

## Octadienediyl Dichlorides of Ruthenium(IV) as Synthetic Reagents in Organoruthenium Chemistry; Isolation of a Protonated 'Open Metallocene' $[\text{Ru}(\eta^5\text{-C}_7\text{H}_{11})_2\text{H}][\text{BF}_4]$

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Chloride extraction from  $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2]_2$  or  $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{L}]$  [ $\text{L} = \text{P}(\text{OMe})_3$  or  $\text{Bu}^t\text{NC}$ ], in the presence of diolefins, results in labilisation of the 2,7-dimethyloctadienediyl ligand and provides syntheses of some new organoruthenium complexes, including the protonated 'open metallocene'  $[\text{Ru}(\eta^5\text{-C}_7\text{H}_{11})_2\text{H}][\text{BF}_4]$ .

An established synthesis of ruthenium complexes containing two polyolefinic ligands is the reduction of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  by zinc dust in the presence of a diolefin.<sup>1</sup> An alternative synthesis, under non-reducing conditions, could be developed from the direct interaction of very labile  $\text{Ru}^{2+}$  ions with diolefins. Indeed, a recent report of the reactivity of the  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  cation confirms the potential of this method.<sup>2</sup>

We have now found that treatment of  $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2]_2$  (**1**) or the adducts  $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{L}]$  [**(2a)**;  $\text{L} = \text{P}(\text{OMe})_3$ , **(2b)**;  $\text{L} = \text{Bu}^t\text{NC}$ ] with  $\text{AgBF}_4$  in ethanol effectively delivers  $\text{Ru}^{2+}$  or  $[\text{RuL}]^{2+}$  ions, respectively, for *in situ* reaction with diolefins. The facile preparation of (**1**) (from  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and isoprene; yield 75%) and the range of available adducts<sup>3</sup> makes this a synthetically attractive route to polyolefinic ruthenium complexes.

Selected syntheses of previously unreported organoruth-

enium cations are illustrated in Scheme 1. The cations (3)—(6)<sup>+</sup> were all isolated as [BF<sub>4</sub>]<sup>−</sup> salts and satisfactory yields (60–80%) were obtained. The known compounds Ru(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and [Ru(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>)] [BF<sub>4</sub>], however, were only isolated in moderate yields (34 and 20% respectively) on similar treatment of (1) in the presence of cyclopentadiene or cyclohexadiene, respectively.

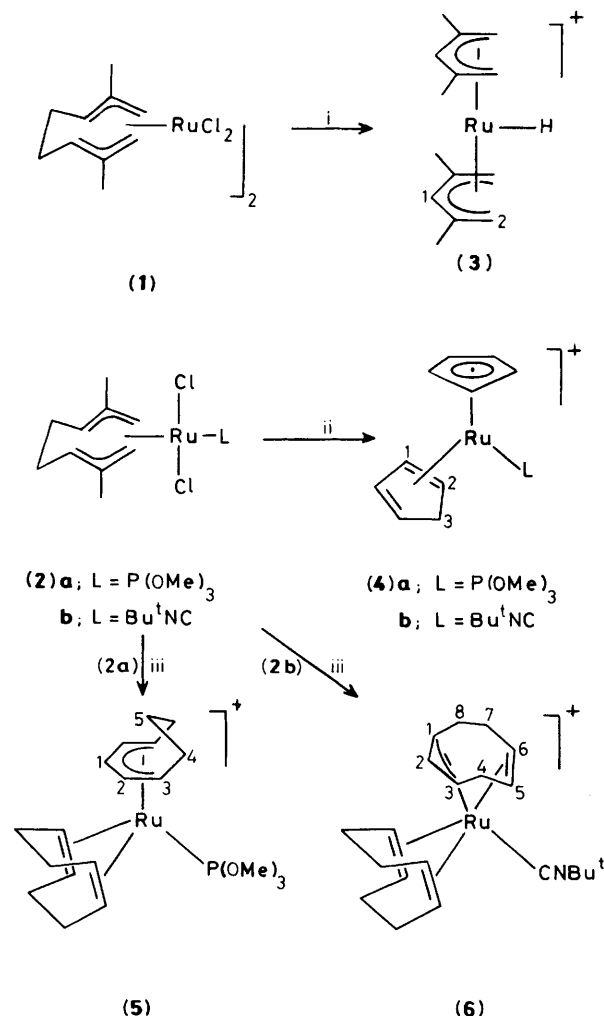
The fate of the 2,7-dimethyloctadienediyl ligand on release from the ruthenium is unknown. A possible internal cyclisation of the ligand chain, however, would account both for its lability and for the formal Ru<sup>IV</sup>/Ru<sup>II</sup> reduction. Interestingly, under favourable conditions, the chloride ligands can be removed from (1) without provoking octadienediyl lability. Hence, [Ru(η<sup>3</sup>:η<sup>3</sup>-C<sub>10</sub>H<sub>16</sub>)(MeCN)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> (7)<sup>+</sup> was isolated (78%) from the reaction of (1) and AgBF<sub>4</sub> in acetonitrile.

Solutions of the [BF<sub>4</sub>]<sup>−</sup> salt of [Ru(η<sup>5</sup>-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>H]<sup>+</sup> (3) exhibit temperature dependent <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra. The <sup>1</sup>H n.m.r. spectrum at 230 K<sup>†</sup> shows a high field resonance (δ −5.77) with additional resonances corresponding to apparently equivalent and symmetrical pentadienyl ligands. Hence, an agostic ground state of the type reported for ML<sub>3</sub>(η<sup>4</sup>-pentadiene) complexes of Cr and Mn<sup>+</sup> can be excluded.<sup>4</sup> A terminal hydride structure for (3), therefore, may be proposed and, indeed, the related cation [Ru(η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub>)<sub>2</sub>H]<sup>+</sup> has such a structure (C<sub>2</sub> symmetry).<sup>5</sup> The (non-limiting) n.m.r. spectra of (3) at 160 K, however, are not easily reconciled to such a structure. At this temperature it is clear, for example, that the central CH groups of the two pentadienyl ligands are inequivalent. This implies that the hydride ligand is no longer on (or averaged onto) the local C<sub>2</sub> axis of the open ruthenocene fragment, possibly owing to a weak [Ru–H ⋯ C] interaction with a terminal methylene group.

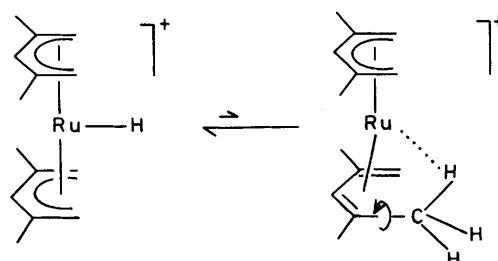
The n.m.r. spectra of (3) above 230 K show both a gradual coalescence of the resonances due to the hydride and the *endo*

and *exo* protons of the methylene groups, and a marked upfield shift of the methylene carbon atoms (Δδ −11 p.p.m. from 230 to 300 K). These changes are explained by invoking agostic intermediates and rotation of the *endo* methyl group, as shown in Scheme 2.

Preliminary studies have shown that (3) is highly reactive towards two- and six-electron ligands (*e.g.* MeCN, CO, arenes, thiophene). One molar equivalent of 2,4-dimethyl-



**Scheme 1.** Reagents and conditions: room temperature ultrasonic irradiation (50 kHz) in deoxygenated ethanol, followed by filtration (AgCl was precipitated) and low temperature crystallisation, for all reactions; (i) AgBF<sub>4</sub>, 2,4-dimethylpenta-1,3-diene, 3 h (65%); (ii) AgBF<sub>4</sub>, cyclopentadiene, 90 min (~75%); (iii) AgBF<sub>4</sub>, 1,5-COD, 90 min, (~65%).



**Scheme 2.** Proposed equilibrium for (3) in solution above 230 K.

<sup>†</sup> Satisfactory elemental analyses of the [BF<sub>4</sub>]<sup>−</sup> salts [cations (3)–(7)] and fast atom bombardment mass spectra [(3)–(6)] have been obtained.

**Selected spectroscopic data** (in CDCl<sub>3</sub>, at room temp., unless otherwise stated) for (3): <sup>1</sup>H n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>, 230 K) δ 5.54 (s, 2H, 1-H), 3.16 (br.s, 4H, *exo*-2-H), 2.02 (s, 12H, Me), 1.17 (br.s, 4H, *endo*-2-H), −5.77 (br.s, 1H, RuH); <sup>13</sup>C n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>, 230 K) δ 108 (br.), 96.5 (d), 58 (br., 2-C), 24.0 (q).

For (4a): <sup>1</sup>H n.m.r. δ 6.30 (m, 2H, 1-H), 5.24 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.38 (m, 2H, 2-H), 3.81 (d, 9H, Me), 3.38 [m, 1H, *J*(PH) 37.5 Hz, *endo*-3-H], 2.69 [m, 1H, *J*(PH) 5.5 Hz, *exo*-3-H]; (4b): ν(CN) 2167 cm<sup>−1</sup> (CHCl<sub>3</sub>); <sup>1</sup>H n.m.r. δ 6.28 (m, 2H, 1-H), 5.22 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.60 (m, 2H, 2-H), 3.34 (m, 1H *endo*-3-H), 2.56 (m, 1H, *exo*-3-H), 1.67 (s, 9H, Me).

For (5) and (6): (CH or CH<sub>2</sub> refer to protons of the 1,5-COD ligand) (5): <sup>1</sup>H n.m.r. δ 7.12 (m, 1H, 1-H), 4.66 (dd, 2H, 2-H), 4.14 (m, 2H, CH), 4.05 (d, 9H, Me), 3.72 (m, 2H, CH), 3.30 (m, 2H, 3-H), 2.49 (m, 2H, CH<sub>2</sub>), 2.39 (m, 2H, CH<sub>2</sub>), 2.09 (d, 2H, CH<sub>2</sub>), 1.92 (d, 2H, CH<sub>2</sub>), 1.80 (m, 2H, 4-H<sub>a</sub>), 1.64 (m, 2H, 4-H<sub>b</sub>), 1.18 (m, 1H, *exo*-5-H), 0.31 (qt, 1H, *endo*-5-H); <sup>13</sup>C n.m.r. δ 104.0 [dd, *J*(PC) 12 Hz, 1-C], 97.5 (d), 97.5 (d), 85.5 (d), 63.4 (d), 55.1 (q), 31.9 (t), 30.0 (t), 25.1 (t), 18.5 (t). (6): ν(CN) 2158 cm<sup>−1</sup> (CHCl<sub>3</sub>); <sup>1</sup>H n.m.r. δ 5.30 (m, 1H, CH), 4.77 (m, 1H, 3-H), 4.62 (m, 1H, 6-H), 4.38 (dd, 1H, 2-H), 4.12 (m, 1H, CH), 3.89 (m, 1H, 1-H), 3.39 (m, 1H, CH), 3.34 (m, 1H, 4-H<sub>a</sub>), 3.29 (m, 1H, CH), 2.91 (m, 1H, 4-H<sub>b</sub>), 2.81 (m, 1H, CH<sub>2</sub>), 2.62 (dd, 1H, CH<sub>2</sub>), 2.47 (m, 1H, 8-H<sub>a</sub>), 2.34 (m, 5H, 4 × CH<sub>2</sub> and 7-H<sub>a</sub>), 2.17 (m, 1H, 8-H<sub>b</sub>), 1.87 (m, 2H, 5-H and 7-H<sub>b</sub>), 1.79 (m, 1H, CH<sub>2</sub>), 1.77 (s, 9H, Me), 1.67 (m, 1H, CH<sub>2</sub>); <sup>13</sup>C n.m.r. δ 152.0 (CNBu<sup>t</sup>), 105.3 (d), 103.3 (d), 94.3 (d), 93.5 (d), 82.6 (d), 80.3 (d), 67.0 (d), 59.6 (s), 57.5 (d), 47.7 (d), 32.8 (t), 32.6 (t), 32.4 (t), 30.6 (q), 28.9 (t), 27.4 (t), 26.8 (t), 21.2 (t).

For (7): <sup>1</sup>H n.m.r. (CD<sub>3</sub>CN) δ 5.09 and 4.02 (2s, 4H, terminal CH<sub>2</sub>), 5.02 (m, 2H, CH), 3.36 and 2.65 (2m, 4H, central CH<sub>2</sub>), 2.55 [s, 3H, MeCN(eq.)], 2.37 [s, 6H, MeCN(ax.)], 2.36 (s, 6H, Me).

penta-1,3-diene is formed, and the reactions provide a convenient entry into monopentadienyl ruthenium chemistry. Further details will be presented in a future publication.

The proposed structures of the cations  $[\text{Ru}(\eta^5\text{-C}_8\text{H}_{11})(1,5\text{-COD})\text{P}(\text{OMe})_3]^+$  (COD = cyclo-octadiene) (**5**) and  $[\text{Ru}(\eta^2:\eta^3\text{-C}_8\text{H}_{11})(1,5\text{-COD})\text{Bu}^t\text{NC}]^+$  (**6**) were derived from their  $^1\text{H}$ ,  $^{13}\text{C}$ , and 2-D  $^1\text{H}$ - $^1\text{H}$  COSY n.m.r. spectra. In the  $^1\text{H}$  n.m.r. spectra of (**5**), the presence of an apparent quartet of triplets at high field ( $\delta$  0.31; *endo* proton on C-5 as labelled in Scheme 1) provides strong support for the presence of an  $\eta^5\text{-C}_8\text{H}_{11}$  ligand in this complex.<sup>6</sup> For cation (**6**), however, there is no corresponding signal in the  $^1\text{H}$  n.m.r. spectra, and furthermore, the  $^{13}\text{C}$  n.m.r. spectra show the inequivalence of all sixteen ring carbon atoms. The contrast of  $\eta^5$  co-ordination of the  $\text{C}_8\text{H}_{11}$  ligand in (**5**) with  $\eta^2:\eta^3$  co-ordination in (**6**) has a precedent in the  $[\text{Ru}(\text{C}_8\text{H}_{11})\text{L}_3]^+$  series of cations, recently reported by Ashworth *et al.*<sup>7</sup> For  $\text{L} = \text{P}(\text{OMe})_3$  only the  $\eta^5$  co-ordination, and for  $\text{L} = \text{Bu}^t\text{NC}$  only the  $\eta^2:\eta^3$  co-ordination, have yet been observed.

The synthetic utility of the octadienediyl dichlorides (**1**) and (**2**) is further illustrated by the synthesis of the cations  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)\text{P}(\text{OMe})_3]^+$  (**4a**) and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)\text{Bu}^t\text{NC}]^+$  (**4b**). Although some related cations  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-1,3-diene})\text{L}]^+$  have previously been reported, all feature  $\text{L} = \text{CO}$ .<sup>8</sup>

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## References

- 1 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.
- 2 M. Stebler-Röthlisberger, A. Salzer, H. B. Bürgi, and A. Ludi, *Organometallics*, 1986, **5**, 298.
- 3 L. Porri, M. C. Gallazzi, A. Colombo, and G. Allegra, *Tetrahedron Lett.*, 1965, 4187; R. A. Head, J. F. Nixon, J. R. Swain, and C. M. Woodard, *J. Organomet. Chem.*, 1974, **76**, 393.
- 4 G. Michael, J. Kaub, and C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 502; J. R. Bleeker, J. J. Kotyk, D. A. Moore, and D. J. Rauscher, *J. Am. Chem. Soc.*, 1987, **109**, 417.
- 5 F. Bouachir, B. Chaudret, F. Dahan, and I. Tkatchenko, *Nouv. J. Chim.*, 1987, **11**, 527.
- 6 K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, and H. Nishiyama, *J. Organomet. Chem.*, 1984, **272**, 179.
- 7 T. V. Ashworth, A. A. Chalmers, D. C. Liles, E. Meintjies, and E. Singleton, *Organometallics*, 1987, **6**, 1543.
- 8 M. Crocker, M. Green, C. E. Morton, K. R. Nagle, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1985, 2145.