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ARYLDIAZENIDO, ARYLDIAZENE, AND ARYLHYDRAZIDO COMPLEXES. FURTHER STUDIES OF *ortho*-METALATED IRIDIUM COMPLEXES DERIVED FROM REACTIONS OF ARYLDIAZONIUM IONS WITH $IrH(CO)(PPh_3)_3$ AND $IrH(CO)_2(PPh_3)_2$

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Summary

The syntheses are described of *ortho*-metalated iridium arylhydrazido complexes $[Ir(NHNHC_6H_3X)(CO)(PPh_3)_2]BF_4$, where X = H, 4-F, 3-F, 2-F, 4-OMe, 2-OMe, 2-NO_2, 3-NO_2, 3-CH_3, 4-CH_3 and 2-CF_3 from the reactions of the corresponding arenediazonium tetrafluoroborates with $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$. A high-yield synthesis of the 2-NO_2 complex from the diazonium salt and $IrCl(CO)(PPh_3)_2$ is also reported, and this complex has been the subject of a multinuclear (^1H, ^{13}C, ^{31}P, ^{15}N) NMR study. Oxidation of these arylhydrazido complexes to *ortho*-metalated aryldiazene complexes $[Ir(NH{=}NC_6H_3X)(Y)(CO)(PPh_3)_2]BF_4$, where Y = F, FBF_3, Cl, Br or I occurs with air and halogens.

Introduction

In a preceding paper [1] we described the characterization of some examples of the *ortho*-metalated iridium arylhydrazido complexes **1a**–**1i** and commented upon their ease of oxidation to six-coordinated *ortho*-metalated iridium(III) aryldiazene complexes **2**. The characterization of **1** was done mainly with the 2-nitrophenylhydrazido analog **1g** since this was found at the time to be the most easily synthesized and the most stable toward potential oxidation; conversely fluoro or trifluoromethyl substituents on the phenyl group appeared to render **1** extremely susceptible to oxidation, to the extent that **1** was destroyed in attempted purification procedures, complex **2** being isolated instead.

To determine more completely the influence of such substituents on the synthesis and stability of the arylhydrazido complexes **1** we have re-examined and extended these syntheses. As a result, we have now succeeded in isolating **1** for F and CF_3

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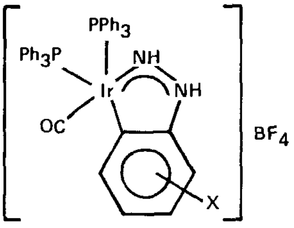
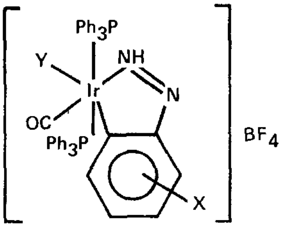
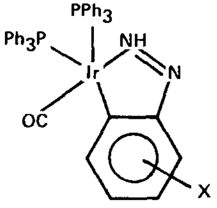
substituents as well as for such electron-donating substituents as OCH_3 and CH_3. This paper presents full details of these syntheses. Also presented is an improved synthesis of the 2-nitrophenylhydrazido complex **1g** by a different method and details of the multinuclear NMR spectra of **1g**. The reaction of **1g** with hydrogen chloride is detailed in the adjacent paper.



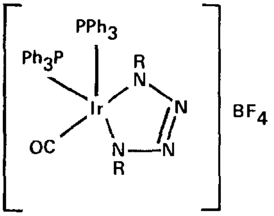
1 (a–k)



2 (a–k); Y = F, FBF_3, Cl, Br, I



3 (a–k)



4 (a, b, d, e, j)
R = C_6H_4X

a, X = H
b, X = 4–F
c, X = 3–F
d, X = 2–F
e, X = 4–OMe
f, X = 2–OMe
g, X = 2–NO_2
h, X = 3–NO_2
i, X = 3–CH_3
j, X = 4–CH_3
k, X = 2–CF_3

Results and discussion

(a) Synthesis

A variety of different approaches have been tried in attempts to optimize the conditions for the synthesis of the arylhydrazido complexes **1** from the hydrido complexes $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$. The preferred method seemed to be the simultaneous dropwise addition of a solution of the hydride in toluene (or benzene) and a solution of the diazonium salt in acetone at room temperature. During subsequent evacuation the desired arylhydrazido complex generally oiled out of a toluene/acetone solution later than other iridium containing products and so could be partially purified immediately by decanting. Microcrystalline samples of **1** were then obtained by addition of methanol acidified with aqueous HBF_4. These generally were analytically and spectroscopically (IR) pure (Table 1). Attempted recrystallization of **1** from mixed solvents such as acetone/ether/hexane with

TABLE 1

ANALYTICAL DATA FOR ARYLHYDRAZIDO COMPLEXES $[Ir(NHNHC_6H_3X)(CO)(PPh_3)_2]BF_4$ (**1**)

Complex	X	Analysis (Found (calcd.) (%))		
		C	H	N
1a	H	54.8 (55.1)	4.06 (3.87)	2.77 (2.99)
1b	4-F	54.0 (54.0)	3.73 (3.69)	2.89 (2.93)
1d	2-F	54.2 (54.0)	3.74 (3.69)	3.02 (2.93)
1f	$2\text{-}OCH_3$	54.6 (54.6)	3.98 (3.96)	2.85 (2.89)
1g	$2\text{-}NO_2$	52.8 (52.6)	3.74 (3.59)	4.09 (4.28)
1i	$3\text{-}CH_3$	49.9 [a] (55.5)	4.04 (4.02)	2.93 (2.94)
1j	$4\text{-}CH_3$	55.1 (55.5)	4.12 (4.02)	2.93 (2.94)

[a] Carbon analyses for this complex were always below theoretical and showed wide variation, suggesting incomplete combustion.

cooling always resulted in contamination of **1** with **2** (X = F), detectable easily by ν(CO) absorption near 2040 cm^{-1}. The crude isolates from the reaction of each mono-substituted benzenediazonium salt tried showed IR absorptions indicating the production of **1** even in those cases where the pure arylhydrazido complex could not be separated subsequently. However, no arylhydrazido complex could be detected using disubstituted (2,6-difluoro- or 3,5-dimethyl-)benzenediazonium ions.

The arylhydrazido complexes have been obtained in only quite low yields from these reactions, and are accompanied by other iridium products, some of which may well arise from further reaction of the former prior to isolation, as discussed later. However, some products are clearly the result of competing reactions. A white solid having analysis and properties in agreement with the composition $[IrH_2(CO)_2(PPh_3)_2]BF_4$ was the first material to solidify from crude product mixtures from the reaction of various arenediazonium tetrafluoroborates and $IrH(CO)_2(PPh_3)_2$. It has IR absorptions (Nujol) at 2071wm (νCO,A_1) 2021vs (νIrH) and 1999vvs (νCO,B_1) cm^{-1}. It is assigned a stereochemistry having *trans*-carbonyl groups and *cis*-hydrides on the basis of the empirical observation that complexes of *cis*-dihydrides almost always show only one IR ν(MH) absorption if the hydrogens are *trans* to equivalent ligands (in this case the phosphines) [6]. The previously known isomer has *trans*-phosphines and *cis*-hydrides and has the IR spectrum ν(IrH) 2180s, 2155m, ν(CO) 2085s, 2050vs [7]. This salt proved somewhat difficult to remove from **1** so that $IrH(CO)_2(PPh_3)_2$ is not a preferred starting material, despite the relative cleanness of the reaction, compared with $IrH(CO)(PPh_3)_3$. The latter was also found to yield a similar protonated derivative when used in the syntheses, but this salt $[IrH_2(CO)(PPh_3)_3]BF_4$ did not solidify at all easily and so did not interfere with the isolation of the hydrazido complex. Its IR spectrum agrees best with the known meridional structure having *cis*-hydrides: IR: 2150m, sh (ν(IrH) + ν(CO)), 2105s

(ν(IrH) *trans* to P), 2005s (ν(CO)+ν(IrH)) cm^{-1} [8]. This was, understandably, produced in larger amounts when the reaction was carried out in the presence of HBF_4, and no arylhydrazido complex was then formed. Protonation of the iridium hydrido carbonyls is a competing reaction, and the salts so formed are not attacked by diazonium ions.

Diaryltetrazene complexes **4** [1,3] have frequently been isolated from these preparations and the range of known examples has been extended by the isolation of bis(4-methylphenyl)- and bis(2-fluorophenyl)-tetrazene complexes in this work. The latter confirms that mono-substitution at the 2-position of the phenyl ring does not block tetrazene formation so that previous inability to obtain solid products is due to crystallization difficulties [3].

The other principal products of these reactions are the aryldiazene complexes **2**. These occur as a result of oxidation of the arylhydrazido complexes as will be discussed below.

Another reaction which produces some of the *ortho*-metalated arylhydrazido complexes **1** is the in situ ethanol reduction of $[\{IrCl(N_2R)(CO)(PPh_3)_2\}_2][BF_4]_2$, but the yield is poor due to concurrent formation of the dichloro complex $IrCl_2(N_2R)(CO)(PPh_3)_2$ [9]. In the case of the 2-nitro derivative **1g** we have found that the addition of a stoichiometric amount of $AgBF_4$ eliminates this second product, and produces a near quantitative yield of **1g**. Unfortunately, we have not found this method to be widely useful for similar synthesis of differently substituted analogs, either because the reaction of $IrCl(CO)(PPh_3)_2$ and the corresponding diazonium salt is not efficient at the low temperature required to prevent decomposition of the binuclear chloro complex intermediate, or because this is too unstable to give the desired product on addition of ethanol and $AgBF_4$. Because of the ready availability of the 2-nitro complex **1g** by this route, most of the reactions studied have used this derivative. The advent of the new mass spectrometric technique of fast atom bombardment [10] has recently allowed us for the first time to obtain mass spectra for such ionic compounds as these. The mass spectrum of **1g**, obtained by xenon bombardment of a sample dispersed in sulfolane exhibited a dominant cluster of lines corresponding to the mass of the cation, *m/e* 896 (^{193}Ir), with the correct intensity distribution expected for the isotopic abundances present. Fragment ions, if present, were barely observable above background.

The hydrazido complexes are generally crystalline solids with colours which are various shades of red depending on the substituent. With nitro groups the colour is shaded toward purple or maroon, and with less electronegative groups toward orange. The complexes dissolve in polar solvents such as MeCN, $CHCl_3$, CH_2Cl_2, Me_2CO, EtOH and MeOH and are insoluble in acetic acid, benzene, toluene, ether, hexanes and water.

(b) Oxidation of arylhydrazido complexes 1 to aryldiazene complexes 2

(i) With halogens. The arylhydrazido complexes **1g** were oxidized in solution by stoichiometric amounts of Cl_2, Br_2 or I_2 to give the corresponding orthometallated aryldiazene complexes **2**, with Y = Cl, Br or I, according to equation 1:

$$\underset{\textbf{(1g)}}{[Ir(NHNHC_6H_3NO_2)(CO)(PPh_3)_2]^+} + Y_2 \rightarrow \underset{\textbf{(2g)}}{[Ir(Y)(NHNC_6H_3NO_2)(CO)(PPh_3)_2]^+} + HY \qquad (1)$$

These were identified by comparison with the complexes reported previously, the IR bands ν(NH) near 3150 and ν(CO) near 2060 cm^{-1} being particularly characteristic [4]. When an excess of Cl_2 was used, followed by addition of HBF_4 during work-up, a solid was recovered analyzing as the aryl complex $IrCl_2(C_6H_4NO_2)(CO)(PPh_3)_2$. Similar compounds have been synthesized previously by a direct route [5].

(ii) Air oxidation. This is the most obvious property of these arylhydrazido complexes. The least susceptible is the 2-nitro derivative **1g**; all others go yellow as quickly as air or oxygen dissolves in the solutions, to give the aryldiazene complexes **2** with Y = F or FBF_3. We presume that the proton is removed as hydroxide ion, but have no experimental evidence for this. Neither do we have evidence for $[BF_3(OH)]^-$ being present either coordinated or as the counter ion, though this can be a possibility [11]. However, the occurrence of F and FBF_3 in the Y position has been demonstrated neatly by the isolation of both examples analytically and spectroscopically pure and unsolvated from the same reaction for the 4-fluoro derivative. For the FBF_3 complex ν(CO) was about 40 cm^{-1} higher than for the F complex, the only useful IR-spectroscopic difference between them. In the more general cases, varying analyses and spectra have indicated that the products are frequently mixtures of **2** with Y present as both F and FBF_3, along with different degrees of solvation.

(c) Nuclear magnetic resonance

The hydrazido complexes **1** all showed ^{1}H NMR resonances from two hydrogens bound to different nitrogen atoms well downfield from the aromatic resonances (Table 2). Their position was quite sensitive to solvent. On addition of D_2O both signals disappeared within the time required to reobtain a spectrum (0.1 h). The integrated intensity could be obtained quite accurately by comparing it with the OCH_3 intensity of the 2-OCH_3 derivative; it was found to be 1.0/1.0/3.0 for N(1)H/N(2)H/OCH_3.

The spectrum of the 4-F derivative **1b** isotopically substituted with ^{15}N at N(1) showed splitting of only the upfield NH signal ($^1J(^{15}N(1)–H)$ 84 Hz), allowing this to be assigned as N(1)–H and the lower field signal as N(2)–H. A similar result was obtained for the 2-NO_2 derivative **1g**-^{15}N(1), giving $^1J(^{15}N(1)–H) = 86$ Hz. The somewhat broad N(1)–H resonances were not significantly sharpened by ^{15}N-substitution so the width probably arises from the effect of slow exchange rather than the ^{14}N quadrupole. A small splitting (ca. 3 Hz) of the N(2)–H resonance appeared consistently in spectra of both $^{14}N–^{14}N$ and $^{15}N(1)–^{14}N$ complexes **1b**, and may be due to ^3J(HH) though it was not resolvable for the N(1)–H resonance.

In 100 MHz ^{1}H NMR spectra the aromatic region is complex, and it is difficult to make precise assignments to distinguish resonances of the phenyl group protons from those of the *ortho*-metalated aryl ring (Table 2). However, the 2-NO_2 derivative **1g** has also been examined at 400 MHz. Now the spectrum exhibits well-separated resonances due to the phenyl protons (Fig. 1) and assignments have been confirmed using selective decoupling (Table 2). In addition to the doublet and apparent triplet due to the 3-aryl and 4-aryl protons of the *ortho*-metalated ring, there is a resonance due to the 5-aryl protons hidden under the 4-phenyl multiplet. This is identified by intensity and by irradiation at this multiplet (whereupon the 4-aryl signal reduces to a doublet). Irradiation at the 3-phenyl multiplet reduces the 4-phenyl multiplet to a broadened singlet, but reduces the 2-phenyl multiplet to a doublet, due to a residual ^{31}PH coupling of ca. 13 Hz (the 3-aryl and 5-aryl signals are unaffected). Irradiation

TABLE 2

100 MHz ^{1}H NMR DATA FOR ARYLHYDRAZIDO COMPLEXES $[Ir(NHNHC_6H_3X)(CO)(PPh_3)_2]BF_4$ (**1**)

Complex	X	Solvent	δ [a]		Assignment
1b	4-F	$CDCl_3$	13.25 app.d [b]	[ca. 1]	N(2)H
			11.94 br [c]	[ca. 1]	N(1)H
			7.80 app. t (d of d) [d]	[ca. 33]	2-aryl
			ca.7.32c		3-,4-phenyl; aryl
			6.50–7.01 c		2-phenyl; aryl
1d	2-F	$(CD_3)_2CO$	13.81 br	[ca. 1]	N(2)H
			13.12 br	[ca. 1]	N(1)H
			7.46 c	[21]	3-,4-phenyl; aryl
			6.80–7.17 c	[12]	2-phenyl
1f	2-OCH_3	$CDCl_3$	13.24 br	[1]	N(2)H
			12.26 br	[1]	N(1)H
			ca. 7.30 c	[33]	3-,4-phenyl; aryl
			6.69–7.03 c		2-phenyl; aryl
			6.42 app.d [e]		3- or 5-aryl
			3.86 s	[3]	OCH_3
1g	2-NO_2	$(CD_3)_2CO$	14.1 br	[ca. 1]	N(2)H
			12.6 br	[ca. 1]	N(1)H
			8.09 d [e]	[1]	3-aryl
			ca. 7.46 m	[ca. 21]	3-,4-phenyl;
			7.36 m		4-,5-aryl
			6.86–7.15 m	[12]	2-phenyl
		$CDCl_3$	14.1 br	[ca. 1]	N(2)H
			13.1 br [f]	[ca. 1]	N(1)H
			8.00 d [e]	[ca. 33]	3-aryl
			ca. 7.33 m		3-,4-phenyl; 4-,5-aryl
			6.73–7.06 m		2-phenyl
		$CDCl_3$ (at 400 MHz)	14.20 br	[1]	N(2)H
			13.15	[1]	N(1)H
			8.15 d [e]	[1]	3-aryl
			7.55 app.t (8 Hz) of m	[7]	4-phenyl and 5-aryl
			7.45 over lapping d (8 Hz) of d (8 Hz) of d (3 Hz)	[12]	3-phenyl
			7.10 d (13 Hz(PH)) of d (9 Hz) of d (1.5 Hz)	[6]	2-phenyl
			7.00 t (8 Hz)	[1]	4-aryl

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[a] In ppm downfield relative to internal Me_4Si, s = singlet, d = doublet, t = triplet, c = complex, m = multiplet, br = broad, app. = apparent. Integration given in square brackets. [b] Possible ^3J(HNNH) 3 Hz. [c] With $^{15}N(1)$, br d, $^1J(^{15}N(1)H)$ 84 Hz. [d] ^3J(HH) 9 Hz, ^4J(FH) 9 Hz. [e] ^3J(HH) ca. 8 Hz. [f] With $^{15}N(1)$, br d, $^1J(^{15}N(1)H)$ 86 Hz.

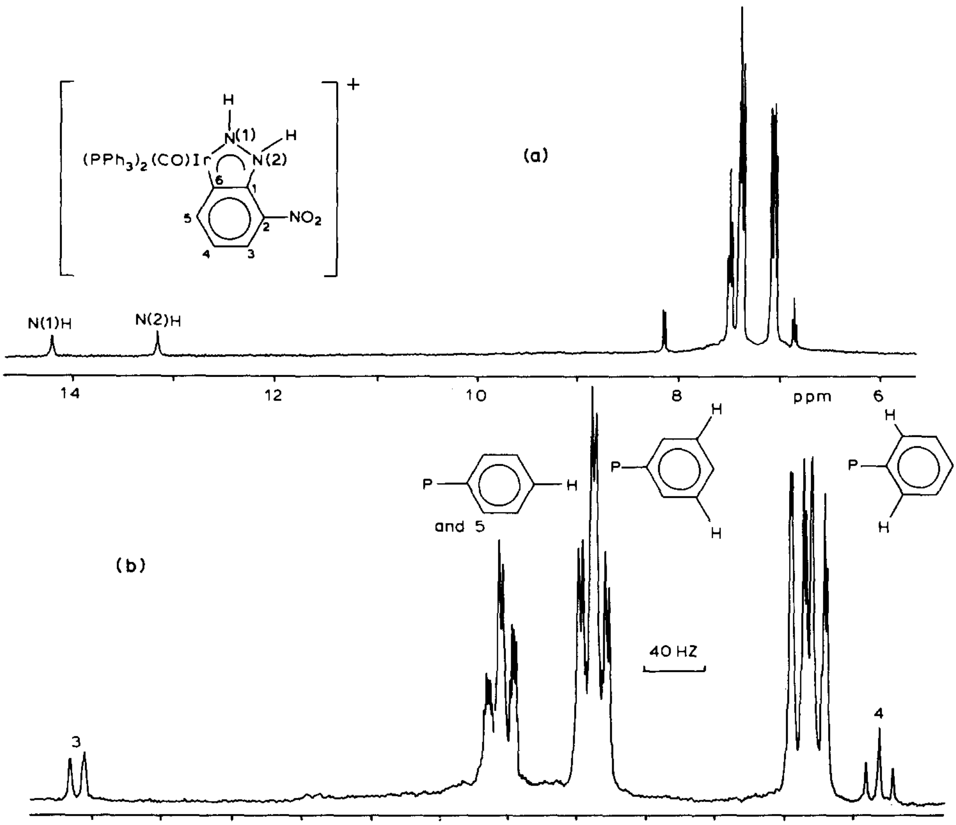

Fig. 1. (a) 400 MHz ^{1}H NMR spectrum of [Ir(NHNHC$_6$H$_3$NO$_2$)CO(PPh$_3$)$_2$]BF$_4$ (**1g**) in CDCl$_3$. (b) Detail of aromatic region.

at the 2-phenyl multiplet reduces the 3-phenyl signal to an apparent doublet and simplifies the fine structure in the 4-phenyl triplet as expected.

The ^{13}C spectrum (100.6 MHz) in CDCl$_3$ at room temperature of **1g** also exhibits well-separated resonances due to the carbons of the triphenylphosphine groups: 133.78 d, $^2J(^{31}$PC) 11.0, C(2); 131.73s, C(4); 130.02d, $^1J(^{31}$PC) 53.7, C(1); 129.06d, $^3J(^{31}$PC) 12.2 C(3). Notably, the C(1) resonance is shifted well upfield compared with triphenylphosphine itself and with some reported PPh$_3$ complexes, and the $^1J(^{31}$PC) coupling constant is rather larger than previously reported for PPh$_3$ complexes [12]. The six resonances expected for the orthometallated ring were located: at 119.59, 123.24 and 146.44 ppm (protonated carbons) and at 138.64, 150.97 and 152.40 ppm (the latter assigned to the IrC by comparison with ref. 13). The carbonyl carbon is at 176.9 ppm. The ^{15}N resonance for **1g**-^{15}N(1) was, as expected, a doublet ($^1J(^{15}$NH) 86 Hz) at 20.89 ppm downfield relative to external ^{15}NH$_4$Cl (10.14 MHz).

The ^{31}P spectrum (40.5 MHz) of **1g** at room temperature in ethanol is a singlet at 13.94 ppm. This broadens at lower temperature and resolves into two equal intensity resonances at 5.64 and 22.66 ppm at −114°C (P–P coupling was not resolved). The low temperature spectrum indicates a stereochemistry with inequivalent phosphines, possibly similar to that observed in the solid state [1]. These become equivalent at higher temperatures by a fluxional process, as expected for a five-coordinate complex.

These hydrazido complexes may be deprotonated by base (e.g., K_2CO_3 in methanol) to yield the neutral *ortho*-metallated aryldiazene complexes **3** [1]. That the deprotonation involves the abstraction of the N(2) proton, leaving N(1) protonated has now been unambiguously determined from the NMR of the $^{15}N(1)$ isotopically substituted derivatives which, after deprotonation, exhibit NH resonances with retention of $^1J(^{15}NH)$ splitting. For example, for the 4-F derivative this is at δ 12.0 ppm with $^1J(^{15}N(1)\text{–}H)$ 81 Hz.

The large ^{15}NH coupling and low field chemical shift of the NH protons in **1** suggest a similarity in the environment of each NH proton with that in complex **2** and with that of the NH protons in aryldiazene complexes in general. In Table 3 we have listed a representative collection of these. The downfield NH chemical shifts of aryldiazene complexes are large, commonly greater than δ 11 ppm. A variety of explanations have been offered for this, including that this is (a) due to the acidity of an aryldiazene NH [14,15] or (b) is a feature of protons at metal-bound nitrogen atoms [16,17]. However, a proton signal does not shift all that much with decrease in electron density, and the pKa of methyldiazene is thought to be ca. 18, barely low enough to be called acidic, yet its NH chemical shift is 15.6 ppm [18,19]. Regarding point (b), the present arylhydrazido complexes illustrate quite clearly that a low-field NH resonance is not exclusively exhibited by metal-bound NH groups since in **1** both N(1)–H and N(2)–H protons resonate beyond δ 12.0 ppm. This is also true for the N(1)–H and N(2)–H protons in the arylhydrazido(1 −) complexes $[CpRe(CO)_2(NHNHAr)][BF_4]$ and $[CpRe(CO)_2(NHN(Me)Ar)]BF_4$ [20]. A more plausible explanation for the low field NH resonance of aryldiazene and certain arylhydrazido complexes is that it is due to a neighbour-anisotropy effect exhibited by the nitrogen atom due to its planar coordination environment, π-delocalization of the "lone" pair of electrons, and the greater diamagnetic susceptibility perpendicular to this plane (cf. aldehydic protons) [21]. This, incidentally, is also consistent with the rather wide variation in observed $^1J(^{15}NH)$ coupling constants (ca. 65–95 Hz)

TABLE 3

^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR N-BOUND PROTONS IN SOME ARYLDIAZENE COMPLEXES

Compound	δ(NH) [a]	$^1J(^{15}NH)$ (Hz)	Ref.
$[PtCl(NHNPh)(PEt_3)_2]BF_4$	15.1 [b]	77	23
	14.25 [c]	74	24
$[RhCl_3(NHNC_6H_4\text{-4-OMe})(PPh_3)_2]$	11.60 [b]	65	25
$[IrCl(CO)(NHNC_6H_3\text{-4-Br})(PPh_3)_2]BF_4$ (**2**)	14.8 [d]	92	4
$[Ir(CO)(NHNC_6H_3\text{-4-F})(PPh_3)_2]$ (**3**)	12.0 [b]	81	this work
$[OsCl(FBF_3)(NHNC_6H_4\text{-4-Me})(CO)(PPh_3)_2]$	13.78 [b]	69	25
$[OsCl_2(NHNC_6H_4\text{-4-Me})(CO)(PPh_3)_2]$	13.50 [b]	67	25
$[RuCl(NHNPh)(CO)_2(PPh_3)_2]ClO_4$	11.75 [c]	65	24

[a] ppm downfield relative to tms. [b] In $CDCl_3$. [c] In CD_2Cl_2. [d] In CD_3CN.

and accords with the suggestion by Roberts that the ^{15}N–H coupling constants for a system such as phenyldiazene should not be determined by the Fermi contact term alone [22].

Experimental

Starting materials and general procedures have been described previously [1]. ^{15}N(1) isotopically substituted derivatives were synthesized using diazonium salts 96% enriched at this position. $IrH(CO)_2(PPh_3)_2$ was synthesized according to ref. 2. Methanolic HBF_4 consisted of 48% aqueous HBF_4 added to methanol to give a concentration ca. 0.02 *M*. NMR spectra were obtained using Varian XL-100 FT or Bruker WM400 instruments. Chemical shifts are listed in ppm relative to $SiMe_4$ (^{1}H and ^{13}C), H_3PO_4 (^{31}P) and $^{15}NH_4Cl$ (^{15}N), with positive values in the direction of increasing frequency.

Reaction of diazonium ions with $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$

(a) Benzenediazonium tetrafluoroborate. A solution of $IrH(CO)(PPh_3)_3$ (0.30 mmol) in toluene (30 ml) and a solution of $C_6H_5N_2BF_4$ (0.61 mmol) in acetone (15 ml) were simultaneously added under N_2 to a flask whilst the mixture was stirred at room temperature. Addition of hydride was begun first, and the flow was balanced so that addition of the two reactants ended simultaneously after 0.1 h. The solution became red-orange. It was stirred a further 0.2 h, then evaporated under vacuum. After 1 h, with about 20 ml of the deep red solution remaining, this was decanted from a brownish oil which formed on the walls of the flask and evaporated to dryness. It was redissolved in 1 ml methanolic HBF_4 and then stirred vigorously with 3 ml Et_2O and 4 ml hexane to produce an orange solid **1a** (13%) which was washed with ether and vacuum dried. The brown oil was also evaporated to dryness, treated with methanolic HBF_4 (1.6 ml) and the maroon solid tetrazene complex **4a** which formed was washed with methanol/ether and vacuum dried (30%). It was identified by IR [3]. Anal. Found: C, 56.2; H, 3.94; N, 5.24. $[Ir(N_4Ph_2)(CO)(PPh_3)_2]BF_4$ calcd.: C, 56.5; H, 3.87; N, 5.38%.

(b) 4-Fluorobenzenediazonium tetrafluoroborate. This reaction was carried out as above, and the red solution again decanted from oily material after partial evaporation. The orange-red hydrazido complex **1b** was obtained by evaporation of the red solution, dissolving the solid in methanolic HBF_4 and precipitation with ether (43%). The filtrate which consisted mainly of unprecipitated hydrazido complex **1b** was easily oxidized to the yellow aryldiazene complex **2b**, by leaving overnight at −5°C in a tube with an ungreased stopper. The yellow solid **2b**-F was precipitated with hexane and recrystallized twice from methanol-ether. IR ν(NH) 3160, ν(CO) 2041 cm^{-1}. Anal. Found: C, 52.9; H, 3.55; N, 2.94; F, 11.6. $[Ir(NHNC_6H_3F)(F)(CO)(PPh_3)_2]BF_4$ calcd.: C, 53.0; H, 3.52; N, 2.88; F. 11.7%. The oily material, above, was dissolved in methanol (1 ml) and cooled to −5°C to yield red crystals of the tetrazene complex [3] **4b** (11%). Anal. Found: C, 54.7; H, 3.67; N, 5.08. $[Ir(N_4(C_6H_4F)_2)(CO)(PPh_3)_2]BF_4$ calcd.: C, 54.6; H, 3.55; N, 5.20%.

The collected filtrates from the separation of hydrazido and tetrazene complexes were evaporated to dryness in vacuo at room temperature, redissolved in methanol and treated with benzene and ether to yield an oil which principally contained $[IrH_2(CO)(PPh_3)_3]BF_4$. The filtrate was again evaporated to dryness, redissolved in acetone/toluene and allowed to evaporate slowly in air. The crude solid so formed was washed lightly with acetone to remove brown oily impurity and the slow crystallization repeated several more times until a clean yellow solid **2b**-FBF_3 was obtained. IR: ν(NH) 3165, ν(CO) 2074 cm^{-1}. Anal. Found: C, 49.6; H, 3.52; N, 2.57; F, 16.1. $[Ir(NHNC_6H_3F)(FBF_3)(CO)(PPh_3)_2]BF_4$ calcd.: C, 49.6; H, 3.29; N, 2.69; F, 16.4%.

(c) 3-Fluorobenzenediazonium tetrafluoroborate. The 3-fluorophenylhydrazido complex **1c** was synthesized as for **1a**. The infrared spectrum of the crude product showed a substantial amount of **1c** to be present, but it could be crystallized only with difficulty and in meager amount, so purification was not achieved.

(d) 2-Fluorobenzenediazonium tetrafluoroborate. This synthesis was carried out as in part (a) and the hydrazido complex **1d** (11%) was separated from the decantate (after evaporating it to dryness) by stirring it in methanolic HBF_4 and filtering the solid which reprecipitated spontaneously at room temperature. A small yield (1%) of impure tetrazene complex **4d** (orange) was precipitated with ether at −5°C from an ethanol solution of the early-oiling material, and was identified by IR [3]. Anal. Found: C, 52.4; H, 3.59; N, 4.61. $[Ir\{N_4(C_6H_4F)_2\}(CO)(PPh_3)_2]BF_4$ calcd.: C, 54.6; H, 3.55; N, 5.20%.

(e) 4-Methoxybenzenediazonium tetrafluoroborate. A synthesis carried out in the manner of (a) gave appreciable crude hydrazido complex in the decantate, ν(NH) 3285, ν(CO) 1990 cm^{-1}, but the recovery of pure material from this synthesis was unsuccessful. A similar reaction conducted with $IrH(CO)_2(PPh_3)_2$ yielded some $[IrH_2(CO)_2(PPh_3)_2]BF_4$ (17%) and IR evidence for hydrazido complex in the remainder, but again this could not be obtained pure. A reaction conducted in acetone gave, after stripping, a residue from which $[IrH_2(CO)_2(PPh_3)_2]BF_4$ and the tetrazene complex **4e** were solidified using methanolic HBF_4 and separated by recrystallization from acetone/benzene. Anal. Found: C, 55.6; H, 4.11; N, 4.90. $[Ir\{N_4(C_6H_4OCH_3)_2\}(CO)(PPh_3)_2]BF_4$ calcd.: C, 55.6; H, 4.02; N, 5.08%.

(f) 2-Methoxybenzenediazonium tetrafluoroborate. This was carried out as in part (a), except that benzene was substituted for toluene. As a result, no separation of oil occurred and evaporation in vacuo left an involatile residue from which complex **1f** solidified upon addition of 2 ml methanolic HBF_4. This was washed with 5/1 ether/methanol and then ether and had ν(NH) 3256m, ν(CO) 2000vs cm^{-1}. No attempt was made to separate other products.

(g) 2-Nitrobenzenediazonium tetrafluoroborate. This was carried out as described previously [1]. Note that the bulk of the hydrazido complex was contained in the oil which separated on the walls of the flask rather than in the decantate. The hydrazido complex could be obtained pure by dissolving the crude material in methanolic HBF_4, from which it reprecipitated and was washed with ether (11%).

(h) 3-Nitrobenzenediazonium tetrafluoroborate. Synthesis as in part (a) was successful in producing crude hydrazido complex **1h** in both the oily fraction and the decantate (IR evidence), but it could not be obtained solid using a variety of solvents and conditions.

(i) 3-Methylbenzenediazonium tetrafluoroborate. This reaction was carried out as for part (a), but all solvents were vacuum stripped and the residue then dissolved in methanolic HBF_4 (6 ml). Addition of ether and hexane did not form a precipitate, so the solution was filtered and evacuated to a volume of 3–4 ml, when an orange solid **1i** formed. This was recrystallized from a minimum of methanol by addition of

ether/hexane, and had ν(NH) 3282m, ν(CO) 1993vs cm^{-1}.

(j) 4-Methylbenzenediazonium tetrafluoroborate. The diazonium salt (0.10 mmol) in degassed acetone and $IrH(CO)_2(PPh_3)_2$ (0.10 mmol) in degassed benzene were added together dropwise under N_2 whilst the mixture was stirred at room temperature over 0.1 h. The solution color remained yellow until near the end of the addition but over 0.3 h a full red developed. Solvents were removed in vacuo and the residue dissolved in 1 ml methanolic HBF_4; addition of 6 ml ether precipitated $[IrH_2(CO)_2(PPh_3)_2]BF_4$ as a white solid (16%). The filtrate was again evaporated and retreated with 0.8 ml fresh methanolic HBF_4 and ether (4 ml) giving an orange solid which was the hydrazido complex **1j** (34%). IR: ν(NH) 3276s, ν(CO) 1996 vs cm^{-1}. The filtrate from this procedure also contained hydrazido complex, which was oxidized to the aryldiazene complex **2j**-F by addition of hexane until almost cloudy and placing in the freezer in a tube with an ungreased stopper. A yellow solid **2j**-F (12%) was deposited. Anal. Found: C, 54.7; H, 4.10; N, 2.82%. $[Ir(NHNC_6H_3CH_3)(F)(CO)(PPh_3)_2]BF_4$ calcd.: C, 54.5; H, 3.85; N, 2.89%. IR: ν(NH) 3161m, ν(CO) 2037vs cm^{-1}. From a reaction of $IrH(CO)(PPh_3)_3$ with the diazonium salt in benzene/acetone otherwise conducted as in (a), the residue after stripping solvents appeared by IR not to contain much hydrazido complex **1j**. Recrystallization from acetone/ether allowed separation of first **2j**-F followed by the tetrazene complex **4j**, identified by IR. Anal. Found: C, 57.2; H, 4.26; N, 5.08. $[Ir\{N_4(C_6H_4CH_3)_2\}(CO)(PPh_3)_2]BF_4$ calcd.: C, 57.2; H, 4.14; N, 5.24%.

(k) 2-Trifluoromethylbenzenediazonium tetrafluoroborate. This reaction was attempted in the manner of part (a). As described previously [1], crude material clearly contained hydrazido complex by IR, but on attempted work-up the hydrazido complex appeared always to oxidize to the aryldiazene complex **2k**. The reaction was also attempted using $IrH(CO)_2(PPh_3)_2$, but the crude isolate appeared to contain little or no hydrazido complex. $[IrH_2(CO)_2(PPh_3)_2]BF_4$ was recovered using methanol/ether. Anal. Found: C, 52.8; H, 3.75. $[IrH_2(CO)_2(PPh_3)_2]BF_4$ calcd.: C, 53.0; H, 3.74%. IR: ν(CO) A_1 2071wm, ν(IrH) 2021vs, ν(CO) B_1 1999vvs cm^{-1}. Further work-up of the filtrate again yielded the aryldiazene complex **2k**-F.

Synthesis of $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2][BF_4]$, (1g) from $IrCl(CO)(PPh_3)_2$. Improved method.

$IrCl(CO)(PPh_3)_2$ (161.0 mg; 0.206 mmol) was ground together with $[2\text{-}NO_2C_6H_4N_2][BF_4]$ (48.7 mg; 0.206 mmol) and the mixture dissolved in cold (ca. −25°C) degassed acetone (10 ml) under nitrogen to give an orange solution. The addition of ethanol (ca. 2 ml) may be required for complete dissolution. An equimolar amount of finely ground $AgBF_4$, and ethanol (1 ml) were added and the mixture stirred at −25°C for 2 h. The cold bath was then removed and the mixture allowed to warm to room temperature. The solution became red and a precipitate of AgCl formed, which was filtered off. Vacuum evaporation gave **1g** as a maroon solid which was washed twice with a minimum of cold methanol, then with diethyl ether, and vacuum dried. Yield 92%. IR: ν(CO) 2000, ν(NH) 3280 cm^{-1}. Anal. Found: C, 52.0; H, 3.71; N, 3.99. Calcd. C, 52.7; H, 3.58; N, 4.28%. Mass spectrum (xenon-sulfolane fast atom bombardment, MS9) m/e 896 (^{193}Ir), $[Ir(NHNHC_6H_3NO_2)(CO)(PPh_3)_2]^+$.

Preparation of aryldiazene complexes $Ir(NHNC_6H_3X)(CO)(PPh_3)_2$ *(3)*

$Ir(NHNC_6H_3\text{-}4\text{-}F)(CO)(PPh_3)_2$ (3b). The arylhydrazido complex **1b** was treated with a stoichiometric amount of 0.05 *M* K_2CO_3 in methanol. The orange-red solid dissolved to give a dark red solution which then reprecipitated an orange solid (75%) which was filtered and washed with water. IR (KBr) ν(NH) 3287, ν(CO) 1953 cm^{-1}; IR ($CHCl_3$) ν(NH) 3283, ν(CO) 1961s cm^{-1}; $\nu(BF_4)$ absent. ^{1}H NMR ($CDCl_3$) 12.0br singlet N*H* (with ^{15}N(1), 12.0 doublet $^1J(^{15}NH)$ 81 Hz); 8.2–8.4 complex (aryl and phenyl). Anal. Found: C, 59.2; H, 4.10; N, 3.18. $Ir(NHNC_6H_3F)(CO)(PPh_3)_2$ calcd.: C, 59.5; H, 3.95; N, 3.23%.

$Ir(NHNC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2$ (3d). This compound was synthesized by adding an excess of triethylamine at −73°C to an acetone/toluene solution of hydrazido complex **1d** resulting directly from the synthesis (vide infra). Volatiles were removed from the dark red solution at 0°C and the residue extracted with benzene. The benzene solution was stripped and the residue of **3d** was triturated with hexane to give a red solid. IR (KBr): ν(NH) 3287w, ν(CO) 1956 cm^{-1}; $\nu(BF_4)$ absent.

$Ir(NHNC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2$ (3g). A stoichiometric amount of degassed aqueous 10.0 m*M* NaOH was added to **1g** in acetone to give a purple solution from which a purple solid was precipitated with water. This was dried, extracted into benzene and freeze-dried to give **3g** (80%). IR (KBr) ν(NH) 3280w, ν(CO) 1960vs, no $\nu(BF_4^-)$. ^{1}H NMR ($CDCl_3$) 12.7br,s. N*H*; 7.90–6.55 complex, aryl and phenyl.

$Ir(NHNC_6H_3\text{-}3\text{-}NO_2)(CO)(PPh_3)_2$ (3h). The crude product from the synthesis of hydrazido complex **1h** (vide infra) was neutralized with 0.1 *M* methanolic KOH and a red-brown solid was precipitated with water. This was extracted into acetone, leaving some unreacted $IrH(CO)(PPh_3)_3$, and then chromatographed under nitrogen as a solution in degassed toluene on degassed silica gel, eluting with toluene and collecting the deep red band. The toluene was stripped and the residue ground with ether to give **3h** and a purple solid (65%). IR(KBr) ν(NH) 3278w, 3253wm, ν(CO) 1965s cm^{-1}; no $\nu(BF_4^-)$. Anal. Found: C, 57.4; H, 3.88; N, 4.63. $Ir(NHNC_6H_3NO_2)(CO)(PPh_3)_2$ calcd.: C, 57.7; H, 3.83; N, 4.70%.

$Ir(NHNC_6H_3\text{-}2\text{-}CF_3)(CO)(PPh_3)_2$ (3k). Although a purified sample of the hydrazido complex could not be obtained (vide infra) the aryldiazene complex **3k** was obtained by treating a fresh reaction mixture containing the crude hydrazido complex with 0.1 *M* methanolic KOH until the solution was slightly basic. A red-orange solid, analytically impure **3k**, was filtered and washed repeatedly with water until free from BF_4^- (IR). This was chromatographed in benzene on a silica gel column under N_2 and eluted with benzene, collecting the violet-red band. Solvent was removed in vacuo and the residue triturated with hexane and then ether to leave **3k** as an orange-red solid. IR (KBr) ν(NH) 3278wm, ν(CO) 1943vs, $\nu(BF_4^-)$ absent. Anal. Found: C, 57.7; H, 4.14; N, 2.80. $Ir(NHNC_6H_3CF_3)(CO)(PPh_3)_2$ calcd.: C, 57.6; H, 3.75; N, 3.05%.

Reaction of arylhydrazido complex 1 with halogens

(a) Br_2. When $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$ (**1g**) (0.1 mmol) in methanol (3 ml) was treated with a slight excess of 0.084 *M* Br_2 in water, the intensely colored red solution became pink. Evacuation at room temperature gave a yellow-brown solid which was recrystallized from CH_2Cl_2/hexane to give $[IrBr(NHNC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$, **2g**-Br having ν(NH) 3143wm, ν(CO) 2060s cm^{-1}. Anal. Found: C, 48.3; H, 3.24; N, 3.71. $[IrBr(NHNC_6H_3NO_2)$-

$(CO)(PPh_3)_2]BF_4$ calcd.: C, 48.6; H, 3.23; N, 3.96%.

(b) I_2. A stoichiometric amount of I_2 in benzene was added to **1g** in methanol to give an orange-yellow color. After evaporation to dryness, recrystallization from acetone/hexane gave a reddish solid which was impure **2g**-I. IR ν(NH) 3155w, ν(CO) 2060s, $\nu(NO_2)$ 1532, 1346. Anal. Found: C, 45.7; H, 3.48; N, 3.35%. $[IrI(NHNC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$ calcd.: C, 46.6; H, 3.09; N, 3.79%.

(c) Cl_2. Oxidation of **1g** in methanol/ether (1/2 acidified with a few drops of 48% aqueous HBF_4) by a stoichiometric amount of Cl_2 in benzene was carried out essentially as in (b) to give a yellow-brown solution, from which **2g**-Cl was recovered and identified by IR [4]: ν(NH) 3150w, ν(CO) 2070s, ν(IrCl) 300w cm^{-1}. A 10-fold excess of Cl_2 was used in a second experiment, giving a colorless solution which was evacuated to leave a yellow solid. Extraction with methanolic HBF_4 left a white residue which was $Ir(C_6H_4NO_2)(CO)Cl_2(PPh_3)_2$ [5]. IR ν(CO) 2040s, ν(IrCl) ca. 345, 285vvw. Anal. Found: C, 54.3; H, 3.96; N, 1.43%. $Ir(C_6H_4NO_2)(CO)Cl_2(PPh_3)_2$ calcd.: C, 54.5; H, 3.95; N, 1.44%.

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