

### Preliminary communication

## THE PREPARATION AND SOME REACTIONS OF CHLORO( $\eta^4$ -CYCLOOCTA-1,5-DIENE)( $\eta^5$ -CYCLOPENTADIENYL)- RUTHENIUM(II): A VERSATILE, NEW SYNTHETIC PRECURSOR FOR CYCLOPENTADIENYL RUTHENIUM(II) CHEMISTRY

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### Summary

Facile substitution of the cyclooctadiene and/or chloro ligands in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}]$  ( $\text{C}_8\text{H}_{12}$  = cycloocta-1,5-diene) under mild reaction conditions provides high yield synthetic routes to a range of new neutral and cationic cyclopentadienylruthenium(II) complexes.

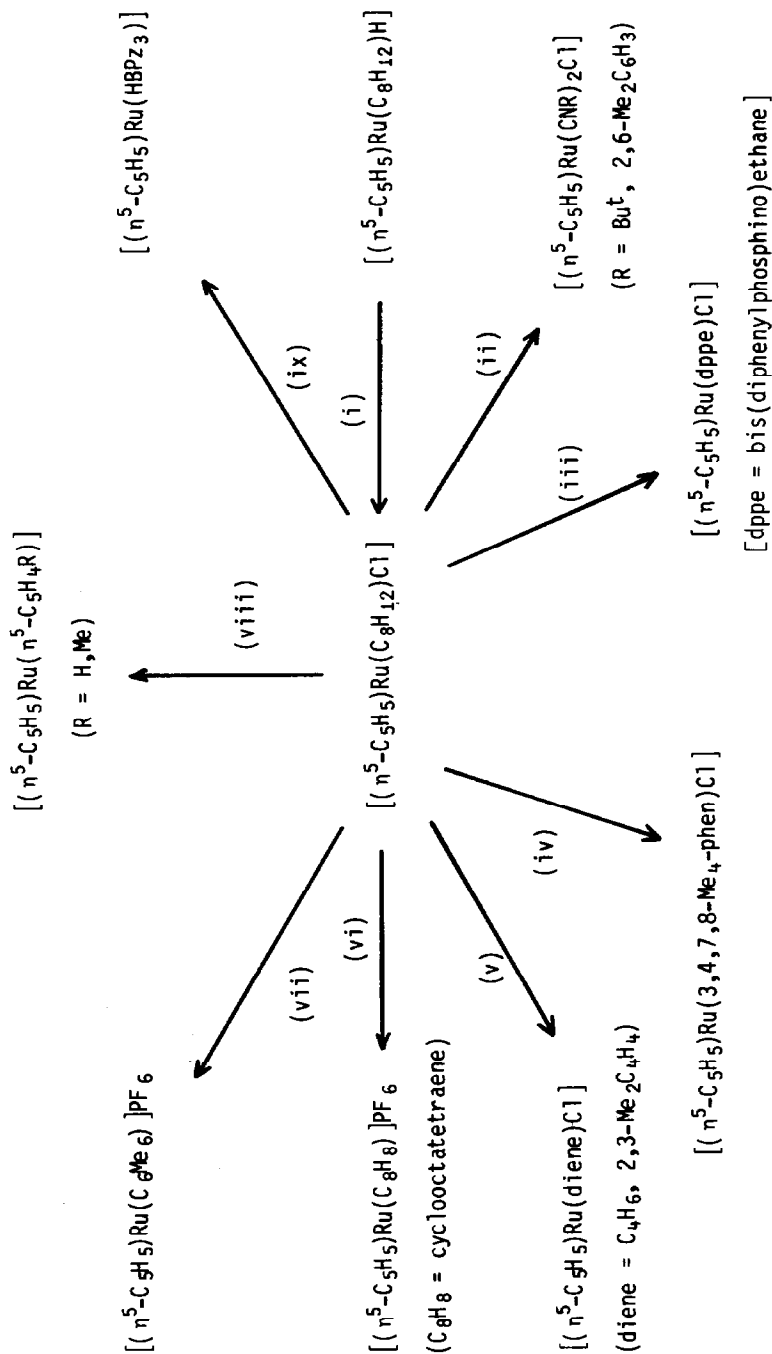
Traditional routes to cyclopentadienylruthenium(II) complexes have relied upon the complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  ( $\text{L} = \text{CO}, \text{PPh}_3$ ) as synthetic precursors, and although numerous reports have appeared on the chemistry of these complexes, the reactions in general require forcing conditions and give low yields of products [1]. We have recently developed synthetic routes to a range of reactive mononuclear and dinuclear cyclopentadienyl derivatives of ruthenium and osmium, and we now describe the preparation of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}]$  (1:  $\text{C}_8\text{H}_{12}$  = cycloocta-1,5-diene) and its use as a precursor for a wide range of cyclopentadienylruthenium(II) complexes\*\*.

Complex 1 is prepared in quantitative yield as golden-yellow crystals by stirring the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{H}]$  [2] in a  $\text{CCl}_4$ /pentane mixture for 5 min at room temperature. Complex 1 has been completely characterized by  $^1\text{H}$  NMR and elemental analysis\*\*\*. It is air-stable and reacts in most solvents in air with no significant decomposition.

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\*\*The complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}]$  has recently been reported by Suzuki and co-workers (N. Oshima, H. Suzuki and Y. Moro-oka, *Chem. Lett.*, (1984) 1161).

\*\*\* $^1\text{H}$  NMR spectroscopic data for all new compounds are given in Table 1. Satisfactory elemental analyses have been obtained for all compounds.



SCHEME 1. Synthesis and selected reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}]$  (1). (i)  $\text{CCl}_4$ , 5 min,  $20^\circ\text{C}$ , pentane, quantitative yield; (ii) RNC (R =  $\text{Bu}^t$ , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ ), 8 h,  $30^\circ\text{C}$ , acetone, yield 85–90%; (iii) dppe, 8 h,  $30^\circ\text{C}$ , acetone, yield 81%; (iv) 3,4,7,8-tetramethyl-1,10-phenanthroline, 8 h,  $30^\circ\text{C}$ , acetone, yield 84%; (v) diene ( $\text{C}_4\text{H}_6$ , 2,3- $\text{Me}_2\text{C}_4\text{H}_4$ ), 20 min, ethanol reflux, yield 80–90%; (vi) cyclooctatetraene,  $\text{NH}_4\text{PF}_6$ , 20 min, ethanol reflux, yield 89%; (vii)  $\text{C}_6\text{Me}_6$ ,  $\text{NH}_4\text{PF}_6$ , 15 min, ethanol reflux, yield 81%; (viii)  $\text{NaC}_5\text{H}_4\text{R}$  (R = H, Me), 12 h,  $25^\circ\text{C}$ , THF, yield 70–75%; (ix)  $\text{NaHBPz}_3$ , 5 min, methanol reflux, yield 83%.

The cyclooctadiene and chloro ligands in **1** are highly labile in acetone or ethanol solution, giving a range of neutral or cationic products by substitution with suitable donor ligands (Scheme 1).

Stoichiometric additions of strong  $\sigma$ -donor ligands to **1** in acetone at 30°C give the neutral substitution products  $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  (**2**: L = RNC, R = Bu<sup>t</sup>, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; L<sub>2</sub> = 1,2-bis(diphenylphosphino)ethane, 3,4,7,8-tetramethyl-1,10-phenanthroline) in yields in excess of 80%. The complexes **2** (L = RNC) are isolated as yellow, crystalline air- and light-stable solids, conflicting with an earlier report [3] which described **2** (L = Bu<sup>t</sup>NC) as a white, unstable solid. These reactions serve to illustrate the synthetic utility of **1**, but the high lability of the cyclooctadiene ligand is best illustrated by its facile displacement by buta-1,3-diene and butadiene derivatives. Thus, treatment of **1** in boiling ethanol solution with excess diene for ten minutes gives quantitative yields of the complexes **2** (L<sub>2</sub> = buta-1,3-diene, 2,3-dimethyl-1,3-butadiene) as air-stable, yellow crystalline solids.

In contrast, however, cyclic polyolefins react with **1** in boiling ethanol to displace both the cyclooctadiene and chloro ligands, giving cationic cyclopentadienylruthenium complexes containing triolefin ligands. Thus, cyclooctatetraene reacts with **1** under these conditions, giving within 5 min, and after addition of NH<sub>4</sub>PF<sub>6</sub>, the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_8)]\text{PF}_6$  (**3**) in 89% yield. Surprisingly, no fluxionality of the C<sub>8</sub>H<sub>8</sub> ring [4] is observed in the <sup>1</sup>H NMR spectrum at room temperature of this salt, and a complete assignment of the ring protons is possible (Table 1). Similarly, **1** reacts readily with arenes (irrespective of the degree of substitution on the arene ring) to give cyclopentadienylareneruthenium cations [5] in high yields. For example, heating of **1** with hexamethylbenzene in ethanol rapidly gives a pale yellow solution, from which the salt  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{Me}_6)]\text{PF}_6$ , (**4**) [6] separates in 81% yield upon addition of NH<sub>4</sub>PF<sub>6</sub>.

Finally, **1** also provides a convenient route to ruthenocene and mixed ruthenocene derivatives. Thus, treatment of **1** with sodium cyclopentadienyl,

TABLE 1

<sup>1</sup>H NMR DATA FOR THE NEW CYCLOPENTADIENYL RUTHENIUM(II) COMPLEXES

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}]^a$	5.32(m,2H,CH), 4.95(s,5H,C <sub>5</sub> H <sub>5</sub> ), 4.40(m,2H,CH), 2.62(m,2H,CH <sub>2</sub> ), 2.03(m,6H,CH <sub>2</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CNBu}^t)_2\text{Cl}]^b$	4.76(s,5H,C <sub>5</sub> H <sub>5</sub> ), 1.48(s,18H,CH <sub>3</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})_2\text{Cl}]^b$	7.18(s,6H,CH), 5.16(s,5H,C <sub>5</sub> H <sub>5</sub> ), 2.42(s,12H,CH <sub>3</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(3,4,7,8\text{-Me}_4\text{-1,10-phen})\text{Cl}]^a$	8.14(s,2H,CH), 7.22(s,2H,CH), 4.31(s,5H,C <sub>5</sub> H <sub>5</sub> ), 2.80(s,6H,CH <sub>3</sub> ), 2.69(s,6H,CH <sub>3</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_4\text{H}_6)\text{Cl}]^{a,c}$	5.38(m,2H,CH <sub>2</sub> ), 4.95(s,5H,C <sub>5</sub> H <sub>5</sub> ), 4.08(m,2H,CH <sub>b</sub> ), 1.35(m,2H,CH <sub>c</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(2,3\text{-Me}_2\text{C}_4\text{H}_4)\text{Cl}]^{a,d}$	4.85(s,5H,C <sub>5</sub> H <sub>5</sub> ), 4.05(d,2H,CH <sub>a</sub> ), 2.10(s,6H,CH <sub>3</sub> ), 1.22(d,2H,CH <sub>b</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_5)]\text{PF}_6^{b,e}$	6.92(m,2H,CH <sub>a</sub> ), 6.04(m,2H,CH <sub>b</sub> ), 5.95(m,2H,CH <sub>c</sub> ), 5.69(s,5H,C <sub>5</sub> H <sub>5</sub> ), 5.11(m,2H,CH <sub>d</sub> )
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{HBPz}_2)]^{a,f}$	8.00(d,3H,CH <sub>a</sub> ), 7.54(d,3H,CH <sub>b</sub> ), 6.12(m,3H,CH <sub>c</sub> ), 4.23(s,5H,C <sub>5</sub> H <sub>5</sub> )

<sup>a</sup> Recorded in CDCl<sub>3</sub>. <sup>b</sup> Recorded in acetone-d<sub>6</sub>. <sup>c</sup> J<sub>a,b</sub> 8.5 Hz, J<sub>b,c</sub> 1.7 Hz, J<sub>a,c</sub> 10.1 Hz. <sup>d</sup> J<sub>a,b</sub> 2.8 Hz.

<sup>e</sup> J<sub>a,b</sub> 4.5 Hz, J<sub>a,b'</sub> 2.3 Hz, J<sub>b,c</sub> 8.4 Hz, J<sub>c,d</sub> 2.3 Hz, J<sub>c,d'</sub> 1.4 Hz. <sup>f</sup> J<sub>a,c</sub> 2.2 Hz, J<sub>b,c</sub> 2.2 Hz.

sodium methylcyclopentadienyl or sodium hydrotris(1-pyrazolyl)borate ( $\text{NaHBPz}_3$ ) [7] gives high yields of the metallocenes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R})]$  ( $\text{R} = \text{H, Me}$ ) [1] and the formal analogue,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{HBPz}_3)]$ .

In conclusion, the ease of synthesis of 1 and its high lability provides a synthetic route to cyclopentadienylruthenium(II) complexes which is exceptional in terms of its versatility and simplicity.

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