[RuH(1—6-η-C_8H_{10})(1′,2′;5′,6′-η-C_8H_{12})]BF_4, The First Isolated Hydridometal Complex Stabilized only by Alicyclic Hydrocarbon Ligands and a Very Efficient Catalyst Precursor for the Transformation of Alkenes

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Low-temperature protonation of [Ru(1—6-η-C_8H_{10})(1′,2′;5′,6′-η-C_8H_{12})] by $HBF_4 \cdot Et_2O$ affords [RuH(1—6-η-C_8H_{10})(1′,2′;5′,6′-η-C_8H_{12})]BF_4 (**4**), a rare example of a hydrido-alkene complex which isomerises at room temperature to, first, [RuH(η^5-C_8H_{11})$_2$]BF_4 and then to [Ru(1—5-η-C_8H_{11})(1′—4′-η-C_8H_{12})]BF_4; all these complexes are efficient catalyst precursors for the isomerisation, oligomerisation, and polymerisation of alkenes and dienes.

We recently reported that cationic allylruthenium complexes (**1**) can be obtained *via* an allyl interchange which occurs during the reaction of allyloxyphosphonium salts (**2**) with zerovalent ruthenium complexes (**3**) [equation (1)].[1] The 18-electron complexes (**1**) which can also be prepared from hydridoruthenium cations[2] are active catalysts for isomerisation and oligomerisation or polymerisation of alkenes.[1] One would expect that the occurrence of vacant sites on the metal centre would lead to the ruthenium cationic complex having a higher activity. Such species could be accessible by the direct protonation of the metal centre in (**3**). The corresponding cations would behave similarly to the hydrides recently described by Singleton and his co-workers[3,4] either to give

$$\underset{\textbf{(3)}}{Ru(1,2,5,6\text{-}\eta\text{-cod})L_3} + \underset{\textbf{(2)}}{[CH_2{=}CRCH_2OP(NMe_2)_3]^+} \rightarrow$$

a, L_3 = cot; **b**, $L_3 = C_6H_6$; **a**, R = H; **b**, R = Me

$$[Ru(1—3,5,6\text{-}\eta\text{-}C_8H_{11})L_3]^+ + CH_2{=}CRMe + hmpa \quad (1)$$

(1)

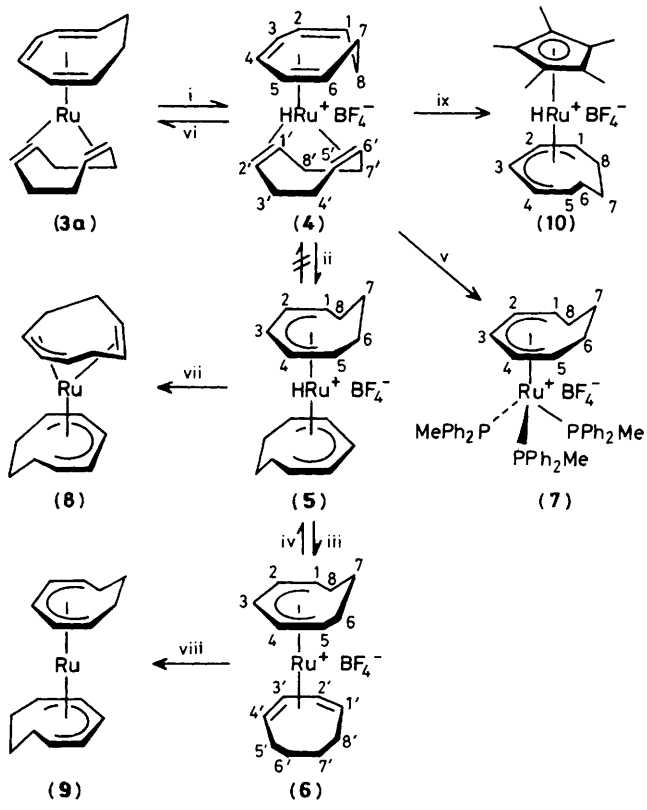
a, L_3 = cot; **b**, $L_3 = C_6H_6$

cot = cyclo-octa-1,3,5-triene; hmpa = hexamethylphosphoric triamide

$[Ru(\eta^3\text{-}C_8H_{13})(\eta^6\text{-}C_8H_{10})]^+$ or to lead by hydrogen transfer to the cot ligand to $[Ru(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_8H_{11})]^+$. Noteworthy is the recent observation that (**3a**) can be protonated in the presence of $HPF_6 \cdot H_2O$ and benzene to give $[Ru(\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6H_6)]PF_6$.[5] We report here the protonation of (**3a**) shown in Scheme 1 and the improved activity of the protonated species for the reactions already described.[1]

Low temperature protonation of (**1a**) by $HBF_4 \cdot Et_2O$ afforded a yellow solution from which yellow microcrystals could be obtained. The compound was found to be thermally unstable and slowly decomposed at room temperature. It is fluxional and shows in its room temperature ^1H n.m.r. spectrum only a broad peak at δ 1—4. If the protonation of (**1a**) is performed at −80 °C in CD_2Cl_2 and the ^1H n.m.r. spectrum recorded shortly afterwards, a well defined spectrum is obtained which we assign to the rigid species (**4**) (Scheme 1). The most noticeable feature of the spectrum† is a resonance at δ −5.5 coupled to two aliphatic (J_{HH} 5 Hz) and one ethylenic (6-H; J_{HH} 7.5 Hz) protons as demonstrated by selective decoupling experiments. This signal appears in the region in which are found the hydride ligands of $[RuH(cod)L_3]^+$ (cod = cyclo-octa-1,5-diene) complexes reported by Singleton *et al.*[3] The ^{13}C n.m.r. spectrum shows only eight of the ten CH resonances expected for a non-symmetrical molecule. A weak resonance is observed at δ 42.2 but cannot be definitely assigned to (**4**); moreover, resonances could be obscured by those of CD_2Cl_2 and diethyl ether.

If the n.m.r. tube is allowed to warm for a few minutes and then recooled to −80 °C features due to a second compound (**5**)† are observed. As in the spectrum of (**4**), a high-field peak is present at δ −5.6. Although it has been difficult to carry out a detailed spectral analysis of (**5**) selective decoupling experiments are in agreement with the presence of symmetrically bonded η^5-cyclo-octadienyl ligands in the complex. This assignment is further supported by the ^{13}C n.m.r. spectrum which exhibits a set of five peaks similar to that reported for $[Ru(\eta^5\text{-}C_8H_{11})_2]$.[6]



Scheme 1. *Reagents and conditions:* i, $HBF_4 \cdot OEt_2$, −80 °C; ii, short time at room temp., then −80 °C; iii, longer time at room temp.; iv, −80 °C; v, PPh_2Me (3 equiv.), warm to room temp.; vi, Et_3N (1 equiv.), −80 °C; vii, Et_3N (1 equiv.), −20 °C; viii, Et_3N (1 equiv.); room temp.; ix, C_5Me_5H, warm to room temp.

† ^1H and ^{13}C N.m.r. spectra of the reported complexes ($SiMe_4$ external reference; *J* values in Hz): (**4**) (CD_2Cl_2, 250 MHz, −70 °C): δ −5.48 (1H, dt, *J* 7.5 and 5, hydride), 0.37 (1H, m, *endo*-8-H), 1.35 (1H, m, 1-H), 1.4—2.5 (5H, br. m, 2-, 7^a, 7^b-, *exo*-8-, and $3'^a$-H), 1.85 (1H, m, $8'^a$-H), 2.32 (1H, m, $7'^a$-H), 2.5 (3H, m, $4'^a$-, $7'^b$-, and $8'^b$-H), 2.84 (1H, m, $4'^b$-H), 3.12 (1H, m, $3'^b$-H), 3.42 (1H, t, *J* 7.5, 2'-H), 3.63 (1H, obscured by Et_2O, 3-H), 3.96 (2H, m, 5'- and 6'-H), 4.08 (1H, t, *J* 7.5, 4-H), 5.13 (1H, q, *J* 7.5, 6-H), 6.07 (1H, q, *J* 7.5, 1'-H), and 7.36 (1H, t, *J* 7.5 Hz, 5-H); ^{13}C (62.8 MHz): CH, δ 32.6, 54.7, 74.9, 82.7, 88.9, 89.2, 103.3, and 110.5; CH_2, δ 16.9, 17.6, 19.7, 25.2, 26.1, and 34.6.

(**5**) (CD_2Cl_2, 250 MHz, −70 °C): δ −5.62 (1H, br., hydride), 0.4 (2H, q, *J* 13, *endo*-7-H), 1.33 (2H, d, *J* 13, *exo*-7-H), 1.79 (4H, m, 6^a- and 8^a-H), 2.06 (4H, d, *J* 16, 6^b- and 8^b-H), 4.06 (4H, br., 1- and 5-H), 4.67 (4H, dd, *J* 7.5, 7.0, 2- and 4-H), and 6.26 (2H, t, *J* 7, 3-H); ^{13}C (62.8 MHz, −80 °C): CH, δ 55.8, 88.6, and 107.4; CH_2, δ 18.0 and 25.7.

(**6**) (CD_3COCD_3, 250 MHz, room temp.): δ −0.47 (2H, a, *J* 10, *endo*-6- and *endo*-8-H), 1.25—1.7 (6H, br., *endo*-5'-, 2 × 6'-, 2 × 7'-, and *endo*-8'-H), 2.25 (2H, br., *exo*-5'- and *exo*-8'-H), 3.5 (2H, br., 1- and 5-H), 3.93 (2H, dd, *J* 6 and 7, 2- and 4-H), 5.70 (2H, m, 1'- and 4'-H), 5.85 (2H, d, *J* 11, 2'- and 3'-H), and 6.45 (1H, t, *J* 6, 3-H).

(**7**) (CD_3COCD_3, 90 MHz, room temp.): δ 0.2—2 (15H, br. m, 2 × 6, 2 × 7, and 2 × 8-H; P-Me), 2.72 (2H, br., 1- and 5-H), 5.09 (2H, br., 2- and 4-H), 6.84 (1H, t, *J* 6.5, 1-H), 7.56 (30 H, br., P-Ph); ^{13}C (62.8 MHz): CH, δ 58.1, 89.4, 97.6, and 130.8—135.0; CH_2, δ 18.9 and 24.9; Me, δ 3.6 (J_{pc} 52).

(**10**) (CD_3COCD_3, 90 MHz, room temp.): δ −10.31 (1H, br., hydride), 2.03 (15H, s, 5 × Me), 2 (6H, br., 2 × 6-, 2 × 7-, and 2 × 8-H), 4.5 (2H, br., 1- and 5-H), 5.5 (2H, br., 2- and 4-H) and 7.85 (1H, t, *J* 7, 3-H).

When left at room temperature, (**5**) isomerises to (**6**). The ^1H n.m.r. spectrum of (**6**) at room temperature shows no hydride resonance but the patterns due to η^5-cyclo-octadienyl and η^4-cyclo-octa-1,3-diene ligands.† The main feature of this spectrum is the presence of a high-field quartet (δ −0.47, 2H) which could indicate the presence in this complex of agostic hydrogen atoms[3,7] or at least of some proximity effect between these hydrogens and the metal centre which has only a 16 electron valence shell.

Finally, addition of 3 equiv. of $PMePh_2$ to a solution of (**4**) at low temperature followed by warming to room temperature for 1 h quantitatively afforded $[Ru(1\text{—}5\text{-}\eta\text{-}C_8H_{11})(PMePh_2)_3]BF_4$ (**7**)† and cyclo-octa-1,3-diene. This compound is very similar to that recently obtained by Singleton *et al.* with PMe_2Ph instead of $PMePh_2$.[2]

Deprotonation is readily achieved by the use of triethylamine in dichloromethane. When this reaction is carried out with (**4**) at −80 °C, (**1a**) is recovered as the major compound (50%). The same reaction with (**5**) at −20 °C gives rise to (**8**)[6] contaminated with (**9**)[8] as judged from the ^1H n.m.r. spectrum. On the other hand, deprotonation of (**6**) occurs mainly on the cyclo-octa-1,3-diene ligand leading to (**9**). Small amounts of (**8**) are formed (30—40%). In both cases, the evolution of (**1a**) is not detected. Therefore, the isomerisation (**4**) ⇆ (**5**) is irreversible, whereas (**5**) and (**6**) may equilibrate under appropriate conditions.

The process depicted in Scheme 1 involves the first example (**4**) of a transition metal hydride stabilized only by alicyclic hydrocarbon ligands. Moreover, although ruthenium(IV)

hydrides like $RuH_4(PPh_3)_3$ are known,[9] (**5**) is also the first representative of a hydridoruthenium complex where only hydrocarbyl residues are borne by the metal centre. A further example of hydridoruthenium(IV) species is provided by the reaction of 1—5-η-pentamethylcyclopentadiene with (**4**). Complex (**10**)† was obtained (30—40%) and would arise from the substitution of the cyclo-octa-1,5-diene ligand followed by a series of hydrogen shifts. However, the exact nature of the processes (**4**) → (**5**) and (**4**) → (**10**) will need further investigation.

Compound (**6**) is electron-deficient and one would expect that it would be an active catalyst precursor. The efficiency of compounds (**4**)—(**6**) in homogeneous catalysis has been tested on a few reactions. Thus, hex-1-ene and oct-1-ene are rapidly isomerised at 25 °C into a mixture of the corresponding 2- and 3-alkenes [turnover rate, t.o.r. 3200 h^{-1}, compared to 40 h^{-1} in the presence of (**1a**); 2-alkenes/3-alkenes 40/60]. Similarly, ethylene dimerisation occurs with higher rates [t.o.r. 800 instead of 160 h^{-1} in the presence of (**1a**)]. A mixture of mainly *cis*- and *trans*-but-2-enes is obtained (90%; but-1-ene: *cis*-but-2-ene : *trans*-but-2-ene 10 : 70 : 20); small amounts of higher oligomers are detected (10%). ^{13}C N.m.r. monitoring of this reaction indicates only the presence of (**4**) and but-2-enes. Isoprene, but not butadiene, is polymerised at room temperature in dichloromethane. G.c. monitoring of the early stages of the reaction shows that the polymerisation proceeds through the intermediacy of light oligomers. Activated alkenes like methyl acrylate are also polymerised in dichloromethane.

We thank C.N.R.S. for continuous support, especially through a research fellowship awarded to F. B.

Received 26th June 1985; Com. 902

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