

## Facile and Reversible CO Insertion into the Ir-CH<sub>3</sub> Bond of [Ir<sub>4</sub>(CH<sub>3</sub>)(CO)<sub>8</sub>(μ<sub>4</sub>-η<sup>3</sup>-Ph<sub>2</sub>PCCPh)(μ-PPh<sub>2</sub>)]

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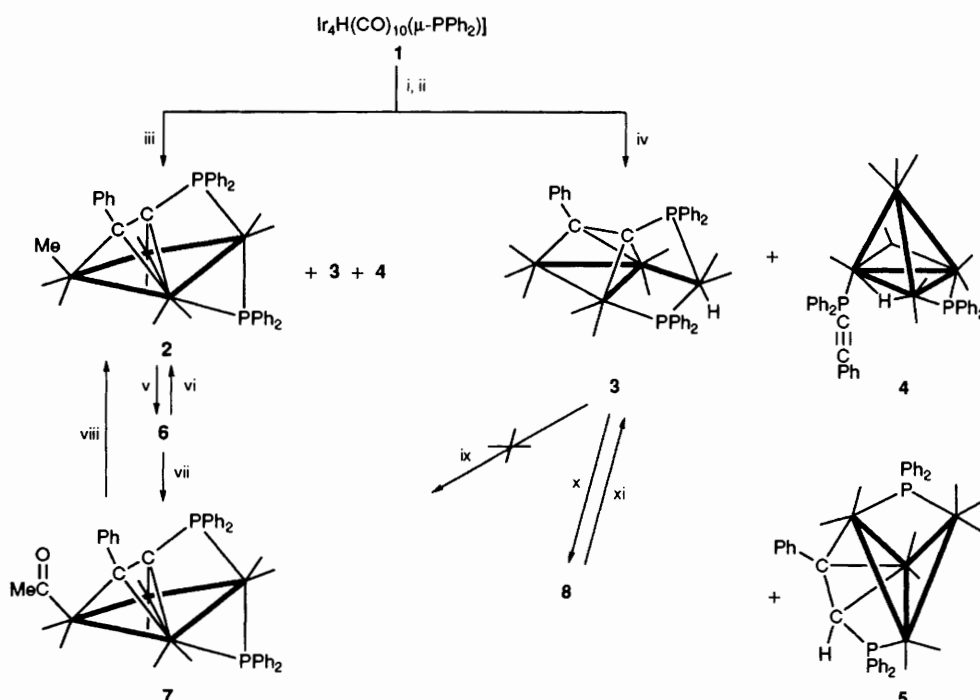
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Reaction of [Ir<sub>4</sub>H(CO)<sub>10</sub>(μ-PPh<sub>2</sub>)] with BuLi, Ph<sub>2</sub>PC≡CPh and then MeI gives [Ir<sub>4</sub>(CH<sub>3</sub>)(CO)<sub>8</sub>(μ<sub>4</sub>-η<sup>3</sup>-Ph<sub>2</sub>PCCPh)(μ-PPh<sub>2</sub>)], which undergoes a reversible two-step CO insertion under extremely mild conditions to yield Ir<sub>4</sub>{(CH<sub>3</sub>C(O))<sub>2</sub>(CO)<sub>8</sub>-(μ<sub>4</sub>: η<sup>3</sup>-Ph<sub>2</sub>PCCPh)(μ-PPh<sub>2</sub>)} as the final product; the structures of both species have been established by X-ray diffraction studies.

Carbonyl cluster compounds containing alkyl and alkyl-derived ligands have been suggested to serve as models for hydrocarbon transformations catalysed by metal surfaces, however, they are still relatively rare.<sup>1</sup> The only known tetranuclear iridium clusters bearing such a ligand, namely [Ir<sub>4</sub>(CO)<sub>11</sub>(CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sup>-</sup> and [Ir<sub>4</sub>(CO)<sub>10</sub>(CH<sub>2</sub>CO<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>]<sup>2-</sup>, were obtained from the reactions of Na[Ir(CO)<sub>4</sub>]

with BrCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>,<sup>2</sup> but generally, carbonyl cluster alkyl species have been produced from preformed polynuclear compounds.<sup>3-7</sup> Although CO insertion into metal-alkyl bonds in mononuclear complexes is a textbook reaction,<sup>8</sup> this process in alkyl containing carbonyl clusters has only been documented in rare cases.<sup>3-5</sup> We now report the formation of [Ir<sub>4</sub>(CH<sub>3</sub>)(CO)<sub>8</sub>(μ<sub>4</sub>-η<sup>3</sup>-Ph<sub>2</sub>PCCPh)(μ-PPh<sub>2</sub>)], and its facile CO



**Scheme 1** Reagents and conditions: i, BuLi-THF, 0 °C; ii, Ph<sub>2</sub>PC≡CPh (1 equiv.); iii, MeI or Me<sub>3</sub>OBF<sub>4</sub> (1 equiv.); iv, CF<sub>3</sub>CO<sub>2</sub>H; v, CO (1 atm)-THF or CDCl<sub>3</sub>, 25 °C, 20 min; vi, Ar-THF or CDCl<sub>3</sub>, 25 °C, 30 min; vii, CO (1 atm)-THF, 40 °C, 7 h; viii, Ar-THF, 60 °C, 6 h; ix, CO (1 atm)-THF or toluene, 40 °C, 24 h; x, H<sub>2</sub> (2 atm)-toluene, 25 °C, 4 h; xi, Ar-toluene, 25 °C, 10 min

insertion reaction that yields  $[\text{Ir}_4\{\text{CH}_3\text{C}(\text{O})\}(\text{CO})_8(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$ .

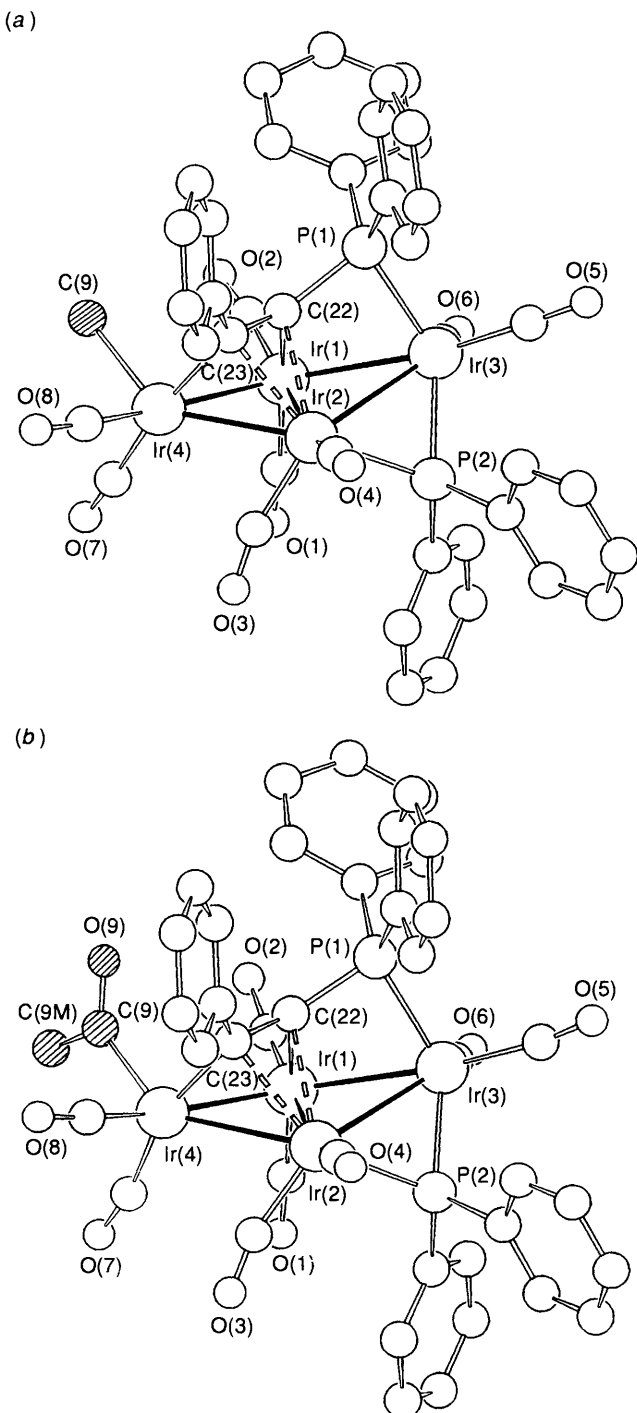
Deprotonation *in situ* of  $[\text{Ir}_4\text{H}(\text{CO})_{10}(\mu\text{-PPh}_2)]$  **1**<sup>9</sup> with BuLi in tetrahydrofuran (THF) at 0 °C, followed by sequential addition of  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  (1 equiv.) and MeI (1 equiv.) gives, after 15 min stirring at room temp. and TLC ( $\text{CH}_2\text{Cl}_2$ -hexane

30% as eluent)  $[\text{Ir}_4(\text{CH}_3)(\text{CO})_8(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$  **2** (up to 40%). The other products of this reaction  $[\text{Ir}_4\text{H}(\text{CO})_9(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$  **3** (20%) and  $[\text{Ir}_4\text{H}(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  **4**, had been previously obtained after protonation of the reaction mixture, instead of methylation, together with  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{Ph})(\mu\text{-PPh}_2)]$  **5**,<sup>10,11</sup> see Scheme 1, and were invariably obtained besides **2**, probably as a result of moisture in the reaction medium.

In compounds **2** and **3** P-C bond cleavage of the  $(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})$  ligand was not observed when these species were heated in  $\text{CH}_2\text{Cl}_2$  under Ar (40 °C, 48 h), and this is in contrast with the lability of this bond in compounds in which this ligand is terminally bound.<sup>11,12</sup> Instead, in both cases this ligand acted as an anchor, holding the metal atoms together and allowing investigation of their chemistry (Scheme 1).

When CO was bubbled through a bright red THF solution of **2** (25 °C, 20 min), a colour change was observed, but the yellow compound **6** formed was found to lose CO readily under Ar to give quantitative amounts of the starting material. Upon heating compound **6** under a flow of CO (40 °C, 7 h), the orange acyl species  $[\text{Ir}_4(\text{CH}_3\text{C}(\text{O}))(\text{CO})_8(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$  **7** was formed in high yield. Interestingly, the terminal acetyl complex **7** underwent CO removal upon heating under Ar (60 °C, 6 h) to give **2**, instead of a  $\mu$ -acetyl complex, as observed for  $[\text{Os}_3(\text{CO})_{11}(\mu\text{-I})(\text{C}(\text{O})\text{CH}_3)]$ ,<sup>3</sup> but under the conditions described, the yellow intermediate **6** was not observed.

Compounds **2** and **7** were fully characterized by spectroscopic and analytical data<sup>†</sup> and by X-ray analyses.<sup>‡</sup> <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR data indicated that only minor structural changes occurred upon CO insertion, but in the case of the



**Fig. 1** Molecular structures of (a) **2** and (b) **7**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Metal-metal bonds (Å) are: Ir(1)-Ir(2) 2.652(1), 2.656(2); Ir(1)-Ir(3) 2.826(1), 2.819(2); Ir(1)-Ir(4) 2.690(1), 2.685(2); Ir(2)-Ir(3) 2.913(1), 2.912(2); Ir(2)-Ir(4) 2.785(1), 2.843(2) for **2** and **7** respectively. Other relevant bond distances (Å): Ir(1)-C(22) 2.09(1), 2.12(4); Ir(4)-C(23) 2.07(1), 2.03(4); Ir(2)-C(22) 2.38(1), 2.47(39); Ir(2)-C(23) 2.30(1), 2.33(3); Ir(3)-P(1) 2.296(3), 2.307(8); Ir(2)-Ir(3) 2.913(1), 2.912(2); Ir(4)-C(9) 2.14(1), 2.00(4) for **2** and **7**, respectively; C(9)-O(9) 1.20(6), C(9)-C(9M) 1.54(9), Ir(4)-C(9)-C(9M) 118(4) for **7**.

<sup>†</sup> *Spectroscopic data* for **2**: IR  $\nu_{\text{CO}}/\text{cm}^{-1}$  (hexane), 2060m 2026s, 2018m, 1993mbr, 1975mbr, 1949wbr; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (s,  $\text{CH}_3$ ) and 6.6-8.4 (m, Ph); <sup>31</sup>P{<sup>1</sup>H} NMR,  $\delta$  -47.2 [<sup>2</sup> $J_{\text{P-P}}$ /Hz 192.6 (d,  $\text{Ph}_2\text{PCCPh}$ )] and 73.8 (d,  $\text{PPh}_2$ ), ref.  $\text{H}_3\text{PO}_4$ ; FAB MS (nitrobenzyl-alcohol matrix) (calc. for <sup>193</sup>Ir) 1482 ( $\text{M}^+$  +  $\text{M}'$ ); 1454 ( $\text{M}' - \text{CO}$ )<sup>+</sup>; 1383 ( $\text{M}' - 3\text{CO} - \text{CH}_3$ )<sup>+</sup>; 1243 ( $\text{M}' - 8\text{CO} - \text{CH}_3$ )<sup>+</sup>; 957 ( $\text{M}' - 8\text{CO} - \text{CH}_3 - \text{Ph}_2\text{PCCPh}$ )<sup>+</sup>.

For **6**: IR  $\nu_{\text{CO}}/\text{cm}^{-1}$  (hexane) 2062w, 2042s, 2032s, 2002m, 1987m, 1851vw; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.07 (s), 1.25 (s) (1:2) and 6.5-7.6 (m, Ph); <sup>31</sup>P{<sup>1</sup>H} NMR -14.4 (s) ( $\text{Ph}_2\text{PCCPh}$ ) and 134.0 (s) ( $\text{PPh}_2$ ).

For **7**: IR,  $\nu_{\text{CO}}/\text{cm}^{-1}$  (hexane) 2074w, 2062m, 2026s, 1995wbr, 1980wbr, 1960w, 1695w; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  2.43 (s,  $\text{C}(\text{O})\text{CH}_3$ ) and 6.6-8.3 (m, Ph); <sup>31</sup>P{<sup>1</sup>H} NMR,  $\delta$  -50.8 [<sup>2</sup> $J_{\text{P-P}}$ /Hz 194 (d,  $\text{Ph}_2\text{PCCPh}$ )] and 79.1 (d,  $\text{PPh}_2$ ) satisfactory elemental analyses (C, H) were obtained for **2** and **7**

<sup>‡</sup> *Crystal data* for **2** and **7**:  $\text{C}_{41}\text{H}_{28}\text{Ir}_4\text{O}_8\text{P}_2$  **2**,  $M = 1475.4$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.452(2)$ ,  $b = 17.386(7)$ ,  $c = 11.231(5)$  Å,  $\alpha = 94.38(5)^\circ$ ,  $\beta = 113.59(2)^\circ$ ,  $\gamma = 89.50(2)^\circ$ ,  $U = 2043$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.40$  g  $\text{cm}^{-3}$ ,  $F(000) = 1352$ ,  $\mu(\text{Mo-K}\alpha) = 12.6$   $\text{cm}^{-1}$ ,  $2 < \theta < 25^\circ$ , final  $R$  value 0.043,  $R_w = 0.049$  for 5682 out of 7798 independent reflections [ $I > 2\sigma(I)$ ].

$\text{C}_{42}\text{H}_{28}\text{Ir}_4\text{O}_9\text{P}_2$  **7**,  $M = 1503.4$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.426(4)$ ,  $b = 17.537(6)$ ,  $c = 11.335(5)$  Å,  $\alpha = 93.96(3)^\circ$ ,  $\beta = 113.24(3)^\circ$ ,  $\gamma = 88.86(3)^\circ$ ,  $U = 2082$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.40$  g  $\text{cm}^{-3}$ ,  $F(000) = 1380$ ,  $\mu(\text{Mo-K}\alpha) = 12.4$   $\text{cm}^{-1}$ ,  $2 < \theta < 25^\circ$ , final  $R$  value 0.078,  $R_w = 0.075$  for 3983 out of 7696 independent reflections [ $I > 2\sigma(I)$ ].

For **2** and **7** diffraction data were collected by the  $\omega/2\theta$  scan method. All non-H atoms in **2** and Ir, P and O atoms in **7** were allowed to vibrate anisotropically. All H atoms were added in calculated positions (C-H 1.08 Å) and refined 'riding' on their respective C atoms. Absorption correction was applied in both **2** and **7** by the Walker and Stuart method<sup>13</sup> (correction range 1.00-0.61, 1.00-0.55 in **2** and **3**, respectively), once complete structural models were obtained and all atoms refined isotropically. The structures were solved by direct methods and refined by full-matrix least-squares. For all calculations the crystallographic program SHELX76 was used.<sup>14</sup> 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.

yellow species **6**, a drastic change, most probably due to CO addition to the metal polyhedron seems to have occurred, and studies are in progress to further characterize this species.

The solid-state molecular structures of **2** and **7** are shown in Fig. 1. They are closely related and their main features will be discussed together. Their metal framework can be described as a flat butterfly, similar to that previously observed in **3**,<sup>10</sup> whose four atoms interact with the ( $\mu_4$ - $\eta^3$ -Ph<sub>2</sub>PCCPh) ligand, via two  $\sigma$ -interactions, one  $\pi$ -interaction and one two-electron P–Ir bond. In both complexes the longest Ir–Ir edge is spanned by the diphenylphosphino ligand. Each Ir-atom does also bear two terminal COs. The most striking feature of the structure of **2** is the presence of a terminally bound methyl group on one of the wing-tip Ir-atoms, which formally takes the place of the ‘ninth CO’ in the structure of **3**. Note, however, that **3** does also bear a H(hydride) atom, so that, considering an one-electron contribution from the methyl group, **2** is a 62-electron cluster, while **3** possesses 64-electrons in agreement with the opening of a second Ir–Ir bond. In place of the CH<sub>3</sub> ligand in **3**, in the structure of **7** there is a C(O)CH<sub>3</sub> group.

Interestingly, **2** and **7** not only possess very similar molecular structures, but their crystals are isomorphous (*i.e.* the two complexes crystallize with extremely similar packing arrangements). Similar relationships between molecular and crystal structures are exhibited by the only other examples of methyl/methoxycarbonyl clusters,<sup>5</sup> namely the anions [Ru<sub>6</sub>C(CO)<sub>16</sub>(CH<sub>3</sub>)]<sup>-</sup> and [Ru<sub>6</sub>C(CO)<sub>16</sub>{C(O)CH<sub>3</sub>}]<sup>-</sup>.

In contrast with the hydrido-species **3**, compound **2** does not obey the 18-electron rule at each metal atom: Ir(1) and Ir(4) formally have 17 valence electrons, while Ir(2) and Ir(3) are associated with 19 valence electrons, so that dative bonds from the latter to the former are implied. This difference in the electronic distribution in the two compounds might well be responsible for their different reactivities. Thus, the yellow hydrido species **3** did not undergo CO insertion into the Ir–H bond when CO was bubbled through a toluene solution (40 °C, 24 h), but it reacted reversibly with H<sub>2</sub> (2 atm, 25 °C, 4 h) to yield a bright red compound **8** only stable under an H<sub>2</sub> atmosphere.

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