In memory of T. A. Stephenson

Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 27.[1] Mixed-valence Triazenido-bridged Di-iridium Compounds *

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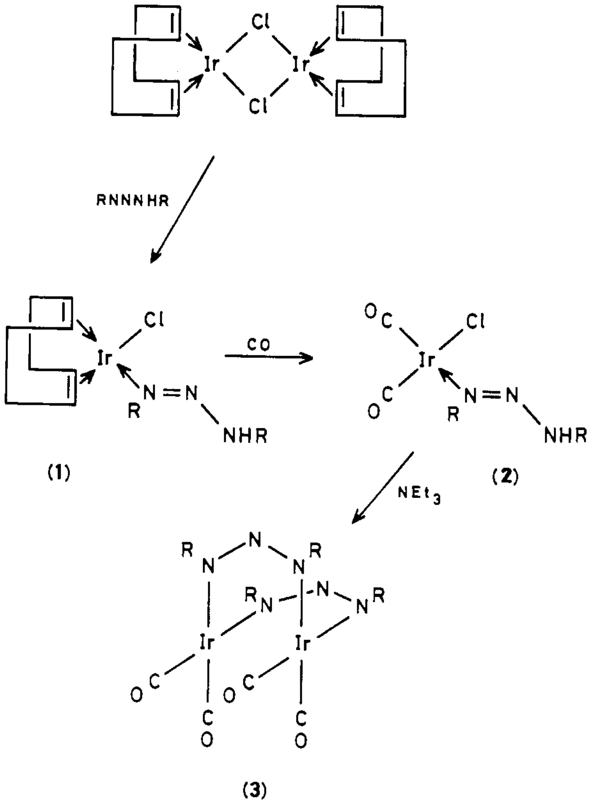
The complex $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$ (cod = cyclo-octa-1,5-diene) reacts with the triazene RNNNHR (R = *p*-tolyl) to give $[IrCl(RNNNHR)(\eta^4\text{-cod})]$ (**1**) which yields $[IrCl(CO)_2(RNNNHR)]$ (**2**) on treatment with CO gas. Deprotonation of (**2**) with NEt_3 in CH_2Cl_2 at −10 °C gives the dimer $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (**3**), which undergoes thermal substitution with PPh_3 to yield $[Ir_2(CO)_3(PPh_3)(\mu\text{-}RNNNR)_2]$ (**4**). Complexes (**3**) and (**4**) undergo reversible one-electron oxidation at a platinum electrode in CH_2Cl_2. In the presence of PPh_3, (**4**) [or (**3**)] reacts with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to give the isolable paramagnetic salt $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2][PF_6]$ which undergoes reversible one-electron reduction and which has been characterised by e.s.r. spectroscopy.

Molecular orbital calculations, supported by *X*-ray structural and ESCA (electron spectroscopy for chemical analysis) studies, suggest[2] that mixed-valence triazenido-bridged complexes such as $[Rh_2(CO)_2L_2(\mu\text{-}RNNNR)_2]^+$ ($L = PPh_3$,[1] L_2 = 2,2′-bipyridyl,[3] R = *p*-tolyl) have delocalised electronic structures. Qualitatively, the e.s.r. spectra of these species also support this conclusion. However, a quantitative analysis[4] of the anisotropic, frozen solution spectra, which would provide a more detailed description of the bonding, has been somewhat hampered by the observation of only small, incompletely resolved ^{103}Rh hyperfine couplings $[A(^{103}Rh)]$.

A comparison of the frozen solution e.s.r. spectra[5] of $[\{M(\mu\text{-}L)(\eta^4\text{-cod})\}_2]^+$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene, L = 3,5-dimethylpyrazolyl) shows that $A(^{192}Ir)$ for the iridium complex is much greater than $A(^{103}Rh)$ for the rhodium analogue (values of 68 G *vs.* 18 G are reported).[5] Thus, on the assumption that larger hyperfine couplings would also be observed for triazenido-bridged iridium complexes (giving rise to better resolved, more easily analysed spectra) we have attempted to synthesise di-iridium analogues of the rhodium compounds mentioned above. We now describe the successful synthesis of $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (R = *p*-tolyl), the thermal and oxidative substitution reactions of the tetracarbonyl with PPh_3, and the e.s.r. spectrum of the stable, paramagnetic cation $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^+$.

Results and Discussion

The simplest route to $[\{Rh(CO)_2(\mu\text{-}RNNNR)\}_2]$, involving the reaction between $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $RNNNR^-$,[1,6] is unavailable for the iridium analogue in that no suitable halogenocarbonyl precursor is known. Other ligand-bridged species of the type $[\{M(CO)_2(\mu\text{-}L)\}_2]$ (M = Rh or Ir, L = nitrogen-donor ligand) have been prepared[7] by reacting $[\{M(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$ with L^- and then carbonylating the product $[\{M(\mu\text{-}L)(\eta^4\text{-cod})\}_2]$, but, once again, this route fails for M = Ir, L = RNNNR. In our hands, the passage of CO through a mixture of $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$ and Na[RNNNR] in tetrahydrofuran (thf), or the addition of NEt_3, as base, to $[\{Ir(\mu\text{-}Cl)(\mu^4\text{-cod})\}_2]$ and RNNNHR under an atmosphere of carbon monoxide, gave only minor quantities of the desired product accompanied by the formation of dark green or blue solutions and/or intractable solids. An alternative synthetic route was therefore devised involving the dimerisation of a preformed mononuclear dicarbonyl precursor (Scheme).



Scheme. R = *p*-tolyl

The reaction of the triazene RNNNHR (R = *p*-tolyl) with orange $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$ in CH_2Cl_2 gives a yellow solution from which a near-quantitative yield of $[IrCl(RNNNHR)(\eta^4\text{-cod})]$ (**1**) was isolated after addition of n-hexane and partial evaporation of the mixture *in vacuo*. Complex (**1**) was

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* *Non-S.I. unit employed*: $G = 10^{-4}$ T.

Table 1. Analytical and i.r. spectral data

Compound[a]	Colour	Yield (%)	Analysis (%)[b]			$\tilde{\nu}$(CO)/cm^{-1} [c]
			C	H	N	
(1) $[\mathrm{IrCl(RNNNHR)}(\eta^4\text{-cod})]$	Yellow	90	47.0 (47.1)	5.0 (4.9)	7.4 (7.5)	—
(2) $[\mathrm{IrCl(CO)_2(RNNNHR)}]$	Dark green	66	37.6 (37.8)	3.1 (3.0)	8.1 (8.3)	2 082, 2 004
(3) $[\{\mathrm{Ir(CO)_2}(\mu\text{-RNNNR})\}_2]$	Red-black	40	42.6 (42.5)	3.6 (3.6)	8.6 (8.5)[d]	2 078vs, 2 045s, 2 010vs
(4) $[\mathrm{Ir_2(CO)_3(PPh_3)}(\mu\text{-RNNNR})_2]$	Black	64	50.0 (49.9)	3.7 (3.7)	7.0 (7.1)	2 046vs, 1 990 (sh), 1 981vs
(5) $[\{\mathrm{Ir(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2][\mathrm{PF_6}]$	Brown	84	48.7 (49.0)	3.7 (3.7)	5.1 (5.1)[e]	2 025, 2 006[f]

[a] R = *p*-tolyl, cod = cyclo-octa-1,5-diene. [b] Calculated values are given in parentheses. [c] Very strong (vs) absorptions in n-hexane unless otherwise stated; s = strong, sh = shoulder. [d] Analysed as 0.5 n-hexane solvate (confirmed by ^{1}H n.m.r. spectroscopy). [e] Analysed as 1:1 $\mathrm{CH_2Cl_2}$ solvate. [f] In $\mathrm{CH_2Cl_2}$.

Table 2. Cyclic voltammetric data for di-iridium complexes

Complex	Process[a]	$E^{\ominus}$/V[b]
$[\{\mathrm{Ir(CO)_2}(\mu\text{-RNNNR})\}_2]$	$0 \rightleftharpoons +1$	0.71
$[\mathrm{Ir_2(CO)_3(PPh_3)}(\mu\text{-RNNNR})_2]$	$0 \rightleftharpoons +1$	0.36
$[\{\mathrm{Ir(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2][\mathrm{PF_6}]$	$+1 \rightleftharpoons 0$	−0.02
	$+1 \rightleftharpoons +2$	1.20[c]

[a] All processes are diffusion controlled and one-electron, obeying the criterion $i/\sqrt{\nu}$ = constant for scan rates, ν, in the range 50—500 mV s^{-1}. Unless stated otherwise, the process is reversible. [b] All potentials are *versus* the aqueous saturated calomel electrode, at a platinum bead in $\mathrm{CH_2Cl_2}$ with 0.1 mol dm^{-3} $[\mathrm{NBu^n{}_4}][\mathrm{PF_6}]$ as supporting electrolyte. Under these conditions, the $E^{\ominus}$ values for the couples $[\mathrm{Fe}(\eta\text{-C_5H_5})_2]^+$–$[\mathrm{Fe}(\eta\text{-C_5H_5})_2]$ and $[\mathrm{Fe}(\eta\text{-C_5Me_5})_2]^+$–$[\mathrm{Fe}(\eta\text{-C_5Me_5})_2]$ are 0.47 and −0.07 V respectively. [c] Irreversible oxidation peak potential at a scan rate of 200 mV s^{-1}.

characterised by elemental analysis (Table 1) and by the ^{1}H n.m.r. spectrum which showed four multiplets [δ(CDCl$_3$) 4.7 (2 H), 3.3 (2 H), 2.3 (4 H), and 1.7 (4 H)] for the η^4-cod protons, a complex pattern centred at δ 7.6 (8 H) due to the $\mathrm{C_6H_4}$ groups, and two singlets [δ 2.36 (3 H) and 2.38 (3 H)] due to the inequivalent methyl groups of the triazene ligand; the NH proton was not detected. The ^{1}H n.m.r. spectrum of (**1**) [and of (**2**), see below] does not allow a distinction to be made between the two possible terminal bonding modes of the RNNNHR ligand, namely *via* the NR or NHR nitrogen atoms. However, the former is favoured by analogy with $[\mathrm{M(CO)(PPh_3)_2(R'NNNHR')}][\mathrm{BF_4}]$ (M = Rh or Ir, R′ = aryl) which has been partially characterised by *X*-ray methods.[8]

On passing a stream of CO gas through (**1**) in $\mathrm{CH_2Cl_2}$, a dark green solution showing i.r. carbonyl bands at 2 083 and 2 005 cm^{-1} is rapidly formed. On treating the solution as above, the *cis* dicarbonyl $[\mathrm{IrCl(CO)_2(RNNNHR)}]$ (**2**) was isolated as a dark green solid, again characterised by elemental analysis (Table 1) and ^{1}H n.m.r. spectroscopy [δ (CDCl$_3$) 7.6 (m, 8 H, $\mathrm{C_6H_4}$), 2.39 (s, 3 H, Me), 2.38 (s, 3 H, Me)].

Complex (**2**) is readily converted into the dimeric tetracarbonyl $[\{\mathrm{Ir(CO)_2}(\mu\text{-RNNNR})\}_2]$ (**3**) when treated with $\mathrm{NEt_3}$ in $\mathrm{CH_2Cl_2}$, but the reaction conditions are critical for optimum yields. At room temperature the predominant product is an intractable black solid which shows no carbonyl bands in the Nujol mull i.r. spectrum. However, addition of the base to (**2**) at −78 °C, followed by slowly warming the mixture to room temperature and stirring for 4 h gave a dark red-brown solution with little of the insoluble by-product. On evaporation of the reaction mixture to dryness, extraction with n-hexane, and chromatography of the extract on an alumina–n-hexane column, a dark red band was eluted from which (**3**) was isolated in moderate yield by cooling to 0 °C. The red-black crystalline product was characterised, as a 0.5 n-hexane solvate, by elemental analysis (Table 1) and by ^{1}H n.m.r. spectroscopy [δ (CDCl$_3$) 7.3 (m, 16 H, $\mathrm{C_6H_4}$), 2.30 (s, 12 H, Me), 1.26 (m, 4 H, n-hexane), and 0.88 (m, 3 H, n-hexane)]. In addition, the mass spectrum of (**3**) shows a parent ion at *m*/*e* 945 (calc., 945) and the i.r. carbonyl spectrum (Table 1) is very similar to that of $[\{\mathrm{Rh(CO)_2}(\mu\text{-RNNNR})\}_2]$.[6,9]

The thermal reaction of (**3**) with $\mathrm{PPh_3}$ differs from that of the dirhodium analogue[6] in that only monosubstitution, rather than disubstitution, occurs readily. Thus, at room temperature equimolar quantities of the reactants in n-hexane give a deep purple solution from which black crystals of $[\mathrm{Ir_2(CO)_3(PPh_3)}(\mu\text{-RNNNR})_2]$ (**4**; Table 1) are obtained on cooling to 0 °C.

Neither the i.r. spectrum of the reaction mixture nor cyclic voltammetry (see below) shows evidence for disubstitution of (**3**) at room temperature even in the presence of two equivalents of $\mathrm{PPh_3}$. However, under these conditions chromatography of the reaction mixture on an alumina–n-hexane column gave (**4**) and a second, red band which on elution gave a very small quantity of a dark red solid. The i.r. carbonyl spectrum of the solid [$\tilde{\nu}$(CO) ($\mathrm{CH_2Cl_2}$) = 1 964 and 1 946 cm^{-1}] is similar to that of $[\{\mathrm{Rh(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2]$; it is also observed when $[\{\mathrm{Ir(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2]^+$ is chemically reduced (see below), and is therefore attributed to $[\{\mathrm{Ir(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2]$.

Cyclic Voltammetry of (**3**) *and* (**4**), *and the Oxidative Substitution of* (**4**) *with* $\mathrm{PPh_3}$.—Both (**3**) and (**4**) undergo a reversible one-electron oxidation at a platinum bead electrode in $\mathrm{CH_2Cl_2}$ (Table 2). Other, ill defined waves are also observed at *ca.* 1.4 V in each case.

Where comparison can be made,[1] the iridium compounds are more easily oxidised to their monocations than are the rhodium analogues, by 0.1—0.2 V. More important, however, is the observation that the di-iridium unit does not seem to support such an extensive sequence of redox reactions. For example, the absence of a well defined second oxidation wave for (**3**) in $\mathrm{CH_2Cl_2}$ is in marked contrast to the three reversible waves associated with the stepwise oxidation of $[\{\mathrm{Rh(CO)_2}(\mu\text{-RNNNR})\}_2]$ to the $\mathrm{Rh_2}^{5+}$-containing trication.[1]

The cyclic voltammogram of (**3**) in the presence of $\mathrm{PPh_3}$ not only confirms that thermal substitution at room temperature gives only (**4**) but also shows that (**4**) undergoes oxidatively induced substitution to $[\{\mathrm{Ir(CO)(PPh_3)}(\mu\text{-RNNNR})\}_2]^+$ (**5**).

Figure 1(*a*) shows the cyclic voltammogram of (**3**) from −0.10 to +0.90 V; only the first, reversible wave at 0.71 V, corresponding to the formation of (**3**)$^+$ is observed in this potential region. On adding one equivalent of $\mathrm{PPh_3}$, and after 45 min, the cyclic voltammogram appears as shown in Figure

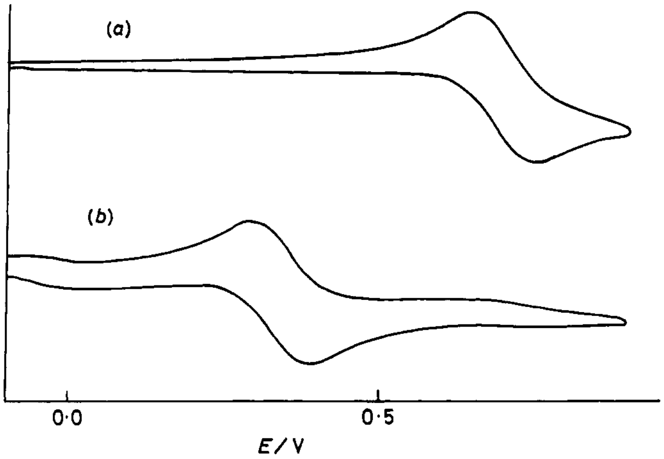

Figure 1. The cyclic voltammogram, from −0.10 to +0.90 V, of $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (**3**) in CH_2Cl_2 at a platinum bead electrode: (*a*) in the absence of PPh_3, (*b*) after 45 min in the presence of one equivalent of PPh_3

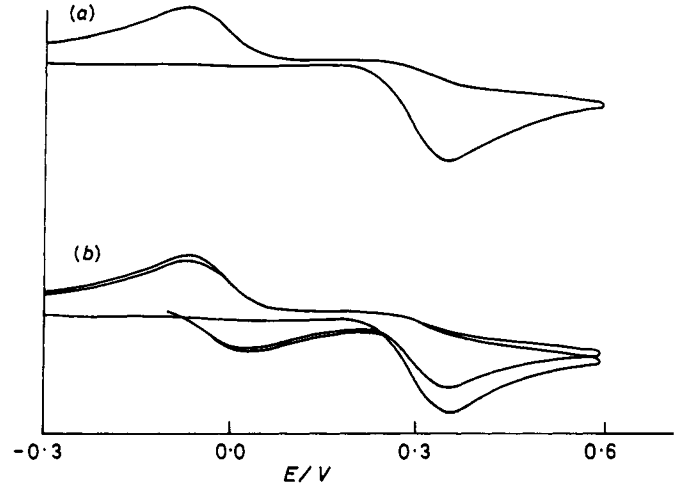

Figure 2. The cyclic voltammogram, from −0.30 to +0.60 V, of $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (**3**) in the presence of two equivalents of PPh_3 in CH_2Cl_2 at a platinum bead electrode: (*a*) single scan, (*b*) multiple scans

1(*b*). The new wave at 0.36 V corresponds to the one-electron oxidation of (**4**); the complete absence of other waves confirms the quantitative and selective formation of the tricarbonyl.

In the presence of a second equivalent of PPh_3, the cyclic voltammogram is again changed. Figure 2(*a*) shows that on scanning from −0.30 V to +0.60 V only the wave corresponding to the oxidation of (**4**) is observed; there is no evidence for further thermal substitution [which should give rise to binuclear species showing oxidation waves at potentials less positive than that of (**4**)]. However, the return sweep reveals that in the presence of PPh_3 the oxidation of (**4**) is irreversible and that a product is formed showing a reduction peak at *ca.* −0.1 V. The multiple-scan cyclic voltammogram shown in Figure 2(*b*) reveals, finally, that the product wave is reversible, and centred at −0.02 V; the chemical studies described below confirm that the new wave is due to the reversible couple $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^{0/1+}$.

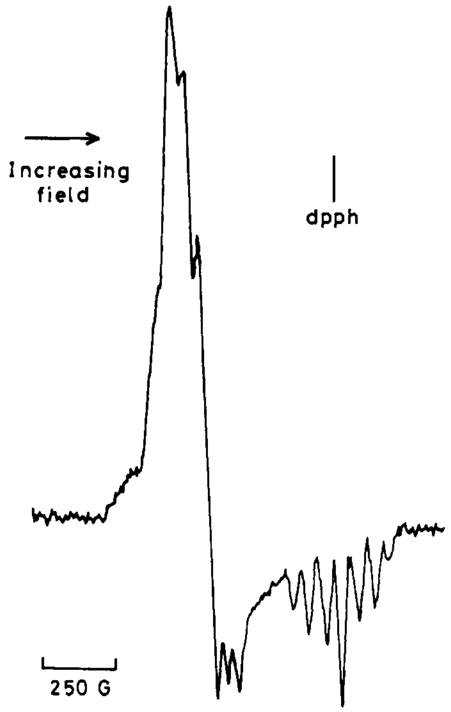

Figure 3. The frozen solution e.s.r. spectrum of $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^+$ (**5**) in CH_2Cl_2–thf (1:2) at −120 °C

The oxidatively-induced substitution reaction detected by cyclic voltammetry is readily effected chemically by adding $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to a 1:2 mixture of (**3**) and PPh_3 in CH_2Cl_2. After stirring for 10 min, orange-brown crystals of $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2][PF_6]$ (**5**; Table 1) were readily isolated in excellent yield.

The cyclic voltammogram of (**5**) shows one reversible one-electron reduction wave at a potential (Table 2) identical to that of the product wave shown in Figure 2(*b*). In addition, the cation (**5**) is further oxidised in an irreversible step, again contrasting markedly with $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^+$ which undergoes two, reversible one-electron oxidations.[1] Chemical reduction of (**5**) with $[NBu^n_4][BH_4]$ in CH_2Cl_2 gave a red-brown solution showing i.r. carbonyl absorptions at 1 964 and 1 946 cm^{-1}. These absorptions, as mentioned above, are as expected for $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]$ (by comparison with the dirhodium analogue[1]); no attempt was made to isolate the neutral iridium complex.

The room-temperature e.s.r. spectrum of (**5**) shows one broad line at $g = 2.243$, similar[1] to that of $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^+$. The anisotropic, frozen solution [−120 °C, CH_2Cl_2–thf (1:2)] spectrum, shown in Figure 3, is also similar to that of the dirhodium analogue[2,4] with $g_\perp$ and $g_\parallel$ components at *ca.* 2.36 and 2.00 respectively. As anticipated, however, the rhodium and iridium hyperfine couplings are very different. For example $A(^{192}Ir)$ on the $g_\parallel$ component of the spectrum of (**5**) (*ca.* 52 G) is much greater than corresponding values of $A(^{103}Rh)$ (*ca.* 19 G)[2,4] for related rhodium complexes.

With the aid of the spectrum shown in Figure 3 we now hope to analyse fully[4] the anisotropic spectra of $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^+$ and related triazenido-bridged complexes.[1,3] In this way, and with the *X*-ray and ESCA studies[2] referred to above, we hope to gain a complete picture of the bonding in these mixed-valence complexes.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, the products are air-stable, dissolving in polar solvents such as CH_2Cl_2 or tetrahydrofuran to give solutions which slowly decompose in air. The compounds $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$,[10] RNNNHR (R = *p*-tolyl),[11] and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$[12] were prepared by published methods.

Infrared spectra were recorded on Nicolet MX-1 or 5ZDX spectrometers. Hydrogen-1 n.m.r. spectra were recorded on a JEOL JNM GX-270 instrument and calibrated against $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical (dpph). Cyclic voltammetry was carried out as previously described;[1] ferrocene was used as an internal calibrant[13] with E° for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ equal to 0.47 V. Mass spectra were recorded on a VG Micromass 3D8 instrument. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Chloro(η^4-*cyclo-octa*-1,5-*diene*)(1,3-*di*-p-*tolyltriazene*)-*iridium*, $[IrCl(RNNNHR)(\eta^4\text{-cod})]$.—To a stirred solution of $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-cod})\}_2]$ (0.10 g, 0.15 mmol) in CH_2Cl_2 (20 cm^3) was added di-*p*-tolyltriazene (0.07 g, 0.30 mmol). After 5 min the yellow solution was filtered, hexane (20 cm^3) was added, and concentration to low volume *in vacuo* gave the product as a yellow solid. Yield 0.15 g (90%).

Dicarbonylchloro(1,3-*di*-p-*tolyltriazene*)*iridium*, $[IrCl(CO)_2(RNNNHR)]$.—Carbon monoxide gas was slowly bubbled for 15 min through a solution of $[IrCl(RNNNHR)(\eta^4\text{-cod})]$ (0.2 g, 0.36 mmol) in CH_2Cl_2 (25 cm^3). Addition of n-hexane (25 cm^3) to the green solution, and concentration to low volume *in vacuo*, gave the product as a dark green solid. Yield 0.12 g (66%). The crude product was pure enough for subsequent syntheses; analytically pure samples may be prepared by dissolving the solid in CH_2Cl_2, with filtration, addition of n-hexane, and concentration.

The complex is slightly soluble in n-hexane and soluble in more polar solvents such as CH_2Cl_2 to give green solutions which slowly decompose in air.

Tetracarbonyl-di-μ-(di-p-*tolyltriazenido*)-*di-iridium–n-Hexane* (2/1), $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]\cdot 0.5C_6H_{14}$.—To a cooled (−78 °C) solution of $[\{IrCl(CO)_2(RNNNHR)]$ (0.32 g, 0.34 mmol) in CH_2Cl_2 (20 cm^3) was added NEt_3 (0.1 cm^3, 0.75 mmol). After allowing the mixture to warm to room temperature, stirring was continued for 4 h. Solvent was then removed *in vacuo*, and the residue extracted with n-hexane (50 cm^3). The dark red extract was evaporated to low volume (*ca.* 10 cm^3) and placed on an alumina–n-hexane chromatography column. Elution with n-hexane gave a red band which was collected, concentrated to low volume (*ca.* 5 cm^3), and cooled to −10 °C to give the product as red-black crystals. Yield 0.125 g (40%).

The complex is soluble in all common organic solvents to give deep red solutions which slowly decompose in air.

Tricarbonyl-di-μ-(*di*-p-*tolyltriazenido*)-*triphenylphosphinedi-iridium*, $[Ir_2(CO)_3(PPh_3)(\mu\text{-}RNNNR)_2]$.—To a stirred solution of $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (0.087 g, 0.09 mmol) in n-hexane (10 cm^3) was added PPh_3 (0.023 g, 0.09 mmol). After stirring for 30 min the purple solution was evaporated to low volume (*ca.* 5 cm^3) and cooled to −10 °C to give black crystals of the product. Yield 0.066 g (64%). If necessary, the complex can be further purified by chromatography on an alumina–n-hexane column, eluting with n-hexane.

The complex is soluble in all common organic solvents to give red-purple solutions which decompose slowly in air.

Dicarbonyl-di-μ-(*di*-p-*tolyltriazenido*)-*bis*(*triphenylphosphine*)*di-iridium Hexafluorophosphate–Dichloromethane* (1/1), $[\{Ir(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2][PF_6]\cdot CH_2Cl_2$.—To a stirred mixture of $[\{Ir(CO)_2(\mu\text{-}RNNNR)\}_2]$ (50 mg, 0.05 mmol) and PPh_3 (26 mg, 0.1 mmol) in CH_2Cl_2 (10 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (17 mg, 0.05 mmol). Filtration of the orange-brown solution, addition of n-hexane (15 cm^3), and concentration *in vacuo* gave the product as brown microcrystals. Yield 66 mg (84%).

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References

1 Part 26, N. G. Connelly, G. Garcia, M. Gilbert, and J. S. Stirling, *J. Chem. Soc., Dalton Trans.*, 1987, 1403.
2 G. C. Allen, T. Brauns, N. G. Connelly, C. J. Finn, M. J. Freeman, G. Garcia, and A. G. Orpen, unpublished work.
3 N. G. Connelly and G. Garcia, *J. Chem. Soc., Chem. Commun.*, 1987 246.
4 W. E. Geiger and P. H. Reiger, unpublished work.
5 D. O. K. Fjeldsted and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1985, 908.
6 N. G. Connelly, H. Daykin, and Z. Demidowicz, *J. Chem. Soc., Dalton Trans.*, 1978, 1532.
7 See, for example, A. Tiripicchio, M. Tiripicchio Camellini, R. Uson, L. A. Oro, M. A. Ciriano, and F. Viguri, *J. Chem. Soc., Dalton Trans.*, 1984, 125; J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zaworotko, *Inorg. Chem.*, 1984, **23**, 4050; L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio, and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.*, 1985, 1891; L. A. Oro, M. J. Fernandez, J. Modrego, and J. M. Lopez, *J. Organomet. Chem.*, 1985, **287**, 409; and refs. therein.
8 N. G. Connelly and Z. Demidowicz, *J. Chem. Soc., Dalton Trans.*, 1978, 50.
9 A. L. Balch and B. Tulyathan, *Inorg. Chem.*, 1977, **16**, 2840; W. H. Knoth, *ibid.*, 1973, **12**, 38.
10 R. H. Crabtree, J. M. Quirk, H. Felkin, and T. F. Khan, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**, 407.
11 W. W. Hartman and J. B. Dickey, *Org. Synth.*, 1943, coll. vol. **2**, 163.
12 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.
13 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1982, **54**, 1527; R. R. Gagne, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2854.

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