Intermolecular versus intramolecular C–H activation reaction in the thermolysis of [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (Cp* = η^5-C$_5$Me$_5$): formation and crystallographic characterisation of [Ru(Ph)Cp*(PMe$_2$Ph)$_2$]

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Abstract

Thermolysis of the ruthenium complex [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (**1**) (Cp* = η^5-C$_5$Me$_5$) in benzene gives methane and [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**), which is converted slowly to [$\overline{Ru(C_6H_4PMe_2)}$Cp*(PMe$_2$Ph)] (**3**) through the loss of benzene. **2** was structurally characterised by single-crystal X-ray diffraction experiments. DFT calculations were performed in order to understand the behaviour of the ruthenium complex **1** towards inter- or intra-molecular C–H bond activation reactions.
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1. Introduction

In 1988, Lehmkuhl and coworkers [1] reported some interesting C–H bond activation reactions which occur by thermolysis of the ruthenium alkyl complexes [Ru(R)Cp*(L)$_2$] (R = Me, CH$_2$CMe$_3$, L = phosphine). Heating in toluene the methyl ruthenium derivatives carrying at least one aromatic phosphine caused orthometallation of the phosphine with concurrent extrusion of methane. The corresponding neopentyl complexes react instead intermolecularly with arenes by eliminating neopentane and giving aryl derivatives.

In particular when [Ru(Me)Cp*(PMe$_2$Ph)$_2$] was heated in toluene at 140 °C, the orthometallated compound [$\overline{Ru(C_6H_4PMe_2)}$Cp*(PMe$_2$Ph)] (**3**) was obtained

and no intermolecular reaction with the aromatic solvent was observed. Instead alkylation of the chloro complex [RuClCp*(PMe$_2$Ph)$_2$] with neopentyl magnesium chloride in benzene at room temperature was reported to yield the corresponding unstable neopentyl intermediate [Ru(CH$_2$CMe$_3$)Cp*(PMe$_2$Ph)$_2$], which reacts immediately with benzene to give the phenyl derivative [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**) (Scheme 1). By analogy with other ruthenium systems, where the reaction in deuteriated benzene gives undeuteriated neopentane, the authors conclude that the first step is the intramolecular C–H activation of the aromatic phosphine to give the orthometallated complex which evolves subsequently to the phenyl derivative by addition of benzene.

In the course of our studies on C–H activation reactions by ruthenium and iridium complexes under oxidative conditions [2], we wanted to prepare some ruthenium complexes like the orthometallated complex **3** and the corresponding phenyl derivative **2**.

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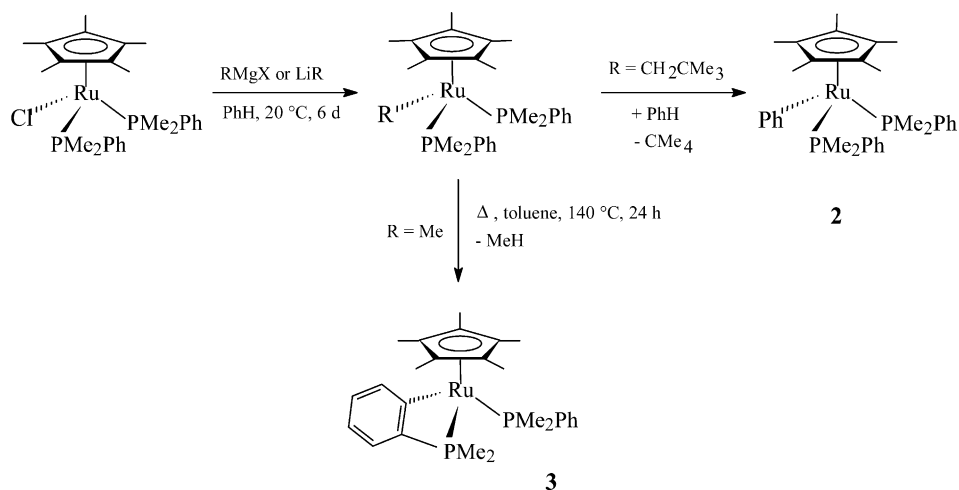
Scheme 1.

Interestingly we found that it is possible to obtain **2** directly by thermolysis of the methyl complex [Ru-(Me)Cp*(PMe$_2$Ph)$_2$] (**1**) in benzene, under slightly different experimental conditions respect to those reported for the cyclometallation to **3**. Compound **2** evolved only slowly to the orthometallated compound **3** and then both compounds can be isolated. In this paper, we report details of this work along with some mechanistic interpretation of the results.

2. Results and discussion

2.1. Thermolysis of [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (1)

Thermolysis of [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (**1**) (48 h, 120 °C, benzene as the solvent instead of 24 h, 140 °C, toluene as reported in the literature [1]), produced, after crystallisation of the crude reaction product from pentane, yellow crystals of a compound which analysed differently from the expected orthometallated complex (**3**). The ^{1}H NMR spectrum was characterised by a triplet at 1.54 ppm (J_{HP} = 1.4 Hz) attributable to the C$_5$Me$_5$ protons and by two virtual triplets at 1.45 ($^2J_{HP}$ + $^4J_{HP}$ = 7.2 Hz) and 1.24 ppm ($^2J_{HP}$ + $^4J_{HP}$ = 7.4 Hz) for the two phosphine methyl groups. Moreover the ^{31}P NMR spectrum in C$_6$D$_6$ (singlet at 20.2 ppm) was entirely different from that reported for **3** in C$_6$D$_5$CD$_3$ [1] (two doublets (J_{AX} = 38.7 Hz) at −47.0 and 32.6 ppm for the orthometallated and non metallated phosphine, respectively). Instead the ^{1}H and ^{31}P NMR data are similar to those reported by Lehmkuhl and co-workers [1] for **3** in deuteriated THF and are quite close to those reported in C$_6$D$_6$ for the phenylderivative [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**), prepared from [Ru(Ph)Cp*(N(O)Et)(PMe$_2$Ph)] by reaction with PMe$_2$Ph in the presence of KN(SiMe$_3$)$_2$ in toluene [3]. This assignment was confirmed by an X-ray structural determina-
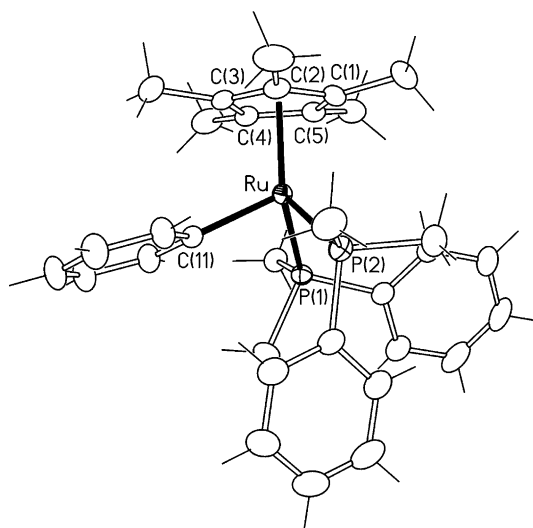
tion on single crystals obtained by slow crystallisation from pentane at −20 °C. The molecular structure of [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] is shown in Fig. 1 and the most significant bond distances and angles are listed in Table 1.

As it is usually encountered in "half-sandwich" derivatives, the co-ordination around ruthenium is three-legged piano stool. The Ru–Cp* (1.931 Å), Ru–P (2.294 Å mean value) and Ru–C(11) (2.104 Å) distances are in keeping with the corresponding distances found in similar compounds of Ru(II) [3–5]. Some features that deserve to be underlined are the heavy upset umbrella deformation of co-ordinated pentamethylcyclopentadienyl ligand and the marked bending of the C(11)–Ru bond out of the phenyl plane. The extent of these effects may be appreciated by comparing the geometry of [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] with that of the analogous [Ru(Ph)Cp*(CO)(PMe$_3$)] and [Ru(Ph)Cp*(N(O)Et)-

Fig. 1. Molecular structure of [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**). Thermal ellipsoids are at 30% probability.

Table 1
Selected bond distances (Å) and angles (°) for [Ru(Ph)Cp*(PMe₂Ph)₂] (**2**) [a,b]

Bond distances

Ru–C(11)	2.104(4)	Ru–C(2)	2.267(4)
Ru–P(1)	2.292(1)	Ru–C(3)	2.281(4)
Ru–P(2)	2.296(1)	Ru–C(4)	2.268(4)
Ru–C(1)	2.281(4)	Ru–C(5)	2.296(4)
Ru–C(2)	2.267(4)	Ru–Cp*	1.931(4)

Bond angles

C(11)–Ru–Cp*	115.3(2)	C(11)–Ru–P(1)	91.1(1)
P(1)–Ru–Cp*	128.3(2)	C(11)–Ru–P(2)	92.4(1)
P(2)–Ru–Cp*	128.5(2)	P(1)–Ru–P(2)	90.89(4)

[a] Estimated standard deviations are given in parentheses.
[b] Cp* denotes the centroid of the pentamethylcyclopentadienyl ligand.

(PMe₂Ph)] [3]. In [Ru(Ph)Cp*(PMe₂Ph)₂] the five methyl carbon atoms C(6) > C(10) stay 0.255 Å (mean value) out of the cyclopentadienyl plane on the opposite side with respect to the ruthenium, while in [Ru(Ph)Cp*(CO)(PMe₃)] and [Ru(Ph)Cp*(N(O)Et)(PMe₂Ph)] the distances are 0.130 and 0.218 Å, respectively. Moreover, the ruthenium atom in [Ru(Ph)Cp*(PMe₂Ph)₂] stays 0.376 Å out of the phenyl ligand plane, while in [Ru(Ph)Cp*(CO)(PMe₃)] and [Ru(Ph)Cp*(N(O)Et)(PMe₂Ph)] the corresponding distances are 0.258 and 0.063 Å, respectively. The easiest explanation of these deformations may be found in the heavy crowding around the metal produced by the presence of the two phosphine ligands.

Apparently [Ru(Ph)Cp*(PMe₂Ph)₂] (**2**) formed by direct reaction of **1** with benzene. In fact heating **1** in C₆D₆ at 120 °C in a sealed NMR tube causes the signals of **1** to decrease up to disappear completely after 2 days with the concurrent formation (in addition to the methane resonance) of signals due to **2** (almost quantitatively). No spectroscopic evidence for the intermediacy of the orthometallated complex **3** was found. Instead when the thermolysis was carried out in C₆D₆ at 140 °C and monitored by ¹H NMR spectroscopy, we found that after a few hours the initially formed phenyl derivative **2** started to be converted into the orthometallated compound **3**: the mixture resulted 50/50 after 24 h, and 70/30 (the orthometallated derivative being prevalent) after further 48 h. After 5 days the ¹H NMR and ³¹P NMR spectra indicated only the presence of the orthometallated compound, the ¹H NMR spectrum showing a triplet at 1.72 ppm (J_{HP} = 1.6 Hz) for the C₅Me₅ protons, a doublet at 1.37 ppm (J_{HP} = 8.7 Hz) due to the two methyl groups of the non metallated phosphine and two doublets at 1.0 (J_{HP} = 7.7 Hz) and 0.87 ppm (J_{HP} = 7.2 Hz) for the two methyl groups of the ortho-metallated phosphine. Finally under the above conditions thermolysis of isolated **2** gave **3** with a qualitatively similar reaction rate. On the other hand, it has to be remarked that by following strictly the published procedure, we were able to obtain the same results as Lehmkuhl et al. [1].

This means that, when the temperature of thermolysis is relatively lower (120 °C), the transformation of the phenyl into the orthometallated derivative is slow enough that the kinetically favoured product **2** is exclusively obtained at low reaction times (Scheme 2). Since the inter- and intra-molecular paths have probably quite close thermodynamic parameters, slightly different experimental conditions (temperature, aromatic substrate) may be important in order to drive preferentially the reaction along one or the other of the two reaction paths. For instance it is well known [2b] that in general increased substitution at the arene ring makes more and more difficult the activation of the arene C–H bonds: then it is without surprise that in toluene as the solvent the intramolecular reaction may prevail on the intermolecular one.

2.2. Reaction energies

The question of intra- versus inter-molecular C–H activation by transition metal complexes has been addressed many times in the literature both on experimental and theoretical grounds [6]. As early as 1983 Bergman and Janowicz [7] found an approximate 1:1 ratio of the intra- and inter-molecular products in the reaction of [IrCp*(PR₃)H₂] with hydrocarbons. Later Jones and Feher [8] investigated the selectivity of the phosphine cyclometallation vs. benzene activation by the [RhCp*(PCH₂PhMe₂)] system (this phosphine was chosen in order to have similar steric constraints for the inter- and intra-molecular pathways) finding out a moderately high thermodynamic preference for the intramolecular activation and a kinetic selectivity for the intermolecular reaction (in neat solvent). In a theoretical study [9] Niu and Hall showed that for the system [Ir(Me)Cp(PMe₃)]⁺ (Cp = η⁵-C₅H₅) the intermolecular
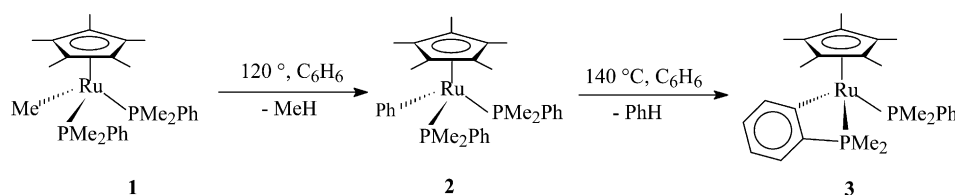
Scheme 2.

Table 2
Calculated relative energies (ΔE (kcal/mol)) for the complexes involved in the C–H activation reactions described in the text[a]

Complex	ΔE
[Ru(Me)Cp*(PMe$_2$Ph)$_2$] (**1**)	0
[Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**)	36.4
[Ru(C$_6$H$_4$PMe$_2$)Cp*(PMe$_2$Ph)] (**3**)	9.7
[Ru(*o*-C$_6$H$_4$Me)Cp*(PMe$_2$Ph)$_2$]	45.8
[Ru(*m*-C$_6$H$_4$Me)Cp*(PMe$_2$Ph)$_2$]	27.3
[Ru(*p*-C$_6$H$_4$Me)Cp*(PMe$_2$Ph)$_2$]	27.2
[Ru(CH$_2$CMe$_3$)Cp*(PMe$_2$Ph)$_2$]	1.8
[Ir(Me)$_2$Cp*(PPh$_3$)] (**4**)	0
[Ir(Me)(Ph)Cp*(PPh$_3$)] (**6**)	17.9
[Ir(C$_6$H$_4$PPh$_2$)(Me)Cp*] (**5**)	11.6
[Ir(Ph)$_2$Cp*(PPh$_3$)] (**7**)	40.8
[Ir(Me)(*o*-C$_6$H$_4$Me)Cp*(PPh$_3$)]	15.2
[Ir(Me)(*m*-C$_6$H$_4$Me)Cp*(PPh$_3$)]	7.7
[Ir(Me)(*p*-C$_6$H$_4$Me)Cp*(PPh$_3$)]	8.6

[a] The calculated values in the table are referred to two different zero energies for the two sets of compounds (**1** and **4** for the ruthenium and iridium compounds, respectively). The energies (kcal/mol) of the organic molecules involved in the reactions are: methane, −12.9; neopentane, −35.8; benzene, +23.5; toluene, +14.1.

C–H activation is a lower energy process compared to the cyclometallation of the phosphine which involves the formation of a quite strained three-membered iridacyclic intermediate; evidence for the existence of this intermediate has been acquired by generation of [Ir-(Me)Cp(PMe$_3$)]$^+$ in the gas phase [10].

Different results have been recently obtained for such systems in solution by Bergman which has found that the [Ir(Me)Cp*(PMe$_3$)]$^+$ complex reacts with hydrocarbons without proceeding through an initial cyclometallation step [11].

In the course of our work on the [Ir(Me)$_2$Cp*(PR$_3$)] systems, we have observed that the thermal activation of aromatic C–H bonds by [Ir(Me)$_2$Cp*(PPh$_3$)] produces only intermolecular reaction products, while by oxidatively catalysed activation the orthometallated compound is kinetically preferred over the intermolecular one, which eventually results to be the thermodynamically favoured product: for instance in the case of benzene activation the intermolecular/intramolecular product ratio at equilibrium is 85/15 [2b].

In order to better understand the reactivity of the above ruthenium complexes, we have estimated relative ground-state energies by performing density functional theory (DFT) calculations on the compounds **1**–**3**. The calculated relative energies (ΔE) are summarised in Table 2, from which the energy variations for the intramolecular (exothermic, −3.2 kcal/mol) and the intermolecular reaction (thermoneutral, 0.0 kcal/mol) can be calculated. As a consequence, the **2** → **3** transformation, i.e., the elimination of benzene from the phenyl derivative **2**, is exothermic (−3.2 kcal/mol). This energy difference permits to rationalize **2** and **3** as the kinetic and thermodynamic products, respectively, and is in

agreement with the observed conversion of **2**–**3**. The **1** → **3** reaction in the case of the thermolysis carried out in toluene becomes probably both thermodynamically and kinetically preferred over the intermolecular activation, since, as it was already observed [2a], the inter- versus the intra-molecular product ratio depends on the number of reactive C–H bonds available. As a matter of fact DFT calculations show that in this case the formation of the tolyl isomers is slightly endothermic for the *meta* and *para* isomer (0.3 and 0.2 kcal/mol, respectively), while markedly endothermic for the *ortho* isomer (18.8 kcal/mol).

In the case of the neopentyl analog [Ru(CH$_2$C-Me$_3$)Cp*(PMe$_2$Ph)$_2$] the energy changes for the intermolecular and the cyclometallation reaction are −24.7 and −27.9 kcal/mol, respectively. By considering the other way round, i.e., the sequence neo-pentyl → ortho-metallated → phenyl derivative, proposed by Lehmkuhl and co-workers on the basis of the formation of undeuteriated neopentane during thermolysis in C$_6$D$_6$, the first step does result exothermic (−27.9 kcal/mol), but the second one is endothermic (+3.2 kcal/mol). Then the direct reaction of the neopentyl complex with benzene is preferred being even more favorable than the reaction of the methyl analog **1** with benzene (ΔE = 0 kcal/mol). Indeed the transformation proceeds rapidly at room temperature (actually the neopentyl complex cannot be isolated since once prepared reacts immediately with benzene to give **2**), while the methyl complex **1** reacts slowly at 120 °C.

The **1** → **3** and the **2** → **3** reactions have been mechanistically examined by DFT methods. The preferred logical pathways which emerge from these calculations seem to be entirely unprecedented: in the intermolecular reaction (see Fig. 2) the first step involves the elimination of methane via a concerted mechanism where the incoming benzene molecule interacts with the P–Me bond. In other words methane is eliminated from a P-bonded methyl group and a benzene hydrogen to give a coordinated methyldiphenylphosphine (then the findings of undeuteriated methane in the reaction in C$_6$D$_6$ does not prove the intermediacy of an ortho-metallated species). In the following step the resulting intermediate undergoes Ru–Me/P–Ph metathesis to give finally **2**. As for the **2** → **3** reaction the results (see Fig. 3) show a rather high activation energy according to the fact that the conversion of the inter- to the intra-molecular product occurs only at long thermolysis times. Interestingly the mechanistic pattern which emerges is a sort of replica of the inter molecular one: actually it is the phosphine phenyl ring which is lost together with an *ortho* hydrogen atom of the ruthenium bound phenyl ligand.

At the moment we have no experimental evidence for such mechanistic pathways although we are working in this direction.
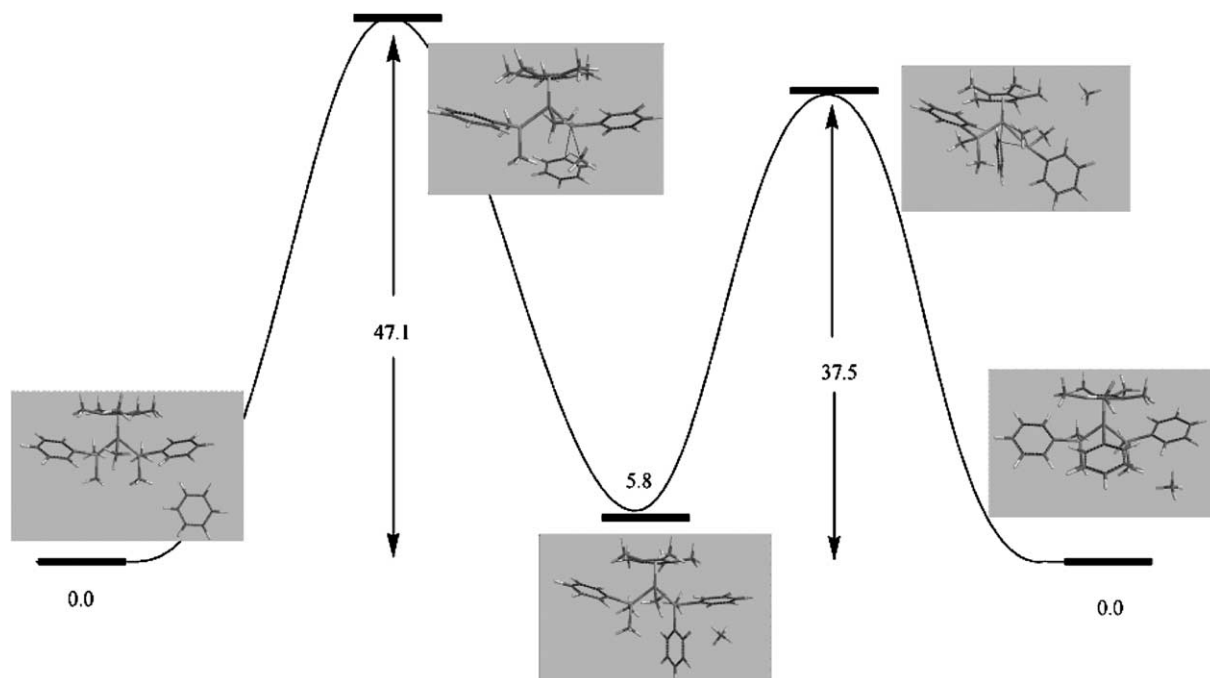
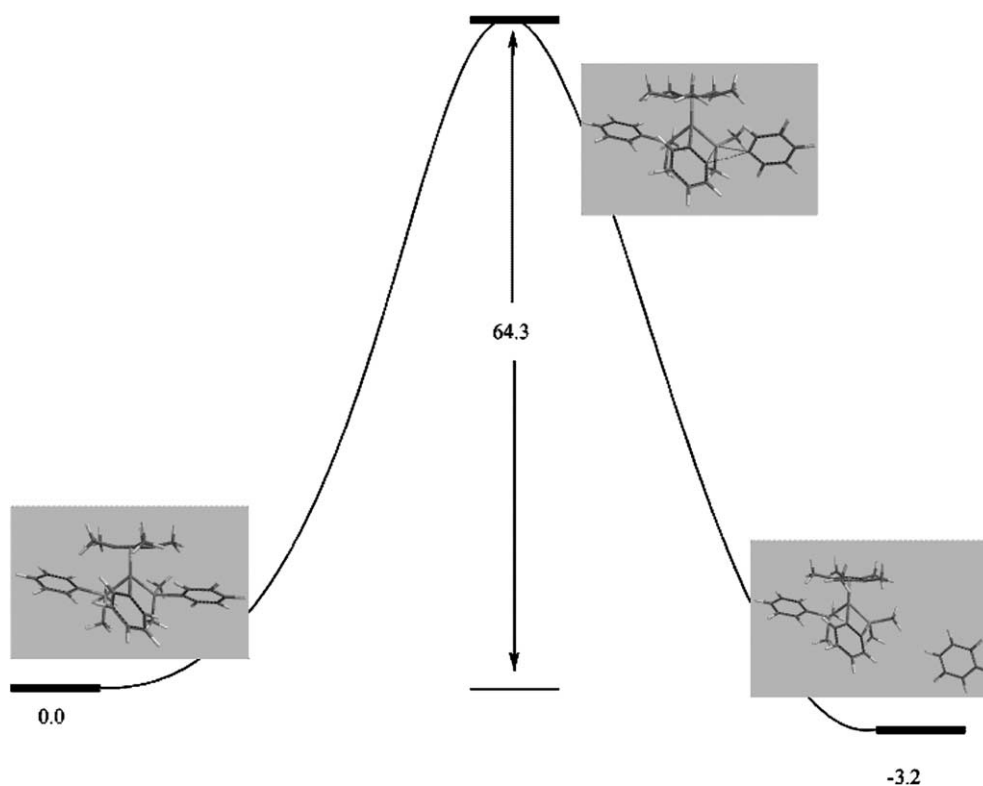Fig. 2. Energy profiles and geometries of the reaction of **1** with benzene to give **2** and methane.

Fig. 3. Energy profiles and geometries of the thermolysis of **2** to give **3** and benzene.

We have also extended our calculations to the reactions of the iridium(III) system [Ir(Me)₂Cp*(PPh₃)] with arenes under thermal conditions, which we have reported in a precedent paper [2a,b]. Now the thermal reactions of **4** with benzene to give first the methylphenyl **6** and then the diphenyl iridium derivative **7**, are both favoured, being exothermic for 18.5 kcal/mol and 13.5 kcal/mol, respectively. It is remarkable that the orthometallated complex **5** was never formed under thermal conditions, but only under electron transfer
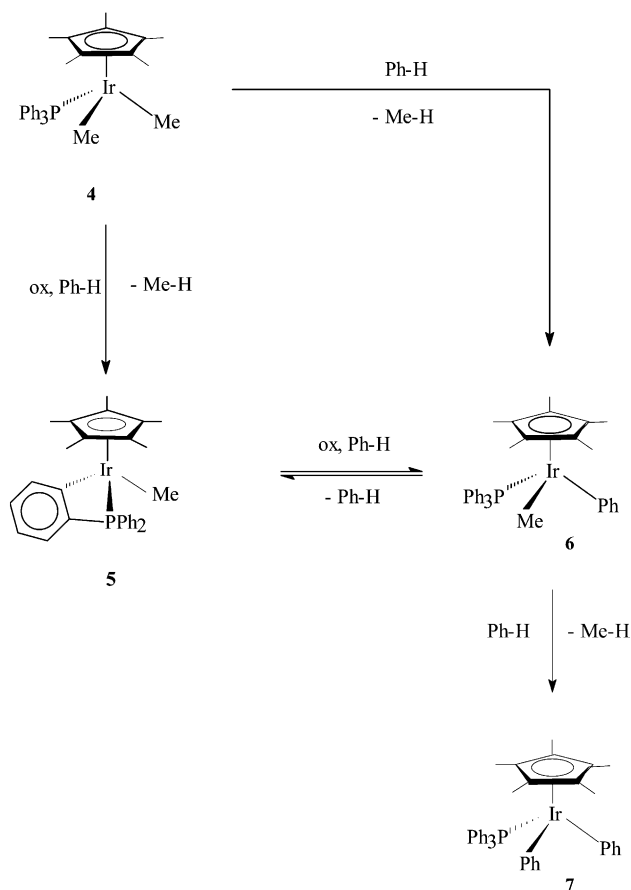
Scheme 3.

catalysis (Scheme 3). Accordingly, our calculations show that the **4 → 5** conversion is only slightly favoured (−1.3 kcal/mol).

Finally, we have performed an even more stringent test of the reliability of our calculations, by examining the case of the activation of toluene by the same above iridium complex **1**, which is complicated by isomerism: in fact only the *meta* and *para* C–H bonds react giving [Ir(Me)(C$_6$H$_4$Me)Cp*(PPh$_3$)] as a 2/1 mixture of the *meta* and *para* isomers, according to the statistically expected value. The calculations confirm the observed thermodynamic preference for the *meta* (−19.3 kcal/mol) respect to the *para* isomer (−18.4 kcal/mol), the calculated *meta/para* ratio (1.9) being practically identical to the experimental one.

3. Conclusions

The main conclusions of the work here reported are that the methyl half-sandwich ruthenium derivative [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (**1**) is able to activate not only the coordinated phosphine aromatic C–H bonds but also benzene used as the solvent. Then under the appropriate conditions **1** activates intermolecularly benzene as the analogous neopentyl derivative does.

The hypothesis that orthometallated complexes are intermediates of the intermolecular C–H activation seems to be uncorrected (at least in the activation of benzene by **1**), since apparently the phenyl derivative **2** (the kinetically favoured product) evolves eventually to **3** (the thermodynamically favoured product) and not the other way round. Theoretical calculations agree with these experimental results. Then if a similar pattern holds also for the neopentyl complex [Ru(CH$_2$C-Me$_3$)Cp*(PMe$_2$Ph)$_2$], the formation of undeuteriated neopentane observed in the reaction with deuteriated benzene [1] could be attributed to the cyclometallation of some other ligand. As shown above, energy profile calculations in our case point out to an unprecedented reaction pattern for the methyl (**1**) to phenyl (**2**) derivative conversion, which could account for the formation of undeuteriated methane without necessarily invoking an orthometallated intermediate. We are planning further work in order to get experimental support for such possibility.

It is possible that Lemhkuhl and co-workers did not observe the formation of the tolyl derivative by thermolysis of **1** in toluene owing to a fortuitous concourse of circumstances (the reactivity of toluene should be lower than that of benzene [2b], as it is confirmed by theoretical calculations), or the initially formed tolyl complex could rapidly eliminate toluene to give the thermodynamically favoured orthometallated product.

4. Experimental

The reactions and manipulation of organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compound [Ru(Cl)Cp*(PMePh$_2$)$_2$] was prepared from [RuCl$_2$Cp*]$_2$ by reaction with an excess of phosphine, according to the procedure described by Tilley for the trimethylphosphine analog [12]. [Ru-(Me)Cp*(PMe$_2$Ph)$_2$] (**1**) was prepared according to a modification [13] of the published procedure [1].

4.1. Thermolysis of [Ru(Me)Cp*(PMe$_2$Ph)$_2$] (1) in C$_6$D$_6$: formation of [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (2)

A Carius tube was loaded with 45 mg (0.084 mmol) of **1** and 3 ml of benzene. The tube was degassed and flame-sealed under argon. It was kept in a thermostated oil bath at 120 °C for 2 days. The vial was broken and the solvent was eliminated under vacuum. The solid residue was crystallized from pentane at −20 °C to give yellow crystals (80%) having the same properties as [Ru(Ph)Cp*(PMe$_2$Ph)$_2$] (**2**) [3]. Anal. Found: C, 65.1; H, 6.9%. C$_{32}$H$_{42}$P$_2$Ru. Calc. C, 65.5; H, 7.2%. ^{1}H NMR (C$_6$D$_6$): δ1.54 (15H, t, J_{HP} = 1.3 Hz, C$_5$Me$_5$), 1.45 (6H, vt, $^2J_{HP}$ + $^4J_{HP}$ = 7.1 Hz, PMe), 1.24 (6H, vt,

$^2J_{HP}$ + $^4J_{HP}$ = 7.4 Hz, PMe), 6.95–7.55 (15H, bm, Ph). ^{31}P NMR (C_6D_6): δ20.2.

The course of the reaction was also monitored by ^{1}H NMR spectroscopy following the thermolysis in C_6D_6.

4.2. Thermolysis of [Ru(Ph)Cp*(PMe_2Ph)_2] (2) in C_6D_6: formation of [Ru(C_6H_4PMe_2)Cp*(PMe_2Ph)] (3)

A NMR tube was charged with a C_6D_6 (1 ml) solution of **2** (15 mg) and heated at 140 °C. ^{1}H NMR spectroscopy showed the progressive transformation of **2** into the orthometallated complex [Ru(C_6H_4PMe_2)Cp*(PMe_2Ph)] (**3**). The conversion was complete after 5 days. ^{1}H NMR (C_6D_6): δ1.72 (15H, t, J_{HP} = 1.6 Hz, C_5Me_5), 1.37 (6H, d, J_{HP} = 8.7 Hz, PMe), 1.0 (3H, d, J_{HP} = 7.7 Hz, Ru(C_6H_4PMe)), 0.87 (3H, d, J_{HP} = 7.2 Hz, Ru(C_6H_4PMe)), 6.5–7.5 (9H, bm, Ph). ^{31}P NMR (C_6D_6): δ−47.0 (d, J_{PP} = 38.7 Hz, Ru(C_6H_4PMe)), 32.6 (d, J_{PP} = 38.7 Hz, PMe_3).

4.3. Crystallographic studies

Yellow tabular crystals of [Ru(Ph)Cp*(PMe_2Ph)_2] (**2**) were obtained by slow evaporation of a pentane solution. One of them was cut in air and the fragment was sealed in a glass capillary under dinitrogen atmosphere. It was then mounted on a Siemens P4 four-circle diffractometer, equipped with graphite monochromated Mo Kα radiation. The lattice parameters listed in Table 3 were obtained. The intensity data collection was made by following the conditions listed in the same Table. The data were corrected for Lorentz, polarisation and absorption effects by means of the ψ-scan method [14]. The structure was solved by the standard Patterson and Fourier methods and was refined by full-matrix least-squares methods contained in SHELX 97 program [15]. The hydrogen atoms were in part localized by means of the difference Fourier map and in part placed in calculated positions. Some reliability factors obtained in the last refinement cycle are listed at the bottom of Table 3. The programme PARST 97 [16] was also used for geometric calculations.

4.4. Computational details

Full optimization of the molecular geometries, transition state geometries and calculation of the energy profile of the ruthenium and iridium complexes involved in the C–H activation reactions were carried out using the '02 version of Spartan computer program [17], running on an Unix workstation. The minima and the transition states were characterized by performing a DFT vibrational frequency analysis. DFT data were obtained by adopting the BP scheme that uses the functional pro-

Table 3
Crystal data and structure refinement for [Ru(Ph)Cp*(PMe_2Ph)_2] (2)

Empirical formula	$C_{32}H_{42}P_2Ru$
Formula weight	589.67
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$ (Nr. 14)
Unit cell dimensions	
a (Å)	16.766(3)
b (Å)	14.019(3)
c (Å)	12.809(3)
β (°)	106.45(3)
V (Å^3)	2887.4(10)
Z	4
D_{calc} (mg/m^3)	1.356
Crystal size (mm^3)	$0.58 \times 0.33 \times 0.20$
θ Range for data collection (°)	2.20–24.01
Reflections collected	4754
Independent reflections [R_{int}]	4523 [0.0261]
Completeness to θ = 24.01°	95.3%
Data/restraints/parameters	4523/0/316
Goodness-of-fit[a] on F^2	1.002
Final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0351, wR_2 = 0.0768
R indices[a] (all data)	R_1 = 0.0600, wR_2 = 0.0873
Largest diff. peak and hole (e · Å^{-3})	0.370 and −0.277

[a] Goodness-of-fit = $\left[\sum\left[w(F_o^2 - F_c^2)^2\right]/(N-P)\right]^{1/2}$, where N, P are the numbers of observations and parameters, respectively, $R_1(F_o)$ = $\sum||F_o|-|F_c||/\sum|F_o|$; $wR_2(F_o^2)$ = $\left[\sum\left[w(F_o^2 - F_c^2)^2\right]\Big/\sum\left[w(F_o^2)^2\right]\right]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0418Q)^2 + 1.83Q]$ where $Q = [MAX(F_o^2, 0) + 2F_c^2]/3$.

posed by Becke [18] and the Perdew [19] correlation functional, adopting the 6-31G** base functions set, which is appropriate for calculations of split-valence-plus-polarization quality.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 23002. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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