Spin-delocalization in Mixed-valence Binuclear Cations of Rhodium and Iridium. A Stable Iridium(II) Radical

D. O. Kim Fjeldsted and Stephen R. Stobart*

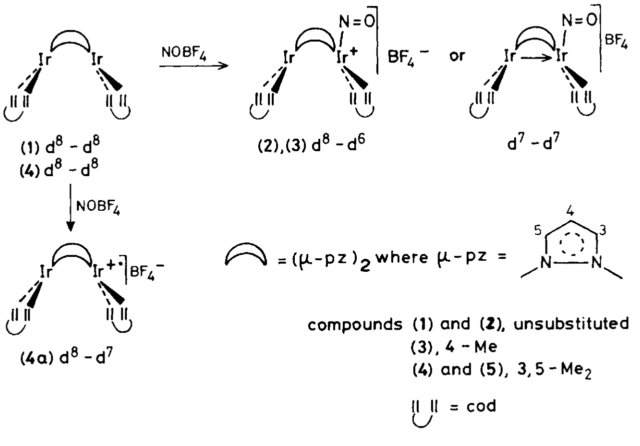
Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2

Oxidation of [Ir(cod)(μ-L)]$_2$ (cod = cyclo-octa-1,5-diene; L = pz or 4-Mepz, pzH = pyrazole) using NOBF$_4$ affords cationic binuclear nitrosyl adducts [Ir$_2$(cod)$_2$(μ-L)$_2$NO]BF$_4$; by contrast similar reactions of [M(cod)(μ-L)]$_2$ (M = Rh or Ir; L = 3,5-Me$_2$pz) yield binuclear cationic radicals [{M(cod)(μ-L)}$_2$$^{+\cdot}$]BF$_4$$^-$ which in e.s.r. spectra show hyperfine-coupling to both metals consistent with delocalized mixed-valence character.

The chemistry of rhodium(II) has a long history; representative complexes may be synthesized by reductive or oxidative routes, the latter affording principally binuclear species.[1] By contrast and partly as a result of the kinetic stability of d^5 Ir^{IV} and d^6 Ir^{III}, iridium(II) has been regarded as an unusual oxidation state. Recently, however, we[2] and others[3] described two-centre addition of oxidizing substrates to di-iridium(I) complexes, giving access to d^7–d^7 iridium(II) dimers which have been structurally characterized. We have also shown[4] using cyclic voltammetry that reversible one-electron oxidation occurs with [Ir(cod)(μ-pz)]$_2$ (**1**) (cod = cyclo-octa-1,5-diene; pzH = pyrazole) and related compounds, suggesting that the corresponding chemical oxidation might yield novel isolable products. We report the synthesis of a new class of stable bimetallic radical cations which exhibit resolved e.s.r. spectra consistent with spin-delocalization over both metal centres M (M = Rh or Ir) in a d^8–d^7 configuration.

Addition to compound (**1**) of nitrosyl tetrafluoroborate (CH$_2$Cl$_2$ soln.) led to immediate darkening of the reaction mixture from purple-red to deep purple. Filtration followed by addition of Et$_2$O precipitated a product (**2**) which was obtained as purple-black, air-stable microcrystals† from CH$_2$Cl$_2$–Et$_2$O. The i.r. spectrum of this material contained strong absorptions at 1715 and 1070 cm^{-1} attributable to ν(NO) and ν(BF) respectively; formulation as a cationic di-iridium nitrosyl (Scheme 1) was substantiated by microanalytical results as well as by the appearance of distinguishable μ-pz H^3 and H^5 proton signals in the ^{1}H n.m.r. spectrum. Using the same preparative routine, an analogue† (**3**) of compound (**2**) was isolated from reaction of [Ir(cod)(μ-4-Mepz)]$_2$, but with 3,5-bridge disubstituted relatives of dimer (**1**) different behaviour was observed.

Oxidation of [Ir(cod)(μ-3,5-Me$_2$pz)]$_2$ (**4**) with NOBF$_4$ or NOPF$_6$ in CH$_2$Cl$_2$ solution afforded products (**4a**) and (**4b**) as red-purple powders‡ with i.r. spectra distinguishable only by ν(E–F) absorption, near 1100 (E = B) or 850 cm^{-1} (E = P) respectively. Complete paramagnetic quenching of ^{1}H n.m.r. was evident in both cases and accordingly strong e.s.r. signals



Scheme 1. (**5**) is Rh analogue of (**4**).

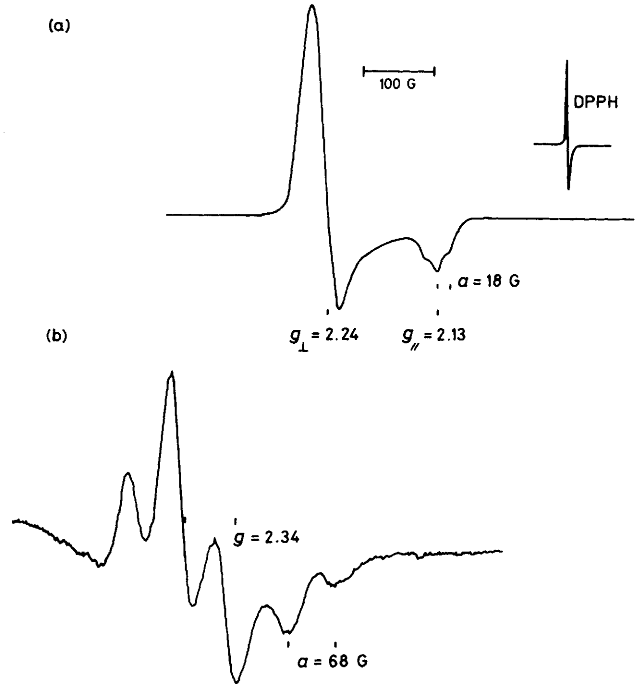


Figure 1. First derivative e.s.r. spectra of (a) compound (**5a**); (b) compound (**4a**), recorded as frozen solutions in CH$_2$Cl$_2$ at 77 K, Varian E6 e.s.r. spectrometer, calibrated with diphenylpicrylhydrazyl (DPPH). 1 G = 10^{-4} T.

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† Satisfactory elemental analysis results were obtained. *Spectroscopic data:* for compound (**2**), n.m.r. (^{1}H, 250 MHz, CDCl$_3$ soln.) δ (μ-pzH$^{3/5}$, H^4): δ 7.67 (2H, d), 7.57 (2H, d), 6.49 (2H, t); (cod–CH=): 5.74 (2H, m), 5.66 (2H, m), 4.69 (2H, m), 3.64 (2H, m); (cod–CH$_2$–): 2.80 (4H, m), 2.69 (4H, m), 2.27 (8H, m); u.v./vis. (tetrahydrofuran soln.) λ 556 nm, ε 746 dm^3 mol^{-1} cm^{-1}; for compound (**3**), n.m.r. (^{1}H, 250 MHz, CD$_2$Cl$_2$ soln.) δ (μ-4-Mepz-H$^{3/5}$): 7.48 (2H, s), 7.26 (2H, s); (cod–CH=): 5.65 (2H, m), 5.46 (2H, m), 4.69 (2H, m), 3.61 (2H, m); (cod–CH$_2$–): 2.60 (8H, m), 2.28 (8H); (4-Me) 2.08 (6H, s); u.v./vis. (tetrahydrofuran soln.) λ 542 nm, ε 3410 dm^3 mol^{-1} cm^{-1}. The *X*-ray crystal and molecular structure of compound (**2**), full details of which will be published subsequently, has been determined in this Department by Dr. M. J. Zaworotko, confirming the proposed geometry with Ir–Ir = 3.225(1) Å, Ir–N = 2.06(4) Å and ∠ Ir–N–O = 115(5)°.

‡ This preparative procedure afforded samples contaminated with *ca.* 5% diamagnetic inorganic impurity, possibly residual NOBF$_4$. Analytically pure materials were isolable however *via* oxidation of [Ir(cod)(μ-3,5-R$_2$pz)]$_2$ (R = Me or R$_2$ = MePh) using[4] [{Ir(cod)(μ-3,5-R$_2$pz)}$_2$$^{+\cdot}$]BF$_4$$^-$, R = CF$_3$, a synthetic route which further supports the binuclear formulation for (**4a**) and (**4b**).

were observed, consistent with one-electron oxidation to $[Ir(cod)(\mu\text{-}3,5\text{-}Me_2pz)]_2^{+\cdot}$ accompanied by elimination of NO (Scheme 1). Facile conversion of the dirhodium(I) complex $[Rh(cod)(\mu\text{-}3,5\text{-}Me_2pz)]_2$ (**5**) to its corresponding radical cation (**5a**), the analogue of (**4a**), proved to be possible using a similar procedure and e.s.r. spectra for these two species are compared in Figure 1. Radical (**5a**) exhibits strongly anisotropic behaviour, with g values of 2.13 and 2.24 for the well separated components of a recognizably axial spectrum (Figure 1, a) implying metal-centred character. Hyperfine splitting of the parallel absorption into a triplet, a = 18 G, is attributable[5] to spin-coupling to both rhodium nuclei (^{103}Rh, 100%, $I = 1/2$). The spectrum of the di-iridium congener (**4a**) (Figure 1, b) is closer to isotropic but $g_{av.}$ at *ca.* 2.34 is again well removed from the free-electron value: metal hyperfine splitting is also conspicuous, a = 68 G, with a splitting pattern resembling the central portion of a seven-line multiplet derived from coupling to two nuclear spins of 3/2 (^{191}Ir, 37%; ^{193}Ir, 63%: both $I = 3/2$). Thus in each of the d^8–d^7 species (**4a**) and (**5a**) there is clear evidence for delocalization of the unpaired electron spin over both metal centres.

A reduction of 0.262 Å in Rh_2 separation accompanying oxidation of the d^8–d^8 triazenido-bridged dimer $[Rh(CO)(PPh_3)(\mu\text{-}RNNNR)]_2$ (**6**: R = *p*-tolyl) to the derived monocation (**6a**) has been reported very recently by Connelly, Orpen, and co-workers;[6] this corresponds to electron-loss from a Rh_2 ($d\sigma^*$) antibonding orbital and increase in formal bond-order from 0 to 1/2. No hyperfine coupling could be detected in the e.s.r. signal ($g_{av.}$ 2.135) due to (**6a**) so that 'trapped-valence' $[Rh^IRh^{II}]$ character[7] could not be ruled out. Conversely, while we have shown that the mixed-valence cation (**4a**) is a spin-delocalized system we expect no contraction along the Ir_2 axis because when the dimer (**1**) (in which there is evidence[8] for significant interaction between the formally non-bonded Ir centres) is oxidized such a change will be sterically opposed by the terminal dialkene ligands.[4,8] Accordingly, Ir_2 distances remain long[9] even when complex (**1**) is further oxidized to d^7–d^7 adducts (formal bond-order 1). With MeI this latter process appears[10] to proceed by a two-step nucleophilic mechanism[11] in which the intermediate may be modelled structurally and electronically by the cationic species (**2**) and (**3**).

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