

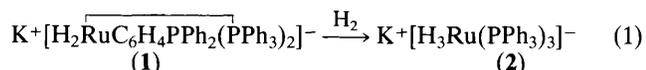
New Synthesis and Molecular Structure of Potassium Trihydridotris(triphenylphosphine)ruthenate

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A convenient, high yield method for the synthesis of ruthenium hydrides, including anionic ruthenium hydrides, has been developed; the molecular structure of potassium trihydridotris(triphenylphosphine)ruthenate (**2**) complexed with 18-crown-6 ether has been determined by single crystal X-ray diffraction.

Recently there has been increased interest in anionic ruthenium hydride species and their role in homogeneous catalysis.^{1,2} *Pez et al.*¹ reported the synthesis and characterization of $K[H_2RuC_6H_4PPh_2(PPh_3)_2]$ (**1**) and its use as a catalyst precursor for the hydrogenation of ketones, nitriles, esters, and arenes. According to Halpern *et al.*² complex (**1**) is immediately converted into $K[H_3Ru(PPh_3)_3]$ (**2**) upon exposure to hydrogen gas in solution, equation (1). Since the synthesis and isolation of (**1**) is relatively inconvenient and complex (**2**) is the predominant form of the catalyst under hydrogenation conditions, we have designed a simple method for the synthesis of complex (**2**) at high yields to allow further studies on the chemistry of anionic ruthenium hydrides. We report here a simple and high yield synthesis of complex (**2**) and other ruthenium hydride species.



When $RuHCl(PPh_3)_3$ was stirred with 2 equiv. KBH_4 in tetrahydrofuran (THF) at ambient temperature and under

inert atmosphere for two days, complex (**2**) was formed at higher than 95% yield. After filtering off KCl and washing the precipitate with small amounts of THF to dissolve any precipitated complex (**2**), the filtrate was evaporated to dryness. The crude product was then washed with excess of diethyl ether. Higher than 85% isolated yields of the bright yellow product were obtained. The spectroscopic data of this species were identical to those reported by Halpern *et al.*² [$^{31}P\{^1H\}$ n.m.r. ($[^2H_8]$ THF, $-70^\circ C$): δ 63 (s) p.p.m.; 1H n.m.r., a six-peak multiplet hydride signal at δ -9.5 ; i.r.: $\nu(Ru-H)$, (THF) 1835, (Nujol) 1857, 1815 cm^{-1}].

After adding a slight excess of 18-crown-6 ether to a solution of complex (**2**) in THF, single crystals of (**2**) complexed with 18-crown-6 ether were obtained by slowly adding diethyl ether to the solution. An X-ray diffraction study of this crown ether complex of (**2**) revealed a highly distorted octahedral structure for the anion. The *fac* disposition of the hydrogen atoms attached to the ruthenium is in agreement with the previous suggestion by Halpern *et al.*² The high degree of distortion from the ideal octahedral structure, as illustrated by the large P–Ru–P bond angles, is obviously due to the large steric bulk of the phosphines relative to the small hydride ligands. The least-squares plane of the crown ether molecule has a standard deviation of ± 0.31 Å. The potassium cation occupies a site 0.75 Å away from the crown ether plane and points toward the ruthenium. The K–Ru distance is 3.613 Å which is outside the range of a covalent bond.¹ The only interaction between the potassium cation and the ruthenium anion is Coulombic. A THF molecule is also found to be trapped in the crystal cage; however, it has no interaction with the complex. † A perspective view of the crystal structure is shown in Figure 1. ‡

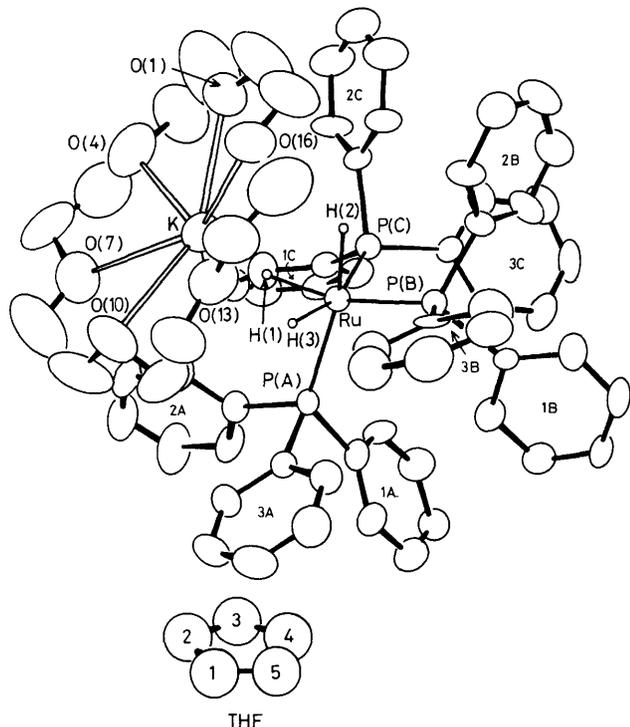
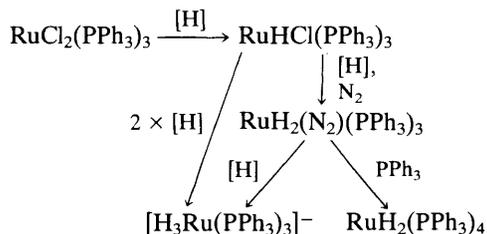


Figure 1. A perspective view of $[K(C_{12}H_{24}O_6)][H_3Ru(PPh_3)_3] \cdot THF$. Selected bond lengths (Å): Ru–P(A) 2.338(2); Ru–P(B) 2.318(2); Ru–P(C) 2.312(3); Ru–H(1) 1.60(6); Ru–H(2) 1.59(7); Ru–H(3) 1.71(7). Selected bond angles ($^\circ$): P(A)–Ru–P(B) 111.22(8); P(A)–Ru–P(C) 104.90(9); P(A)–Ru–H(1) 90(3); P(A)–Ru–H(2) 167(2); P(A)–Ru–H(3) 81(2); P(B)–Ru–P(C) 102.18(9); P(B)–Ru–H(1) 151(2); P(B)–Ru–H(2) 76(2); P(B)–Ru–H(3) 93(2); P(C)–Ru–H(1) 90(2); P(C)–Ru–H(2) 84(3); P(C)–Ru–H(3) 160(2); H(1)–Ru–H(2) 80(3); H(1)–Ru–H(3) 70(3); H(2)–Ru–H(3) 88(3).

† The THF molecule is highly disordered due to the lack of interaction with the complex. For the purpose of refinement five idealized models of THF molecules with occupancy factor of 0.2 were used to pick up the residual electron density that appeared in the difference Fourier map. Their positional and temperature parameters were fixed during all the refinement cycles.

‡ The complex, $[K(C_{12}H_{24}O_6)][H_3Ru(PPh_3)_3] \cdot THF$, crystallized in yellow plate form. $M = 1266.51$, monoclinic, $a = 17.234(5)$, $b = 13.260(2)$, $c = 28.257(6)$ Å, $\beta = 94.42(2)^\circ$, $U = 6438(4)$ Å³, $D_c = 1.307$ g cm⁻³, space group $P2_1/c$, $Z = 4$. The structure was solved by Patterson heavy atom methods and refined by a full matrix least-squares procedure to an R value of 0.069 on 5043 observed [$I > 2.33 \sigma(I)$] reflections. The three hydrogen atoms attached to the ruthenium were found in the difference Fourier map and their positional parameters were refined. Since the refined value of the metal centre has an equivalent isotropic temperature factor ($B_{equiv.}$) of 2.38 Å², the temperature factors (B) of these hydrogen atoms were fixed at a value of 3.0 Å² in the final refinements. The final difference Fourier map showed no residual electron density at levels greater than 0.70 electron/Å³ and all of the major residual electron densities were located around the region of the disordered THF molecule. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. [H] = 1 equiv. LiBHET₃ or KBHBU₃ in THF.

The lithium salt of [H₃Ru(PPh₃)₃]⁻ was obtained at similarly high yields by using LiBHET₃ as a hydride source. Other ruthenium hydride species such as RuHCl(PPh₃)₃, RuH₂(N₂)(PPh₃)₃, or RuH₂(PPh₃)₄ were also conveniently prepared by this method. Thus, when RuCl₂(PPh₃)₃ was treated with 1 equiv. LiBHET₃ or KBHBU₃ in THF, RuHCl(PPh₃)₃ [i.r. (Nujol): ν(Ru-H) 2020 cm⁻¹]³ was formed in virtually quantitative yield. Upon further addition of 1 equiv. LiBHET₃ or KBHBU₃ under nitrogen atmosphere, RuH₂(N₂)(PPh₃)₃ was obtained at similarly high yield [i.r.

(Nujol): ν(Ru-H) 2032, ν(N₂) 2146 cm⁻¹; ³¹P{¹H} n.m.r. in [²H₈]THF: δ 55.7 (d, 2P), 43 p.p.m. (t, 1P', J(P-P') 15 Hz)]. In the presence of excess of PPh₃, RuH₂(PPh₃)₄ was obtained as the product [i.r. (Nujol): ν(Ru-H) 2080 cm⁻¹; ³¹P{¹H} n.m.r. in [²H₈]THF: δ 48.2 (t, 2P), 40.2 p.p.m. (t, 2P', J(P-P') 13.5 Hz)].

These reactions are depicted in Scheme 1.

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