Structures of Cationic Di-iridium Complexes derived from $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, including the Dication $[(\eta^5\text{-}C_5Me_5)(CO)_2Ir\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)]^{2+}$ and the Bridging Methylenetetramethylcyclopentadienyl (Tetramethylfulvene) Complex $[(\eta^5\text{-}C_5Me_5)(CO)\overline{Ir\text{–}Ir(CO)_2\ (\eta^5\text{-}C}H_2C_5Me_4)]^+$

Frederick W. B. Einstein, Richard H. Jones, Xiaoheng Zhang,† Xiaoqian Yan, Ruby Nagelkerke, and Derek Sutton*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

$(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (**1**) reacts with Ph_3C^+ to give the dinuclear dication $[(\eta^5\text{-}C_5Me_5)(CO)_2Ir\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)]^{2+}$ (**4**) and with $(\eta^5\text{-}C_5Me_5)Ir(CO)Cl_2$ in the presence of one equivalent of Ag^+ to give $[(\eta^5\text{-}C_5Me_5)(CO)\underline{(Cl)Ir\text{–}Ir(CO)_2(}\eta^5\text{-}C_5Me_5)]^+$ (**2**); both (**2**) and (**4**) may be converted to the complex $[(\eta^5\text{-}C_5Me_5)(CO)\overline{Ir\text{–}Ir(CO)_2(\eta^5\text{-}C}H_2C_5Me_4)]^+$ (**3**) containing a rare bridging methylenetetramethylcyclopentadienyl (tetramethylfulvene) ligand.

Since it was reported by Maitlis and co-workers in 1969[1] the half-sandwich complex $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (**1**) has become established as a fundamental reagent in organometallic chemistry by virtue of its properties. It is, for example, an excellent nucleophile (or electron-rich metal base[2]) as illustrated by its protonation,[3] and it is one of a small group of precursors for the activation of aliphatic hydrocarbons, including methane.[4] Here, we describe a new aspect to the chemistry of (**1**): the formation of various dinuclear cationic species with Ir–Ir bonds, including the simple dication in (**4**).

$(\eta^5\text{-}C_5Me_5)Ir(CO)_2$
(**1**)

$[(\eta^5\text{-}C_5Me_5)(CO)(Cl)Ir\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$
(**2**)

$[(\eta^5\text{-}C_5Me_5)(CO)\overline{Ir\text{–}Ir(CO)_2(\eta^5\text{-}C}H_2C_5Me_4)][BF_4]$
(**3**)

$[(\eta^5\text{-}C_5Me_5)(CO)_2Ir\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]_2$
(**4**)

$[(\eta^5\text{-}C_5Me_5)(CO)_2Ir\text{–}Ag\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$
(**5**)

In one of many unsuccessful attempts to synthesize the unknown iridium aryldiazenide (N_2R) complex $[(\eta^5\text{-}C_5Me_5)Ir(CO)(N_2R)]^+$ for a comparison with the well studied[5] rhenium analogue $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2R)]^+$, (**1**) was treated with an arenediazonium tetrafluoroborate in CH_2Cl_2 (Scheme 1). Consumption of 0.5 equiv. of the diazonium salt yielded (**2**); $[NO][BF_4]$ reacted similarly with (**1**). Complex (**2**) was subsequently synthesized from (**1**) and $(\eta^5\text{-}C_5Me_5)Ir(CO)Cl_2$ in the presence of $AgBF_4$ for comparison.‡ This synthesis may simply be viewed as proceeding by the formation of the unsaturated (or solvated) 16-electron intermediate $[(\eta^5\text{-}C_5Me_5)Ir(CO)Cl]^+$ which is then attacked by the base (**1**); *i.e.*, (**2**) may be considered to have a

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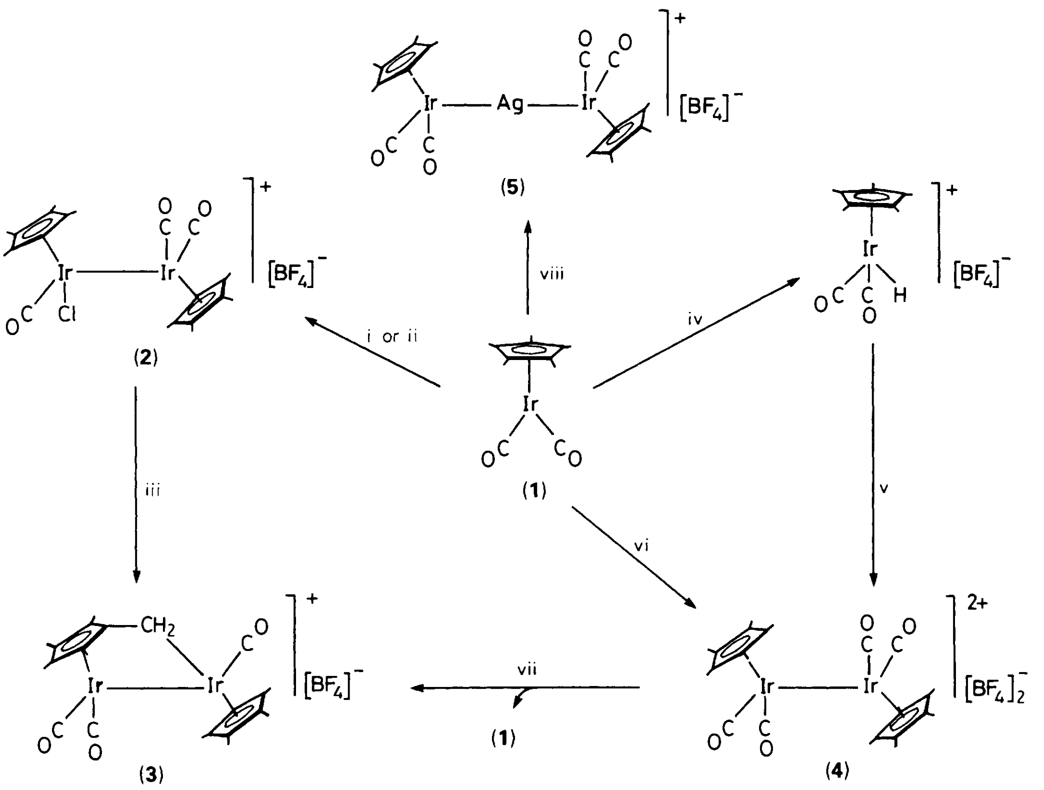
† Visiting scientist from Instrumental Research and Analysis Center, Zhongshan University, Guangzhou, People's Republic of China.

‡ Satisfactory analytical and spectroscopic data have been obtained for all new compounds. (**2**) i.r. (CH_2Cl_2, cm^{-1}, ν_{co}) 2058m, 2017 s,br.; ^1H n.m.r. ($CDCl_3$) δ 1.94 (s), 2.23 (s); ^{13}C n.m.r. ($CDCl_3$) δ 10.17, 10.39, 103.05, 106.67, 171.37 [separates into 172.95 and 168.21 at −86 °C in $C_2H_2Cl_4$]; m.s. (fast-atom bombardment, f.a.b., thioglycerol–xenon, most intense peak of isotope pattern) *m/z* 775, 745, 717. (**3**) i.r. (CH_2Cl_2, cm^{-1}, ν_{co}) 2058s, 2009s, 1978m; ^1H n.m.r. δ 1.57 (s, 3H), 1.64 (s, 3H), 2.15 (s, 15H), 2.18 (d, 1H, *J* 8.9 Hz), 2.34 (s, 3H), 2.38 (s, 3H), 3.30 (d, 1H, *J* 8.9 Hz); ^{13}C n.m.r. ($CDCl_3$) δ −13.5 (CH_2), 8.72 (Me), 9.45 (Me), 10.01 ($C_5\mathit{Me}_5$), 10.47 (Me), 10.80 (Me), 89.80, 91.18, 92.14, 98.57 (C_5Me_5), 111.70, 109.40, 166.08, 168.94, 173.63; m.s. (f.a.b.) *m/z* 737, 709, 681, 653. (**4**) i.r. ($MeNO_2$, cm^{-1}, ν_{co}) 2073m, 2058m; ^1H n.m.r. (CD_3NO_2) δ 2.41 (s); ^{13}C n.m.r. (CD_3NO_2) δ 10.18, 109.45, 165.54; m.s. (f.a.b.) *m/z* 739 $[(C_5Me_5)_2Ir_2(CO)_3H]^+$, 709.



Scheme 1. *Reagents and conditions:* [NO][BF_4]/CH_2Cl_2 or [PhN_2][BF_4]/CH_2Cl_2; ii, $AgBF_4$ + (C_5Me_5)Ir(CO)Cl_2/acetone; iii, $AgBF_4$ + (1)/acetone; iv, HBF_4/Et_2O; v, air exposure; vi, [Ph_3C][BF_4]/$MeNO_2$; vii, 1 atm CO/acetone; viii, $AgBF_4$/acetone.

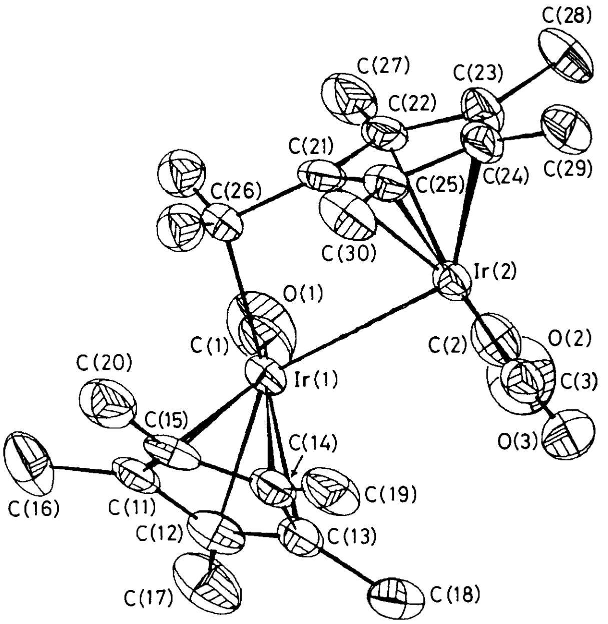


Figure 1. Perspective view of the cation in (3). Selected bond lengths (Å) and angles (°): Ir(1)–Ir(2) 2.794(1), Ir(1)–C(1) 1.817(10), Ir(1)–C(26) 2.154(10), Ir(2)–C(2) 1.867(11), Ir(2)–C(3) 1.877(10), C(1)–O(1) 1.159(12), C(2)–O(2) 1.137(14), C(3)–O(3) 1.137(12), C(21)–C(26) 1.464(14); C(1)–Ir(1)–Ir(2) 90.2(3), C(26)–Ir(1)–Ir(2) 77.6(3), C(26)–Ir(1)–C(1) 90.9(5), C(2)–Ir(2)–Ir(1) 89.4(3), C(3)–Ir(2)–Ir(1) 100.6(4), C(3)–Ir(2)–C(2) 90.2(4), Ir(1)–C(26)–C(21) 101.0(6).

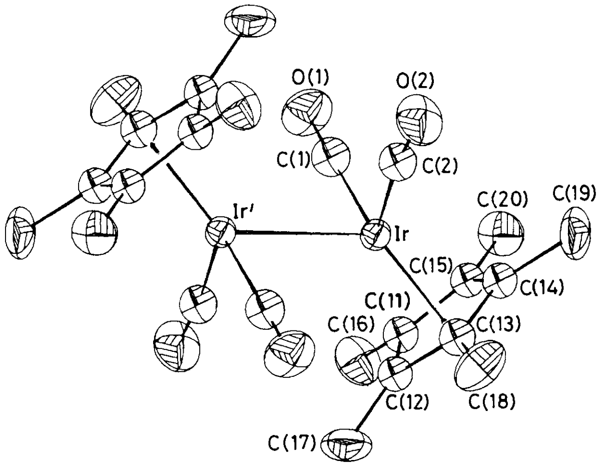


Figure 2. Perspective view of the centrosymmetric cation in (4). Selected bond lengths (Å) and angles (°): Ir–Ir' 2.8393(12), Ir–C(1) 1.891(11), Ir–C(2) 1.866(10), C(1)–O(1) 1.140(13), C(2)–O(2) 1.162(13); C(1)–Ir–Ir' 84.7(3), C(2)–Ir–Ir' 81.9(3), C(1)–Ir–C(2) 96.9(4).

donor–acceptor Ir→Ir bond. With this in mind complex (2) was treated with further $AgBF_4$ in the presence of (1) with the intention of replacing the remaining chloride by a further equivalent of (1) to give a tri-iridium cation. Instead, compound (3)‡ was formed, in which one η^5-C_5Me_5 group of (2) has been converted into a rare[6] bridging methylenetetramethylcyclopentadienyl ligand in (3), which differs from (2) formally by elimination of HCl (Figure 1). The presence of (1) is not required for this conversion, but it does occur most cleanly when (1) is present.

Compound (1) complexes directly with $AgBF_4$ in acetone to give [{(η^5-C_5Me_5)(CO)$_2$Ir}$_2$Ag][BF_4] (5) which has a linear

Ir–Ag–Ir skeleton.[7] However, (**1**) is oxidized by $[Ph_3C][BF_4]$ in $MeNO_2$ to give the new complex dication (**4**) (Figure 2), possibly as a result of one-electron oxidation to the 17 e^- radical cation[8] followed by dimerization. Complex (**4**) was also observed to be formed cleanly from the complex $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2H][BF_4]$ on exposure to air. The structures of (**2**), (**3**), (**4**), and (**5**)[7] have been established by *X*-ray crystallography.§ On the basis of the observed bond lengths, the $C_5Me_4CH_2$ group in (**3**) is comparable to a previous structure,[6] and does not adopt the alkenoid fulvene structure.

The mechanism for the formation of (**2**) and (**3**) have still to be fully established. Interestingly, (**3**) is formed cleanly and in good yield (by i.r. and ^1H n.m.r.) when (**4**) is heated to *ca.* 200 °C as a solid; this thermal stability of the methylene bridge in (**3**) is remarkable. Compound (**4**) also reacts with 1 atm of CO in acetone to produce (**1**) and (**3**). It is possible that the formation of the bridging methylene in (**3**) is a result of intramolecular C–H addition to give an intermediate dicationic hydrido complex which then deprotonates to give (**3**). Attempts to intercept this intermediate have not yet been successful, and are continuing.

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§ *Crystal data.* Crystallographic results for (**2**) will be reported separately. (**3**): $C_{23}H_{29}BF_4Ir_2O_3$, monoclinic, space group $P2_1/n$, a = 12.736(1), b = 14.301(2), c = 14.417(1) Å, β = 104.55(1)°, T = 298 K, U = 2541.5 Å^3, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 104.77 cm^{-1}; Enraf-Nonius CAD-4F, Mo-K_α radiation (graphite monochromated, λ = 0.71069 Å), 4453 unique data collected using the ω–2θ scan method, $2° < 2\theta < 50°$, 2928 reflections with $I \geqslant 2.5\,\sigma(I)$ used in solution and refinement, solution by heavy atom method, refinement by full-matrix least squares, analytical absorption correction, 299 variables, all non-H atoms anisotropic, H atoms included in found or calculated positions but not refined, final maximum shift/error ratio 0.1, R = 0.029, R_w = 0.033.

(**4**): Crystals were obtained as the dioxane solvate from $MeNO_2$–dioxane. ($4\cdot C_4H_8O_2$): $C_{28}H_{38}B_2F_8Ir_2O_6$, orthorhombic, space group *Pbca* (No. 61), a = 14.642(2), b = 14.763(1), c = 15.483(1) Å, T = 293 K, U = 3346.8 Å^3, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 79.56 cm^{-1}; Enraf-Nonius CAD-4F, Mo-K_α radiation (graphite monochromated, λ = 0.71069 Å), 2948 unique data measured using the ω–2θ scan method, $0° < 2\theta < 50°$, 1800 reflections with $I \geqslant 2.5\,\sigma(I)$ used in solution and refinement, solution by heavy atom method, refinement by full-matrix least squares, empirical absorption correction, 169 variables, anisotropic thermal parameters for Ir, F, O, and methyl carbon atoms, isotropic parameters for all other atoms, H atoms included in calculated positions but not refined, final maximum shift/error ratio 0.38, R = 0.026, R_w = 0.037.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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