A Dinuclear Iridium Aryldiazenide Complex with a μ^2-η^2-*N,N'* Bridge. Synthesis of $[(C_5Me_5)_2Ir_2(CO)_2(\mu^2\text{-}\eta^2\text{-}NNC_6H_4OMe)][BF_4]$ from $[(C_5Me_5)Ir(C_2H_4)(N_2C_6H_4OMe)][BF_4]$

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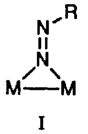
$[(C_5Me_5)Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$, **2** and the nitrosyl analogue $[(C_5Me_5)Ir(C_2H_4)(NO)][BF_4]$, **3** have been synthesized from $(C_5Me_5)Ir(C_2H_4)_2$, **1** and $[p\text{-}N_2C_6H_4OMe][BF_4]$ or $[NO][BF_4]$; **2** reacts with $(C_5Me_5)Ir(CO)_2$ to give the title dinuclear complex, **4** in which the aryldiazenide ligand bridges in the four-membered dimetalladiaza-ring fashion.

Compounds in which the aryldiazenide (N_2R) ligand bridges a metal–metal bond are very rare.[1] Isolated examples have been structurally verified for each of the geometries I–III.[2–4] In each case the synthesis has involved introducing the N_2R ligand into a suitable metal–metal bonded precursor. Here, we describe only the second example of structure II, and in this instance the dimetalladiaza ring has been assembled from a terminal aryldiazenide complex and an appropriate second metal fragment.

Reaction of $(C_5Me_5)Ir(C_2H_4)_2$ **1** with $[p\text{-}N_2C_6H_4OMe][BF_4]$ in acetone at −78 °C affords red crystals of the terminal aryldiazenido (ethylene) complex **2** (R = $p\text{-}MeOC_6H_4$). The corresponding nitrosyl complex **3** is synthesized analogously from $[NO][BF_4]$ and **1**.† Compounds **2** and **3** possess singly bent N_2R and linear NO groups respectively, as expected for 18 electron complexes, on the basis of spectroscopic properties, and a crystal structure determination for **2** at −40 °C (Fig. 1).‡ Compounds **2** and **3** should be valuable for the synthesis of a range of aryldiazenide or nitrosyl derivatives by ethylene displacement. Here, we describe that complex **2** reacts with $(C_5Me_5)Ir(CO)_2$ in acetone to produce the dinuclear complex **4**.†

The structure of the cation in **4** is shown in Fig. 2.‡ The only other example of structure II that we are aware of is a triosmium complex in which this arrangement resulted from photochemical isomerization of the related complex with structure I.[2b] In the present case, we presume that the base[5]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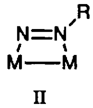
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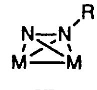
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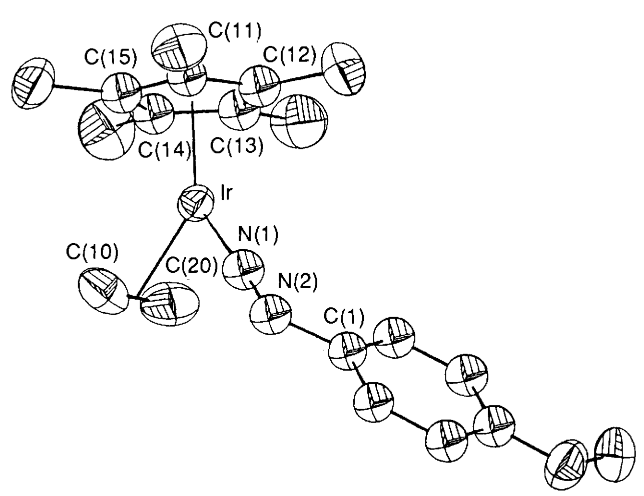
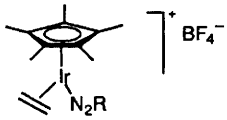


Fig. 1 Perspective view of the cation in **2**. Selected bond lengths (Å) and angles (°): Ir–C(10) 2.190(8), Ir–C(20) 2.172(9), Ir–N(1) 1.811(7), N(1)–N(2) 1.205(9), N(2)–C(1) 1.438(10); C(10)–Ir–C(20) 37.1(4), C(10)–Ir–N(1) 91.3(3), C(20)–Ir–N(1) 89.3(3), Ir–N(1)–N(2) 176.2(6), N(1)–N(2)–C(1) 120.4(6), Ir–C(10)–C(20) 70.8(5), Ir–C(20)–C(10) 72.2(5)



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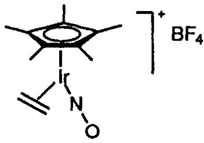

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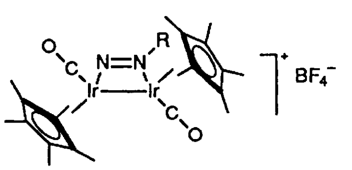

4

$[(C_5Me_5)(CO)_2Ir\text{–}Ir(N_2R)(C_5Me_5)][BF_4]$

5

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† X-Ray structures for **2** and **4**, satisfactory elemental analyses and spectroscopic properties have been obtained. **2**: ν(NN) 1710 cm^{-1} (KBr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25s (C_5Me_5), 3.25s (C_2H_4), 3.91s (OMe) 7.23q (C_6H_4); ^{14}N NMR ($MeNO_2$-d_3) δ −140 (N_β), −37 (N_α); FABMS *m/z* 491 (M^+, ^{193}Ir). **3**: ν(NO) 1822 cm^{-1} (acetone); ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.20s (C_5Me_5); FABMS *m/z* 386 (M^+, ^{193}Ir). **4**: ν(CO) 1992, 1970 cm^{-1} (KBr); ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.13s (C_5Me_5), 2.01s (C_5Me_5), 3.89s (OMe), 7.05q (C_6H_4).

‡ *Crystal data* for **2**: $C_{19}H_{26}BF_4IrN_2O$, FW = 577.22, monoclinic, space group $P2_1/n$, a = 8.578(1), b = 20.531(2), c = 12.031(2) Å, β = 93.50(1)°, Z = 4, ρ = 1.814 (g cm^{-3}); μ(Mo-Kα) = 63.35 cm^{-1}; Enraf-Nonius CAD-4F, Mo-Kα radiation (graphite monochromatized) λ = 0.71069 Å, 3716 unique data collected at −40 °C using the ω −2θ scan method, $0 < 2\theta < 50°$, 2611 reflections with $I \geqslant 2.5\sigma(I)$ used in solution and refinement by full-matrix least-crystal squares analysis, crystal ground to a sphere with an appropriate absorption correction, 183 variables, anisotropic thermal parameters for Ir, F, O, C (methyl) and C (ethylene), H atoms included in calculated positions but not refined, R_F = 0.0281, R_{wF} = 0.0308. For **4**: $C_{29}H_{37}BF_4Ir_2N_2O_3$, FW = 932.71, orthorhombic, space group $Pc2_1b$, a = 8.821(1), b = 20.237(3), c = 34.808(2) Å, Z = 8, ρ = 1.995, analytical absorption correction, transmission: 0.2191–0.3759; μ(Mo-Kα) = 85.85 cm^{-1}; Enraf-Nonius CAD-4F, Mo-Kα radiation (graphite monochromatized) λ = 0.71069 Å, 3038 unique data collected using the ω −2θ scan method, $0° < 2\theta < 42°$, 1661 reflections with $I \geqslant 2.5\sigma(I)$ used in solution and refinement, solution by Patterson method. Disordered cation sites (85 and 15% occupancy); refinement by restrained large block-matrix least-squares analysis; the 15% site modelled as rigid groups based on geometry of 85% site; 259 variables, H atoms included in calculated positions (0.95 Å); R_F = 0.0438. R_{wF} = 0.0492. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

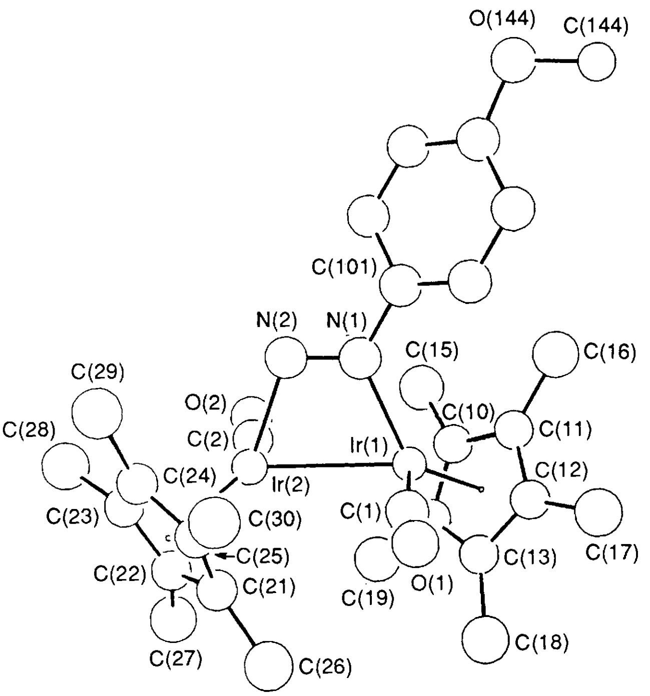

Fig. 2 Perspective view of the cation in **4**. Selected bond lengths (Å) and angles (°): Ir(1)–Ir(2) 2.723(4), N(1)–N(2) 1.29(2), Ir(1)–C(1) 1.81(2), Ir(2)–C(2) 1.79(2), Ir(1)–N(1) 2.02(2), Ir(2)–N(2) 2.06(2), Ir(1)–C(10) 2.26(2), Ir(2)–C(20) 2.26(2), Ir(1)–C(11) 2.27(2), Ir(2)–C(21) 2.27(2), Ir(1)–C(12) 2.24(2), Ir(2)–C(22) 2.26(2), Ir(1)–C(13) 2.26(2), Ir(2)–C(23) 2.28(2), Ir(1)–C(14) 2.26(2), Ir(2)–C(24) 2.25(2), C(1)–O(1) 1.21(2), C(2)–O(2) 1.20(2), N(1)–C(101) 1.41(3); Ir(2)–Ir(1)–N(1) 68.0(10), Ir(2)–Ir(1)–C(1) 84.8(19), Ir(1)–Ir(2)–N(2) 70.7(10), Ir(1)–Ir(2)–C(2) 91.4(24), Ir(1)–N(1)–N(2) 115.1(25), Ir(2)–N(2)–N(1) 106.2(24), N(1)–N(2)–C(101) 114.9(24), C(1)–Ir(1)–N(1) 94.0(16), C(2)–Ir(2)–N(2) 94.2(22), Ir(1)–C(1)–O(1) 162.9(51), Ir(2)–C(2)–O(2) 170.3(49), Ir(1)–N(1)–C(101) 130.0(20)

$(C_5Me_5)Ir(CO)_2$ coordinates to the iridium centre in **2** with displacement of ethylene to give an unobserved intermediate such as **5** that then rearranges by a pathway involving terminal–bridge–terminal transfer of a CO group assisted by bridging of the N_2R ligand to give **4**. Support for this suggestion can be found in related reactions of $(C_5Me_5)Ir(CO)_2$. We have shown that the dinuclear complex $[(C_5Me_5)(CO)_2Ir\text{–}Ir(CO)Cl(C_5Me_5)][BF_4]$, **6** is synthesized by Ag^+-mediated displacement of one Cl ligand from $(C_5Me_5)Ir(CO)Cl_2$ by the base $(C_5Me_5)Ir(CO)_2$. This closely parallels the way in which we suggest that **5** would be formed, and indeed the structure of **6** is analogous to that suggested for **5**. Additionally, the CO groups in **6** undergo exchange at room temperature, presumably by a bridge interchange mechanism.[6]

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