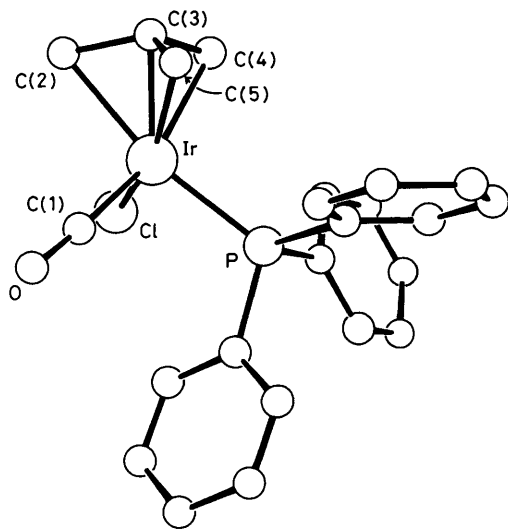




unreacted *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] can be recovered from the reaction mixture. Attempts to obtain (2) by treatment of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with the acetate (1a) have not been successful. However, the acetate (1a) reacts with [Os(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>9</sup> in refluxing benzene to afford a low yield (11%) of the η<sup>4</sup>-trimethylenemethane osmium complex (4).

The η<sup>4</sup>-trimethylenemethane complexes (2)–(4) have been characterised on the basis of microanalytical data and their spectroscopic properties.† Assignments in the <sup>1</sup>H n.m.r. spectra were made on the basis of the existence of strong 'W' couplings, H<sup>1</sup>–H<sup>4</sup>, H<sup>2</sup>–H<sup>5</sup>, and H<sup>3</sup>–H<sup>6</sup> in (2) and H<sup>1</sup>–H<sup>3</sup> in (3). These assignments were confirmed by selective decoupling experiments and nuclear Overhauser effect difference spectra. No sign of rotation of the trimethylenemethane ligand in (2) could be detected by a magnetisation transfer experiment at 70 °C giving a lower limit of Δ*G*‡ for this process of the order of 90 kJ mol<sup>-1</sup>. This is somewhat higher than values of 71–79 kJ mol<sup>-1</sup> for the rotational barrier found for substituted trimethylenemethane–Fe(CO)<sub>3</sub> derivatives.<sup>10</sup> We were also unable to observe changes in the <sup>1</sup>H n.m.r. spectrum of the osmium complex (4) between ±60 °C.

The n.m.r. spectra† of the complexes (2)–(4) are consistent with the illustrated staggered conformation as predicted by theoretical considerations.<sup>11,12</sup> A single crystal *X*-ray study



**Figure 1.** Molecular structure of (2), with H atoms of phenyl rings and methylene groups omitted. Interatomic distances: Ir–P 2.332(3), Ir–Cl 2.448(3), Ir–C(1) 1.898(15), Ir–C(2) 2.288(15), Ir–C(3) 2.053(12), Ir–C(4) 2.201(12), Ir–C(5) 2.173(15) Å.

† Selected spectroscopic data (coupling constants in Hz). Compound (2), i.r. (CsCl disc):  $\nu_{\text{CO}}$  2025,  $\nu_{\text{IrCl}}$  282 cm<sup>-1</sup>; n.m.r. (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H (400 MHz), δ 0.70 [dt, 1H, H<sup>2</sup>, *J*(H<sup>2</sup>H<sup>5</sup>) = *J*(H<sup>2</sup>P) 3.8, *J*(H<sup>2</sup>H<sup>1</sup>) 0.7], 1.66 [br., d, 1H, H<sup>1</sup>, *J*(H<sup>1</sup>H<sup>4</sup>) 4.1], 2.40 [dd, 1H, H<sup>3</sup>, *J*(H<sup>3</sup>H<sup>6</sup>) 3.9, *J*(H<sup>3</sup>P) 6.4], 2.94 [dd, 1H, H<sup>6</sup>, *J*(H<sup>3</sup>H<sup>6</sup>) 3.9, *J*(H<sup>6</sup>P) 7.5], 3.03 [dd, 1H, H<sup>4</sup>, *J*(H<sup>4</sup>H<sup>1</sup>) 4.1, *J*(H<sup>4</sup>H<sup>3</sup>) or *J*(H<sup>4</sup>P) 0.5], and 3.16 [dd, 1H, H<sup>5</sup>, *J*(H<sup>5</sup>H<sup>2</sup>) 3.8, *J*(H<sup>5</sup>P) 7.0]; <sup>13</sup>C{<sup>1</sup>H} (100 MHz), δ 175.0 [d, C<sup>1</sup>, *J*(C<sup>1</sup>P) 4.4], 108.8 [d, C<sup>3</sup>, *J*(C<sup>3</sup>P) 3.1], 57.8 (s, C<sup>4</sup> or C<sup>5</sup>), 54.0 [d, C<sup>2</sup>, *J*(C<sup>2</sup>P) 37.7], and 40.2 (s, C<sup>4</sup> or C<sup>5</sup>). Compound (3), i.r. (CsCl disc):  $\nu_{\text{CO}}$  2040 cm<sup>-1</sup>; n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H (400 MHz), δ 2.02 [1:2:6:2:1 quintet, 2H, H<sup>2</sup>, AA'XX' system, *J*(H<sup>2</sup>H<sup>2</sup>) 0, *J*(PP') 4.1, *J*(H<sup>2</sup>P) = –*J*(H<sup>2</sup>P) ± 5.8], 2.27 [dd, 2H, H<sup>1</sup>, *J*(H<sup>1</sup>H<sup>3</sup>) 4.1, *J*(H<sup>1</sup>P) 8.5], and 3.26 [dd, 2H, H<sup>3</sup>, *J*(H<sup>3</sup>H<sup>1</sup>) 4.1, *J*(H<sup>3</sup>P) 6.4]; <sup>13</sup>C{<sup>1</sup>H} (100 MHz), δ 172.2 (s, C<sup>1</sup>), 108.2 (s, C<sup>3</sup>), 58.5 (s, C<sup>4</sup>), and 54.9 [d, C<sup>2</sup>, *J*(C<sup>2</sup>P) 29.8]. Compound (4), i.r. (Nujol mull):  $\nu_{\text{CO}}$  1995s and 1927s cm<sup>-1</sup>; n.m.r. (CDCl<sub>3</sub>): <sup>1</sup>H (100 MHz), δ 1.02 [dd, 2H, H<sup>1</sup>, *J*(H<sup>1</sup>H<sup>3</sup>) 4.2, *J*(H<sup>1</sup>P) 6.6], 2.08 (br., s, 2H, H<sup>2</sup>), and 2.15 [d, 2H, H<sup>3</sup>, *J*(H<sup>1</sup>H<sup>3</sup>) 4.2].

of the neutral iridium complex (2) confirms this geometry.‡ The molecular structure is illustrated in Figure 1. The trimethylenemethane ligand adopts the usual umbrella arrangement with the iridium atom closer to the central carbon atom than the outer ones. The outer carbon atoms are bent towards the iridium atom with an average Ir–C–CH<sub>2</sub> angle of 76(0.8)°. The union of the trimethylenemethane ligand with the IrCl(CO)(PPh<sub>3</sub>) fragment creates a distorted octahedral arrangement about iridium with the methylene carbon atoms occupying three facial vertices. It is interesting to note that the trimethylenemethane ligand is not symmetrically bound to the iridium, the Ir–CH<sub>2</sub> bond lengths reflecting the markedly differing *trans* influences of chlorine, carbon monoxide, and triphenylphosphine.<sup>13,14</sup>

Preliminary studies indicate that the chemistry of the osmium derivative (4) is markedly different to the neutral iridium derivative (2). Thus (4) reacts rapidly with HCl at room temperature to give the methallyl complex [Os(η<sup>3</sup>-CH<sub>2</sub>CMeCH<sub>2</sub>)(CO)<sub>2</sub>(Cl)(PPh<sub>3</sub>)] characterised by comparison with an authentic sample prepared by the action of methallyl chloride upon [Os(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]. In contrast there is no similar reaction between HCl and (2).

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‡ Crystal data for (2): C<sub>23</sub>H<sub>21</sub>ClIrOP, *M* = 572.6, monoclinic, space group C2/c, *a* = 17.727(1), *b* = 13.705(10), *c* = 17.848(2) Å, β = 102.68(1)°, *U* = 4230.4 Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.80 g cm<sup>-3</sup>, *F*(000) = 2208, Mo–K<sub>α</sub> X-radiation, λ = 0.71069 Å, μ(Mo–K<sub>α</sub>) = 62.6 cm<sup>-1</sup>; current *R* 0.0526 (*R<sub>w</sub>* 0.0540) for 2622 independent reflections [*I* > 3σ(*I*)] collected at 293 K on a Stoe STADI-2 Weissenberg diffractometer in the range 7 ≤ 2θ ≤ 60°.

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.