Photoactivation of Alkanes by Carbonyl(η^5-cyclopentadienyl)dihydridoiridium: Solution and Matrix Isolation Studies

Peter E. Bloyce,[a] Antony J. Rest,*[a] Ian Whitwell,[a] William A. G. Graham,*[b] and Rupert Holmes-Smith[b]

[a] *Department of Chemistry, The University, Southampton SO9 5NH, U.K.*

[b] *Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2*

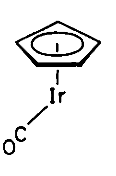
Photoactivation of neopentane at 298 K and CH_4 in a matrix at 12 K by $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ proceeds with overall H_2 loss and intermediates are detected in gas matrices at 12 K; H/D scrambling observed during neopentane activation at 298 K by $[Ir(\eta^5-C_5H_5)(CO)(D)_2]$ is incompatible with initial D_2 loss as the exclusive pathway.

Attention has recently been focused on the activation of carbon–hydrogen bonds following the discovery that complexes such as $[Ir(\eta^5-C_5Me_5)(PMe_3)(H)_2]$[1] and $[Ir(\eta^5-C_5R_5)(CO)_2]$[2] form isolable hydrido-alkyl and -aryl compounds of the type $[Ir(\eta^5-C_5R_5)(L)(H)(R')]$ (R = Me, L = PMe_3, CO; R = H, L = CO; R′ = alkyl or aryl group) by photolytically induced loss of H_2 or CO. Indeed, matrix isolation studies have shown that methane activation by $[Ir(\eta^5-C_5R_5)(CO)_2]$ will take place even at *ca.* 12 K.[3] The scientific interest in such reactions is reinforced by their longer range potential as the bases of efficient new approaches to hydrocarbon functionalisation. In this communication we describe experiments with $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ (**1**)[4] in solution at 298 K and in matrices at *ca.* 12 K which provide further insight into the mechanisms of C–H activation processes.

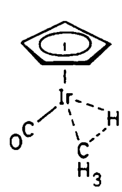
$$[Ir(\eta^5-C_5H_5)(CO)(H)_2]$$
(**1**)

$$[Ir(\eta^5-C_5H_5)(CO)(H)(CH_2CMe_3)]$$
(**2**)

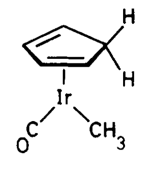
U.v. irradiation of a 10 mM neopentane solution of (**1**) (ν_{CO} 2018 cm^{-1} in cyclohexane) with Pyrex-filtered Hg arc radiation at room temperature (298 K) afforded the C–H activation product $[Ir(\eta^5-C_5H_5)(CO)(H)(CH_2CMe_3)]$ (**2**)† in 55% yield (by ^1H n.m.r., with the only other peaks observed being due to starting material). The obvious interpretation is that an intermediate, **I**, $[Ir(\eta^5-C_5H_5)(CO)]$, is produced by H_2 loss, and that it attacks the solvent forming (**2**). The dihydride complex (**1**) would, in this view, represent an alternative to $[Ir(\eta^5-C_5H_5)(CO)_2]$ for generation of intermediate **I**. More details were sought by carrying out the reaction of the dideuterio complex $[Ir(\eta^5-C_5H_5)(CO)(D)_2]$ with unlabelled neopentane under the same conditions. Formation exclusively of D_2 and unlabelled (**2**) would have been consistent with **I** as the only intermediate in the reaction. In fact, there was extensive and complex scrambling of the deuterium labels. Using $[Ir(\eta^5-C_5H_5)(CO)(D)_2]$ of 94% isotopic purity [*ca.* 6% of the Ir(H)(D) complex], chemical conversion to the hydridoneopentyl complex was 39%. The mass spectrum of the evolved gas showed 48% D_2, 39% HD, and 13% H_2. Combined ^1H and ^2H n.m.r. spectroscopy showed that *ca.* 80% of the product was $[Ir(\eta^5-C_5H_5)(CO)(H)(CH_2CMe_3)]$, with 20% $[Ir(\eta^5-C_5H_5)(CO)(D)(CH_2CMe_3)]$, while *ca.* 25% of the methylene protons in these products had been substituted by deuterium. Moreover, 'unreacted' starting complex after the experiment comprised $IrD_2 : IrHD : IrH_2$ in the ratio 2.1 : 3.4 : 1.0.



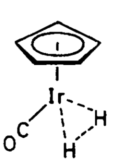
I



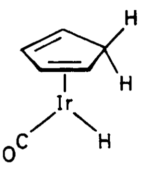
II



III



IV



V

The foregoing results appear to exclude initial D_2 loss and subsequent solvent activation by **I** as the *only* process involved. We think it necessary to invoke intermediates which incorporate H, D, and R (R = CH_2CMe_3) as ligands so that H/D exchange can precede reductive elimination. Three *a priori* possibilities are outlined in equations (1)—(3). Possibility (1) involves ejection and later return of CO, with an Ir^V intermediate related to known[5] stable $[Ir(\eta^5-C_5Me_5)]$ complexes, *e.g.* $[Ir(\eta^5-C_5Me_5)(H)_4]$[5a] and $[Ir(\eta^5-C_5Me_5)(Me)_4]$.[5b,c] Possibility (2) visualises a ring hapticity change, while (3) entails a metal-to-ring deuterium transfer. All three result in the necessary involvement of co-ordinatively unsaturated/supersaturated intermediates. Scrambling of deuterium into the methylene protons of $[Ir(\eta^5-C_5H_5)(CO)(D)(CH_2CMe_3)]$ is reasonable in view of the intramolecular exchange recently observed for $[Ir(\eta^5-C_5Me_5)(PMe_3)(D)(R')]$ (R′ = Me, cyclohexyl).[6]

$$[^2H_2]\,(\mathbf{1}) \xrightarrow[-CO]{h\nu} [Ir(\eta^5-C_5H_5)(D)_2] \xrightarrow{R-H} [Ir(\eta^5-C_5H_5)(D)_2(H)(R)] \xrightarrow[HD,\ or\ D_2]{-RH,\ RD,} \xrightarrow{+CO} \quad (1)$$

$$[^2H_2]\,(\mathbf{1}) \xrightarrow{h\nu} [Ir(\eta^3-C_5H_5)(CO)(D)_2] \xrightarrow{R-H} [Ir(\eta^3-C_5H_5)(CO)(D)_2(H)(R)] \xrightarrow[\substack{HD,\ or\ D_2 \\ and\ \eta^3 \rightarrow \eta^5}]{-RH,\ RD} \quad (2)$$

$$[^2H_2]\,(\mathbf{1}) \xrightarrow{h\nu} [Ir(\eta^4-C_5H_5D)(CO)(D)] \xrightarrow{R-H} [Ir(\eta^4-C_5H_5D)(CO)(D)(H)(R)] \xrightarrow[or\ HD]{-RH,\ RD,} \quad (3)$$

---

† *Spectroscopic data* for (**2**): i.r. (n-hexane) ν_{IrH} 2210w, br., ν_{CO} 2006s cm^{-1}; ^1H n.m.r. (200 MHz, CD_2Cl_2, *J* in Hz) δ 5.43 (s, C_5H_5), 2.50[d, ^2J(HH) 10.9, C*H*H′], 1.94 [dd, ^2J(HH) 10.9, ^3J(HH) 0.4, CH*H*′], 0.85 (s, CH_3), −16.30 (s, Ir*H*); m.s. (70 eV, 65 °C) *m/z* M^+, $(M - C_5H_{12} - CO)^+$.

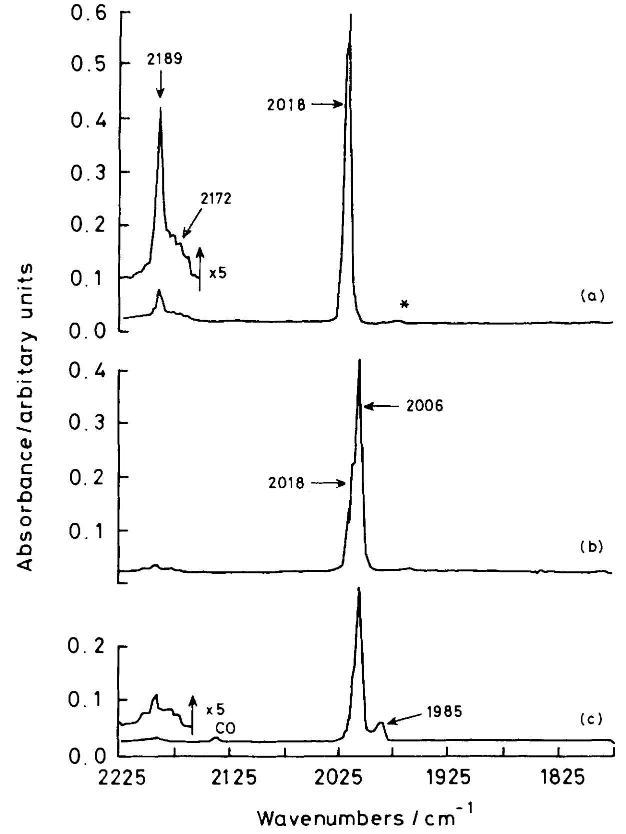


Figure 1. Fourier transform i.r. spectra (Nicolet 7199 Ftir; *ca.* 1 cm^{-1} resolution; number of data points = 16384; number of transform points = 32768) from an experiment with $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ isolated at high dilution in a CH_4 matrix (pulsed deposition of gas phase mixture): (a) after deposition, (b) after 12 h irradiation ($290 < \lambda < 370$, $\lambda > 550$ nm), (c) after 15 min irradiation ($\lambda < 280$, $\lambda > 550$ nm). The band marked * arises from $[Ir(\eta^5-C_5H_5)(^{13}CO)(H)_2]$ present in natural abundance.

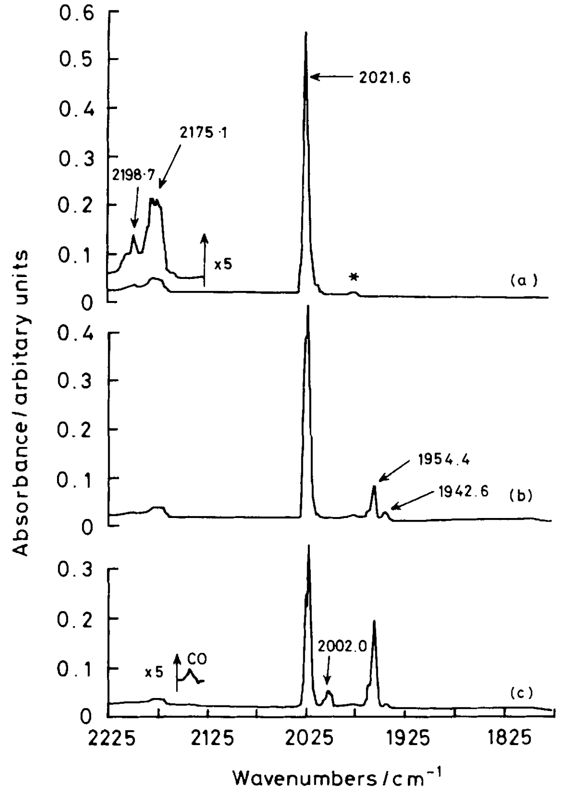


Figure 2. F.t.i.r. spectra (Nicolet 7199 Ftir; *ca.* 1 cm^{-1} resolution) from an experiment with $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ isolated at high dilution in an Ar matrix: (a) after deposition, (b) after 15 h irradiation ($290 < \lambda < 370$ nm, $\lambda > 550$ nm), (c) after 40 min irradiation ($\lambda < 290$ nm, $\lambda > 550$ nm). The band marked * arises from $[Ir(\eta^5-C_5H_5)(^{13}CO)(H)_2]$ present in natural abundances.

In the hope of gaining further insight into the processes involved, photolysis of (**1**) was investigated at 12 K in methane and argon matrices. In a methane matrix, photolysis with light corresponding to the solution reactions ($290 < \lambda < 370$ nm)‡ resulted in high conversion to $[Ir(\eta^5-C_5H_5)(CO)(H)(Me)]$ (ν_{CO} 2006 cm^{-1}), assigned by comparison with previous solution[2b] and matrix isolation[3] studies (Figure 1b). It is apparent from the short photolysis times required that H_2 loss from (**1**) provides a much more efficient route to methane activation than previously observed[3] for CO loss from $[Ir(\eta^5-C_5H_5)(CO)_2]$. Continued photolysis with radiation of higher energy ($200 < \lambda < 280$ nm) produced a further band at 1985 cm^{-1} and some CO (Figure 1c). Subsequent photolysis with the initial source brought about a decrease in the 1985 cm^{-1} band and an increase in the intensity of the band at 2006 cm^{-1} {$[Ir(\eta^5-C_5H_5)(CO)(H)(Me)]$}. The band at 1985 cm^{-1} corresponds exactly with one observed on high energy photolysis of $[Ir(\eta^5-C_5H_5)(CO)_2]$ in CH_4 matrices.[3b] In the present experiment it is clear that the 1985 cm^{-1} band is due to a species produced by secondary photolysis. A likely possibility for the 1985 cm^{-1} species is the methane complex, **II**. However, a diene isomer **III**, where hydrogen has been transferred to the ring, as considered earlier,[3b] cannot be excluded.§

In CD_4 matrices photolysis of (**1**) gave bands assigned to $[Ir(\eta^5-C_5H_5)(CO)(CD_3)(D)]$ (ν_{CO} 2006, ν_{IrD} 1564 cm^{-1}).[3b] When the corresponding dideuteride complex $[Ir(\eta^5-C_5H_5)(CO)(D)_2]$ was photolysed in CH_4 matrices the product was $[Ir(\eta^5-C_5H_5)(CH_3)(H)]$. No scrambling products, *i.e.* $[Ir(\eta^5-C_5H_5)(CO)(CD_3)(H)]$ or $[Ir(\eta^5-C_5H_5)(CO)(CH_3)(D)]$ were observed in these gas matrix experiments.

Photolysis ($290 < \lambda < 370$ nm) of (**1**) in argon (ν_{CO} 2022 cm^{-1} in this matrix) gave new bands at 1954 and 1943 cm^{-1}, but no indication of 'free' CO (Figure 2b). Upon subsequent photolysis at higher energy ($240 < \lambda < 390$ nm and $200 < \lambda < 280$ nm) the intensity of the 1954 cm^{-1} band increased and a weak band appeared at 2002 cm^{-1}, together with a trace of 'free' CO (Figure 2c). Photolysis at longer wavelengths ($\lambda > 370$ nm) caused the band at 1954 cm^{-1} to decrease significantly along with the weak 2002 cm^{-1} band, while the parent band at 2022 cm^{-1} increased in intensity. Annealing the matrices to *ca.* 30 K produced no significant change in the i.r. spectra. The most likely assignment of the major product band in the argon

---

‡ See ref. 3b for details of equipment, spectrometers, light sources, filters, and sample handling in the matrix isolation experiments.

§ A referee has made the interesting suggestion that a reasonable model for $[Ir(\eta^5-C_5H_5)(CO)(\eta^2-CH_4)]$ is provided by $[Ir(\eta^5-C_5H_5)(CO)(\eta^2-C_2H_4)]$, which has ν_{CO} at 1980 cm^{-1} in a CO matrix. An appropriate model compound for the diene isomer **III** is not available.

matrix at 1954 cm^{-1} is to the monocarbonyl $[Ir(\eta^5\text{-}C_5H_5)(CO)]$ **I** produced by H_2 elimination. This assignment is supported by the observed reversal to the parent complex on long wavelength photolysis {*cf.* the recombination of $[Fe(CO)_4]$ with H_2, ref. 7} and by the exact agreement with the band previously assigned to **I** when $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ was photolysed in Ar matrices.[3] Assignments for the weaker bands at 1943 and 2002 cm^{-1} are more speculative. One possibility for the 1943 cm^{-1} band is that it corresponds to the bands seen at 1941 cm^{-1} (in Ar)[3b] or 1937 cm^{-1} (in N_2)[8] which had been tentatively ascribed to the dimer $[\{Ir(\eta^5\text{-}C_5H_5)(CO)\}_2]$. The species giving rise to the band at 2002 cm^{-1} in Ar may be **IV**, the H_2 analogue of **II**. Both are seen to form on high energy photolysis and decrease in intensity during low energy photolysis. The decrease in ν_{CO} upon substitution of H by CH_3 (*i.e.* from **IV** to **II**) is appropriate, and, moreover, the decrease in ν_{CO} in moving from parent dihydride (**1**) to the proposed $\eta^2\text{-}H_2$ complex **IV** is consistent with shifts observed in a series of $\eta^2\text{-}H_2$ complexes and their equilibrium dihydride isomers.[9] On the basis of these arguments, **IV** seems to be the species most likely to be responsible for the 2002 cm^{-1} in Ar matrices; the diene isomer **V** of the parent cannot be excluded, *cf.* **III** as an alternative to **II**.

The matrix experiments show that loss of H_2 by (**1**) is the dominant process at the irradiation wavelengths used in solution experiments, and that possibility (1) which involves initial CO loss is unlikely. However, solution experiments have shown that other transient species, such as those invoked in equations (2) and (3), are likely to be involved in the C–H activation processes. These have not been positively identified in the gas matrices. The activation energy for H/D scrambling in any of the proposed intermediates is likely to be substantial, and the process would not be expected at 12 K, and indeed was not observed.

The Southampton group thanks the S.E.R.C. and British Gas for Studentships (to P. E. B. and I. W., respectively) and for support (to A. J. R.). The Edmonton group thanks the National Sciences and Engineering Research Council for support. We thank Dr. J. K. Hoyano for kindly providing samples of $[Ir(\eta^5\text{-}C_5H_5)(CO)(H)_2]$ and $[Ir(\eta^5\text{-}C_5H_5)(CO)(D)_2]$. We also thank the referees for helpful comments and suggestions.

Received, 1st May 1987;¶ Com. 588

References

1 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352.

2 (a) J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723; (b) J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *ibid.*, 1983, **105**, 7190.

3 (a) A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano, and A. D. McMaster, *J. Chem. Soc., Chem. Commun.*, 1984, 624; (b) *J. Chem. Soc., Dalton Trans.*, 1987, 1181.

4 J. R. Shapley, P. C. Adair, and R. J. Lawson, *Inorg. Chem.*, 1982, **21**, 1702.

5 (a) T. M. Gilbert and R. G. Bergman, *Organometallics*, 1983, **2**, 1458; (b) K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 808; (c) K. Isobe, A. Vasquez de Miguel, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 929.

6 J. M. Buchanan, J. M. Stryker, and R. G. Bergman, *J. Am. Chem. Soc.*, 1986, **108**, 1537.

7 R. L. Sweany, *J. Am. Chem. Soc.*, 1981, **103**, 2410.

8 I. Whitwell, PhD Thesis, University of Southampton, 1986.

9 G. J. Kubas, C. J. Unkefer, B. I. Swanson, and E. Fukushima, *J. Am. Chem. Soc.*, 1986, **108**, 7000.

¶ Received in revised form, 28th March 1988.