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NEW HIGH YIELD SYNTHESES OF RUTHENOCENE AND OSMOCENE AND THEIR DECAMETHYL DERIVATIVES. THE CRYSTAL STRUCTURE OF $[Ru(\eta^5\text{-}C_5Me_5)_2]$

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Summary

Reaction of $[\{MCl_2(cod)\}_x]$ ($x > 2$; cod = cycloocta-1,5-diene) with $SnBu_3(C_5R_5)$ (R = H, Me) gives $[M(\eta^5\text{-}C_5R_5)_2]$ (M = Ru, R = H, Me; M = Os, R = H) and $[Os(\eta^5\text{-}C_5Me_5)H(cod)]$. Decamethylosmocene, $[Os(\eta^5\text{-}C_5Me_5)_2]$, has been prepared from $Na_2[OsCl_6]$ and pentamethylcyclopentadiene. The crystal structure of $[Ru(\eta^5\text{-}C_5Me_5)_2]$ has been determined.

Although the chemistry of ferrocene has developed rapidly since its discovery in 1951, that of ruthenocene has received little attention [1], and the chemistry of osmocene remains virtually unexplored [2]. This can largely be attributed to the lack of suitable synthetic routes that produce these metallocenes in high yields, and particularly, in substantial quantities. Current interest in the rich and varied chemistry of pentamethylcyclopentadienylrhodium [3,4] and -iridium [5—7] complexes has, however, stimulated recent investigations [8,9] into new synthetic routes to ruthenium complexes containing this ligand. In this regard we have now devised high yield synthetic routes to ruthenium and osmium metallocenes. These preparative procedures are reported here.

The polymeric material $[\{RuCl_2(cod)\}_x]$ (**1**, $x > 2$) reacts in ethanol with $SnBu^n_3(C_5R_5)$ to give $[Ru(\eta^5\text{-}C_5R_5)_2]$ (**2**, R = H, Me) in yields in excess of 70%. In a typical experiment, a suspension of **1** (5.6 g, 20 mmol) in refluxing ethanol (150 ml) containing $SnBu^n_3(C_5Me_5)$ (42.5 g, 100 mmol) gave, on cooling and reduction of the volume of the solution, white crystals of **2** (R = Me; yield 5.2 g, 70%). Because of the continuing interest in the structural

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chemistry of metallocenes and their derivatives [1,2,10] the X-ray crystal structure of 2 (R = Me) has been determined*

The complex (Fig. 1) has crystallographic mirror symmetry with an eclipsed conformation of cyclopentadienyl ligands. A similar eclipsed conformation has been observed [11] for ruthenocene itself where calculations have confirmed that this is the thermodynamically preferred orientation (by 4.66 kJ mol^{-1}) [12]. For decamethylferrocene though, a staggered conformation of the cyclopentadienyl moieties has been reported [13,14] and calculated to be 4.2 kJ mol^{-1} more stable than the eclipsed form. Unfavourable methyl—methyl interactions in decamethylferrocene are probably responsible for the adoption of the staggered conformation. However, the greater separation of the cyclopentadienyl rings in 2 (interplanar distance of 3.616(6) relative to 3.314 Å in [Fe(η^5-C$_5$Me$_5$)$_2$]) apparently accommodates the eclipsed conformation with no more significant steric interactions than in the staggered iron analogue. (Eclipsed C(Me)···C(Me) distances for 2 (R = Me) are in the

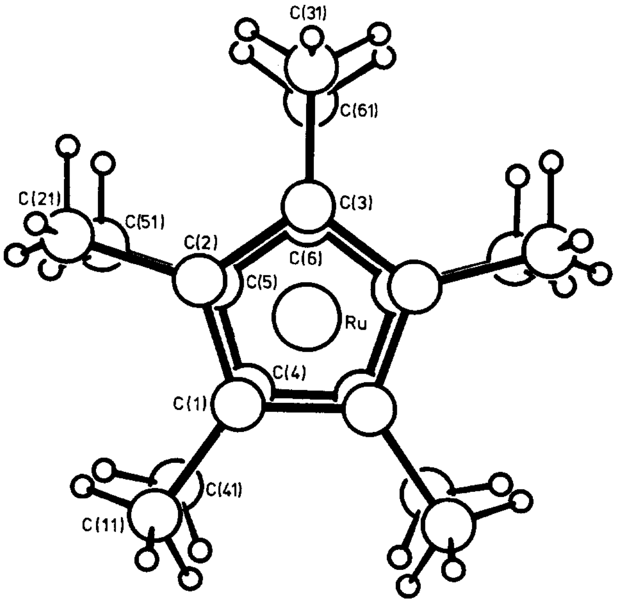

Fig. 1. A perspective view of 2 (R = Me) viewed perpendicular to the planes of the rings. Selected bond lengths (Å) and angles (°): Ru—C(1) 2.182(3), Ru—C(2) 2.175(4), Ru—C(3) 2.176(5), Ru—C(4) 2.179(3), Ru—C(5) 2.177(4), Ru—C(6) 2.158(6), C(1)—C(1′) 1.418(7), C(1)—C(2) 1.428(5), C(2)—C(3) 1.418(5), C(4)—C(4′) 1.415(7), C(4)—C(5) 1.420(5), C(5)—C(6) 1.434(5), C—C(Me) (mean) 1.501(7), C—H(mean) 0.93(9); C(1′)—C(1)—C(2) 107.9(4), C(1)—C(2)—C(3) 108.1(4), (C(2)—C(3)—C(2′) 108.1(5), C(4′)—C(4)—C(5) 108.5(4), C(4)—C(5)—C(6) 107.5(4), C(5)—C(6)—C(5′) 107.9(5), C—C—C(Me) (mean) 126.0(8).

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*Crystal data for 2 (R = Me): M = 371.53; monoclinic, space group $P2_1/m$, a 7.732(2), b 14.676(2), c 8.641(1) Å, β 106.57(2)°, U 939.8 Å^3, D_c 1.313 Mg m^{-3} for Z = 2. $F(000)$ = 388, Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 0.737 mm^{-1}. The structure was solved by heavy atom (Patterson and Fourier) methods and was refined by standard least-squares procedures [with $w = 1/\sigma^2(F_o)$]. The current residual R is 0.0517 for 2113 unique, observed [$F_o \geqslant 4\sigma(F_o)$] reflections collected at 295 K. (The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain).

range 3.750(7) to 3.767(7) Å. Staggered C(Me)···C(Me) distances for $[Fe(\eta^5\text{-}C_5Me_5)_2]$ [13] are in the range 3.79 to 3.85 Å.)

The corresponding reactions of $SnBu^n_3(C_5H_5)$ with the polymer $[\{OsCl_2(cod)\}_x]$ (3, $x > 2$) in methanol (2 h) have provided a simple, reproducible route to osmocene $[Os(\eta^5\text{-}C_5H_5)_2]$ (4) in yields typically greater than 70%. In contrast though, treatment of 3 with $SnBu^n_3(C_5Me_5)$ produced only the osmium-hydride complex $[(\eta^5\text{-}C_5Me_5)OsH(cod)]$ (5)*, in 80% yield. Although 5 can be converted quantitatively to the corresponding chloride $[(\eta^5\text{-}C_5Me_5)OsCl(cod)]$ (6)* further reaction of 5 or 6 with either $SnBu^n_3(C_5Me_5)$ or other cyclopentadienylating reagents to give $[Os(\eta^5\text{-}C_5R_5)_2]$ and related products could not be achieved. (The hydride complex 5 was the eventual product of the reaction between 6 and $SnBu^n_3(C_5Me_5)$. It is possible that this occurs via the intermediacy of $[Os(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)(cod)]$ and this is being investigated.)

We believe that the reactions between the materials $[\{MCl_2(cod)\}_x]$ (M = Ru, Os; $x > 2$) and the $SnBu^n_3(C_5R_5)$ reagents giving the metallocenes 2 and 4, proceed via intermediates similar to 5 or 6. We have, however, found no direct evidence for the intermediacy of such species, even with equimolar additions of $SnBu^n_3(C_5R_5)$ reagent to 1. As indirect evidence though, we have synthesized the complexes $[(\eta^5\text{-}C_5R_5)RuCl(cod)]$ (7) [15], by reaction of the ruthenium hydride complex $[RuH(cod)(NH_2NMe_2)_3]PF_6$ with TlC_5R_5 (R = H, Me) in pentane/CCl_4. We have found the cyclooctadiene ligands in these complexes to be highly labile in ethanol or acetone solvent, rapidly with $SnBu^n_3(C_5R_5)$ under these conditions to give the metallocenes $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5R_5)]$ (R = H, Me) in good yields. We thus conclude that the introduction of the first cyclopentadienyl moiety into 1 is the rate determining step, and that the high lability of the cyclooctadiene ligand in an intermediate such as 7, results in a rapid further reaction with the tin reagent to give the metallocene product. The failure to synthesize decamethylosmocene from 3 is thus attributable to the unusual stability of either 5 or 6 to cyclooctadienes displacement. This suggested to us that alternative synthetic routes to $[Os(\eta^5\text{-}C_5Me_5)_2]$ that avoided intermediates similar to 5 or 6 could be more successful. Indeed, reaction of $Na_2[OsCl_6]$ directly with pentamethylcyclopentadiene in refluxing ethanol (2 h) gives $[Os(\eta^5\text{-}C_5Me_5)_2]$ (8)* in 80% yield. Similarly, reaction of $H_2[OsCl_6]$ with C_5Me_5H in boiling alcohols was found to give 8 (yield ca. 25%), although in this case the oxidized species, $[OsCl(\eta^5\text{-}C_5Me_5)_2]Cl$, was a significant contaminant.

In accordance with the known reactivity patterns of ruthenocene and osmocene [1,2], the complexes 2 (R = Me) and 8 have been found to undergo rapid redox reactions, for instance giving $[M(\eta^5\text{-}C_5Me_5)_2]PF_6$ (M = Ru, Os) and $[MX(\eta^5\text{-}C_5Me_5)_2]X$ (M = Ru, Os; X = Br, I) on treatment with $AgPF_6$ or the respective halogen. Further, strong acids reversibly protonate the elec-

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*Selected NMR data ($CDCl_3$), δ in ppm: 5, ^1H NMR: δ —12.26 (s, 1H, OsH), 1.51—2.01 (m, 8H, CH_2), 1.85 (s, 15H, C_5Me_5), 2.52 (m, 2H, CH), 2.74 (m, 2H, CH); ^{13}C NMR, δ 10.3 ($C_5\mathit{Me}_5$), 33.0, 34.9, (C_8H_{12}), 47.1, 54.2 (C_8H_{12}), 90.4 (C_5Me_5). 6, ^1H NMR, δ 1.56 (s, 15H, C_5Me_5), 1.53—2.48 (m, 8H, C_8H_{12}), 3.38 (m, 2H, C_8H_{12}), 4.14 (m, 2H, C_8H_{12}); ^{13}C NMR, δ 9.94 ($C_5\mathit{Me}_5$), 31.12, 32.73 (C_8H_{12}), 68.28, 71.06 (C_8H_{12}), 94.52 (C_5Me_5). 8, ^1H NMR, δ 1.7 (s, $C_5\mathit{Me}_5$). ^{13}C NMR, δ 10.3 ($C_5\mathit{Me}_5$), 77.8 (C_5Me_5).

tron-rich metal centres in 2 (R = Me) and 8. For instance, with HPF_6, the cationic hydride complexes $[MH(\eta^5\text{-}C_5Me_5)_2]PF_6$ are inferred from the high-field ^1H NMR resonances at δ −8.30 (M = Ru) and −15.67 ppm (M = Os).

In conclusion, the discovery of simple, reliable synthetic routes to the metallocenes $[M(\eta^5\text{-}C_5R_5)_2]$ (M = Ru, Os; R = H, Me) provides an entry to the inorganic and organic chemistry of these complexes. We are currently furthering our studies in this regard.

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References

1 M.A. Bennet, M.I. Bruce and T.W. Matheson, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Vol. 4, pp. 759—776.
2 R.D. Adams and J.P. Selegue in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Vol. 4, pp. 1018—1019.
3 K. Isobe, S. Okeya, N.J. Meanwell, A.J. Smith, H. Adams, and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1984) 1215.
4 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 106 (1984) 1650.
5 M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 1121.
6 J.K. Hoyario and W.A.G. Graham, J. Am. Chem. Soc., 104 (1982) 2723.
7 P.M. Maitlis, Coord. Chem. Rev., 43 (1982) 377.
8 T.D. Tilley, R.H. Grubbs and J.E. Bercaw, Organometallics, 3 (1984) 274.
9 N. Oshima, H. Suzuki and Y. Moro-Oka, Chem. Lett., 1984, 1161.
10 A.J. Deeming in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Vol. 4, pp. 475—480.
11 G.L. Hardgrove and D.H. Templeton, Acta Crystallogr., 12 (1959) 28.
12 S. Carter and J.N. Murrell, J. Organomet. Chem., 192 (1980) 399.
13 Yu.T. Struchkov, V.G. Andrianov, T.N. Sal'nikova, I.R. Lyatifov and R.B. Materikova, J. Organomet. Chem., 145 (1978) 213.
14 D.P. Freyberg, J.L. Robbins, K.N. Raymond and J.C. Smart, J. Am. Chem. Soc., 101 (1979) 892.
15 M.O. Albers, H.E. Oosthuizen, D.J. Robinson, A. Shaver and E. Singleton, J. Organomet. Chem., 282 (1985) C49.