Unexpected Dehydrogenation of a Cyclohexyl Group at Low Temperature through Protonation of $RuH_3(\eta^5\text{-}C_5Me_5)(PCy_3)$ (Cy = cyclohexyl). *X*-Ray Structure of $[(\eta^5\text{-}C_5Me_5)Ru\{(C_6H_9)P(C_6H_{11})\}_2]BF_4$

Thérèse Arliguie,[a] Bruno Chaudret,*[a] Felix Jalon,[a]† and Fernando Lahoz[b]

[a] *Laboratoire de Chimie de Coordination du CNRS, lié par convention à l'Université Paul Sabatier, 205 route de Narbonne, 31077 Toulouse Cedex, France*

[b] *Departemento de Quimica Inorganica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Low temperature protonation of $RuH_3(\eta^5\text{-}C_5Me_5)(PR_3)$ (R = Pr^i, Ph, cyclohexyl) leads either to decomposition (R = Pr^i), to a mixture of *cis*- and *trans*-$[RuH_2(\eta^5\text{-}C_5Me_5)(PR_3)_2]BF_4$ (R = Ph), or to dehydrogenation of a cyclohexyl group to afford the complex $[Ru(\eta^5\text{-}C_5Me_5)\{(C_6H_9)P(C_6H_{11})_2\}]BF_4$ which shows a strong agostic interaction between a C–H bond of the cyclohexenyl group and the metal; a possible application of the later observation is proposed for the dehydrogenation of alkanes.

Protonation of polyhydrides has been shown in some cases to lead to extensive evolution of dihydrogen. These reactions, at first surprising, have been better understood after the discovery of co-ordination of H_2 to a metal.[1] It was then shown that the protonation of a polyhydride could lead to a structural change in the complex and to the formation of dihydrogen ligands, as for the reaction $IrH_5(PR_3)_2 + H^+ \rightarrow [IrH_2(H_2)_2(PR_3)_2]^+$.[2]

Furthermore, the protonation of a series of *trans*-$MH_2(L_2)_2$ complexes (M = Fe, Ru, Os; L_2 = $Et_2PCH_2CH_2PEt_2$, $Ph_2PCH_2CH_2PPh_2$) has been studied by Morris *et al.* who have shown that the stability of the M–H_2 interaction in the [*trans*-$MH(H_2)(L_2)_2]^+$ derivatives they obtained depends on the nature of the metal in the order Ru < Fe < Os.[3]

In the case of complexes such as $(\eta^5\text{-}C_5H_5)RuHLL'$, it was shown by Simpson *et al.*[4] and Heynekey *et al.*[5] that protonation leads to either dihydride or molecular hydrogen derivatives depending on the ligand. We and others have recently prepared a series of complexes of the type $(\eta^5\text{-}C_5Me_5)RuH_3L$ (L = PPh_3, PCy_3, PPr^i_3)[6] (Cy = cyclohexyl) and we have demonstrated that these compounds show non-classical n.m.r. behaviour related to the possible presence of a trihydrogen ligand.[7]

Since protonation of a polyhydride could lead to under-co-ordinated derivatives which could show a high reactivity, especially in C–H activation, we have been interested in such reactions of $RuH_3(\eta^5\text{-}C_5Me_5)(PR_3)$. We describe here our unexpected results.

The reaction of $RuH_3(\eta^5\text{-}C_5Me_5)(PPr^i_3)$ with $HBF_4{\cdot}Et_2O$ at −78 °C in acetone leads to extensive decomposition of the complex and formation of $[HPPr^i_3]BF_4$. However, the same reaction with $RuH_3(\eta^5\text{-}C_5Me_5)(PPh_3)$ in toluene leads to precipitation of the dihydride $[RuH_2(\eta^5\text{-}C_5Me_5)(PPh_3)_2]BF_4$ (1) [^{1}H n.m.r., δ −6.85 t ($J_{P\text{-}H}$ 26 Hz), 1.56 s (C_5Me_5) integration ratio: 2H : 1C_5Me_5]. When the reaction is carried out in acetone, it yields the same complex along with a very similar one [^{1}H n.m.r., δ −6.55 t ($J_{P\text{-}H}$ 19 Hz)]. We tentatively propose that these compounds are the *cis*- and *trans*-isomers of the dihydrides. We observed no sign of the presence of a molecular hydrogen derivative. The results are in agreement with those obtained by Simpson *et al.*[4] who found that increasing the steric bulk of the ligands favoured the formation of the dihydride. However, they only found the *trans*-dihydride whereas in our case the *cis*-dihydride can also exist and is not a molecular hydrogen derivative. This is probably due to

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† On leave from the University of Alcala de Henares.

the greater electron richness of our compounds which favours H_2 dissociation through back-donation.

It is surprising to obtain a bisphosphine derivative, resulting from the disproportionation of the complex. In the case of the reaction in toluene, a π-toluene derivative, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}PhMe)]BF_4$ (**2**) was also obtained.‡ This shows the great instability of the $Ru(\eta^5\text{-}C_5Me_5)(PR_3)^+$ fragments as also demonstrated in the case of PPr^i_3.

The protonation of $RuH_3(\eta^5\text{-}C_5Me_5)(PCy_3)$ in acetone at −78 °C led to a yellow–brown solution which, after evaporation to dryness and recrystallization from ethanol, afforded yellow crystals of a compound with analytical data consistent with the formula $[Ru(\eta^5\text{-}C_5Me_5)\{P(C_6H_{11})_2(C_6H_9)\}]BF_4$ (**3**). In addition to C_5Me_5 as a doublet at δ 2.,04 (J_{P-H} 1.5 Hz) and a broad set of peaks between δ 1 and 2 due to alkyl protons, its ^1H n.m.r. spectrum shows a quartet at δ −10.5 (H^0, J_{P-H} ~ 11 Hz), a doublet of triplets at δ 4.04 (H^1, J_{H-H} 6.5, 1.2 Hz), a triplet at δ 3.85 (H^2, J_{H-H} 6.5 Hz), and a broad multiplet centred at δ 3.18 (H^3). Upon ^{31}P decoupling, the quartet transformed into a triplet due to the coupling of H^0 to H^3 and to another proton near δ 2.0. Double irradiation experiments showed that H^2 was coupled to H^1 and H^3 while H^1 was coupled to H^3 but with a small coupling constant (1.2 Hz). The ^{13}C n.m.r. spectrum shows peaks at δ 96.8 (C_5Me_5), 10.3 (C_5Me_5, J_{C-H} 128 Hz), 69.7 (C–H, J_{C-H} 159 Hz), 69.15 (C–H, J_{C-H} 174 Hz), 41.1 (CH_2, J_{C-H^3} 159 Hz, J_{C-H^0} 39 Hz) and peaks for CH_2 and CH–P groups between δ 37 and 26.

These data are consistent with the presence of a cyclohexenyl group bonded to the metal with an agostic interaction[9] between a proton of this group and the ruthenium atom. This fact has been confirmed by an *X*-ray crystal structure determination.§

The crystals of (**3**) consist of mononuclear cations, BF_4^- anions, and ethanol of crystallization. An ORTEP drawing of the cation with the atomic numbering is given in Figure 1. The co-ordination around the ruthenium atom involves the C_5Me_5 ligand, the phosphorus atom of the phosphine, and a cyclohexenyl group with three carbon atoms located at bonding distances from the metal centre [Ru–C(33) 2.315(5), Ru–C(34) 2.109(5), Ru–C(35) 2.286(6) Å]. The C(34)–C(35) distance [1.403(8) Å] is significantly shortened compared to the observed values for the single C–C bond in the cyclohexyl groups (range 1.50—1.56 Å) and indicates the presence of an olefinic group. Another C–C bond [C(33)–C(34) 1.487(9) Å] is slightly shortened. These data are in agreement with the proposed dehydrogenation of a cyclohexyl group of the PCy_3 into a cyclohexenyl group.

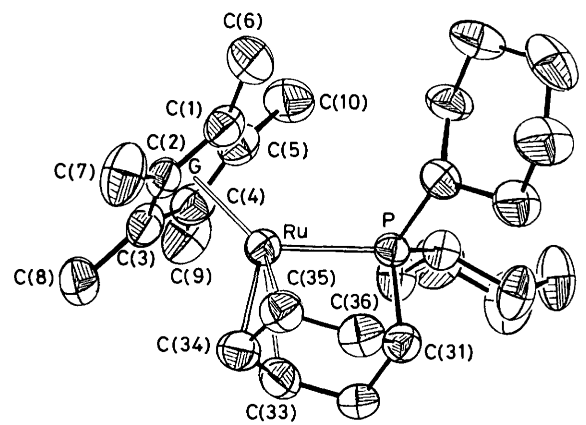
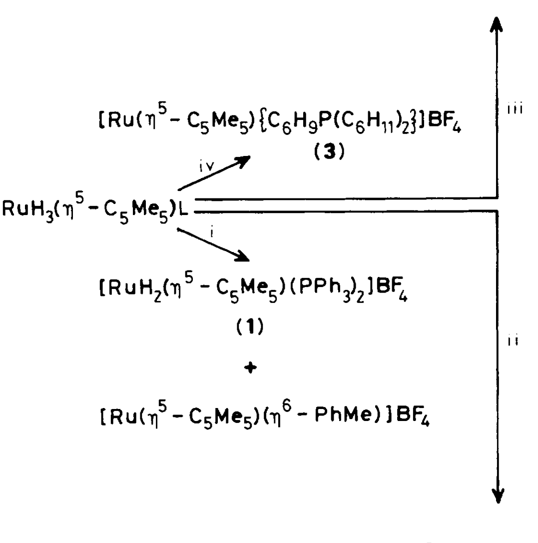


Figure 1. Molecular structure of the cation $[Ru(\eta^5\text{-}C_5Me_5)(C_6H_9)P(C_6H_{11})_2]^+$. Selected bond lengths (Å) and angles (°): Ru–P 2.327(1), Ru–G 1.855(3), Ru–C(1) 2.213(5), Ru–C(2) 2.200(6), Ru–C(3) 2.212(6), Ru–C(4) 2.236(6), Ru–C(5), 2.237(6), Ru–C(33) 2.315(5), Ru–C(34) 2.109(5), Ru–C(35) 2.286(6), C(33)–C(34) 1.487(9), C(34)–C(35), 1.403(8); G–Ru–P 134.0(1), G–Ru–C(33) 137.0(2), G–Ru–C(34) 125.7(2), G–Ru–C(35) 133.0(2), P–Ru–C(33) 81.4(2), P–Ru–C(34) 99.9(2), P–Ru–C(35) 79.9(1), C(32)–C(33)–C(34) 115.5(5), C(33)–C(34)–C(35) 116.8(5), C(34)–C(35)–C(36) 119.2(5); G = centroid of C_5Me_5.



Scheme 1. Some protonation reactions of $(\eta^5\text{-}C_5Me_5)RuH_3L$. *Reagents and conditions:* i, $HBF_4\cdot Et_2O$ (1 equiv.), toluene, L = PPh_3; ii, $HBF_4\cdot Et_2O$ (1 equiv.), acetone, L = PPh_3; iii, CF_3CO_2H (1 equiv.), hexane, L = PCy_3; iv, $HBF_4\cdot Et_2O$ (1 equiv.), acetone, L = PCy_3.

Furthermore, the placement of hydrogen atoms in calculated positions, the disorder for the anion and the solvent molecule preventing clear location in the structure determination, shows the presence of a short H–Ru distance

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‡ $Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}PhMe)]BF_4$: ^1H n.m.r.: δ 2.15 (s, 15H, C_5Me_5), 2.34 (s, 3H, Me), 6.09 (s, 5H, Ph). This complex can be obtained directly from the reaction of $[(\eta^5\text{-}C_5Me_5)RuCl]_n$ with toluene like its benzene congener.[8]

§ Crystals of (**3**) are monoclinic, space group $P2_1$, with $a = 9.305(1)$, $b = 16.101(2)$, $c = 10.621(1)$ Å, $\beta = 97.92(1)\infty$, $U = 1576(3)$ Å^3, $Z = 2$, $D_c = 1.365$ g/cm^3. A yellow prismatic block of dimensions 0.456 × 0.524 × 0.418 mm was used for data collection, on a Siemens AED-2 diffractometer using graphite-monochromated Mo-K_α radiation. A total of 8842 reflections were measured ($3 \leqslant 2\theta \leqslant 45°$) using the ω/2θ scan technique. The data were corrected for Lorentz and polarization effects, and for absorption (ψ-scan method from 7 reflections) ($\mu = 5.806$ cm^{-1}). 4052 unique reflections with $I \geqslant 3.0\,\sigma(I)$ were considered observed and used in refinement. The structure was solved by standard Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions riding upon their respective carbon atoms and included in the last cycle of refinement. The final values of the agreement indices were $R = 0.043$ and $R_w = 0.046$. The disorder observed for the anion and the solvent molecule prevented a clear location of the hydrogen atoms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[1.786(6) Å], corroborating the agostic interaction proposed from the n.m.r. data between a proton of the olefinic carbon atom C(33) and the metal.

This result is interesting for two reasons. First this agostic interaction is very strong as can be deduced from the large J_{H-P} coupling (12 Hz) and the low J_{C-H} coupling (39 Hz), which both indicate a significant lengthening of the carbon–hydrogen bond. Such compounds are not very common although a similar phenomenon has been recently reported for a cobalt compound.[9,10]

Secondly, the reaction reported here corresponds to a 'spontaneous' dehydrogenation of a cyclohexyl group at low to room temperature. Of course, dehydrogenation of PCy_3 is known to occur in iridium compounds but in refluxing toluene in the presence of cyclo-octene which can serve as a hydrogen acceptor.[11] The mechanism we propose involves a β-elimination step followed by formation of molecular hydrogen in the co-ordination sphere of ruthenium and, finally, elimination of H_2. This is a step of great significance for alkane dehydrogenation and could mean that complexes able to bind loosely molecular hydrogen could be good candidates for such reactions.

An intermediate for this reaction was obtained by carrying out the protonation using an acid containing a co-ordinating anion. Thus, $RuH_3(\eta^5\text{-}C_5Me_5)(PCy_3)$ does not react with CF_3COOH in acetone while in hexane a red–purple solution is obtained from which purple crystals are formed upon recrystallization from ethanol. The complex was identified as $Ru(\eta^5\text{-}C_5Me_5)(OCOCF_3)(PCy_3)$,¶ an unusual 16-electron half-sandwich complex similar to $Ru(\eta^5\text{-}C_5Me_5)Cl(PR_3)$[7b] that we prepared independently. This is most probably the first step of the dehydrogenation reaction with $HBF_4 \cdot Et_2O$, *i.e.* formation of a bisdihydrogen derivative and evolution of two moles of hydrogen. However, since BF_4^- is unable to stabilize the $Ru(\eta^5\text{-}C_5Me_5)(PCy_3)^+$ fragment, dehydrogenation occurs.

To conclude, we have reported an unusual example of dehydrogenation of a cyclohexyl group. This reaction is possible probably thanks to the ability of ruthenium to form H–H bonds in its co-ordiantion sphere and to the weakness of the $Ru\text{–}H_2$ bond in cationic complexes already demonstrated by Morris *et al.*[3] It is now important to see whether this mechanism could apply to intermolecular reactions. It is noteworthy that the same reaction which leads to dehydrogenation of PCy_3 {*e.g.* $[IrCl_2(\eta^2\text{-}C_8H_{14})_2]_2$ + PCy_3/toluene}[11] has been shown by Werner *et al.* to lead to an intermolecular C–H activation reaction in the presence of PPr^i_3.[12]

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¶ ^{1}H n.m.r. δ 1.55 (s, 15H, C_5Me_5), 1.32—1.91 (m, 33H, Cy). ν(CO) 1620 cm^{-1}; elemental analyses were satisfactory.

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