

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 -CH₂ is converted to μ -CH⁺ and μ -CHMe to μ -CHCH₂⁺; the mono-cationic products react with nucleophiles to produce derivatives of the original μ -alkylidene, while μ -CH⁺ yields μ -CH₃⁺ readily under pressure of hydrogen.

In a recent communication we described the slow, low yield formation of the cation [Ru₂(μ -CH)(μ -CO)(μ -dppm)(η -C₅H₅)₂]⁺ (**3**) [dppm = bis(diphenylphosphino)methane] from [Ru₂(μ -CH₃)(μ -CO)(μ -dppm)(η -C₅H₅)₂]⁺ (**5**) in solution.¹ As a result of efforts to clarify this intriguing μ -CH₃ 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 following² communication.

A possible first step in the conversion of μ -CH₃ 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 fission³), generating a radical cation

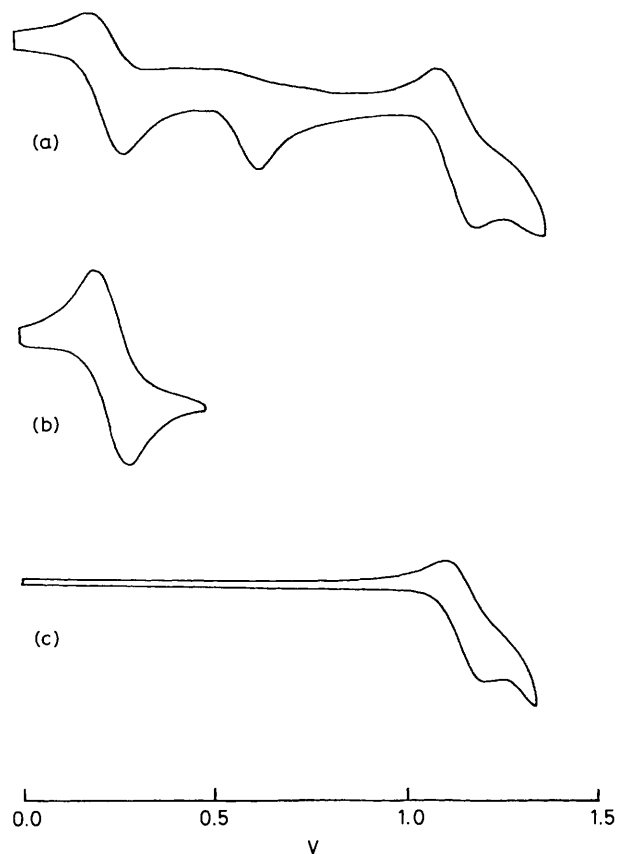
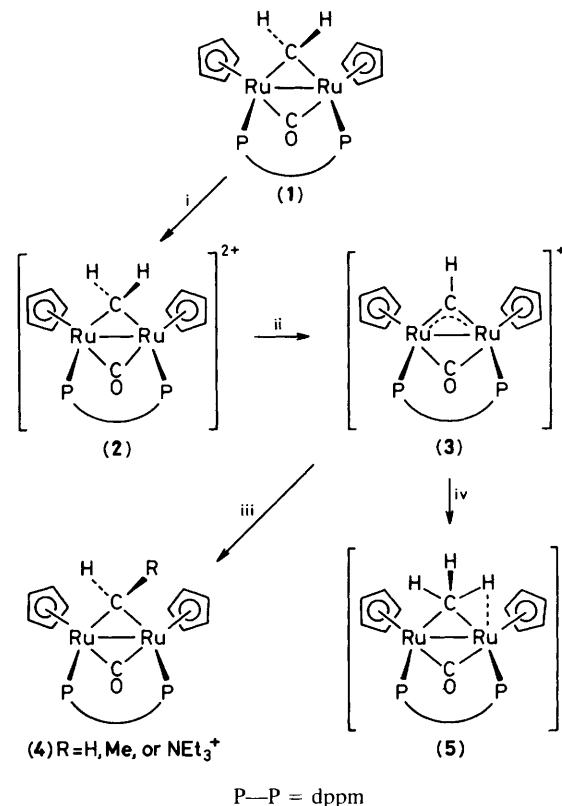


Figure 1. Cyclic voltammograms of (1) (a and b) and (3) (c).

$[\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2]^+$. The additional possibility that the latter could be obtained in high yield by oxidation of $[\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2]^1$ (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 ($E^\circ = 0.24$ V) is diffusion-controlled and fully reversible (Figure 1b), and corresponds to the formation of the radical cation $[\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2]^+$; the second is irreversible with a peak potential, $E_{\text{ox.}}$, of 0.65 V at a scan rate of 200 mV s^{-1} . Our suspicion that the third, reversible wave ($E^\circ = 1.16$ V) was due to the one-electron oxidation of (3), formed via an EEC (electrochemical–electrochemical–chemical) mechanism in which the dication $[\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2]^{2+}$ (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 $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ 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 $E^\circ = 1.16$ 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

† Electrochemical studies were performed at a Pt bead electrode in dichloromethane containing $0.1 \text{ mol dm}^{-3} [\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte. Potentials are vs. the saturated calomel electrode; under these conditions E° for the oxidation of ferrocene is 0.48 V.



Scheme 1. Reagents: i, $2[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{PF}_6]$, CH_2Cl_2 ; ii, 2,6-dimethylpyridine, $^- \text{H}^+$; iii, NaBH_4 , MeLi, or NEt_3 ; iv, H_2 (150 atm), 100°C , 16 h.

complexes (4), the sequence (1) \rightarrow (2) \rightarrow (3) \rightarrow (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 original¹ synthesis of (3) from (5) involves concerted elimination of H_2 . The hydrogenation of $\mu\text{-CH}$ to give $\mu\text{-CH}_3$ may play an important role in catalytic CO hydrogenation.

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 $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHMe})(\eta\text{-C}_5\text{Me}_5)_2]$ 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 $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHCH}_2)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$ in high yield. The μ -vinyl cation reacts readily with nucleophiles, giving, for example, $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHEt})(\eta\text{-C}_5\text{Me}_5)_2]$ with methyl-lithium, and completing an homologation of $\mu\text{-CHMe}$. Application of this approach to the $\mu\text{-CHEt}$ 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

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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