

## Loss of Pentamethylcyclopentadiene from Pentamethylcyclopentadienylrhodium Hydride Complexes

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Pentamethylcyclopentadienylrhodium hydride complexes eliminate pentamethylcyclopentadiene on reaction with trimethylphosphine.

A most useful feature of the pentamethylcyclopentadienylrhodium complexes is the inertness of the ring to metal bond. This has allowed the development of an extensive stoichiometric and catalytic chemistry involving the other co-ordination sites on the metal, but where the ring stays intact.<sup>1</sup> Indirect evidence has indicated that this inertness is only relative and that the ring is sometimes lost.<sup>2</sup> We here report two stoichiometric reactions where this occurs under quite mild conditions, when hydride as a co-ligand is present on the metal.

The n.m.r. spectra of a C<sub>6</sub>D<sub>6</sub> solution containing [(C<sub>5</sub>Me<sub>5</sub>)RhH<sub>3</sub>(SiEt<sub>3</sub>)] (**1**)<sup>3</sup> and one equivalent of PMe<sub>3</sub> showed (0.5 h, 25 °C) the presence of only starting material and [HRh(PMe<sub>3</sub>)<sub>4</sub>]<sup>4</sup> (**2**) {<sup>1</sup>H n.m.r., δ 1.29 (s, Me), -12.33 [H, dquin, *J*(H-P) = *J*(Rh-H) = 14 Hz]; <sup>31</sup>P{(C<sup>1</sup>H<sub>3</sub>)<sub>3</sub>} n.m.r. δ -19.5 dd; *J*(Rh-H) = 146, *J*(P-H) 14 Hz}. On addition of a 10-fold excess of PMe<sub>3</sub>, (**1**) was completely converted into (**2**); the other products were C<sub>5</sub>Me<sub>5</sub>H and Et<sub>3</sub>SiH, identified by comparison of their <sup>13</sup>C and <sup>1</sup>H n.m.r. spectra with those of authentic specimens.

When the reaction was repeated at lower temperature

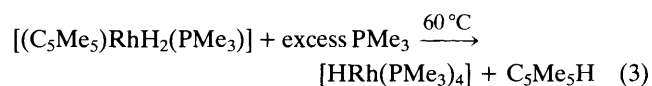
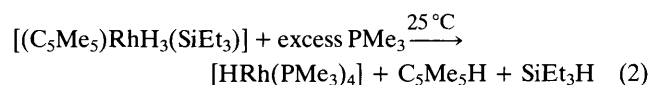
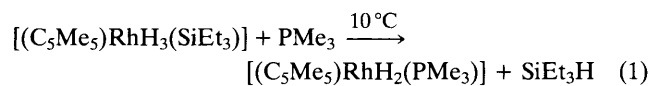
(10 °C) with a 1 : 1.8 molar ratio of PMe<sub>3</sub> to [(C<sub>5</sub>Me<sub>5</sub>)RhH<sub>3</sub>(SiEt<sub>3</sub>)] (**1**), the <sup>1</sup>H n.m.r. spectrum showed the presence of (**1**) and [(C<sub>5</sub>Me<sub>5</sub>)RhH<sub>2</sub>(PMe<sub>3</sub>)] (**3**),<sup>5</sup> in the ratio of 43 : 57. When excess of PMe<sub>3</sub> was then added at 25 °C, the remaining [(C<sub>5</sub>Me<sub>5</sub>)RhH<sub>3</sub>(SiEt<sub>3</sub>)] was converted directly into [HRh(PMe<sub>3</sub>)<sub>4</sub>]. This mixture did not change its composition further on standing at 25 °C.

One interpretation of these data is that (**1**) reacts with PMe<sub>3</sub> via an η<sup>1</sup>-intermediate such as [(η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub>)RhH<sub>3</sub>(SiEt<sub>3</sub>)(PMe<sub>3</sub>)<sub>x</sub>]<sup>6</sup> which, at lower temperature reductively eliminates SiHEt<sub>3</sub> to give (**3**), or at rather higher temperatures reacts further with PMe<sub>3</sub> via [(η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub>)RhH<sub>3</sub>(SiEt<sub>3</sub>)(PMe<sub>3</sub>)<sub>x</sub>] (*x* = 2, 3) to yield (**2**), C<sub>5</sub>Me<sub>5</sub>H, and SiHEt<sub>3</sub>.

However even [(C<sub>5</sub>Me<sub>5</sub>)RhH<sub>2</sub>(PMe<sub>3</sub>)] (**3**) lost the ring at 60 °C (C<sub>6</sub>D<sub>6</sub> solution) when reacted with excess of PMe<sub>3</sub> (1 : 10; 45% conversion after 5 h, 70% after 9 h), to give a solution which was shown by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P n.m.r. spectroscopy to contain only [HRh(PMe<sub>3</sub>)<sub>4</sub>] (**2**), C<sub>5</sub>Me<sub>5</sub>H, and excess of PMe<sub>3</sub>.

The reactions may be summarised as in equations (1)–(3).

By contrast, [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> reacted stepwise with three



equivalents of  $PMe_3$  to displace the three chlorines on each rhodium, giving, successively,  $[(C_5Me_5)RhCl_2(PMe_2)]$ ,  $[(C_5Me_5)RhCl(PMe_3)_2]Cl$ , and  $[(C_5Me_5)Rh(PMe_3)_3]Cl_2$ , but there was no further reaction, even with an excess of  $PMe_3$  at  $60^\circ C$ .

The ease of ring displacement is related to the stability of the leaving group. Thus pentamethylcyclopentadiene can be eliminated when the rhodium bears a hydride, whereas the driving force for the formation of the presumably very unstable  $C_5Me_5Cl$ , the corresponding product from  $[(C_5Me_5)RhCl_2]_2$ , would be expected to be much less.

We draw attention to these results since they illustrate that in some circumstances, and under mild conditions, the  $C_5Me_5$  ring on rhodium is not just an innocent spectator ligand. Loss of  $C_5H_6$  has also been reported to occur when  $[(C_5H_5)ReH(CO)(NO)]$  was heated with  $PMe_3$  ( $80^\circ C$ ).<sup>7</sup> Loss of  $[C_5H_5PMe_3]I$  also occurs from  $[(C_5H_5)M(NO)_2]_2$ <sup>8</sup> ( $M = Mo, W$ ), on reaction with  $PMe_3$ , but this does not appear to have been observed with  $C_5Me_5$ -complexes yet.

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