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Reactivity of Ruthenium Polyhydrides: Reactions of $RuH_6[P(C_6H_{11})_3]_2$ with C_5-Cyclic Hydrocarbons. Preparation of New Ruthenium(IV)Trihydrides $RuH_3(C_5Me_5)L$ [L = PMe_3, PPh_3, PPr^i_3, or $P(C_6H_{11})_3$]

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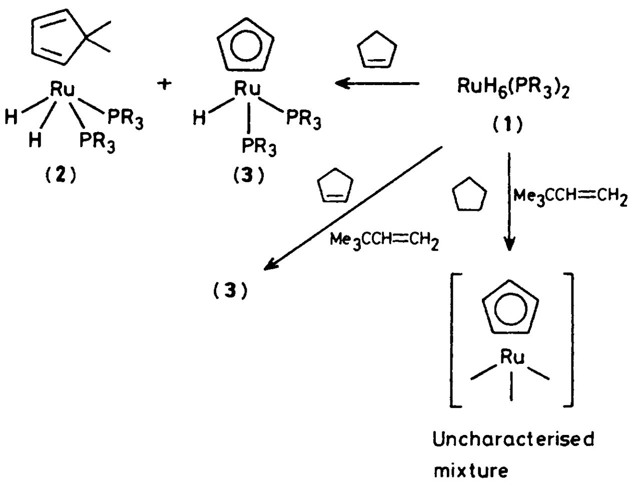
The hydrides $RuH_2(C_5H_6)(Pcy_3)_2$ (**2**) and $RuH(C_5H_5)(Pcy_3)_2$ (**3**) (cy = cyclohexyl) are formed in the reaction of $RuH_6(Pcy_3)_2$ (**1**) with cyclopentene, although in the presence of 3,3-dimethylbut-1-ene only (**3**) is formed quantitatively, but treatment of (**1**) with C_5Me_5H gives no C_5Me_5 complex (although in C_6D_6 active H–D exchange with the phosphine protons is observed); however $[Ru(C_5Me_5)Cl_2]_n$ when treated with phosphine (L = PMe_3, PPh_3, PPr^i_3, or Pcy_3) gives the paramagnetic complexes $RuCl_2(C_5Me_5)L$, which on treatment with $LiBHEt_3$ in tetrahydrofuran yields the new trihydrides $RuH_3(C_5Me_5)L$.

We have recently reported the preparation and reactivity of $RuH_6(Pcy_3)_2$ (cy = C_6H_{11}, cyclohexyl), the first hexahydride of ruthenium.[1] It was shown to react readily with ethylene at room temperature to give $RuH[C_6H_{10}P(C_6H_{11})_2][P(C_6H_{11})_3](C_2H_4)_2$ and thus is more reactive than comparable polyhydrides such as ReH_7L_2.[2] In view of the great interest in hydrogen transfer reactions and C–H activation,[3] we have investigated the reactivity of ruthenium hydrides with cyclopentene, cyclopentane, and pentamethylcyclopentadiene, C_5Me_5H (cp*H). The discovery by Bergman *et al.*[4] and Graham *et al.*[5] that cp* complexes of iridium could oxidatively add C–H bonds of alkanes after photochemical activation with loss of H_2 or CO has prompted the study of such complexes of different transition metals. The cp* ligand can stabilize low-valent complexes such as $cp^*Ir(CO)_2$,[5] as well as high-valent organometallic (*e.g.* cp^*IrMe_4),[6] hydrido (cp^*IrH_4),[7] or even oxo (cp^*ReO_3)[8] complexes. As far as ruthenium is concerned, with the exception of carbonyl derivatives, very few such compounds are known. Grubbs, Bercaw, *et al.*[9] then Suzuki, Moro-Oka, *et al.*[10] proposed two syntheses of the polymeric derivative $[RuCl_2cp^*]_n$ which they then used to prepare trimethylphosphine complexes including $RuHcp^*(PMe_3)_2$ and $[RuHClcp^*(PMe_3)_2]PF_6$, and various ruthenium(II) as well as ruthenium(IV) allylic compounds.[11] We have now prepared and characterised some C_5Me_5-ruthenium hydrides and studied their reactivity.

The room temperature reaction of $RuH_6(Pcy_3)_2$, (**1**), with an excess of cyclopentene in pentane produces a white precipitate (Scheme 1) shown to consist of a mixture of two compounds , (**2**) and (**3**).† Their most noticeable spectroscopic features are in the ^1H n.m.r. spectra, where the hydrides are observed as a triplet at δ −10.9 (J_{PH} 27.5 Hz), (**2**), or at δ −13.1 (J_{PH} 38.2 Hz), (**3**). The C_5 rings appear as broad peaks at δ 5.81, 4.61, 2.81, and 2.23 for (**2**), and as a singlet at δ 4.93 for the C_5H_5 ligand in (**3**).‡ If the reaction is performed in the presence of 3,3-dimethylbut-1-ene, only (**3**) is obtained quantitatively. The complexes are both white, a little air-sensitive, and soluble in aromatic solvents, from which (**3**) could be recrystallized. The structure of (**3**) has been unambiguously attributed as $RuH(\eta^5\text{-}C_5H_5)(Pcy_3)_2$ whereas for (**2**), always obtained as a minor component of a mixture,



Scheme 1

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† (**2**): ^1H n.m.r.: (C_6D_6) δ −10.9 (t, J_{PH} 27.5 Hz); 5.81, 4.61, 2.81 and 2.23 (C_5H_6, all broad). (**3**): ν(RuH) 1945 cm^{-1}; ^1H n.m.r.: (C_6D_6) δ −13.1 (t, J_{PH} 38.2 Hz), 4.93 (C_5H_5); ^{13}C n.m.r.: (C_6D_6) δ 77.56 (C_5H_5), 29—33 (C_6H_{11}).

‡ See δ −11.7 (t, $J_{P\text{-}H}$ 34 Hz, Ru–H); δ 4.04 (C_5H_5) for $RuHC_5H_5(PPh_3)_2$ (ref. 13).

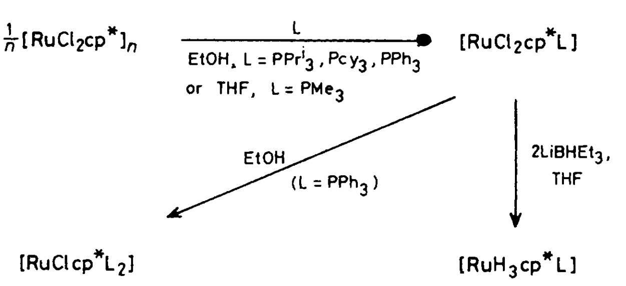
we propose the formulation $RuH_2(C_5H_6)(Pcy_3)_2$ by comparison with other known C_5H_6 complexes.[12] The reaction proceeds through hydrogen transfer from cyclopentene in the co-ordination sphere of the ruthenium, after initial removal of the hydrides. This demonstrates once more the ease of such ruthenium-mediated hydrogen transfer reactions[14,15] and also the greater reactivity of $RuH_6(Pcy_3)_2$ when compared with ReH_7L_2.

It was of interest to see whether this reactivity could apply to saturated hydrocarbons. We carried out the reaction of $RuH_6(Pcy_3)_2$ with cyclopentane in the presence and absence of 3,3-dimethylbut-1-ene at 120 °C. In the absence of 3,3-dimethylbut-1-ene, we observed the decomposition of the complex but no formation of a cyclopentadienyl derivative whereas with an excess of 3,3-dimethylbut-1-ene, a mixture of cyclopentadienyl compounds was obtained as observed by ^1H n.m.r. spectroscopy [δ 5.18, 5.15, and 5.06 (C_5H_5)]. The complexes could not be separated by conventional recrystallization or chromatography techniques and we attributed the production of a mixture to the low stability of the compounds at 120 °C.

If $RuH_6(Pcy_3)_2$ is treated with pentamethylcyclopentadiene (cp*H), n.m.r. investigations on the resulting brown solution show the presence of several fluxional hydrido complexes (δ −8.2, −8.9, −12.3, and −14.2) which could not be characterized, but apparently no cp* derivative is formed. However, this solution is able, within 10 min, to exchange 19% of its alkyl phosphine protons with the deuterium atoms of C_6D_6. Assuming that all the ruthenium species in solution catalyse this exchange, this would represent a turnover rate (TOR) of 75 h^{-1} at room temperature in the dark. Furthermore the real TOR must be higher since most probably only one species is active for the H–D exchange.

As it proved very difficult to crystallize complexes out of this solution, we attempted the direct preparation of similar cp* hydride phosphine complexes. $[RuCl_2cp^*]_n$ reacts with one equivalent of a bulky phosphine L (L = Pcy_3, PPh_3, PPr^i_3) in ethanol to yield a red precipitate analysing as $RuCl_2cp^*L$ (Scheme 2). The complexes are red, paramagnetic, air-stable powders [$\mu_{eff.}$ 1.95 (L = PPr^i_3), 1.93 (L = PPh_3)] and show a broad e.s.r. signal at g 2.096 (L = PPr^i_3) and 2.135 (L = PPh_3) as expected for ruthenium(III) complexes. In the presence of excess of PPh_3 in ethanol, $RuClcp^*(PPh_3)_2$ was obtained, but if Pcy_3 or PPr^i_3 is used, a bright blue complex is formed that is yet uncharacterised.

However $RuCl_2cp^*L$ reacts with two equivalents of $LiBHEt_3$ in tetrahydrofuran (THF) to give RuH_3cp^*L as the only detected hydride-containing compound (Scheme 2).[§] The same complex can be obtained with less bulky ligands using a different procedure. Thus, addition of a stoicheiometric quantity of PMe_3 to $(RuCl_2cp^*)_n$ in THF followed by 'super hydride' reduction afforded $RuH_3cp^*(PMe_3)$[¶][||] as well as a very small yield of the known $RuHcp^*(PMe_3)_2$.[9] All the trihydride complexes are yellow-brown and show a sharp doublet in the high field region in the ^1H n.m.r. spectra. Integration of the hydride peaks against the cp* and phosphine protons unambiguously supports a 3 : 1 : 1 ratio for these ligands. Furthermore, a partially-decoupled ^{31}P n.m.r. spectrum of RuH_3cp^*L (L = PPh_3, Pcy_3, PPr^i_3) shows a quartet in agreement with a coupling of the phosphorus with three hydrides. For RuH_3cp^*L (L = PMe_3, PPr^i_3) the electron impact mass spectrum shows parent ions at m/z 316 and 400 (^{102}Ru), respectively, and peaks for loss of H_2 at m/z 314 and 398. In the case of PPr^i_3 we could also detect the loss of one and two isopropyl groups at m/z 355 and 312 while for L = PMe_3 a small amount of $RuHcp^*(PMe_3)_2$ was detected at m/z 392.



Scheme 2

This result represents an easy high yielding synthesis of a new class of ruthenium(IV) polyhydrido complexes, of which only one similar complex $RuH_3(C_5H_5)PPh_3$[16] is known.[||] The mechanism most probably involves abstraction of hydrogen from the solvent but needs further study. The complexes RuH_3cp^*L do not exchange phosphine protons with deuteriated aromatic hydrocarbons and are very thermally stable (little, if any, decomposition up to 140 °C).

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[§] $RuH_3cp^*PPr^i_3$: ν(Ru–H) 1990s, 1905m cm^{-1}; ^1H n.m.r.: (C_6D_6) δ −10.99 (d, J_{PH} 24.3 Hz, Ru–H); δ 2.12 (C_5Me_5); ^{31}P n.m.r.: (C_6D_6–C_6H_6) 95.2 p.p.m. (s). $RuH_3(C_5Me_5)PPh_3$: ν(Ru–H) 1965, 1935 cm^{-1}; ^1H n.m.r.: (C_6D_6) δ −9.73 (d, J_{PH} 20.6 Hz, Ru-H), 2.10 (C_5Me_5); ^{31}P n.m.r.: (C_6D_6–C_6H_6) 79.13 p.p.m. (s). $RuH_3(C_5Me_5)Pcy_3$: ν(Ru–H) 1987s, 1895m cm^{-1}; ^1H n.m.r.: (C_6D_6) δ −10.98 (d, J_{PH} 22.1 Hz, Ru–H), 2.16 (C_5Me_5), ^{31}P n.m.r.: (C_6D_6–C_6H_6) δ 83.93 p.p.m.

[¶] $RuH_3cp^*PMe_3$: ^1H n.m.r.: δ −10.35 (d, J_{PH} 22.2 Hz, Ru–H).

[||] *Note added in proof:* R. Paciells and J. E. Bercaw have recently prepared $RuH_3cp^*(PMe_3)$ *via* hydrogenation of $Ru(CH_2SiMe_3)cp^*(PMe_3)_2$: Abstract, 191 st. Am. Chem. Soc. National Meeting, New York, 1986, INORG 82.