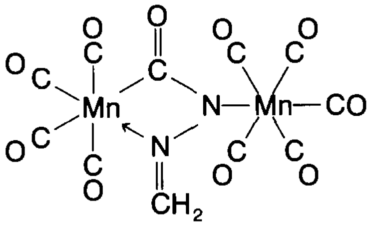
Upon re-examining the early literature on cyclopentadienylmetal derivatives it now appears that alkyldiazenido metal derivatives were first prepared but not identified in ca. 1955, approximately a decade before the preparation of *p*-$\mathrm{CH_3OC_6H_4N_2Mo(CO)_2C_5H_5}$ in 1964 [7] and 20 years before the identification of $\mathrm{MeN_2Mo(CO)_2C_5H_5}$ (**I**: R = Me) in 1975 [25,26]. Thus Piper and Wilkinson reported [6] in 1956 the reaction of diazomethane with $\mathrm{HMo(CO)_3C_5H_5}$ in diethyl ether under ambient conditions to give after chromatographic separation not only a 3% yield of the σ-methyl derivative $\mathrm{MeMo(CO)_3C_5H_5}$ but also a then-unidentified volatile red oil with two ν(CO) frequencies; this latter product clearly appears to be the methyldiazenido derivative $\mathrm{MeN_2Mo(CO)_2C_5H_5}$. In addition, the reac-



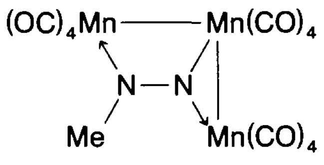
V

tion of $HW(CO)_3C_5H_5$ with diazomethane was first used in 1955 by Fischer, Hafner and Stahl [28] to synthesize the σ-methyl derivative $MeW(CO)_3C_5H_5$ without any mention of the formation of the corresponding methyldiazenido derivative $MeN_2W(CO)_2C_5H_5$. However, the red color of $MeW(CO)_3C_5H_5$ prepared by this method as compared with the very pale yellow color of $MeW(CO)_3C_5H_5$ prepared by the reaction of $NaW(CO)_3C_5H_5$ with MeI [6], suggests that the $MeW(CO)_3C_5H_5$ prepared in 1955 from the CH_2N_2/$HW(CO)_3C_5H_5$ reaction contained a then-unrecognized impurity of the red $MeN_2W(CO)_2C_5H_5$.

Herrmann et al. [29] also report reactions of $HM(CO)_5$ (M = Mn or Re) with diazomethane in Et_2O/THF to give yellow binuclear products of the general formula $(\mu_2\text{-}CH_2N_2)M_2(CO)_{10}$ (M = Mn or Re), shown by X-ray diffraction [30] to have structure **XII** (M = Mn), in which a diazomethane ligand functions as a four-electron donor to two manganese atoms but with insertion of CO into one of the Mn–N bonds leading to a diazametallacyclobutanone ring. The reaction of $HMn(CO)_5$ with CH_2N_2 also gives the red trinuclear methyldiazenido derivative $(\mu_3\text{-}CH_3N_2)[Mn(CO)_4]_2$, indicated by X-ray diffraction [30,31] to have structure **XIII** in which a μ_3-bridging methyldiazenido ligand donates a total of five electrons to the chain of three manganese atoms.



XII



XIII

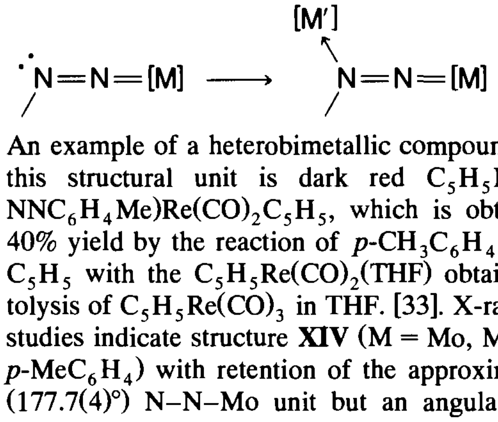
3. Chemical reactivity of aryldiazenido metal carbonyl derivatives

3.1. Ligand substitution reactions

The failure to obtain stable aryldiazenido derivatives from reactions of the homoleptic metal carbonyl anions $V(CO)_6^-$, $Mn(CO)_5^-$ and $Co(CO)_4^-$ has been attributed to the labilization of carbonyl groups by the aryldiazenido ligand so that compounds of the type $RN_2V(CO)_5$, $RN_2Mn(CO)_4$ and $RN_2Co(CO)_3$ are not stable at ambient conditions. A further indication of the labilization of CO groups by aryldiazenido ligands is the ready replacement of a CO group in $RN_2Mo(CO)_2C_5H_5$ by other ligands using thermal reaction conditions rather than the photochemical reaction conditions required for CO substitution in other cyclopentadienylmetal carbonyl derivatives such as $C_5H_5M(CO)_3$ (M = Mn or Re). For example, reaction of $p\text{-}MeC_6H_4N_2Mo(CO)_2C_5H_5$ with triphenylphosphine in boiling methylcyclohexane (ca. 100°C) for 1–3 d [8] was found to give a 66% isolated yield of red $p\text{-}MeC_6H_4N_2Mo(CO)(PPh_3)C_5H_5$. The aryldiazenido tris(pyrazolyl)borate complexes $RN_2Mo(CO)_2(Pz_3BH)$ undergo similar carbonyl substitution reactions with triphenylphosphine, but at higher reaction temperatures (e.g. ca. 140°C in boiling xylene for several days) to give lower yields (20%–40%) of the corresponding substitution products $RN_2Mo(CO)(PPh_3)(Pz_3BH)$ [32]. Reactions of this type provide one of several methods for preparing QMXYZ complexes (Q = neutral five-electron donor ligand such as Cp or Pz_3BH) with four different ligands around a central metal atom. Such compounds are of interest in the study of optically active metal complexes.

3.2. Ligating properties of the complexed aryldiazenido ligand

The aryldiazenido ligand, when bonded to a transition metal, still has a lone pair on the nitrogen atom not bonded to the transition metal which is available for coordination to a second transition metal, i.e.



$$\ddot{N}{=}N{=}[M] \longrightarrow \overset{[M']}{N}{=}N{=}[M]$$

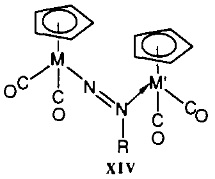
An example of a heterobimetallic compound containing this structural unit is dark red $C_5H_5Mo(CO)_2(\mu\text{-}NNC_6H_4Me)Re(CO)_2C_5H_5$, which is obtained in ca. 40% yield by the reaction of $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with the $C_5H_5Re(CO)_2(THF)$ obtained by photolysis of $C_5H_5Re(CO)_3$ in THF. [33]. X-ray diffraction studies indicate structure **XIV** (M = Mo, M′ = Re, R = $p\text{-}MeC_6H_4$) with retention of the approximately linear (177.7(4)°) N–N–Mo unit but an angular (118.9(3)°) unit.

3.3. Oxidative addition reactions of aryldiazenido complexes

In 1966 we first reported [8] the reaction of $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with iodine at ambient temperature with gas evolution to give a black solid of stoichiometry $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_n$ suggesting oxidative addition of I_2 to Mo(0) in $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ to give Mo(II) in $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_n$. Reactions of this type were subsequently studied in more detail in 1983 by Lalor, Deane and Condon [34] who showed that the original oxidative addition product of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with I_2 at low temperatures (−78°C) is the labile green mononuclear monocarbonyl *p*-$CH_3C_6H_4N_2Mo(CO)I_2C_5H_5$, which they characterized by elemental analyses and a single $\nu(CO)$ frequency at 2040 cm^{-1}. Stirring the monocarbonyl *p*-$CH_3C_6H_4N_2Mo(CO)I_2C_5H_5$ in dichloromethane solution at ambient temperature for 20 min or keeping the solid in vacuum for 8 h at room temperature was found to result in complete decomposition to give the carbonyl-free $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_n$ identical to the material reported in 1966 [8]. Simple electron counting considerations suggest that this product is the halogen-bridged dimer $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_2$ (**XV**), although this does not appear to have been confirmed by X-ray diffraction. Similar low-temperature reactions of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with Cl_2 and Br_2 at low temperatures were found to give spectroscopic $\nu(CO)$ evidence for the formation of the corresponding monocarbonyls *p*-$CH_3C_6H_4N_2Mo(CO)X_2C_5H_5$ (X = Cl or Br), but these products were too unstable to be isolated and the corresponding decarbonylation products $[p\text{-}CH_3C_6H_4N_2MoX_2C_5H_5]_n$ (X = Br or Cl) could not be obtained analytically pure, possibly owing to side reactions with the more reactive Br_2 and Cl_2 leading to inseparable byproducts.

Some similar oxidative reactions of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with tin halides were also investigated by Lalor, Deane and Condon [34]. Thus the reaction of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with SnI_4 at −78°C was found to give the monocarbonyl *p*-$CH_3C_6H_4N_2Mo(CO)(SnI_3)(I)C_5H_5$, which is unusual in being an organometallic complex containing five different ligands. An initially formed kinetic isomer of this product was found to rearrange readily to a thermodynamic isomer, which was sufficiently stable to be isolated for analysis. Analytically pure products could not be obtained either by the decarbonylation of *p*-$CH_3C_6H_4N_2Mo(CO)(SnI_3)(I)C_5H_5$ in dichloromethane at room temperature or by corresponding reactions of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with $SnCl_4$ or $SnBr_4$. The organotin halides Me_3SnCl and Ph_3SnCl failed to undergo oxidative addition reactions with *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$.

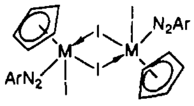
These oxidative addition products undergo a variety of reactions with Lewis base ligands. For example, Lalor and Condon [35] obtained brown *p*-$CH_3C_6H_4N_2MoI_2(PPh_3)C_5H_5$, olive-green $[MePPh_3]^+[p\text{-}CH_3C_6H_4N_2MoI_3C_5H_5]^-$, purple *p*-$CH_3C_6H_4N_2MoI(\eta^2\text{-}S_2CNEt_2)C_5H_5$, and red $[p\text{-}CH_3C_6H_4N_2MoI(bipy)C_5H_5]^+I^-$ from reactions of *p*-$CH_3C_6H_4N_2Mo(CO)I_2C_5H_5$ or $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_2$ (**XV**) with Ph_3P, $MePPh_3^+I^-$, Et_2NCS_2Na and 2,2-bipyridyl, respectively.



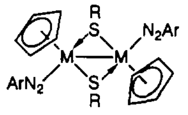
XIV

The other oxidative addition product of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ that we reported in our original 1966 paper [8] was $[p\text{-}CH_3C_6H_4N_2Mo(SMe)C_5H_5]_2$ (**XVI**), a brown solid obtained in 31%–51% yield by reaction of *p*-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with dimethyl disulfide in boiling methylcyclohexane (ca. 100°C) for 1–3 d. In our original work the dimeric nature of **XVI** corresponding to a formal Mo(I) complex (assuming $C_5H_5^-$, RN_2^+ and RS^-) with a direct Mo–Mo single bond was suggested by an osmometric molecular weight determination. In 1982 Lalor et al. [32] reported that the corresponding reaction of $PhN_2Mo(CO)_2(Pz_3BH)$ (**IV**: M = Mo, R = Ph) with dimethyl disulfide in boiling xylene did not give any tractable products. However, the reactions of the tris(pyrazolyl)borate derivatives $ArN_2Mo(CO)_2(Pz_3BH)$ (**IV**: M = Mo; Ar = *p*-$CH_3C_6H_4$ and *p*-FC_6H_4) with di-*p*-tolyl disulfide in boiling xylene were found to give 72% isolated yields of brown $ArN_2Mo(SC_6H_4\text{-}p\text{-}Me)_2(Pz_3BH)$. The structure of *p*-$FC_6H_4N_2Mo(SC_6H_4\text{-}p\text{-}Me)_2(Pz_3BH)$ was shown by X-ray diffraction to be the mononuclear octahedral derivative **XVII** (Ar = *p*-F-C_6H_4, R = *p*-$CH_3C_6H_4$). The Mo–S distances of ca. 2.33 Å in **XVII** are intermediate between the Mo–S single bond distances of 2.45 Å in Mo-thiolato complexes and Mo=S double bond distances of 2.10 Å in complexes with sulfide ligands suggesting some molybdenum–sulfur multiple bonding in accord with the 16-electron configuration of **XVII** if both Mo–S bonds are regarded as ordinary single bonds. These observations suggest that $RN_2Mo(CO)_2Q$ derivatives can undergo oxidative additions with organic disulfides to give either dimeric Mo(I) or monomeric Mo(II) derivatives depending on the reaction conditions and the various substituents.

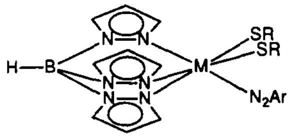
Oxidative addition reactions of $RN_2Mo(CO)_2Q$ derivatives (Q = C_5H_5 or Pz_3BH) with nitrosyl chlo-



XV



XVI



XVII

ride in dichloromethane at −25°C were found [36] to give orange derivatives containing the $Mo(NO)(N_2R)^{2+}$ unit according to the following equation:

$$RN_2Mo(CO)_2Q + ClNO \rightarrow RN_2Mo(NO)(Q)Cl + 2CO \qquad (5)$$

The chlorine in these $RN_2Mo(NO)(Q)Cl$ derivatives is relatively unreactive towards nucleophilic substitution by reagents such as C_5H_5Tl, KCN, PPh_3 or CF_3CO_2Ag in acetone, MeMgI in boiling diethyl ether, or CH_3CN or $AlCl_3$ in boiling benzene. A similar reaction of $NO^+PF_6^-$ with $ArN_2Mo(CO)(PPh_3)Q$ ($Q = C_5H_5$ or Pz_3BH; $Ar = C_6H_5$, p-$CH_3C_6H_4$, p-FC_6H_4, and m-FC_6H_4) in acetone at −78°C was found to give the brown cations $[ArN_2Mo(NO)(PPh_3)Q]^+$, which could be isolated as their PF_6^- salts. The structures of p-$FC_6H_4N_2Mo(NO)(Pz_3BH)Cl$ and $[p$-$FC_6H_4N_2Mo(NO)(PPh_3)(Pz_3BH)][PF_6]$ were confirmed by X-ray diffraction [36].

3.4. Preparation of bis(aryldiazenido) derivatives

The oxidative addition chemistry of $RN_2M(CO)_2Q$ derivatives can be extended to the preparation of bis(aryldiazenido) derivatives containing the $(RN_2)_2$-M^{2+} structural unit. This relates to the original observation [7,8] that the reaction of $NaMo(CO)_3C_5H_5$ with arenediazonium salts to give the corresponding $ArN_2Mo(CO)_2C_5H_5$ was found to be very sensitive to the reaction conditions. Thus, use of excess diazonium salt or even addition of the solid diazonium tetrafluoroborate at too high a temperature or at too fast a rate was found to lead to complete decomposition of the original $ArN_2Mo(CO)_2C_5H_5$ derivative to give a red–purple solid insoluble in pentane and benzene, soluble in THF, and shown by its IR spectrum in the ν(CO) region to contain no metal carbonyl groups.

The nature of these reactions of $NaMo(CO)_3C_5H_5$ with excess arenediazonium cations was clarified by later studies by Lalor and coworkers [37–39]. They found that the reaction of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with ArN_2^+ ($Ar = p$-$CH_3C_6H_4$ or p-FC_6H_4) in acetone at −78°C gives purple reactive solutions which were suggested to contain the bis(aryldiazenido) cations $[C_5H_5Mo(CO)(N_2Ar)(N_2Ar')]^+$ on the basis of their chemical reactivity. Thus, addition of Ph_3P or halide anion to these solutions at low temperatures was found to give excellent yields of the stable purple cationic complexes $[C_5H_5Mo(PPh_3)(N_2Ar)(N_2Ar')]^+$ isolated as their BF_4^- or PF_6^- salts or stable red neutral compounds $C_5H_5Mo(N_2Ar)(N_2Ar')X$, respectively [37]. A closely related species $MeC_5H_4Mo(N_2C_6H_4$-F-$p)_2Cl$ was found to be a byproduct in ca. 14% yield from the preparation of p-$FC_6H_4N_2Mo(CO)_2C_5H_4Me$ from the reaction of $NaMo(CO)_3C_5H_4Me$ with an equimolar amount of p-$FC_6H_4N_2^+BF_4^-$ in THF followed by extraction of the product from the reaction mixture with dichloromethane. An X-ray diffraction study of $MeC_5H_4Mo(N_2C_6H_4$-F-$p)_2Cl$ indicated a "singly bent" molybdenum–aryldiazenido geometry with Mo–N–N angles of 176.5° and 167.4(2)° to the two aryldiazenido groups [38].

A similar method, namely reaction of an aryldiazenido complex with additional arenediazonium ion, can also be used to prepare bis(aryldiazenido) complexes of manganese [23]. Thus, reaction of PhN_2-$Mn(CO)_2(PPh_3)_2$ with $PhN_2^+PF_6^-$ in dichloromethane gives the chocolate brown $[(PhN_2)_2Mn(CO)(PPh_3)_2]^+$-$PF_6^-$. The lone remaining CO group in $[(PhN_2)_2Mn(CO)(PPh_3)_2]^+PF_6^-$ can be displaced with halide by reactions with the corresponding bis(triphenylphosphine)iminium salts, $(PPh_3)_2N^+X^-$, in acetone solution to give the burgundy-red neutral complexes $(PhN_2)_2$-$Mn(PPh_3)_2X$ (X = Cl, Br or NCO).

3.5. Dearylation of an aryldiazenido ligand to a dinitrogen ligand

Diazenido complexes are of interest as possible intermediates in studies of the binding and activation of N_2 at a transition metal center since they can arise from the protonation or alkylation of metal dinitrogen complexes [9,10]. The opposite reaction, namely dearylation of an aryldiazenido ligand to a dinitrogen ligand, has been achieved in organometallic aryldiazenido chemistry. Thus, attempts to effect nucleophilic substitutions of a carbonyl group in $[(MeC_5H_4)M(CO)_2N_2Ar]^+$ (**VIII**: M = Mn, R = 2-$CF_3C_6H_4$, 2-FC_6H_4, or Ph: M = Re, R = 2-FC_6H_4) by reaction with KX (X = Cl, Br, I, CN or SCN) in acetone lead instead to dearylation to give the corresponding dinitrogen complex according to the following equation [21]:

$$[(MeC_5H_4)M(CO)_2N_2Ar]^+ + I^- \rightarrow (MeC_5H_4)M(CO)_2N_2 + ArI \qquad (6)$$

The original aryldiazenido derivatives can be regenerated by reaction of the dinitrogen complex with arenediazonium salts according to the following equation:

$$(MeC_5H_4)M(CO)_2N_2 + ArN_2^+ \rightarrow [(MeC_5H_4)M(CO)_2N_2Ar]^+ + N_2 \qquad (7)$$

Reaction of $(MeC_5H_4)Mn(CO)_2N_2$ with labelled $[p$-$FC_6H_4{}^{14}N^{15}N]^+BF_4^-$ gives $[(MeC_5H_4)M(CO)_2$-$N_2C_6H_4$-p-F$]^+$ exhibiting a ν(NN) frequency at 1770 cm^{-1} rather than 1796 cm^{-1} indicating incorporation of the ^{15}N into the aryldiazenido ligand and thus showing that this reaction is a displacement of coordinated N_2 by RN_2^+ rather than the diazonium salt being simply a source of R or R^+ for addition to the existing dinitrogen ligand.

4. Summary

Research during the thirty years since the discovery of the first aryldiazenido derivative [7] p-$CH_3OC_6H_4$-$Mo(CO)_2C_5H_5$ has established the versatility of the aryldiazenido ligand in organometallic chemistry. Thus numerous aryldiazenido transition metal complexes are readily accessible by reactions of arenediazonium salts with suitably chosen organometallic derivatives. Most such reactions can be considered as attack of an arenediazonium electrophile on a nucleophilic transition metal species. The neutral aryldiazenido ligand, RN_2, functions as a three-electron donor ligand in organometallic chemistry similar to the nitrosyl ligand. Although most aryldiazenido organometallic complexes contain terminal aryldiazenido ligands, bridging aryldiazenido ligands are found in $[PhN_2Mn(CO)_4]_2$ (**V**). Special features of aryldiazenido organometallic chemistry include coordination of the second aryldiazenido nitrogen to give bimetallic derivatives containing bridging aryldiazenido ligands such as $C_5H_5Mo(CO)_2(\mu\text{-}NNC_6H_4\text{-}Me)Re(CO)_2C_5H_5$ (**XIV**: M = Mo, M′ = Re) as well as dearylation of an aryldiazenido ligand to a dinitrogen ligand such as conversion of $[(MeC_5H_4)Mn(CO)_2N_2\text{-}Ar]^+$ to $MeC_5H_4Mn(CO)_2N_2$ by reactions with certain nucleophiles.

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