Cationic Diaryltriazene, Hydrido(diaryltriazenido)-, and Diarylacetamidine Complexes of Rhodium and Iridium †

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Protonation of $[M(CO)L_2(RNNNR)]$ with HBF_4 affords either $[IrH(CO)L_2(RNNNR)][BF_4]$ (1; L = PPh_3, R = p-MeC_6H_4 or p-FC_6H_4; L = $PMePh_2$, R = p-FC_6H_4) or $[M(CO)L_2(RNNNHR)][BF_4]$ (2; M = Rh, L = PPh_3, R = Ph, p-MeC_6H_4, or p-FC_6H_4). Complexes (2; M = Rh or Ir), and $[M(CO)L_2\{MeC(=NR)NHR\}][BF_4]$ (3; M = Rh or Ir, L = PPh_3, R = Ph or p-MeC_6H_4), may be prepared directly from the appropriate diaryltriazene or diarylacetamidine and $[M(CO)L_2(OCMe_2)][BF_4]$.

A WIDE variety of transition-metal complexes of the triazenido-group, $[RNNNR]^-$ (R = aryl), has recently been synthesised;[1-3] structural studies show the anion can bond as a unidentate[4,5] or bidentate[6,7] ligand to one metal, or as a bridging ligand to two.[8] Surprisingly, the reactions of co-ordinated nitrogen ligands such as $[RNNNR]^-$ and the acetamidine anion $[R^2C(=NR^1)NR^1]^-$, which bear some resemblance to the allyl and carboxylate groups, have been neglected. Unco-ordinated diaryltriazenes, RNNNHR, react with protons according to equation (1), the equilibrium lying to the

$$RNNNHR + H^+ \rightleftharpoons [RN_2]^+ + NH_2R \qquad (1)$$

left in the presence of base. In addition, diaryltriazenes may be deprotonated, for example by reaction with sodium hydride or with lithium alkyls or aryls, to give the triazenide salts M[RNNNR] (M = Li or Na). Our interest[9,10] in arenediazo-complexes has prompted us, therefore, to investigate the protonation of the co-ordinated triazenido-group in that a two-stage protonation might be expected to result in amine elimination and formation of the co-ordinated $[RN_2]^+$ ligand. We have, however, observed only one-stage protonation of $[M(CO)L_2(RNNNR)]$ which results in the formation of either hydrido-complexes (M = Ir) or triazene derivatives (M = Rh) *via* protonation at nitrogen. We also report the direct synthesis of the iridium triazene complexes, and analogous diarylacetamidine complexes, from $[M(CO)L_2(OCMe_2)]^+$ and the appropriate organic ligand.

RESULTS AND DISCUSSION

Addition of aqueous HBF_4 (42% w/w) to $[Ir(CO)L_2(RNNNR)]$ (L = PPh_3, R = p-MeC_6H_4 or p-FC_6H_4;

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† No reprints available.

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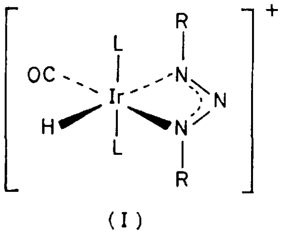
$L = PMePh_2$, $R = p\text{-}FC_6H_4$) in CH_2Cl_2 affords yellow solutions from which the yellow hydridotriazenido-complexes $[IrH(CO)L_2(RNNNR)][BF_4]$ (1) may be isolated by addition of diethyl ether. The characterisation of (1) as cationic hydrides follows from i.r., microanalytical (C, H, and N), and conductance data (Table 1) and ^1H n.m.r. spectroscopy (Table 2). The observation of the metal hydride resonance as a 1 : 2 : 1 triplet in each case, and of an apparent triplet [τ 7.80, $|J(PH) + J(P'H)|$ 3.8 Hz] for the phosphine methyl groups for (1; $R = p\text{-}FC_6H_4$, $L = PMePh_2$) is consistent with the presence of equivalent *trans* phosphines *cis* to the hydride ligand; the inequivalence of the methyl resonances for (1; $R = p\text{-}MeC_6H_4$, $L = PPh_3$) allows structure (I) to be assigned unequivocally to (1). *X*-ray structural studies have revealed[7] the same stereochemistry for $[RuH(CO)(PPh_3)_2(RNNNR)]$ ($R = p\text{-}MeC_6H_4$).



(I)

TABLE 1

Analytical, conductance, and i.r. data for $[IrH(CO)L_2(RNNNR)][BF_4]$ (1), $[M(CO)L_2(RNNNHR)][BF_4]$ (2), and $[M(CO)L_2\{MeC(=NR)NHR\}][BF_4]$ (3)

Complex	M	L	R	Colour	Yield (%)	Λ [a] S cm^2 mol^{-1}	Analysis [b] (%) C	H	N	$\bar{\nu}$(CO) [c] cm^{-1}
(1)	Ir	PPh_3	$p\text{-}MeC_6H_4$	Golden-yellow	18	131	56.6(56.5) [d]	4.5(4.5)	3.7(3.7)	2 060
(1)	Ir	PPh_3	$p\text{-}FC_6H_4$	Yellow	55	130	55.2(55.3)	4.0(3.7)	3.7(4.0)	2 061
(1)	Ir	$PMePh_2$	$p\text{-}FC_6H_4$	Yellow	80	132	50.0(49.8)	4.1(3.8)	4.1(4.5)	2 061
(2)	Rh	PPh_3	Ph	Yellow	90	158	62.4(62.6) [e]	4.9(4.8)	3.7(4.2)	2 023
(2)	Rh	PPh_3	$p\text{-}MeC_6H_4$	Yellow	91	166	63.7(63.3)	5.1(4.7)	4.4(4.3)	2 022
(2)	Rh	PPh_3	$p\text{-}FC_6H_4$	Yellow	98	176	59.8(60.3)	4.1(4.0)	4.2(4.3)	2 024
(2)	Ir	PPh_3	Ph	Yellow	89	187	57.4(57.2)	4.6(4.0)	3.8(4.1)	2 012
(2)	Ir	PPh_3	$p\text{-}MeC_6H_4$	Yellow	93	179	57.6(58.0)	4.4(4.3)	3.6(4.0)	2 011
(2)	Ir	PPh_3	$p\text{-}FC_6H_4$	Yellow	95	175	52.6(52.2) [f]	3.8(3.6)	3.2(3.6)	2 014
(3)	Rh	PPh_3	Ph	Yellow	90	195	64.3(64.3)	5.0(4.7)	2.8(2.9)	2 009
(3)	Rh	PPh_3	$p\text{-}MeC_6H_4$	Yellow	63	160	60.4(60.9) [f]	4.8(4.7)	2.5(2.6)	2 009
(3)	Ir	PPh_3	Ph	Yellow	95	185	58.5(58.8)	4.8(4.3)	2.5(2.7)	1 999
(3)	Ir	PPh_3	$p\text{-}MeC_6H_4$	Yellow	85	130	59.1(59.5)	4.7(4.5)	2.8(2.6)	1 998

[a] 10^{-4} mol dm^{-3} in acetone. [b] Calculated values are given in parentheses. [c] In CH_2Cl_2. [d] Calculated figures for $[IrH(CO)(PPh_3)_2(p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)][BF_4]\cdot 0.5CH_2Cl_2\cdot 0.5Et_2O$. The presence of the solvent molecules in the ratios given was confirmed by the ^1H n.m.r. spectrum. [e] Calculated for a 1 : 1 acetone solvate and confirmed by the ^1H n.m.r. spectrum. [f] Calculated for a 1 : 1 CH_2Cl_2 solvate and confirmed by the ^1H n.m.r. spectrum.

TABLE 2

Hydrogen-1 n.m.r. data for $[IrH(CO)L_2(RNNNR)][BF_4]$ (1), $[M(CO)L_2(RNNNHR)][BF_4]$ (2), and $[M(CO)L_2\{MeC(=NR)NHR\}][BF_4]$ (3)

Complex	M	L	R	τ (in $CDCl_3$)
(1)	Ir	PPh_3	$p\text{-}MeC_6H_4$	2.0—4.0(m, 38 H, PPh_3 and C_6H_4), 7.66(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 7.86(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 26.55[t, 1 H, J(PH) 11 Hz, Ir–H]
(1)	Ir	PPh_3	$p\text{-}FC_6H_4$	2.0—4.0(m, 38 H, PPh_3 and $p\text{-}FC_6H_4$), 26.98[t, 1 H, J(PH) 11 Hz, Ir–H] [a]
(1)	Ir	$PMePh_2$	$p\text{-}FC_6H_4$	2.2—3.4(m, 28 H, $PMe\mathit{Ph}_2$ and $p\text{-}FC_6H_4$), 7.8[apparent t, 6 H, $|J(PH) + J(P'H)|$ 3.8 Hz], 26.7(t, 1 H, J(PH) 12 Hz, Ir–H] [a]
(2)	Rh	PPh_3	$p\text{-}MeC_6H_4$	2.0—3.2(m, 38 H, PPh_3 and C_6H_4), 7.68(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 7.74(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$)
(2)	Ir	PPh_3	$p\text{-}MeC_6H_4$	2.2—3.4(m, 38 H, PPh_3 and C_6H_4), 7.70(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 7.76(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$)
(3)	Rh	PPh_3	$p\text{-}MeC_6H_4$	1.71(s, 1 H, NH), 2.51(m, 30 H, PPh_3), [2.86(d, 2 H), 3.25(d, 2 H), 3.63(d, 2 H), 3.96(d, 2 H)],[b] 7.66(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 7.74(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 8.49(s, 3 H, C–Me)
(3)	Ir	PPh_3	$p\text{-}MeC_6H_4$	1.36(s, 1 H, NH), 2.58(m, 30 H, PPh_3), [2.90(d, 2 H), 3.30(d, 2 H), 3.66(d, 2 H), 4.02(d, 2 H)],[b] 7.68(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 7.78(s, 3 H, $p\text{-}\mathit{Me}C_6H_4$), 8.48(s, 3 H, C–Me)

[a] In CD_2Cl_2. [b] $|J_O + J_P|$ 8 Hz; these peaks are attributed to two inequivalent phenylene groups.

In contrast to the iridium case, addition of aqueous HBF_4 to a suspension of $[Rh(CO)(PPh_3)_2(RNNNR)]$ (R = Ph, $p\text{-}MeC_6H_4$, or $p\text{-}FC_6H_4$) in diethyl ether yields a pale yellow precipitate of (2) (Table 1). The absence of a metal hydride resonance in the ^1H n.m.r. spectrum of (2), analytical and conductance data, and the considerable difference between ν(CO) for (1) and (2), suggest that the (2) has a similar composition to (1) with protonation at nitrogen the most likely. Although no resonance due to the NH proton has been detected in the ^1H n.m.r. spectrum, the direct preparation of (2) from the free diaryltriazene and $[Rh(CO)(PPh_3)_2(OCMe_2)]^+$ confirms its identity as $[Rh(CO)(PPh_3)_2(RNNNHR)][BF_4]$. The inequivalence of the methyl resonances in the ^1H n.m.r. spectrum of (2; $R = p\text{-}MeC_6H_4$), and a preliminary *X*-ray structural study,* show (2) to have structure (II).

In ethanol, the reaction of aqueous HBF_4 with

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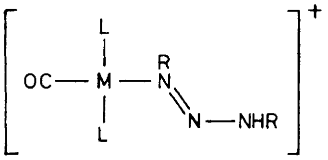
* Severe disorder problems have hampered full refinement of the structure of $[Rh(CO)(PPh_3)_2(PhNNNHPh)][BF_4]$. The gross geometry as shown in (II) is, however, certain (L. E. Smart and P. Woodward, personal communication).

$[Rh(CO)(PPh_3)_2(RNNNR)]$ results in removal of the nitrogen-donor ligand and isolation of the known[11] cationic complex $[Rh(CO)(PPh_3)_2(OCMe_2)][BF_4]$ after recrystallisation from acetone–diethyl ether.



(II)

Complex (2) undergoes triazene displacement with chloride ion or with iodine, to give $[RhCl(CO)(PPh_3)_2]$ and $[RhI_3(CO)(PPh_3)_2]$ respectively, and quantitative deprotonation with NEt_3 or *NNN'N'*-tetramethylnaphthalene-1,8-diamine (Proton Sponge). Attempts to alkylate the co-ordinated triazenido-ligand were apparently unsuccessful. Although green (R = Ph) and yellow (R = *p*-MeC_6H_4 or *p*-FC_6H_4) crystalline solids containing the fluorosulphate anion were isolated from the reaction between $[Rh(CO)(PPh_3)_2(RNNNR)]$ and $MeOSFO_2$ in diethyl ether, no methyl groups could be detected in the ^1H n.m.r. spectra of the products.

When (1; L = PPh_3, R = Ph) was allowed to stand in the solid state a new carbonyl absorption at 2 001 cm^{-1} (Nujol mull) appeared after several weeks. The possibility that (1) partially isomerises to (2; M = Ir) in the solid state, suggested by the similarity in stretching frequency of the new carbonyl absorption and that of (2; M = Rh) (Table 1), led us to attempt the synthesis of (2; M = Ir) by other methods. Addition of a diethyl ether solution of a diaryltriazene, RNNNHR, to a solution of $[M(CO)(PPh_3)_2(OCMe_2)][BF_4]$[11] in CH_2Cl_2 afforded (2; M = Rh or Ir) confirming that protonation of $[Rh(CO)L_2(RNNNR)]$ occurs at nitrogen and that isomerisation of (1) to (2; M = Ir) may occur in the solid state; an authentic sample of $[Ir(CO)(PPh_3)_2(PhNNNHPh)][BF_4]$ shows one carbonyl absorption at 2 005 cm^{-1} (Nujol mull).

The direct synthesis of (2) from diaryltriazenes and $[M(CO)(PPh_3)_2(OCMe_2)][BF_4]$ has enabled us to prepare related cationic diarylacetamidine complexes by the same method. Thus, addition of MeC(=NR)NHR in diethyl ether to $[M(CO)(PPh_3)_2(OCMe_2)][BF_4]$ in CH_2Cl_2 gives pale yellow $[M(CO)(PPh_3)_2\{MeC(=NR)NHR\}][BF_4]$ (3; R = Ph or *p*-MeC_6H_4) in good yield. Formulation of (3) as acetamidine complexes follows from i.r., analytical (C, H, and N), conductance, and ^1H n.m.r. data (Tables 1 and 2). The ^1H n.m.r. spectra not only show the inequivalence of the methyl resonances of (3; R = *p*-MeC_6H_4) but also broad but definite signals due to the NH protons. The i.r. spectra show strong absorptions, due to C=N stretching vibrations, in the 1 550—1 600 cm^{-1} region [*e.g.* M = Rh, R = Ph; ν(C=N) (Nujol) at 1 571 cm^{-1}], and a comparison of the carbonyl-stretching frequencies for (2) and (3) suggests that diarylacetamidines are better σ-donor (or worse π-acceptor) ligands than diaryltriazenes.

Attempts to deprotonate (3) with NEt_3 or Proton Sponge to give complexes of the ligand $[MeC(=NR)NR]^-$ have failed. We have also found that the reaction between $[MH(CO)(PPh_3)_3]$ (M = Rh or Ir) and a diarylacetamidine, or between $[M^1Cl(CO)(PPh_3)_2]$ (M^1 = Rh or Ir) and $M^2[MeC(=NR)NR]$ (M^2 = Li or Na) did not yield acetamidinato-complexes. The analogous reactions using RNNNHR or $M^2[RNNNR]$ (M^2 = Li or Na) are those used to prepare $[M(CO)L_2(RNNNR)]$ (M = Rh or Ir).

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds $[Ir(CO)L_2(RNNNR)]$ (L = PPh_3, R = *p*-MeC_6H_4 or *p*-FC_6H_4; L = $PMePh_2$, R = *p*-FC_6H_4),[1] $[Rh(CO)(PPh_3)_2(RNNNR)]$ (R = Ph, *p*-MeC_6H_4, or *p*-FC_6H_4),[2] $[IrCl(CO)(PPh_3)_2]$,[12] RNNNHR,[13] and MeC(=NR)NHR[14] were prepared by published procedures. Aqueous HBF_4 (42% w/w) was obtained from B.D.H., and $Ag[BF_4]$ from Ozark-Mahoning Co., Tulsa, Oklahoma. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on Perkin-Elmer PE 257 and 457 spectrophotometers and calibrated against the band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA 100 and Jeol JNM-PS-100 spectrometers at 100 MHz using tetramethylsilane as internal reference. Microanalyses were by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

*Carbonyl(di-*p*-fluorophenyltriazenido)hydridobis(triphenylphosphine)iridium Tetrafluoroborate,* $[IrH(CO)(PPh_3)_2(p\text{-}FC_6H_4NNNC_6H_4F\text{-}p)][BF_4]$.—To a stirred solution of $[Ir(CO)(PPh_3)_2(p\text{-}FC_6H_4NNNC_6H_4F\text{-}p)]$ (0.50 g, 0.51 mmol) in CH_2Cl_2 (80 cm^3) was added 42% (w/w) aqueous HBF_4 (0.15 g, 0.51 mmol). After 24 h the orange solution was filtered, reduced in volume to *ca.* 10 cm^3, and treated with diethyl ether (*ca.* 50 cm^3). On cooling to 0 °C a yellow precipitate formed, yield 0.30 g (55%). Recrystallisation from CH_2Cl_2–OEt_2 gave an analytically pure sample of the *complex* as yellow crystals.

The *complexes* $[IrH(CO)(PMePh_2)_2(p\text{-}FC_6H_4NNNC_6H_4F\text{-}p)][BF_4]$, recrystallised from CH_2Cl_2–n-hexane and $[IrH(CO)(PPh_3)_2(p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)][BF_4]$ were prepared similarly. Crystallisation of the latter was only achieved after drying the initial reaction mixture in CH_2Cl_2 over anhydrous $Na_2[SO_4]$ for 15 min.

Carbonyl(diphenyltriazene)bis(triphenylphosphine)rhodium Tetrafluoroborate, $[Rh(CO)(PPh_3)_2(PhNNNHPh)][BF_4]$.—To a suspension of orange-red $[Rh(CO)(PPh_3)_2(PhNNNPh)]$ (0.20 g, 0.24 mmol) in diethyl ether (40 cm^3) was added, dropwise, 42% (w/w) aqueous HBF_4 (0.067 g, 0.23 mmol). After stirring for 5 min the resulting yellow precipitate was removed, washed with n-hexane and then with diethyl ether, and dried in air, yield 0.20 g (90%). Recrystallis-

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ation from acetone–diethyl ether gave the *complex* as 1 : 1 acetone solvate.

The *complexes* [Rh(CO)(PPh$_3$)$_2$(RNNNHR)][BF$_4$] (R = pMeC$_6$H$_4$ *or* p-FC$_6$H$_4$) were prepared similarly.

Carbonyl(diphenyltriazene)bis(triphenylphosphine)iridium Tetrafluoroborate, [Ir(CO)(PPh$_3$)$_2$(PhNNNHPh)][BF$_4$].—To a solution of [IrCl(CO)(PPh$_3$)$_2$] (0.20 g, 0.26 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added a solution of Ag[BF$_4$] (0.05 g, 0.26 mmol) in acetone (3 cm^3). After stirring for 10 min, the precipitated AgCl was removed and the filtrate evaporated to dryness. To the resulting yellow residue of [Ir(CO)(PPh$_3$)$_2$(OCMe$_2$)][BF$_4$], dissolved in CH$_2$Cl$_2$ (5 cm^3), was rapidly added, with stirring, PhNNNHPh (0.05 g, 0.25 mmol) in diethyl ether (40 cm^3). After 5 min the yellow precipitate was removed by filtration and recrystallised from acetone–diethyl ether to give the *complex*, yield 0.23 g (89%).

The complexes [Ir(CO)(PPh$_3$)$_2$(RNNNHR)][BF$_4$] (R = p-MeC$_6$H$_4$ or p-FC$_6$H$_4$) and [M(CO)(PPh$_3$)$_2${MeC(=NR)-NHR}][BF$_4$] (M = Rh or Ir, R = Ph or p-MeC$_6$H$_4$) were prepared by similar methods using the appropriate diaryltriazene or diarylacetamidine.

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