Photochemistry of Alkyltricarbonyl(η^5-cyclopentadienyl)tungsten (alkyl = Et, Pr^n, Pr^i, Bu^n, or CH_2Ph), Tricarbonyl(η^5-cyclopentadienyl)-(phenyl)tungsten, Tricarbonyl(η^5-pentamethylcyclopentadienyl)-(n-propyl)tungsten, and Tricarbonyl(η^5-cyclopentadienyl)(ethyl)-molybdenum in Gas Matrices at 12 K and in Solutions at 243 K †

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The photoreactions of $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes (M = Mo or W; R = Et, Pr^n, Pr^i, Bu^n, Ph, or CH_2Ph; R' = H or Me) have been studied in solution (−30 to 20 °C) and in gas matrices (12—30 K). In alkane solutions in the absence of ligands the alkyl complexes that contain β-hydrogens initially undergo β-photoelimination at −30 °C to give $[MH(CO)_2(\text{olefin})(\eta^5\text{-}C_5R'_5)]$ complexes of which only the *trans* isomers could be detected, isolated, and characterised (i.r., n.m.r., and mass spectra). Intramolecular rotation of the olefin ligands about the tungsten–olefin bond axis was observed by low-temperature (−80 °C) n.m.r. spectroscopy; asymmetric olefins gave rotamers in different proportions. Prolonged photolysis of $[M(CO)_3(\text{alkyl})(\eta^5\text{-}C_5R'_5)]$ complexes in alkane solutions gave $[MH(CO)_3(\eta^5\text{-}C_5R'_5)]$ complexes and ultimately $[\{M(CO)_3(\eta^5\text{-}C_5R'_5)\}_2]$. The dimer $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ was the only metal-containing photoproduct when $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ was photolysed alone in pentane at −30 °C, while for $[W(CO)_3(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)]$ the major photoproduct was $[W(CO)_2(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)]$. In the presence of C_2H_4, the phenyl and benzyl complexes gave the *new* monosubstitution products $[W(CO)_2(C_2H_4)R(\eta^5\text{-}C_5H_5)]$ (R = Ph or CH_2Ph) whereas the alkyl complexes all gave $[MH(CO)_2(C_2H_4)(\eta^5\text{-}C_5R'_5)]$ as the main metal-containing product. In CH_4 and CO gas matrices at 12 K the primary photolysis step was shown to be photo-ejection of a CO ligand and the formation of the 16-electron species $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ (R = alkyl or aryl). The identity of the co-ordinatively unsaturated species was confirmed by ^{13}CO-labelling in $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ and fitting the terminal CO stretching bands using an energy-factored force-field program. For the alkyl complexes with β-hydrogens, thermal and photochemical reactions led to the conversion of $[M(CO)_2(\text{alkyl})(\eta^5\text{-}C_5R'_5)]$ species into the olefin–hydride complexes $[MH(CO)_2(\text{olefin})(\eta^5\text{-}C_5R'_5)]$. Gas matrix studies for the W complexes at 12 K showed the presence of both *cis* and *trans* isomers together with intramolecular *cis* $\rightleftharpoons$ *trans* isomerisation whereas in a previous paraffin-wax disc study of $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes (M = Mo or W; R = Et or n-C_5H_{11}; R' = H or Me) at 77 K only *trans* isomers were observed. Photolysis of the benzyl complex, $[W(CO)_3(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)]$, led to the formation of the η^3-bonded benzyl complex, $[W(CO)_2(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)]$ in CH_4, Ar, and CO matrices. The olefin–hydride species with asymmetric olefins, $[MH(CO)_2(\text{olefin})(\eta^5\text{-}C_5H_5)]$, were found to be formed and to exist as rotamers in gas matrices at 12 K. Prolonged photolysis of the alkyl complexes resulted in the formation of $[MH(CO)_3(\eta^5\text{-}C_5R'_5)]$ complexes. In the presence of ligands L (L = C_2H_4 or N_2) the 16-electron intermediate $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$ gave addition products $[W(CO)_2(L)Ph(\eta^5\text{-}C_5H_5)]$ at 12 K but no such products were observed for $[W(CO)_2(CH_2Ph)(\eta^5\text{-}C_5H_5)]$. The combination of solution and matrix isolation studies established that the primary photolysis step for $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes is photo-ejection of a CO ligand and that this can be followed by β-hydrogen transfer to give *cis* and *trans* isomers of $[MH(CO)_2(\text{olefin})(\eta^5\text{-}C_5R'_5)]$. The very low temperature used in this study enabled the *cis* isomer to be observed for the first time.

The photo-induced substitution of carbonyl ligands in complexes of the general formula $[M(CO)_3R(\eta^5\text{-}C_5H_5)]$ (M = Cr, Mo, or W; R = alkyl or aryl) has been known for many years and has been proposed to proceed dissociatively *via* 16-electron $[M(CO)_2R(\eta^5\text{-}C_5H_5)]$ species.[1-4] Only recently, however, has it been recognised that $[M(CO)_3Me(\eta^5\text{-}C_5H_5)]$ complexes can be dealkylated in solution,[2,5-8] if the solvent is not able to stabilise the 16-electron species $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$ formed initially or when a potential ligand is absent. For example, the photolysis of $[M(CO)_3Me(\eta^5\text{-}C_5H_5)]$ (M = Cr, Mo, or W) complexes in solution resulted in the formation of CH_4 *via* hydrogen abstraction.[5-9] Radicals could be detected during the course of these photo-induced dealkylation reactions.[6,9] Derivatives with alkyl ligands that contain more than one carbon atom behave differently. For example, the ethyl complex $[W(CO)_3Et(\eta^5\text{-}C_5H_5)]$ [4,10,11] and the n-pentyl complex $[W(CO)_3(C_5H_{11})(\eta^5\text{-}C_5H_5)]$ [12] undergo photo-induced dealkylation in alkane solution to form the same final metal-containing product, $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$, but in this case the reaction is thought to involve β-hydrogen transfer and the formation of intermediate olefin-hydrido-species, *e.g.* $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$.

The matrix isolation technique has been shown to be very useful for investigating photochemical reactions and for characterising reactive species, in particular metal carbonyl species.[13] Using frozen gas matrices at 12 K we have shown that the principal photoprocess for isolated $[Mo(CO)_3Me(\eta^5\text{-}C_5H_5)]$ molecules is ejection of CO to give the 16-electron species $[Mo(CO)_2Me(\eta^5\text{-}C_5H_5)]$, whose reactivity was demonstrated by its facile recombination with CO at *ca.* 30 K.[14]

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† *Non-S.I. unit employed:* 1 Torr = (101 325/760) Pa.

In polyvinyl chloride film matrices over the temperature range 12—293 K, however, i.r. spectroscopic evidence was found for a photochemical reaction pathway involving radicals.[15] In order to gain a more detailed understanding of the mechanisms of photo-induced dealkylation and dearylation reactions of alkyl- and aryl-transition metal complexes we report here a matrix isolation study of the photolysis of [W(CO)$_3$R(η^5-C$_5$R$'_5$)] complexes (R = Et, Pr^n, Pr^i, Bu^n, Ph, or CH$_2$Ph; R$'$ = H or Me) in frozen gas matrices at 12 K. The results in gas matrices are compared with photolysis studies in solution. A comparison with a metal in another series was effected by studying [Mo(CO)$_3$Et(η^5-C$_5$H$_5$)] in gas matrices at 12 K and in solution. Some low temperature studies have already been performed with [M(CO)$_3$R(η^5-C$_5$R$'_5$)] complexes (M = Mo or W; R = Me, Et, or n-C$_5$H$_{11}$; R$'$ = H or Me) in paraffin wax at 77 K.[11,12] From wide experience of the critical effects of temperature in matrix isolation studies,[13] *e.g.* the recombination of [Mo(CO)$_2$Me(η^5-C$_5$H$_5$)] with CO at *ca.* 30 K,[14] it seemed probable that a study of [M(CO)$_3$R(η^5-C$_5$R$'_5$)] complexes in gas matrices at 12 K might reveal additional species compared to the study at 77 K. A detailed study of the dearylation of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] in solution and in gas matrices at 12 K has not been carried out previously.

Experimental

Preparation of [W(CO)$_3$R(η^5-C$_5$R$'_5$)] *Complexes*.—The starting materials [W(CO)$_3$R(η^5-C$_5$R$'_5$)] were prepared according to literature procedures [16–18] with several modifications.*

(*i*) *Solution Studies*.—All operations were carried out under N$_2$ using the Schlenk technique (Duran-glass Schlenk tubes, transparent at $\lambda > 300$ nm). Solvents were dried over Na/K alloy and freshly distilled. A mercury high-pressure lamp (Hanovia L, 450 W) was used for photolyses. Solutions to be irradiated were cooled to −30 °C by a cryostat and placed 1—2 cm from the water-cooled Hg lamp. Gases produced during photochemical reactions were analysed using a gas chromatograph (Packard 427) equipped with a thermal conductivity detector. Gas samples were separated on a 7-ft Porapak Q column (hydrocarbons) or a 7-ft Carbosieve S column (CO and H$_2$). Organometallic products were characterised by their n.m.r. spectra (JEOL FX-90Q multi-nuclei Fourier-transform spectrometer) and i.r. spectra (Perkin-Elmer 297).

Photolysis of [W(CO)$_3$R(η^5-C$_5$R$'_5$)] *complexes* (R = Et, Pr^n, *or* Bu^n; R$'$ = H *or* Me): *preparation of* [WH(CO)$_2$(olefin)(η^5-C$_5$R$'_5$)] *complexes*. The appropriate starting material [W(CO)$_3$R(η^5-C$_5$R$'_5$)] (2 mmol) was dissolved in pentane (300 cm^3) in a Schlenk tube equipped with a magnetic follower and a mercury pressure relief valve. The yellow solution was cooled to −30 °C and irradiated using the Hg arc lamp when a rapid colour change (yellow ⟶ red) was observed. After 10 min the i.r. spectra indicated the maximum yields of [WH(CO)$_2$(olefin)(η^5-C$_5$R$'_5$)] complexes (*ca.* 40%) together with unreacted starting materials and some [WH(CO)$_3$(η^5-C$_5$R$'_5$)] (*ca.* 20%). Continued photolysis (1 h) resulted in the precipitation of dimers [{W(CO)$_3$(η^5-C$_5$R$'_5$)}$_2$] as the only products. Gas chromatographic analyses showed that the photolysis gas was mainly alkenes (ethene, propene, 1-butene) with some alkanes (ethane, propane, n-butane), CO, and H$_2$. The alkene : alkane ratio was *ca.* 3 : 1. Higher concentrations of starting material favoured the formation of the free olefins.

In order to isolate the [WH(CO)$_2$(olefin)(η^5-C$_5$R$'_5$)] complexes the photolysis was stopped after 10 min and the red solution was chromatographed on a silica column. At −30 °C unreacted starting material was eluted with pentane. A mixture of pentane and toluene (20 : 1) eluted the [WH(CO)$_2$(olefin)(η^5-C$_5$R$'_5$)] complexes as faint yellow fractions. Higher proportions of toluene resulted in fractions containing [WH(CO)$_3$(η^5-C$_5$R$'_5$)] and a little [{W(CO)$_3$(η^5-C$_5$R$'_5$)}$_2$]. The solvent was removed under vacuum (*ca.* 10^{-2} Torr, 0 °C) to give a residue which was dissolved in pentane, filtered through a frit, and cooled to −78 °C to yield (6—11%) yellow crystals of the [WH(CO)$_2$(olefin)(η^5-C$_5$R$'_5$)] complexes, which were characterised by their i.r. and n.m.r. spectra (Table 1). Additional characterisation was afforded by the parent ions in the mass spectra {[WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)], *m/e* = 334; [WH(CO)$_2$(C$_3$H$_6$)(η^5-C$_5$H$_5$)], *m/e* = 348; [WH(CO)$_2$(C$_4$H$_8$)(η^5-C$_5$H$_5$)], *m/e* = 362; [WH(CO)$_2$(C$_3$H$_6$)(η^5-C$_5$Me$_5$)], *m/e* = 418; all *m/e* values quoted with respect to ^{184}W}.

The photolysis of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] was conducted in an analogous manner. After photolysis (1 h) the pentane was removed by distillation and the remaining products, C$_6$H$_6$ and [{W(CO)$_3$(η^5-C$_5$H$_5$)}$_2$], were identified by i.r. and n.m.r. spectroscopy. Carrying out the reaction in an n.m.r. tube {[W(CO)$_3$Ph(η^5-C$_5$H$_5$)] in C$_6$D$_6$} confirmed that no other products were detected besides C$_6$H$_6$ and [{W(CO)$_3$(η^5-C$_5$H$_5$)}$_2$].

Photo-induced reactions of [W(CO)$_3$R(η^5-C$_5$R$'_5$)] *complexes with* C$_2$H$_4$ *in pentane solutions*. The course of the photo-induced reactions of [W(CO)$_3$R(η^5-C$_5$R$'_5$)] complexes with ethylene at −30 °C in pentane solutions depends on the ligand R. When the alkyl ligand is able to undergo β-hydrogen transfer, *i.e.* R = Et, Pr, or Bu, no [W(CO)$_2$(C$_2$H$_4$)R(η^5-C$_5$R$'_5$)] could be detected after photolysis. Instead, the main products were the hydrido–ethylene complexes [WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$R$'_5$)]. The complex [W(CO)$_3$Ph(η^5-C$_5$H$_5$)], however, does not undergo photo-induced β-hydrogen transfer and gave the *new* monosubstitution compound [W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)] as the major product. The σ-benzyl complex gave primarily the η^3-benzyl complex, [W(CO)$_2$(η^3-CH$_2$Ph)(η^5-C$_5$H$_5$)] but also a small amount of the *new* substitution product [W(CO)$_2$(C$_2$H$_4$)(σ-CH$_2$Ph)(η^5-C$_5$H$_5$)].

[W(CO)$_3$Ph(η^5-C$_5$H$_5$)] (2 mmol) was dissolved in pentane (300 cm^3). Ethylene was bubbled through the solution which was irradiated at −30 °C. When no more starting compound could be detected (i.r. spectroscopy; *ca.* 1 h) the yellow-brown solution was filtered through a frit covered with a filter paper. The clear solution was concentrated to 20 cm^3 by removing some solvent under vacuum (*ca.* 10^{-2} Torr) and on standing in solid CO$_2$ (−78 °C) gave good yields (*ca.* 80—85%) of yellow-brown crystals of [W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)]. The *new* [W(CO)$_2$(C$_2$H$_4$)R(η^5-C$_5$H$_5$)] complexes (R = Ph or CH$_2$Ph) were identified by i.r. and n.m.r. spectroscopy (Table 1) and by mass spectroscopy (R = Ph, *m/e* = 410; R = CH$_2$Ph, *m/e* = 424; all *m/e* values quoted with respect to ^{184}W).

(*ii*) *Matrix Studies*.—Details of the 12 K cryostat and vacuum system, i.r. and u.v.–visible spectrometers, the photolysis lamp, and matrix gases have been described previously.[14] The complexes [M(CO)$_3$R(η^5-C$_5$R$'_5$)] were sublimed from a glass

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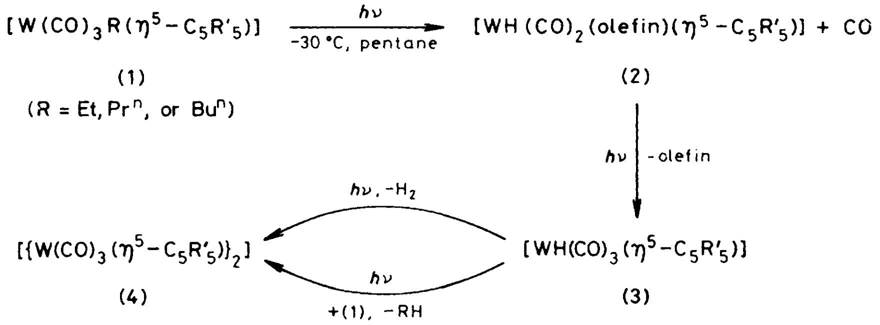
* [W(CO)$_6$] was refluxed with equivalent amounts of Na(C$_5$H$_5$) or Li(C$_5$Me$_5$) respectively in dimethylformamide (dmf) for 1 h. After removal of the dmf, the residue was dissolved in tetrahydrofuran (thf) and refluxed for 2 h with an excess of the corresponding alkyl halide, with the exception of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] [19] which used [2] Ph$_2$ICl as arylating agent at room temperature. After removing the solvent, the oily residue was extracted with pentane and the resulting yellow solution was filtered through a frit. Cooling the concentrated pentane solution to −78 °C afforded good yields (70—80%) of crystals of the [W(CO)$_3$R(η^5-C$_5$R$'_5$)] complexes which were dried *in vacuo* (10^{-2} Torr).

Table 1. Infrared and n.m.r. spectroscopic data for $[\mathrm{W(CO)_3R(\eta^5\text{-}C_5R'_5)}]$ and $[\mathrm{WH(CO)_2(olefin)(\eta^5\text{-}C_5R'_5)}]$ complexes in solution

		^{1}H N.m.r.[b]			^{13}C N.m.r. (^{1}H decoupled)			
Complex	ν(CO) [a]/cm^{-1}	δ($\mathrm{C_5H_5}$) or δ($\mathrm{C_5Me_5}$)	δ(alkyl), δ(aryl), or δ(olefin) [J(HH)/Hz]	δ(W–H)	δ($\mathrm{C_5H_5}$) or δ($\mathrm{C_5Me_5}$)	δ(M–CO) [J(WC)/Hz]	δ(alkyl), δ(aryl), or δ(olefin) [J(WC)/Hz]	Temp. of n.m.r. spectra (°C)
$[\mathrm{WH(CO)_3(\eta^5\text{-}C_5H_5)}]$	2 038, 1 937	5.72	—	−7.35 (s)	89.8	218.1 [c]	—	20
$[\mathrm{W(CO)_3Et(\eta^5\text{-}C_5H_5)}]$	2 015, 1 923	5.67	1.50 (m)	—	93.1	230.8, 219.5	20.6, −17.1 [28.1]	20
$[\mathrm{W(CO)_3Pr^n(\eta^5\text{-}C_5H_5)}]$	2 018, 1 925	5.61	1.53 (m), 0.92 (m)	—	92.7	230.5 [130.9], 219.0 [160.2]	30.5, 20.9, −7.1 [29.3]	20
$[\mathrm{W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)}]$	2 009, 1 920	5.64	2.77 (h), 1.48 (d) [7.0]	—	93.2	230.4, 221.2 [164.1]	31.8, −2.0 [29.1]	20
$[\mathrm{W(CO)_3Bu^n(\eta^5\text{-}C_5H_5)}]$	2 019, 1 925	5.61	1.55 (m), 1.26 (m), 0.87 (m)	—	92.9	230.7 [134.2], 219.2 [159.8]	39.8, 29.4, 13.7, −10.2 [29.0]	20
$[\mathrm{W(CO)_3(}n\mathrm{\text{-}C_{10}H_{21})(\eta^5\text{-}C_5H_5)}]$	2 011, 1 924	5.58	1.58 (m), 1.29 (m), 0.88 (m)	—	92.9	223.0, 219.3	57.6, 36.8, 32.6, 30.6, 30.1, 23.3, 14.4, −9.7	20
$[\mathrm{W(CO)_3Pr^n(\eta^5\text{-}C_5Me_5)}]$	1 999, 1 910	2.02	1.56 (m), 0 97 (m)	—	103.9, 10.4	234.0, 224.2	30.3, 21.8, 4.2 [31.2]	20
$[\mathrm{W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)}]$	2 010, 1 924	5.55	7.12 (m), 2.97 (s)	—	94.0	230.6, 220.2	152.8, 128.5, 128.3, 124.3, −6.9	20
$[\mathrm{W(CO)_3Ph(\eta^5\text{-}C_5H_5)}]$	2 022, 1 935	5.70	7.65 (m), 6.96 (m)	—	93.8	229.7, 220.2	147.6, 128.7, 125.7, 124.7	20
$[\mathrm{WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)}]$	1 978, 1 903	5.43	2.00 (s,br)	−5.71 (m)	90.6	217.8	21.1 [13.0]	20
$[\mathrm{WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)}]$ [d]	1 972, 1 899	5.48; 5.44	2.70 (m), 1.63 (m); n.c.[e]	−6.13 (m); −6.54 (m)	90.9; 91.2	220.4, 217.9; 221.3, 218.5	33.4, 24.8, 21.5; 33.3, 23.9, 20.7	−80
$[\mathrm{WH(CO)_2(1\text{-}C_4H_8)(\eta^5\text{-}C_5H_5)}]$ [f]	1 972, 1 899	5.46; 5.50	2.65 (m), 1.07 (m); n.c.[e]	−6.14 (m); −6.51 (m)	90.8; 90.1	219.7, 217.9; 220.5	40.4, 30.3, 23.0, 20.4; 39.3, 23.9, 19.6	−80
$[\mathrm{WH(CO)_2(1\text{-}C_{10}H_{20})(\eta^5\text{-}C_5H_5)}]$ [g]	1 970, 1 900	5.36; n.c.[e]	1.27 (m), 0.89 (m); n.c.[e]	−6.09 (m); −6.47 (m)	90.8; 90.6	223.0, 219.3; n.c.[e]	32.3, 30.2, 29.9, 23.2, 14.3; n.c.[e]	−80
$[\mathrm{WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5Me_5)}]$	1 960, 1 886	1.96	1.75 (m)	−5.53 (m)	102.2, 10.8	223.1, 219.4	39.6, 31.5, 22.3	−80
$[\mathrm{W(CO)_2(C_2H_4)(CH_2Ph)(\eta^5\text{-}C_5H_5)}]$	1 970, 1 899	5.09	7.01 (m), 3.01 (d), 2.79, 1.80 (d)	—	96.5	222.8	24.6, 4.4	−30
$[\mathrm{W(CO)_2(C_2H_4)Ph(\eta^5\text{-}C_5H_5)}]$ [h,i]	1 965, 1 883	5.32	8.04 (m), 7.00 (m), 2.25 (s,br)	—	94.5	219.8	146.3, 128.2, 128.0, 124.2, 26.3	−20
$[\mathrm{W(CO)_2(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)}]$	1 952, 1 878	5.60	7.24 (m), 2.87 (s)	—	91.4	232.2	142.6, 129.2, 129.0, 123.8, 19.1	20

[a] In pentane solution at 20 °C. [b] In [^{2}H$_6$]acetone solution; δ values in p.p.m.; s = singlet, d = doublet, h = heptet, m = multiplet, br = broad, n.c. = not clear. [c] At −80 °C: two CO signals at 225.7 and 215.5 p.p.m. [d] Two rotamers present in the ratio 85 : 15 (see text); data for the more abundant isomer presented first. [e] Signals for second rotamer not clearly defined. [f] Two rotamers present in the ratio 80 : 20 (see text); data for the more abundant isomer presented first. [g] W–H resonance indicates the presence of two rotamers, *cf.* $[\mathrm{WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)}]$ (see above and text), rotamer ratio 80 : 20; data for the more abundant rotamer presented first. [h] I.r. data in $\mathrm{C_6H_6}$ solution; n.m.r. data in $\mathrm{CDCl_3}$ solution. [i] Characterisation: (*i*) analysis for $[\mathrm{W(CO)_2(C_2H_4)Ph(\eta^5\text{-}C_5H_5)}]$ (Found: C, 43.55; H, 3.5; W, 44.8. Calc.: C, 43.95; H, 3.45; W, 44.85%); (*ii*) mass spectrum, expected *m*/*e* 410, found *m*/*e* 410 based on ^{184}W; (*iii*) melting point 104 °C; (*iv*) $\Delta G^{\ddagger}$ (olefin rotation) $\simeq$47.6 kJ mol^{-1} in $\mathrm{CDCl_3}$.



Scheme 1.

finger held at a specific temperature (10—15 °C for M = Mo and R = Et; 25—30 °C for M = W and R = Et; 30—35 °C for M = W and R = Pr^n, Pr^i, and Bu^n; 55—60 °C for M = W and R = Ph or CH_2Ph; 55—60 °C for M = W, R' = Me and R = Pr^n) and co-condensed on to the cooled CaF_2 window simultaneously with matrix gas introduced *via* a needle valve, *i.e.* a slow spray-on technique was used. Monomer isolation (dilution *ca.* 1 : 2 000) was ensured by having a substantially higher gas flow for the host matrix than for the complex to be isolated. Deposition (*ca.* 90 min) was monitored throughout by running i.r. spectra of the matrix and checking that the half-width at half-height of the terminal CO stretching bands did not exceed *ca.* 2 cm^{-1} and that there was no tailing of the bands to lower wavenumbers.

Wavelength-selective photolysis was achieved using the following combinations of absorbing materials: filter A, $\lambda > 430$ nm, CS 3-73 Corning glass filter; filter B, $\lambda > 410$ nm, CS 3-74 Corning glass filter; filter C, $\lambda > 370$ nm, CS 0-51 Corning glass filter; filter D, $\lambda > 530$ nm, CS 3-68 Corning glass filter; filter E, $310 < \lambda < 370$ and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr) + Pyrex glass disc (thickness 18 mm).

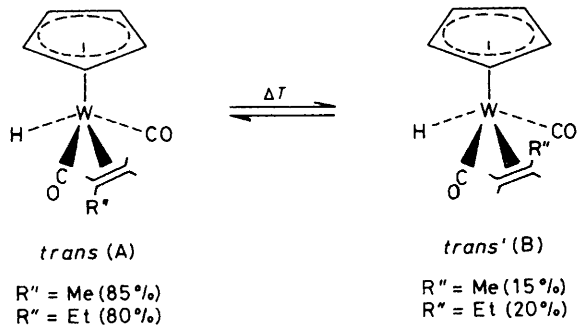
The ^{13}CO-enriched complex $[W(^{12}CO)_{3-n}(^{13}CO)_nPh(\eta^5\text{-}C_5H_5)]$ was prepared by photolysing (filter C) $[W(^{12}CO)_3Ph(\eta^5\text{-}C_5H_5)]$ in n-hexane (25 mg in 100 cm^3) in an atmosphere of ^{13}CO (300 Torr) in a sealed glass vessel for 1 h.* The solvent was removed by pumping under vacuum (*ca.* 10^{-2} Torr) and the solid was purified by sublimation (*ca.* 10^{-3} Torr, 65 °C).

Results

(*i*) *Studies in Solution.*—In the series of $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes (M = Cr, Mo, or W) the tungsten derivatives are the most stable. An additional advantage in studying the tungsten complexes is that ^{183}W–^{13}C coupling constants can be used to gain direct information concerning the hybridisation of the carbon atoms that are co-ordinated to the metal (see Table 1).

The photolysis ($\lambda > 300$ nm) of the alkyl complexes $[W(CO)_3R(\eta^5\text{-}C_5R'_5)]$ (R = alkyl) in pentane solution at −30 °C proceeds rapidly and after 10 min photolysis the olefin–hydrido-complexes $[WH(CO)_2(olefin)(\eta^5\text{-}C_5R'_5)]$ represent the main products with the exception of the isopropyl complex, $[W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)]$, for which no olefin–hydrido-species but only $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ could be detected. Further photolysis led to the disappearance of starting materials and the olefin–hydrido-species and the emergence of hydrido-complexes $[WH(CO)_3(\eta^5\text{-}C_5R'_5)]$ as the most abundant species. Ultimately, after 1 h photolysis, the only detectable products were the dimeric complexes $[\{W(CO)_3(\eta^5\text{-}C_5R'_5)\}_2]$. The main organic photoproducts (see Scheme 1) were the olefins and free alkanes RH, in the approximate ratio 3 : 1, together with a little CO and H_2.

The organometallic products (2)—(4) could be separated and isolated using column chromatography (silica) at −30 °C. The i.r. spectra of the olefin–hydrido-species (2) exhibit two terminal CO stretching bands. The fact that the upper band was very much less than the lower band was taken to indicate that the hydrido-ligand and the olefin are occupying *trans* positions in the tetragonal pyramid below the η^5-cyclopentadienyl ring (see below). No evidence could be found for the existence of a *cis* isomer in solution. The olefin–hydrido-complexes $[WH(CO)_2(C_3H_6)(\eta^5\text{-}C_5H_5)]$ and $[WH(CO)_2(C_4H_8)(\eta^5\text{-}C_5H_5)]$ both contain asymmetric alkene ligands and, therefore, the observation of an additional species in the ^1H and ^{13}C n.m.r. spectra at −80 °C was not unexpected. The two species at low temperatures are assigned as the rotameters (A) and (B) (see Table 1 for spectroscopic data). Surprisingly, the pentamethyl derivative $[WH(CO)_2(C_3H_6)(\eta^5\text{-}C_5Me_5)]$ showed only one species in the ^1H and ^{13}C n.m.r. spectra in the temperature range −90 to +30 °C. It is noteworthy that the pentamethyl derivative is thermally and kinetically more stable than the corresponding cyclopentadienyl complex.



In contrast to the alkyl complexes, the aryl derivative $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ does not give any photoproducts that would be characteristic of a β-elimination pathway, *e.g.* $[WH(CO)_2(C_6H_4)(\eta^5\text{-}C_5H_5)]$. Instead, i.r. and n.m.r. spectra identify the dimer (4) (Scheme 1) and benzene as the only products. This result is comparable with the dealkylation of some other transition metal methyl complexes where hydrogen abstraction to give CH_4 plays a key role in the mechanism. Dearylation in solution has been observed on photolysis of $[Fe(CO)_2Ph(\eta^5\text{-}C_5H_5)]$ [20] and $[TiPh_2(\eta^5\text{-}C_5H_5)_2]$.[21-23]

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* Only partial $^{12}CO/^{13}CO$ scrambling was achieved.

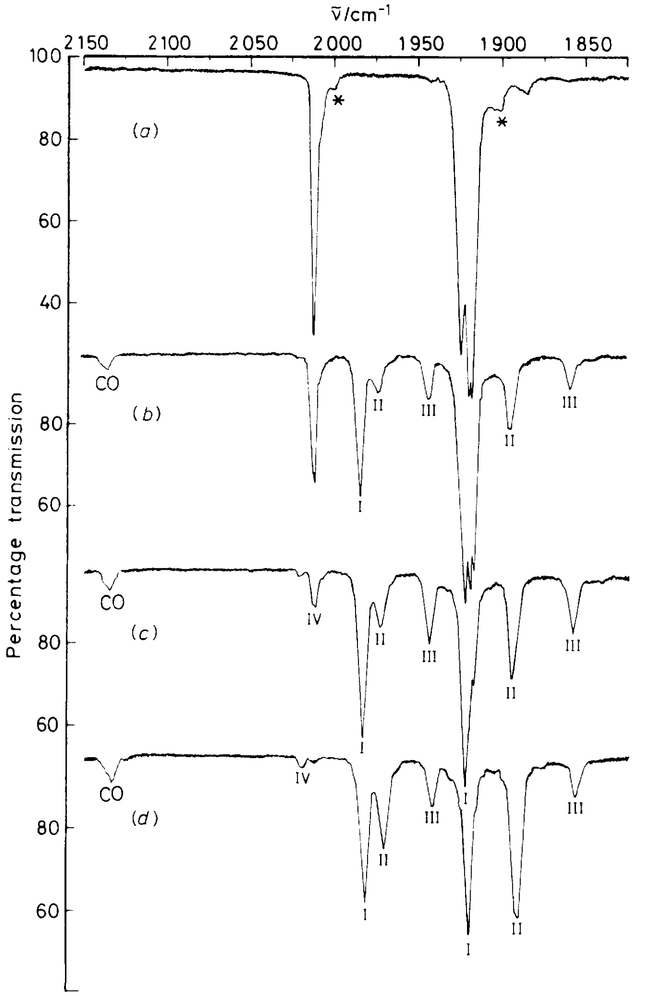

Figure 1. Infrared spectra from an experiment with [W(CO)$_3$Et(η^5-C$_5$H$_5$)] isolated at high dilution in a CH$_4$ matrix at 12 K: (*a*) after deposition, (*b*) after 60 min photolysis using $\lambda > 410$ nm radiation (filter B), (*c*) after 10 min photolysis using $\lambda > 370$ nm radiation (filter C), and (*d*) after further 75 min photolysis with $\lambda > 370$ nm radiation. Bands marked (*) are due to [W(^{12}CO)$_2$(^{13}CO)Et(η^5-C$_5$H$_5$)] in natural abundance. Bands marked (I)—(IV) arise from photoproducts (see text)

Table 2. Infrared band positions (cm^{-1}) observed in the terminal CO stretching region for [M(CO)$_3$Et(η^5-C$_5$H$_5$)] complexes (M = Mo or W) and their photoproducts in CH$_4$ and CO matrices at 12 K

Complex	CH$_4$	CO
[Mo(CO)$_3$Et(η^5-C$_5$H$_5$)]	2 019.5	2 019.3
	1 939.5 1 932.8 [a]	1 938.8 1 928.0 [a]
[W(CO)$_3$Et(η^5-C$_5$H$_5$)]	2 016.8	2 016.0
	1 930.4 1 924.6 [a]	1 931.7 1 925.0 [a]
[Mo(CO)$_2$Et(η^5-C$_5$H$_5$)]	1 957.8	1 956.6
	1 876.2	1 876.3
[W(CO)$_2$Et(η^5-C$_5$H$_5$)]	1 948.7	1 949.8
	1 862.8	1 861.5
trans-[MoH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)] [b]	1 977.4	1 980.0
	1 904.7	1 908.5
cis-[WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)] [c]	1 988.5	1 988.1
	1 929.2	1 930.3
trans-[WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)] [d]	1 977.4	1 976.7
	1 899.7	1 901.2
[MoH(CO)$_3$(η^5-C$_5$H$_5$)]	2 028.0	2 028.0
	1 947.6 1 940.3 [a]	1 947.1 1 941.3 [a]
[WH(CO)$_3$(η^5-C$_5$H$_5$)]	2 024.8	2 026.4
	1 938.6 1 934.4 [a]	1 938.8 1 933.2 [a]

[a] Overlapping *A′* and *A″* bands (see text). [b] Energy-factored CO force constants: $K = 1\ 522.0$, $k_1 = 57.0$ N m^{-1}. [c] Energy-factored CO force constants: $K = 1\ 549.9$, $k_1 = 46.9$ N m^{-1}. [d] Energy-factored CO force constants: $K = 1\ 518.2$, $k_1 = 60.8$ N m^{-1}.

(*ii*) *Matrix Isolation Studies.**—*Photolysis of* [M(CO)$_3$Et(η^5-C$_5$H$_5$)] (M = Mo *or* W) *in* CH$_4$, N$_2$, *and* CO *matrices*. The i.r. spectra of [M(CO)$_3$R(η^5-C$_5$R′$_5$)] complexes in solution show *two* terminal CO stretching bands (Table 1) whereas *three* bands are expected for a *C$_s$* M(CO)$_3$R fragment. Similarly the i.r. spectra of *C$_s$* [Mo(CO)$_3$Me(η^5-C$_5$H$_5$)] in gas matrices at 12 K showed two i.r.-active terminal CO stretching bands.[14] The *C$_s$* symmetry of the Mo(CO)$_3$Me fragment was confirmed by an energy-factored force-field fitting of the terminal CO stretching bands of matrix isolated [Mo(^{12}CO)$_n$(^{13}CO)$_{3-n}$Me(η^5-C$_5$H$_5$)].[14] The upper wavenumber band for [M(CO)$_3$R(η^5-C$_5$R′$_5$)] complexes in solution must, therefore, be the symmetric stretch (*A′*, *ca.* 2 000 cm^{-1}) while the lower band arises from an accidental coincidence of *A″* and *A′* bands (*ca.* 1 920 cm^{-1}, Table 1). All the [M(CO)$_3$R(η^5-C$_5$R′$_5$)] complexes studied in matrices in this work showed a single upper-wavenumber band and a split lower-wavenumber band, *e.g.* the spectrum of [W(CO)$_3$Et(η^5-C$_5$H$_5$)] [Figure 1(*a*)]. The splittings of the lower-wavenumber bands (*ca.* 8 cm^{-1}) are of similar magnitude to those for matrix effects[24] and, therefore, in summarising the i.r. data for [M(CO)$_3$R(η^5-C$_5$R′$_5$)] complexes, the split bands (Table 2) are assigned to *A′* + *A″* modes.

Irradiation of [W(CO)$_3$Et(η^5-C$_5$H$_5$)] in a CH$_4$ matrix using the filtered medium-pressure arc (filter B), giving light corresponding to the long-wavelength absorption [Figure 2(*a*)] produced free CO (*ca.* 2 138 cm^{-1}) and five new bands at 1 988.5, 1 977.4, 1 948.7, 1 899.7, and 1 862.8 cm^{-1} [Figure 1(*b*)]. A further period of irradiation (filter C) showed an increase in free CO, increases in all the new bands, a decrease in the upper *A′* parent band, and a change in the splitting pattern of the combined parent *A′* + *A″* band [Figure 1(*c*)]. The latter observation indicates that a further new band is growing (1 929.6 cm^{-1}) under the parent *A′* + *A″* band. An extended period of irradiation confirmed this [Figure 1(*d*)] because the parent bands had disappeared but a band remained at 1 929.6 cm^{-1}. Comparison of the growth and disappearance of bands under various times of photolysis identified that there were three pairs of new bands (Figure 1): (I) 1 988.5 and 1 929.2 cm^{-1}, (II) 1 977.4 and 1 899.7 cm^{-1}, and (III) 1 948.7 and 1 862.8 cm^{-1}.

The pair (II) (1 977.4 and 1 899.7 cm^{-1}) can be confidently assigned to *trans*-[WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)] by comparison with the bands for this complex in solution (1 978 and 1 903 cm^{-1}, Table 1) and in separate matrix isolation experiments (1 974.2 and 1 897.3 cm^{-1}).[25] The pair (III) (1 948.7 and 1 862.8 cm^{-1}) may be assigned to the 16-electron species [W(CO)$_2$Et(η^5-C$_5$H$_5$)] by analogy with the formation of [Mo(CO)$_2$Me(η^5-C$_5$H$_5$)] (1 966.0 and 1 880.4 cm^{-1}) on photolysis of [Mo(CO)$_3$Me(η^5-C$_5$H$_5$)] in gas matrices at 12 K [14] and by comparison

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* Monitoring and analysing the effects of photolysis has been confined to observations in the C–O stretching region (2 200—1 800 cm^{-1}). While this is less than ideal, vibrations for other ligands, *e.g.* M–H, M–alkene, σ- or η^3-benzyl, are very much weaker than for CO ligands and are less well documented and understood. Future work will aim to provide just such documentation and understanding and will involve an extensive program of work using Fourier-transform i.r. spectroscopy.

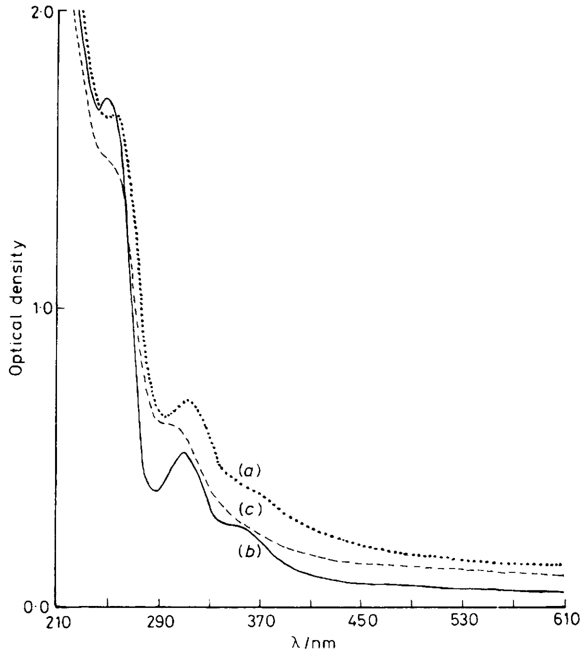


Figure 2. Ultraviolet–visible spectra from experiments with (*a*) [$W(CO)_3Et(\eta^5-C_5H_5)$] and (*b*) [$W(CO)_3Pr^n(\eta^5-C_5H_5)$] isolated at high dilution in CH_4 matrices at 12 K and (*c*) [$W(CO)_3Pr^n(\eta^5-C_5H_5)$] after 60 min photolysis using $\lambda > 430$ nm

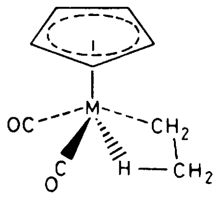
with the band positions of [$W(CO)_2Et(\eta^5-C_5H_5)$] (1 952 and 1 865 cm^{-1}) in a paraffin-wax disc at 77 K.[11,12] The remaining pair of bands [pair (I), 1 988.5 and 1 929.2 cm^{-1}] must belong to a species with at least two CO ligands. The most likely candidates are [$WH(CO)_3(\eta^5-C_5H_5)$] and *cis*-[$WH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$]. Of these species, the former can be eliminated because it has bands at 2 024.2, 1 938.6, and 1 934.4 cm^{-1} as shown in a separate matrix isolation study at 12 K; [25] the upper band of [$WH(CO)_3(\eta^5-C_5H_5)$] was observed to appear [(IV), Figure 1(*c*)] and to grow [Figure 1(*d*)] on extended photolysis. Assuming the pair (I) belong to a $W(CO)_2$ fragment, a OC–W–CO bond angle (θ) may be calculated from the expression $\tan^2(\theta/2) = I_{asym}/I_{sym}$ [26] and compared with that for *trans*-[$WH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$]. Weighed tracings of the spectra of the two sets of bands in absorbance mode yielded values of *ca.* 90° [pair (I)] and 110° [pair (II)]. These values together with the similar band positions for pairs (I) and (II) suggest strongly that the pair (I) may be assigned to *cis*-[$WH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$].* Additionally the energy-factored CO interaction force constant [26] for the pair (I) ($k_i = 46.9$ N m^{-1}) is less than that for *trans*-[$WH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$] ($k_i = 60.8$ N m^{-1}) and this is indicative of two *cis* CO groups in the species giving rise to pair (I).

Analogous results for [$W(CO)_3Et(\eta^5-C_5H_5)$] were obtained for N_2 and CO matrices except that the amounts of the various species were different from those observed for CH_4 matrices and that a much higher yield of [$WH(CO)_3(\eta^5-C_5H_5)$] was produced on extended photolysis in the case of CO matrices.

Photolysis of [$Mo(CO)_3Et(\eta^5-C_5H_5)$] in CH_4 and CO matrices yielded all the species identified above for [$W(CO)_3Et(\eta^5-C_5H_5)$] with the *noteworthy* exception of *cis*-[$MoH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$], *cf.* the failure to observe *cis*-[$WH(CO)_2(C_2H_4)(\eta^5-C_5H_5)$] in paraffin-wax discs at 77 K.[11,12]

Infrared data for all the species are collected in Table 2.

In the study by Kazlauskas and Wrighton [12] using paraffin-wax discs at 77 K two of the most important species cited were the 16-electron dicarbonyl species, [$M(CO)_2Et(\eta^5-C_5H_5)$], where it was proposed that a β-hydrogen became co-ordinated to the metal (C). The evidence for (C) was a large shift in the optical spectrum, *e.g.* 405 and 535 nm, between species which were proposed to be dicarbonyls with and without M ··· H interactions, respectively. We noticed no difference of colour in our matrices for [$M(CO)_2Et(\eta^5-C_5H_5)$] species in CH_4, N_2, and CO matrices nor could we observe new absorptions in the u.v.–visible spectra on photolysis of [$M(CO)_3Et(\eta^5-C_5H_5)$] complexes. It may well be that there was insufficient chromophore in the very thin gas matrices compared to the thicker and more concentrated paraffin-wax discs.



(C)

Photolysis of [$W(CO)_3R(\eta^5-C_5R'_5)$] ($R = Pr^n$, $R' = H$ *or* Me; $R = Bu^n$, $R' = H$) *in* CH_4 *and* CO *matrices.* The photoreactions of the three complexes are typified by that of [$W(CO)_3Pr^n(\eta^5-C_5H_5)$], which is described in detail below.

The i.r. spectrum of [$W(CO)_3Pr^n(\eta^5-C_5H_5)$] isolated at high dilution in a CH_4 matrix in the terminal CO stretching region [Figure 3(*a*), Table 3] is very similar to that already described for [$W(CO)_3Et(\eta^5-C_5H_5)$]. Irradiation of the matrices using the filtered medium-pressure Hg arc (filter A, $\lambda > 430$ nm), giving radiation corresponding to the long-wavelength absorption band [Figure 2(*b*)], produced ' free ' CO (2 138 cm^{-1}) and new bands at 1 986.0, 1 978.6, 1 970.3, 1 963.7, 1 949.4, 1 937.5, 1 893.5, 1 883.8, and 1 863.5 cm^{-1} [Figure 3(*b*)]. Further photolysis using slightly higher energy radiation (filter C, $\lambda > 370$ nm) caused a rapid increase in all the new bands [Figure 3(*c*)]. When this was followed by a further period of long-wavelength photolysis (filter A), the bands at 1 949.4 and 1 863.5 cm^{-1} decreased dramatically [Figure 3(*d*)]. At this stage the parent bands have almost disappeared. Comparison of the growth and disappearance of bands in several experiments and under various times of photolysis with different energies of radiation identified that there were five pairs of new bands (Figure 3): (I) 1 986.0 and 1 937.5 cm^{-1}, (II) 1 978.6 and 1 919.5 cm^{-1}, (III) 1 970.3 and 1 893.5 cm^{-1}, (IV) 1 963.7 and 1 883.8 cm^{-1}, and (V) 1 949.4 and 1 863.5 cm^{-1}. On extended photolysis a further band (VI) begins to grow [Figure 3(*d*)].

The pair (V) (1 949.4 and 1 863.5 cm^{-1}) can confidently be assigned to the 16-electron co-ordinatively unsaturated species [$W(CO)_2Pr^n(\eta^5-C_5H_5)$] by comparison with the bands for [$W(CO)_2Et(\eta^5-C_5H_5)$] (1 948.7 and 1 862.8 cm^{-1}). The other

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* Reservations have been expressed about the validity of deriving geometries by calculating interbond angles for [$M(CO)_n$] fragments from band intensities.[27] It is stated that the method can only be a legitimate one in those molecules where vibrational coupling between M–X and CO oscillators is small, *e.g.* [$Mn(CO)_5Br$]. Where coupling is strong, the errors involved in the method may be unacceptable, *e.g.* [$Mo(CO)_5(N_2)$]. In our experience, however, where ν(M–X) and ν(CO) bands are separated by *ca.* 200 cm^{-1}, bond angle calculations and energy-factored force-field fittings of bands of ^{13}CO-enriched species can be satisfactorily carried out without recourse to the inclusion of perturbations from X ligands, *e.g.* N_2 in [$Co(CO)(N_2)(\eta^5-C_5H_5)$] [28] and CO in [$Mn(CO)(NO)_2(NO^*)$] (where NO* represents a nitrosyl ligand acting as a one-electron donor).[29]

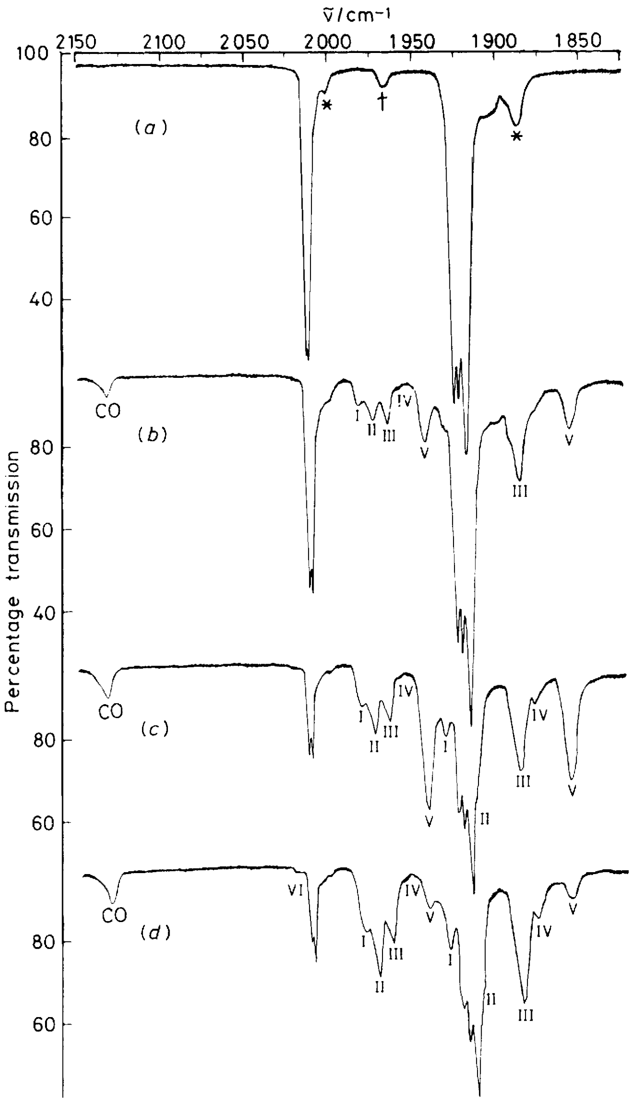


Figure 3. Infrared spectra from an experiment with [W(CO)$_3$Pr^n-(η^5-C$_5$H$_5$)] isolated at high dilution in a CH$_4$ matrix at 12 K: (*a*) after deposition, (*b*) after 110 min photolysis using $\lambda > 430$ nm, (*c*) after 15 min photolysis using $\lambda > 370$ nm, and (*d*) after 100 min photolysis using $\lambda > 430$ nm. Bands marked (*) are due to [W(^{12}CO)$_2$(^{13}CO)Pr^n(η^5-C$_5$H$_5$)] present in natural abundance and that marked (†) is due to [W(CO)$_6$] present as a trace impurity. Bands marked (I)—(VI) arise from photoproducts (see text)

bands, by analogy with *cis* and *trans* isomers for [WH(CO)$_2$-(C$_2$H$_4$)(η^5-C$_5$H$_5$)] in matrices (see above) are most probably due to *cis* and *trans* isomers of [WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)]. In solution *trans*-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] has terminal CO stretching bands at 1 972 and 1 899 cm^{-1} and these correlate well with the pair (III) (1 970.3 and 1 893.5 cm^{-1}). Taking the upper bands in pairs, (I) + (II) (1 986.0 and 1 978.6 cm^{-1}) and (III) + (IV) (1 970.3 and 1 963.7 cm^{-1}) it could be argued that each new pair represented a fundamental mode with a typical matrix splitting (0—10 cm^{-1}),[24] *i.e.* (I) + (II) belong to the *cis* isomer and (III) + (IV) belong to the *trans* isomer. Treating the lower-wavenumber bands in the same manner, giving pairs (I) + (II) (1 937.5 and 1 919.5 cm^{-1}) and (III) + (IV) (1 893.5 and 1 883.8 cm^{-1}), shows that the matrix splitting explanation is false because the (I) + (II) pair have a splitting of 18 cm^{-1} which is well outside the range for matrix splittings.

Table 3. Infrared band positions (cm^{-1}) observed in the terminal CO stretching region for [W(CO)$_3$R(η^5-C$_5$R′$_5$)] complexes (R′ = H, R = Pr^n, Pr^i, or Bu^n; R′ = Me, R = Pr^n) and their photoproducts, in CH$_4$ and CO matrices at 12 K

Complex	CH$_4$	CO
[W(CO)$_3$Pr^n(η^5-C$_5$H$_5$)]	2 016.6	2 016.6
	1 929.9 1 923.2 [a]	1 929.5 1 921.8 [a]
[W(CO)$_3$Pr^i(η^5-C$_5$H$_5$)]	2 014.1	2 013.2
	1 929.0 1 919.3 [a]	1 927.5 1 915.2 [a]
[W(CO)$_3$Pr^n(η^5-C$_5$Me$_5$)]	2 002.0	2 002.5
	1 908.7 1 904.4 [a]	1 909.0 1 902.6 [a]
[W(CO)$_3$Bu^n(η^5-C$_5$H$_5$)]	2 017.5	2 014.1
	1 930.2 1 924.5 [a]	1 925.8 1 916.8 [a]
[W(CO)$_2$Pr^n(η^5-C$_5$H$_5$)]	1 949.4	1 948.7
	1 863.5	1 862.5
[W(CO)$_2$Pr^i(η^5-C$_5$H$_5$)]	1 946.3	1 946.8
	1 860.8	1 862.0
[W(CO)$_2$Pr^n(η^5-C$_5$Me$_5$)]	1 932.2	1 931.8
	1 845.8	1 844.2
[W(CO)$_2$Bu^n(η^5-C$_5$H$_5$)]	1 948.2	1 945.0
	1 862.8	1 860.0
cis-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)]	1 986.0	*b*
	1 937.5	1 936.2
cis′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)]	1 978.6	1 982.7
	1 919.5	1 923.7
trans-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)]	1 970.3	1 971.4
	1 893.5	1 894.3
trans′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)]	1 963.7	*c*
	1 883.8	1 885.0
cis-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$Me$_5$)]	*d*	*d*
	1 922.4	1 924.5
cis′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$Me$_5$)]	1 967.8	1 970.3
	1 904.0	1 910.5
trans-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$Me$_5$)]	1 954.1	1 955.0
	1 875.2	1 875.3
trans′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$Me$_5$)]	*e*	*e*
	1 860.0	1 865.4
cis-[WH(CO)$_2$(1-C$_4$H$_8$)(η^5-C$_5$H$_5$)]	1 986.3	1 987.1
	1 937.3	1 937.4
cis′-[WH(CO)$_2$(1-C$_4$H$_8$)(η^5-C$_5$H$_5$)]	1 980.7	1 982.3
	1 921.8	1 922.6
trans-[WH(CO)$_2$(1-C$_4$H$_8$)(η^5-C$_5$H$_5$)]	1 971.1	1 969.7
	1 894.3	1 891.4
trans′-[WH(CO)$_2$(1-C$_4$H$_8$)(η^5-C$_5$H$_5$)]	*f*	*f*
	1 882.5	1 881.6
[WH(CO)$_3$(η^5-C$_5$H$_5$)]	2 024.2	2 024.3
	1 937.5 1 932.3 [a]	1 936.8 1 934.6 [a]
[WH(CO)$_3$(η^5-C$_5$Me$_5$)]	2 012.1	2 011.4
	1 922.2	1 923.2

[a] Overlapping *A*′ and *A*″ bands. [b] Band obscured by broad band at 1 982.7 cm^{-1}. [c] Band obscured by broad band at 1 971.4 cm^{-1}. [d] Band obscured by broad upper band of *cis*′ isomer. [e] Band obscured by broad upper band of *trans* isomer. [f] Band obscured by broad upper band of *trans* isomer.

In solution at −80 °C, ^{1}H n.m.r. studies show that *trans*-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] exists as two rotamers, (A) and (B). It seems reasonable, therefore, that rotamers of *cis*- and *trans*-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] could be formed and frozen out at 12 K. We assign the pair (I) to *cis*-[WH(CO)$_2$-(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] the pair (II) to *cis*′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)], the pair (III) to *trans*-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] (A) and the pair (IV) to *trans*′-[WH(CO)$_2$(1-C$_3$H$_6$)(η^5-C$_5$H$_5$)] (B). On extended photolysis with high-energy radiation (filter E, 310 < λ < 370 nm) bands of [WH(CO)$_3$(η^5-C$_5$H$_5$)] grew at the expense of those of the rotamers of $[WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)]$ and those of $[W(CO)_2Pr^n(\eta^5\text{-}C_5H_5)]$.

Analogous results were obtained for $[W(CO)_3Pr^n(\eta^5\text{-}C_5H_5)]$ isolated in CO matrices, except that bands due to $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ [(VI) in Figure 3(*d*)] appeared after a much shorter period of irradiation. Similarly, the photoreactions of $[W(CO)_3Pr^n(\eta^5\text{-}C_5Me_5)]$ and $[W(CO)_3Bu^n(\eta^5\text{-}C_5H_5)]$ in CH_4 and CO matrices followed the pattern described for $[W(CO)_3Pr^n(\eta^5\text{-}C_5H_5)]$. Infrared data for the new species are presented in Table 3.

Photolysis of $[W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)]$ *in* CH_4 *and* CO *matrices*. The i.r. spectrum of $[W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)]$ isolated at 12 K in a CH_4 matrix before photolysis is analogous to those for other $[W(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes (Tables 2 and 3).

Irradiation of the matrix with long-wavelength radiation (λ > 410 nm, filter B) for a similar length of time as that used initially for $[W(CO)_3Pr^n(\eta^5\text{-}C_5H_5)]$ produced bands due to ' free CO ', pairs (I)—(V) seen previously for $[W(CO)_3Pr^n(\eta^5\text{-}C_5H_5)]$ [*cf.* Figure 3(*b*)], and an additional band at 2 024.2 cm^{-1} [*cf.* (VI) in Figure 3(*d*)]. Further photolysis (λ > 370 nm, filter C) showed that the band at *ca.* 1 937 cm^{-1} grew out of proportion with the other band of the band pair (I), *i.e.* there is another species with a band at 1 937 cm^{-1}. Careful comparison of band intensities showed that the 1 937 cm^{-1} band could be correlated with the band at 2 024.2 cm^{-1} (VI). The pair (VI) can be identified as belonging to $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ by comparison with band position from separate experiments [25] (Table 2). In the experiments using CO matrices the production of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ was even more predominant than for CH_4 matrices.

Photolysis of $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ *and* $[W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)]$ *in* CH_4 *and* CO *matrices*. The photoreactions of these two complexes are very similar and, because of the ^{13}CO-labelling study with $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ (see below), the results for this complex will be described first.

The i.r. spectrum of $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ isolated in a CH_4 matrix before irradiation is analogous to those for other $[W(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes [Figure 4(*a*), Tables 2 and 3].

Irradiation of the matrices with long-wavelength radiation (λ > 430 nm, filter A) produced new bands at 2 138.0 (' free ' CO), 1 955.0, and 1 869.7 cm^{-1} [Figure 4(*b*)]. A short period of higher-energy irradiation ($310 < \lambda < 370$ nm, filter E) produced marked increases in the new bands at the expense of the parent bands [Figure 4(*c*)]. Irradiation then with longer-wavelength radiation (λ > 530 nm, filter D) and annealing the matrix for 2 min to *ca.* 30 K caused the new product bands to decrease and those of the starting complex, $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$, to increase [Figure 4(*d*)]. The relative intensity of the bands at 1 955.0 and 1 869.7 cm^{-1} remained constant under a variety of forward and reverse photolyses and annealing cycles indicating that the bands arose from a single product species. The dilution used, the absence of bands due to $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$, and the reversibility of the photoreaction enable the new bands to be assigned to the 16-electron species $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$. This was confirmed using $[W(^{12}CO)_n(^{13}CO)_{3-n}Ph(\eta^5\text{-}C_5H_5)]$ (see below). Analogous results were obtained for $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ in CO matrices, *i.e.* an excess of CO does not prevent the photoejection of a CO ligand.

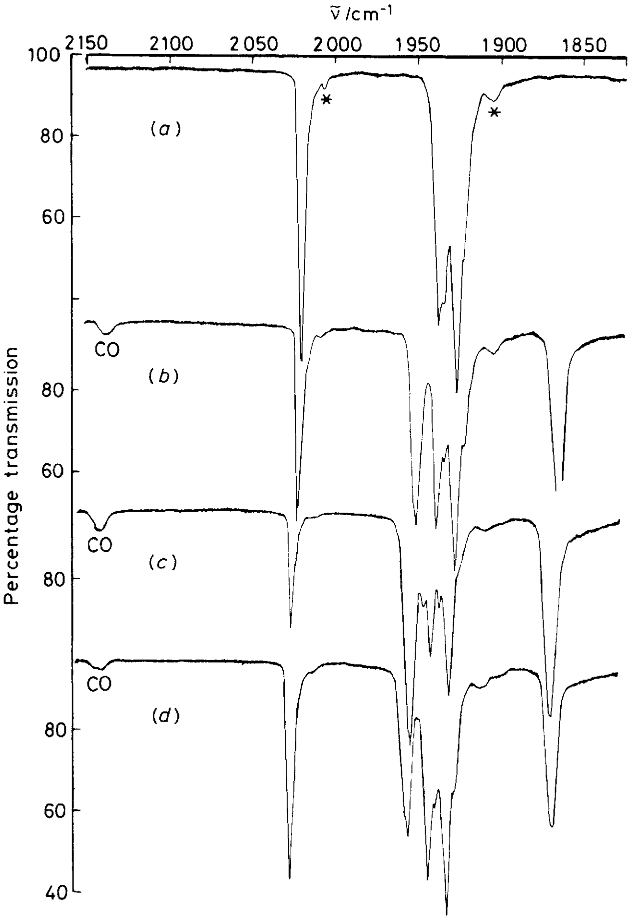


Figure 4. Infrared spectra from an experiment with $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 30 min photolysis using λ > 430 nm, (*c*) after 5 min photolysis using $310 < \lambda < 370$ nm and (*d*) after 120 min photolysis using λ > 530 nm. Bands marked (*) are due to $[W(^{12}CO)_2(^{13}CO)Ph(\eta^5\text{-}C_5H_5)]$ present in natural abundance

Irradiation of $[W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)]$ in CH_4 and CO matrices produced analogous results to those described above for $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$, *i.e.* there was no evidence for the hydrides $[WH(CO)_2(olefin)(\eta^5\text{-}C_5H_5)]$ and $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$. There were, however, four new bands [1 946.2, 1 942.4, 1 871.7, and 1 859.3 cm^{-1} (CO matrix)] for species derived from $[W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)]$, in addition to a band due to ' free ' CO, whereas only two new bands were observed in experiments starting from $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$. The four bands grew under various types of irradiation in such a way that two pairs could be identified: (I) 1 942.4 and 1 859.3 cm^{-1} and (II) 1 946.2 and 1 871.7 cm^{-1} of which the latter pair were much more intense. Surprisingly there was no reversal of the forward photolysis step on long-wavelength irradiation (λ > 530 nm, filter D). The fact that two distinct species are involved was deduced from observations that the pairs (I) and (II) had different relative intensities at various stages of irradiation and that the separation of the lower pair of bands (*ca.* 12 cm^{-1}) is rather large for a matrix splitting (0—8 cm^{-1}).

The more intense pair of bands, pair (I) (1 942.4 and 1 859.3 cm^{-1}), are at similar positions to the bands of $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$ (1 955.0 and 1 869.7 cm^{-1}) and those of other 16-electron $[W(CO)_2R(\eta^5\text{-}C_5R'_5)]$ species (Tables 2 and 3). The pair (I) bands, which grow with the growth of the band due to ' free ' CO, can, therefore, be assigned to the co-ordinatively unsaturated 16-electron species $[W(CO)_2(CH_2Ph)(\eta^5\text{-}C_5H_5)]$. There are two possible explanations for pair (II): (*i*) another conformation of a σ-CH_2Ph ligand has been frozen out or (*ii*) the CH_2Ph ligand has changed its mode of co-ordination from a σ-bonded to a π-bonded η^3-CH_2Ph configuration. Precedent for the latter type of bonding comes from the fact that $[W(CO)_2(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)]$ is a known compound (Table 1) which has band positions (1 952 and 1 878 cm^{-1}, solution) which are identical to those of pair (II) (1 946.2 and 1 871.7

Table 4. Infrared band positions (cm^{-1}) observed in the terminal CO stretching region for [W(CO)$_3$R(η^5-C$_5$H$_5$)] complexes (R = CH$_2$Ph or Ph) and their photoproducts in a variety of matrices at 12 K

Complex	CH$_4$	Ar	CO	N$_2$	5% C$_2$H$_4$-CH$_4$
[W(CO)$_3$(σ-CH$_2$Ph)(η^5-C$_5$H$_5$)]	2 014.1	2 021.4	2 015.0		
	1 930.6 1 919.3 [a]	1 936.6 1 925.8 [a]	1 931.1 1 917.1 [a]	—	—
[W(CO)$_3$Ph(η^5-C$_5$H$_5$)]	2 025.1		2 024.3	2 024.3	2 022.1
	1 944.3 1 932.2 [a]	—	1 938.9 1 927.8 [a]	1 941.7 1 929.6 [a]	1 938.0 1 924.5 [a]
[W(CO)$_2$(σ-CH$_2$Ph)(η^5-C$_5$H$_5$)]	1 939.4	1 949.4	1 942.4	—	—
	1 857.5	1 868.5	1 859.3		
[W(CO)$_2$Ph(η^5-C$_5$H$_5$)]	1 955.0	—	1 954.4	1 958.7	1 951.5
	1 869.7		1 865.7	1 873.6	1 861.5
[W(CO)$_2$(η^3-CH$_2$Ph)(η^5-C$_5$H$_5$)]	1 945.0	b	1 946.2		
	1 871.3	1 880.5	1 871.7		
[W(CO)$_2$(N$_2$)Ph(η^5-C$_5$H$_5$)] [c]	—	—	—	1 971.0	—
				1 902.3	
[W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)] [d]	—	—	—	—	1 990.2
					1 922.5

[a] Overlapping A' and A'' bands. [b] Band obscured by broad band of [W(CO)$_2$(σ-CH$_2$Ph)(η^5-C$_5$H$_5$)] at 1 949 cm^{-1}. [c] ν(NN) too weak to observe. [d] *cis* Isomer in matrices at 12 K [K = 1 546.0 and k_i (*cis*) = 53.5 N m^{-1}] but *trans* isomer in solution [Table 1, K = 1 495.6 and k_i (*trans*) = 63.7 N m^{-1}].

cm^{-1}) if a 6 cm^{-1} solvent shift is allowed for. It seems most reasonable to assign the pair of bands (II) to [W(CO)$_2$(η^3-CH$_2$Ph)(η^5-C$_5$H$_5$)], especially since this is the major product formed when [W(CO)$_2$(σ-CH$_2$Ph)(η^5-C$_5$H$_5$)] is photolysed in pentane solutions (see above). The same two product species were formed when [W(CO)$_3$(CH$_2$Ph)(η^5-C$_5$H$_5$)] was irradiated in CO and Ar matrices at 12 K.

Infrared data in the terminal CO stretching region for all the new species are presented in Table 4.

Photolysis of ^{13}CO-*enriched* [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] *in* CH$_4$ *matrices*. The i.r. spectrum of ^{13}CO-enriched [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] (see Experimental section) isolated in a CH$_4$ matrix showed bands due to the full range (n = 0—3) of [W(^{12}CO)$_n$(^{13}CO)$_{3-n}$Ph(η^5-C$_5$H$_5$)] species. A good correspondence was obtained between observed and calculated band positions using an energy-factored force-field fitting procedure (Table 5).

Irradiation of the matrix with medium-energy radiation (λ > 410 nm, filter B) gave new ^{13}CO-enriched product bands at 1 936.3, 1 910.2, 1 839.1, and 1 824.1 cm^{-1} in addition to the bands of the ^{12}CO species at 1 954.0 and 1 865.6 cm^{-1}. Subjecting these six bands to the energy-factored force-field fitting procedure gave an excellent fit for a C_s W(CO)$_2$ fragment (Table 5). Photoproducts produced with the liberation of 'free' CO and pairs of bands at *ca.* 1 950 and *ca.* 1 860 cm^{-1} can therefore confidently be assigned the structures [W(CO)$_2$R(η^5-C$_5$R'$_5$)].

The observed relative intensity of the two terminal CO bands for [W(CO)$_2$Ph(η^5-C$_5$H$_5$)], obtained by tracing and weighing the A' and A'' bands from spectra run in absorbance units, was used to calculate a OC–W–CO bond angle of 90 ± 1° from the standard expression $I_{asym}/I_{sym} = I_{A''}/I_{A'}$ (0.9966) $\tan^2(\theta/2)$.[26]

Photolysis of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] *in* N$_2$ *and* 5% C$_2$H$_4$-*doped* CH$_4$ *matrices*. The i.r. spectrum of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] isolated at high dilution in a 5% C$_2$H$_4$-doped CH$_4$ matrix shows very much broader bands than obtained in pure gas matrices [Figure 5(*a*)]. The broadness of the bands is a common feature of all doped matrices and reflects not a lack of isolation but rather that substrate molecules are isolated in matrix cages with varying probabilities and orientations of dopant.

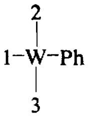
A period of photolysis using long-wavelength radiation (λ > 430 nm, filter A) produced new bands at 2 138.0, 1 990.2, 1 951.5, and 1 861.5 cm^{-1} of which the band at 2 138.0 cm^{-1} corresponds to CO liberated during photolysis [Figure 5(*b*)]. A short period of higher-energy photolysis (λ > 370 nm, filter C) caused all the product bands to increase while those of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] decreased [Figure 5(*c*)]. Irradiation with much longer wavelength radiation (λ > 530 nm) [Figure 5(*d*)], or annealing the matrix to *ca.* 30 K [Figure 5(*e*)] revealed a band growing at 1 922.5 cm^{-1} which was formerly obscured by the bands of the parent molecule. Annealing the matrix also showed that the bands at 1 951.5 and 1 861.5 cm^{-1} [pair (I)] were not related to those at 1 990.2 and 1 922.5 cm^{-1} [pair (II)] because the former decreased in intensity whereas the latter increased, while there was little or no change in the intensities of the parent bands [Figure 5(*e*)].

The more intense pair of bands, (II) [1 951.5 and 1 861.5 cm^{-1}, Figure 5(*b*)], which reverse on annealing and long-wavelength photolysis, can be assigned to the co-ordinatively unsaturated 16-electron species [W(CO)$_2$Ph(η^5-C$_5$H$_5$)] by comparison with those observed in CH$_4$ matrices (Table 4) and their analogous reversal behaviour. The pair of bands at higher wavenumbers, (I) [1 990.2 and 1 922.5 cm^{-1}, Figure 5(*e*)], are typical of a situation where a CO ligand has been replaced by another ligand, *e.g.* [Mo(CO)$_2$(N$_2$)Me(η^5-C$_5$H$_5$)] (1 969.7 and 1 913.7 cm^{-1}) compared with [Mo(CO)$_2$Me(η^5-C$_5$H$_5$)] (1 972.8 and 1 884.4 cm^{-1}).[14] The bands can probably be assigned to the 18-electron species [W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)]. The band positions in the matrix (1 990.2 and 1 922.5 cm^{-1}) are, however, different from those of *trans*-[W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)] observed in solution (1 965 and 1 883 cm^{-1}, Table 1). We assign the bands at 1 990.2 and 1 922.5 cm^{-1} to *cis*-[W(CO)$_2$(C$_2$H$_4$)Ph(η^5-C$_5$H$_5$)] because (*a*) the relative magnitude of the energy-factored CO interaction force constant for this species (53.5 N m^{-1}) is smaller than that for the *trans* isomer (63.7 N m^{-1}, solution) and these values are similar to the relative magnitudes of the *cis* (46.9 N m^{-1}) and *trans* (60.8 N m^{-1}) interaction force constants for the isomers of [WH(CO)$_2$(C$_2$H$_4$)(η^5-C$_5$H$_5$)] (Table 2), and (*b*) *cis* and *trans* isomers of [WH(CO)$_2$(olefin)(η^5-C$_5$H$_5$)] complexes are formed in matrices but only the *trans* isomers can be isolated as crystalline compounds.

Irradiation of [W(CO)$_3$Ph(η^5-C$_5$H$_5$)] in N$_2$ matrices with medium-energy radiation (λ > 430 nm, filter A) produced two

Table 5. Observed and calculated [a] band positions (cm^{-1}) of terminal CO stretching bands in an experiment with a ^{13}CO-enriched sample of $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ in a CH_4 matrix at 12 K

Complex (symmetry point group)			Observed	Calculated
$[W(^{12}CO)_3Ph(\eta^5\text{-}C_5H_5)]$	(C_s)	A'	2 023.0	2 023.1
		A'	1 940.0	1 939.6
		A''	1 930.0	1 930.7
$[W(^{12}CO)_2(^{13}CO)Ph(\eta^5\text{-}C_5H_5)]$	(C_s) [b]	A'	2 012.3	2 012.8
		A''	1 931.3	1 930.7
		A'	1 906.4	1 906.2
	(C_1) [c]	A	2 010.0	2 011.9
		A	1 937.2	1 937.8
		A	*d*	1 900.0
$[W(^{12}CO)(^{13}CO)_2Ph(\eta^5\text{-}C_5H_5)]$	(C_1) [e]	A	1 998.1	1 998.8
		A	1 914.4	1 913.6
		A	*f*	1 893.7
	(C_s) [f]	A'	1 996.7	1 998.4
		A'	*d*	1 919.9
		A''	1 887.2	1 887.8
$[W(^{13}CO)_3Ph(\eta^5\text{-}C_5H_5)]$	(C_s)	A'	1 978.2	1 978.1
		A'	1 896.0	1 896.4
		A''	1 888.4	1 887.8
$[W(^{12}CO)_2Ph(\eta^5\text{-}C_5H_5)]$	(C_s)	A'	1 954.0	1 953.8
		A''	1 865.6	1 865.5
$[W(^{12}CO)(^{13}CO)Ph(\eta^5\text{-}C_5H_5)]$	(C_1)	A	1 936.3	1 937.0
		A	1 839.1	1 839.9
$[W(^{13}CO)_2Ph(\eta^5\text{-}C_5H_5)]$	(C_s)	A'	1 910.2	1 910.4
		A''	1 824.1	1 824.0

[a] Refined energy-factored force constants for $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$: $K_1 = 1\,562.8$, $K_2 = 1\,558.2$, $k_{12} = 44.2$, and $k_{23} = 52.3$ N m^{-1} as defined by the numbering  $1-\overset{\overset{2}{|}}{\underset{\underset{3}{|}}{W}}-Ph$ $(1 \neq 2 = 3)$. Refined energy-factored force constants for $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$: $K = 1\,474.1$ and $k_i = 68.1$ N m^{-1}. [b] ^{13}CO in position 1. [c] ^{13}CO in position 2. [d] Band obscured. [e] ^{12}CO in position 2. [f] ^{12}CO in position 1.

new strong bands at 1 958.7 and 1 873.6 cm^{-1}, which can be assigned to $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$ (see above and Table 4), and two weak bands at 1 971.0 and 1 902.3 cm^{-1}. Unfortunately the yield of these latter two bands was always low no matter what irradiation sources were employed. Comparison of these weak bands with those of $[Mo(CO)_2(N_2)Me(\eta^5\text{-}C_5H_5)]$ (see above) suggests that they may be assigned to the dinitrogen complex $[W(CO)_2(N_2)Ph(\eta^5\text{-}C_5H_5)]$. Since NN stretching bands are always very much less intense than CO stretching bands it is perhaps not surprising that no new band in the 2 200 cm^{-1} region could be observed, *cf.* ν(NN) at 2 190.8 cm^{-1} for $[Mo(CO)_2(N_2)Me(\eta^5\text{-}C_5H_5)]$.[14]

No new bands assignable to $[W(CO)_2(C_2H_4)(CH_2Ph)(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_2(N_2)(CH_2Ph)(\eta^5\text{-}C_5H_5)]$ species were observed when $[W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)]$ was photolysed in 5% C_2H_4-doped CH_4 and pure N_2 matrices respectively.

Infrared data in the terminal CO stretching region for the new species are presented in Table 4.

Discussion

In the $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes the dissociation energy of the transition metal–carbon σ-bond is comparable with the bond strength of the metal–carbon(carbonyl) bond as determined calorimetrically.[30] In principle both M–R and M–CO bonds could be cleaved by u.v. radiation ($\lambda > 300$ nm). The combination of solution and matrix isolation studies should provide a complete understanding of the mechanisms of the photo-induced CO substitution, dealkylation, and dearylation reactions of $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes because both final products and intermediates can be characterised.

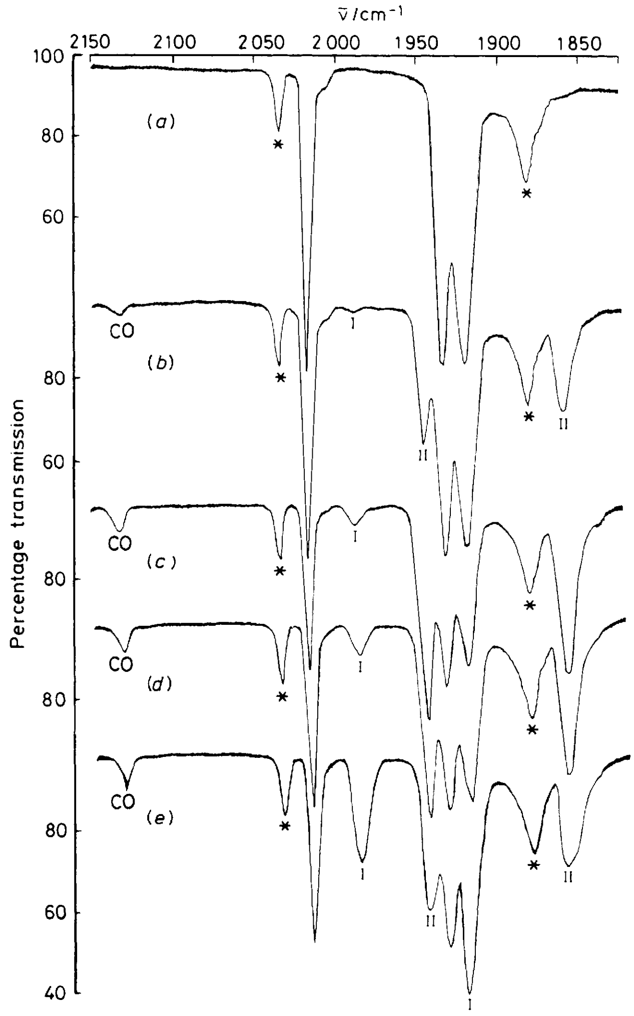
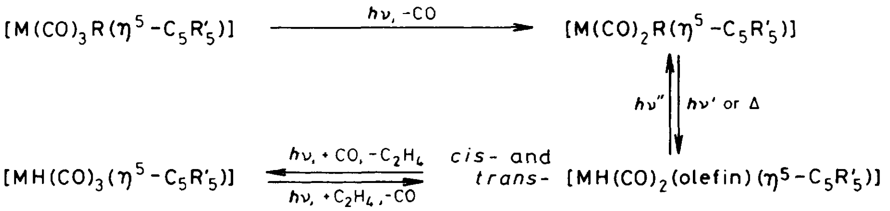


Figure 5. Infrared spectra from an experiment with $[W(CO)_3Ph(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a 5% C_2H_4–CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 45 min photolysis using $\lambda > 430$ nm, (*c*) after 2 min photolysis using $\lambda > 370$ nm, (*d*) after 120 min photolysis using $\lambda > 530$ nm and (*e*) after annealing the matrix to *ca.* 30 K for 2 min. Bands marked (*) are due to C_2H_4. Bands marked (I) and (II) arise from $[W(CO)_2(C_2H_4)Ph(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_2Ph(\eta^5\text{-}C_5H_5)]$ respectively

The photoreactions of the $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$ complexes (M = Mo, R = Et, R′ = H; M = W, R = Et, Pr^n, or Bu^n, R′ = H; M = W, R = Pr^n, R′ = Me) at high dilution in CH_4 and CO matrices are summarised in Scheme 2. The primary photoprocess in all cases is the ejection of a CO ligand. The resulting co-ordinatively unsaturated 16-electron species $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ can be identified in CH_4 and CO matrices at 12—30 K and in paraffin-wax discs at 77 K (M = Mo or W; R = Me, Et, or n-C_5H_{11}; R′ = H or Me)[11,12] but not in n-pentane solutions at −30 °C.

The fragments $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ do not readily recombine with photoejected CO at 12 K to reform the starting complexes $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$; this is in striking contrast to the behaviour of $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$ (M = Mo or W).[11,12,14,15] Instead the formation of the olefin–hydrido-complexes $[MH(CO)_2(\text{olefin})(\eta^5\text{-}C_5R'_5)]$ is observed, *i.e.* β-hydrogen transfer is a more favoured process than recombin-

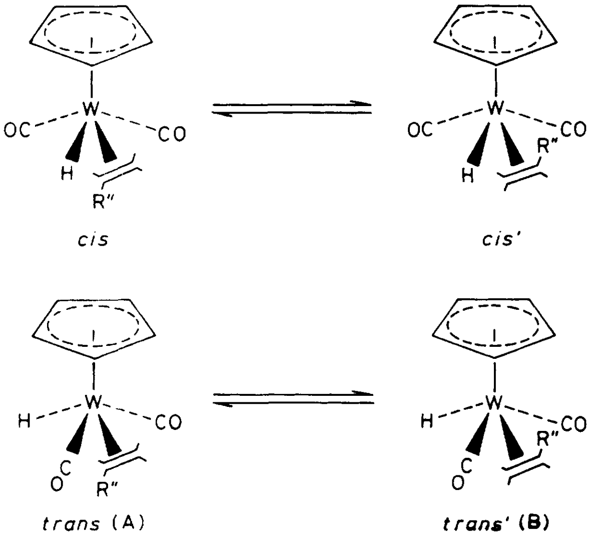


Scheme 2. M = Mo, R = Et, R' = H; M = W, R = Et, Pr^n, Pr^i, or Bu^n, R' = H; M = W, R = Pr^n, R' = Me

ation with photo-ejected CO. The growth and decay of the i.r. bands of $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ and $[MH(CO)_2(olefin)(\eta^5\text{-}C_5R'_5)]$ species suggest that there is a reversible reaction (Scheme 2). This was confirmed in separate experiments with $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ isolated in matrices at 12 K when the formation of $[W(CO)_2Et(\eta^5\text{-}C_5H_5)]$ was observed.[25]

It is important to note that in low-temperature matrices at 12 K both *cis* and *trans* isomers of $[WH(CO)_2(olefin)(\eta^5\text{-}C_5H_5)]$ complexes can be observed. In solution [10] and even in paraffin-wax discs at 77 K,[11,12] however, only the *trans* isomer could be detected. The fact that $[MoH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ could only be detected as the *trans* isomer even at 12 K reveals that the *cis* ⟶ *trans* isomerisation proceeds more rapidly for Mo than for W. In all cases the formation of the *cis* isomer may be considered to be the first step; this was axiomatically assumed in the work of Kazlauskas and Wrighton [11,12] although they detected only *trans*-$[MH(CO)_2(olefin)(\eta^5\text{-}C_5H_5)]$.

In the cases of olefin–hydrido-complexes with asymmetric olefins, *e.g.* $[WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)]$ and $[WH(CO)_2(1\text{-}C_4H_8)(\eta^5\text{-}C_5H_5)]$, the situation becomes more complicated because the *cis* and *trans* isomers can exist as rotamers, *e.g.* *cis* and *cis'* or *trans* and *trans'*. In fact all these four forms could exist in an additional configuration, *e.g.* the *cis'* has a counterpart *cis''* with R'' pointing away from the CO ligand. We differentiated (Figure 3, Table 3) between R'' near to H or to CO (as below) but we were unable to resolve whether R'' (Me or Et) was towards or away from H or CO. In the solution studies two rotamers, (A) and (B), of the *trans* isomers can be observed and characterised at −80 °C by ^1H and ^{13}C n.m.r. spectroscopy (see Table 1). The barrier for the intramolecular rotation of the 1-propene and 1-butene ligands around the tungsten–olefin bond axis ($\Delta G^{\ddagger} \simeq 50$ kJ mol^{-1} in [$^2H_8$]toluene) is approximately in the same range as that for the rotation of the C_2H_4 ligands in $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_2(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$.[31,32] Such a barrier indicates very strong metal ⟶ olefin back donation; in this situation the bonding may approximate to a metallocycle (D) rather than the more conventional Chatt–Dewar representation (E). A metallocycle resonance form is suggested by the presence of $^{183}W-^{13}C$(olefin) coupling constants [$J(WC) \simeq 29$ Hz] [32,33] that are typical for W–C σ bonds. The conversion of the olefin–hydrido-species $[MH(CO)_2(olefin)(\eta^5\text{-}C_5R'_5)]$ to the co-ordinatively unsaturated species $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ ($\lambda > 370$ nm; CH_4 matrix) by olefin insertion is interesting because such a process is postulated as a step in the hydroformylation of olefins catalysed by metal carbonyl hydrides.[34,35]

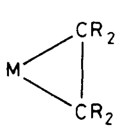


cis

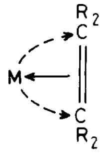
cis'

trans (A)

trans' (B)



(D)



(E)

Further photolysis of the olefin–hydrido-complexes $[MH(CO)_2(olefin)(\eta^5\text{-}C_5R'_5)]$ in CH_4 and CO matrices at 12 K and also in alkane solutions leads to the loss of the olefin and re-capture of the photo-ejected CO ligand (Scheme 2) to give good yields of $[MH(CO)_3(\eta^5\text{-}C_5R'_5)]$ complexes. In CH_4 matrices even further photolysis ($290 < \lambda < 390$ nm) took place (not illustrated in Figures 1 and 3) to give the 16-electron species $[WH(CO)_2(\eta^5\text{-}C_5R'_5)]$. These species were not detected in CO matrix experiments, and they were also not detected by Kazlauskas and Wrighton [11,12] when they photolysed $[M(CO)_2R(\eta^5\text{-}C_5R'_5)]$ (M = Mo or W; R = Et or n-C_5H_{11}; R' = H or Me) in paraffin-wax discs at 77 K. In solution the $[MH(CO)_3(\eta^5\text{-}C_5R'_5)]$ complexes can be photolysed to produce $[\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ and H_2 or can react photochemically with unreacted starting material, $[M(CO)_3R(\eta^5\text{-}C_5R'_5)]$, to give $[\{M(CO)_3(\eta^5\text{-}C_5R'_5\}_2]$ and the free alkane RH.[25]

In the series of alkyl complexes $[M(CO)_3R(\eta^5\text{-}C_5H_5)]$ (R = alkyl) the isopropyl derivative is noteworthy because of the very rapid appearance of bands due to $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ on photolysis, while there are modest yields of the $[W(CO)_2Pr^i(\eta^5\text{-}C_5H_5)]$ and $[WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)]$ species. Solution photolysis did not produce any $[WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)]$ but only $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$. Since $[W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)]$ has six hydrogens in the β-position of the alkyl ligand it should be a more favourable candidate for β-elimination than the Pr^n derivative which has only two β-hydrogens. Marks and co-workers [36,37] have shown that $[ThPr^i(\eta^5\text{-}C_5H_5)_3]$ can be readily photolysed in solution to give good yields of the complex '$[Th(\eta^5\text{-}C_5H_5)_3]$'. The organic products were propane and propene. When the reaction was carried out in frozen benzene the yields of propane and propene on thawing were in the ratio 26 : 74. In these reactions β-hydrogen transfer was considered to be the key process but no olefin–hydrido-species could be detected. In the case of $[W(CO)_3Pr^i(\eta^5\text{-}C_5H_5)]$ the rapid generation of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ is possibly caused by efficient generation of the olefin–hydrido-species [$WH(CO)_2(1\text{-}C_3H_6)(\eta^5\text{-}C_5H_5)$] followed by secondary photolysis which photo-ejects $1\text{-}C_3H_6$ and adds a CO ligand.

In contrast to the alkyl complexes, the aryl complexes [$W(CO)_3Ph(\eta^5\text{-}C_5H_5)$] and [$W(CO)_3(CH_2Ph)(\eta^5\text{-}C_5H_5)$] do not undergo β-elimination reactions either in solution or in matrices. The complexes do, however, show photo-ejection of CO ligands to give [$W(CO)_2Ph(\eta^5\text{-}C_5H_5)$] and [$W(CO)_2(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)$]. A ^{13}CO-labelling study of [$W(CO)_3Ph(\eta^5\text{-}C_5H_5)$] established beyond doubt the formation of the co-ordinatively unsaturated 16-electron species [$W(CO)_2Ph(\eta^5\text{-}C_5H_5)$] in this case and for [$M(CO)_2R(\eta^5\text{-}C_5R'_5)$] species in general. The reactivity of the [$W(CO)_2Ph(\eta^5\text{-}C_5H_5)$] species was demonstrated by its ready recombination with CO, and its reaction with N_2 and C_2H_4 ligands. Surprisingly [$W(CO)_2(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)$] did not show reactions with N_2 and C_2H_4. In solution the photolysis of [$W(CO)_3Ph(\eta^5\text{-}C_5H_5)$] alone leads to the formation of [$\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2$] and benzene, which presumably arises *via* hydrogen abstraction from the solvent or from a $\eta^5\text{-}C_5H_5$ ring.

An interesting feature of the matrix photochemistry of [$W(CO)_3(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)$] was the observation of additional bands besides those assigned to [$W(CO)_2(\sigma\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)$]. In view of the fact that [$W(CO)_2(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)$] is well characterised in solution (Table 1), we may assign the additional bands in CH_4 and CO matrices to the formation of this species rather than to a matrix splitting effect. Further work on other benzyl complexes will be carried out to establish whether $\sigma \longrightarrow \eta^3$ conversion of CH_2Ph ligands in other complexes can take place in matrices at 12 K.

Conclusions

A combination of studies in solution at 243 K and in gas matrices at 12 K has confirmed that the primary step in the photoreactions of [$M(CO)_3R(\eta^5\text{-}C_5R'_5)$] (R = alkyl and aryl) complexes is the ejection of a CO ligand in agreement with studies using paraffin-wax discs.[11,12] In contrast to the latter work, the lower temperature used in the gas matrix work was instrumental in detecting the *key* secondary photoproduct *cis*-[$WH(CO)_2(\text{olefin})(\eta^5\text{-}C_5H_5)$], which was assumed to be formed in the 77 K study and was crucial to the β-elimination mechanism proposed. Additionally the gas matrix study revealed the existence of rotamers for olefin–hydrido-species with asymmetric olefins; these were not observed in paraffin-wax discs at 77 K. The importance of temperature in the design of experiments to trap and characterise unstable species, proposed as reaction intermediates, has been underlined. The only species detected in paraffin-wax discs at 77 K and not detected in gas matrices at 12 K was a species (C), where, on the basis of a large optical shift, it was proposed that a β-hydrogen became co-ordinated to the metal in [$M(CO)_2Et(\eta^5\text{-}C_5H_5)$] species.[11,12] We noticed no differences of colour in our matrices for [$M(CO)_2Et(\eta^5\text{-}C_5H_5)$] in CH_4 and CO matrices nor could we observe new absorptions in the u.v.–visible spectra after photolysis. It may well be that there is insufficient chromophore in the very thin gas matrices compared to the thicker wax matrices.

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