

Preliminary communication

BENZENE CARBON–HYDROGEN BOND ACTIVATION USING $\text{Ru}(\text{C}_6\text{Me}_6)[\text{PH}(\text{C}_6\text{H}_{11})_2]\text{H}_2$

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(Received July 27th, 1983)

Summary

The dihydride $\text{Ru}(\text{C}_6\text{Me}_6)[\text{PH}(\text{C}_6\text{H}_{11})_2]\text{H}_2$ is synthesized in high yield by reducing $\text{Ru}(\text{C}_6\text{Me}_6)[\text{PH}(\text{C}_6\text{H}_{11})_2]\text{Cl}_2$ with $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$. In benzene it loses hydrogen under UV irradiation to give $\text{Ru}(\text{C}_6\text{Me}_6)[\text{PH}(\text{C}_6\text{H}_{11})_2]\text{H}(\text{C}_6\text{H}_5)$.

Some of the most active complexes for the intermolecular activation of carbon–hydrogen bonds have the formulae $\text{M}(\text{C}_5\text{Me}_5)(\text{PMe}_3)_2\text{H}_2$, $\text{M} = \text{Ir}$ [1], Rh = [2] and $\text{Ir}(\text{C}_5\text{Me}_5)(\text{CO})_2$ [3]. It is significant that stable alkyl hydride products can be isolated from the photochemical or thermal reactions of these compounds with alkanes; the “piano stool” geometry of the complexes appears to discourage reductive elimination of alkane from the products. We are studying the activity of the iron group elements toward C–H bond cleavage [4] and in particular the complexes $\text{Ru}(\text{C}_6\text{Me}_6)(\text{L})\text{H}_2$ which are isoelectronic with the cobalt group complexes listed above and which have the favorable “piano stool” geometry. Indeed we find that such complexes do activate carbon–hydrogen bonds under photolysis conditions. Here we report that the secondary phosphine ligand dicyclohexylphosphine ($\text{L} = \text{PHCy}_2$) promotes the activation of benzene under conditions where phosphorus–hydrogen bond cleavage might be expected to occur.

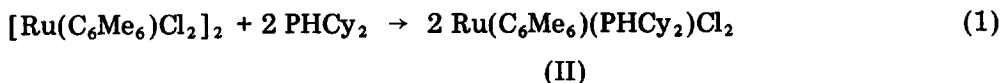
The new dihydride $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PHCy}_2)_2\text{H}_2$ (I) was prepared in two steps from $[\text{Ru}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2$ by a modification of literature methods [5,6]. First the chloride-bridged dimer was treated with 2 mol PHCy_2 in methylene chloride at 22°C under nitrogen for 24 h to give, after precipitation, air-stable red crystals of $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PHCy}_2)(\text{Cl})_2$ (II) in 95% yield (eq. 1).

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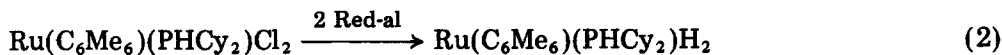
TABLE 1
SPECTROSCOPIC AND ANALYTICAL DATA FOR THE COMPLEXES $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PhCy}_2)(\text{X})(\text{Y})$.

Complex XY	¹ H NMR ^a				³¹ P NMR ^b				Analysis				
	Solvent	δ(PH) (ppm)	¹ J(PH) (Hz)	³ J(PH) (Hz)	³ J(PH) (Hz)	δ(C ₆ Me ₆) (ppm)	δ(RuH) (ppm)	² J(PH) (Hz)	δ(PHCy ₂) (ppm)				
									C	H			
I	H ₂	C ₆ D ₆	4.03dt	282	4.7	—	2.16s	-11.12d	43.5	pentane	63.0s	62.17 (62.33)	9.34 (9.52)
II	Cl ₂	CDCl ₃	4.39dt	326	5.6	—	2.00d	—	—	CH ₂ Cl ₂	35.1s	54.12 (53.56)	7.76 (7.88)
III	HCl	C ₆ D ₆	4.00dm	299	—	—	1.87s	-8.82d	50.7	THF	56.6s	—	—
IV	HPh	C ₆ D ₆	3.97ddd	299	6.8	3.3	1.91s	-10.38d	50.3	pentane	52.8s	66.75 (66.56)	8.77 (9.19)
V	D(C ₆ D ₅)	C ₆ D ₆	3.97ddd	299	6.8	3.3	1.91s	—	—	pentane	52.9t (J 7 Hz)	—	—

^a 200 MHz spectra from a Varian XL200. $\delta(\text{Cy})$ for all complexes: 1.2–2.0 ppm. $\delta(\text{C}_6\text{H}_6)$ for complex IV 7.64 ppm (d, $^3J(\text{HH})$ 7.2 Hz, 2H, *ortho*), 7.1 ppm (m, 3H, *meta* + *para*). ^b 32.3 MHz spectra from a Bruker WP80 instrument. Chemical shifts are referenced to 85% H_3PO_4 .

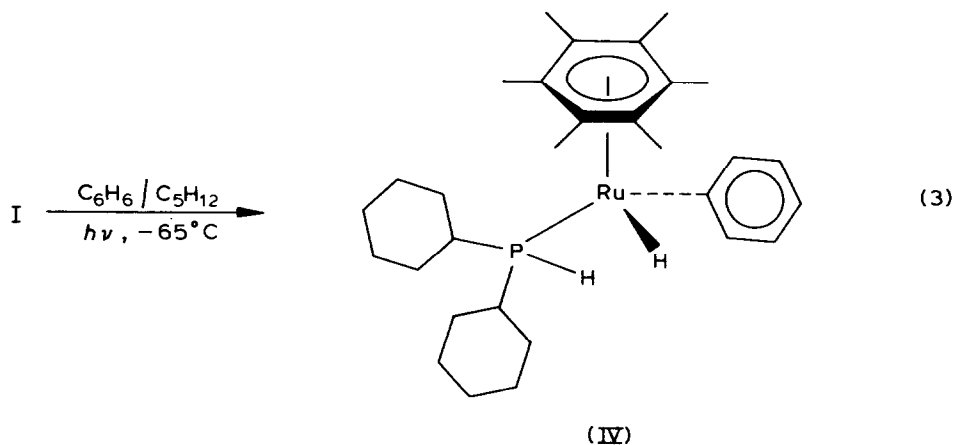


Then complex II was dissolved in dry THF and reduced at 22°C with two equivalents of $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ "Red-al" to give, after workup, complex I as air-sensitive, pale-yellow crystals in 90% yield (eq. 2). This dihydride is ob-



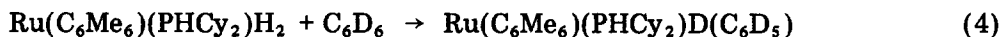
tained in higher yield than the complexes $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PR}_3)_2\text{H}_2$, $\text{R} = \text{Me}$ [5,6], and Pr^i [7] because of its ready separation from ionic solids produced in reaction 2 by filtration through alumina (activity I) and possibly its lower solubility in pentane. Use of one equivalent of Red-al per ruthenium yields mainly the monohydride compound $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PHCy}_2)\text{HCl}$ (III) which has been characterized in solution. The ^1H NMR spectra (Table 1) of the complexes I–III contain characteristic signals due to the C_6Me_6 ligands, multiplets assigned to the P–H groups and doublets in the hydride region for I and III. The ^{31}P NMR spectra show singlets for the complexes (Table 1). Distinctive absorptions in the IR spectra are due to $\nu(\text{P–H}) \sim 2230 \text{ cm}^{-1}$ for all the complexes and $\nu(\text{Ru–H}) 1945 \text{ cm}^{-1}$ for I and 1980 cm^{-1} for III.

The activation of a carbon–hydrogen bond of benzene by complex I is clearly demonstrated by the photolysis ($\lambda > 280 \text{ nm}$) of a $1.25 \times 10^{-2} \text{ M}$ solution of I in a benzene/pentane mixture (0.1 vol./vol.) at -65°C . After 4 h of irradiation, 0.9 mol hydrogen per ruthenium is evolved and tan coloured crystals of the phenyl hydride complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PHCy}_2)\text{H}(\text{C}_6\text{H}_5)$ (IV) can be isolated in 50% yield, eq. 3. Complex IV is identified in the ^1H NMR spectrum by a new hydride resonance at -10.4 ppm (d, $^2J(\text{PH}) 50.3 \text{ Hz}$, 1H, RuH), phenyl resonances at 7.64 ppm (d, $^3J(\text{HH}) 7.2 \text{ Hz}$, 2H, *ortho*) and 7.1 ppm (m, 3H, *meta* + *para*) and the secondary phosphine hydrogen at 3.97 ppm (ddd, $^1J(\text{PH}) 299.3 \text{ Hz}$, $^3J(\text{HH}) 6.8 \text{ Hz}$, $^3J'(\text{HH}) 3.3 \text{ Hz}$ (coupling to two diastereotopic cyclohexyl protons [8]), 1H, PH). The IR spectrum shows $\nu(\text{P–H}) 2225$ and $\nu(\text{Ru–H}) 1930 \text{ cm}^{-1}$. Complex IV is thermally more stable than $\text{Rh}(\text{C}_5\text{Me}_5)(\text{PMe}_3)\text{H}(\text{C}_6\text{H}_5)$ [9] since it decomposes under nitrogen in toluene- d_8 with a half-life at 100°C of about



30 min compared to 4 h at 60°C for the rhodium complex. Benzene is cleanly eliminated during the decomposition; the metal-containing products are under investigation.

A typical reaction of low valent complexes containing secondary phosphine ligands is P—H bond cleavage to give dimers or clusters containing phosphido bridges [10–12]. A ^{31}P NMR study of solutions from photolysis reaction 3 shows that complex IV is the major product using these concentrations. In addition the secondary phosphine hydrogen does not take part in hydrogen exchange with the activated benzene during the photolysis reaction. This was demonstrated by irradiating complex I in a C_6D_6 /pentane mixture under the same conditions as reaction 3 and isolating pure $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PHCy}_2)\text{D}(\text{C}_6\text{D}_5)$ (V), eq. 4. Complex V in pentane appears as a triplet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum because of



phosphorus—deuterium coupling. A strong stretch $\nu(\text{P—H})$ is observed at 2225 cm^{-1} and P—H resonances are seen in the ^1H NMR spectrum with intensities consistent with the formulation for V (Table 1). We have no evidence for the activation of pentane during the reactions described here.

The photoinduced elimination of *cis*-hydride ligands as dihydrogen from transition metal complexes and the insertion of the unsaturated complexes so produced into carbon—hydrogen bonds are well known reactions [1,2,4,13–17]. The reactions of complex I provide yet another example. A unique aspect of the reactivity of I is its preference for C—H over P—H bond cleavage. This selectivity may arise because C—H activation can proceed via a favorable intramolecular process involving the reactive intermediate $\text{Ru}(\text{C}_6\text{Me}_6)(\text{PH}(\text{C}_6\text{H}_{11})_2)(\eta^2\text{-C}_6\text{H}_6)$ [18] whereas intermolecular P—H bond cleavage would be hindered by the bulky ligands around the ruthenium. We have no information regarding intramolecular P—H activation although reversible 1,2-shifts of hydrogen between nitrogen and iridium have been observed [19]. Other transition metal complexes display unusual intramolecular selectivities [1] for cleavage of C—H bonds over reactive bonds such as C—I [20] or C—F [14] and intermolecular selectivities [1] for cleavage of C—H bonds in alkanes over C—H or C—Cl bonds of chlorinated solvents [21]. Exploiting such properties may lead to the design of valuable homogeneous catalysts or reagents for hydrocarbon functionalization. Further work is in progress in our laboratory using ruthenium and secondary phosphine ligands.

We thank the Natural Sciences and Engineering Research Council of Canada for the support of this work and Johnson-Matthey for a generous loan of ruthenium chloride.

References

- 1 A.H. Janowicz and R.G. Bergman, *J. Am. Chem. Soc.*, **105** (1983) 3929.
- 2 W.D. Jones and F.J. Feher, *Organometallics*, **2** (1983) 562.
- 3 J.K. Hoyano and W.A.G. Graham, *J. Am. Chem. Soc.*, **104** (1982) 3723.
- 4 H. Azizian and R.H. Morris, *Inorg. Chem.*, **22** (1983) 6.
- 5 H. Werner and H. Kletzin, *J. Organomet. Chem.*, **228** (1982) 289.
- 6 K. Isobe, P.M. Bailey and P.M. Maitlis, *J. Chem. Soc. Dalton Trans.*, (1981) 2003.
- 7 H. Werner and H. Kletzin, *J. Organomet. Chem.*, **243** (1983) C59.
- 8 Complexes III and IV contain chiral ruthenium centres and have similar P—H spin systems.

- 9 W.D. Jones and F.J. Feher, *J. Am. Chem. Soc.*, **104** (1982) 4240.
- 10 E. Keller and H. Vahrenkamp, *Angew. Chem. Int. Ed. Engl.*, **16** (1977) 731.
- 11 R.B. English, R.J. Haines and N.D. Steen, *J. Organomet. Chem.*, **238** (1982) C34.
- 12 K. Yasufuku and H. Yamazaki, *J. Organomet. Chem.*, **28** (1971) 415.
- 13 C. Giannotti and M.L.H. Green, *J. Chem. Soc. Chem. Comm.*, (1972) 1114.
- 14 M. Berry, K. Elmitt and M.L.H. Green, *J. Chem. Soc. Dalton Trans.*, (1979) 1950.
- 15 G.L. Geoffroy, *Prog. Inorg. Chem.*, **27** (1980) 123.
- 16 M.G. Bradley, D.A. Roberts and G.L. Geoffroy, *J. Amer. Chem. Soc.*, **103** (1981) 379.
- 17 S. Muralidharan, G. Ferraudi, M.A. Green and K.G. Caulton, *J. Organomet. Chem.*, **244** (1983) 47.
- 18 Similar η^3 -arene complexes that activate aromatic C—H bonds have been reported: (a) J.R. Sweet and W.A.G. Graham, *Organometallics*, **2** (1983) 135; (b) ref. 9.
- 19 M.D. Fryzuk and P.A. MacNeil, *Organometallics*, **2** (1983) 683.
- 20 M. Gomez, D.J. Robinson and P.M. Maitlis, *J. Chem. Soc. Chem. Commun.*, (1983) 825.
- 21 R.H. Crabtree, M.F. Mellea, J.M. Mihelcic and J.M. Quick, *J. Am. Chem. Soc.*, **104** (1982) 107.