Photo-activation of Methane at 12 K by (η^5-Cyclopentadienyl)- and (η^5-Pentamethylcyclopentadienyl)-dicarbonyl-rhodium and -iridium Complexes

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I.r. spectroscopic evidence, including ^{2}H labelling, is presented to show that photolysis of [(η^5-C_5R_5)M(CO)$_2$] complexes (M = Rh, R = Me; M = Ir, R = H, Me) in CH_4 matrices at 12 K leads primarily to [(η^5-C_5R_5)M(CO)(H)(Me)] species whereas in Ar and N_2 matrices only *small* yields of [(η^5-C_5R_5)M(CO)] species are observed.

One of the most important goals in the petrochemicals industry is to find catalysts which will activate saturated hydrocarbons, particularly CH_4, so as to enable their use as feedstocks.[1] The recent discoveries that [(η^5-C_5R_5)Ir(CO)$_2$] complexes [R = H (**1**), Me (**2**)] would photochemically activate C–H bonds in CH_4,[2a] neopentane,[2b] cyclohexane,[2b] and benzene,[2b] and that [(η^5-C_5Me_5)M(PMe$_3$)H$_2$] (M = Rh,[3] Ir[4]) could similarly activate C–H bonds in alkanes have indicated that the goal may be attainable under mild conditions. In the photoreactions the reactive intermediates were presumed to be the 16 electron co-ordinatively unsaturated

[(η^5-C_5R_5)M(CO)$_2$]
(**1**) M = Ir, R = H
(**2**) M = Ir, R = Me
(**3**) M = Rh, R = Me

[(η^5-C_5Me_5)Ir(CO)(H)(Me)]
(**4**)

Table 1. Observed band positions (cm^{-1}) of [(η^5-C_5R_5)M(CO)$_2$] complexes (**1**)—(**3**) and their photoproducts in various matrices at 12 K.

Complex	Matrix CH$_4$(CD$_4$)	Ar	N$_2$	CO
(**2**)[a,b]	2020.7(2020.7)	2025.4	2022.9	2020.3
	1954.7(1953.5)	1958.8	1957.0	1954.3
(**4**)[c,d]	2150.1[e](1548.8)[f]			
	1991.5(1990.2)			
[(η^5-C_5Me_5)Ir(CO)][g]	1971.4(1970.5)	1984.2	1989.3	
[(η^5-C_5Me_5)Ir(CO)$_3$][h]				2053.5
				1998.6
				1980.5

[a] ν_{CO} for (**3**) at 2027.5 and 1964.1 cm^{-1}. [b] ν_{CO} for (**1**) at 2039.9 and 1972.9 cm^{-1}. [c] ν_{RhH} for [(η^5-C_5Me_5)Rh(CO)(H)(Me)] vvw and not unambiguously assigned and ν_{CO} at 2007.7 cm^{-1}. [d] ν_{IrH} for [(η^5-C_5H_5)Ir(CO)(H)(Me)] at 2174.6 cm^{-1} and ν_{CO} at 2004.7 cm^{-1}. [e] ν_{IrH}. [f] ν_{IrD}. [g] ν_{CO} for [(η^5-C_5Me_5)Rh(CO)] and [(η^5-C_5H_5)Ir(CO)] at 1981.1 and 1984.0 cm^{-1}, respectively, in CH$_4$ matrices. [h] ν_{CO} for [(η^3-C_5H_5)Co(CO)$_3$] occur at 2075.0 and 2018.0 cm^{-1}; data from ref. 7.

species [(η^5-C_5R_5)Ir(L)] (L = CO, R = H, Me;[2a,2b] L = PMe$_3$, R = Me[4]). We describe here a matrix isolation[5,6] study of [(η^5-C_5R_5)M(CO)$_2$] complexes [M = Rh, R = Me (**3**); M = Ir, R = H (**1**), Me (**2**)] in which C–H bond activation has been observed even at 12 K. We relate the species formed to the intermediates proposed in solution reactions.

The i.r. spectra of [(η^5-C_5R_5)M(CO)$_2$] complexes in various matrices (Table 1) are typified by the spectrum of (**2**) at high dilution (*ca.* 1 : 2000—1 : 5000) in a pure CH$_4$ matrix at 12 K [Figure 1(a)]. On irradiation ($290 < \lambda < 370$ and $\lambda > 550$ nm†) one new strong terminal CO band appeared (1991.5 cm^{-1}) together with a weak band at 2136.8 cm^{-1} ('free' CO) and a weak band at 2150.1 cm^{-1} [Figure 1(b) and (c)]. Further photolysis with higher energy u.v. light ($200 < \lambda < 370$ nm and $\lambda > 550$ nm‡) afforded a weak band at 1971.4 cm^{-1} [Figure 1(e)], but only after a very extended period of photolysis. When the irradiation of (**2**) was carried out with a pure CD$_4$ matrix bands at 2136.8 and 1990.2 cm^{-1} were observed but no weak band was observed at 2150.1 cm^{-1} [Figure 1(d)]. Instead a weak band was observed at 1548.8 cm^{-1}. The band shift is appropriate for H/D isotope exchange and, therefore, the 2150.1 band in the CH$_4$ matrix can be assigned to an Ir–H stretching mode. Comparison of the matrix isolation data with that for [(η^5-C_5Me_5)Ir(CO)(H)(Me)] (**4**) in solution (ν_{IrH} at 2134vw and ν_{CO} at 1990s cm^{-1} in n-hexane) enables the major matrix product to be identified as (**4**), *i.e.*, photoactivation of CH$_4$ has occurred at 12 K.

In contrast with the reactivity of (**2**) in CH$_4$ matrices, irradiation for *three* days in Ar and N$_2$ matrices was required to produce even small yields of photoproducts. In the case of Ar this is perhaps not so surprising since [(η^5-C_5H_5)Co(CO)$_2$] underwent no apparent photoreaction in Ar at 12 K.[7] The same complex in N$_2$ matrices was, however, speedily converted into [(η^5-C_5H_5)Co(CO)(N$_2$)].[7] The positions of the new bands in Ar and N$_2$ matrices (1984.2 and 1989.3 cm^{-1}, respectively) are consistent with loss of CO from an [M(CO)$_2$] fragment to form an [M(CO)] species. For example, the terminal CO stretching bands for [(η^5-C_5H_5)Fe(CO)$_2$(COMe)] are at 2020 and 1960 cm^{-1} while that for

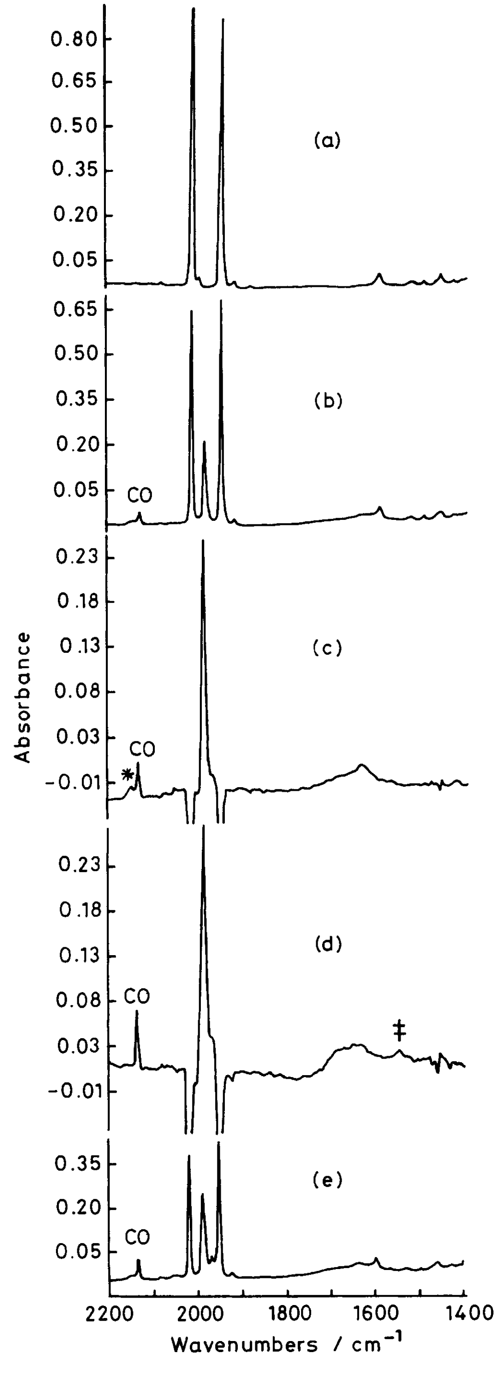

Figure 1. Infrared spectra (Nicolet 7199 Fourier transform i.r. spectrometer; 1000 scans, 1 cm^{-1} resolution) from experiments with (**2**) isolated at high dilution (1 : 2000—1 : 5000) in CH$_4$ [(a)—(c) and (e)] and CD$_4$ [(d)] matrices at 12 K: (a) after deposition; (b) after 70 h photolysis ($290 < \lambda < 370$ nm and $\lambda > 550$ nm); (c) subtraction spectrum [(b) − *A*(a)], where *A* is a scaling factor; (d) analogous subtraction for experiment using CD$_4$ matrix; (e) further photolysis of a CH$_4$ matrix (17 h, $290 < \lambda < 370$ nm and $\lambda > 550$ nm followed by 3 h, $200 < \lambda < 370$ nm and $\lambda > 550$ nm). Bands marked * and ‡ are assigned as ν_{IrH} and ν_{IrD}, respectively.

[(η^5-C_5H_5)Fe(CO)(COMe)] occurs at 1948 cm^{-1}.[8] The minor new matrix species may provisionally be identified as [(η^5-C_5Me_5)Ir(CO)].

In pure CO matrices photolysis leads to new bands at higher wavenumbers (ν_{CO} at 2053.5, 1998.6, and 1980.5 cm^{-1}) in a

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† Quartz gas cell (path length 25 mm) containing Br$_2$ gas (300 Torr) + Pyrex glass disc (thickness 18 mm).

‡ Quartz gas cell (path length 25 mm) containing Br$_2$ gas (300 Torr).

manner analogous to that for [(η^5-C_5H_5)Co(CO)$_2$] in CO matrices. The product in the latter case was assigned as [(η^3-C_5H_5)Co(CO)$_3$],[7] *i.e.*, ring slippage occurs to give [(η^3-C_5Me_5)Ir(CO)$_3$].§ Additionally in 5% ^{13}CO doped Ar matrices (**2**) undergoes ^{13}CO/^{12}CO exchange but this process is considerably slower than for [(η^5-C_5H_5)Co(CO)$_2$]. Interestingly in 5% ^{13}CO doped CH_4 matrices there was no evidence for ^{13}CO incorporation into either (**2**) or (**4**).¶

Photolysis of (**1**) and (**3**) in CH_4 matrices yielded the same band patterns as observed for (**2**) in CH_4 (Table 1), *i.e.* C–H activation occurs.

The failure to generate more than trace amounts of [(η^5-C_5Me_5)Ir(CO)] in Ar and N_2 matrices together with the very slow exchange of bound ^{12}CO with ^{13}CO doped into matrices suggests that the proposed dissociative C–H activation mechanism *via* 16 electron co-ordinatively unsaturated species [(η^5-C_5R_5)Ir(L)] (L = CO, PMe_3; R = H, Me) should be regarded with some scepticism. An alternative mechanism, *i.e. via* a change of ring hapticity η^5-$C_5R_5 \rightleftarrows \eta^3$-$C_5R_5$ as has been demonstrated for [(η^5-C_5H_5)Co(CO)$_2$], deserves serious consideration. Such a change in ring hapticity affords a site at the metal for the incoming ligand whether an exchanging ^{13}CO ligand, a CO affording [(η^3-C_5Me_5)Ir(CO)$_3$], or an interaction with a CH_4 molecule.

The photoactivation of CH_4 at 12 K is the *first* example encountered in matrix isolation studies of metal complexes. It is interesting to note that the Rh complex (**3**) activates CH_4 at 12 K. Irradiation of (**3**) in cyclohexane at 298 K affords [{(η^5-C_5Me_5)Rh(CO)}$_2$],[9] presumably owing to instability of the primary activation products at this temperature.[3]

The Southampton group thanks the S.E.R.C. for support (to A. J. R.) and British Gas for a Scholarship (to I. W.). The Edmonton group thanks the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Received, 28th February 1984; Com. 269

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§ The three band pattern for [(η^3-C_5Me_5)Ir(CO)$_3$] compared with the two band pattern for [(η^3-C_5H_5)Co(CO)$_3$)][7] possibly arises because of the bulky Me groups.

¶ In a thermal reaction at 298 K in n-hexane, exchange of ^{13}CO with (**2**) proceeded readily (half life *ca.* one hour).

References

1 J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, U.S.A., 1980; C. Masters, 'Homogeneous Transition Metal Catalysis,' Chapman and Hall, London, 1981.

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

3 W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562.

4 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; 1983, **105**, 3929.

5 'Matrix Isolation Spectroscopy,' eds. A. J. Barnes, W. J. Orville-Thomas, A. Müller, and R. Gaufrès, NATO ASI Series, D. Reidel, Dordrecht, The Netherlands, 1981.

6 R. B. Hitam, K. A. Mahmoud, and A. J. Rest, *Coord. Chem. Rev.*, 1984, in the press.

7 O. Crichton, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 167.

8 D. J. Fettes, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1981, 2311.

9 M. Stephenson, unpublished work.