

## Facile $\delta$ -Hydrogen Abstraction from a Ruthenium Complex; Possible 1—4 $\eta$ -Bonding of the *o*-Xylylene Ligand

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**Summary** Reaction of  $\text{RuCl}_2\text{L}_4$  ( $\text{L} = \text{PMe}_2\text{Ph}$  or  $\text{PMePh}_2$ ) with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$  in diethyl ether at room temperature leads to  $\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3$ , whose spectroscopic and chemical characteristics suggest a possible 1—4 $\eta$ -bonding of the *o*-xylylene ligand.

ALKYL complexes of transition metals decompose either *via* reductive elimination or by hydrogen abstraction giving an alkane. We have recently reported<sup>1</sup> a rare example in which hydrogen abstraction occurs from a  $\delta$ -carbon atom; the platinum-containing product contains a 2,3-benzoplatinacyclopentene ring, and very forcing conditions (refluxing xylene; 16 h) were required to effect the transformation. We now report that a similar reaction occurs for ruthenium but that the  $\delta$ -hydrogen abstraction is so facile that even at room temperature we have been unable to isolate the presumed dialkyl intermediate.

A similar marked difference in reactivity between ruthenium<sup>2</sup> and platinum<sup>3</sup> has been observed in the formation of analogous metallacyclobutane complexes from neopentyl derivatives.

Reaction of  $\text{RuCl}_2\text{L}_4$  ( $\text{L} = \text{PMe}_2\text{Ph}$  or  $\text{PMePh}_2$ ), obtained by metathetical exchange of L with  $\text{RuCl}_2(\text{PPh}_3)_3$  in hexane

at room temperature,<sup>4</sup> with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$  in ether at room temperature affords yellow solutions from which crystals of  $\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3^\dagger$  ( $\text{L} = \text{PMe}_2\text{Ph}$ , yellow;  $\text{L} = \text{PMePh}_2$ , orange) may be isolated. The mass spectra of these complexes show parent ions at 620 and 806 a.m.u. (based on  $^{102}\text{Ru}$ ), respectively, together with fragmentation patterns showing loss of the phosphine groups and of the  $\text{C}_8\text{H}_8$  moiety.

From the  $^1\text{H}$  n.m.r. spectra of  $\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3$  it is clear that the methyl groups on  $\text{P}_A$  are diastereotopic and give rise to two doublets at  $\delta$  1.21 and 1.29 ( $J_{\text{PH}} + J_{\text{PH}} = 5$  Hz), whilst those on  $\text{P}_B$  give a doublet at  $\delta$  1.73 ( $J_{\text{PH}} = 7$  Hz). The methylene groups give two doublets of doublets at  $\delta - 0.16$  ( $J_{\text{PH}} = 8$  Hz) and 1.9 ( $J_{\text{PH}} = 6$  Hz). Decoupling studies show that the two methylene groups are chemically equivalent but that the lack of a plane of symmetry coincident with the plane of the ring causes the two hydrogen atoms on each methylene group to be non-equivalent; thus  $J_{\text{HH}} = 4$  Hz. The  $^1\text{H}$  n.m.r. spectrum of  $\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMePh}_2)_3$  is qualitatively similar except that only two signals are observed from the phosphine methyl groups:  $\delta$  2.22 (d,  $J_{\text{PH}} = 6$  Hz) and 1.7 (d, with some

<sup>†</sup> Satisfactory analyses have been obtained for both complexes.

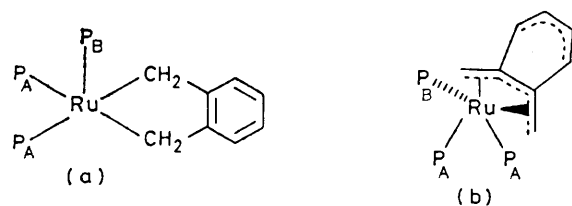


FIGURE 1. Possible structures of  $\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3$ .

intensity between the lines). The methylene groups again give rise to two doublets of doublets,  $\delta$  0.63 ( $J_{\text{PH}} = 8$  Hz) and 1.99 ( $J_{\text{PH}} = 6$  Hz);  $J_{\text{HH}} = 4$  Hz.

These n.m.r. data could qualitatively be accounted for assuming a five-coordinate structure as shown in Figure 1(a). Such a five-coordinate complex should readily co-ordinate small molecules, e.g. CO, into the sixth coordination position. However, CO does not react with

$\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3$  at room temperature in the dark. Under more forcing conditions (100 °C; 100 atm) no simple addition product is obtained but mass spectral data show that substitution of one or two phosphorus atoms occurs along with the formation of  $\text{Ru}(\text{CO})_3\text{L}_2$ . In u.v. light,

$\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_2\text{CO}$  is apparently the only product.

The  $^{31}\text{P}$  n.m.r. spectrum for the complex with  $\text{L} = \text{PMe}_2\text{Ph}$  consists of two singlets of intensity ratio 1:2 at  $\delta$  25.71 ( $\text{P}_\text{B}$ ) and 5.05 ( $\text{P}_\text{A}$ ).<sup>‡</sup> The lack of P-P coupling is, at first sight, surprising since, in general, five-coordinate complexes of ruthenium(II)<sup>4</sup> or ruthenium(0)<sup>5</sup> have  $J_{\text{PP}} > 20$  Hz. The only ruthenium complexes for which  $J_{\text{PP}}$  is ca. 0 are zerovalent and contain dienes. For example,  $\text{Ru}(\text{PPh}_3)_3(\text{C}_4\text{H}_6)$  has<sup>6</sup>  $J_{\text{PP}} = 4.9$  Hz and we now believe that the  $^{31}\text{P}$  n.m.r. spectra of  $\text{Ru}(\text{styrene})(\text{PPh}_3)_2(\text{C}_4\text{H}_5\text{R})$  ( $\text{R} = \text{H}$  or  $\text{Et}$ ) are best interpreted as arising from a single isomer with non-equivalent phosphorus atoms and  $J_{\text{PP}} = 0$  rather than, as one of us has previously suggested,<sup>7</sup> from different isomers each with equivalent phosphorus atoms.

<sup>‡</sup>  $^{31}\text{P}$  Chemical shifts are in p.p.m. to high frequency of external 85%  $\text{H}_3\text{PO}_4$ .

<sup>§</sup> This high-field shift could also arise from interaction with phenyl rings on  $\text{P}_\text{B}$ .

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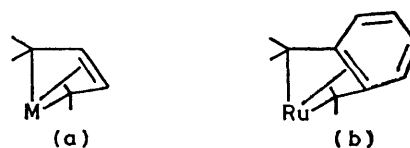


FIGURE 2. (a) Extreme resonance hybrid for co-ordinated butadiene. (b) Possible similar bonding of the *o*-xylylene ligand.

An extreme resonance hybrid for co-ordinated buta-1,3-diene is shown in Figure 2(a) and it is conceivable that a similar mode of bonding could exist [Figure 2(b)] for the *o*-xylylene ligand. In its delocalised form, this would give the structure shown in Figure 1(b) for the

$\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3$  complexes making them isoelectronic with  $\text{Ru}(\text{butadiene})(\text{PPh}_3)_3$ , and rationalising the zero value of  $J(\text{P}_\text{A}\text{P}_\text{B})$ .

Further evidence that supports the 18-electron formulation [Figure 1(b)] is the following: (i) the observed lack of formation of simple addition products with CO; (ii) the yellow colour of the complexes, which is generally associated with 18-electron complexes of ruthenium(-II) or -(0);<sup>7,8</sup> (iii) the high-field shift<sup>§</sup> of one of the sets of protons of the methylene groups in each complex, which is similar to that found<sup>6</sup> for the endo-methylene protons of co-ordinated butadiene in  $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$ . Although confirmation of this unusual<sup>1,9,10</sup> bonding mode for the *o*-xylylene ligand awaits crystallographic studies, a similar bonding mode has been observed for  $\text{Fe}(\text{C}_8\text{H}_8)(\text{CO})_2\text{L}$  ( $\text{L} = \text{PPh}_3$ <sup>11</sup> or  $\text{CO}$ <sup>12</sup>).

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