Aryldiazenido- and Aryldiazene Complexes: Reaction of Ethanol with Aryldiazenido-complexes of Iridium(III) to form Orthometallated Derivatives

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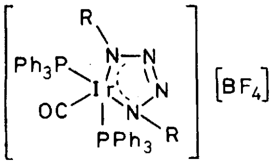
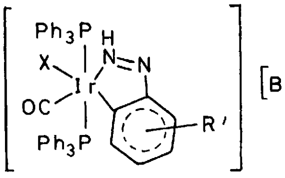
A re-examination of the products of the reaction of $[IrCl(CO)(PPh_3)_2]$ with diazonium salts, $[RN_2][BF_4]$, in benzene–ethanol or benzene–propan-2-ol shows them now to include the complexes $[IrCl_2(N_2R)(CO)(PPh_3)_2]$ (4) and the orthometallated arylhydrazido-complex $[Ir(NHNHR)(CO)(PPh_3)_2][BF_4]$ (5), in addition to the previously found diaryltetrazenido-complex $[Ir(N_4R_2)(CO)(PPh_3)_2][BF_4]$ (1) and orthometallated aryldiazene complex $[IrX(NHNR)(CO)(PPh_3)_2][BF_4]$ (2; X = Cl). Complex (5) readily oxidizes to (2; X = Cl, F, or BF_4), depending on the availability of the ligand X. These results, taken together with those from reactions of (*a*) $[IrCl(CO)(PPh_3)_2]$ and $[RN_2][BF_4]$ in acetone, which yield $[\{IrCl(N_2R)(CO)(PPh_3)_2\}_2][BF_4]_2$, (*b*) $[IrH(CO)(PPh_3)_3]$ and $[RN_2][BF_4]$ in acetone, yielding (5), and (*c*) $[\{IrCl(N_2R)(CO)(PPh_3)_2\}_2][BF_4]_2$ with ethanol or propan-2-ol, yielding variously (2), (4), and (5), allow a mechanism for the reactions in benzene–ethanol to be proposed. It envisages that the chlorine-bridged aryldiazenido-complex $[\{IrCl(N_2R)(CO)(PPh_3)_2\}_2][BF_4]_2$ is first formed, and subsequently undergoes hydrogen transfer from the alcohol to yield (4) plus the intermediate $[Ir(NHNR)(CO)(PPh_3)_2][BF_4]$. The latter then (*a*) orthometallates to give (5), and hence (2), or (*b*) reacts with further $[RN_2][BF_4]$ to give (1).

FOR some time we have been interested in the reactions of diazonium ions with Vaska's complex $[IrCl(CO)(PPh_3)_2]$. The products obtained using benzene–ethanol as solvent are not simple aryldiazenido-complexes,† but are instead an iridium(III) diaryltetrazenido-complex (1) and an iridium(III) orthometallated aryldiazene complex (2; X = Cl).[1-4] In previous papers [1,2] we described the evidence then available as to the possible mechanism, and showed that α-hydrogen abstraction from the alcohol is involved. Subsequently, we have examined these reactions in greater detail and have carried out related reactions, the results of which now enable a reasonable mechanism to be formulated.



(1)



(2) X = F, Cl, or BF_4

RESULTS AND DISCUSSION

(a) *Reactions of* $[IrCl(CO)(PPh_3)_2]$ *with Diazonium Salts in Acetone*.—These have been reported in detail elsewhere,[5] so we shall simply summarize the results here [equations (1) and (2)]. The diazonium ion oxidatively adds to produce the iridium(III) aryldiazenido-complexes

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† The proposed I.U.P.A.C. rule whereby the ArNN ligand was named aryldiazenato has not been adopted. Instead the I.U.P.A.C. Commission now recommends reversion to the original aryldiazenido terminology.

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

[2] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645; A. B. Gilchrist and D. Sutton, *J.C.S. Dalton*, 1977, 677.

[3] F. W. B. Einstein and D. Sutton, *Inorg. Chem.*, 1972, **11**, 2827.

[4] F. W. B. Einstein and D. Sutton, *J.C.S. Dalton*, 1973, 434.

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

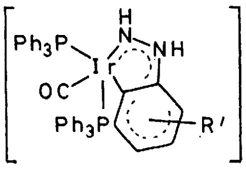
(3) or (4). Complex (3) is indicated by ν(Ir–Cl) to be at least binuclear with chlorine bridges,[5] and for the purpose of the present discussion we shall formulate it as

$$[\mathrm{IrCl(CO)(PPh_3)_2}] \xrightarrow[\mathrm{Me_2CO},\ -25\ ^{\circ}\mathrm{C}]{[\mathrm{RN_2}][\mathrm{BF_4}]} \underset{(3)}{[\{\mathrm{IrCl(N_2R)(CO)(PPh_3)_2}\}_2][\mathrm{BF_4}]_2} \quad (1)$$

$$[\mathrm{IrCl(CO)(PPh_3)_2}] \xrightarrow{[\mathrm{RN_2}][\mathrm{BF_4}],\ \mathrm{LiCl}} \underset{(4)}{[\mathrm{IrCl_2(N_2R)(CO)(PPh_3)_2}]} \quad (2)$$

$[\{\mathrm{IrCl(N_2R)(CO)(PPh_3)_2}\}_2][\mathrm{BF_4}]_2$. Both reactions are clean, and in neither case are complexes (1) or (2) produced. In particular, the simple idea that (2) might arise by an isomerization of the mononuclear form of (3) is untenable; whilst (3) does have poor stability in solution, this is mainly due to dissociation to $[\mathrm{IrCl(CO)(PPh_3)_2}]$ and diazonium ion, which is considerable with most substituents at room temperature.

(b) *Reactions of Diazonium Ions with* $[\mathrm{IrH(CO)(PPh_3)_3}]$.—Reaction in acetone–benzene or acetone–toluene yields the orthometallated arylhydrazido-complex (5), the structure of which has been established by i.r. and n.m.r. spectroscopy and *X*-ray crystallography.[6] This product results from insertion of the diazonium ion into the Ir–H bond to form the aryldiazene complex intermediate (6) followed by orthometallation, resulting from attack of the electron-rich $\mathrm{Ir^I}$ on the aromatic ring [equation (3)]. Complex (5) is characterized by ν(CO) at *ca.* 2 000 cm^{-1} and ν(NH) of the hydrazido-group at *ca.* 3 280 cm^{-1}.



(5)

$$[\mathrm{IrH(CO)(PPh_3)_3}] \xrightarrow{[\mathrm{RN_2}]\,[\mathrm{BF_4}]} \underset{(6)}{[\mathrm{Ir(NHNR)(CO)(PPh_3)_2}][\mathrm{BF_4}]} \longrightarrow \underset{(5)}{[\mathrm{Ir(NHNHR)(CO)(PPh_3)_2}][\mathrm{BF_4}]} \quad (3)$$

We have observed (5) in reactions using diazonium salts with a variety of substituents. Notably, there is a general tendency for (5) to oxidize to six-co-ordinate iridium(III) orthometallated *aryldiazene* complexes of the type (2) in which an available anionic ligand $\mathrm{X^-}$ (in these cases $\mathrm{X = BF_4}$ or F) is incorporated [equation (4)]. These exhibit the usual absorptions of ν(CO) at 2 040—2 070 cm^{-1} and ν(NH) at 3 150 cm^{-1} noted previously for this type of complex.[2,6] This conversion is slow for R = *o*-nitrophenyl, but occurs so readily in the case of *o*-trifluoromethylphenyl that (5) is largely lost on work-up; slow crystallization under $\mathrm{N_2}$ using normal Schlenk-tube handling procedures has yielded (2; X = F or $\mathrm{BF_4}$) as the only crystalline products, and this structure has also been established by *X*-ray crystallography for X = F.[6] Generally, both (5) and (2) are obtained.

$$\underset{(5)}{[\mathrm{Ir(NHNHR)(CO)(PPh_3)_2}][\mathrm{BF_4}]} \xrightarrow[\text{oxidation}]{\mathrm{X^- = F^-\ or\ [BF_4]^-}} \underset{(2)\ \mathrm{X = F\ or\ BF_4}}{[\mathrm{IrX(NHNR)(CO)(PPh_3)_2}][\mathrm{BF_4}]} \quad (4)$$

The $[\mathrm{IrH(CO)(PPh_3)_3}]$ reactions also produced the diaryltetrazenido-complex (1), most readily where excess of a *p*-substituted diazonium salt was used, but also for *ortho* and *meta* substituents in smaller yield. Its formation can be simply accounted for by attack of a second diazonium ion on the aryldiazene intermediate (6) [equation (5)] or perhaps on its conjugate base $[\mathrm{Ir(NNR)(CO)(PPh_3)_2}]$. A possible mechanism for this reaction has been suggested previously.[1]

$$\underset{(6)}{[\mathrm{Ir(NHNR)(CO)(PPh_3)_2}][\mathrm{BF_4}]} + [\mathrm{RN_2}]^+ \longrightarrow [\mathrm{Ir(N_4R_2)(CO)(PPh_3)_2}][\mathrm{BF_4}] + \mathrm{H^+} \quad (5)$$

(c) *Reinvestigation of Reactions of* $[\mathrm{IrCl(CO)(PPh_3)_2}]$ *and Diazonium Ions in Benzene–Ethanol.*—A re-inspection of the i.r. spectrum of the initial crude products obtained in the original reactions[1,2] of $[o\text{-}\mathrm{O_2NC_6H_4N_2}][\mathrm{BF_4}]$ with $[\mathrm{IrCl(CO)(PPh_3)_2}]$ in benzene–ethanol clearly showed absorptions at 3 280 and 2 000 cm^{-1}, typical of (5), to be present. Similar bands could also be found in the spectra of material from runs with a few other substituents. A selection of these reactions were therefore re-examined, special care being taken to try to isolate any complexes present in addition to (1) and (2; X = Cl) by changing the work-up from that originally reported[1,2] to reduce the time that products are in solution and to minimize the oxidation of (5).

Complex (5) was isolated in the case of R′ = *o*- and *p*-$\mathrm{NO_2}$; for *o*-$\mathrm{CF_3}$, the complex was converted into (2) on attempted isolation and it was presumably too unstable in this regard to be observed in the case of *p*-Br. Complex (2; X = F, $\mathrm{BF_4}$, or Cl) was found in all cases as expected, and the diaryltetrazenido-complex (1) was found for R′ = *p*-Br and *p*-$\mathrm{NO_2}$ and believed to be present (but could not be isolated) for *o*-$\mathrm{CF_3}$ and *o*-$\mathrm{NO_2}$. Interestingly, the complex $[\mathrm{IrCl_2(N_2R)(CO)(PPh_3)_2}]$ (4) was also always present, and could be readily separated by precipitation with ethanol.

(d) *Reaction of* $[\{\mathrm{IrCl(N_2R)(CO)(PPh_3)_2}\}_2][\mathrm{BF_4}]_2$ (3) *with Ethanol or Propan-2-ol.*—Complex (3), either as the pure solid or formed *in situ* as a solution in acetone at low temperature, reacted with the alcohol during *ca.* 1—2 h to give a precipitate of (4) in the cases of R = $\mathrm{C_6H_4}$-$\mathrm{NO_2}$-*o*, -$\mathrm{NO_2}$-*p*, or -$\mathrm{CF_3}$-*o*. In the last case it was contaminated with $[\mathrm{IrCl(CO)(PPh_3)_2}]$ as a result of the

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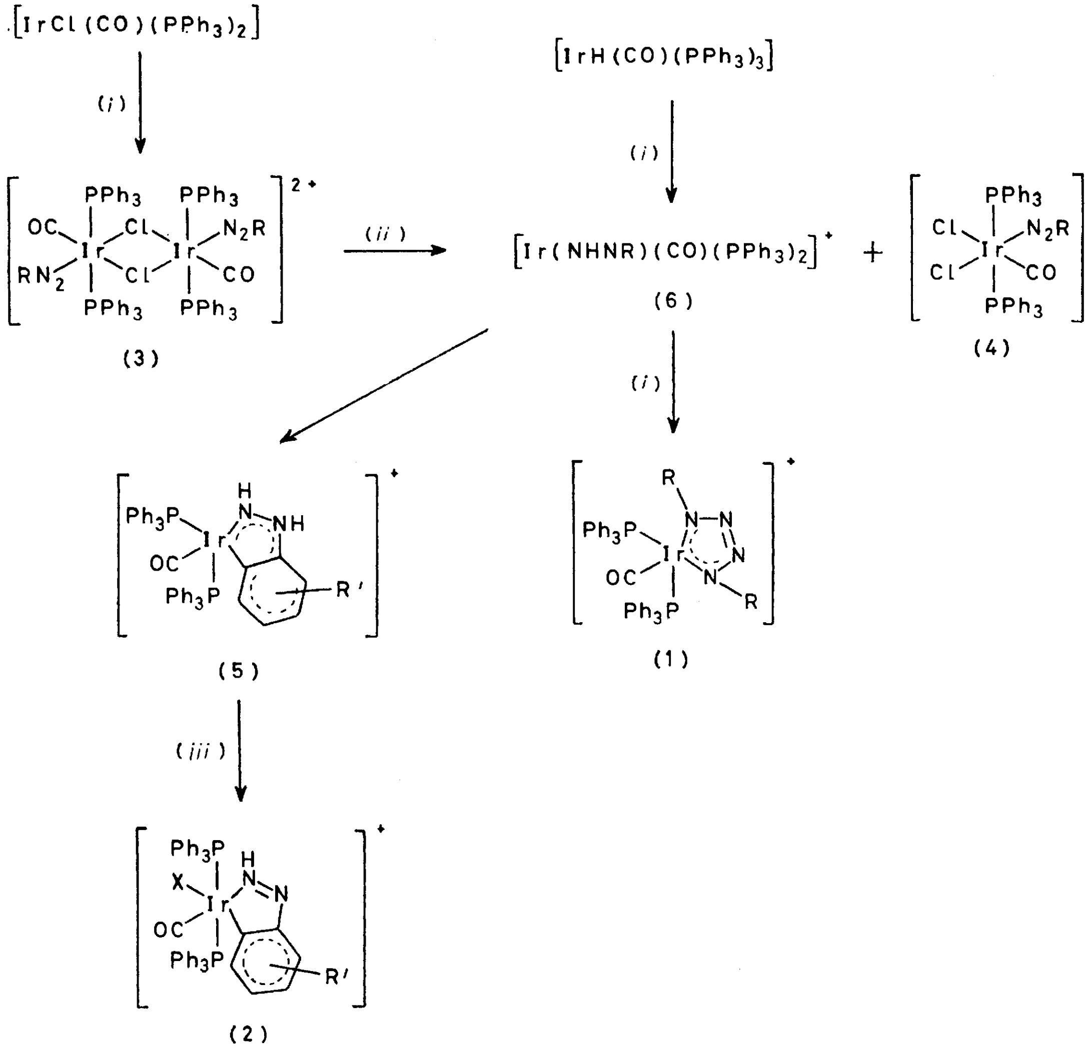
[6] J. A. Carroll, R. E. Cobbledick, F. W. B. Einstein, N. Farrell, D. Sutton, and P. L. Vogel, *Inorg. Chem.*, 1977, **16**, in the press.

instability of (3) in solution, and for R = C_6H_4-F-*p*, -Br-*p*-, or -F-*o* this decomposition is so pronounced that recovered material from reactions at 25 °C was substantially $[IrCl(CO)(PPh_3)_2]$ and $[RN_2][BF_4]$ with some evidence for orthometallated products (2) but no tetrazenido-complex; at $\leqslant 0$ °C virtually no reaction occurred within a few hours. No useful results could therefore be obtained using these halogen substituents. The remaining products observed for R = C_6H_4-NO_2-*o*, -NO_2-*p*, or -CF_3-*o* paralleled almost exactly those found in the benzene–ethanol reactions. For R = $C_6H_4NO_2$-*o* the product was substantially (5) which could be converted separately into (2; X = BF_4), for $C_6H_4NO_2$-*p* (5) was accompanied by (2; X = Cl or F), and for $C_6H_4CF_3$-*o* (5) was formed but easily converted into (2; X = F). The virtual absence of the tetrazenido-complex in these reactions reflects the absence of excess of diazonium ion.



SCHEME (*i*) $[RN_2]^+$; (*ii*) RR′CHOH, $-$RR′CO $-H^+$; (*iii*) $X^- = [BF_4]^-$, F^-, or Cl^-

Mechanism.—There are a number of related features in the above reactions which point to a probable mechanism in benzene–ethanol. First, we see that the products of the latter reactions actually include complexes (4) and (5) in addition to those [(1) and (2)] originally found. Secondly, the observation that (2) is readily formed as a result of the oxidation of (5) in the presence of an anionic ligand X establishes a route for the formation of (2). In the presence of Cl^- (2; X = F or BF_4) is converted readily into (2; X = Cl) due to the greater nucleophilicity of Cl^-. Thirdly, the reaction of (3) with ethanol, which gives rise to (2), (4), and (5), strongly suggests that these same products arise in benzene–ethanol due to initial formation of (3) and its subsequent reaction with the alcohol. This is most reasonable, since (3) is formed alone by the addition of $[RN_2]^+$ to $[IrCl(CO)(PPh_3)_2]$ in a non-reacting solvent such as acetone. Fourth, the production of (5) in the reactions in benzene–ethanol and in those of $[IrH(CO)(PPh_3)_3]$ (alcohol absent) points to an intermediate common to both these reactions, probably complex (6).

The suggested mechanism for the reactions in benzene–ethanol is shown in the Scheme, and may be summarized as follows. (*i*) The chloride-bridged aryldiazenido complex (3) is formed initially, just as in the reactions in acetone. (*ii*) This reacts with the alcohol at one iridium centre, causing the chloride bridges to break asymmetrically to yield $[IrCl_2(N_2R)(CO)(PPh_3)_2]$ (4). Hydrogen is abstracted from the alcohol to yield $[Ir(NHNR)(CO)(PPh_3)_2]^+$ (6) presumably *via* an (aryldiazenido)hydrido-complex $[IrH(N_2R)(CO)(PPh_3)_2]^+$. [As pointed out by a referee, an alternative possibility is symmetric cleavage of (3) by the alcohol with loss of Cl^- to give (6), with subsequent addition of Cl^- to (3) to yield (4).] In reactions of $[IrH(CO)(PPh_3)_3]$ with diazonium ions, (6) is formed by addition of $[RN_2]^+$ followed by insertion [equation (3)]. Hence the similarity in the products such as (2; $X = F$ or BF_4) and (5), from both the reactions in benzene–ethanol and those of $[IrH(CO)(PPh_3)_3]$. (*iii*) The intermediate (6) rearranges to the orthometallated arylhydrazido-complex (5) which is sufficiently stable in cases such as $R' =$ *o*- or *p*-NO_2 to be isolated from the reactions in benzene–ethanol. However, in most cases (5) oxidizes to an orthometallated iridium(III) aryldiazene complex (2), and in so doing it binds a sixth (anionic) ligand. In the reactions in benzene–ethanol this ligand is generally Cl which may arise from a number of sources such as the labile Cl *trans* to RN_2 in (4).[5] It is frequently F or BF_4 in cases (such as $R' =$ *o*-NO_2, *p*-NO_2, or *o*-CF_3) in which (3) and (4) have the highest stability and the availability of Cl^- is presumably low. (*iv*) The formation of the diaryltetrazenido-complex (which notably contains no chloride ligand) arises [1] by reaction of (6) with $[RN_2]^+$.

EXPERIMENTAL

Manipulations were carried out in Schlenk-type glassware connected to a double manifold for evacuation and backfilling with dry nitrogen. Solvents were dried by the usual methods and saturated with dry nitrogen directly before use. Aryldiazonium salts were recrystallized from acetone–diethyl ether before use.

Infrared spectra were recorded using Perkin-Elmer 457, Beckman IR-12, and Shimadzu IR 27-G instruments with samples pressed in KBr. Elemental analyses were by the Simon Fraser University and the University of Otago (New Zealand) microanalytical units. Satisfactory analyses were obtained for all the complexes, and the majority have been synthesized previously.[1,2,6] The reactions of $[IrCl(CO)(PPh_3)_2]$ with diazonium salts in acetone,[5] and of $[IrH(CO)(PPh_3)_3]$ with diazonium salts,[6] have been described elsewhere.

Reactions of Diazonium Ions with $[IrCl(CO)(PPh_3)_2]$ *in Benzene–Ethanol*.—(*i*) $[p\text{-}O_2NC_6H_4N_2][BF_4]$. The complex $[IrCl(CO)(PPh_3)_2]$ (0.08 mmol) in benzene (15 cm^3) was treated with the solid diazonium salt followed immediately by ethanol (5 cm^3) and the solution was stirred. The solution rapidly became deep red, and after 1 h it was reduced to *ca.* 5 cm^3 *in vacuo*. Ethanol (15 cm^3) was added to give a purple precipitate [5] of $[IrCl_2(N_2C_6H_4NO_2\text{-}p)(CO)(PPh_3)_2]$ (4) (0.025 mmol) having $\nu(CO)$ at 2 060 cm^{-1}.

Solvent was stripped from the red filtrate which was then stirred with benzene, resulting in a yellow insoluble fraction of $[IrCl(NHNC_6H_3NO_2\text{-}p)(CO)(PPh_3)_2][BF_4]$ (2; $X = Cl$, $R' = p\text{-}NO_2$) (0.003 mmol) having $\nu(CO)$ at 2 058 cm^{-1} and $\nu(NH)$ at 3 150 cm^{-1}. From the red benzene filtrate, the complexes $[Ir\{N_4(C_6H_4NO_2\text{-}p)_2\}(CO)(PPh_3)_2][BF_4]$ (1) having $\nu(CO)$ at 2 061 cm^{-1} and $[Ir(NHNHC_6H_3NO_2\text{-}p)(CO)(PPh_3)_2][BF_4]$ (5) having $\nu(CO)$ at 2 000 and $\nu(NH)$ at 3 280 cm^{-1} could be isolated with difficulty by fractional crystallization from benzene–hexane.

(*ii*) $[o\text{-}O_2NC_6H_4N_2][BF_4]$. This reaction was performed as in (*i*), to give a similar deep red solution, and analogous work-up gave an orange precipitate of $[IrCl_2(N_2C_6H_4NO_2\text{-}o)(CO)(PPh_3)_2]$ having $\nu(CO)$ at 2 060 cm^{-1}.[5] No evidence for (2; $X = Cl$, $R' = o\text{-}NO_2$) was found when the residue was stirred in benzene, and the residue consisted mainly of the maroon complex $[Ir(NHNHC_6H_3NO_2\text{-}o)(CO)(PPh_3)_2][BF_4]$ (5) having $\nu(CO)$ at 2 000 and $\nu(NH)$ at 3 280 cm^{-1}. Attempted crystallization of (5) from methanol–diethyl ether–hexane at 0 °C for 4 d resulted in a yellow-brown solution and yellow-brown crystals of $[Ir(BF_4)(NHNC_6H_3NO_2\text{-}o)(CO)(PPh_3)_2][BF_4]\cdot 2MeOH$ (2; $X = BF_4$, $R' = o\text{-}NO_2$) having $\nu(CO)$ at 2 062 and $\nu(NH)$ at 3 150 cm^{-1}.

(*iii*) $[o\text{-}F_3CC_6H_4N_2][BF_4]$. This reaction was performed as in (*i*), and the solution quickly became orange. After 2 h the solution was reduced to 5 cm^3 *in vacuo* and ethanol (15 cm^3) was added. The orange precipitate consisted of $[IrCl_2(N_2C_6H_4CF_3\text{-}o)(CO)(PPh_3)_2]$ (4) having $\nu(CO)$ at 2 045 cm^{-1}, and $[IrCl(CO)(PPh_3)_2]$. The filtrate was evaporated to give a yellow-orange solid which recrystallized from methanol–diethyl ether–hexane to give $[IrCl(NHNC_6H_3CF_3\text{-}o)(CO)(PPh_3)_2][BF_4]\cdot 2Et_2O$ having $\nu(CO)$ at 2 055 and $\nu(NH)$ at 3 150 cm^{-1}.

(*iv*) $[p\text{-}BrC_6H_4N_2][BF_4]$. In this case the reaction proceeded to give a deep red solution but no precipitate of (4) was obtained with ethanol. The solution yielded only the tetrazenido-complex (1) and the orthometallated aryldiazene complex (2; $X = Cl$, $R' = p\text{-}Br$) as described previously.[1]

Reactions of $[\{IrCl(N_2C_6H_4R')(CO)(PPh_3)_2\}_2][BF_4]_2$ (3) *with Ethanol*.—(*i*) $R' = p\text{-}NO_2$. The complex $[IrCl(CO)(PPh_3)_2]$ (0.1 mmol) and $[p\text{-}O_2NC_6H_4N_2][BF_4]$ (0.1 mmol) were intimately mixed and cooled to −25 °C. Acetone (10 cm^3) at −25 °C was added with vigorous stirring to yield a pale red-pink solution of the aryldiazenido-complex (3).[5] After 15 min, ethanol (5 cm^3) at −25 °C was added, stirring continued, and the cooling bath removed. The solution attained room temperature within 20 min and was stirred for another 2 h. The solution was now deep red and usually contained a precipitate of (4). It was evaporated to *ca.* 5 cm^3 and ethanol (15 cm^3) was added to complete the precipitation of $[IrCl_2(N_2C_6H_4NO_2\text{-}p)(CO)(PPh_3)_2]$ (4) (0.03 mmol). The solvent was pumped off the red filtrate and the resulting deep red solid was stirred with benzene (10 cm^3), then filtered to remove the insoluble yellow complex $[IrCl(NHNC_6H_3NO_2\text{-}p)(CO)(PPh_3)_2][BF_4]$ (2; $X = Cl$) (0.01 mmol). The red filtrate was pumped to remove solvent and the residue found to consist of complex (5; $R' = p\text{-}NO_2$) with $\nu(CO)$ at 2 000 and $\nu(NH)$ at 3 280 cm^{-1}, contaminated with other material having $\nu(CO)$ at 2 055 cm^{-1}. Reprecipitation from benzene–hexane diminished the proportion of this second product, but (5) could not be obtained pure. Reactions with the previously isolated complex (3) were identical.

(*ii*) $R' = o\text{-}NO_2$. This reaction was carried out as above; runs in which the orange aryldiazenido-complex (3) was isolated [5] and treated separately with ethanol gave identical results. The orange ethanol-insoluble complex $[\mathrm{IrCl_2(N_2C_6H_4NO_2\text{-}}o\mathrm{)(CO)(PPh_3)_2}]$ (4) having [5] ν(CO) at 2 062 cm^{-1} was obtained in the usual way. Removal of solvent from the maroon filtrate, followed by stirring the maroon solid in benzene, gave no precipitate of (2; X = Cl, R′ = *o*-$\mathrm{NO_2}$). The maroon solid recrystallized from methanol–diethyl ether–hexane to give $[\overline{\mathrm{Ir(NHNHC_6}}\mathrm{H_3NO_2\text{-}}o\mathrm{)(CO)(PPh_3)_2}][\mathrm{BF_4}]$ having ν(CO) at 2 000 and ν(NH) 3 280 cm^{-1}.[6]

(*iii*) R′ = *o*-$\mathrm{CF_3}$. This reaction was carried out similarly to (*i*). An orange material was precipitated with ethanol which consisted of $[\mathrm{IrCl(CO)(PPh_3)_2}]$ and $[\mathrm{IrCl_2(N_2C_6H_4\text{-}CF_3\text{-}}o\mathrm{)(CO)(PPh_3)_2}]$ (4). These were separated by fractional crystallization from benzene–ethanol, and the latter complex was obtained as an adduct containing one molecule of $\mathrm{C_6H_6}$ and having ν(CO) at 2 045 cm^{-1}. The residue from the ethanolic filtrate gave no precipitate of (2) at the benzene-extraction stage, and contained (5) [ν(CO) at 2 000 and ν(NH) at 3 280 cm^{-1}] together with material having ν(CO) at 2 060 cm^{-1}. Recrystallization from methanol–diethyl ether–hexane gave only golden crystals of (2; X = F, R′ = *o*-$\mathrm{CF_3}$) as an adduct containing two molecules of MeOH and having [6] ν(CO) at 2 050 and ν(NH) at 3 150 cm^{-1}.

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