# Aryldiazenato- and Aryldiazene Complexes. Some Orthometallated Compounds derived from Reactions of Diazonium Ions with Carbonylchlorobis(triphenylphosphine)iridium

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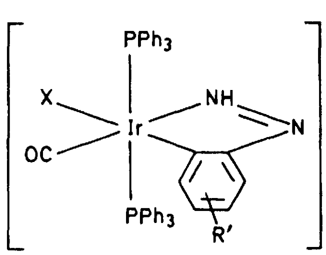
A wide range of variously substituted aryldiazonium ions ($RN_2^+$) react with $[Ir(CO)Cl(PPh_3)_2]$ and its analogues in benzene–ethanol or benzene–propan-2-ol to yield orthometallated aryldiazene complexes $[Ir(CO)X(NH{:}NC_6H_3\text{-}R')(PPh_3)_2]Y$ (1) of iridium(III). These may be deprotonated to yield orthometallated aryldiazenato-complexes $[Ir(CO)X(NNC_6H_3R')(PPh_3)_2]$ (2), and hydrogenated by $H_2$ at 1 atm and 25 °C in the presence of a palladium catalyst to give orthometallated arylhydrazine complexes $[Ir(CO)X(NH_2NHC_6H_3R')(PPh_3)_2][Y]$ (3) ($X = F$, Cl, Br, I, or $OClO_3$; $R' = H$, F, Br, Cl, Me, $CF_3$, $NH_2$, $NO_2$, or OMe; $Y = BF_4$ or $ClO_4$).

THE reaction of Vaska's complex $[Ir(CO)Cl(PPh_3)_2]$ with diazonium ions leads to a variety of products which are critically dependent on the conditions employed. Substitution of CO by $RN_2^+$ ($R =$ aryl) to give what appears to be the iridium(I) $RN_2^+$ complex $[IrCl(N_2R)(PPh_3)_2]^+$ has been described by Haymore and Ibers.[1] Under most conditions, however, the CO group of $[Ir(CO)Cl(PPh_3)_2]$ is not substituted, and the iridium is instead oxidised by the $RN_2^+$ group to $Ir^{III}$. The syntheses and properties of a number of such iridium(III) $RN_2^-$ complexes of the type $[IrCl_2(CO)(N_2R)(PPh_3)_2]$ and $[\{IrCl(CO)(N_2R)(PPh_3)_2\}_n][BF_4]_n$ have been described in a previous paper.[2]

A more complicated process involves the participation of a primary or secondary alcohol in the reaction, with the formation of iridium(III) diaryltetrazene complexes.[3,4] Iridium(III) complexes containing the bidentate orthometallated aryldiazene ligand are also formed in these reactions, and we have described the crystal structure of one such complex.[5] The present paper now describes in detail the syntheses, properties, and reduction by $H_2$ of variously substituted orthometallated aryldiazene and aryldiazenato-complexes derived from $[Ir(CO)Cl(PPh_3)_2]$ and its analogues. More recent studies in this laboratory on the reactions of the simple aryldiazenato-complexes[2] with ethanol, and on the reactions of diazonium ions with the iridium(I) complex $[Ir(CO)H(PPh_3)_2]$, have also led to orthometallated complexes and have helped to shed some light on the mechanism of the reaction. These will be reported in subsequent publications.

## RESULTS AND DISCUSSION

*Compounds Derived from* $[Ir(CO)Cl(PPh_3)_3]$.—The generally yellow or orange [(1k) is violet] orthometallated aryldiazene complexes of structure (1) were obtained in small yield from work-up of solutions from the reaction of diazonium salts with $[Ir(CO)Cl(PPh_3)_2]$ in benzene–ethanol or benzene–propan-2-ol. The yield could usually be optimised in relation to that of the diaryltetrazene where formed[3] by adjusting the solvent ratio and isolation procedure. Complexes were obtained for a wide range of diazonium salts with *ortho*, *meta*, and *para* substituents and for $[Ir(CO)X(PPh_3)_2]$ ($X = F$, Cl, Br, I, or $OClO_3$). Analytical and other data are included in the Table. Preliminary attempts to obtain analogous complexes by a similar procedure with $[Ir(CO)Cl(PMePh_2)_2]$ and $[Ir(CO)Cl(PMe_2Ph)_2]$ were unsuccessful. Complexes (1) are diamagnetic, indefinitely stable to air and moderate temperature, and are much more easily handled and stored than are the (non-orthometallated) iridium(III) aryldiazenato-complexes[2] with which they are isomeric. They are soluble in methanol, ethanol, acetone, acetonitrile, chloroform, and dichloromethane but insoluble in diethyl ether, water, and hydrocarbons. The electrical conductance in nitromethane of a representative selection is typical of 1 : 1 electrolytes. The $pK_a$ values are 6.3—6.8 and the complexes are readily deprotonated to give neutral orthometallated aryldiazenato-complexes of structure (2) as discussed below.



(1) $X = Cl$, $Y = BF_4$: $R' =$ (a) H, (b) *p*-F, (c) *p*-Cl, (d) *p*-Me, (e) *p*-Br, (f) *p*-$NO_2$, (g) *p*-$CF_3$, (h) *o*-F, (i) *o*-Cl, (j) *o*-Br, (k) *o*-$NO_2$, (l) *m*-Me, (m) *m*-OMe, (n) *m*-Br, (o) *m*-Cl, (p) *m*-$NO_2$, (q) *m*-F
$R' =$ *o*-Br: (r) $X = F$, $Y = BF_4$; (s) $X = I$, $Y = BF_4$; (t) $X = Br$, $Y = BF_4$; (u) $X = OClO_3$, $Y = ClO_4$.

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[1] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3052.

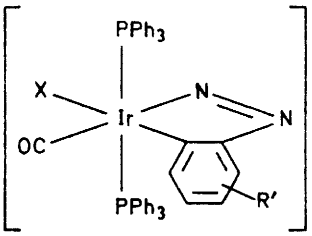
[2] R. E. Cobbledick, F. W. B. Einstein, N. Farrell, A. B. Gilchrist, and D. Sutton, *J.C.S. Dalton*, 1977, 373.

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

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

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

In the i.r. spectra: ν(NH) occurred in the 3 150—3 180 cm$^{-1}$ region and disappeared on deprotonation; ν(CO) occurred in the range 2 048—2 093 cm$^{-1}$ typical of Ir$^{III}$; ν(Ir–Cl) was at *ca.* 285 cm$^{-1}$ consistent with the rather long Ir–Cl bond [5] and the *trans* influence of the Ir–C$^6$ bond; and a band which we assign to ν(NN) occurred weakly, when observed, in the 1 403—1 443 cm$^{-1}$ region. Assignment of ν(NN) has been aided, in selected examples, by $^{15}$N substitution at the iridium-bonded nitrogen atom N$^1$. Thus, the band at 1 410 cm$^{-1}$ for (1e) shifted to 1 397 cm$^{-1}$, and the band at 1 442 cm$^{-1}$ in (1j) shifted to 1 426 cm$^{-1}$, in the $^{15}$N$^1$ derivatives. The magnitude of these shifts is smaller than theoretical and undoubtedly coupling of ν(NN) with other vibrations is occurring.[6]



(2)(a)-(u) R′ and X as for (1)

Analytical and other data for orthometallated aryldiazene complexes $[\mathrm{Ir(CO)X(NH{:}NC_6H_3R')(PPh_3)_2}][\mathrm{Y}]$ [a]

| | | | | | Analysis (%) | | | | | | | | I.r. (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Found | | | | Calc. | | | | | $(\mathrm{HN{:}NC_6H_3R'})$ | | | |
| | R′ [b] | X | Solvent of crystallisation | Yield (%) | C | H | N | Other | C | H | N | Other | ν(CO) | ν(NN) | δ(CH) | Λ [c] S cm$^2$ mol$^{-1}$ | p$K_a$ [d] |
| (1a) | H | Cl | $C_6H_6$ | 2 | 55.4 | 3.65 | 2.70 | | 56.05 | 3.95 | 2.65 | | 2 048 | 1 410 | [e] | | |
| (1b) | *p*-F | Cl | $Me_2CO$ | 13 | 52.65 | 3.90 | 2.85 | | 52.7 | 3.85 | 2.65 | | 2 048 | 1 419 | 825, 875 | 123 | |
| (1c) | *p*-Cl | Cl | 0.5 $C_6H_6$ | 8 | 52.85 | 3.55 | 2.60 | | 52.85 | 3.55 | 2.70 | | 2 048 | 1 409 | 820, 870 | | |
| (1d) | *p*-Me | Cl | | 4 | 53.4 | 3.75 | 2.80 | | 53.60 | 3.80 | 2.85 | | 2 050 | 1 410 | 810, | | |
| (1e) | *p*-Br | Cl | | 22 | 49.0 | 3.25 | 2.75 | C 13.25,<br>Br 7.55 | 49.15 | 3.25 | 2.65 | C 13.35,<br>Br 7.60 | 2 050 | 1 410 [f] | 830, 880 | | |
| (1f) | *p*-$NO_2$ | Cl | | 3 | 50.2 | 3.60 | 4.05 | Cl 3.40 | 50.8 | 3.75 | 4.15 | Cl 3.50 | 2 058 | 1 408 | 840, 890 | | |
| (1g) | *p*-$CF_3$ | Cl | $Me_2CO$ | 8 | 51.55 | 3.75 | 2.35 | | 51.4 | 3.65 | 2.55 | | 2 060 | 1 403 | 840, 885 | | |
| (1h) | *o*-F | Cl | | 13 | 52.1 | 3.45 | 2.80 | | 52.15 | 3.45 | 2.80 | | 2 065 | | 785 | | |
| (1i) | *o*-Cl | Cl | $Me_2CO$ | 13 | 52.1 | 3.95 | 2.70 | | 51.9 | 3.80 | 2.65 | | 2 066 | 1 443 [g] | 795 | | |
| (1j) | *o*-Br | Cl | $Me_2CO$ | 17 | 50.05 | 3.80 | 2.50 | | 49.8 | 3.65 | 2.55 | | 2 068 | 1 442 [g,h] | 790 | 126 | 6.6 |
| (1k) | *o*-$NO_2$ | Cl | | 13 | 50.6 | 3.55 | 3.90 | | 50.8 | 3.35 | 4.15 | | 2 072 | | 800 | | |
| (1l) | *m*-Me | C | | 22 | 53.5 | 3.85 | 3.10 | | 53.6 | 3.80 | 2.85 | | 2 051 | | 775 | | 6.3 |
| (1m) | *m*-OMe | Cl | $Me_2CO$ | 8 | 53.65 | 4.10 | 2.70 | | 53.25 | 4.10 | 2.65 | | 2 061 | | 770 | | |
| (1n) | *m*-Br | Cl | | 8 | 49.3 | 3.30 | 2.60 | | 49.15 | 3.25 | 2.65 | | 2 066 | | 770 | | |
| (1o) | *m*-Cl | Cl | | 13 | 50.9 | 3.55 | 2.70 | | 51.3 | 3.40 | 2.80 | | 2 068 | | 770 | | |
| (1p) | *m*-$NO_2$ | Cl | | 14 | 50.15 | 3.35 | 3.95 | | 50.8 | 3.35 | 4.15 | | 2 072 | | 780,<br>830,<br>880 | | |
| (1q) | *m*-F | Cl | $Me_2CO$ | 14 | 50.9 | 3.55 | 2.65 | | 52.15 | 3.45 | 2.85 | | 2 075 | | 785 | | |
| (1r) | *o*-Br | F | $Me_2CO$ | 29 | 50.45 | 3.75 | 2.70 | F 8.55 | 50.55 | 3.70 | 2.55 | F 8.70 | 2 056 | | 790 | 139 | 6.5 |
| (1s) | *o*-Br | I | | 14 | 45.65 | 3.05 | 2.55 | I 11.1 | 45.2 | 3.00 | 2.45 | I 11.1 | 2 063 | | 790 | 131 | 6.9 |
| (1t) | *o*-Br | Br | 0.5 $C_6H_4$ | 16 | 48.55 | 2.30 | 2.50 | | 48.7 | 3.30 | 2.45 | | 2 067 | | 835 | 128 | |
| (1u) | *o*-Br | $OClO_3$ | $Me_2CO$ | 43 | 46.7 | 3.25 | 2.40 | Cl 6.10<br>Br 7.20 | 46.6 | 3.40 | 2.35 | Cl 6.00<br>Br 6.75 | 2 093 | | 795 | 124 | 6.8 |

[a] (1a)—(1t), Y = $BF_4$; (1u), Y = $ClO_4$. [b] Designated as *o*, *m*, or *p* relative to the diazo-group, as in the diazonium ion. [c] In nitromethane at 25 °C. Concentrations: (1b) 8.4 × 10$^{-5}$, (1u) 4.0 × 10$^{-4}$, others 1.7 × 10$^{-4}$ mol dm$^{-3}$. [d] In ethanol at 25 °C. [e] Masked by $PPh_3$. [f] Observed in i.r. and Raman: ν($^{15}$N=$^{14}$NR) at 1 397 cm$^{-1}$. [g] Raman spectrum only. [h] ν($^{15}$N=$^{14}$NR) at 1 426 cm$^{-1}$.

A spectroscopic clue to the existence of the orthometallated aromatic ring in these complexes is provided by a careful inspection of the out-of-plane aromatic CH-bending region, δ(CH), which occurs at 680—900 cm$^{-1}$. Band positions are sensitive to the number of CH groups and their relative proximity. Strong absorption due to triphenylphosphine, at *ca.* 700 and 750 cm$^{-1}$, was of course always present and may in some instances partly mask the absorptions due to the aryldiazene ligand. In the *para*-substituted ligands in particular, where δ(CH) bands were widely separated from $PPh_3$ absorption, there was an excellent correlation of observation with expectation.[7] In substituted benzenes, a simple 1,4-substitution pattern usually gives a single absorption at 810—833 cm$^{-1}$, whilst a 1,2,4-substitution pattern produces two bands at 805—825 and 870—885 cm$^{-1}$. The *para*-substituted complexes (1b)—(1g) usually exhibited a quite distinct two-band pattern of a 1,2,4-substituted aromatic ring, thereby confirming orthometallation. For *ortho* and *meta* substituents the results were also consistent with orthometallation, although less definitive.

The electronic spectra of the yellow complexes in ethanol showed only broad, asymmetric, and ill defined bands. Two maxima, near 300—400 and 400—450 nm respectively with molar absorption coefficients of *ca.* 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$, were generally present, and the orange-yellow complexes (1e), (1s), and (1u) showed an additional weak band near 500 nm (ε *ca.* 10$^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$).

Hydrogen-1 n.m.r. spectra were recorded (with some difficulty due to inadequate solubility in [$^2H_6$]acetone and $CDCl_3$) for complexes (1e; R′ = *p*-Br), (1i; R′ = *o*-Cl), and (1j; R′ = *o*-Br). Multiplet structure due to the aromatic protons occurred at τ 2.46. A weak signal integrating to a single proton was observed in each case at τ 3.61 [(1e) in $(CD_3)_2CO$], 3.67 [(1e) in $CDCl_3$], 3.14 [(1i) in $(CD_3)_2CO$], and 3.70 [(1j) in $(CD_3)_2CO$], and was originally [5] assigned to the NH proton in view of an apparent doublet at this position in the spectrum of (1e) ($^{15}$N$^1$). However, for this assignment the chemical shift and apparent coupling constant were not in accord with reasonable expectation. On re-examination of the spectrum of (1e) and its $^{15}$N$^1$ derivative using improved

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[6] B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, 1975, **14**, 541.

[7] R. T. Conley, 'Infrared Spectroscopy,' Allyn and Bacon Inc., Boston, 1966, p. 107.

instrumentation, more concentrated solutions in $CD_3CN$, and spectrum accumulation, we found conclusively that a single resonance occurred near $\tau$ 3.6 in both cases (which must be assigned to an aryldiazene ring proton). The NH proton was observed as a very broad weak resonance at $\tau$ −4.8, split in the $^{15}N^1$ complex into a sharp doublet [$J(^{15}NH)$ 92 Hz]. The signal disappeared on addition of $D_2O$ or on deprotonation. The magnitudes of $^{15}NH$ coupling constants have been discussed recently and this is close to the expected value for an *sp*$^2$ nitrogen atom. The large downfield chemical shift is similar to those observed previously for several classes of simple aryldiazene complexes.[8-14] These include $[PtCl(NH{:}NC_6H_4F\text{-}p)(PEt_3)_2]^+$ [$\tau$ −5.1, $^1J(^{15}NH)$ 77 Hz] and $[IrH_2(NH{:}NC_6H_4NO_2\text{-}p)(PPh_3)_3]^+$ ($\tau$ −3.5)[8,9]; Laing *et al.*[10] reported an extensive series of aryldiazene complexes having $\tau$(NH) −4.0 to −1.6 and $^1J(^{15}NH)$ 65—70 Hz. In a single report of aryldiazene complexes having positive $\tau$(NH) values, (7.2—7.62) is listed for $[Pt(NH{:}NR)(PPh_3)_3]^{2+}$ (R = aryl) but this assignment requires confirmation by isotopic substitution.[13]

Complexes (1) were readily deprotonated by base to give generally pink neutral orthometallated aryldiazenato-complexes (2) as in equation (1), the reaction being reversed by $HBF_4$. This may be achieved by treating

$$\underset{(1)}{[\overline{\mathrm{Ir(CO)Cl(NH{:}NC_6H_4}})(\mathrm{PPh_3})_2][\mathrm{BF_4}]} \underset{\mathrm{HBF_4}}{\overset{\text{base}}{\rightleftharpoons}} \underset{(2)}{[\overline{\mathrm{Ir(CO)Cl(NNC_6H_4}})(\mathrm{PPh_3})_2]} \qquad (1)$$

methanol solutions of (1) with $NEt_3$, aqueous methanolic Na[OH], or $Na[O_2CMe]$ [whereupon (2) precipitates as a pink solid in 70% yield], or by treating a suspension of (1) in diethyl ether with $NEt_3$. A suspension of (2) in ethanol was reconverted into (1) in 70% yield by the careful addition of 48% aqueous $HBF_4$.

The neutral complexes (2) are diamagnetic air-stable pink solids, readily soluble in benzene, chloroform, and dichloromethane, only slightly soluble in ethanol, methanol, and diethyl ether, and insoluble in water and acetone. The i.r. spectra exhibited no frequencies attributable to $\nu$(NH) or $\nu(BF_4)$; $\nu$(CO) occurred near 2 000 cm$^{-1}$. There is some irregularity in the assignment of $\nu$(NN) since in the example studied by $^{15}N$ substitution, (2e), a band at 1 450 cm$^{-1}$ in the spectrum of the $^{14}N$ complex is absent in that of the $^{15}N^1$ derivative, which instead has an additional band at 1 413 cm$^{-1}$. This corresponds to an isotopic shift of *ca.* 37 cm$^{-1}$, much greater than the calculated value (*ca.* 25 cm$^{-1}$). Probably coupling is occurring and $\nu$(NN) is near 1 440 cm$^{-1}$ in the $^{14}N$ complex. Attempted confirmation by Raman spectroscopy was unsuccessful as the stationary sample decomposed in the He–Ne laser. The continued presence of the aromatic $\delta$(CH) pattern typical of orthometallation (see above) was confirmed [*e.g.* $\delta$(CH) at 812 and 863 cm$^{-1}$ for (2e)]. In this system, protonation of the aryldiazenato-ligand leads to an increase in $\nu$(CO) and a probable decrease in $\nu$(NN). The increase in $\nu$(CO) for the cationic complex is an expected result, as the iridium atom is likely to be a site of partial positive charge. The changes in $\nu$(NN) on protonation of aryldiazenato-complexes are more complicated, and are quite possibly dependent on the individual metal, its oxidation state, and its electronic configuration.[14]

Hydrogen-1 n.m.r. spectra of (2e) showed the usual multiplet due to $PPh_3$ at $\tau$ 2.58 (30 H) and a poorly resolved group of three peaks near $\tau$ 3.17 (3 H) assigned to the protons of the orthometallated aromatic ring.

*Hydrogenation Studies*.—A feature of interest in complexes containing a co-ordinated unsaturated diazo-group is the extent to which the diazo-group is capable of reduction.[15,16] Most frequently, direct or catalytic hydrogenation of the group under mild conditions has been attempted. There is an evident (although at present incompletely documented) correlation of reducibility with the stretching frequency of the N=N bond and hence with the fine details of the electronic population of the diazo-group inasmuch as it is ' tuned ' by the adjacent metal atom.

From the examples which we have been able to locate the following situation appears to exist [observed rather than adjusted[6,17,18] $\nu$(NN) values (cm$^{-1}$) are quoted]. (*i*) A number of complexes containing doubly bent aryldiazenato-ligands have been hydrogenated under mild conditions to yield hydrazine complexes, *e.g.* $[PtCl(N_2R)(PEt_3)_2]$ [$\nu$(NN) at[14] *ca.* 1 460][8,15,16,19] and $[RhCl_2(N_2Ph)(PPh_3)_2]$ [$\nu$(NN) at 1 549 and 1 614 cm$^{-1}$].[10] There is no reported inability to hydrogenate doubly bent aryldiazenato-ligands [which generally have relatively low $\nu$(NN) values], although most have not been tested. (*ii*) Several $N^1$-protonated doubly bent aryldiazenato-complexes (*i.e. cis*-aryldiazene complexes) have been hydrogenated, *e.g.* $[PtCl(NH{:}NR)(PEt_3)_2]^+$ [$\nu$(NN) at[14] *ca.* 1 480][8,15,16,20] and $[RhCl_3(NH{:}NR)(PPh_3)_2]$ [$\nu$(NN) at 1 500—1 530 cm$^{-1}$].[10] (*iii*) Most singly bent aryldiazenato-complexes studied [which are notable in having relatively high $\nu$(NN) values] are not hydrogenated

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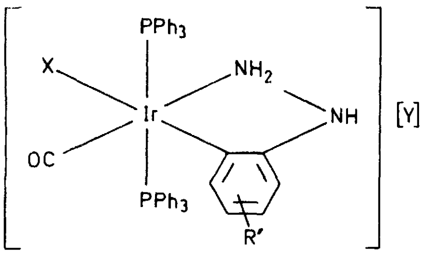
[20] S. D. Ittel and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4804.

under mild conditions, including $[Mo\{BH(pz)_3\}(CO)_2(N_2Ph)]$ [ν(NN) at [21] 1 559],[22,23] $[Fe(CO)_2(N_2R)(PPh_3)_2]^+$ [ν(NN) at 1 715—1 725],[24,25] $[RuX_3(N_2R)(PPh_3)_2]$ [X = Cl or Br; ν(NN) at 1 881—1 895],[10,18] and $[OsBr_3(N_2C_6H_4Me\text{-}p)(PPh_3)_2]$ [ν(NN) at 1 855 $cm^{-1}$].[10] Hydrogenation of $[Mo(\eta\text{-}C_5H_5)(CO)_2(N_2R)]$ [ν(NN) at 1 545—1 562 $cm^{-1}$] [15] has been reported, without details.[22] (*iv*) No protonated singly bent aryldiazenato-complexes (protonated on $N^2$) appear to have been tested.

We found that the orthometallated aryldiazene (1) and aryldiazenato-complexes (2) are readily hydrogenated by $H_2$ at 1 atm and 25 °C in the presence of a catalyst consisting of Pd supported on $Ba[SO_4]$; * no hydrogenation occurred in the absence of catalyst. In the case of (1), hydrogenation produced arylhydrazine complexes (3). The reaction appeared to be a general one for *ortho*-, *meta*-, and *para*-substituted derivatives, from a comparison of i.r. spectra; elemental analyses were only obtained for representative complexes (see Experimental section). The evidence that the orthometallated aromatic ring is retained in (3) again comes from an inspection of δ(CH) absorptions, which were unchanged from those of the parent complexes (1). Complexes (3) are generally pale yellow [(3v) is brownish purple], soluble in ethanol and chloroform, but insoluble in diethyl ether. The i.r. spectra showed typical absorptions for $[BF_4]^-$ and co-ordinated $PPh_3$, the absence of ν(NN) absorptions seen in the parent complexes (1), ν(CO) near 2 050 $cm^{-1}$, and ν(Ir–Cl) near 280 $cm^{-1}$. Several bands (usually four) occurred in the ν(NH) region from 3 150 to 3 330 $cm^{-1}$, and δ(NH) occurred at 1 610—1 620 $cm^{-1}$. In the case of (1k) reduction of the $o$-$NO_2$ group to $o$-$NH_2$ also occurred to give (3v), as indicated by the absence of typical absorptions for the nitro-group and the presence of additional $\nu(NH_2)$ bands at 3 380 and 3 410 $cm^{-1}$. Further exposure of (3e; R′ = $p$-Br) to $H_2$ at 60 lbf $in^{-2}$ and 30 °C for 30 h in the presence of Pd–$Ba[SO_4]$ catalyst failed to achieve hydrogenolysis of the N–N bond, or other changes.



(3e),(3i),(3j),(3n) R′, X, and Y designated as for (1)

(3v) R′ = $o$-$NH_2$, X = Cl, Y = $BF_4$

Hydrogenation of one of the orthometallated aryldiazenato-complexes, namely (2e; R′ = $p$-Br) was carried out similarly, and the deep pink-red solid obtained was recrystallised from diethyl ether. This was at first presumed to be the expected neutral orthometallated arylhydrazido-complex, $[Ir(CO)Cl(NH{\cdot}NHC_6H_3Br\text{-}p)(PPh_3)_2]{\cdot}OEt_2$. However, it now appears more probable that hydrogenation has occurred with elimination of HCl to give the complex $[Ir(CO)(NH{:}NC_6H_3Br\text{-}p)(PPh_3)_2]{\cdot}OEt_2$, formally containing $Ir^I$.† The evidence for this is the improved analytical agreement and the absence of ν(Ir–Cl) in the i.r. spectrum, together with a relative paucity of ν(NH) bands compared with (3e). The observed value of 1 960 $cm^{-1}$ for ν(CO) is important as it is quite inconsistent with the previous formulation as an iridium(III) hydrazido-complex since ν(CO) is seen to change very little in going from (1) to (3), and it would therefore be expected to be near 2 000 $cm^{-1}$ by comparison with (2); the observed lower value is consistent with a more reduced iridium. Once again, the presence of orthometallation is confirmed by δ(CH) at 810 and 865 $cm^{-1}$, and diethyl ether solvent is responsible for bands at 2 860, 2 925, and 2 965 $cm^{-1}$. No clear band assignable to ν(NN) could be seen.

*Mechanism of Formation of* (1).—Several experiments were conducted to try to elucidate the mechanism of the reaction leading to the formation of the orthometallated aryldiazene complexes (1). Of particular interest are (*i*) the involvement of the alcohol in the reaction, (*ii*) the orthometallation step, and (*iii*) the actual source of the NH proton. In this paper it is convenient only to describe those experiments relating to the synthesis of (1) by the route described; at a later time we shall present additional observations and discuss possible mechanisms.

The role played by the alcohol is overwhelmingly likely to be that of a hydrogen donor, either by a radical mechanism or quite probably as hydride. This is also true for the synthesis of the diaryltetrazene complexes, for which the arguments have been presented already.[3] Neither the tetrazene complex nor (1) was formed when ethanol was replaced by methanol, t-butyl alcohol, acetone, dichloromethane, nitromethane, or acetic acid, but both were readily formed for propan-2-ol, which like ethanol has an activated α-hydrogen atom. Because of the lack of a suitable visible-absorption band specific for (1), kinetic studies comparable to those for the tetrazene complexes [3] were not made to compare the behaviour of EtOH with $C_2D_5OD$. Although any discussion of the possible processes in this reaction is always complicated by the formation of both tetrazene complex and (1), it does appear that the consumption of ethanol or propan-2-ol is directly related to the production of both products. Thus, the acetone production required by the hydride-abstraction reaction (2) for propan-2-ol has been found

$$R^1R^2CHOH \longrightarrow R^1R^2CO + H^+ + H^- \qquad (2)$$

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* Throughout this paper: 1 atm = 101 325 Pa.

† We are grateful to Mr. J. A. Carroll for pointing this out.

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[23] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

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to agree quantitatively with the total isolated amounts of both products.[3] When formation of both products is prevented by employing the ' blocked ' diazonium ion $2,6\text{-}F_2C_6H_3N_2^+$, acetone is still formed in comparable amounts,[3] suggesting that hydride abstraction is an early step which leads to a (possibly common) intermediate which normally proceeds to products, but which under ' blocked ' conditions either remains in limbo or decays by some other route.

A systematic search was made to attempt to identify by process of elimination the source of the NH proton using deuteriated reagents and the i.r. spectra of the isolated products. Syntheses were performed with (*a*) EtOH replaced by EtOD and $C_2D_5OD$, (*b*) $PhN_2BF_4$ replaced by $C_6D_5N_2BF_4$, (*c*) both EtOH and $PhN_2BF_4$ replaced by $C_2D_5OD$ and $C_6D_5N_2BF_4$, and (*d*) both $C_6H_6$ and EtOH replaced by $C_6D_6$ and $C_2D_5OD$. Surprisingly, in each case $\nu$(NH) was clearly visible in the i.r. spectrum of the product and no $\nu$(ND) absorption could be identified. Reluctantly, but seemingly inescapably, we are forced to conclude that ND bonds must have been formed, but were being converted into NH bonds either by adventitious hydrogen in the form of insufficiently dry solvents, mulling agents, or KBr, or through a dynamic mechanism causing exchange of ND with hydrogen atoms of triphenylphosphine, which could occur, for example, if scrambling of ND with the *o*-hydrogens and deuteriums of all the aromatic rings were to occur *via* facile reversible orthometallation of both aryldiazene and phosphine phenyl groups. The results were inconclusive as to the source of the NH group.

It is remarkable, and possibly instructive, to note that despite an already considerable number of reported syntheses of complexes using diazonium ions,[26] frequently in ethanol, only one other report of an orthometallated aryldiazene ligand exists currently, and this is also an iridium(III) complex closely related to those described here.[27]

## EXPERIMENTAL

The complexes $[Ir(CO)X(PPh_3)_2]$ (X = Cl, Br, or I) were obtained from Strem Chemicals Inc. and were found not to require further purification; $[Ir(CO)F(PPh_3)_2]$ was synthesised.[28] Infrared spectra were recorded on samples pressed in KBr or dispersed in Nujol or Fluorolube using Perkin-Elmer 457 or Beckman IR-12 instruments. Hydrogen-1 n.m.r. spectra were obtained with Varian A56/60 and XL 100 spectrometers at 60 and 100 MHz respectively, relative to $SiMe_4$ as internal standard. Electrical conductance was recorded at room temperature using a Radiometer (Copenhagen) type CHM2 conductivity meter. The p$K_a$ values were obtained potentiometrically by titrating $10^{-4}$ mol dm$^{-3}$ ethanol solutions of the appropriate complexes against $2 \times 10^{-4}$ mol dm$^{-3}$ ethanolic K[OH] using a Radiometer type 4D pH meter; p$K_a$ values were taken as the pH at half-equivalence. Microanalyses were by Mr. M. K. Yang of the Simon Fraser Microanalytical Laboratory and by A. Bernhardt, Germany. All the manipulations were carried out under dry argon or nitrogen in Schlenk-type apparatus. Solvents were dried by conventional methods and distilled under inert gas before use.

*Orthometallated Aryldiazene Complexes* (1).—Unless stated otherwise, these complexes were all prepared by essentially the same procedure now described. In each case the ethanol may be replaced by propan-2-ol.

$[\overline{Ir(CO)Cl(NH{:}NC}_6H_4)(PPh_3)_2][BF_4]$ (1a). Benzenediazonium tetrafluoroborate (0.024 g, 0.125 mmol) was added to a solution of $[Ir(CO)Cl(PPh_3)_2]$ (0.098 g, 0.125 mmol) in benzene (15 cm$^3$) followed immediately by absolute ethanol (5 cm$^3$). The mixture was stirred at room temperature for 3 h and the resulting orange-red solution was evaporated to dryness by freezing and pumping. The residual solid was stirred in benzene (15 cm$^3$) for 2 h and the insoluble material was filtered off, and washed with benzene and then diethyl ether. It was redissolved in the minimum of acetone and diethyl ether was added until the solution became cloudy. The solution was maintained at room temperature, when crystallisation occurred. (The addition of too much diethyl ether, or cooling, frequently caused co-crystallisation of the diaryltetrazene complex.) The yellow *crystals* were filtered off, washed with diethyl ether containing a little acetone, and dried *in vacuo*.

In the case of (1f; R′ = *p*-$NO_2$) the crude solid was not the desired product, which was instead obtained by crystallisation of the filtrate at 5 °C after addition of diethyl ether. For (1g; R′ = *p*-$CF_3$) the diaryltetrazene crystallised first at room temperature and was removed. Addition of diethyl ether (10 cm$^3$) yielded crystals of (1g) at 5 °C. In synthesising (1n; R′ = *m*-Br) the crude solid dissolved completely in benzene and the product was crystallised from this solution by use of diethyl ether at room temperature.

$[\overline{Ir(CO)F(NH{:}NC}_6H_3Br\text{-}p)(PPh_3)_2][BF_4]$ (1r). The complex $[Ir(CO)F(PPh_3)_2]$ (0.095 g, 125 mmol) was incompletely soluble in benzene (15 cm$^3$); *o*-$BrC_6H_4N_2BF_4$ (0.338 g, 125 mmol) was added in the usual manner followed by absolute ethanol (5 cm$^3$). After 3 h the resulting orange-red solution was freeze-dried, and orange *crystals* of the product were obtained by treating an acetone solution of the crude solid with diethyl ether until it was just cloudy and maintaining it at 3 °C for 4 h. In the case of (1s; X = I, R′ = *o*-Br) crystals of the product were obtained from both the benzene–insoluble material and the filtrate obtained by stirring the crude freeze-dried solid in benzene. The filtrate precipitated crystals of (1s) at 10 °C over 24 h. The ' benzene-insoluble ' solid was dissolved in the minimum of acetone and crystallised by addition of benzene (20 cm$^3$) and cooling for 12 h.

$[\overline{Ir(CO)(NH{:}NC}_6H_3Br\text{-}o)(OClO_3)(PPh_3)_2][ClO_4]$ (1u). The complex $[Ir(CO)(OClO_3)(PPh_3)_2]$ was synthesised *in situ* by stirring anhydrous $Ag[ClO_4]$ (0.104 g, 0.5 mmol) with a solution of $[Ir(CO)Cl(PPh_3)_2]$ (0.195 g, 0.25 mmol) in benzene (30 cm$^3$) in the dark for 15 min. The resulting yellow-orange solution was filtered from suspended AgCl, *o*-$BrC_6H_4N_2BF_4$ (0.678 g, 0.25 mmol) was added followed by absolute ethanol (10 cm$^3$), and stirring was continued in the dark for 3 h. The $Ag[BF_4]$ was filtered off, and the

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deep red-orange filtrate was evaporated by freeze drying. The crude solid was stirred in benzene, in which it dissolved, later precipitating the product (1u) which was recrystallised from acetone–diethyl ether at room temperature. The presence of both perchlorato-ligand and perchlorate ion was indicated by the massive, broad, and structured absorption at 1 050—1 200 cm$^{-1}$ ($OClO_3$ and $ClO_4$) and a medium-intensity band at 932 cm$^{-1}$ [$\nu_2(OClO_3)$].

*Orthometallated Aryldiazenato-complexes* (2).—These were synthesised as described below for one example. Most were identified by i.r. but were not analysed.

$[Ir(CO)Cl(NNC_6H_3Br\text{-}p)(PPh_3)_2]$ (2e). A solution (1.0 cm$^3$) of $Na[OH]$ (0.032 g) in aqueous methanol (1 : 1; 20 cm$^3$) was added to a solution of (1e) (0.018 g) in methanol (3 cm$^3$). The yellow solution immediately became pink, followed by precipitation of a pink solid. After cooling to 0 °C and stirring for 15 min, the pink product was filtered off, washed several times with 1 : 1 aqueous methanol, and dried *in vacuo*, yield 0.012 g (73%) (Found: C, 53.4; H, 3.4; N, 2.7. Calc. for $C_{43}H_{33}BrClIrN_2OP_2$: C, 53.6; H, 3.6; N, 2.9%). The deprotonation was also carried out by (*a*) using $Na[O_2CMe]$ in 1 : 1 aqueous methanol, (*b*) $NEt_3$ in aqueous methanol, and (*c*) suspending (1e) in diethyl ether and stirring with a slight excess of $NEt_3$ until the colour of the suspension was completely pink.

Reconversion of (2e) into (1e) was effected in >70% yield by adding 48% $HBF_4$ solution dropwise to a stirred suspension of (2e) in diethyl ether until it was completely yellow.

$[Ir(CO)Cl(NH_2NHC_6H_3Br\text{-}p)(PPh_3)_2][BF_4]$ (3e).—A solution of (1e) (0.02 g) in absolute ethanol (10 cm$^3$) was saturated with $H_2$, a catalyst of 10% Pd on $Ba[SO_4]$ was added, and the mixture was stirred at room temperature for 2 h whilst bubbling a slow stream of $H_2$. The mixture was then centrifuged to remove the solid catalyst, and the mother liquor was evaporated to dryness *in vacuo*. The residual pale yellow solid was extracted with benzene, and the solid obtained from evaporation of the extract *in vacuo* was recrystallised from ethanol–diethyl ether, yield 75% (Found: C, 48.4; H, 3.4; N, 2.65. Calc. for $C_{43}H_{36}BBrClF_4IrN_2OP_2$: C, 48.9; H, 3.4; N, 2.65%); $\nu$(CO) at 2 048 (KBr) and 2 046 (Nujol) cm$^{-1}$, $\nu$(NH) at 3 170, 3 230, 3 250, and 3 310 cm$^{-1}$.

Similarly synthesised were: (3i; R′ = *o*-Cl), $\nu$(CO) at 2 052 and $\nu$(NH) at 3 174, 3 240, 3 256, and 3 330 cm$^{-1}$; (3j; R′ = *o*-Br), $\nu$(CO) at 2 054 and $\nu$(NH) at 3 174, 3 239, 3 256, and 3 330 cm$^{-1}$; (3n; R′ = *m*-Br), $\nu$(CO) at 2 056 and $\nu$(NH) at 3 150, 3 180, 3 200, 3 270, and 3 320 cm$^{-1}$; and (3v; R′ = *o*-$NH_2$) which was prepared from (1k; R′ = *o*-$NO_2$) (Found: C, 51.2; H, 3.6; N, 3.5. Calc. for $C_{43}H_{38}BClF_4IrN_3OP_2$: C, 52.1; H, 3.8; N, 4.2%), $\nu$(CO) at 2 050 and $\nu$(NH) at 3 180, 3 230, 3 290, 3 380, and 3 410 cm$^{-1}$.

$[Ir(CO)(NH{:}NC_6H_3Br\text{-}p)(PPh_3)_2]\cdot OEt_2$. The pink neutral complex (2e) (0.02 g) was suspended in absolute ethanol (10 cm$^3$) under $H_2$ (1 atm) and stirred with the Pd–$Ba[SO_4]$ catalyst (10 mg) for 2 h with slow $H_2$ bubbling. The resulting mixture was centrifuged and ethanol was stripped from the red solution to give a reddish pink solid which was recrystallised by slow evaporation of a solution in diethyl ether {Found: C, 56.15; H, 4.55; N, 2.65. Calc. for $C_{47}H_{44}BrIrN_2O_2P_2$: C, 56.3; H, 4.40; N, 2.80. Calc. for $[Ir(CO)Cl(NH\cdot NHC_6H_3Br\text{-}p)(PPh_3)_2]\cdot OEt_2$: C, 54.3; H, 4.35; N, 2.70%}; $\nu$(CO) at 1 960, $\nu$(NH) at 3 225 and 3 285 cm$^{-1}$.

*Determination of Acetone from Propan-*2*-ol Reactions.*—Benzene and propan-2-ol were purified by fractional distillation on a spinning-band column and carefully checked for the absence of acetone and low-boiling components by g.l.c. under conditions identical to those used to analyse the solvents after reaction. Typically, $[Ir(CO)Cl(PPh_3)_2]$ (0.0976 g, 0.125 mmol) and *p*-$BrC_6H_4N_2BF_4$ (0.0338 g, 0.125 mmol) were placed in a flask (A) (100 cm$^3$) which was thoroughly degassed on a vacuum line. A degassed mixture of pure benzene (15 cm$^3$) and propan-2-ol (5 cm$^3$) was vacuum-distilled into (A) cooled in liquid $N_2$. Flask (A) was sealed off and the contents were stirred at 25 °C for 3 h, becoming orange-red. The flask was again cooled in liquid $N_2$, reattached to the vacuum line, the seal broken, and the volatiles condensed into a separate tube. Samples (1.5 µl) were analysed on a 10% 20M Carbowax column (6 ft × 0.125 in) at 30 °C using a Varian Aerograph 1400. Peak areas were calibrated by running samples (1.5 µl) of standard solutions of acetone in the mixed solvent under identical conditions.

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