

## CHAPTER 7

# Complex formation

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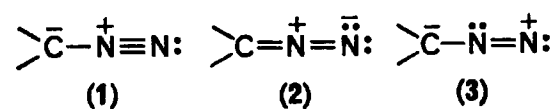
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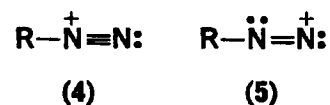
### I. INTRODUCTION

The structure of diazoalkanes may be described in the valence-bond formalism in terms of the canonical structures 1, 2 and 3, and their reactions may be classified



on this basis. Thus diazoalkanes may react as 1,3-dipoles (3) or as nucleophiles through carbon (1) or through the terminal nitrogen (2). In addition, the unsaturated nature of these compounds renders possible the formation of  $\pi$ -type complexes.

Diazonium ions on the other hand may be described as 4 and 5, and they react normally as electrophiles through the terminal nitrogen (5).



The possibility of certain metal derivatives acting as Lewis acids and bases enables them to form complexes with diazoalkanes and with diazonium ions. Few complexes have been isolated where a diazoalkane molecule as such is present as a

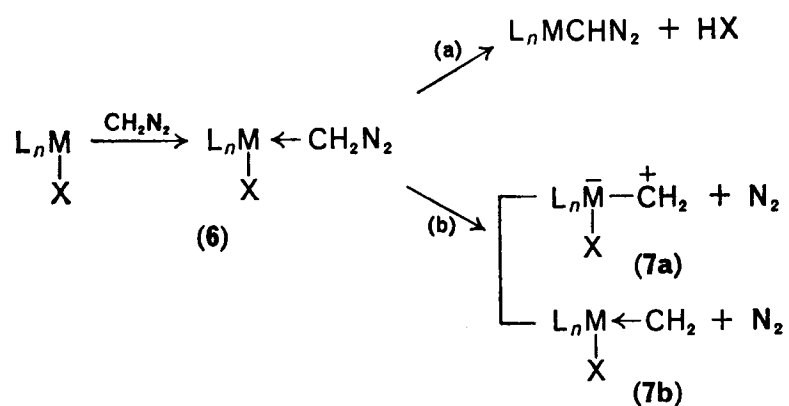
ligand, but their presence as reactive intermediates has been invoked in numerous occasions. Consequently most of the evidence presented is of an indirect nature. On the other hand, diazonium ions have yielded numerous stable complexes with transition metal derivatives. While this manuscript was in preparation, an authoritative review appeared in this field<sup>1</sup>. Hence, the emphasis will be on the most recent developments.

## II. COMPLEX FORMATION BY DIAZOALKANES

The number of stable complexes of diazoalkanes reported in the literature is severely limited. Nevertheless in the few examples described the metal has been proposed to bind the diazoalkane in three different ways. Hence, metal-carbon, metal-nitrogen and 'side-on' bonding have been suggested.

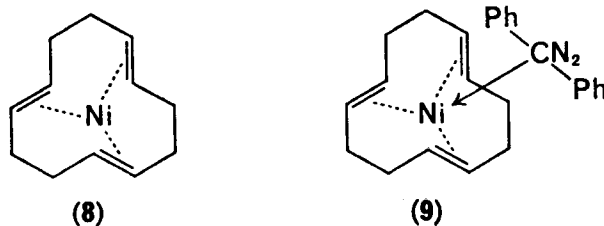
### A. Carbon Coordination

There is a wealth of reactions in which diazoalkanes are thought to act towards metal derivatives as nucleophiles through the diazo carbon to give intermediates of type 6 (Scheme 1) but their direct observation has been limited to two reports.



SCHEME 1

Upon treatment of 8 with diphenyl diazomethane at  $-78^\circ\text{C}$  the observed colour change from red to brown was attributed to the formation of a complex whose structure has been assigned as 9 on the basis of chemical evidence<sup>2</sup>. Furthermore, the less stable diazomethane apparently forms with 8 an analogous complex at lower temperatures<sup>2</sup>.



It has been postulated that a similar complex is formed in the reaction of  $\text{AlEt}_3$  with diazomethane, which at  $-78^\circ\text{C}$  yields a colourless solution without nitrogen evolution<sup>3</sup>. Spectroscopic and other methods to probe further into the nature of the bonding in these complexes have not been used.



The reactions of diazoalkanes with transition metal derivatives, such as those shown in equations (4), (5) and (6), have not been studied from a mechanistic viewpoint. In the formation of disilverdiazomethane (equation 6), acetate may be replaced by other anions provided that they give silver salts soluble in the solvent employed. Yields are better with anions deriving from weak acids. Added base helps the reaction, presumably by partially bonding an outgoing proton and/or the terminal nitrogen in the diazoalkane thus rendering the carbon more nucleophilic.

Spectroscopic studies on  $\alpha$ -heterosubstituted diazoalkanes provide some basis for judging factors that contribute to their stability. In the i.r. spectrum, these compounds present a band in the region 2150–1950  $\text{cm}^{-1}$  attributed to an N–N stretching vibration, sensitive to the nature of the substituent.

For compounds 11, the  $\nu_{(\text{NN})}$  values decrease with progression down the Periodic

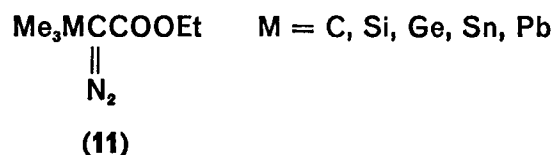
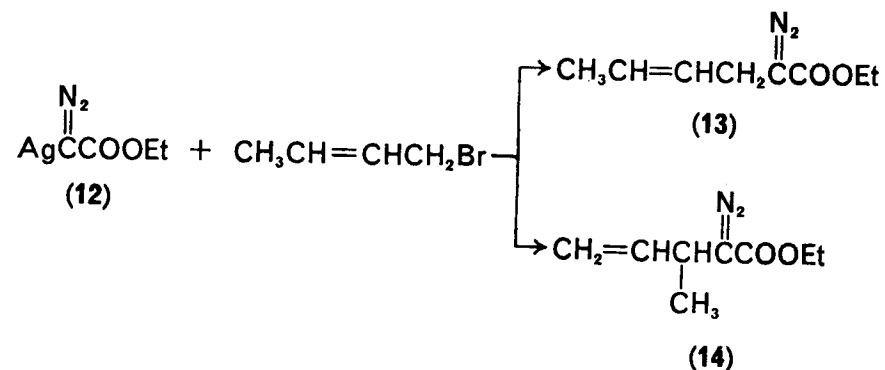


Table. This trend may be interpreted by invoking the increasing electron-donating effect in the series partially compensated, in particular, in the case of the silicon compound, by  $p_\pi-d_\pi$  resonance interaction<sup>22</sup>.

The possibility of the metal in a metal-substituted diazoalkane expanding its valence shell has also been shown for compound 12. In its reaction with crotyl bromide, an 85/15 mixture of 13 and 14 is obtained pointing to the intermediacy of an ion pair<sup>23</sup>.



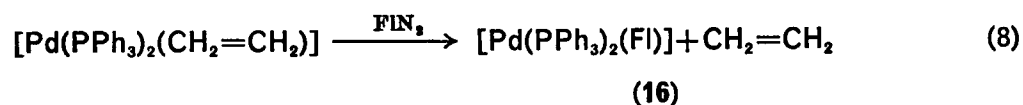
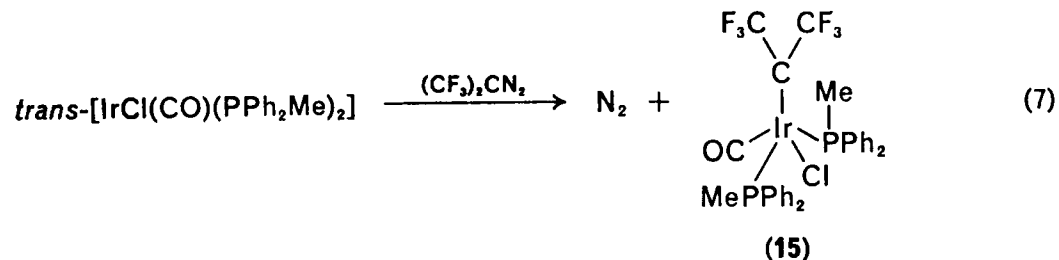
The intermediacy of metal-carbene complexes<sup>24, 25</sup> or 'inverse' metal ylides has been invoked in numerous metal derivative-catalysed decompositions of diazoalkanes<sup>26–42</sup>. The nature of the rate-determining step of the reaction has been established by kinetic measurements in only a few cases. In the reaction of diphenyldiazomethane catalysed by  $\text{ZnCl}_2$  or  $\text{ZnBr}_2$  to yield, after work up, mixtures of benzophenone and benzophenone azine, the kinetics and product proportions are consistent with rate-limiting formation of the complex  $\text{Ph}_2\overset{+}{\text{C}}\text{ZnX}_2^-$ <sup>36</sup>. When  $\text{CuBr}_2$  is employed as catalyst, a copper complex which may have diphenylmethylene as a ligand is formed in a rapid first step, the further consumption of diazoalkane occurring at a slower rate<sup>32</sup>.

Correlations have been found between the rates of decomposition of diazoalkanes and their basicity and the strength as Lewis acid of the metal compound. Thus, while diphenyldiazomethane shows no reaction with  $\text{ZnCl}_2$  below  $-15^\circ\text{C}$ , phenyldiazomethane reacts at  $-50^\circ\text{C}$ . The decreased basicity of the former compound

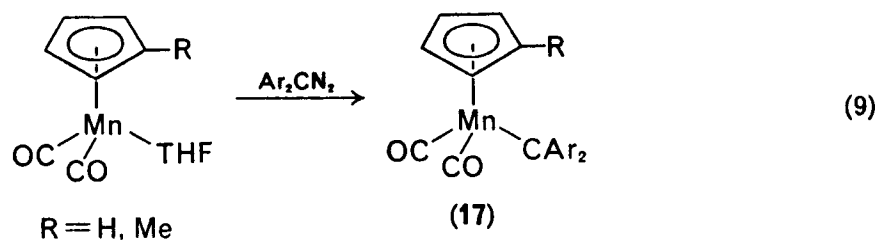
may be attributed to inductive electron withdrawal and to the additional steric hindrance of the second phenyl ring<sup>30</sup>. On the other hand, in the presence of the typically strong Lewis acids  $\text{AlCl}_3$  and  $\text{SnCl}_4$ , 0.1 mmol of diphenyldiazomethane reacts completely in air in less than 1 minute while the reaction takes hours in the presence of the weaker acids  $\text{ZnCl}_2$  or  $\text{SnCl}_2$ <sup>30</sup>.

In the decomposition of diphenyldiazomethane aided by different metal salts the observation was made that the products were related to the reduction potential of the salt in  $\text{H}_2\text{O}$ <sup>38</sup>. Thus, when  $\text{Tl}^{\text{III}}(\text{OAc})_3$  ( $E = +1.21$  V) or  $\text{Cu}^{\text{II}}(\text{OAc})_2$  ( $E = +0.15$  V) was used the products resulted from a two-electron or one-electron transfer with formation of  $\text{Tl}^{\text{I}}\text{OAc}$  and  $\text{Cu}^{\text{I}}\text{OAc}$  respectively, whereas when  $\text{Cr}^{\text{III}}(\text{OAc})_3$  ( $E = -0.41$  V) was employed no reduction of the metal ion took place. The mechanism proposed involves internal acetate transfer within a metal-carbene complex<sup>38</sup>.

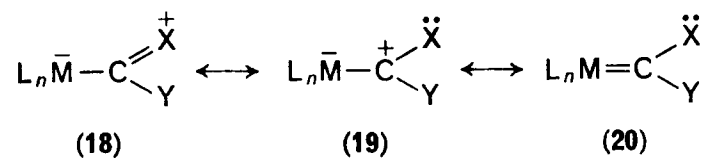
In a very limited number of cases stable metal-carbene complexes have been isolated from the reaction of metal derivatives and diazoalkanes (equations 7<sup>41</sup>, 8<sup>31</sup> and 9<sup>43</sup>).



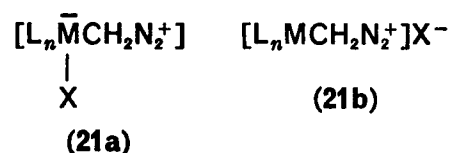
FI = 9-Fluorenylidene



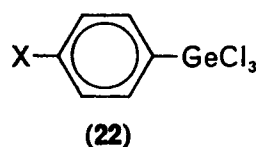
On the other hand, methods different from path (b) (Scheme 1) have been used to synthesize numerous complexes, most of which possess oxy, thio, seleno or amino substituents on the carbene carbon atom<sup>24, 25</sup>. These complexes may be said to originate from nucleophilic carbenes<sup>44, 45</sup> and their bonding is interpreted in terms of the limiting structures 18, 19 and 20. Complexes 15, 16 and 17 would thus constitute exceptions by being electrophilic carbene complexes. Presumably the electron-withdrawing character of the carbene substituents induces strong  $\pi$ -back donation from the metal and hence produces a strong M-C bond.



The methylene insertion reaction has been the subject of several structure-reactivity studies that have confirmed that a nucleophilic attack on the metal is involved in the rate-determining step<sup>46, 47</sup>. The data available do not distinguish either between a stepwise and a concerted process or between a zwitterionic intermediate such as **21a** and an ion pair intermediate such as **21b**.



In general it is found that organic substitution in the Group IVa halides tends to decrease the reactivity of the M—X bond towards diazomethane. Thus, while SiCl<sub>4</sub> reacted rapidly with CH<sub>2</sub>N<sub>2</sub> in ether even at -50 °C to give ClCH<sub>2</sub>SiCl<sub>3</sub>, further methylenation was found to be increasingly difficult. Et<sub>3</sub>PbCl, on the other hand, did react to give Et<sub>3</sub>PbCH<sub>2</sub>Cl in high yield<sup>46</sup>. A quantitative study of the substituent influence upon the reaction of **22** with CH<sub>2</sub>N<sub>2</sub> has produced a ρ value

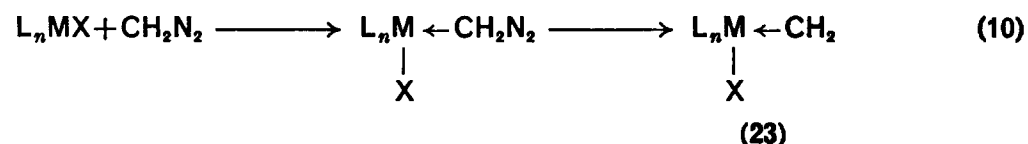


of 2.3<sup>46</sup>. These data show that more electrophilic character in the metal favours the reaction.

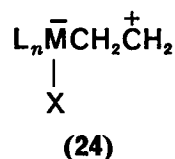
An initial association of diazoalkanes to the metal has also been proposed for their reaction with Group IIIa derivatives. The adduct reacts further to give either methylenation products<sup>3, 48-52</sup> or/and polymerization of the diazoalkane<sup>3, 53</sup>.

Qualitative experiments have led to the conclusion that the rate of the reaction depends on the Lewis acidity of the metal derivative. Thus, while BEt<sub>3</sub> reacts vigorously with CH<sub>2</sub>N<sub>2</sub> at room temperature to give polymethylene, B(OEt)<sub>3</sub> requires hours under the same conditions<sup>3</sup>.

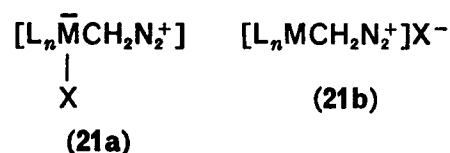
The fate of the intermediate adduct has been found to depend on the Lewis acidity of the metal derivative as well, weaker acids favouring polymerization over insertion<sup>50</sup>. Thus higher proportions of polymerization over insertion are found for boron derivatives as compared with analogous aluminium ones, for derivatives substituted with OR groups rather than R, H or X, and for reactions in which additional donor molecules have been added<sup>3</sup>. A mechanistic interpretation may be given (equation 10). Intermediate **23** behaves as a strong electrophile and can add



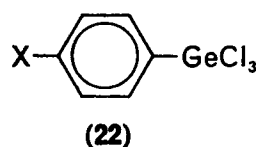
further diazomethane to form **24**. However, the stronger the interaction between the metal and the diazo carbon, the more effective will be the competition of M—X bond rupture and migration of X to carbon<sup>54</sup>.



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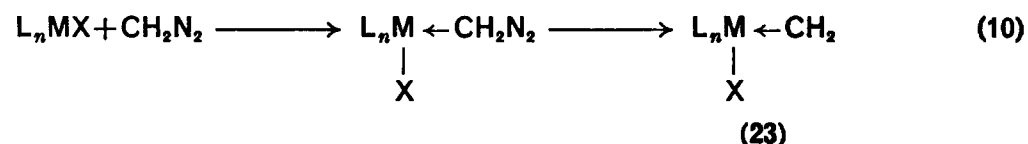


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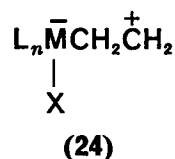
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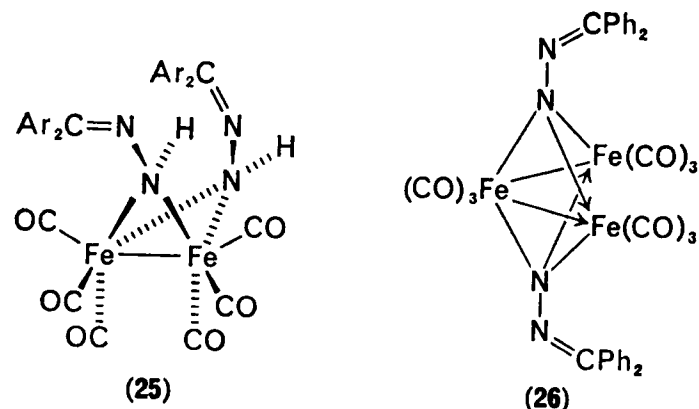


further diazomethane to form **24**. However, the stronger the interaction between the metal and the diazo carbon, the more effective will be the competition of M—X bond rupture and migration of X to carbon<sup>54</sup>.



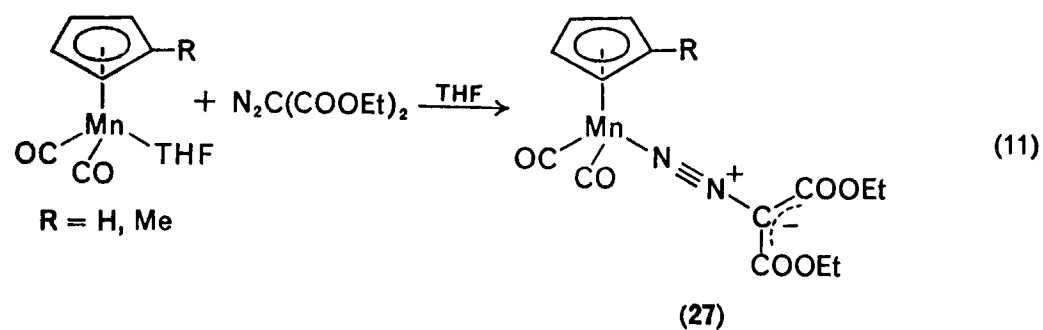
### B. Nitrogen Coordination

The reaction of diphenyldiazomethane with dodecacarbonyltri-iron and also its irradiation in the presence of pentacarbonyliron in benzene leads to two compounds<sup>55, 56</sup>, whose structures have been determined by X-ray studies to be **25**<sup>55</sup>

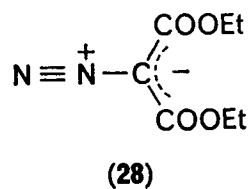


and **26**<sup>56</sup>. The N atoms in both complexes show angles characteristic of  $sp^3$  hybridization and the N—Fe bond lengths are close to those found in other complexes known to contain  $N(sp^3)$ —Fe bonds.

A single case has been reported where a diazo compound as such is bonded to a metal through its terminal nitrogen<sup>57</sup>, as shown in equation (11). The product of the reaction is stable up to 80 °C, diamagnetic, and it liberates the diazomalonate ester upon treatment with  $PPh_3$  under irradiation or with CO.



The structure proposed may be compared with those determined by X-ray studies for aryldiazenato complexes (see Section III.A), the basis for the comparison being the importance of limiting structure **28** in the ground state of the diazoester.

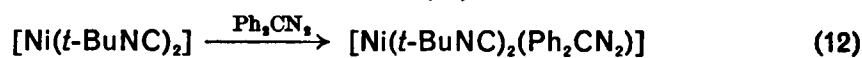
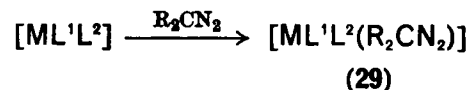


Complexes **27** show i.r. absorptions at 2025, 1982 and 1951  $cm^{-1}$  ( $R = H$ ) and 2022, 1979 and 1948  $cm^{-1}$  ( $R = Me$ ). By analogy with  $[M(\pi-C_5H_5)(CO)_2(N_2Ar)]$  ( $M = Cr$ <sup>58</sup>,  $Mo$ <sup>59-61</sup> or  $W$ <sup>62, 63</sup>), the first two bands may be assigned to  $\nu_{(CO)}$  and the last to  $\nu_{(NN)}$ . The high value of  $\nu_{(NN)}$  points to a ligand with an NNC angle close to 180° (see Section III.C.1).



### C. 'Side-on' Coordination

A series of complexes of Ni and Pd have been synthesized in which a diazoalkane ligand is claimed to be bonded 'side-on'<sup>31, 64</sup>. They have the general composition  $[ML^1L^2(\text{diazoalkane})]$  (29) with the ligands being *t*-BuNC, PPh<sub>3</sub> or 1,5-cyclo-octadiene and the diazoalkanes, 9-diazo-fluorene or diphenyldiazomethane. These complexes have been synthesized via addition reactions to  $[ML^1L^2]$ <sup>65</sup> or ligand substitution reactions with  $[ML^1L^2(\text{CH}_2=\text{CH}_2)]$ , as shown in the examples (12) and (13).



FI = 9-Fluorenylidene

The complexes 29 present an i.r. absorption attributed to  $\nu_{(\text{NN})}$  between 1550 and 1450  $\text{cm}^{-1}$ ; a linear end-on coordination involving the terminal nitrogen would presumably show in the region around 2000  $\text{cm}^{-1}$  and a coordination through carbon presumably still higher. Furthermore, the trends observed in the i.r. spectra upon changing the metal, the ligands and the diazoalkane parallel the trends found upon similar changes in complexes containing an alkyne ligand, which is known to be bonded 'side-on'<sup>31</sup>.

The structure of the ketenimine complex  $[Ni(t\text{-BuNC})_2\{t\text{-BuN}=\text{C}=\text{C}(\text{CN})_2\}]$  has been determined by X-ray studies to involve a 'side-on' coordination in which the Ni atom is nearly equidistant to the N and the adjacent C<sup>66</sup>. A similar proposal has been made for the bonding in the diazoalkane complexes, where the orbital picture would involve the donation from an occupied  $\pi$  orbital localized between the nitrogen atoms to the metal and  $\pi$  back donation from the metal into the corresponding unoccupied  $\pi^*$  orbital. 'Side-on' coordination has also been suggested for analogous derivatives with dicyanodiazomethane as ligand<sup>66</sup>.

## III. COMPLEX FORMATION BY DIAZONIUM IONS

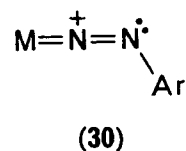
Since the first synthesis of an aryldiazonato† complex of a transition metal in 1964<sup>59</sup>, this area of chemistry has been continuously expanding both in the quantity and in the scope of the research carried out in it. Among the transition metals belonging to Groups VIb, VIIb and VIII, there only remain to be isolated complexes of Tc, Ni and Pd. On the other hand, the vast majority of the complexes reported involve the aryldiazonato ligand, only a handful of alkyldiazonato complexes having been characterized.

### A. Structure

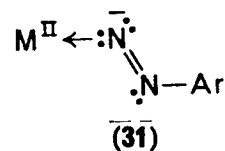
The terminal aryldiazonato ligand has been observed in two geometrical forms: singly bent and doubly bent. In the first instance the bonding is described as  $\sigma$ -donation from an sp hybrid orbital on the terminal nitrogen with  $\pi$  back donation from d orbitals of the metal into a p orbital on the terminal nitrogen ( $N_{(1)}$ ). A simple valence bond description of this type of complex has been given (structure 30)<sup>67</sup>. Evidence exists to show that upon reaction of an arenediazonium salt to form a

† The following nomenclature will be used<sup>1</sup>: diazene ( $\text{HN}=\text{NH}$ ), aryldiazene ( $\text{ArN}=\text{NH}$ ), aryldiazonato ( $\text{ArN}_2-$  or  $\text{ArN}_2\langle$ ) and arenediazonium ( $\text{ArN}_2^+$ ).

complex where the aryldiazonato ligand is coordinated in this fashion, the oxidation state of the metal suffers no change. Hence, the ligand may formally be regarded as an  $\text{ArN}_2^+$  two-electron donor ligand.



The doubly bent terminal ligand has been described as having a single bond by overlap between an  $\text{sp}^2$  orbital on  $\text{N}_{(1)}$  with a hybrid orbital on the metal, as shown in structure 31<sup>67</sup>. In this case, the evidence available indicates that when an arene-diazonium ion becomes coordinated as a doubly bent ligand, the metal suffers a formal two-electron oxidation. The bonding may hence be formally described as that between a two-electron donor  $\text{ArN}_2^-$  ligand and a doubly oxidized metal.



The X-ray studies reported<sup>1, 68, 69</sup> for complexes containing a singly bent ligand<sup>70, 71</sup> show that the NNC angles lie within the range 118–124°, the only exception being  $[\text{RuCl}_3(\text{PPh}_3)_2(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})]$ , with a value of 137°. It has been suggested that slight back donation from the metal into  $\pi^*$  orbitals on the aryldiazonato moiety leaves the N–N bond largely as a triple bond and the NNC angle close to 180° (hypothetical linear terminal diazenato ligand)<sup>1</sup>, whereas stronger back donation as described above predicts this angle to be 120°. Intermediate values of the angle might be expected depending upon the relative importance of the linear and singly bent formalisms to the electronic structure or, equivalently, upon the degree of the metal to ligand electron transfer process<sup>67</sup> (see Section III.C.1). Detailed discussions on the electronic structure of the isoelectronic nitrosyl ligand have been reported<sup>72, 73</sup>.

### B. Synthesis

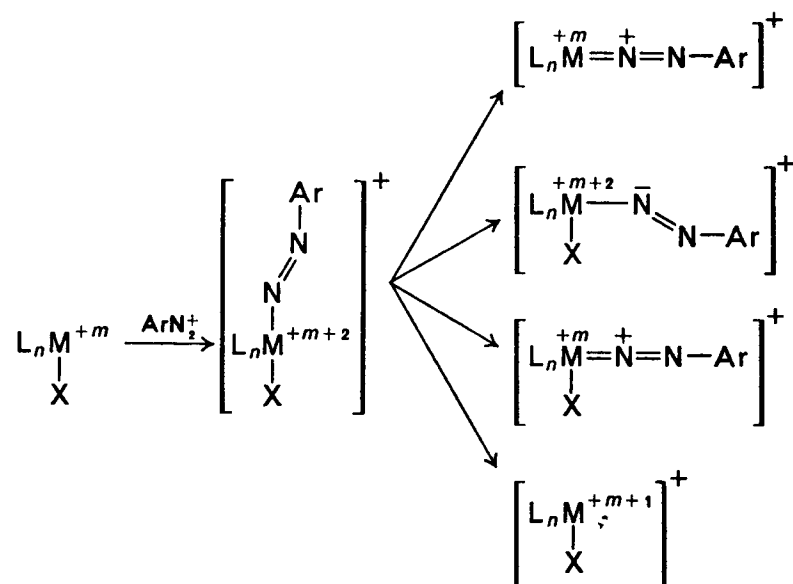
The most frequently used reagents for preparing aryldiazonato complexes have been diazonium salts, either as such or as compounds that generate them *in situ*. The complexes are produced via ligand substitution, oxidative addition or Lewis base association reactions<sup>74</sup>.

A general mechanism has been proposed<sup>1</sup>, which has received additions and partial confirmation from comparative electrochemical studies on nitrosyl and aryldiazonato complexes<sup>75</sup>; it is shown in Scheme 2. The nature of the products has been observed to depend on the metal and its ligand, but with the exception mentioned above<sup>75</sup> no quantitative studies have yet been reported.

Complexes between diazonium ions and transition metal derivatives have been postulated as reactive intermediates in the Sandmeyer<sup>76–79</sup> and related<sup>80</sup> reactions, but structural proofs are not available.

Several other methods have been used to prepare aryldiazonato complexes including<sup>1</sup> apparent insertion of diazonium ions into metal–hydrogen bonds

followed by deprotonation of the aryldiazene complex formed<sup>81</sup>, reaction of coordinated nitrosyl with aromatic amines, reaction of metal complexes with arylhydrazines<sup>82</sup>, organodiazenes or diazoalkanes<sup>83</sup>, and modification of complexes already containing an aryldiazene ligand<sup>81</sup>.



SCHEME 2

### C. Spectroscopic Properties

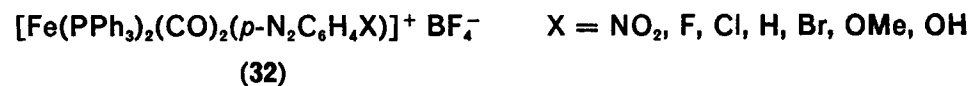
#### I. Infrared spectroscopy

Infrared studies have provided a useful tool for examining the interaction of the aryldiazene ligand with the transition metal to which it is bonded and with other ligands present in the complex. Several studies have shown that although overlap of  $\nu_{(NN)}$  with the absorption of other groups in the complex and coupling between the N—N stretching vibration with aryl vibrational modes occur<sup>81, 84, 85</sup>, the isolation of  $\nu_{(NN)}$  is possible by mathematically decoupling the interacting bands which shift upon <sup>2</sup>H or <sup>15</sup>N substitution<sup>85</sup>.

The N—N stretching vibration is found within the broad region defined between *c.* 1440 and 2100  $\text{cm}^{-1}$ . This wide range is a reflection of the different coordination modes of the aryldiazene ligand, i.e. 30 and 31. High values of  $\nu_{(NN)}$  ( $> c.$  1650  $\text{cm}^{-1}$ ) can generally be attributed to the occurrence of complexes of type 30, whereas low values of  $\nu_{(NN)}$  ( $< c.$  1500  $\text{cm}^{-1}$ ) can be generally identified with complexes of type 31. With values in the intermediate overlap region, the assignment is not trustworthy.

A method has been proposed<sup>70</sup> which brings the  $\nu_{(NN)}$  values to a common scale and reduces the region where the ligand structure assignment is doubtful, the basis of it being the variations expected in  $\nu_{(NN)}$  upon changing the nature of the metal and its ligands.

The mutual influence of the aryldiazene ligand and other ligands present in the same complex can be studied in CO-containing complexes, since  $\nu_{(CO)}$  is an easily identifiable absorption. An increase in  $\nu_{(CO)}$  implies an increase in the C—O bond order, a consequence of diminished  $d_{\pi}-p_{\pi}$  back donation by the metal<sup>60</sup>. This effect may be induced by substituents in the aryldiazene ligand. Thus, in complexes 32,

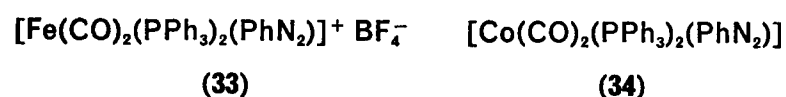


the better electron-withdrawing substituents produce the highest  $\nu_{(\text{CO})}$  and the lowest  $\nu_{(\text{NN})}$  of the series<sup>86</sup>, pointing to electron flow from the CO groups to the aryldiazonato ligands.

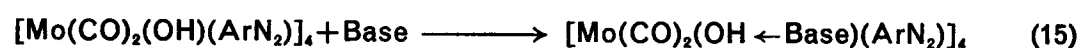
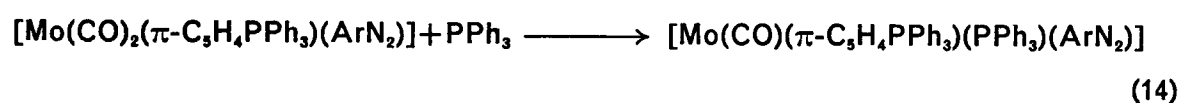
The complexes of the heavier metals present lower  $\nu_{(\text{NN})}$  values (or/and lower  $\nu_{(\text{CO})}$  values when appropriate) indicating that they are better electron donors than the lighter ones. Thus for example,  $[\text{RuBr}_3(\text{PPh}_3)_2(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})]$ ,  $\nu_{(\text{NN})} = 1895 \text{ cm}^{-1}$ , may be compared with  $[\text{OsBr}_3(\text{PPh}_3)_2(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})]$ ,  $\nu_{(\text{NN})} = 1855 \text{ cm}^{-1}$ <sup>87</sup>.

The electronic configuration of the metal influences its capability of back donating electron density, a comparison of the  $\nu_{(\text{NN})}$  values for the aryldiazonato complexes reported showing that they exhibit a general trend in which  $\nu_{(\text{NN})}$  decreases as the  $d^n$  configuration of the metal increases<sup>88</sup>. Since the data available are rather scarce, simultaneous variations in the ligands, the charge and the metal are included in the comparison.

The i.r. spectra of complexes 33 ( $\nu_{(\text{NN})} = 1723$ ,  $\nu_{(\text{CO})} = 2030$ ,  $1978 \text{ cm}^{-1}$ )<sup>89</sup> and 34 ( $\nu_{(\text{NN})} = 1689$ ,  $\nu_{(\text{CO})} = 2010$ ,  $1960 \text{ cm}^{-1}$ )<sup>90</sup>, show that a positive charge, which may be assumed to reside mainly on the metal<sup>86</sup>, diminishes the electron density available on the latter to share with the ligands.



The nature of the ligands influences the availability of electrons on the metal. In equation (14), replacement of CO by the relatively poorly accepting  $\text{PPh}_3$  ligand



results in an increased electron release from the metal and  $\nu_{(\text{NN})}$  and  $\nu_{(\text{CO})}$  occur at lower wave numbers in the products<sup>91</sup>. In equation (15) the lower  $\nu_{(\text{NN})}$  and  $\nu_{(\text{CO})}$  values observed in the adducts<sup>92</sup> may be related to increased electron release from the metal caused by donation of electron density from the Lewis base to the OH ligand through a hydrogen bond.

TABLE 1. Correction parameters to  $\nu_{(\text{NN})}$  ( $\text{cm}^{-1}$ )

Metal	Group	Charge	Ligands	Coordination number
First row	VIb	+100	Third $\text{PPh}_3$	4
Second row	VIIb	+50	Fourth $\text{PPh}_3$	5, 6, 7
(Mo, -10)	VIII	0	$\text{HBPz}_3^-$ <sup>a</sup>	0
Third row		-1	$\pi\text{-C}_5\text{H}_4\text{PPh}_3$	
		-2	$\text{H}^-$	
		-3		

<sup>a</sup> Pz = 1-Pyrazolyl.

Table 1 collects the suggested correction parameters which should be added (or subtracted) to  $\nu_{(\text{NN})}$ <sup>70</sup> to obtain a modified frequency  $\nu_{(\text{NN})}$ . The magnitudes of the corrections have been chosen so as to give the best agreement with data collected from several hundred known complexes of the isoelectronic nitrosyl ligand.

The number of X-ray structure determinations being very limited, the  $\nu_{(NN)}$  values provide a useful tool to predict confidently the type of ligand present in the great majority of aryldiazene complexes, a value above  $1550\text{ cm}^{-1}$  indicating a complex of type **30** and one below  $1530\text{ cm}^{-1}$  of type **31**.

A relationship between electron back donation by the metal and i.r. spectra has been demonstrated in complexes containing the *monohapto*-dinitrogen ligand<sup>93, 94</sup>, isoelectronic with  $\text{NO}^+$  and with  $\text{ArN}_2^+$ <sup>95</sup>. In a series of these complexes, X-ray photoelectron spectroscopy studies show that increasing electron density on the  $\text{N}_2$  fragment, as measured by the binding energy of its core electrons<sup>96</sup>, is coupled with decreasing NN stretching frequencies<sup>97</sup>.

## 2. N.m.r. spectroscopy

Although the  $^1\text{H}$ -n.m.r. spectra of many of the aryldiazene complexes reported have been determined, the information they yield is very unspecific and hence they have been utilized as an analytical tool rather than as a probe into the electronic distribution in the complexes. On the other hand,  $^{19}\text{F}$ -n.m.r. studies are severely limited in number<sup>61, 98, 99</sup>, but they have yielded valuable information on the interaction at the electronic level between metal, aryldiazene ligand and other ligands in the complex.

The most recent and complete study<sup>61</sup> has applied the technique of Taft<sup>100</sup> and coworkers where the differences in chemical shifts between a *para*- and a *meta*-F substituent are taken as a measure of the electronic effects acting on the ring that holds these substituents. Thus, the more positive the value of  $\delta_p - \delta_m$  is, the less shielded the *para*-F is relative to the *meta*-F substituent, and hence the less electron flow into the aryl ring has taken place.

Some results obtained are collected in Table 2. Comparisons among them lead to the same conclusions concerning the influence of the metal and its ligands on the aryldiazene ligand, as reached on the basis of i.r. spectra.

TABLE 2.  $^{19}\text{F}$ -N.m.r. data for aryldiazene complexes<sup>a</sup>

Complex	$\delta_p - \delta_m$ (p.p.m.)
$[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)(\text{N}_2\text{Ar})]$	-5.02
$[\text{W}(\text{HBPz}_3)(\text{CO})_2(\text{N}_2\text{Ar})]^b$	-4.54
$[\text{Mo}(\pi\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})(\text{PPh}_3)(\text{N}_2\text{Ar})]^+ \text{BF}_4^-$	-3.86
$[\text{Mo}(\text{HBPz}_3)(\text{CO})_2(\text{N}_2\text{Ar})]^b$	-3.58
$[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}_2\text{Ar})]$	-2.20
$[\text{Mo}(\text{HCPz}_3)(\text{CO})_2(\text{N}_2\text{Ar})]^+ \text{BF}_4^-$	-2.11
$[\text{Mo}(\pi\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})_2(\text{N}_2\text{Ar})]^+ \text{BF}_4^-$	-0.14

<sup>a</sup> Chemical shifts for  $\text{CH}_2\text{Cl}_2$  solutions and referred to external hexafluorobenzene.

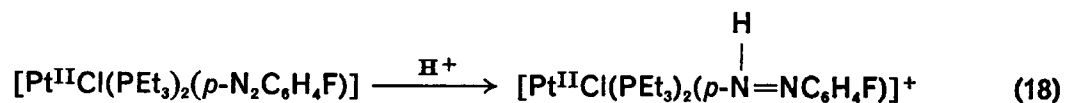
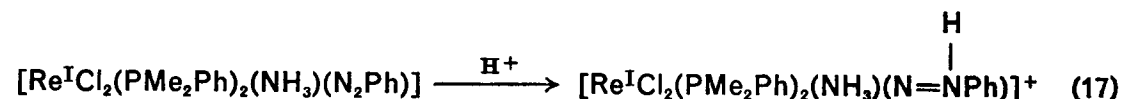
<sup>b</sup> Pz = 1-pyrazolyl.

## D. Chemical Properties

No quantitative study on the reactivity of aryldiazene complexes has yet appeared in the literature. Conclusions concerning the influence of the metal, of the substituents on the aryldiazene ligand and of the rest of the ligands on the reactivity of the complexes have been based on a reaction failing to produce the



expectations have been confirmed by X-ray studies in the cases of equations (17)<sup>103</sup> and (18)<sup>104</sup>.



Finally, although the discussion has been centred on aryldiazenato complexes, most of it should apply as well to alkyl, acyl and aroyl diazenato complexes. Caution should be exercised however in not extending the generality too far because the stability of the aryldiazenato as ligand is greatly influenced by its capability to accept  $\pi$  electrons from a metal, a characteristic not shared by alkyl diazenato groups<sup>105</sup>.

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