C–H activation of benzene with Cp*Ru(CO)$_2$CH$_3$

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ABSTRACT

Irradiation of Cp*Ru(CO)$_2$CH$_3$ (**1**) in C$_6$D$_6$ at room temperature yields Cp*Ru(CO)$_2$C$_6$D$_5$ and CH$_3$D (where Cp* = n^5-C$_5$Me$_5$). Cp*Ru(CO)$_2$CD$_3$ (**2**) has also been prepared and similar irradiation in C$_6$H$_6$ yields Cp*Ru(CO)$_2$C$_6$H$_5$ (**3**) and CD$_3$H. This latter reaction confirms that it is the methyl group bonded to ruthenium that is involved in the C–H activation process and not the methyl groups on the Cp* ligand system. The compound Cp*Ru(CO)$_2$C$_6$H$_5$ (**3**) has been prepared for the first time in good yield by the reaction of Cp*Ru(CO)$_2$Br with NaBPh$_4$. X-ray crystal structures of both Cp*Ru(CO)$_2$CH$_3$ (**1**) and Cp*Ru(CO)$_2$C$_6$H$_5$ (**3**) have been determined and the results are reported and discussed.

1. Introduction

The intermolecular activation of C–H bonds by metal complexes is an important process, which may comprise the first step in the catalytic conversion of alkanes into more useful products [1–3]. Platinum group metal compounds are particularly useful in this regard [3]. Metal–alkyl complexes L$_m$M—R in particular have been shown to undergo a variety of C–H activation reactions; recent reviews discuss the current understanding of the sigma-bond metathesis reactions of L$_m$MR with R′–H [4].

There have been a number of recent studies of reactions of L$_m$RuR (with various ligand systems L$_m$; R = CH$_3$ or C$_6$H$_5$) with arenes. Diversi et al. reported the thermolysis (48 h, 120 °C) of Cp*Ru(PMe$_2$Ph)$_2$CH$_3$ in benzene to give Cp*Ru(PMe$_2$Ph)$_2$C$_6$H$_5$ [5]. Oxgaard and Goddard have carried out calculations on the system TpRu(CO)(MeCN)C$_6$H$_5$ which catalyzes hydroarylation via C–H activation [6]. More recently, Cundari et al. have investigated the use of complexes of the type TpRu(L)(MeCN)R (L = CO, PMe$_3$; R = Me or Ph; Tp = hydridotris(pyrazolyl) borate) toward hydroarylation of isonitriles [7].

There are few reports on C–H activation by species generated from the "classical" organometallic complexes CpRu(CO)$_2$CH$_3$ or Cp*Ru(CO)$_2$CH$_3$. Photolysis of [CpRu(CO)$_2$]$_2$ in toluene generates (*inter alia*) CpRu(CO)$_2$H, presumably via H-atom abstraction by the 17-electron intermediate CpRu(CO)$_2$ [8]. Photolysis of a bridged dicylopentadienyl-dirutheniun species leads to (thermally reversible) activation of a ring C–H bond [9]. These various studies prompted us to report our findings on the reaction of the related system Cp*Ru(CO)$_2$CH$_3$ with benzene under irradiation.

2. Results and discussion

Irradiation of a solution of Cp*Ru(CO)$_2$CH$_3$ in C$_6$D$_6$ results in the clean formation of a new species, as judged by the disappearance of the Ru–CH$_3$ peak in the ^{1}H NMR spectrum and the appearance of a single new Cp* peak at δ 1.46 ppm. The IR spectrum of this solution also showed the appearance of two new ν(CO) peaks. High resolution mass spectrometry was consistent with the new species being Cp*Ru(CO)$_2$C$_6$D$_5$. The ^{1}H NMR spectrum of this reaction solution was also consistent with the main organic product being CH$_3$D (Eq. (1)).


$$(1)$$
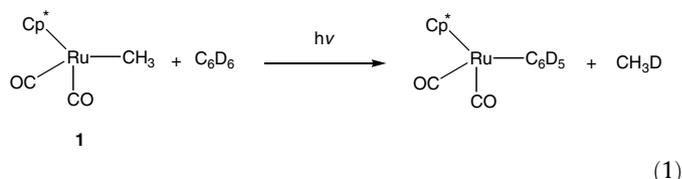
A possible mechanism for this reaction involves loss of CO, oxidative addition of a benzene C–D bond, elimination of CH$_3$D and then re-coordination of CO. Alternatively, the mechanism could involve a concerted process, as has been suggested by others for related systems [5,6]. There is also the possibility that the methane is generated from one of the methyl groups on the pentamethylcyclopentadienyl ring. In order to rule this out, we made the

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perdeuterated methyl compound $Cp^*Ru(CO)_2CD_3$ and reacted it with benzene; NMR spectra were consistent with the formation of CD_3H and $Cp^*Ru(CO)_2C_6H_5$ as shown in Eq. (2).

The reaction of $Cp^*Ru(CO)_2CD_3$ with C_6D_6 yielded $Cp^*Ru(CO)_2$-C_6D_5 and no protio methanes. It is quite conclusive that the CH_3 of the Cp^* is not being involved with the formation of methane (Eq. (3)).

$$\text{2} \quad + C_6H_6 \xrightarrow{h\nu} \text{3} \quad + CD_3H \tag{2}$$

$$\text{2} \quad + C_6D_6 \xrightarrow{h\nu} \quad + CD_4 \tag{3}$$
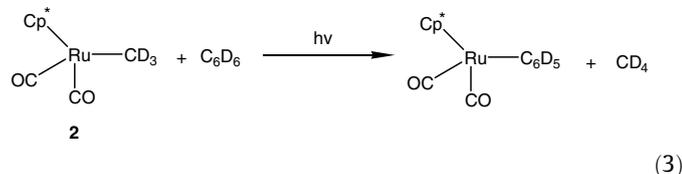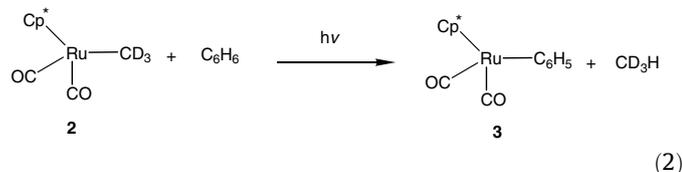
Since the phenyl compound $Cp^*Ru(CO)_2C_6H_5$ (**3**) had not previously been reported, we prepared it independently by a method which has been used for preparing related phenyl compounds [9], shown in Eq. (4). The spectroscopic data obtained for compound (**3**) was completely consistent with the Ru–phenyl compound being produced as described in Eqs. (2) and (4).

$$\text{} + NaBPh_4 \xrightarrow{reflux} \text{3} \quad + \text{Other products} \tag{4}$$
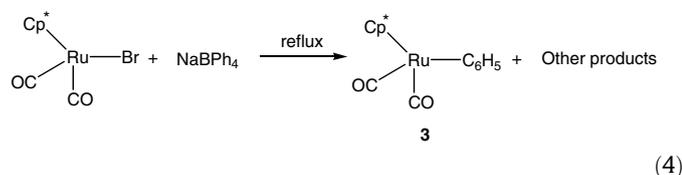
Since no crystal structures have been previously reported on simple alkyl compounds of the type $Cp^*Ru(CO)_2R$, we determined the crystal structures of both the methyl (Fig. 1) and phenyl (Fig. 2) complexes for comparison (Table 1). The molecular struc-
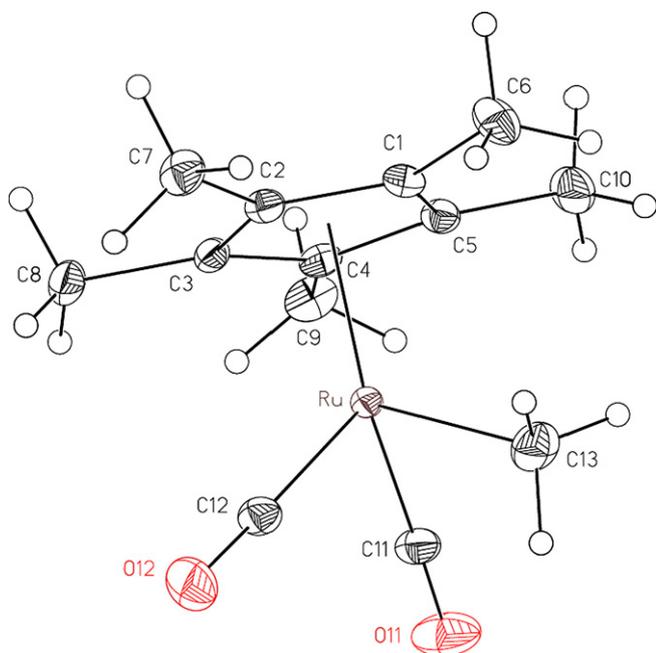

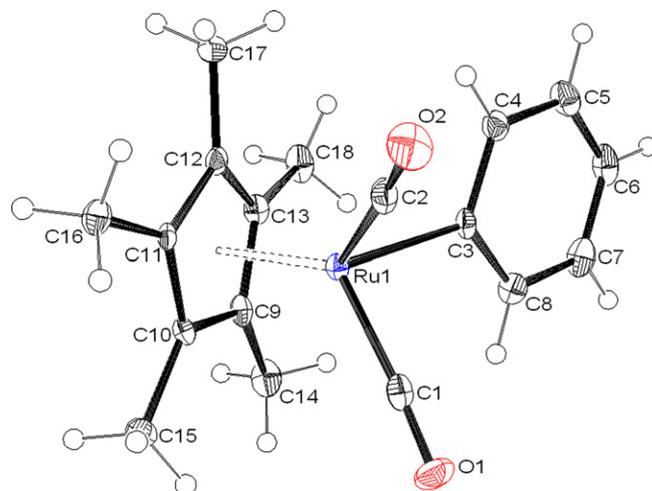**Fig. 2.** Molecular structure of $Cp^*Ru(CO)_2C_6H_5$ (**3**) showing the atom numbering scheme.

Table 1
Comparison of X-ray structures of complexes **1** and **3**

	$Cp^*Ru(CO)_2CH_3$	$Cp^*Ru(CO)_2C_6H_5$
Ru–CO$_{(1)}$	1.8774 (11)	1.871 (4)
Ru–CO$_{(2)}$	1.8803 (11)	1.874 (4)
Ru–R	2.1441 (15)	2.105 (3)
Ru–C$_5$Me$_5$ (average)	2.2669 (12)	2.260 (3)
C–O$_{(1)}$	1.1443 (14)	1.151 (4)
C–O$_{(2)}$	1.1457 (14)	1.147 (4)
OC$_{(1)}$–Ru–CO$_{(2)}$	90.32 (5)	92.68 (15)
OC$_{(1)}$–Ru–R	87.92 (6)	90.70 (13)
OC$_{(2)}$–Ru–R	89.76 (6)	90.71 (13)

tures of compounds **1** and **3** are similar; as one would expect, the Ru–C bond length in the phenyl compound (2.105 (3) Å) is shorter than that in the methyl compound (2.1441 (15) Å). The Ru–C$_6$H$_5$ distance in (**3**) is very similar to that found in $Cp^*Ru(PMe_2Ph)_2C_6H_5$ (2.104 Å) [5]. The angles given in Table 1 are all bigger for the phenyl compound as compared with the methyl compound, which may be due to steric crowding at the metal centre.

3. Conclusions

We have shown that the complex $Cp^*Ru(CO)_2CH_3$ can activate the C–H bond of benzene to give the new Ru–phenyl complex $Cp^*Ru(CO)_2C_6H_5$ and methane. We have also demonstrated that the methyl group in the methane is derived from the methyl group directly bonded to the Ru. The Ru–phenyl complex has also been prepared by another route and successfully characterized. The Ru–C$_6$H$_5$ distance of 2.105(3) Å is significantly shorter than Ru–CH$_3$ (2.144 (2) Å) in $Cp^*Ru(CO)_2R$.

4. Experimental

4.1. General

All preparations were carried out in dry nitrogen saturated solvents using standard Schlenk techniques. Irradiations were carried out with a Englehard Hanovia Lamp (125 W) at a distance of 16 cm from the reaction vessel. Many reactions were carried out in J. Young re-sealable NMR tubes. ^1H and ^{13}C NMR spectra were re-

Fig. 1. Molecular structure of $Cp^*Ru(CO)_2CH_3$ (**1**) showing the atom numbering scheme.

corded on a Varian Mercury 300 or Varian INOVA – 500 spectrometers at room temperature. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane. IR spectra were recorded on a Bio Rad Merlin spectrophotometer. Mass spectra were recorded on a JEOL JMS 600 mass spectrometer.

4.2. Synthesis of compounds 1–3

[Cp*Ru(CO)$_2$]$_2$ was prepared by the method of King et al. [10], and Cp*Ru(CO)$_2$CH$_3$ (1) was prepared by the method of Malisch et al. [11]. The mass spectrum of 1 shows a parent ion at m/e 308 P (16%) with the expected isotope pattern and other peaks at 293 P–CH$_3$ (10%), 279 P–CO (40%), 264 P–CH$_3$–CO (7%), 252 P–2CO (98%) and 235 P–2CO–CH$_3$ (77%). IR ν(CO) (pentane) 2005 (s) and 1946 (s) cm^{-1}. Cp*Ru(CO)$_2$CD$_3$ (2) was also prepared by the method of Malisch et al. [11] using CD$_3$I. The product was characterized by IR, ^{1}H NMR and mass spectra.

4.2.1. Preparation of Cp*Ru(CO)$_2$C$_6$H$_5$ (3)
A solution of Cp*Ru(CO)$_2$Br (0.101 g, 0.2713 mmol) was refluxed with NaBPh$_4$ (93.6 mg, 0.2735 mmol) in methanol for 4 h as reported by Haines et al. [12]. The solvent was removed and the product recrystallized from 3 ml of CH$_2$Cl$_2$/n-hexane (1:2) to give pure (3) as off-white prisms in good yield (72 mg, 72%). Anal. Calc. for C$_{18}$H$_{20}$O$_2$Ru: C, 58.52; H, 5.46. Found: C, 58.36; H, 5.58%. IR (ν(CO) in CH$_2$Cl$_2$): 2005 (s) and 1945 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 6.82-7.42 (m, 5H, Ph), 1.84 (s, 15H, Cp*CH$_3$); ^{13}C NMR: δ 202.8 (Ru–CO), 142.5, 127.7, 123.2, 100.1 (Ru–C$_6$H$_5$), 9.95 (CH$_3$–Cp*).

4.3. Reaction of Cp*Ru(CO)$_2$CH$_3$ with C$_6$D$_6$

Cp*Ru(CO)$_2$CH$_3$ (5.4 mg) was transferred to a J. Young NMR tube and C$_6$D$_6$ (0.6 ml) was added. The resulting solution was subjected to three freeze–thaw cycles, and then allowed to warm to room temperature. The colourless solution was then irradiated for 4 h. The ^{1}H NMR spectrum now showed the peaks of Cp*Ru(CO)$_2$CH$_3$ to have disappeared and a new Cp* peak appeared at δ 1.46 ppm corresponding to Cp*Ru(CO)$_2$C$_6$D$_5$ as well as a singlet at δ 0.14 corresponding to CH$_4$ (23%) and a triplet centred at δ 0.13 corresponding to CH$_3$D (77%). After removing the solvent, the residue in pentane showed ν(CO) peaks in the IR spectrum at 2012 and 1956 cm^{-1}. A mass spectrum of this residue showed a parent ion measured at m/e 375.0812 (calculated for C$_{18}$H$_{15}$D$_5$O$_2$Ru: 375.0821). The data is consistent with the product being Cp*Ru(CO)$_2$C$_6$D$_5$.

4.4. X-ray crystal structure determinations

Cp*Ru(CO)$_2$CH$_3$ (1): Crystals of Cp*Ru(CO)$_2$CH$_3$ were obtained by slow evaporation of the solvent from a cold pentane solution. X-ray data was collected on a Bruker SMART 1000 diffractometer and details of the crystal, data collection and refinement are given in Table 2 (see Supplementary Information).

Cp*Ru(CO)$_2$C$_6$H$_5$ (3): Crystals of Cp*Ru(CO)$_2$C$_6$H$_5$ were grown from hexane solutions on cooling. X-ray data was collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and details of the crystal, data collection and refinement are given in Table 3 (see Supplementary Information).

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