

Photochemical C–H bond activation; NMR, matrix and laser kinetic studies

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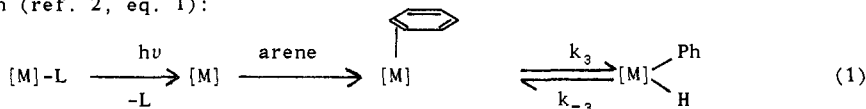
Abstract - Experiments are reported on the combined application of product studies, matrix isolation and laser flash photolysis to organotransition metal complexes which act as C–H bond activators. Direct evidence for precoordination of arenes in the η^2 -mode is reported. Several complexes containing coordinated ethene were found to isomerise to metal(vinyl)hydride complexes. The proposed intermediates in C–H bond activation, CpRhCO and $(\text{mes})\text{OsCO}(\text{Cp} = \eta^5\text{-C}_5\text{H}_5, \text{mes} = \eta^6\text{-C}_6\text{H}_3\text{Me}_3)$, may be detected by matrix isolation. Both species react with methane at 20 K.

INTRODUCTION

Many C–H bond activation reactions are initiated photochemically from neutral precursors making them suitable (i) for kinetic investigations by laser flash photolysis and (ii) for investigations of reactive intermediates by matrix isolation (ref. 1). When combined with information from conventional product studies, especially NMR, a detailed reaction mechanism may be built up. In this paper, examples are taken from the photochemistry of $\text{CpRh}(\text{CO})\text{L}$, $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$, $(\eta^6\text{-arene})\text{Os}(\text{CO})\text{L}$ and $(\eta^6\text{-arene})\text{Os}(\text{CO})\text{H}_2$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, arene = C_6H_6 , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$). Photolysis of these compounds may induce insertion into the C–H bonds of arene or alkane solvents, or intramolecular insertion into one of the ligands.

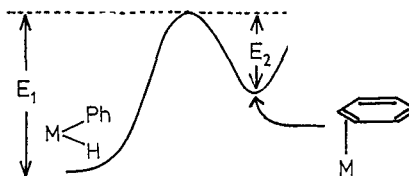
ARENE ACTIVATION

The typical mechanism of photochemical arene activation involves three stages, generation of a coordinatively unsaturated intermediate, η^2 -coordination of the arene and C–H insertion (ref. 2, eq. 1):

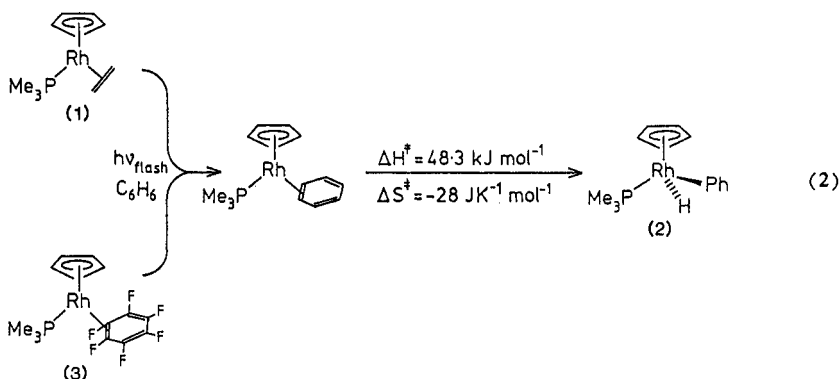


Studies of fluxional rearrangements of (phenyl)hydride complexes provide estimates of the barrier, E_1 corresponding to process k_{-3} , but barrier, E_2 for the forward process, k_3 , has never been measured (see figure 1).

Figure 1: Schematic potential energy diagram for arene C–H activation

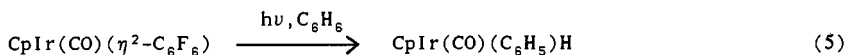
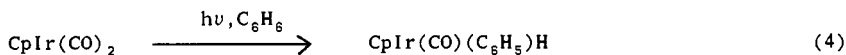
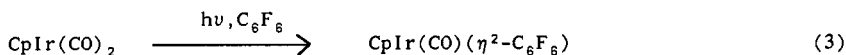


We have demonstrated that photolysis of $\text{CpRh}(\text{C}_2\text{H}_4)(\text{PMe}_3)$, **1**, in benzene yields $\text{CpRh}(\text{PMe}_3)(\text{Ph})\text{H}$, **2**. When **1** is photolysed in C_6F_6 , the product is established by NMR and crystallography to be $\text{CpRh}(\text{C}_2\text{H}_4)(\eta^2\text{-C}_6\text{F}_6)$, **3**. This stereochemically rigid complex is thermally stable in benzene, but is rapidly photolysed to give **2**. Laser flash photolysis of either **1** or **3** in benzene leads to a transient with very similar kinetic and absorption properties. The decay of this species is unaffected by the presence of 1 atm C_2H_4 or by dilution of the benzene with cyclohexane. However the yield of transient decreases as the benzene concentration is reduced. These observations are consistent with an assignment of this transient as $\text{CpRh}(\text{C}_2\text{H}_4)(\eta^2\text{-C}_6\text{H}_6)$. The activation parameters for its conversion to **2** have been determined (eq. 2, ref. 3):

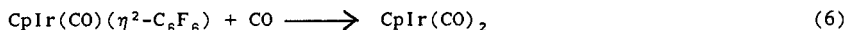


The value of ΔH^\ddagger of 48.3 kJ mol⁻¹ for E₂ (figure 1) may be compared to the value of E₁ = 76 kJ mol⁻¹ measured for the η⁵-C₅Me₅ analogue. (The value of E₁ for the C₅H₅ complexes is not yet available).

The C₆F₆ complex, **3**, the first of its kind, reacts thermally with CO to form CpRh(PMe₃)₂CO and photochemically with benzene or Et₃SiH giving **2** and CpRh(PMe₃)₂(SiEt₃)H respectively. The stability of **3** proves that C₆F₆ is not an inert solvent contrary to recent claims in the context of CpIr(CO)₂ photochemistry (ref. 4). Moreover, it offers an explanation for the lack of variation with CO pressure of the quantum yield for formation of CpIr(CO)(Ph)H in C₆F₆ solutions doped with benzene. Three photoprocesses probably occur in this system (eq. 3-5)



The lifetime of any intermediate will be too short to be quenched significantly by CO, since the solvent is reactive. However slow thermal reaction with CO may occur (eq. 6). In conclusion, the experiments reported in ref. 4 do not distinguish between ring-slip and dissociative mechanisms for the photolysis of CpIr(CO)₂.



ETHENE ACTIVATION

One of the principal problems of C-H activation lies in the prediction of whether intermolecular activation will occur in preference to insertion into C-H bonds of the complex. We first demonstrated insertion into ethene C-H bonds in a mononuclear complex for the case of CpIr(C₂H₄)₂ (ref. 5, eq. 7):



Other examples have also been reported (ref. 6). We have now demonstrated that a reaction of this type occurs on photolysis of both CpRh(PMe₃)(C₂H₄) and (η⁶-arene)Os(CO)(C₂H₄) (arene = C₆H₆ or 1,3,5-C₆H₃Me₃) in low-temperature matrices. In both cases the identity of the product has been confirmed by C₂D₄ substitution, in the former also by P(CD₃)₃ substitution. Comparison of the IR spectra of the complete group of metal(vinyl)hydride complexes show that the vinyl vibrations are very characteristic. Three bands are observed for each complex with frequencies within the ranges 1565 ± 5, 1375 ± 4, 1255 ± 12 cm⁻¹. The isomerisation of (mes)Os(CO)(C₂H₄) (mes = η⁶-1,3,5-C₆H₃Me₃) in C₂D₄-saturated toluene and of (mes)Os(CO)(C₂D₄) in

TABLE 1 Isomerisation of Ethene Complexes

Complex	Matrices	Solution
CpRh(C ₂ H ₄) ₂	No	No, but scrambling*
CpRh(C ₂ H ₄)(PMe ₃)	Yes	No
CpIr(C ₂ H ₄) ₂	Yes	Yes
(mes)Os(CO)(C ₂ H ₄)	Yes	Yes

*Photolysis under C₂D₄ atmosphere generates C₂D_{4-x}H_x

C₂H₄-saturated toluene, occurs without ethene exchange, implying that the reaction is either intramolecular or occurs within the solvent cage. The behaviour of different ethene complexes in solution and matrices is summarised in Table 1.

COORDINATIVELY UNSATURATED INTERMEDIATES AND ALKANE ACTIVATION

Most mechanisms proposed for C-H activation reactions involve coordinatively unsaturated intermediates ([M]) in eq. 1, ref. 2,7). Such species have proved too reactive to observe directly in solution, but may be observed in matrices. For instance, Rest et al have observed CpIrCO by photolysis of CpIr(CO)(H)₂ and CpRhCO from CpRh(CO)₂ (ref. 8). We have observed CpRhCO on photolysis of CpRh(CO)(C₂H₄) (ref. 9). Studies of the arene osmium complexes are assisted by the availability of several precursors. Photolysis of either (mes)Os(CO)(H)₂ or (mes)Os(CO)(CH₃)H in argon matrices generates (mes)OsCO. ($\nu(\text{CO}) = 1889 \text{ cm}^{-1}$). (N.B. Other products are also formed which are not yet identified).

When CpRh(CO)C₂H₄ is photolysed in methane matrices instead of argon, CpRhCO is replaced by a product with a higher frequency $\nu(\text{CO})$ mode assigned as CpRh(CO)(CH₃)H (ref. 9). Rest has made similar observations and has observed the $\nu(\text{Ir-H})$ mode of the corresponding iridium complex (ref. 8). Such studies demonstrate that there can be no substantial barrier to insertion into methane C-H bonds once the coordinatively unsaturated intermediate is formed. This conclusion is supported by our recent investigations of CpRh(CO)L (L = CO, C₂H₄) in cyclohexane solution by laser flash photolysis with UV and IR detection (ref. 10). By these means, we discovered that CpRh(CO)(*c*-C₆H₁₁)H is formed within 400 ns of the laser flash. However, it may be argued that we have built an edifice on one $\nu(\text{CO})$ band - all our conclusions depend on the assignment of a single IR band.

The studies of (arene)osmium complexes allow us to rectify this situation since (mes)Os(CO)(CH₃)H is available for comparison. Indeed photolysis of (mes)Os(CO)₂ or (mes)Os(CO)(H)₂ in methane matrices leads to a product with $\nu(\text{CO})$, $\nu(\text{Os-H})$ and at least 12 further IR bands in common with a spectrum obtained by direct sublimation of (mes)Os(CH₃)H into a methane matrix (Figure 2). In conclusion, the evidence for methane activation at temperatures of ca. 20 K is now wholly conclusive.

CONCLUDING REMARKS

The complementary application of matrix isolation, solution flash photolysis and product studies has enabled us

- (i) to find strong evidence in favour of arene coordination in the η^2 -mode prior to C-H insertion and to measure the energy barrier between these two isomers;
- (ii) to use ethene complexes as precursors both for intermolecular C-H activation and for generation of (vinyl)hydride complexes;
- (iii) to observe coordinatively unsaturated intermediates implicated in C-H activation;
- (iv) to demonstrate that C-H activation of alkanes occurs with minimal activation energy in solution and in matrices.

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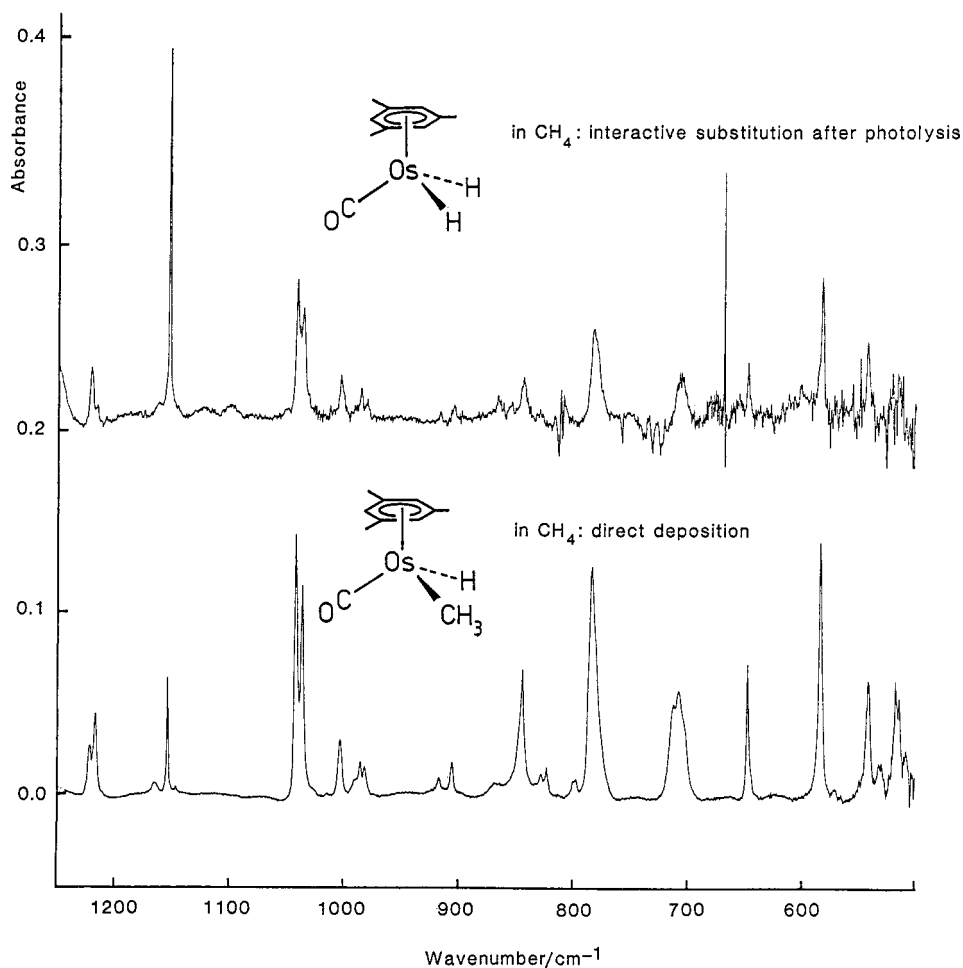


Figure 2. IR spectra in the fingerprint region: above spectrum of (mes)Os(CO)(CH₃)H generated by photolysis of (mes)Os(CO)H₂ in a methane matrix with interactive subtraction of the precursor bands; below spectrum of (mes)Os(CO)(CH₃)H in methane obtained by direct deposition.

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