

## Photochemistry of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3]$ in Benzene Solution; Crystal Structure of $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\}_2(\mu\text{-}\eta^2,\eta^{2'}\text{-C}_6\text{H}_6)]$

Harry van der Heijden,<sup>a</sup> A. Guy Orpen,<sup>b</sup> and Peter Pasman<sup>a\*</sup>

<sup>a</sup> Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), P.O. Box 3003, 1003 AA Amsterdam, The Netherlands

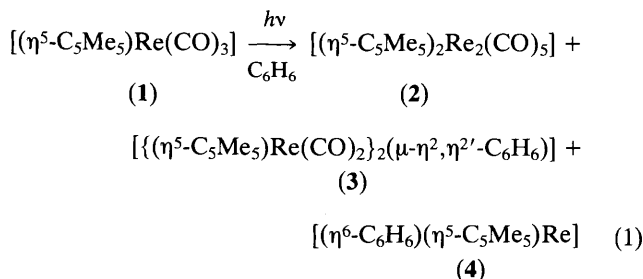
<sup>b</sup> Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

U.v. irradiation of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3]$  in benzene yields the stable complex  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\}_2(\mu\text{-}\eta^2,\eta^{2'}\text{-C}_6\text{H}_6)]$ ; X-ray diffraction reveals a pronounced double-bond localization in the doubly co-ordinated benzene ligand.

Arene molecules co-ordinated in an  $\eta^2$  fashion to transition metals have often been assumed to participate in a number of catalytic processes.<sup>1</sup> In particular their involvement in the activation of carbon-hydrogen bonds in aromatic molecules has recently been the subject of a number of reports.<sup>2</sup> Direct crystallographic evidence for  $\eta^2$ -co-ordination of arene mole-

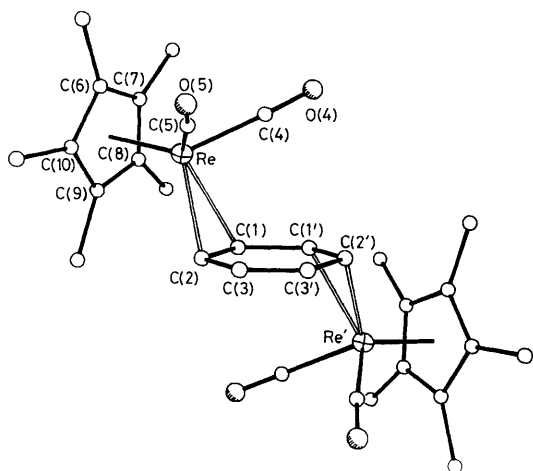
cules to transition metals is only abundant for the coinage metals<sup>3</sup> and few examples are known for the other transition elements.<sup>4</sup> We report here the synthesis of a new rhenium derivative of this class of compound.

When  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3]$  (**1**) was irradiated with u.v. light in benzene (20 °C; argon purge) three rhenium com-



plexes could be isolated† [equation (1)]. Compound (3) was isolated (ca. 5%)‡ as an off-white, air-stable, crystalline material. The formulation of this complex was suggested by spectroscopic data§ and confirmed by X-ray methods.

**Crystal data for (3):**  $\text{C}_{30}\text{H}_{36}\text{O}_4\text{Re}_2$ ,  $M = 833.0$ , monoclinic, space group  $C2/c$ ,  $a = 14.142(5)$ ,  $b = 8.955(5)$ ,  $c = 23.053(14)$  Å,  $\beta = 100.29(4)^\circ$ ,  $U = 2872(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.93$  g cm<sup>-3</sup>,  $\mu = 85.7$  cm<sup>-1</sup>,  $F(000) = 1591.5$ ,  $\lambda = 0.71069$  Å. Diffraction data were collected on a Nicolet P3m/F diffractometer using Mo- $K_\alpha$  radiation and an  $\omega/2\theta$  scan technique. The structure was solved by conventional heavy atom methods (Patterson and difference Fourier). All non-hydrogen atoms were assigned anisotropic vibrational parameters and were refined without constraints. Crystallographic calculations were car-



**Figure 1.** The structure of complex (3). Selected bond lengths (Å) and angles (°): Re–C(1) 2.263(8), Re–C(2) 2.276(10), C(1)–C(2) 1.401(13), C(1)–C(1') 1.473(16), C(2)–C(3) 1.456(14), C(3)–C(3') 1.312(20), C(1)–Re–C(2) 35.9(3), Re–C(1)–C(2) 72.5(5), Re–C(2)–C(1) 71.5(5), C(1)–C(2)–C(3) 118.0(8), C(2)–C(1)–C(1') 119.8(5), C(2)–C(3)–C(3') 122.2(5).

† In some cases trace amounts of the known<sup>8</sup> dimer  $[(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CO})_3\text{Re}_2]$  were found.

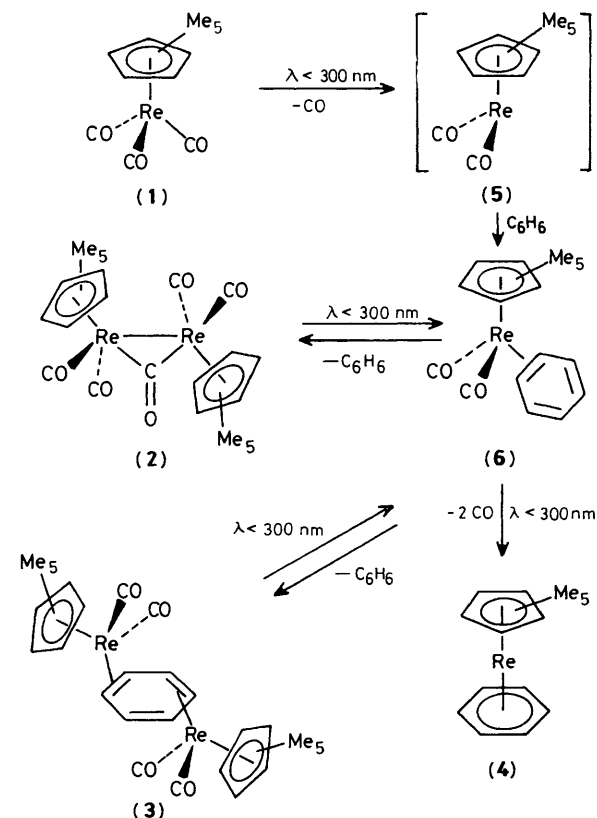
‡ Isolation of (3) involves removal of benzene, extraction with hexane, trituration of the insoluble material with ethanol, resulting in solidification of (3), which is isolated and recrystallized from toluene (yield based on unrecovered starting material: 7.5%).

§ **Spectroscopic data:** (3), i.r. ( $\text{C}_6\text{H}_6$ )  $\nu_{\text{CO}}$  1937s and 1871s cm<sup>-1</sup>; <sup>1</sup>H n.m.r. ( $\text{C}_6\text{D}_6$ )  $\delta$  1.66 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 2.85 (m, 2 H), 4.14 (d, 2 H,  $J$  8 Hz), and 6.41 (m, 2 H); <sup>13</sup>C n.m.r. ( $\text{CDCl}_3$ )  $\delta$  10.2 (Me), 96.9 ( $\text{C}_5\text{Me}_5$ ); 40.9, 50.6, and 127.3 ( $\text{C}_6\text{H}_6$ ); 206.6 and 206.8 (CO); (6), i.r. ( $\text{C}_6\text{H}_6$ ):  $\nu_{\text{CO}}$  1938s and 1870s cm<sup>-1</sup>; <sup>1</sup>H n.m.r. ( $\text{C}_6\text{H}_6\text{-C}_6\text{D}_6$ , 95:5)  $\delta$  1.59 (s, 15 H,  $\text{C}_5\text{Me}_5$ ) and 5.87 (s, 6 H,  $\text{C}_6\text{H}_6$ ); (4), <sup>1</sup>H n.m.r. ( $\text{C}_6\text{D}_6$ )  $\delta$  2.01 (s, 15 H,  $\text{C}_5\text{Me}_5$ ) and 4.24 (s, 6 H,  $\text{C}_6\text{H}_6$ ); <sup>13</sup>C n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  13.5 (Me), 62.5 ( $\text{C}_6\text{H}_6$ ), and 89.8 ( $\text{C}_5\text{Me}_5$ ).

ried out on a Data General Eclipse computer using programs of the SHELXTL packages. In the final cycle 163 parameters were refined using 2040 observations having  $I > 3\sigma(I)$ ; final  $R$  and  $R_w$  values were 0.038 and 0.047.¶

The molecular structure of (3), which has crystallographic  $C_2$  symmetry (Figure 1), shows a benzene molecule  $\eta^2$ -bonded to each of two  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$  fragments. The rhenium atoms lie on opposite faces of the benzene ring and are co-ordinated to the 1–2 and 3–4 bonds of the ring [*i.e.* C(1)–C(2) and C(1')–C(2')] in Figure 1]. The benzene ring in (3) is essentially planar; the r.m.s. deviation of carbon atoms from the  $\text{C}_6$  plane is 0.005 Å. The C–C distances within the benzene ring show considerable and significant variations. The C(1)–C(2) bond lengths are 1.401(13) Å, *i.e.* in the range observed for a variety of transition metal  $\eta^2$ -olefin complexes.<sup>5</sup> The C(1)–C(1') and C(2)–C(3) bond lengths are 1.473(16) and 1.456(14) Å, respectively, both lengths being slightly shorter than that of the central bond in buta-1,3-diene [1.483(10) Å].<sup>6</sup> By contrast, C(3)–C(3') is short: 1.312(20) Å; this length is consistent with that of an isolated C=C double bond (1.337 Å).<sup>7</sup>

Compound (3) is not a primary photo-product, but is formed in a dark reaction following the photolysis. Thus when the reaction mixture is analysed *directly* after photolysis *two* photo products are observed, one of which is the  $\eta^2$ -benzene complex  $[(\eta^2\text{-C}_6\text{H}_6)(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2]$  (6),§ which is



**Scheme 1**

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

formed *via* complexation of benzene to the photochemically generated 16-electron intermediate  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2]$ , (5); the other is  $[(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_5\text{Me}_5)\text{Re}]$  (4)§ (see Scheme 1).

The intermediacy of (6) accounts for the formation of all products. Thus reaction with unconverted (1) gives the known dimer (2),<sup>8</sup> while dimerization with loss of one molecule of benzene gives (3). Prolonged irradiation of (6) results in loss of two more moles of CO to form (4). It is noteworthy that both dimers (2) and (3) are unstable under photolysis conditions in benzene and are primarily converted into (1) and (6), respectively.

The  $\eta^2$ -benzene adduct (6) can be observed in dilute benzene solutions at room temperature over a period of several hours. This stability is in marked contrast to the thermal instability of  $\eta^2$ -benzene complexes which have been reported recently,<sup>2</sup> and it shows that the loss of resonance energy<sup>4b</sup> of the benzene ring upon complexation is amply compensated for by the binding interaction with the  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$  fragment. The introduction of a second interaction with an  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$  fragment, as in (3), results in a further stabilization of the system since now only a minor amount of resonance energy (comparable to that in butadiene) is lost. Hence it is not surprising that (3) has great

thermal stability, both in solution and in the solid state, and may, *e.g.*, be recrystallized from boiling toluene without arene exchange or decomposition.

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