

## The Cyclometallation of Benzoic Acid and the X-Ray Crystal Structure of $[C_5Me_5Ir(O_2CC_6H_4)(Me_2SO)]$

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The complexes  $[C_5Me_5M(C_6H_4CO_2)(Me_2SO)]$  (**1a**, M = Rh; **1b**, M = Ir), and  $[(p\text{-cymene})Os(C_6H_4CO_2)(Me_2SO)]$ , containing cyclometallated benzoic acid, have been prepared and characterised; carbonylation of (**1a**) yields phthalic anhydride.

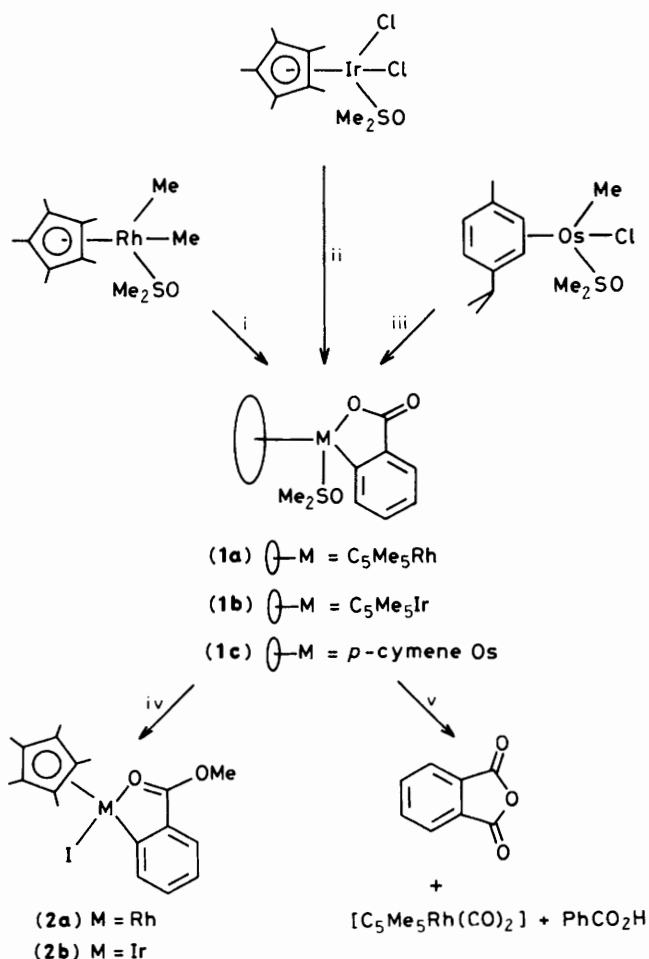
Many cyclometallation reactions have been described where a 4-, 5-, or 6-membered chelate ring is formed, in which an aromatic ring, bearing a functional group bonded to a metal, is attacked by the metal *ortho* to the functional group.<sup>1</sup> Related reactions have also been used synthetically, for example the orthothallation of benzoic acid, followed by transmetalation with Pd<sup>II</sup>, offers useful synthetic routes to phthalic anhydride or isocoumarins.<sup>2,3</sup> However the cyclometallation of benzoic acid itself, a very attractive starting material for many reactions, does not appear to have been described. We here report on the cyclometallation of benzoic acid by rhodium, iridium, and osmium complexes, on the X-ray structure of the iridium complex (**1b**), and on some of the reactions of the cyclometallated benzoic acid complexes.

The most convenient routes to the complexes (**1a–c**) are: for (**1a**) (90%), by reaction of  $[C_5Me_5RhMe_2(Me_2SO)]^4$  with one equivalent of benzoic acid; for (**1b**) (60%), by reaction of  $[C_5Me_5IrCl_2(Me_2SO)]$  with two equivalents of silver benzoate; and for (**1c**) (68%), by reaction of  $[(p\text{-cymene})OsMe(Cl)(Me_2SO)]^5$  with one equivalent of silver benzoate. Complexes (**1a**) and (**1b**) were quite air-stable, but the osmium complex (**1c**) was air-sensitive. They were characterised by elemental analysis, spectroscopy,<sup>†</sup> and an X-ray structure determination of (**1b**).<sup>‡</sup>

The X-ray structure of (**1b**) showed the expected approximately octahedral arrangement of ligands about the iridium

[Figure 1; S–Ir–O(1) 90.7(5), S–Ir–C(12) 90.5(8), O(1)–Ir–C(12) 78.4(10)°, the remaining 'three' sites being occupied by the  $C_5Me_5$  ring], and with the  $Ir(O_2CC_6H_4)$  moiety approximately planar [Ir +0.26, C(17) –0.07, O(1) +0.018, and O(2) –0.165 Å vertically out of the plane of the  $C_6$ -ring]. The bond lengths Ir–C(12) 2.08(3) and Ir–O(1) 2.09(2) Å are normal.<sup>6</sup>

The complexes (**1a**) and (**1b**) [but not (**1c**)] reacted with methyl iodide to give (**2a**) and (**2b**) where the dimethyl sulphoxide had been replaced by iodide and the methyl had added on to the benzoate oxygen. This was accompanied by a change in  $\nu(CO_2)$  from 1730 and 1740  $cm^{-1}$  in (**1b**) to 1575 and 1600  $cm^{-1}$  in (**2b**).



Scheme 1. Reagents: i,  $PhCO_2H$  (1 equiv.); ii,  $PhCO_2Ag$  (2 equiv.); iii,  $PhCO_2Ag$  (1 equiv.); iv, MeI; v, CO (80 °C, 5 atm).

† N.m.r. spectra in  $CDCl_3$  ( $J$  in Hz). <sup>1</sup>H: (**1a**) at  $\delta$  1.68 ( $C_5Me_5$ ), 2.18 and 2.94 (2  $\times$  s,  $Me_2SO$ ), 7.50 (dd,  $J$  7.5, 1.1, H-3), 7.08 (td,  $J$  7.5, 1.3, H-4), 7.25 (td,  $J$  7.5, 1.1, H-5), and 7.54 (dd,  $J$  7.5, 1.3, H-6); (**1b**), 1.78 ( $C_5Me_5$ ), 2.49 and 2.90 (2  $\times$  s,  $Me_2SO$ ), 7.53 (dd,  $J$  7.5, 1.5, H-3), 7.10 (td,  $J$  7.5, 1.3, H-4), 7.24 (td,  $J$  7.5, 1.5, H-5), and 7.60 (dd,  $J$  7.5, 1.3, H-6); and (**1c**) 2.28 (s), 5.64 (m), 2.74 (septet,  $J$  7), 1.07 and 1.19 (2  $\times$  d,  $J$  7), all *p*-cymene; 2.71 and 2.49 (2  $\times$  s,  $Me_2SO$ ); 6.96 (td,  $J$  1.5, 7.3, H-4), 7.15 (td,  $J$  7.3, 1.8, H-5), 7.35 (ddd,  $J$  7.3, 1.8, 0.8, H-3), and 7.78 (ddd,  $J$  7.3, 1.5, 0.8, H-6), all benzoate. <sup>13</sup>C: (**1a**) at  $\delta$  8.9 and 99.8 (d,  $J_{Rh}$  5.5,  $C_5Me_5$ ), 43.2 and 43.8 ( $Me_2SO$ ), 168.0 (d,  $J_{Rh}$  29.1, C-1), 140.7 (C-2), 131.8 (C-3), 124.4 (C-4), 129.9 (C-5), 134.7 (C-6), and 179.9 ( $CO_2$ ); (**1b**), 8.7 and 94.0 ( $C_5Me_5$ ), 42.5 and 43.8 ( $Me_2SO$ ), 150.1 (C-1), 138.5 (C-2), 131.9 (C-3), 123.9 (C-4), 130.1 (C-5), 134.8 (C-6), and 183.5 ( $CO_2$ ); (**1c**), 18.3, 22.2, 22.8, 31.1, 79.0, 80.2, 80.3, 82.0, 98.6, 107.7 (all *p*-cymene), 41.9 and 45.6 ( $Me_2SO$ ), 123.7 (C-4), 128.9 (C-5), 131.8 (C-3), 138.9 (C-2), 139.5 (C-6), and 156.1 (C-1) (benzoate), and 183.3 ( $CO_2$ ).

‡ Crystal data:  $C_{10}H_{25}IrO_3S$ ,  $M = 525.68$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.274(12)$ ,  $b = 13.753(10)$ ,  $c = 15.304(34)$  Å,  $\beta = 99.25(15)^\circ$ ,  $U = 1926.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.863$  g  $cm^{-3}$ , Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å;  $\mu = 70.20$   $cm^{-1}$ ), crystal dimensions  $0.04 \times 0.05 \times 0.35$  mm<sup>3</sup>. X-Ray data collected ( $3.5 \leq 2\theta \leq 40^\circ$ ) on Nicolet R3M four-circle diffractometer to give 989 independent reflections,  $I \geq 5\sigma(I)$ . Structure solved and refined by SHELXTL programs to a final  $R = 0.0577$ . The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

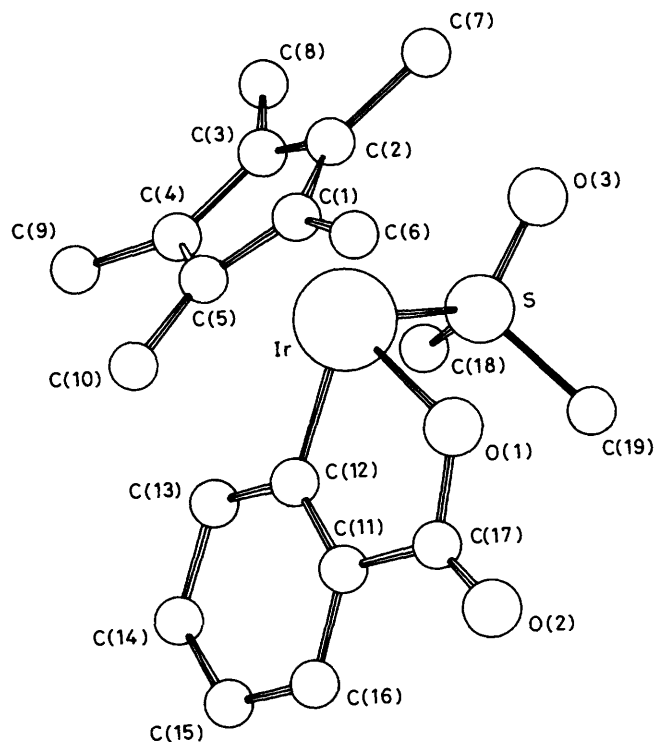


Figure 1. The X-ray crystal structure of  $[\text{C}_5\text{Me}_5\text{Ir}(\text{O}_2\text{CC}_6\text{H}_4)(\text{Me}_2\text{SO})]$  (**1b**) (hydrogen atoms omitted).

The rhodium complex (**1a**) also reacted readily with excess of benzoic acid to give  $[\text{C}_5\text{Me}_5\text{Rh}(\text{O}_2\text{CC}_6\text{H}_5)_2]$  (dichloromethane, 20 °C); interestingly, both the iridium and the osmium complexes were inert to benzoic acid under these conditions.

Reaction of  $[\text{C}_5\text{Me}_5\text{RhMe}_2(\text{Me}_2\text{SO})]$  with *m*-toluic or *m*-nitrobenzoic acids gave  $[\text{C}_5\text{Me}_5\text{Rh}(\text{XC}_6\text{H}_3\text{CO}_2)(\text{Me}_2\text{SO})]$  ( $\text{X} = \text{Me}$  or  $\text{NO}_2$ ), analogous to (**1a**), where attack on the ring had occurred *para* to the substituent and *ortho* to the carboxylic acid function.<sup>7</sup>

Complex (**1a**) reacted with carbon monoxide (80 °C, 5 atm, 18 h) in tetrahydrofuran or toluene to give a red-purple solution which contained phthalic anhydride (95%, by g.c.-mass spectrometry) and  $[\text{C}_5\text{Me}_5\text{Rh}(\text{CO})_2]$  [ $\nu(\text{CO})$  1943 and 2015  $\text{cm}^{-1}$ ]; some benzoic acid (5%) was also present.

We thank the S.E.R.C. for support, I.C.I. New Sciences Group for a CASE award (to G. J. S.) and Johnson Matthey for the loan of iridium trichloride.

Received, 15th March 1985; Com. 344

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