# Co-ordination Chemistry of Aryldiazonium Cations: Aryldiazenato (Arylazo) Complexes of Transition Metals, and the Aryldiazenato–Nitrosyl Analogy

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## 1 Introduction

During the past ten years there has been a growing interest in the synthesis and structure elucidation of transition-metal compounds containing the aryldiazenato-ligand (ArNN). The first reported compound, by King and Bisnette in 1964,[1] was [Mo(C$_5$H$_5$) (CO)$_2$(N$_2$C$_6$H$_4$OMe-$p$)]. Its synthesis utilized displacement of a carbonyl group in [Mo(C$_5$H$_5$) (CO)$_3$]$^-$ by the aryldiazonium ion. Subsequently, reactions involving aryldiazonium ions have become an important general route to aryldiazenato-compounds. An immediately obvious analogy exists between this compound and the corresponding nitrosyl [Mo(C$_5$H$_5$) (CO)$_2$NO]. In each compound an 18-electron molybdenum configuration requires nitrosyl and aryldiazenato-ligands to be three-electron donors, and the pursuit of this analogy between the formally isoelectronic nitrosyl and aryldiazenato-ligands has underscored much of the subsequent development. Fortuitously, this has also coincided with certain renewed interest in nitrosyl complexes themselves, when structural evidence showed in 1968 that a formal distinction could be drawn between the familiar three-electron donor nitrosyl ligands with near-linear MNO geometry and a second group of nitrosyl complexes which are characterized by a bent (*ca.* 120°) MNO geometry. The latter correspond to a description of the nitrosyl group acting as a one-electron donor, as in organic nitroso-compounds.[2] Similar geometrical differences in aryldiazenato-compounds would be expected and have been found.[3] This convergence of structural results on aryldiazenato and nitrosyl compounds, together with the considerable number of new aryldiazenato-compounds reported in the past ten years, makes this an opportune time for a comparative review of these complexes.
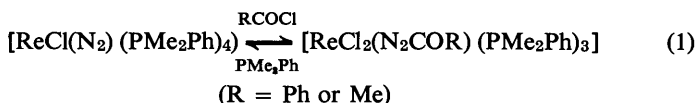
A further point of interest and potential utility is the close relationship of the

[1] R. B. King and M. B. Bisnette, (*a*) *J. Amer. Chem. Soc.*, 1964, **86**, 5694; (*b*) *Inorg. Chem.*, 1966, **5**, 300.
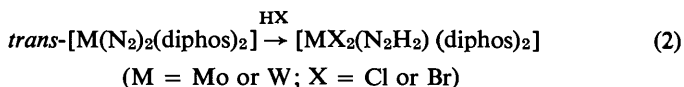
[2] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1968, **90**, 4486; D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345; B. A. Frenz and J. A. Ibers, in 'Chemical Crystallography', ed. J. M. Robertson, MTP International Review of Science, Physical Chemistry, Series One, Vol. 11, Butterworths, London, 1972, p.33.

[3] (*a*) A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 6859; (*b*) A. P. Gaughan and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 352.

aryldiazenato-ligand with dinitrogen. It presently seems that a continued study of the synthesis and properties of aryldiazenato-complexes may prove worthy in understanding the activation of dinitrogen by transition metals and the role of iron and molybdenum in biological nitrogen fixation. The following examples will illustrate. Generally, the co-ordinated dinitrogen ligand has been found to be hardly at all more reactive than molecular dinitrogen itself. One of the few reactions which it has been observed to undergo, in appropriate complexes with Mo, W, or Re, is attack by electrophilic alkyl, aroyl, or acyl groups to form diazenato-complexes as in equation (1).[4]

$$\text{[ReCl(N}_2\text{) (PMe}_2\text{Ph)}_4\text{]} \overset{\text{RCOCl}}{\underset{\text{PMe}_2\text{Ph}}{\rightleftharpoons}} \text{[ReCl}_2\text{(N}_2\text{COR) (PMe}_2\text{Ph)}_3\text{]} \qquad (1)$$

$$(R = Ph \text{ or } Me)$$

A second reaction, and clearly one of considerable consequence in regard to nitrogen fixation, is protonation to yield a co-ordinated $N_2H_2$ moiety[5] [equation (2)].

$$trans\text{-[M(N}_2\text{)}_2\text{(diphos)}_2\text{]} \overset{\text{HX}}{\rightarrow} \text{[MX}_2\text{(N}_2\text{H}_2\text{) (diphos)}_2\text{]} \qquad (2)$$

$$(M = Mo \text{ or } W; X = Cl \text{ or } Br)$$

A recent $X$-ray structure determination[6] indicates that in $[MX(N_2H_2)(diphos)_2]$ $BPh_4$ the ligand has the hydrazido(2−) structure $M{=}N{=}NH_2$, in which case an obvious and close comparison exists between the stereochemistry and electronic configuration of this arrangement and that of an aryldiazenato-ligand protonated on $N^2$. This seems to be confirmed by the $X$-ray structure[7] of $[ReCl_2\{NN(H)Ph\} (PMe_2Ph)_2(NH_3)]^+$, formed by the protonation of the aryldiazenato-ligand in the complex $[ReCl_2(N_2Ph) (PMe_2Ph)_2(NH_3)]$, where the observed dimensions indicate the presence of the $Re{=}N{=}N(H)Ph$ group. Other compounds formed in the protonation of co-ordinated dinitrogen appear to be complexes of diazene ($HN{=}NH$), which has long been postulated as a possible intermediate in nitrogen fixation but never identified. Possibilities for the binding of this ligand include a $\sigma$-complex ($M{-}NH{=}NH$) and a $\eta$-complex (1). Consequently the binding of diazene itself and substituted diazenes to transition metals is receiving attention,[8] and an important route to the

[4] (a) J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc. (A)*, 1971, 2631; (b) J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organometallic Chem.*, 1973, **57**, C67; (c) A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organometallic Chem.*, 1975, **84**, C11.

[5] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 1010; *J.C.S. Dalton*, 1974, 2074.

[6] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259.

[7] R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Amer. Chem. Soc.*, 1974, **96**, 260.

[8] S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 1973, **12**, 2290; A. Nakamura, M. Aotake, and S. Otsuka, *J. Amer. Chem. Soc.*, 1974, **96**, 3456; P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *ibid.*, 1972, **94**, 8640.

$$M - - \overset{\displaystyle NH}{\underset{\displaystyle NH}{\big|\big|}}$$
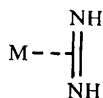
(1)

latter complexes can be through reaction of aryldiazenato-complexes with electrophiles.

The purpose of this article, then, is to review the synthetic and structural chemistry of aryldiazenato-complexes and their present distribution among the elements, so as to bring out parallels with the corresponding nitrosyls and their relationship with other complexes of nitrogen ligands.

## 2 Nomenclature

The most notable feature regarding the nomenclature currently in use in relation to the compounds described in this Review is its variety and inconsistency. This extends to the diazonium ions themselves, which are properly named by adding the suffix 'diazonium' to the name of the parent hydrocarbon, rather than that of the aryl group.[9] Nevertheless, the latter terminology is quite common, especially in journals of inorganic or organometallic chemistry.

Products containing the M—N$_2$Ar group have been most often called *arylazo* complexes, though recently[3] *aryldiazo* was introduced on the basis of its derivation from *aryldiazonium*. However, neither name conforms with established rules of nomenclature. A survey of the names currently adopted for related species reveals the following: the molecule HNNH is still frequently called *di-imine*[6] or *di-imide*,[10] even though general adoption of the name *diazene* has been urged;[11,12] similarly, PhNNH is variously called *phenyldi-imide*,[10,13] *phenyldi-imine*,[7,14] and *phenyldiazene*,[3,11] and an identical name should be, and has been, used for PhNNH as a neutral ligand. As mentioned in the introduction, protonation of M—NN and M—NNPh may give rise to M—NNH$_2$ and M—NN(H)Ph. These ligands have been described as the hydrazido dianion[6] and phenylhydrazido dianion[7] respectively.

First it must be decided whether different names should be adopted to distinguish the two limiting structural possibilities represented by the linear M—N—N and the bent M—N—N systems which will be discussed in the following Section. It is a principle of chemical nomenclature that a compound must be named without recourse to a determination of its dominant electronic

[9] I.U.P.A.C. Nomenclature of Organic Chemistry, Section C, Butterworths, London, 1965, p. 216.
[10] E. K. Jackson, G. W. Parshall, and R. W. F. Hardy, *J. Biol. Chem.*, 1968, **243**, 4952.
[11] E. M. Kosower, *Accounts Chem. Res.*, 1971, **4**, 193.
[12] J. H. Fletcher, O. C. Dermer, and R. B. Fox, 'Nomenclature of Organic Compounds', *Adv. Chem. Ser.*, 1974, No. 126, p. 247.
[13] G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.
[14] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1973, 2713.

structure; these systems are essentially different electronic structures and so need not be distinguished by name. Secondly we must decide the systematic name for the ArNN ligand. The names *diazene* (HN=NH) and *aryldiazene* (ArN= NH), recommended[12] by the American Chemical Society, will eventually be universally endorsed. According to proposed I.U.P.A.C. rules, the ArNN ligand then logically becomes *aryldiazenato* (not *aryldiazenido*[15]) and this name will be used throughout this Review. Other related groups are usually named according to I.U.P.A.C. rules. The nitrogen atoms will be numbered as Ar—$N^2$=$N^1$—M.

## 3 Electronic Structure and Geometry

**A. Three-electron Donor ($N_2Ar^+$) Terminal Ligand.**—By exact analogy with terminal, so-called $NO^+$, nitrosyl complexes there is a group of aryldiazenato-complexes in which the aryldiazenato-ligand may be viewed formally as a three-electron donor terminal ligand or, equivalently, as the aryldiazonium ion ($N_2Ar^+$) co-ordinated through the $\sigma$-lone pair on the terminal nitrogen together with strong back donation of electrons from the metal.

A conventional, simplified picture of the electronic structure is shown in Scheme 1(a). It should be noted that, in its usual interpretation, this picture does not imply any change of hybridization at oxygen. However, the simple valence-bond model of back-bonding [Scheme 1(b)] generates a second lone pair on
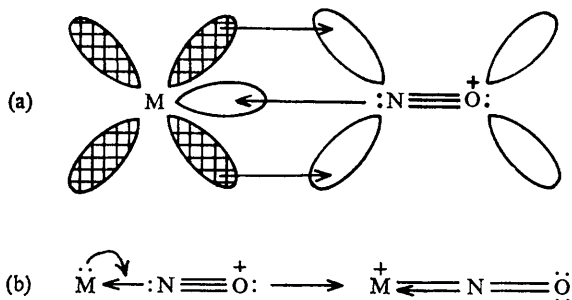


**Scheme 1**

oxygen and implies a hybridization change at oxygen from *sp* to *sp²*. Unfortunately, there are no possible observable geometric changes at oxygen capable of reflecting the adequacy of either picture.

The situation in aryldiazenato-complexes is different in this respect. Now, the mere population of $\pi^*$-orbitals on $N_2Ar$ leaves the angle at $N^2$ close to 180°, [Scheme 2(a)] whereas the simple valence-bond picture in Scheme 2(b) predicts this angle to be about 120°.
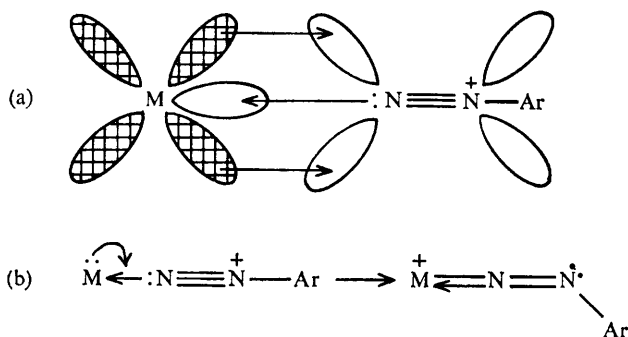
In the majority of presently available *X*-ray structure determinations on formally $N_2Ar^+$ complexes the angle at $N^2$ is indeed near to 120° (see the Table), attesting to the importance of back-bonding in these complexes and to the

[15] S. D. Ittel and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4804.

**Table** *Dimensions of aryldiazenato-complexes from X-ray diffraction studies*

| Compound | M—N$^1$/Å | N$^1$—N$^2$/Å | N$^2$—C/Å | M—N$^1$—N$^2$/° | N$^1$—N$^2$—C/° | Ref. |
|---|---|---|---|---|---|---|
| *Group 1  Terminal 3e$^-$-donor* (N$_2$Ar$^+$) | | | | | | |
| [{HB(pz)$_3$}Mo(CO)$_2$(N$_2$Ph)] | 1.825(4) | 1.211(6) | 1.432(7) | 174.2(1) | 121.1(2) | 16 |
| [Re(N$_2$Ph)Cl$_2$(PMe$_2$Ph)$_3$] | 1.80 | 1.23 | | 172 | 118 | 17 |
| | 1.77(2) | 1.23(2) | 1.43(2) | 173(2) | 119(2) | 7 |
| [Fe(N$_2$Ph)(CO)$_2$(PPh$_3$)$_2$]$^+$ | 1.702(6) | 1.201(7) | 1.404(8) | 179.2(5) | 124.2(6) | 18, 19 |
| [Ru(*p*-N$_2$C$_6$H$_4$Me)Cl$_3$(PPh$_3$)$_2$] | 1.796(9) | 1.14(1) | 1.40(1) | 171.2(9) | 136(1) | 20 |
| | 1.784(5) | 1.158(6) | 1.376(6) | 171.9(5) | 137.1(5) | 19 |
| [ReCl$_2$(N$_2$COPh) (PMe$_2$Ph)$_3$] | 1.74(2) | 1.22(3) | 1.42(3) | 170(2) | 124(2) | 7 |
| *Group 2  Terminal 1e$^-$-donor* (N$_2$Ar$^-$) | | | | | | |
| [Rh(N$_2$Ph)Cl(PPP)]$^+$* | 1.961(7) | 1.172(9) | 1.445(11) | 125.1(6) | 118.9(8) | 3b |
| *Group 3  Bridging 3e$^-$-donor* | | | | | | |
| [Mn(N$_2$Ph) (CO)$_4$]$_2$ | 2.031(2) | 1.234(3) | 1.445(3) | 134.4(2) | 119.7(2) | 35 |
| | 2.021(2) | | | 119.6(2) | | |

*PPP = PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$

* PPP = PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$

16 G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, B**27**, 725.
17 V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1970, 1083.
18 W. E. Carroll and F. J. Lalor, *J.C.S. Dalton*, 1973, 1754.
19 J. A. Ibers and B. L. Haymore, *Inorg. Chem.*, 1975, **14**, 1369.
20 J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 1676.

(a)  M $\equiv$ :N $\equiv\equiv$ $\overset{+}{N}$—Ar

(b)  $\overset{..}{M}$ $\leftarrow$ :N $\equiv\equiv$ $\overset{+}{N}$—Ar $\longrightarrow$ $\overset{+}{M}$ $\equiv\equiv$ N $\equiv\equiv$ $\overset{.}{N}$ $\diagdown$ Ar

**Scheme 2**

qualitative usefulness of the simple VB description. Understandably then, it is this nitrogen atom which is the site for protonation, as indicated by the *X*-ray structure determination[7] of $[ReCl_2\{NN(H)Ph\}(PMe_2Ph)_2(NH_3)]^+$. The extent to which other $N_2Ar^+$ complexes may undergo protonation or reaction with other electrophiles at $N^2$ has at the time of writing received little attention, but this is expected to become an increasingly important aspect of their chemistry. Of course, examples of NNC angles intermediate between 180° and 120° may be expected depending upon the relative importance of the 'linear' and 'singly bent' formalisms (2) and (3) to the electronic structure. In this connection, the

$$M \leftarrow N \equiv \overset{+}{N}Ar \qquad\qquad M = \overset{+}{N} = \overset{.}{N}$$
$$\diagdown Ar$$

(2)          (3)
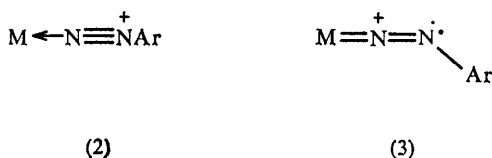
136° angle in the listed ruthenium complex is not unexpected. It may be possible eventually to correlate vibrational frequencies with the intra-ligand angles, but at present there are insufficient structural as well as spectral data to allow this in detail.

At this point it is worthwhile examining other ligands isoelectronic with $N_2Ar^+$ to see whether these display similar geometric changes upon co-ordination. Examples are cyanides $R—C\equiv N$,[21] isocyanides $R—\overset{+}{N}\equiv\overset{-}{C}$,[22] and acetylides $R—C\equiv\overset{-}{C}$. There appear to be no recorded instances of a corresponding geometry change of this magnitude for these ligands. Especially interesting is isocyanide, where the nitrogen carries a formal positive charge as in diazonium. The

[21] M. Kilner, *Adv. Organometallic Chem.*, 1972, **10**, 115.
[22] P. M. Treichel, *Adv. Organometallic Chem.*, 1973, **11**, 21.

chemistry of this ligand points to it being a much better σ-donor and a weaker π-acceptor than CO. On the basis of available *X*-ray structure determinations, of which some recent examples are cited,[23-26] terminal isocyanide complexes exhibit angles close to 180° at nitrogen, presumably reflecting the importance of σ-donor rather than π-acceptor capacity in its binding to metals in the presently determined examples.

**B. One-electron Donor (N₂Ar⁻) Terminal Ligand.**—The conventional occurrence of the nitrosyl (nitroso) group or the aryldiazenyl (arylazo) group in carbon chemistry is where these contribute one electron to a two-electron, two-centre σ-bond in R—NO or R—N₂Ar compounds. These ligands can form analogous bonds to transition metals, and in such complexes they can be viewed formally as one-electron donors and formulated as NO⁻ and N₂Ar⁻ ligands. An important difference from the previously described NO⁺ and N₂Ar⁺ complexes is the expected change in geometry. As a one-electron ligand the nitrosyl group should give rise to an angle of about 120° at nitrogen (4); the corresponding aryldiazenato-complexes should possess 120° angles at both nitrogen atoms, *i.e.* be 'doubly bent' and capable of *trans-* and *cis-*geometric isomers (5) and (6).
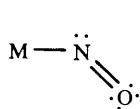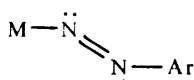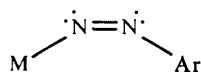


(4)                    (5)                    (6)

The ions NO⁺ and N₂Ar⁺ do, of course, exist and may be utilized directly in the synthesis of many of their complexes, lending at least some degree of reality to their formulation as complexes of the positive ions. This is not true, to any extent, of the ions NO⁻ and N₂Ar⁻, and, as yet, NO⁻ and N₂Ar⁻ complexes have not been synthesized by direct co-ordination of these anions, nor by reactions involving reagents likely to give rise to these ions *in situ*. Instead, present methods yield these compounds indirectly, an important route being the formal transfer of two electrons from the metal to the ligand, either as a redistribution of electrons in the formal NO⁺ or N₂Ar⁺ complexes or by electrophilic attack of NO⁺ or N₂Ar⁺ at an electron-rich metal atom. As an example of the former, nitrosyl complexes of the type [Co(NO)(PR₃)₂Cl₂] are believed[27] to exhibit structural isomerism between a trigonal-bipyramidal form having a linear equatorial nitrosyl group [Co^I(NO⁺)], and a square-pyramidal form having

[23] C. J. Gilmore, S. F. Watkins, and P. Woodward, *J. Chem. Soc. (A)*, 1969, 2833.
[24] B. Jovanović, L. Manojlović-Muir, and K. W. Muir, *J.C.S. Dalton*, 1972, 1178.
[25] D. Baumann, H. Endres, H. J. Keller, and J. Weiss, *J.C.S. Chem. Comm.*, 1973, 853.
[26] R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, 1974, **13**, 257.
[27] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.

a bent apical nitrosyl group, $[Co^{III}(NO^-)]$. Other examples have been cited.[28] The relationship between the limiting forms in this electron redistribution is simply indicated in Scheme 3, and an analogous representation for aryldiazenato-complexes is shown in Scheme 4.
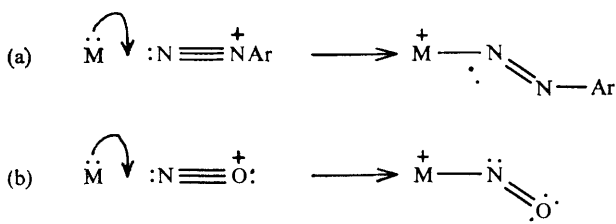
**Scheme 3**
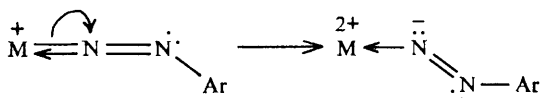
**Scheme 4**

The synthesis of $NO^-$ and $N_2Ar^-$ complexes by reactions of nitrosonium or aryldiazonium salts can similarly be represented, albeit in a somewhat arbitrary and cumbersome manner, in terms of Schemes 3 and 4, in which it is envisaged that Lewis-base co-ordination by the cation occurs first, followed by an extreme back-bonding process, going beyond (using the aryldiazenato example) the singly bent species to a complete transfer of two electrons from the metal to give the doubly bent ligand. A simpler, and chemically more appealing, viewpoint is that the reaction proceeds directly to the doubly bent ligand by virtue of the $N_2Ar^+$ group acting as an electrophile (*i.e.* Lewis acid co-ordination) as depicted in Scheme 5. In support of this, the metals which undergo such reactions

(a)

(b)

**Scheme 5**

are typically those for which oxidative addition and other two-electron oxidation processes are important, for example $d^8$ complexes of $Co^I$, $Rh^I$, and $Ir^I$, and $d^{10}$ complexes of $Pt^0$. A particularly well documented example, which also illustrates the nitrosyl-aryldiazenato analogy very well, is the co-ordination of the dissociation-stabilized rhodium(I) phosphine complex [Rh(PPP)Cl] {PPP = [Ph$_2$P(CH$_2$)$_3$]$_2$PPh} by $NO^+$ and $N_2Ph^+$ to give structurally similar square-pyramidal complexes containing apical bent nitrosyl (4) and doubly bent
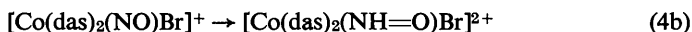
[28] J. H. Enemark and R. D. Feltham, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 3534; *Co-ordination Chem. Rev.*, 1974, **13**, 339.

aryldiazenato (5) ligands respectively.[3,29] As can be seen from the Table, the M—N distance in the aryldiazenato-complex (12) (see p. 456) is considerably longer than that of any singly bent aryldiazenato-complex, in keeping with the one-electron donor formalism and with observed lengths in linear and bent nitrosyl complexes.[2]

Of the two possible sites for protonation of the doubly bent aryldiazenato-ligand, the presently available evidence, primarily from the magnitude of $^{15}N-^{1}H$ coupling constants,[14] is that protonation occurs at $N^1$, the nitrogen atom adjacent to the metal, as for example equation (3).[14] No example is presently known of protonation at $N^2$ or at both sites. Protonation therefore yields complexes containing co-ordinated aryldiazenes (NH=NAr) such as phenyldiazene, molecules that are quite unstable in the uncomplexed state.[11]

$$[RhCl_2(N_2Ar)(PPh_3)_2] \underset{Et_3N}{\overset{HCl}{\rightleftharpoons}} [RhCl_3(NH=NAr)(PPh_3)_2] \qquad (3)$$
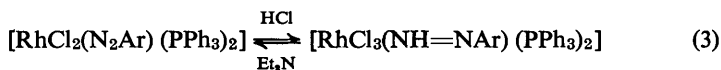
Here again, the analogy with nitrosyl complexes is illustrated by equation (4), in which protonation of co-ordinated nitrosyl occurs at the site of co-ordination to give a complex containing co-ordinated HNO.[30]

$$[OsCl(CO)(NO)(PPh_3)_2] \underset{-HCl}{\overset{HCl}{\rightleftharpoons}} [OsCl_2(CO)(NH=O)(PPh_3)_2] \qquad (4a)$$

$$[Co(das)_2(NO)Br]^+ \rightarrow [Co(das)_2(NH=O)Br]^{2+} \qquad (4b)$$

The stereochemistry of $[OsCl(CO)(NO)(PPh_3)_2]$ has not been determined by *X*-rays, but it may be expected that the reaction involves an isomer having the bent Os—N—O form, rather than the linear. The closely related isoelectronic complex $[Os(OH)(NO)_2(PPh_3)_2]^+$ possesses both linear and bent nitrosyl groups,[31] where the linear $NO^+$ group may be considered to be the counterpart of CO.

As a final comment in this section, the question is raised as to what extent it is realistic, in view of their positive charge, to consider that $NO^+$ and $N_2Ar^+$ are actually ever capable of attacking metal complexes as Lewis bases, for example in the displacement of CO and the formation of $NO^+$ and $N_2Ar^+$ complexes in equations (5) and (6).[18,32,33]

$$[Fe(CO)_3(PPh_3)_2] + NO^+ \rightarrow [Fe(CO)_2(NO)(PPh_3)_2]^+ + CO \qquad (5)$$

$$[Fe(CO)_3(PPh_3)_2] + N_2Ph^+ \rightarrow [Fe(N_2Ph)(CO)_2(PPh_3)_2]^+ + CO \qquad (6)$$

[29] (a) T. E. Nappier, D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 4194; (b) T. E. Nappier and D. W. Meek, *ibid.*, 1972, **94**, 306.

[30] (a) K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Comm.*, 1970, 1501; (b) J. H. Enemark, R. D. Feltham, J. Ricker-Nappier, and K. F. Bizot, *Inorg. Chem.*, 1975, **14**, 624.

[31] J. M. Waters and K. R. Whittle, *Chem. Comm.*, 1971, 518; G. R. Clark, J. M. Walters, and K. R. Whittle, *J.C.S. Dalton*, 1975, 463.

[32] (a) B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1972, 1268; (b) S. Cenini, F. Porta, and M. Pizzotti, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 983.

[33] D. R. Fisher and D. Sutton, *Canad. J. Chem.*, 1973, **51**, 1697.

An alternative view which merits greater attention is that attack by NO⁺, N₂Ar⁺, and similar cationic species may always be electrophilic at the electron-rich low-valent metal atom, and that displacement of CO, PPh₃, *etc.* occurs by virtue of the competition for the metal's *d*-electrons between the incumbent ligands and the electrophile. This is illustrated, for a metal carbonyl residue, in simple valence-bond terms in Scheme 6. The entering NO⁺ attacks an electron

(7)          (8)
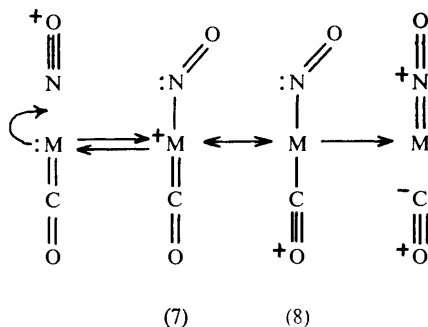
**Scheme 6**

pair in a non-bonding *d*-orbital to give (7), causing no formal change in the electron count for M. By virtue of the increased positive charge on M, it will now be less capable of back-bonding to CO, leading to an electronic arrangement more in favour of (8). Competition then arises between the capability of NO and CO to form multiple-bonds with M. Where this lies in favour of CO, the NO⁺ may either be expelled or be retained in the bent geometry of the NO⁻ formalism, as occurs[2] in the reaction of [IrCl(CO) (PPh₃)₂] with NO⁺. Where this lies in favour of NO, building of the N=M multiple bond from the nitrogen lone pair will weaken and expedite cleavage of the M—C bond. At the same time this process replaces the electrons being lost with the departure of the CO ligand, maintaining the electron count of the metal. The M(NO⁺) formalism for the complex results and the geometry is linear.

**C. Bridging N₂Ar.**—The aryldiazenato-ligand may bridge two metal atoms in structures such as (9) and (10) and in both cases it supplies three electrons to the
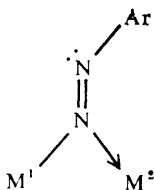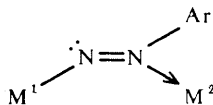
(9)                    (10)

system. Bridging nitrosyls bound in a manner comparable to (9) are well-known,[34] and this is the geometry of the single well established example[35] of a bridging aryldiazenato-ligand in the complex $[Mn(N_2Ph)(CO)_4]_2$ (24) (see p. 463). The bonds from $N^1$ to the two manganese atoms are almost identical (Table) indicating that the three electrons are shared equally by them. As expected, they are also somewhat longer than in the terminal aryldiazenato-complexes.

## 4 Synthesis

A major route to nitrosyl complexes is by reaction with NO itself, and here an immediate difference in the case of aryldiazenato-complexes becomes apparent: presently $ArN_2\cdot$ is not a readily accessible reagent on account of its instability toward dissociation to $Ar\cdot + N_2$. As a consequence, aryldiazenato-complexes have been obtained most frequently from diazonium ions, paralleling a number of recent applications of $NO^+$ to the synthesis of nitrosyl complexes.[34,36] However, new reagents such as $Me_3SiN_2Ph$ promise to be important alternatives for the introduction of $ArN_2$ ligands.[35]

**A. Substitution by Diazonium Ions.**—A metal complex frequently reacts directly with an aryldiazonium salt, the product being formed by the displacement of another ligand. Generally, an 18-electron configuration is maintained by the replacement of a two-electron donor ligand such as CO or $PR_3$ by $ArN_2^+$. Such a process is favoured by attack at an electron-rich metal site such as a substituted metal carbonyl anion, as in equations (7) and (8), but can also occur with a neutral substituted carbonyl.
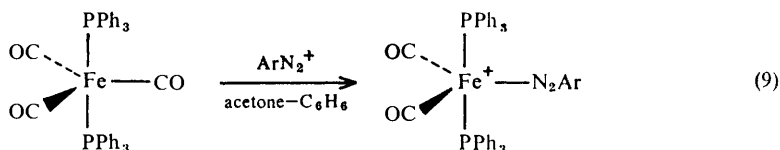


$$[\{RB(pz)_3\}Mo(CO)_3]^- \xrightarrow[DMF]{ArN_2^+} [\{RB(pz)_3\}Mo(CO)_2(N_2Ar)] + CO$$

(ref. 69)   (8)
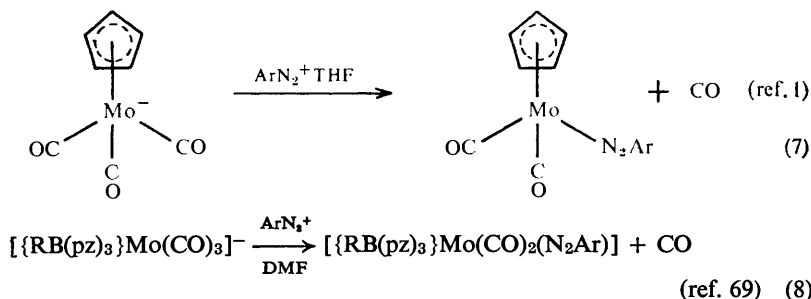
For example, $[Fe(CO)_3(PPh_3)_2]$ readily undergoes replacement of one carbonyl group by either $NO^+$ or $N_2Ar^+$ to form analogous cationic complexes $[Fe(NO)(CO)_2(PPh_3)_2]^+$ and $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+$ which are trigonal bipyramids with apical phosphines [equation (9)]. These are formally complexes of iron(0) with $NO^+$ or $N_2Ar^+$, on the basis of i.r. spectroscopy [$\nu(NN) \approx 1730$ cm$^{-1}$], and a structure determination shows a singly bent $FeN_2Ar$ group[19] (Table). Both

[34] N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.
[35] E. W. Abel, C. A. Burton, M. R. Churchill, and K.-K.G. Lin, *J.C.S. Chem. Comm.*, 1974, 268.
[36] N. G. Connelly and J. D. Davies, *J. Organometallic Chem.*, 1972, **38**, 385.

compounds may be converted into the neutral five-co-ordinate complexes [Fe(NO)X(CO)(PPh$_3$)$_2$] and [Fe(N$_2$Ar)X(CO)(PPh$_3$)$_2$] by [Ph$_3$P=N=PPh$_3$]$^+$ X$^-$(X = Cl or Br), but differ in the inertness of the aryldiazenato-complexes

$$
\begin{array}{ccc}
\underset{OC}{\overset{PPh_3}{\text{Fe}}}\text{---CO} & \xrightarrow[\text{acetone--C}_6\text{H}_6]{\text{ArN}_2{}^+} & \underset{OC}{\overset{PPh_3}{\text{Fe}^+}}\text{---N}_2\text{Ar}
\end{array}
\tag{9}
$$

towards substitution of CO by PPh$_3$, compared with the nitrosyl complexes.[37] It is also possible for the diazonium ion to react with, and abstract, the co-ordinated phosphine group from [Fe(CO)$_3$(PPh$_3$)$_2$] with the formation of highly coloured [R$_3$P—N=NAr]$^+$ cations, which have varying stability depending upon the substituents on phosphorus or the aromatic nucleus.[38] Where these cations are unstable and decompose to dinitrogen and a quaternary phosphonium salt, the erroneous impression may be obtained of the formation of transient transition-metal aryldiazenato-complexes, whereas we have found that addition of further diazonium salt may frequently yield isolable derivatives.[39]

It is appropriate at this point to examine how successful have been the attempted syntheses of other aryldiazenato-complexes of the 3d elements. The binary carbonyls [Fe(CO)$_5$], [Co$_2$(CO)$_8$], and [Ni(CO)$_4$] react with diazonium salts with vigorous evolution of N$_2$ and CO, whereas [Cr(CO)$_6$] {and [Mo(CO)$_6$]} show little reaction.[40,41] No derivatives could be obtained from [CpFe(CO)$_2$]$^-$, [Ph$_3$SnFe(CO)$_4$]$^-$, [Co{P(OMe)$_3$}$_4$]$^-$, or [CpNiCO]$^-$.[1b,42–44] The zwitterion (11)
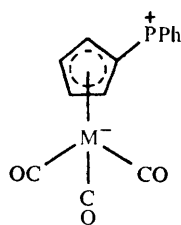
(11) M = Cr or Mo

[37] W. E. Carroll, F. A. Deeney, and F. J. Lalor, *J.C.S. Dalton*, 1974, 1430.
[38] J. A. Carroll, D. R. Fisher, G. W. Rayner Canham, and D. Sutton, *Canad. J. Chem.*, 1974, **52**, 1914.
[39] N. Farrell and D. Sutton, unpublished results.
[40] G. N. Schrauzer, *Chem. Ber.*, 1961, **94**, 1891.
[41] J. C. Clark and R. C. Cookson, *J. Chem. Soc.*, 1962, 686.
[42] W. E. Carroll and F. J. Lalor, *J. Organometallic Chem.*, 1973, **54**, C37.
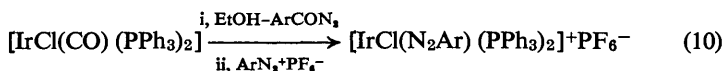[43] A. N. Nesmeyanov, Y. A. Chapovskii, and L. G. Makarova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965, 1310.
[44] E. L. Muetterties and F. J. Hirsekorn, *J.C.S. Chem. Comm.*, 1973, 683.

yields an aryldiazenato-derivative by replacement of one CO group in the case of Mo but not Cr.[45] The first aryldiazenato-complexes of chromium have been synthesized by reaction of the compounds $[(C_5H_5)Cr(CO)_3]^-$ or $[(C_6Me_6)Cr(CO)_3]$ with a variety of aryldiazonium salts.[46] The latter yields $[(C_6Me_6)Cr(N_2Ar)(CO)_2]^+$ salts, which undergo nucleophilic attack by $H^-$ at the arene ring to yield neutral complexes $[(C_6Me_6H)Cr(N_2Ar)(CO)_2]$ in apparent preference to attack at the aryldiazenato-ligand. Surprisingly, in view of the iron results already described, the phosphine-substituted complex $[(C_6Me_6)Cr(CO)_2(PPh_3)]$ is not substituted by $ArN_2^+$, but is instead oxidized to the monocation.[46a]

Thus far, attempts to secure isolable aryldiazenato-derivatives of unsubstituted metal carbonyls or metal carbonyl anions have been notably unsuccessful. King[1] failed to obtain derivatives from $[V(CO)_6]^-$, $[Mn(CO)_5]^-$, and $[Co(CO)_4]^-$, and attributed this to labilization of metal–carbon monoxide bonds by the presence of the good electron-withdrawing aryldiazenato-group. More recently, Carroll and Lalor[18] confirmed that at $-70$ °C reaction does occur with these anions to give highly coloured species which may be aryldiazenato-derivatives, but that these do not survive warming to room temperature. In the case of $[Co(CO)_4]^-$, but not the others, they were able to isolate an unstable triphenylphosphine derivative, believed to be $[Co(N_2Ph)(CO)_2PPh_3]$ from i.r. spectroscopy. The stable complex $[Fe(N_2Ph)(NO)(CO)PPh_3]$ was obtained similarly from $[Fe(NO)(CO)_3]^-$. The manganese complex $[Mn(N_2Ph)(CO)_4]_2$, containing bridging $N_2Ph$ ligands,[35] presently stands as the sole example of an unsubstituted metal carbonyl aryldiazenato-complex, and its synthesis is described in Section 4F.

As a matter of contrast, the CO group in the 16-electron Vaska's complex is tightly held, and its reactions with diazonium ions (to be described in Section 5C) give a variety of products, in none of which has the CO group been displaced. However, by allowing the carbonyl to react with an aroyl azide followed immediately by the addition of an aryldiazonium salt,[47] the CO group is effectively substituted by $ArN_2^+$, almost certainly owing to the formation of the more labile dinitrogen complex as an intermediate [equation (10)].

$$[IrCl(CO)(PPh_3)_2] \xrightarrow[\text{ii, ArN}_2^+\text{PF}_6^-]{\text{i, EtOH–ArCON}_3} [IrCl(N_2Ar)(PPh_3)_2]^+PF_6^- \qquad (10)$$

The stoichiometry, synthesis, and high $\nu(NN)$ value of 1868 cm$^{-1}$ of this green salt all point to a square-planar Ir$^I$ complex possessing a singly bent $N_2Ar^+$ ligand. Like its carbonyl and nitrosyl analogues, $[IrCl(N_2Ar)(PPh_3)_2]^+$ displays numerous reactions. Addition of neutral ligands L, such as CO, PR$_3$, AsR$_3$, SbR$_3$, and RNC, occurs to form five-co-ordinate cationic species. These compounds may alternatively be synthesized from $IrCl(PPh_3)_2L$ and $ArN_2^+$. From experience with related compounds, the geometries of these compounds are

[45] D. Cashman and F. J. Lalor, (*a*) *J. Organometallic Chem.*, 1970, **24**, C29; (*b*) *ibid.*, 1971, **32**, 351.
[46] (*a*) N. G. Connelly and Z. Demidowicz, *J. Organometallic Chem.*, 1974, **73**, C31; (*b*) M. Heberhold and W. Bernhagen, *Z. Naturforsch.*, 1974, **29b**, 801.
[47] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3052.

postulated to be trigonal bipyramids (with singly bent $N_2Ar$) for the tris-($ER_3$) complexes (E = P, As, or Sb) and square pyramids (with apical doubly bent $N_2Ar$) for the bisphosphine carbonyl or isocyanide.

An example[14] of the displacement of phosphine, accompanied by co-ordination of halide to give the preferred six-co-ordinate complex,[20,48] is given in equation (11).



$$\text{(11)}$$
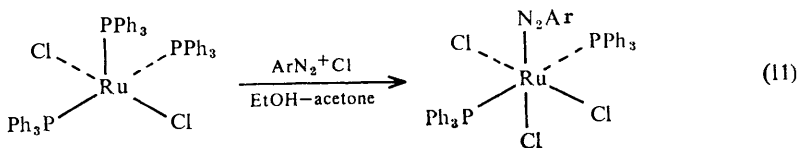
The *X*-ray structure[20] of the product indicates it to be a complex of ruthenium(II) (Table) involving no change in ruthenium oxidation state. The reaction therefore belongs to the substitution type, and not to the class of oxidative–addition reactions now to be described.

**B. Oxidative Addition of Diazonium Ions.**—There does not appear, as yet, to be any established instance of the simple addition of the diazonium ion (*i.e.* as a Lewis base) to a transition-metal complex without either ligand displacement or an increase in the oxidation state of the metal. An inspection of all known instances of simple addition indicates to this author that they fall into the general category of Lewis-acid addition, *i.e.* a reaction of the type illustrated in Schemes 4 or 5 is implied and the product is of the $N_2Ar^-$ complex type.* In only one instance is this presently established by *X*-ray diffraction, but the chemical, spectroscopic, and structural properties of the remainder, especially where nitrosyl analogues of known structure exist, point strongly to this conclusion.

The structurally established example[3] is (12), the product of diazonium ion addition to the dissociation-stabilized phosphine analogue (13) of Wilkinson's compound [RhCl(PPh_3)_3]. Although no analogous compound has been isolated from [RhCl(PPh_3)_3] itself, probably owing in part to dissociation of a phosphine ligand, simultaneous addition of $Cl^-$ yields $[Rh(N_2Ar)Cl_2(PPh_3)_2]$, which must be expected to be a complex of rhodium(III) also.[14] These are examples of the oxidative–addition conversion of $d^8$ complexes into $d^6$; the reaction is also exhibited in the conversion of $d^{10}$ complexes into square-planar $d^8$ species. Cenini *et al.*,[49] have described the reaction of a series of *p*-substituted phenyldiazonium salts with [Pt(PPh_3)_3] to yield the platinum(II) complexes $[Pt(N_2C_6H_4X)(PPh_3)_3]Y$ (X = *p*-NO_2, F, H, OMe, Me, NEt_2, or NMe_2; Y = BF_4 or BPh_4) [equation (12)].

*Note added in proof: The crystal structure of $[IrCl(NPh)(PPh_2Me)_3]^+$ synthesized from $[IrCl(PPh_2Me)_3]$ and $PhN_3^+$ indicates a $Ir^I(N_3Ph^+)$ structure. (B. J. Haymore and J. A. Ibers, personal communication.)

[48] (a) J. A. McCleverty and R. N. Whiteley, *Chem. Comm.*, 1971, 1159; (b) J. A. McCleverty, D. Seddon, and R. N. Whiteley, *J.C.S. Dalton*, 1975, 839.

[49] S. Cenini, R. Ugo, and G. LaMonica, *J. Chem. Soc. (A)*, 1971, 3441.

(12)                                    (13)

$$[Pt(PPh_3)_3] \xrightarrow[\text{Et}_2\text{O-EtOH}]{\text{ArN}_2^+} [Pt(N_2Ar)(PPh_3)_3]^+ \qquad (12)$$
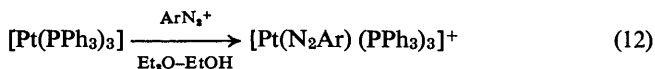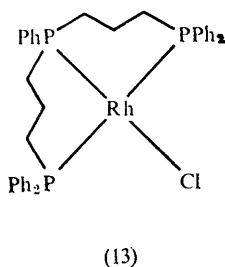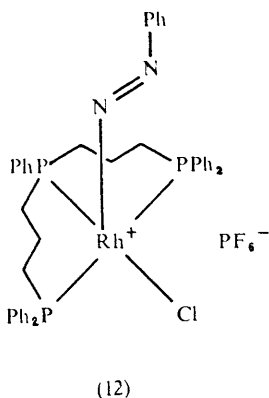
Partial replacement of PPh₃ from these complexes can be accomplished to yield some examples of the neutral complexes $[Pt(N_2C_6H_4X)(PPh_3)_2Z]$ (Z = N₃ or I). These complexes are presumably square planar, with a doubly bent aryldiazenato-ligand. Similar derivatives could not be isolated with $[Pt(PPh_3)_2L]$, where L is $CH_2{=}CH_2$ or $CH_2{=}CHCN$. The cations react with H₂ at 1 atm and room temperature in the absence of catalyst to evolve N₂ and give $[PtH(PPh_3)_3]^+$ $BF_4^-$, and no intermediate aryldiazene or hydrazine complexes were observed. They can, however, be reversibly protonated by non-co-ordinating acids to yield the aryldiazene complexes $[Pt(NH{=}NC_6H_4X)(PPh_3)_3]^{2+}$ $(BF_4)_2$.

These compounds are analogues of the platinum triethylphosphine complexes synthesized by Parshall[50] and by Garner and Mays,[51] using insertion of ArN₂⁺ into $[PtHL(PEt_3)_2]$ complexes as described in Section 4C. It is therefore surprising that these neutral and cationic aryldiazenato-complexes are all considered to have $\nu(NN)$ at about 1580 cm⁻¹, whereas it has been verified by ¹⁵N substitution[13] to occur at 1463 cm⁻¹ in the neutral complex $[PtCl(N_2C_6H_4F)(PEt_3)_2]$ and appears to occur at about 1580 cm⁻¹ in the corresponding cationic triethylphosphine complexes,[51] though this has not been confirmed by ¹⁵N substitution. A band at *ca.* 1150 cm⁻¹ has also been assigned to $\nu(NN)$ in the triphenylphosphine aryldiazene complexes,[49] but this appears to be unusually low and the assignment must await additional confirmation. Cook and Jauhal[52] have used potentially chelating ligands to displace co-ordinated ethylene from $[Pt(PPh_3)_2(C_2H_4)]$; for example benzenediazonium-1,2-carboxylate (14) reacts to form the Ptᴵᴵ complex (15). Several other examples of oxidative addition of diazonium ions to noble metal compounds will be found in Section 5.
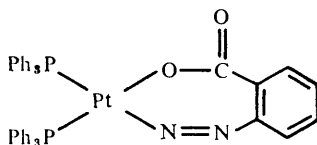
⁵⁰ G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133.
⁵¹ A. W. B. Garner and M. J. Mays, *J. Organometallic Chem.*, 1974, **67**, 153.
⁵² C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, 1968, **90**, 1464; T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *Chem. Comm.*, 1968, 821.
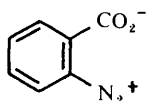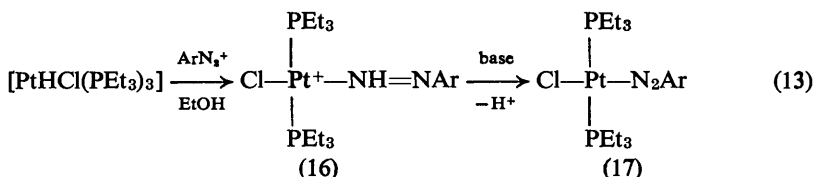
(14)                                        (15)

## C. Apparent Insertion by Diazonium Ions.

This reaction was first recorded by Parshall,[50] who showed that diazonium ion would react with *trans*-[PtHCl(PEt₃)₂] to yield initially the product of 'insertion' of the diazonium ion into the Pt—H bond namely, the aryldiazene complex (16), which could be deprotonated to the aryldiazenato-complex (17) [equation (13)]. The overall reaction is equivalent to



$$[\text{PtHCl(PEt}_3)_3] \xrightarrow[\text{EtOH}]{\text{ArN}_2^+} \text{Cl—Pt}^+\text{—NH}{=}\text{NAr} \xrightarrow[-\text{H}^+]{\text{base}} \text{Cl—Pt—N}_2\text{Ar} \qquad (13)$$

(16)                    (17)

replacement of H⁻ by ArN₂⁻ and involves no change in oxidation state of the metal. This reaction was subjected to detailed comparison with the enzymatic reduction of dinitrogen by nitrogenase, and led to important postulates as to the nature of the binding and reduction of dinitrogen in the enzyme system.[10,13] The square-planar geometry of (16) has been established by *X*-rays,[15] confirming the formal $\text{Pt}^{\text{II}}$ oxidation state and, by implication, the $\text{N}_2\text{Ar}^-$ nature of (17). Additionally the hydrogen atom is found to be located on $\text{N}^1$, confirming the conclusion arrived at by Parshall on the basis of ¹H n.m.r. spectroscopy using ¹⁵N at this position.

By replacing Cl with a neutral ligand L such as $\text{NH}_3$, pyridine (py), $\text{PEt}_3$, and EtNC these compounds have been converted[51] into the cationic aryldiazenato-complexes (18) and the dicationic aryldiazene complexes (19). The instability of (18) in favour of decomposition to $[\text{Pt(Ar)L(PEt}_3)_2]^+$ by extruding dinitrogen appears to follow a sequence $\text{NH}_3 \approx \text{py} < \text{PEt}_3 \approx \text{EtNC} < \text{CO}$, and in the case of CO only the σ-aryl complex was obtained. The mechanism of this reaction is not known, but it clearly appears to be enhanced by the presence of
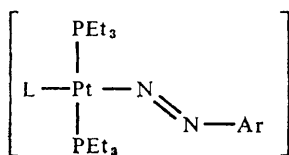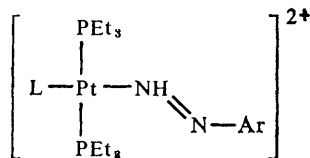


(18)                                        (19)

a $\pi$-acceptor ligand *trans* to the aryldiazenato-ligand. The *X*-ray results on the diazene complex (16) show little *trans*-influence on the part of either Cl or NH=NC$_6$H$_4$F, and since ArNNH and ArN$_2^-$ appear at present to be primarily $\sigma$-bonding ligands, the absence of a *trans*-ligand high in the *trans*-influence series readily can be appreciated as a criterion for the stability of these platinum complexes.

The $^{19}$F n.m.r. of the *p*- and *m*-fluorophenyldiazenato-complexes have been compared in efforts to estimate the importance of $\sigma$ and $\pi$ effects in the bonding of the aryldiazenato-ligand to platinum, and the interpretation of the results has been the subject of some controversy. Parshall[13] initially interpreted the difference $(\delta_p - \delta_m)$ in the $^{19}$F chemical shifts of the neutral *p*- and *m*-fluoro-complexes [PtCl(N$_2$C$_6$H$_4$F) (PEt$_3$)$_2$] to indicate a substantial contribution of resonance structures such as (20) to the electronic structure of the complexes. Garner and

$$F-\langle\phantom{x}\rangle=N-N=Pt^+-Cl$$

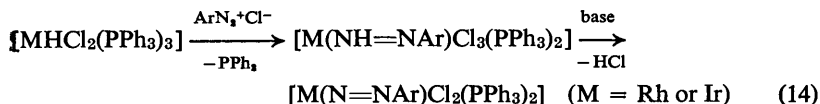with PEt$_3$ above and PEt$_3$ below the Pt centre.
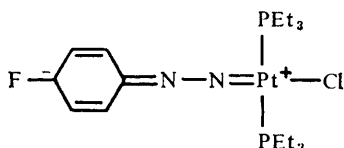
(20)

Mays,[51] however, consider that this criterion overestimates resonance effects. They interpret the results for the neutral complexes (and additional new results for the cationic complexes) in terms of the Taft $\sigma_I$ and $\sigma_R$ parameters. They conclude that in neutral [PtCl(N=NAr) (PEt$_3$)$_2$] there is weak $\pi$-donor and weak $\sigma$-acceptor behaviour on the part of the (PEt$_3$)$_2$ClPtN$_2$ fragment towards the FC$_6$H$_4$ ring, and that in the cationic complexes [Pt(N=NAr)L(PEt$_3$)$_2$]$^+$ the (PEt$_3$)$_2$LPtN$_2$ group acts as a distinctly better $\sigma$-acceptor (as expected) with the $\pi$-donor ability suffering minimal change. It is regrettable that these studies have not included the aryldiazene complexes for better comparison with the crystallographic dimensions. Nevertheless, this interpretation seems to correlate sensibly with the expected properties of the doubly bent ArN$_2^-$ ligand. In this connexion, Lalor and co-workers[53] have measured the $^{19}$F n.m.r. chemical shifts of the *m*- and *p*-fluorophenyldiazenato-group for a wide selection of complexes of iron, molybdenum, tungsten, and platinum and have attempted to correlate the $(\delta_p - \delta_m)$ values with $\nu$(NN) determined from $^{15}$N-substitution studies* and $\pi$-effects. A re-examination of these results in terms of the Taft $\sigma_R$ and $\sigma_I$ parameters would clearly also be of some interest.

*Note that $\nu$(NN) values were not corrected (see ref. 80*b*).
[53] W. E. Carroll, M. E. Deane, and F. J. Lalor, *J.C.S. Dalton*, 1974, 1837.

Insertion of $ArN_2^+$ into M—H bonds has also been observed for ruthenium,[14,54] rhodium,[14] and iridium,[14,55,56] for example equation (14).[14]
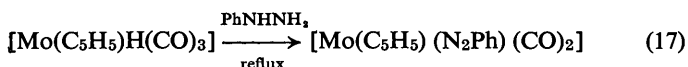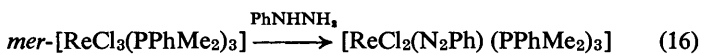
$$[MHCl_2(PPh_3)_3] \xrightarrow[\substack{-PPh_3}]{ArN_2^+Cl^-} [M(NH{=}NAr)Cl_3(PPh_3)_2] \xrightarrow[\substack{-HCl}]{base}$$

$$[M(N{=}NAr)Cl_2(PPh_3)_2] \quad (M = Rh \text{ or } Ir) \quad (14)$$

It should be pointed out, however, that sometimes 'insertion' occurs to give an identifiable aryldiazene complex but the corresponding aryldiazenato-derivative is not easily isolated after attempted deprotonation.[14,56]

**D. Reaction of Co-ordinated NO with ArNH₂.**—Nitrosyl complexes which correspond to the $NO^+$ formalism are potential electrophiles, to an extent which may be loosely related to the direct magnitude of $\nu(NO)$.[57] Attack by $RNH_2$ may yield aryldiazenato-complexes according to equation (15), and in this way

$$M{-}NO + RNH_2 \rightarrow M{-}N_2R + H_2O \quad (15)$$

the compounds $[Ru(bipy)_2(N_2R)Cl](PF_6)_2$ ($R = p\text{-}MeOC_6H_4$ or $p\text{-}MeC_6H_4$) have been synthesized from $[Ru(bipy)_2(NO)Cl](PF_6)_2$.[58] These possess remarkably high $\nu(NN)$ values of 2095 and 2080 $cm^{-1}$ respectively, which at least attest to their formulation as $N_2Ar^+$ complexes of ruthenium(II) and possibly may indicate a molecular geometry in which the NNAr angle is considerably greater than 120°, *i.e.* tending towards structure (2). This synthesis is probably restricted to nitrosyl complexes having $\nu(NO)$ greater than about 1900 $cm^{-1}$ and may be of less general usefulness than even this, as in the author's laboratory and elsewhere the NO group in a number of such nitrosyl complexes has been found not to react similarly with amines.[57,59,60]

**E. Reaction with Arylhydrazines.**—There are several instances where arylhydrazines have reacted with a transition-metal complex to form an aryldiazenato-complex by an *in situ* oxidation of the hydrazine as in equations (16) and (17).[17,61]

$$mer\text{-}[ReCl_3(PPhMe_2)_3] \xrightarrow{PhNHNH_2} [ReCl_2(N_2Ph)(PPhMe_2)_3] \quad (16)$$

$$[Mo(C_5H_5)H(CO)_3] \xrightarrow[\substack{reflux}]{PhNHNH_2} [Mo(C_5H_5)(N_2Ph)(CO)_2] \quad (17)$$

The linearity of the Re—N—N skeleton and the 118° angle at $N^2$ (Table) suggest

[54] D. F. Gill, B. E. Mann, and B. L. Shaw, *J.C.S. Dalton*, 1973, 311.

[55] L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455.

[56] G. Caglio and M. Angoletta, *Gazzetta*, 1972, **102**, 462.

[57] F. Bottomley, W. V. F. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919; F. Bottomley, personal communication.

[58] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.

[59] L. Busetto, A. Palazzi, D. Pietropaolo, and G. Dolcetti, *J. Organometallic Chem.*, 1974, **66**, 453.

[60] J. A. Carroll and D. Sutton, unpublished results.

[61] M. L. H. Green, J. R. Sanders, and R. N. Whiteley, *Z. Naturforsch.*, 1968, **23b**, 106.

formulation of $[ReCl_2(N_2Ph)(PPhMe_2)_3]$ as an $N_2Ph^+$ compound of rhenium(I) rather than an $N_2Ph^-$ complex as originally proposed.[17] The molybdenum compound may be formulated as a $N_2Ph^+$ complex by analogy with the dimensions in the Table of the corresponding $HB(pz)_3$ derivative.[16]

An interesting example of the ligand tautomerism which may occur is the reaction of benzoylhydrazine with $[ReOCl_3(PPh_3)_2]$.[4a] Spectroscopy favours the presence of a benzoylhydrazido(3 −) ligand as in (21) rather than the chelating benzoyldiazenato-ligand illustrated in the resonance structure (22). However,



(21)                    (22)
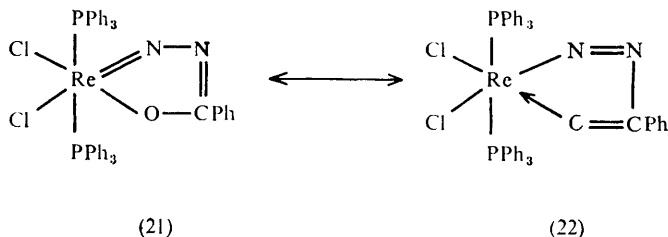
reaction with chlorine or with nucleophiles opens the ring to yield benzoyldiazenato-complexes, as in Scheme 7. These were described[4a] as $Re^{IV}$ and $Re^{III}$
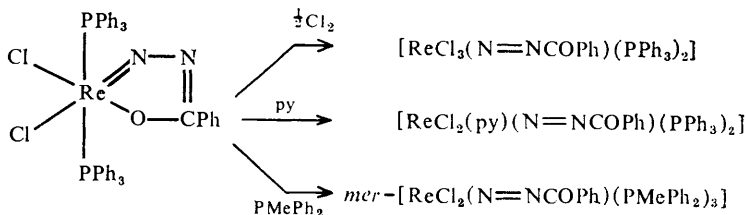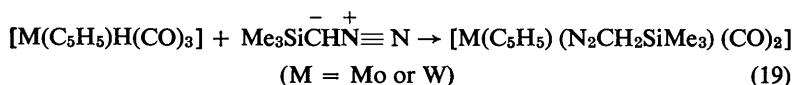


**Scheme 7**

complexes, implying the presence of $(N_2COPh^-)$, but a $Re^I(N_2COPh^+)$ formulation seems to be more in keeping with the $X$-ray-determined linear Re—N—N skeleton reported[4a,7] for $[ReCl_2(N_2COPh)(PMe_2Ph)_3]$ (Table); it is also consistent with the 18-electron rule, though it is by no means certain that these compounds need necessarily conform to this rule. Apparently rhenium acyldiazenato-complexes could not be synthesized in a comparable manner from acylhydrazines such as $MeCONHNH_2$. However, the rhenium(I) dinitrogen compound $[ReCl(N_2)(PMe_2Ph)_4]$ may be converted[4b] into the benzoyldiazenato- or acetyldiazenato-complex using benzoyl or acetyl chloride [equation (1)]. The disphosphine complex $[ReCl(N_2)(diphos)_2]$, does not undergo this reaction, which requires the loss of a labile monophosphine ligand; it may be compared with the aroylation or acylation of the molybdenum and tungsten compounds in equation (18) which proceeds accompanied by the loss of the

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second labile dinitrogen ligand.[5,62] The original rhenium(I) dinitrogen complex is

$$[M(N_2)_2(PR_3)_4] \xrightarrow{RCOX} [M(N_2COR)(PR_3)_4X] \xrightarrow{HX} [M(N_2(H)COR)(PR_3)_4X] \quad (18)$$

$$(M = Mo \text{ or } W)$$
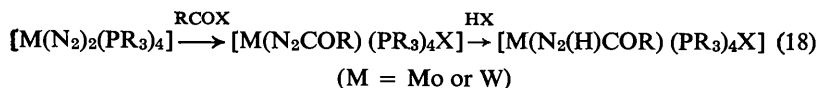
regenerated in the presence of excess phosphine. The reaction illustrated in equation (18) is not confined to acid halides, and importantly it occurs with HX and MeX (X = Cl or Br). The former[5] is the first example of protonation of a co-ordinated dinitrogen ligand in a stable complex; it has not proved possible[4b] to protonate the $[ReCl(N_2)(PR_3)_4]$ complexes or to protonate, acylate, or aroylate the dinitrogen in $[OsCl_2(N_2)(PEt_2Ph)_3]$. The second[4c,63] is important in providing rare examples of alkyldiazenato-complexes. The latter are generally inaccessible by the more convenient routes used for aryldiazenato-complexes by virtue of the instability of alkyldiazonium ions, but a methyldiazenato-molybdenum complex, $[Mo(N_2Me)(S_2CNR_2)_3]$, has been obtained by the reaction of methylhydrazine with $[MoO_2(S_2CNR_2)_2]$[64] and a trimethylsilylmethyldiazenato-complex has been synthesized by the 1,3-insertion reaction [equation (19)].[65]

$$[M(C_5H_5)H(CO)_3] + Me_3SiCH\overset{-}{N}\equiv\overset{+}{N} \rightarrow [M(C_5H_5)(N_2CH_2SiMe_3)(CO)_2]$$

$$(M = Mo \text{ or } W) \quad (19)$$

This compound may be compared with the structure of (23)[66] established by *X*-rays[67] where 1,3-addition of $EtO_2CCH\overset{-}{N}\equiv\overset{+}{N}$ across a molybdenum carbonyl centre in $[Mo(C_5H_5)(CO)_3]^-$ has taken place, followed by protonation and rearrangement to the carbene.
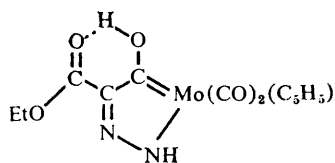


(23)

**F. Reaction with Organodiazenes.**—This reaction is in principle the replacement of $R^2$ in an organic diazene by a metal [equation (20)]. It has received little

[62] J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 444.
[63] (*a*) J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, Abstracts of the International Symposium on Nitrogen Fixation, Pullman, Washington, June 1974, p. 2; (*b*) T. A. George and S. D. A. Iske, *ibid.*, p. 4.
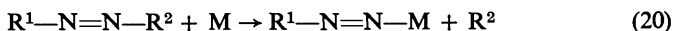[64] M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Organometallic Chem.*, 1974, **73**, C59.
[65] M. F. Lappert and J. S. Poland, *Chem. Comm.*, 1969, 1061.
[66] M. L. H. Green and J. R. Sanders, *Chem. Comm.*, 1967, 956.
[67] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1952.

attention so far, but recent results for silyl compounds indicate that this may

$$R^1—N{=}N—R^2 + M \rightarrow R^1—N{=}N—M + R^2 \qquad (20)$$

well turn out to be a generally useful method. Trimethylsilyl(phenyl)diazene, $Me_3SiN{=}NPh$, removes the bromide ligand from $[Mn(CO)_5Br]$ with the formation[35] of the novel dimer $[Mn(N_2Ph)(CO)_4]_2$ [equation (21)].

$$[Mn(CO)_5Br] + Me_3SiN{=}NPh \xrightarrow{-CO} [\{Mn(N_2Ph)(CO)_4\}_2] + Me_3SiBr \quad (21)$$
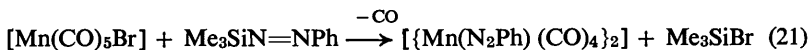
The molecular structure (24) of this first established example of a bridging aryldiazenato-ligand has been discussed in Section 3C.

*N*-Methyl-*N*-nitrosotoluene-*p*-sulphonamide is a convenient source of nitrosyl ligands in the single-step synthesis of numerous nitrosyl complexes of the platinum metals, but the analogous aryldiazenes, $p$-$MeC_6H_4SO_2N(Me)N_2Ar$ do not appear to afford clean syntheses of corresponding aryldiazenato-complexes.[14] 1,3-Diaryltriazenes, ArHN—N=NAr or Ar(Me)N—N=NAr, cleave readily in acid solution to produce the diazonium ion *in situ*, and these reagents have been found to give rise to aryldiazenato-complexes in some instances.[14]



(24)
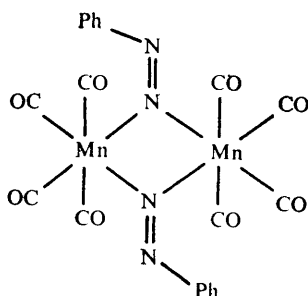
# 5 Aryldiazenato-complexes of 4*d* and 5*d* Metals

At present, aryldiazenato-complexes have been synthesized containing chromium, manganese, iron, cobalt, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, and platinum. The main features of the compounds of the 3*d* metals and of rhenium and platinum have been dealt with in the preceding sections. The most extensive studies have been concerned with the pairs of elements molybdenum and tungsten, ruthenium and osmium, and rhodium and iridium. An abbreviated review of the aryldiazenato-complexes of these metals is presented here in order to indicate the nature and scope of the present situation.

## A. Molybdenum and Tungsten.—King[1] prepared the prototype aryldiazenato-complexes (25) for molybdenum [equation (7)] but was unable to obtain a
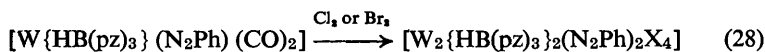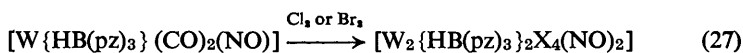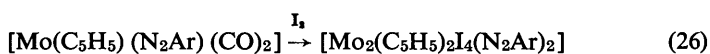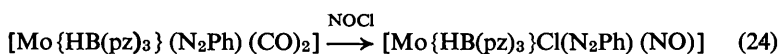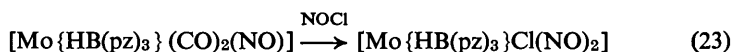
tungsten analogue, though this was soon synthesized by Nesmeyanov[68] *via* a similar reaction at $-60\ °C$. The $\sigma$-aryl complex $[W(C_5H_5)Ph(CO)_2]$ was obtained also, but it is not clear whether this arises from competitive nucleophilic attack at carbon or as a result of nitrogen extrusion from the aryldiazenato-complex
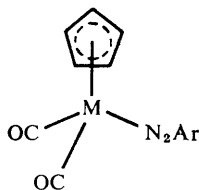


(25)  M = Mo or W

(*cf.* the platinum compounds[50,51]). The aryldiazenato-complexes may be obtained alternatively from the cyclopentadienylcarbonylhydrides and phenylhydrazine[61] [equation (17)]. An extensive series of analogous complexes in which $\eta$-$C_5H_5$ is replaced by a polypyrazolylborate ligand $[RB(pz)_3^-]$ has been synthesized by Trofimenko.[69]

The similarities in the chemistries of the analogous NO and $N_2Ar$ complexes are illustrated by equations (23)—(28).[70–72]

$$[Mo\{HB(pz)_3\}(CO)_2(NO)] \xrightarrow{NOCl} [Mo\{HB(pz)_3\}Cl(NO)_2] \qquad (23)$$

$$[Mo\{HB(pz)_3\}(N_2Ph)(CO)_2] \xrightarrow{NOCl} [Mo\{HB(pz)_3\}Cl(N_2Ph)(NO)] \qquad (24)$$

$$[Mo(C_5H_5)(CO)_2(NO)] \xrightarrow{X_2} [Mo_2(C_5H_5)_2X_4(NO)_2] \qquad (25)$$

$$[Mo(C_5H_5)(N_2Ar)(CO)_2] \xrightarrow{I_2} [Mo_2(C_5H_5)_2I_4(N_2Ar)_2] \qquad (26)$$

$$[W\{HB(pz)_3\}(CO)_2(NO)] \xrightarrow{Cl_2\ or\ Br_2} [W_2\{HB(pz)_3\}_2X_4(NO)_2] \qquad (27)$$

$$[W\{HB(pz)_3\}(N_2Ph)(CO)_2] \xrightarrow{Cl_2\ or\ Br_2} [W_2\{HB(pz)_3\}_2(N_2Ph)_2X_4] \qquad (28)$$

However, interesting differences in the $HB(pz)_3$ *vs.* $(C_5H_5)$ and $N_2Ar$ *vs.* NO relationships become evident upon closer examination, and the former may in part be accounted for by the greater bulk of the $HB(pz)_3$ ligand. For example, the products in equations (27) and (28) might appear to be of similar structure, but the observation that $\nu(NN)$ is so much lower than $\nu(NO)$ in the i.r. spectrum

[68] A. N. Nesmeyanov, Y. A. Chapovskii, N. A. Ustyniuk, and L. G. Makarova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 449.

[69] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675; *J. Amer. Chem. Soc.*, 1970, **92**, 5118.

[70] M. E. Deane and F. J. Lalor, *J. Organometallic Chem.*, 1973, **57**, C61.

[71] M. E. Deane and F. J. Lalor, *J. Organometallic Chem.*, 1974, **67**, C19.

[72] T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1971, 1068.

points to an entirely different structure for the aryldiazenato-complex containing ($N_2Ar^-$) rather than ($N_2Ar^+$); furthermore, considerable differences occur in the behaviour of analogous molybdenum and tungsten aryldiazenato-complexes upon halogenation.[71] The synthesis of other molybdenum and tungsten aryldiazenato-complexes has been reported.[48,73]

**B. Ruthenium and Osmium.**—The obvious question to be asked when comparison is made of $ArN_2^+$ with isoelectronic molecules is the possibility of synthesizing $[Ru(NH_3)_5(N_2Ar)]^{3+}$, analogous to the known $[Ru(NH_3)_5X]^{n+}$ ions, where X is $NO^+$, $N_2$, or CO.[74] The answer is presently negative: attempted direct displacement of $H_2O$ from $[Ru(NH_3)_5(H_2O)]^{2+}$ by $N_2Ar^+$ yielded dinuclear dinitrogen complexes,[75] and various other attempts involving phenylhydrazine *etc.* have led to the same product.[60] There is no obvious reason why this ion should not exist, but no method has yet achieved the correct experimental conditions, *i.e.* to avoid a cation–cation reaction or the *in situ* liberation of $N_2$.

The reaction of $ArN_2^+$ with $[RuCl_2(PPh_3)_3]$ does not seem to be simple, and leads to compounds such as $[Ru_n(N_2Ar)_n(PPh_3)_{2n}Cl_{2n}]$ $[BF_4]_n$, where probably $n = 2$.[48] However, ruthenium and osmium aryldiazenato-complexes of the type $[MX_3(N_2Ar)(PPh_3)_2]$ result from addition of LiX to the reaction.[14,20,48] These exhibit $\nu(NN)$ frequencies in the range 1850—1900 $cm^{-1}$, strongly indicative of an $N_2Ar^+$ formulation, and this is confirmed by two independent crystal-structure determinations of solvates of *mer*-$[RuCl_3(N_2C_6H_4Me$-$p)$-$(PPh_3)_2]$ in which a singly bent $N_2Ar$ ligand is observed[19,20] (Table). There is a parallel series of nitrosyl complexes $[MX_3(NO)(PPh_3)_2]$[76] having $\nu(NO)$ values closely similar to these $\nu(NN)$ values, indicative of analogous linear $NO^+$ formulations. The aryldiazenato-complexes are resistant to protonation under mild conditions.[14] $[RuCl_3(N_2Ar)(PPh_3)_2]BF_4$ is also reported to be the product of chlorination of the interesting compound described[48] as the bis(aryldiazenato) complex $[RuCl(N_2Ar)_2(PPh_3)_2]BF_4$. A complex of this composition may be analogous to the known bis(nitrosyl) $[RuCl(NO)_2(PPh_3)_2]PF_6$, which has been shown by Pierpont and Eisenberg[77] to be formally a $Ru^{II}$ complex with both linear ($NO^+$) and bent ($NO^-$) nitrosyl groups. A full *X*-ray structure determination would establish this analogy; unfortunately the attempted preparation of single crystals of this compound led instead to isolation of a solvate of $[RuCl_3(N_2Ar)(PPh_3)_2]$.[20] This interesting compound deserves a renewed effort at characterization and structure elucidation. Indeed, its synthesis from $[RuHCl(PPh_3)_3]$ and $ArN_2^+$ alone deserves further work to elucidate the nature and stability of possible intermediates such as $[Ru(NHNAr)Cl(PPh_3)_3]^+$ and their ease of deprotonation.

[73] F. J. Lalor and P. L. Pauson, *J. Organometallic Chem.*, 1970, **25**, C51.
[74] J. N. Armor, *Inorg. Chem.*, 1973, **12**, 1959; J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Chem. Soc. (A)*, 1971, 3168.
[75] V. B. Shur, I. A. Tikhonova, and M. E. Vol'pin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1972, 212.
[76] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1972, 1.
[77] C. G. Pierpoint and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1088.

The reactions of ruthenium and osmium carbonyls and carbonyl hydrides have received some attention. The reaction of nitrosonium ions with $[Ru(CO)_3(PPh_3)_2]$ differs from the case of the corresponding iron compounds in that no nitrogen-containing complexes result,[32a] bu trecently[32b] complexes $[Ru(N_2Ar)(CO)_2(PPh_3)_2]^+$ have been obtained with diazonium ions, paralleling the iron case. The monohydrido-complexes $[RuHCl(CO)(PPh_3)_3]$ and $[OsHCl(CO)(PPh_3)_3]$ react with diazonium tetrafluoroborates to yield complexes of stoicheiometry $MCl(BF_4)(NH=NAr)CO(PPh_3)_2$, believed to contain co-ordinated $BF_4$. These compounds in solution probably have $BF_4$ replaced by solvent[48b] and readily absorb CO to yield the *cis*-dicarbonyl complexes $[MCl(NH=NAr)(CO)_2(PPh_3)_2] BF_4$ or react with LiCl to yield $[MCl_2(NH=NAr)CO(PPh_3)_2]$. The dicarbonyl salts react with LiCl to yield mixtures of $[MCl_2(NH=NAr)(CO)(PPh_3)_2]$ and *cis*-$[MCl_2(CO)_2(PPh_3)_2]$; the fate of the liberated aryldiazene in the formation of the latter product is intriguing, but was not ascertained. The aryldiazene ligand is also removed from $[MCl_2(NH=NAr)CO(PPh_3)_2]$ by CO to give $[MCl_2(CO)_2(PPh_3)_2]$, and is not hydrogenated under mild conditions.[14] Shaw *et al.*[54] observed the insertion of $PhN_2^+$ into the Ru—H bond of $[RuHCl(CO)_2(PPr^n_2Bu^n)_2]$ to produce $[RuCl(NH=NPh)(CO)_2(PPr^n_2Bu^n)_2]BF_4$ $[\tau(NH) = -3.57]$ but no attempt at deprotonation was reported.

The dihydrido-complexes $[MH_2(CO) (PPh_3)_3]$ react with *p*-tolyldiazonium fluoroborates to give $[MH(NH=NAr)CO(PPh_3)_3] BF_4$; reaction of the second M—H bond is not reported to occur, despite the fact that an almost $2:1 [ArN_2^+]$ : [complex] ratio was employed.[14] The aryldiazene complexes react with LiCl to yield $[MCl_2(NH=NAr)CO(PPh_3)_2]$ and, for ruthenium, also $[RuHCl(NH=NAr)CO(PPh_3)_2]$. Deprotonation of several of these aryldiazene complexes described above probably occurs in solution (as judged by colour changes) but no aryldiazenato-complex analogues of the corresponding known nitrosyls were isolated. The $\tau(NH)$ values for all these complexes were in the range $-3.8$ to $-1.6$, indicating acidic protons, and the $J(^{15}NH)$ values were *ca.* 69 Hz. Reactions of diazonium salts with $[RuH_2(PPh_3)_4]$ and $[OsH_4(PPh_3)_3]$ are immediate, but the products decompose spontaneously with evolution of $N_2$.[14]
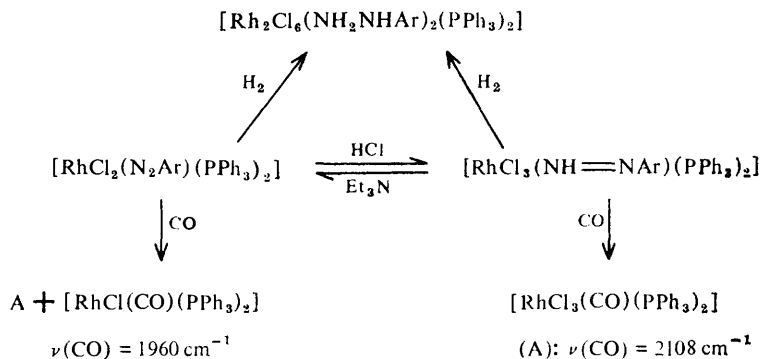
**C. Rhodium and Iridium.**—Baird and Wilkinson[78] were the first to report the reaction of diazonium ions with rhodium(I) complexes. $[RhCl(PPh_3)_3]$ did not yield an isolable aryldiazenato-complex, but more recently Meek *et al.* have demonstrated that when a chelating triphosphine ligand {$PPP = PhP[(CH_2)_3PPh_2]_2$} replaces $PPh_3$ the resulting complex (13) easily adds to $NO^+$ and $N_2Ph^+$ to yield the expected singly bent nitrosyl complex $[RhCl(NO) (PPP)]^+$ and doubly bent aryldiazenato-complex $[RhCl(N_2Ph) (PPP)]^+$ (12) of $Rh^{III}$ respectively.[3,29] These compounds have been fully elucidated structurally by X-rays (Table). It may be noted parenthetically that when a slurry of $[RhCl(N_2Ph) (PPP)]^+BF_4$ in methanol is warmed to 50 °C $[RhHCl(PPP)]BF_4$ may be isolated in good yield,[29b] accompanied by anisole, PhOMe. Perhaps MeOH is sufficiently acidic for $H^+$ to displace the aryldiazenato-group as $PhN_2^+$ from the

⁷⁸ M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.

co-ordination sphere, possibly *via* a phenyldiazene complex. The $Rh^I$ cation $[Rh(CNBu^t)_4]^+$ reacts with $NO^+$ and $ArN_2^+$ to give $[Rh(NO) (CNBu^t)_4]^{2+}$ and $[Rh(N_2Ar) (CNBu^t)_4]^{2+}$, presumably by oxidative addition.[79]

When $[RhX(PPh_3)_3]$ (X = Cl or Br) reacts with diazonium ions in the presence of LiX the rhodium(III) complexes $[RhX_2(N_2Ar) (PPh_3)_2]$ are obtained.[14] These are notable for exhibiting *two* i.r. bands in the 1550—1615 $cm^{-1}$ region which are sensitive to $^{15}N$ substitution, but each shifts by less than the calculated amount for $\nu(^{15}N=NAr)$. This effect is not restricted to these compounds, but seems to be due to vibrational coupling[53,80] rather than *cis–trans* isomerism of the aryldiazenato-ligand or the complex. Measured values of $\nu(NN)$ require correction if this effect is observed.[80b]

Aryldiazonium fluoroborates are believed to react with $[RhHCl_2(PPh_3)_3]$ (free from excess HCl) with the formation of $[RhCl_2(NH=NAr) (PPh_3)_3]BF_4$ by apparent insertion into the Rh—H bond. However, attempts to purify and characterize these salts have been unsuccessful.[14,78] When the reaction is conducted in the presence of excess HCl or LiCl, the products are now believed to be[14] the neutral trichlorobis(phosphine) complexes $[RhCl_3(NH=NAr) (PPh_3)_2]$ rather than the (less expected) aryldiazenato-complexes of the type $[RhCl_2(N=NAr) (PPh_3)_2(solvent)]$ claimed at first[78] and subsequently examined as such by Raman and i.r. spectroscopy.[81] This reformulation follows naturally from the synthetic conditions employed, and from the fundamental differences in the nature of the products compared with the $[RhCl_2(N_2Ar)(PPh_3)_2]$ complexes synthesized separately[14] and described above. Thus the compounds show a weak broad resonance at *ca.* $\tau$ −2.0 which is replaced by a sharp doublet $[J(^{15}NH)65$—70 Hz] in the compounds synthesized from $^{15}N\equiv NAr^+$, indicating protonation of $N^1$. The aryldiazenato and aryldiazene complexes may be interconverted according to Scheme 8.

$$[Rh_2Cl_6(NH_2NHAr)_2(PPh_3)_2]$$

$H_2$ ⟋       ⟍ $H_2$

$$[RhCl_2(N_2Ar) (PPh_3)_2] \underset{Et_3N}{\overset{HCl}{\rightleftharpoons}} [RhCl_3(NH=NAr)(PPh_3)_2]$$

↓CO                    CO↓

A + $[RhCl(CO)(PPh_3)_2]$          $[RhCl_3(CO)(PPh_3)_2]$

$\nu(CO) = 1960\ cm^{-1}$          (A): $\nu(CO) = 2108\ cm^{-1}$

**Scheme 8**

[79] J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J.C.S. Dalton*, 1973, 2039.
[80] (*a*) D. Sutton, *Canad. J. Chem.*, 1974, **52**, 2634; (*b*) B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, 1975, **14**, 541.
[81] G. W. Rayner Canham and D. Sutton, *Canad. J. Chem.*, 1971, **49**, 3994.

Insertion into Ir—H bonds has been a common source of iridium aryldiazene and aryldiazenato-complexes also. [IrHCl$_2$(PPh$_3$)$_3$] may be converted into the complexes [IrCl$_2$(NH=NAr) (PPh$_3$)$_3$]BF$_4$ and [IrCl$_3$(NH=NAr) (PPh$_3$)$_2$] by reactions analogous to those described above.[14] Like the rhodium analogues, [IrCl$_3$(NHNAr) (PPh$_3$)$_2$] may be converted by means of HCl into an unstable brown complex. This reaction may be reversed with NEt$_3$, and the brown complex is therefore tentatively identified as the aryldiazenato-complex [IrCl$_2$(N$_2$Ar) (PPh$_3$)$_2$]. Toniolo and Eisenberg[55] and Caglio and Angoletta[56] obtained [IrH$_2$(NH=NAr) (PPh$_3$)$_3$]BF$_4$ from the insertion of diazonium ions into *mer*-[IrH$_3$(PPh$_3$)$_3$]. The results of a preliminary *X*-ray investigation[55] indicated structure (26) for the cation. No further hydrogenation of the aryldia-



(26)
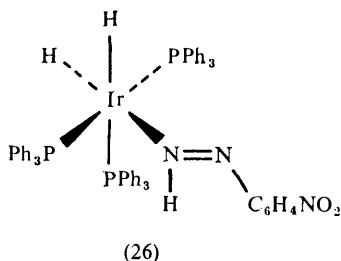
zene ligand occurred at 1—3 atm H$_2$ at 50—80 °C, and no indication was made whether insertion of further ArN$_2$$^+$ into the remaining Ir—H bonds could be accomplished. On attempted deprotonation with base no aryldiazenato-complex was formed; instead the original complex [IrH$_3$(PPh$_3$)$_3$] was regenerated. The compounds are unstable in chloroform or chloroform–ethanol, depositing orange crystals for which $\nu$(IrH) is absent. The product from chloroform has been shown by *X*-rays[82] to be the orthometallated diazene (27), in which the initial hydride ligands have been replaced by chloride derived from the solvent.

Vaska's complex, [IrCl(CO) (PPh$_3$)$_2$], occupies a central place in Ir$^{\rm I}$ chemistry,



(27)



(28)
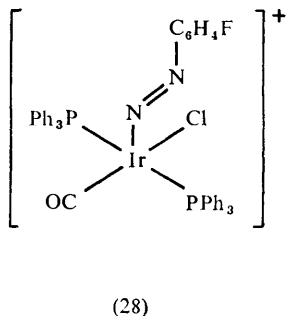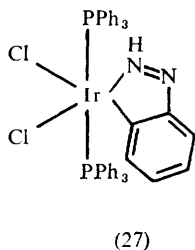
[82] P. L. Bellon, G. Caglio, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1974, 897.

and several groups[47],[83-85] have examined its aryldiazenato and aryldiazene derivatives. The synthesis of the $Ir^I(N_2Ar^+)$ complex $[IrCl(N_2Ar)(PPh_3)_2]^+$, isoelectronic with the nitrosyl complex[86] $[Ir(NO)Cl(PPh_3)_2]^+$, has been described in Section 4A. This complex has a considerable chemistry, being a precursor to numerous five- and six-co-ordinate aryldiazenato-complexes which may be expected to show interesting redox properties reflecting $N_2Ar^+$ and $N_2Ar^-$ formalisms, as do the corresponding nitrosyls.[47] Thus, the reaction of $[IrCl(N_2Ar)(PPh_3)_2]^+$ with CO, or the reaction of $[IrCl(CO)(PPh_3)_2]$ with diazonium ions, yields the five-co-ordinate cation $[IrCl(N_2Ar)CO(PPh_3)_2]^+$, believed to contain doubly bent $ArN_2^-$ and to have structure (28) analogous to the structurally determined[3] $NO^-$ bent-nitrosyl complex of iridium(III). From this, an extensive series of six-co-ordinate iridium(III) aryldiazenato-complexes may be obtained by further addition of neutral or negative ligands.[47]

Studies in the author's laboratory have indicated that the reactions of $[IrCl(CO)(PPh_3)_2]$ with diazonium ions in the presence of ethanol or propan-2-ol may be considerably more complex than the simple additions just described. The principal products then obtained are the cationic orthometallated diazene[85] (29) and the iridium(III) tetrazene complex cation (30).[87] A tentative mechanism for
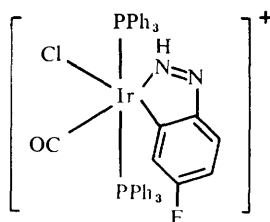


(29)
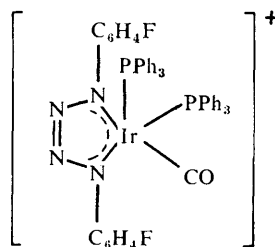


(30)

the synthesis of the tetrazene has been proposed.[88] The diazene is closely analogous to the orthometallated complex (27) described by Bellon *et al.*,[82] and it might be concluded that it arises as a result of an orthometallation isomerization of the five-co-ordinate simple addition complex (28) with which it is isomeric. Such a mechanism is attractive in view of the vacant co-ordination site in (28), yet there remain doubts about the validity of this mechanism as we have never

[83] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 1128.

[84] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

[85] (a) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645; (b) F. W. B. Einstein and D. Sutton, *J.C.S. Dalton*, 1973, 436.

[86] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 1459.

[87] (a) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1971, **93**, 1826; (b) F. W. B. Einstein and D. Sutton, *Inorg. Chem.*, 1972, **11**, 2827.

[88] A. B. Gilchrist and D. Sutton, *Canad. J. Chem.*, 1974, **52**, 3387.

been able to induce the orthometallation of (28) to occur other than in the presence of ethanol, propan-2-ol, or similar α-hydridic alcohols.[89] From this it seems to us that an intermediate hydride abstraction from the solvent is a necessary step.

## 6 Conclusion

Whilst the chemistry of aryldiazenato-complexes is mostly of very recent origin, it can be said already that they display much of the expected structural and electronic similarity with the isoelectronic nitrosyl complexes, underlining the usefulness of classifying them pragmatically in terms of $N_2Ar^+$ and $N_2Ar^-$ ligands. Despite many aryldiazenato-complexes presently appearing to be less 'stable' than their nitrosyl counterparts, the number of successful syntheses to date, the vast number of known nitrosyl compounds, and the already evident greater versatility of the aryldiazenato-ligand toward electrophiles promise much for the future development of their chemistry.

[89] N. Farrell, A. B. Gilchrist, and D. Sutton, unpublished results.