Activation of μ-Alkylidene Ligands through Oxidation–Deprotonation: A New Synthesis of μ-Methyne, and its Hydrogenation to μ-Methyl

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A new method of activating μ-alkylidene complexes is described, involving oxidation to dications followed by deprotonation, so that μ-CH_2 is converted to μ-CH^+ and μ-CHMe to μ-$CHCH_2^+$; the mono-cationic products react with nucleophiles to produce derivatives of the original μ-alkylidene, while μ-CH^+ yields μ-CH_3^+ readily under pressure of hydrogen.

In a recent communication we described the slow, low yield formation of the cation $[Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(\mu\text{-dppm})(\eta\text{-}C_5H_5)_2]^+$ (**3**) [dppm = bis(diphenylphosphino)methane] from $[Ru_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-dppm})(\eta\text{-}C_5H_5)_2]^+$ (**5**) in solution.[1] As a result of efforts to clarify this intriguing μ-CH_3 to μ-CH transformation we have discovered a new method of activating hydrocarbon species co-ordinated at di- and tri-metal centres, described in this and the following[2] communication.

A possible first step in the conversion of μ-CH_3 into μ-CH was the loss of the agostic hydrogen as a radical (there is evidence that an agostic C–H bond is weakened towards both homolytic and heterolytic fission[3]), generating a radical cation

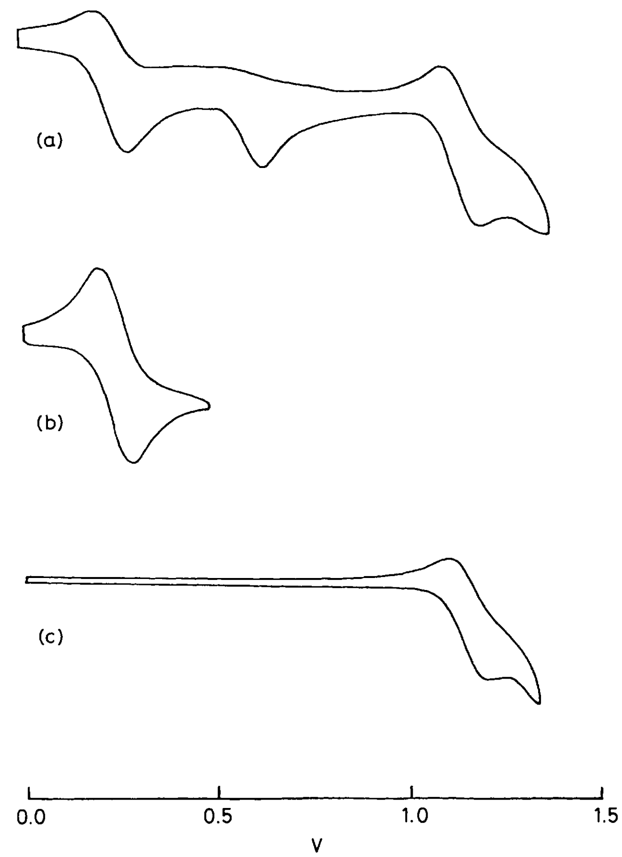
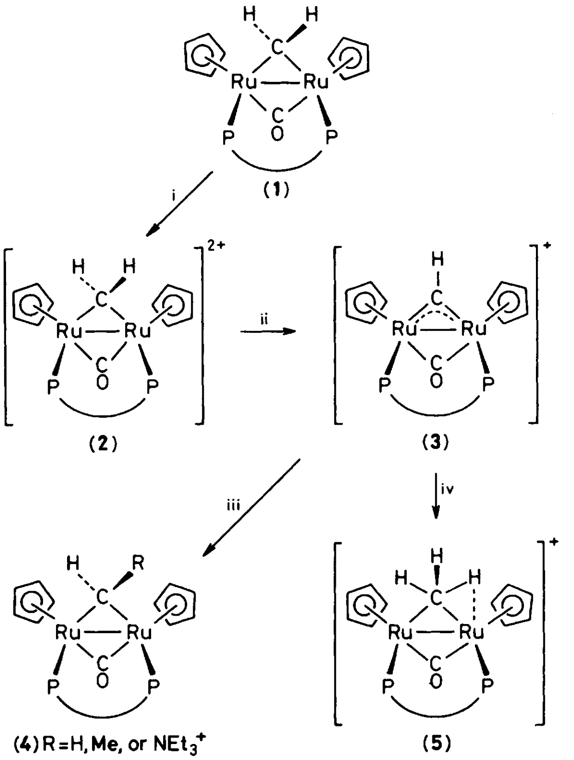


Figure 1. Cyclic voltammograms of (1) (a and b) and (3) (c).

$[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)(\eta\text{-}C_5H_5)_2]^+$. The additional possibility that the latter could be obtained in high yield by oxidation of $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)(\eta\text{-}C_5H_5)_2]$[1] (**1**) was explored by cyclic voltammetry. The cyclic voltammogram† of (**1**) shows (Figure 1a) three oxidation waves in the potential range 0 to 1.5 V. The first (E° = 0.24 V) is diffusion-controlled and fully reversible (Figure 1b), and corresponds to the formation of the radical cation $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)(\eta\text{-}C_5H_5)_2]^+$; the second is irreversible with a peak potential, $E_{ox.}$, of 0.65 V at a scan rate of 200 mV s^{-1}. Our suspicion that the third, reversible wave (E° = 1.16 V) was due to the one-electron oxidation of (**3**), formed *via* an EEC (electrochemical–electrochemical–chemical) mechanism in which the dication $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)(\eta\text{-}C_5H_5)_2]^{2+}$ (**2**) is formed (second wave) and subsequently deprotonates (Scheme 1), was confirmed by the synthesis of (**3**) through chemical oxidation and its subsequent electrochemistry. Thus, addition of two equivalents of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ as oxidant to (**1**) in dichloromethane, in the presence of the sterically-hindered base 2,6-dimethylpyridine, gives a near-quantitative yield of (**3**), the cyclic voltammogram of which shows one reversible one-electron oxidation wave with E° = 1.16 V (Figure 1c).

This oxidation–deprotonation route provides the μ-methyne cation (**3**) readily and allows a thorough study of its chemistry, the preliminary results of which are displayed in Scheme 1. Reaction with nucleophiles gives μ-alkylidene complexes (**4**), the sequence (**1**) → (**2**) → (**3**) → (**4**) representing a fast and efficient method of functionalising a μ-methylene ligand. The cation (**3**) also reacts with hydrogen (150 atm, 100 °C, 16 h) to afford the μ-methyl species (**5**) in greater than 90% yield. This unprecedented hydrogenation of μ-methyne may be related to 'hydrocarbation' [the apparently concerted reaction of $\mu\text{-}CH^+$ with an alkene to give $\mu\text{-}CR^+$ (ref. 4)], and it is then conceivable that the original[1] synthesis of (**3**) from (**5**) involves concerted elimination of H_2. The hydrogenation of μ-CH to give $\mu\text{-}CH_3$ may play an important role in catalytic CO hydrogenation.



P—P = dppm

Scheme 1. *Reagents:* i, $2[Fe(C_5H_5)_2][PF_6]$, CH_2Cl_2; ii, 2,6-dimethylpyridine, $-H^+$; iii, $NaBH_4$, MeLi, or NEt_3; iv, H_2 (150 atm), 100 °C, 16 h.

The EEC mechanism by which (**3**) is obtained from (**1**) is observed in other electron-rich diruthenium complexes. Thus, the cyclic voltammogram of the μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2]$ is qualitatively similar [oxidation waves at 0.55 V (reversible) and 0.98 V (irreversible, scan rate 100 mV s^{-1})] to that of (**1**), but the shifts of the waves to higher potentials (by *ca.* 0.3 V) necessitates the use of a stronger chemical oxidant. Accordingly, an excess of $AgBF_4$ was added, giving the μ-vinyl species $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5Me_5)_2][BF_4]$ in high yield. The μ-vinyl cation reacts readily with nucleophiles, giving, for example, $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHEt)(\eta\text{-}C_5Me_5)_2]$ with methyl-lithium, and completing an homologation of μ-CHMe. Application of this approach to the μ-CHEt complex, in turn, introduces the possibility of chain-branching in addition to linear homologation.

We have shown that diruthenium μ-alkylidene ligands may be rapidly and cleanly functionalised at both the α- and β-positions through activation by oxidation–deprotonation followed by intermolecular nucleophilic attack. The method promises to provide a general route to highly reactive cationic

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† Electrochemical studies were performed at a Pt bead electrode in dichloromethane containing 0.1 mol dm^{-3} $[Bu^n{}_4N][PF_6]$ as supporting electrolyte. Potentials are *vs.* the saturated calomel electrode; under these conditions E° for the oxidation of ferrocene is 0.48 V.

complexes of simple hydrocarbons‡ of this and other dinuclear metal systems.

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‡ The related activation of a complex eight-carbon ligand has been reported (ref. 5).

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