New μ-Methylene-dicobalt Complexes and Evidence for μ-Methylene to Terminal Methylene Transformations

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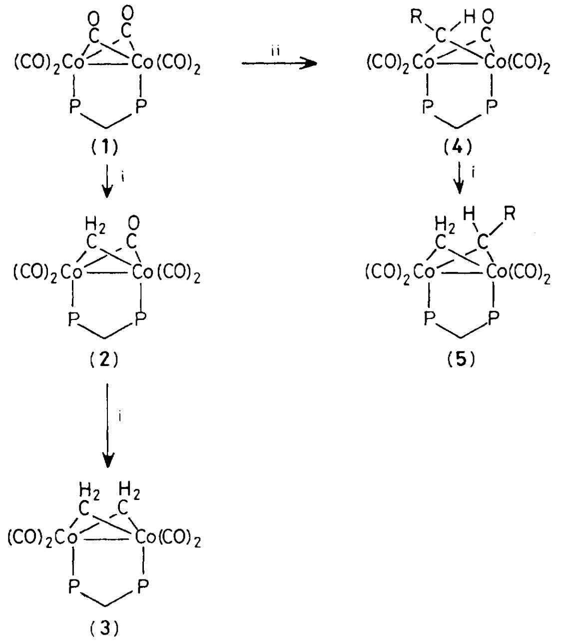
New μ-alkylidene complexes $[Co_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CHR)(\mu\text{-}dppm)]$ and $[Co_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CHR)(\mu\text{-}dppm)]$, R = H or CO_2Et, dppm = $Ph_2PCH_2PPh_2$, have been prepared by displacement of μ-CO groups from $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}dppm)]$ on reaction with $CHRN_2$; dynamic n.m.r. data indicate rapid μ-CH_2 to terminal methylene transformations in these complexes.

There has been great interest in μ-methylene derivatives of transition elements,[1-3] and several cyclopentadienylcobalt derivatives are known.[1,4,5] We now report the first μ-methylene derivatives based on cobalt carbonyl,† and present strong evidence for facile interconversion of bridging and terminal methylene groups in these complexes.

The synthesis is shown in Scheme 1 and involves displacement at room temperature of μ-CO groups by μ-alkylidene groups in the complex $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}dppm)]$, (1),[6] using diazomethane or ethyl diazoacetate as the source of alkylidene groups. Diazomethane gave both the mono- and bis-μ-methylene derivatives, (2) [ν(μ-CO) 1810 cm^{-1}] and (3), but the diazoester gave only the monosubstituted derivative (4).‡ Further reaction of (4) with diazomethane gave the mixed alkylidene derivative (5), but this could not be prepared from (2) and excess of diazoester. This is the first case in which μ-alkylidene complexes have been prepared by direct displacement of μ-CO groups.[1]

The ^1H n.m.r. spectrum (100 MHz) of (3) at room temperature gave single resonances in a 2:1 ratio for $(CH_2)_2Co_2$ and CH_2P_2 protons, but at −80 °C the CH_2Co_2 resonance had split



Scheme 1. i, CH_2N_2, −CO, $-N_2$; ii, $CH(CO_2Et)N_2$, −CO, $-N_2$; $\overset{\wedge}{P\,P}$ = $Ph_2PCH_2PPh_2$, R = CO_2Et.

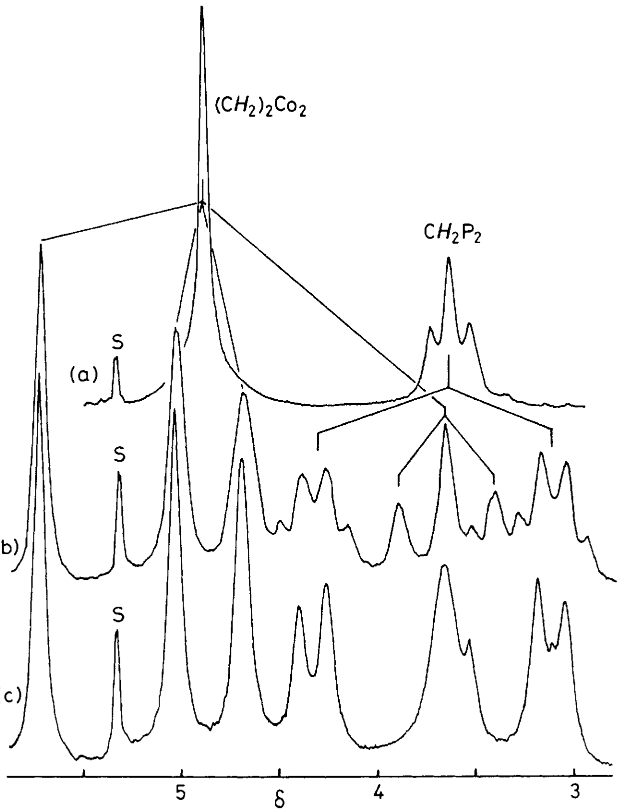
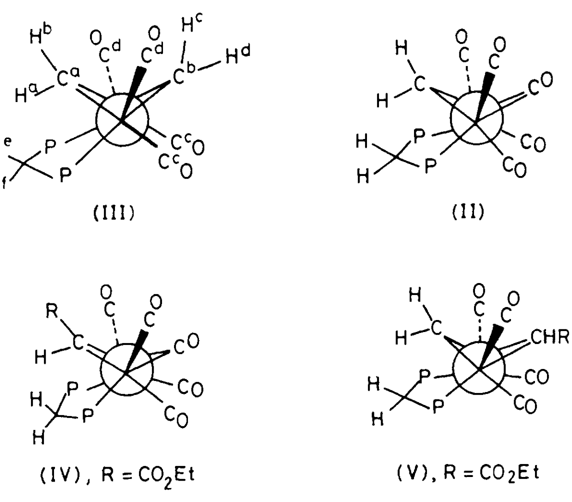


Figure 1. ^1H n.m.r. spectra (100 MHz) of complex (3) in CD_2Cl_2. (a) 30 °C, (b) −80 °C, (c) −80 °C with ^{31}P decoupling. The peaks labelled S are due to $CHDCl_2$.



Newman projections of compounds (2)—(5)

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† Fluorinated derivatives and γ-lactone derivatives have been reported (ref. 1). No bis(μ-alkylidene) complexes are known. For a related complex, see *Inorg. Chem.*, 1983, **22**, 1049.

‡ $[Co_2(CO)_8]$ did not yield μ-methylene derivatives with CH_2N_2.

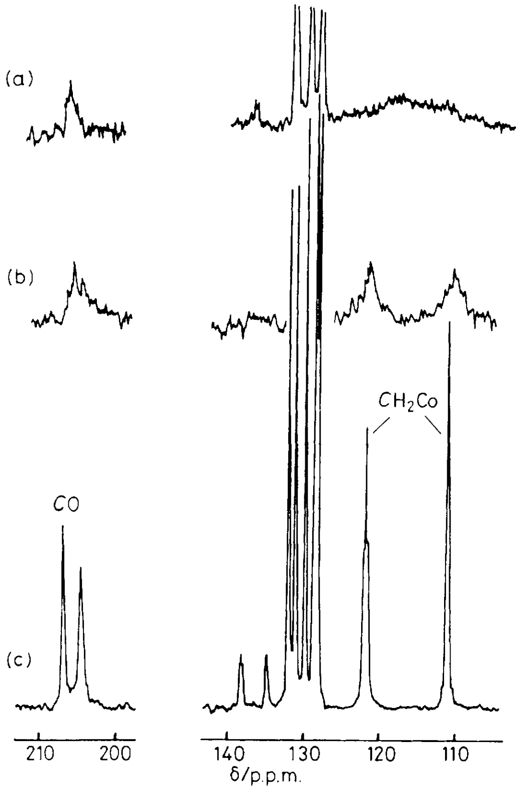
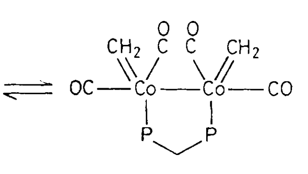


Figure 2. $^{13}C\{^1H\}$ N.m.r. spectra (100.6 MHz) of complex (**3**) in CD_2Cl_2. (a) 30 °C, (b) 10 °C, (c) −50 °C. Note that three of the four phenyl resonances (128—138 p.p.m.), as well as the CO and CH_2Co resonances, are split at −50 °C.

into four equal intensity peaks and the CH_2P_2 resonance had split into two (Figure 1), as expected fo the static structure (III) shown in Newman projection down the Co–Co bond. One of the CH_2Co_2 resonances (Figure 1) occurred at anomalously low chemical shift[1] (δ 3.65) and gave a large triplet coupling to phosphorus [J(PH) 23.5 Hz]; this is assigned to H^a which lies over the diphosphine ligand and is shielded by the phenyl substituents. In the $^{13}C\{^1H\}$ n.m.r. spectrum (100.6 MHz, ^{13}C enriched at both CO and μ-CH_2 sites) the broad resonances at room temperature due to μ-CH_2 and CO carbons each split into two equal intensity peaks at low temperature (Figure 2) due to non-equivalent carbons C^a, C^b, C^c, C^d shown in (III). The activation energy $\Delta G^\ddagger$ was calculated to be 53 ± 1 kJ mol^{-1} from all ^1H and ^{13}C (including phenyl resonances of the dppm ligands) coalescence points, indicating that a single dynamic process was responsible. Since the presence of the bridging phosphine ligand prevents alternative mechanisms which have been considered,[2,5,7] in which the μ-CH_2 groups remain intact during a pseudorotation process, the only reasonable mechanism is that shown in equation (1), which involves rate determining μ-methylene to terminal methylene transformations, followed by rapid pseudorotation of the $Co(CO)_2(=CH_2)$ units and reformation of (**3**). This mechanism was first suggested by Knox,[2] for *cis–trans* isomerization in diruthenium complexes.

(3) $\rightleftharpoons$  (1)

Complex (**2**) shows very similar fluxional behaviour but with a higher activation energy ($\Delta G^\ddagger$ *ca.* 62 kJ mol^{-1}) and includes terminal CO for bridging CO exchange, as expected for the proposed mechanism [^{13}C n.m.r.: δ 247.6 (μ-CO); 207.1, 204.6 (CO); 86.8 p.p.m. (μ-CH_2) at −50 °C]. In contrast, the parent (**1**) is fluxional at temperatures as low as −100 °C,[6] indicating a series of activation energies as (**2**) > (**3**) >> (**1**). The low temperature ^1H n.m.r. spectra of (**2**) and (**4**) each contain μ-alkylidene resonances with a large PH coupling [(**2**), δ 3.66, J(PH) 23 Hz; (**3**), δ 4.64, J(PH) 21 Hz] thus defining the stereochemistries shown in the Newman projections (II) and (IV), while the stereochemistry of compound (**5**), projection (V), is deduced from the chemical shift of the μ-alkylidene proton showing the large J(PH) [(**5**), δ 3.66, J(PH) 22 Hz; compare data for (**2**) and (**3**)]. Note that in structures (II) and (IV) the μ-alkylidene group occupies a position *trans* to CO rather than *trans* to phosphorus, presumably because the π-acceptor carbonyl can better remove excess electron density donated by the μ-CH_2 ligand in this configuration. There was no evidence for minor isomers in the n.m.r. spectra, so that alternative isomers must lie at considerably higher energy.

Complexes (**2**) and (**3**) are thermally stable in the absence of air, but show high reactivity, for example towards alkenes and alkynes, as will be reported separately.

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