# Photochemistry of Tricarbonyl($\eta^5$-cyclopentadienyl)hydrido Complexes of Molybdenum and Tungsten and of Dicarbonyl($\eta^5$-cyclopentadienyl)-(ethylene)hydridotungsten in Solution and in Frozen Gas Matrices at 12 K†

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The photochemical reactions of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ complexes (M = Mo or W) and of *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ have been studied by a combination of conventional solution and low-temperature (12 K) matrix isolation techniques. In pentane solution the photolysis of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ complexes proceeds with the formation of the dimeric complexes $[\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$, $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, and $[\{WH(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ together with evolution of $H_2$ and CO. The photo-induced reactions with $N_2$ and $C_2H_4$ lead to monosubstitution products but only $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ is stable enough at room temperature for it to be fully characterised. The olefin–hydrido-complex $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ exists only as the *trans* isomer at room temperature. Under thermal and especially photochemical reaction conditions the olefin ligand in $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ can be replaced by CO, $N_2$, $PMe_3$, and tetrahydrofuran (thf) ligands leading to substitution products with different thermal stabilities. The photolysis of $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ in pentane solution in the absence of potential ligands leads to the loss of the olefin and the formation of $[\{WH(CO)_2(\eta^5\text{-}C_5H_5)_2\}_2]$. In Ar and $CH_4$ matrices at 12 K u.v. irradiation results in dissociative loss of one of the CO ligands to give the co-ordinately unsaturated 16-electron species$[MH(CO)_2(\eta^5\text{-}C_5H_5)]$(M = Mo or W). This process was reversed using visible light, *i.e.* there is an equilibrium (i). The reactivity of the $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ species was apparent in their reactions with $N_2$ and $C_2H_4$

$$[MH(CO)_3(\eta^5\text{-}C_5H_5)] \underset{h\nu'}{\overset{h\nu}{\rightleftarrows}} [MH(CO)_2(\eta^5\text{-}C_5H_5] + CO \qquad (i)$$

at 12 K to produce *trans*-$[MH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$ complexes and both *cis* and *trans* isomers of $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ but only the *trans* isomer of $[MoH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$. In CO matrices the formation of the radicals $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot}$ and $HCO^{\cdot}$ is indicative of photo-induced metal–hydrogen bond cleavage. The photolysis in $^{13}CO$ matrices results initially in the formation of all possible $[MH(^{13}CO)_{3-n}(CO)_n(\eta^5\text{-}C_5H_5)]$ ($n$ = 0—3) derivatives indicating easy CO exchange. Ultimately bands of $H^{13}CO^{\cdot}$ and $^{13}CO$-enriched $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot}$ species were observed. The identities of $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$, $[MH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$, and $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot}$species were confirmed by energy-factored force-field fitting procedures for the $^{13}CO$-enriched molecules. Upon u.v. irradiation of *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ in $CH_4$ matrices the primary product is the *cis* isomer and this is followed by insertion of $C_2H_4$ into the W–H bond to generate the 16-electron species $[W(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$. A monocarbonyl complex, possibly $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$, is the final product. In CO matrices, however, the olefin is substituted by CO, and the corresponding hydrido-carbonyl complex $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ is formed. The *cis* $\rightleftarrows$ *trans* isomerisation and the insertion of $C_2H_4$ into a M–H bond are relevant to the understanding of hydroformylation reactions catalysed by transition metal hydrides.

Transition metal hydrido-complexes play important roles in a variety of reactions: (*i*) they provide hydrogens for organic or organometallic hydrogenation reactions;[1,2] (*ii*) olefins may insert into the metal–hydrogen bond generating alkyl derivatives,[3-5] (*iii*) they represent efficient catalysts in hydroformylation reactions[6] and other catalytic processes;[7,8] (*iv*) they are highly reactive intermediates in the thermal or photo-induced β-hydrogen elimination process of transition metal alkyl complexes.[9-11] One reason for this versatile reactivity is the fact that the hydrido-ligand has only small steric requirements.[12] Since metal–hydrogen bonds are considered stronger than metal–carbon bonds,[13] selective reactions can be expected for hydrido-carbonyl complexes. So far, however, photochemistry is only known for a few hydrido-complexes,[14] *e.g.* $[ReH(\eta^5\text{-}C_5H_5)_2]$,[15] $[MH_2(\eta^5\text{-}C_5H_5)_2]$ (M = Mo or W),[16-19] $[MH(CO)_5]$ (M = Mn or Re),[20] $[CoH(CO)_4]$,[21] $[IrClH_2(PPh_3)_3]$, $[IrH_3(PPh_3)_3]$,[22] $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuClH(CO)_2(PPh_3)_2]$,[23] and $[OsH(CO)_2(\eta^5\text{-}C_5Me_5)]$.[24] In order to gain more insight into the basic steps of the photochemistry of transition metal hydrido-complexes we chose the compounds $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) and an olefin derivative $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$[10] for photolysis studies in different frozen gas matrices at 12 K. We compare those results with studies in solution, *e.g.* Hoffman and Brown[25] have postulated that the facile thermal and photo-induced reactions of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PBu^n{}_3$ both proceed chiefly *via* radical intermediates rather than by CO dissociation.

## Experimental

The starting materials $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[26-28] and $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$[10] were prepared according to the literature methods; $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ was obtained as the *trans* isomer by the direct photo-induced reaction of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ with ethylene. In a typical preparation 2 mmol (668 mg) of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ was dissolved in n-pentane (300 cm$^3$). A slow stream of

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

**Table 1.** Spectroscopic data [a] for the complexes $[\mathrm{MH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{MH(CO)_2L}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo or W; L = thf or $\mathrm{C_2H_4}$)

| Compound | ν(CO) [b]/cm$^{-1}$ | δ($\mathrm{C_5H_5}$) [c]/p.p.m. | δ(M–H) [c]/p.p.m. [J(WH)/Hz] |
|---|---|---|---|
| $[\mathrm{MoH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 2 018, 1 930 | 5.61 | −5.64 |
| $[\mathrm{WH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 2 015, 1 922 | 5.70 | −7.40 [37.1] |
| *trans*-$[\mathrm{MoH(CO)_2(thf)}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 930br, 1 827br | 5.04 | −4.69 |
| *trans*-$[\mathrm{WH(CO)_2(thf)}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 924, 1 830br | 5.11 | −4.67 [28.9] |
| *cis*-$[\mathrm{WH(CO)_2(thf)}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 928, 1 830br | 5.11 | −4.86 [23.0] [d] |
| *trans*-$[\mathrm{WH(CO)_2(C_2H_4)}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 961, 1 833 | 5.39 | −5.66 (q) [2.9] [e] |

[a] br = Broad; m = multiplet; q = quintet. [b] In thf. [c] In [$^2$H$_8$]thf at −30 °C. [d] δ(thf) = 3.75 (m), 1.79 (m); $^{13}$C n.m.r., δ($\mathrm{C_5H_5}$) = 86.4, δ(CO) = 235.7. [e] δ($\mathrm{C_2H_4}$) = 2.27 (m), 1.67 (m).

ethylene was bubbled through the solution and it was irradiated at −30 °C for 90 min. When nearly all the starting material had been consumed the reaction mixture was filtered over a frit covered with filter pulp, and the solvent was reduced to about 20 cm$^3$. This solution was then cooled to −78 °C overnight yielding 250 mg (37%) of light brown crystals (decomp. 70 °C). Spectroscopic data are given in Table 1.

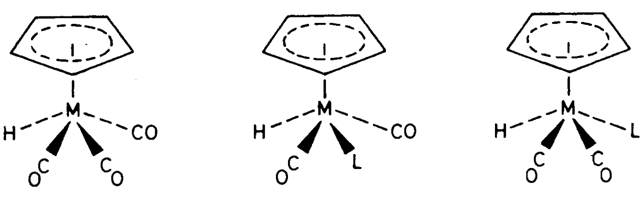
(*i*) *Solution Studies*.—All operations were carried out under nitrogen or argon using Schlenk techniques. The solvents were water free and freshly distilled. For photolyses a mercury high-pressure lamp (Hanovia L, 450 W) was used. The Duran glass of the Schlenk tubes acted as a filter for u.v. light giving $\lambda > 300$ nm. The n.m.r. spectra were obtained with a JEOL FX 90Q multi-nuclei Fourier-transform n.m.r. spectrometer and the i.r. spectra with a Perkin-Elmer 297 instrument.

*Isolation and identification of the reaction products.* Samples of $[\mathrm{MH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo or W) were photolysed at −30 °C in pentane solution. Gaseous compounds, *e.g.* CO, $\mathrm{N_2}$, and $\mathrm{C_2H_4}$, were bubbled through the solution during photolysis. Liquids, *e.g.* tetrahydrofuran (thf), were added before irradiation. The course of the reaction was monitored by i.r. and in some cases by n.m.r. spectroscopy. After photolysis the reaction mixture was filtered and n-pentane removed under high vacuum. Hydrogen-1 and carbon-13 n.m.r. spectra were then obtained. The thermal and photochemical reactions with $[\mathrm{WH(CO)_2(C_2H_4)}(\eta^5\text{-}\mathrm{C_5H_5})]$ and potential ligands were performed in an analogous manner. The spectroscopic data for the products are presented in Table 1.

(*ii*) *Matrix Studies*.—Details of the cryostat, the i.r. and u.v.—visible spectrometers, irradiation source and filters for wavelength photolysis, and matrix gases have been described previously.[5,29a] Matrices containing $[\mathrm{MH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo or W) and $[\mathrm{WH(CO)_2(C_2H_4)}(\eta^5\text{-}\mathrm{C_5H_5})]$ were prepared by the slow spray-on technique, *i.e.* the vapour from the cooled starting material (*ca.* 10 °C) was co-condensed with matrix gas onto the cold $\mathrm{CaF_2}$ window. Monomer isolation (*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 was monitored throughout by running i.r. spectra of the matrix and checking that the half-width of the terminal CO stretching bands did not exceed *ca.* 2 cm$^{-1}$ and that there was no tailing of bands to lower wavenumbers. The $^{13}$C-enriched complex $[\mathrm{WH(^{13}CO)_{3-\mathit{n}}(^{12}CO)_\mathit{n}}(\eta^5\text{-}\mathrm{C_5H_5})]$ was prepared by photolysing ($290 < \lambda < 370$ nm) the complex $[\mathrm{WH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ in n-hexane solution (25 mg in 100 cm$^3$) in an atmosphere of $^{13}$CO (200 Torr) for 2 h. The solvent was removed *in vacuo* and the hydrido-complex separated from the reaction mixture by sublimation at 30 °C (10$^{-3}$ Torr).

## Results

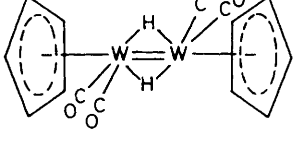
(*i*) *Studies in Solution*.—The pseudo-five-co-ordinated complexes $[\mathrm{MH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo or W) and $[\mathrm{WH(CO)_2(C_2H_4)}(\eta^5\text{-}\mathrm{C_5H_5})]$ are most conveniently represented as tetragonal pyramids (below). Accordingly the carbonyl ligands can occupy either *cis* or *trans* positions in the monosubstitution products. In the i.r. spectra of these products two bands of equal intensity are indicative for a *cis* isomer, while a considerably more intense band at lower energy is characteristic for the *trans* isomer. Because of the high mobility of the hydrido-ligand, both isomers can easily be interconverted.



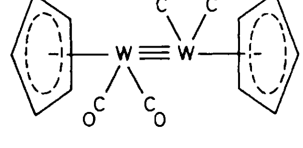
*trans*

*cis*

(*a*) *Photo-induced reactions of* $[\mathrm{MH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo *or* W) *with ligands* L (L = $\mathrm{N_2}$, $\mathrm{C_2H_4}$, *or thf*) *in solution.* The photolysis reactions of $[\mathrm{MoH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{WH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$ in pentane or toluene solution proceed differently.[29b] Upon u.v. irradiation the Mo derivative forms $[\{\mathrm{Mo(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ and hydrogen as the main reaction products besides a little $[\{\mathrm{Mo(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ and carbon monoxide. Depending on the concentration of the solution, the reaction needs 2—4 h photolysis to reach completion. The primary photoproduct upon u.v. irradiation of $[\mathrm{WH(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})]$, however, is the dimeric hydrido-species $[\{\mathrm{WH(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ [structure (I)] and carbon monoxide. This brown coloured *new* hydrido-complex has two CO bands of nearly equal intensity (1 860 and 1 930 cm$^{-1}$ in toluene) in the i.r. spectrum, and strongly shielded bridging hydrogen ligands in the $^1$H n.m.r. spectrum {δ($\mathrm{C_5H_5}$) = 6.14, δ(W–H–W) = −13.24 p.p.m., J(WH) = 83.1 Hz; in [$^2$H$_6$]acetone at −30 °C}. Extended photolysis (*ca.* 3—4 h) results in the formation of $[\{\mathrm{W(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ [structure (II)] and very little $[\{\mathrm{W(CO)_3}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$.



(I)



(II)

In the presence of ligands L (L = $\mathrm{N_2}$, $\mathrm{C_2H_4}$, or thf) a different type of reaction is observed. Instead of cleavage of the metal–hydrogen bond, CO substitution occurs and leads to the formation of the derivatives $[\mathrm{MH(CO)_2L}(\eta^5\text{-}\mathrm{C_5H_5})]$.

However, only the complex [$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] is stable enough to be isolated and fully characterised.

The photolysis of [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] in thf solutions proceeds with evolution of CO and formation of a brown solution. Monitoring of the reaction by i.r. spectroscopy shows the growth of new CO bands that are indicative of the formation of *cis* and *trans*-[$MH(CO)_2(thf)(\eta^5\text{-}C_5H_5)$] complexes (see Table 1). Simultaneously, [{$WH(CO)_2(\eta^5\text{-}C_5H_5)$}$_2$] is generated which exhibits two CO bands at 1 928 and 1 858 cm$^{-1}$. The course of the reaction can also be observed by $^1H$ n.m.r. spectroscopy. In this case photolysis results in a decrease in intensity of the signals of the starting material and the growth of new $C_5H_5$ and W–H signals that can be assigned to *cis* and *trans*-[$WH(CO)_2(thf)(\eta^5\text{-}C_5H_5)$] (see Table 1). Another $C_5H_5$ signal at 6.10 and a terminal W–H signal at $-13.26$ p.p.m. [$J$(WH) = 83.5 Hz] arise from the dicarbonyl by-product, [{$WH(CO)_2(\eta^5\text{-}C_5H_5)$}$_2$].

The photolysis of [$MoH(CO)_3(\eta^5\text{-}C_5H_5)$] in thf gives [{$Mo(CO)_3(\eta^5\text{-}C_5H_5)$}$_2$] [$\nu$(CO) = 1 953 and 1 908 cm$^{-1}$ in thf; $^1H$, $\delta$ ($C_5H_5$) = 5.22 p.p.m. in $CDCl_3$] as the principal product. With Ar bubbling through the solution, however, a mixture of products is obtained. Two products are the dimers [{$Mo(CO)_3(\eta^5\text{-}C_5H_5)$}$_2$] and [{$Mo(CO)_2(\eta^5\text{-}C_5H_5)$}$_2$]. We assign the third product as [$MoH(CO)_2(thf)(\eta^5\text{-}C_5H_5)$] [$\nu$(CO) = 1 930 and 1 827 cm$^{-1}$ in thf; $^1H$, $\delta(C_5H_5)$ = 5.04 and $\delta$ (Mo–H) = $-4.69$ p.p.m.] by comparison with the tungsten analogue (Table 1). The complex is extremely sensitive and labile. A *trans* stereochemistry for [$MoH(CO)_2(thf)(\eta^5\text{-}C_5H_5)$] seems most probable by analogy with the isolation of *cis* and *trans* isomers for [$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] (see below: matrix isolation studies) whereas only a *trans* isomer could be detected for [$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] (Table 1).

(*b*) *Thermal reaction of trans*-[$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] *and ligands* L (L = $N_2$ *or* $PMe_3$). When nitrogen is passed through the pentane solution of *trans*-[$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] at $-30$ °C, the i.r. spectra indicate a fast decrease of the parent complex (within 5 min). Simultaneously, a brown precipitate is formed. However, the generation of new CO bands could not be detected at room temperature. If a dinitrogen complex was formed the species was too labile under the reaction conditions to be observed by i.r. spectroscopy.

Trimethylphosphine reacts instantly with [$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] in pentane solutions. A yellow precipitate is formed and the i.r. spectrum of this precipitate exhibits four CO bands that are assigned to a *cis* and *trans* mixture of the known compound [$WH(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)$].[30]

(*c*) *Photo-induced reaction of trans*-[$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] *and ligands* L (L = thf *or* CO). Though [$WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)$] can be considered as a highly reactive intermediate in the photo-induced $\beta$-elimination of ethylene from [$W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)$], u.v. light is necessary to effect the substitution of the olefin ligand by L (L = CO or thf). The photoreaction takes *ca.* 30 min for CO and *ca.* 8 h for thf, leading to [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] and *trans*-[$WH(CO)_2(thf)(\eta^5\text{-}C_5H_5)$] respectively. The substitution products were characterised directly in the reaction solution by i.r., and, after removal of the solvent *in vacuo* by n.m.r. spectroscopy.

(*ii*) *Matrix Isolation Studies.—Photolysis of* [$MH(CO)_3(\eta^5\text{-}C_5H_5)$] (M = Mo *or* W) *in* $CH_4$ *and* Ar *matrices at* 12 K. Infrared spectra from an experiment with [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] isolated at high dilution in an Ar matrix (*ca.* 1 : 2 000—1 : 5 000) are shown in Figure 1. Before photolysis the spectrum in the terminal CO stretching region contains bands at 2 032.2, 1 946.1, and 1 942.1 cm$^{-1}$ [Figure 1(*a*), Table 2]. The upper band is assigned as a symmetric $A'$ stretch and the lower bands are assigned to overlapping $A'$ (symmetric) and $A''$ (antisymmetric) bands of a $C_s$ symmetry complex by analogy with the bands observed in gas matrices for [$M(CO)_3R(\eta^5\text{-}C_5R'_5)$] complexes (M = Mo or W; R = alkyl or aryl; R$'$ = H or $CH_3$).[5,29a] Irradiation of the matrix with u.v. radiation ($230 < \lambda < 420$ nm) corresponding to the electronic spectrum of [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] [Figure 2(*a*)] produced 'free' CO (2 138.5 cm$^{-1}$) and two new bands at 1 967.0 and 1 881.6 cm$^{-1}$ [Figure 1(*b*)]. Continued photolysis resulted in the latter pair of bands and that of CO growing at the expense of the parent bands.

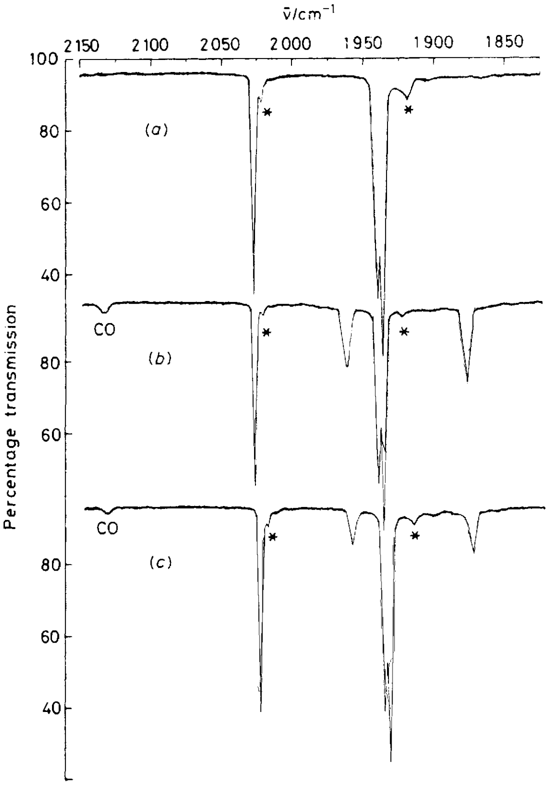


**Figure 1.** Infrared spectra from an experiment with [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] isolated at high dilution in an Ar matrix at 12 K: (*a*) after deposition, (*b*) after 50 min photolysis using $230 < \lambda < 420$ nm light, and (*c*) after 60 min reversal using $\lambda > 430$ nm radiation. Bands marked (*) are due to [$WH(^{12}CO)_2(^{13}CO)(\eta^5\text{-}C_5H_5)$] present in natural abundance

Irradiation with visible light ($430 < \lambda < 460$ nm) caused the new bands to decrease with the simultaneous increase in intensity of the bands of [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] [Figure 1(*c*)]. The relative intensities of the bands at 1 967.0 and 1 881.6 cm$^{-1}$ remained constant under a variety of photolysis conditions (time and wavelength of irradiation) indicating that they arose from a single product species. This species must be a mononuclear species because of the dilutions employed in this work. The facile reversibility of the primary step shows that the W–H linkage is retained in the product species because if cleavage of the W–H bond had occurred H atoms would have been produced and these are known to diffuse freely in gas matrices at 4—30 K.[31] Diffusion of H atoms would have precluded reversibility. The ejection of CO in the primary photolysis with the retention of a W–H bond enables the new species to be identified as [$WH(CO)_2(\eta^5\text{-}C_5H_5)$]. This assignment was confirmed by an experiment with $^{13}CO$-enriched [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] (see below).

Analogous results were obtained for [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] isolated at high dilution in $CH_4$ matrices. Analogous results were also obtained for [$MoH(CO)_3(\eta^5\text{-}C_5H_5)$] isolated at

**Table 2.** Infrared band positions (cm$^{-1}$) observed in the terminal CO stretching region for [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] complexes (M = Mo or W) and *trans*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] and their photoproducts in various matrices at 12 K

| | Matrix | | | | |
|---|---|---|---|---|---|
| Complex | CH$_4$ | Ar | N$_2$ | CO | 5% C$_2$H$_4$–CH$_4$ |
| [MoH(CO)$_3$($\eta^5$-C$_5$H$_5$)] | 2 029.8<br>1 946.9<br>1 940.3 [a] | 2 033.4<br>1 952.4<br>1 948.0 [a] | 2 029.2<br>1 947.2<br>1 942.4 [a] | 2 029.2<br>1 946.7<br>1 940.5 [a] | 2 028.2<br>1 944.0<br>1 939.3 [a] |
| [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] | 2 025.5<br>1 939.5<br>1 935.1 [a] | 2 032.2<br>1 946.1<br>1 942.1 [a] | 2 029.5<br>1 942.5<br>1 932.3 [a] | 2 024.3<br>1 936.1<br>1 931.1 [a] | 2 024.0<br>1 932.5 [b] |
| [MoH(CO)$_2$($\eta^5$-C$_5$H$_5$)] | 1 963.5<br>1 885.2 | 1 972.4<br>1 892.4 | *c* | *d* | 1 962.2<br>1 882.7 |
| [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)] | 1 956.4<br>1 872.0 | 1 967.0<br>1 881.6 | *c* | *d* | 1 956.0<br>1 874.5 |
| [MoH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] [e] | — | — | 1 976.1<br>1 912.8 | — | — |
| [WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] [e] | — | — | 1 972.7<br>1 910.0 | — | — |
| [Mo(CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\cdot$ | — | — | — | 2 008.9<br>1 915.5<br>1 908.4 [f] | — |
| [W(CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\cdot$ | — | — | — | 1 999.3<br>1 900.3<br>1 896.5 [f] | — |
| [Mo(CO)$_6$] | — | — | — | 1 985.1 | — |
| [W(CO)$_6$] | — | — | — | 1 979.7 | — |
| H$^{12}$CO/H$^{13}$CO | — | — | — | 1 859.1/1 817.0 | — |
| *trans*-[MoH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] | — | — | — | — | 1 974.8<br>1 901.3 |
| *cis*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] | 1 987.6<br>1 928.5 | — | — | 1 988.7<br>1 931.4 | 1 986.2<br>1 927.8 |
| *trans*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] | 1 974.2<br>1 897.2 | — | — | 1 979.5<br>1 902.1 | 1 974.0<br>1 897.5 |
| [Mo(CO)$_2$(C$_2$H$_5$)($\eta^5$-C$_5$H$_5$)] | — | — | — | — | 1 955.0<br>1 872.5 |
| [W(CO)$_2$(C$_2$H$_5$)($\eta^5$-C$_5$H$_5$)] | 1 947.8<br>1 861.1 | — | — | 1 949.1<br>1 862.2 | 1 945.3<br>1 859.3 |
| [WH(CO)(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] | 1 904.0 | — | — | — | 1 904.3 |

[a] Overlapping *A′* and *A″* bands (see text). [b] Broad unresolved band due to mixed-matrix effect. [c] [MH(CO)$_2$($\eta^5$-C$_5$H$_5$)] species (M = Mo or W) are not observed in N$_2$ matrices. [d] [MH(CO)$_2$($\eta^5$-C$_5$H$_5$)] species (M = Mo or W) are not observed in CO matrices. [e] ν(NN) (Mo) at 2 192 cm$^{-1}$; ν(NN) (W) at 2 163.5 cm$^{-1}$. [f] Broad band split.

dilution in Ar and CH$_4$ matrices (*ca.* 1 : 2 000 to 1 : 5 000). Spectroscopic data for the new species are given in Table 2.

*Photolysis of* $^{13}$CO *enriched* [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] *in* Ar *matrices at* 12 K. The i.r. spectrum of $^{13}$CO-enriched [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in an Ar matrix at 12 K shows bands due to the range of species [WH($^{12}$CO)$_{3-n}$($^{13}$CO)$_n$($\eta^5$-C$_5$H$_5$)] ($n$ = 0—3) [Figure 3(*a*)]. This was confirmed by an energy-factored force-field analysis of the observed and calculated band positions.[29a,32,33] A very good fit was obtained using $C_s$ symmetry (Table 3). Irradiation of the matrix with u.v. radiation (290 < λ < 410 nm) gave new $^{13}$CO-enriched product bands at 1 965.9, 1 950.1, 1 879.5, 1 854.5, and 1 837.6 cm$^{-1}$ [Figure 3(*b*)]. In this case a good fit was obtained between the observed and calculated bands of a $C_s$ W(CO)$_2$ fragment, *i.e.* [WH($^{12}$CO)$_{2-m}$($^{13}$CO)$_m$($\eta^5$-C$_5$H$_5$)] ($m$ = 0—2) (Table 3). The photoproducts in Ar and CH$_4$ matrices (see above) can, therefore, be conclusively assigned as [MH(CO)$_2$($\eta^5$-C$_5$H$_5$)] species (M = Mo or W).

The observed relative intensities ($I$) of the two bands for [WH($^{12}$CO)$_2$($\eta^5$-C$_5$H$_5$)] [$I$(1 965.9) : $I$(1 879.5) (symmetric : antisymmetric) = 1 : 1.21] were obtained by tracing and weighing bands from spectra in absorbance mode. The ratio $I_{\text{asym}}/I_{\text{sym}}$ (1.21 : 1) gave an OC–W–CO angle (θ) of *ca.* 95° in the standard expression $I_{\text{asym}}/I_{\text{sym}} = \tan^2(\theta/2)$.[33]

*Photolysis of* [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] (M = Mo *or* W) *in* N$_2$ *matrices at* 12 K. The i.r. spectrum of [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a N$_2$ matrix (*ca.* 1 : 2 000 to 1 : 5 000) is shown in Figure 4(*a*). A period of photolysis using medium energy u.v. radiation (290 < λ < 370 nm) produced new i.r. bands at 2 163.5, 2 138.0, 1 972.7, and 1 910.0 cm$^{-1}$, of which the band at 2 138.0 cm$^{-1}$ corresponds to free CO [Figure 4(*b*)]. Long-wavelength irradiation (430 < λ < 460 nm) caused little change in the intensities of the parent bands [Figure 4(*d*)] or new product bands; such long-wavelength photolysis caused reversal of the forward step in the case of [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)] (see above).

The band at 2 163.5 cm$^{-1}$ may be assigned as a N–N stretching mode of an end-on co-ordinated dinitrogen ligand by analogy with bands for [Co(CO)(N$_2$)($\eta^5$-C$_5$H$_5$)] [ν(NN) at 2 164.6 cm$^{-1}$ (N$_2$ matrix)],[34] [Mn(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] [ν(NN) at 2 175.0 cm$^{-1}$ (N$_2$ matrix) and 2 169 cm$^{-1}$ (n-hexane)],[35,36] [Fe(CO)$_2$(N$_2$)($\eta^4$-C$_4$H$_4$)] [ν(NN) at 2 206.8 cm$^{-1}$ (N$_2$ matrix)],[35] [Ni(CO)$_3$(N$_2$)] [ν(NN) at 2 266 cm$^{-1}$ (N$_2$ matrix)],[37] and [Mo(CO)$_2$(N$_2$)(CH$_3$)($\eta^5$-C$_5$H$_5$)][ν(NN) at 2 190.8 cm$^{-1}$ (N$_2$ matrix)].[29a] The bands at 1 972.7 and 1 910.0 cm$^{-1}$ may be assigned as terminal CO stretching modes. Since the product is formed with the ejection of CO (band at 2 138.0 cm$^{-1}$), it may be identified as [WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)], *cf.* [Mo(CO)$_2$(N$_2$)(CH$_3$)($\eta^5$-C$_5$H$_5$)] [ν(CO) at 1 969.7 and 1 913.7 cm$^{-1}$].[29a] This assignment was confirmed by photolysing [WH($^{12}$CO)$_{3-n}$-

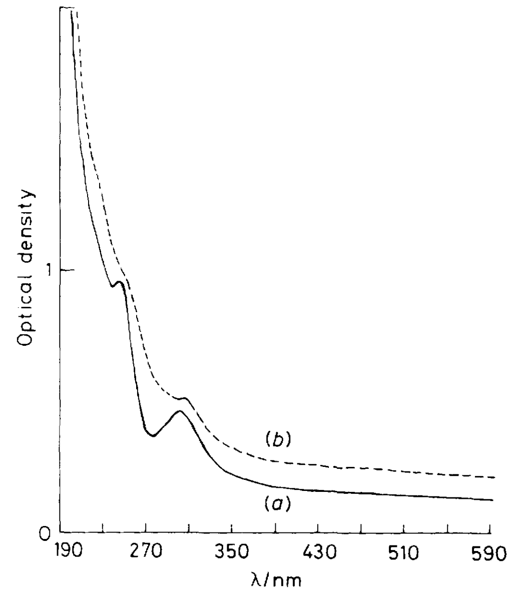


**Figure 2.** Ultraviolet-visible spectra from an experiment with [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in an Ar matrix at 12 K: (*a*) after deposition and (*b*) after 50 min photolysis using 230 < λ < 420 nm light

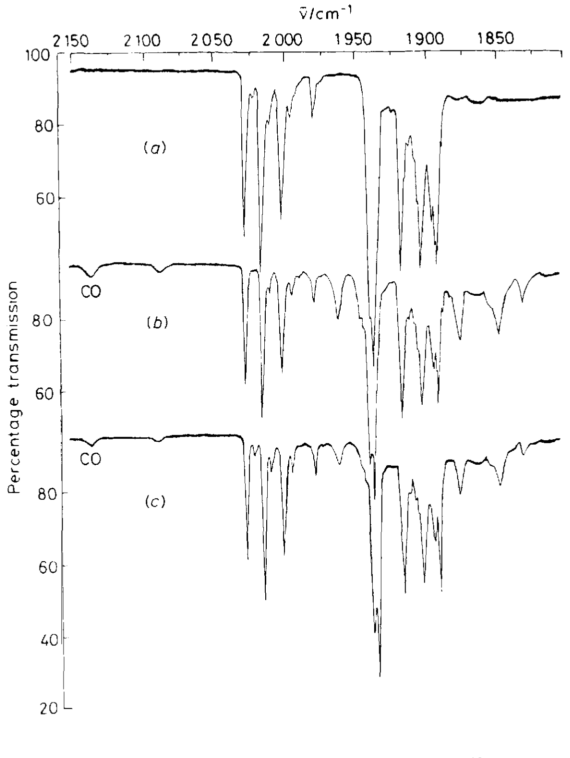


**Figure 3.** Infrared spectra from an experiment with $^{13}$CO-enriched [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in an Ar matrix at 12 K: (*a*) after deposition, (*b*) after 45 min photolysis using 290 < λ < 410 nm radiation, and (*c*) after 2 min annealing

($^{13}$CO)$_n$($\eta^5$-C$_5$H$_5$)] ($n$ = 0–3) in a N$_2$ matrix. The resulting bands were subjected to an energy-factored force-field fitting procedure (see above) and excellent agreement between observed and calculated bands was obtained for a M(CO)$_2$ fragment (see Table 3).

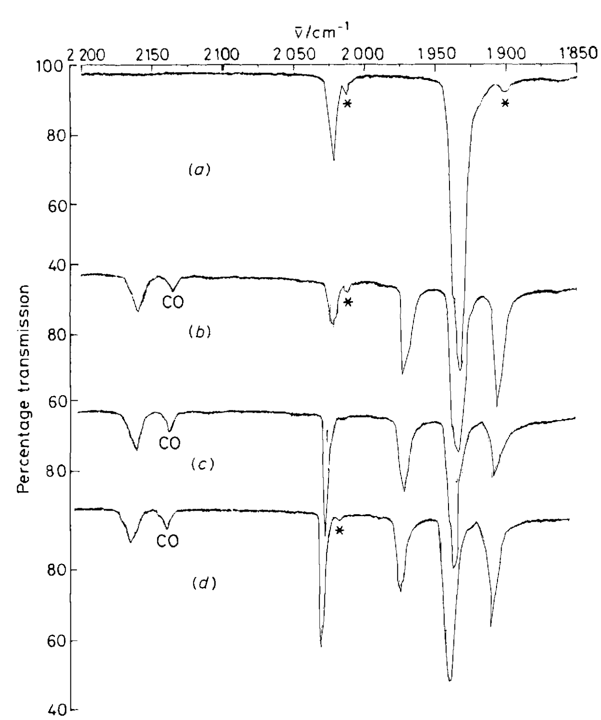


**Figure 4.** Infrared spectra from an experiment with [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a N$_2$ matrix at 12 K: (*a*) after deposition, (*b*) after 10 min photolysis with 290 < λ < 370 nm radiation, (*c*) after further 15 min photolysis using the same source, and (*d*) after reversal for 90 min using λ > 430 nm light. Bands marked (*) are due to [WH($^{12}$CO)$_2$($^{13}$CO)($\eta^5$-C$_5$H$_5$)] present in natural abundance

Considering the relative intensities of the CO stretching bands of [WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)], which may be assigned as the symmetric (1 972.7 cm$^{-1}$) and antisymmetric (1 910.0 cm$^{-1}$) modes of a $C_s$ symmetry W(CO)$_2$ fragment, an OC–W–CO bond angle (θ) can be calculated from the expression $I_{\text{asym}}/I_{\text{sym}} = \tan^2(\theta/2)$, *cf.* [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)]. The value of the OC–W–CO angle was found to be 108° which is indicative of a *trans* geometry of the CO ligands.* An alternative approach to assigning stereochemistry is *via* the calculation[31] of energy-factored CO interaction force constants ($k_i$). For [WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] this gave a value of 49.2 N m$^{-1}$ for $k_i$ and comparison of this value with $k_i$ values for [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] ($k_{12} = k_{cis}$ = 43.9 N m$^{-1}$ and $k_{23} = k_{trans}$ = 51.9 N m$^{-1}$; Table 3) confirms the structure of the new species as *trans*-[WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)].

Analogous results were obtained with [MoH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in N$_2$ matrices except that for this complex the forward photolysis to give [MoH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] could be reversed. Values of the OC–Mo–CO bond angle (θ) of *ca.* 102° and the energy-factored CO-inter-

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* Burdett[38] has concluded that for metal carbonyls containing other ligands, the use of carbonyl band intensities to calculate bond angles is not universally applicable. The method can only be a legitimate one in those molecules where vibrational coupling between the M–X and CO oscillators is small, *e.g.* [Mn(CO)$_5$Br]. 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(CO) and ν(NN) or ν(CO) and ν(NO) 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 including perturbations from the N$_2$ and NO ligands, *e.g.* [Co(CO)(N$_2$)($\eta^5$-C$_5$H$_5$)],[34] [Mo(CO)$_2$(N$_2$)(CH$_3$)($\eta^5$-C$_5$H$_5$)],[29a] and [Mn(CO)(NO)$_2$(NO*)] (where NO* denotes a one-electron donor nitrosyl ligand).[39]

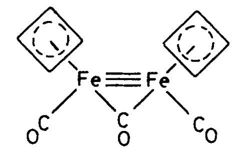
**Table 3.** Observed and calculated band positions (cm$^{-1}$) of terminal CO bands in an experiment with a $^{13}$CO-enriched sample of [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] in various matrices at 12 K

| Complex (symmetry point group) | | | Observed | Calculated |
|---|---|---|---|---|
| [WH($^{12}$CO)$_3$($\eta^5$-C$_5$H$_5$)] [a] | ($C_s$) | $A'$ | 2 029.6 | 2 028.9 |
| | | $A' + A''$ | 1 942.0 | 1 941.1 |
| [WH($^{12}$CO)$_2$($^{13}$CO)($\eta^5$-C$_5$H$_5$)] | ($C_s$) [b] | $A'$ | 2 020.0 | 2 020.5 |
| | | $A''$ | 1 941.2 [c] | 1 941.1 |
| | | $A'$ | 1 906.0 | 1 905.9 |
| | ($C_1$) [d] | $A$ | 2 016.0 | 2 016.7 |
| | | $A$ | 1 941.2 [c] | 1 941.1 |
| | | $A$ | 1 908.6 | 1 909.4 |
| [WH($^{12}$CO)($^{13}$CO)$_2$($\eta^5$-C$_5$H$_5$)] | ($C_1$) [e] | $A$ | 2 005.2 | 2 006.1 |
| | | $A$ | 1 920.8 | 1 919.6 |
| | | $A$ | 1 899.0 | 1 897.9 |
| | ($C_s$) [f] | $A'$ | 1 999.7 | 2 001.0 |
| | | $A'$ | *g* | 1 924.4 |
| | | $A''$ | 1 897.0 | 1 897.9 |
| [WH($^{13}$CO)$_3$($\eta^5$-C$_5$H$_5$)] | ($C_s$) | $A'$ | 1 983.4 | 1 983.9 |
| | | $A' + A''$ | 1 897.1 | 1 897.9 |
| [WH($^{12}$CO)$_2$($\eta^5$-C$_5$H$_5$)] [h] | ($C_s$) | $A'$ | 1 965.9 | 1 966.0 |
| | | $A''$ | 1 879.5 | 1 879.7 |
| [WH($^{12}$CO)($^{13}$CO)($\eta^5$-C$_5$H$_5$)] | ($C_1$) | $A$ | 1 950.1 | 1 949.2 |
| | | $A$ | 1 854.5 | 1 853.8 |
| [WH($^{13}$CO)$_2$($\eta^5$-C$_5$H$_5$)] | ($C_s$) | $A'$ | *g* | 1 922.3 |
| | | $A''$ | 1 837.6 | 1 837.9 |
| [WH($^{12}$CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] [i] | ($C_s$) | $A'$ | 1 972.7 | 1 972.7 |
| | | $A''$ | 1 910.0 | 1 910.0 |
| [WH($^{12}$CO)($^{13}$CO)(N$_2$)($\eta^5$-C$_5$H$_5$)] | ($C_1$) | $A$ | 1 957.2 | 1 957.6 |
| | | $A$ | 1 882.3 | 1 882.0 |
| [WH($^{13}$CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] | ($C_s$) | $A'$ | 1 928.6 | 1 928.9 |
| | | $A''$ | 1 866.4 | 1 867.6 |
| [W($^{12}$CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$ [j] | ($C_{3v}$) | $A_1$ | 1 999.7 | 1 999.3 |
| | | $E$ | 1 899.5 | 1 898.6 |
| [W($^{12}$CO)$_2$($^{13}$CO)($\eta^5$-C$_5$H$_5$)]$^\bullet$ | ($C_s$) | $A'$ | 1 987.8 | 1 988.0 |
| | | $A''$ | 1 899.2 | 1 898.7 |
| | | $A'$ | 1 866.7 | 1 867.0 |
| [W($^{12}$CO)($^{13}$CO)$_2$($\eta^5$-C$_5$H$_5$)]$^\bullet$ | ($C_s$) | $A'$ | 1 974.5 | 1 974.3 |
| | | $A'$ | 1 880.5 | 1 879.9 |
| | | $A''$ | *k* | 1 856.5 |
| [W($^{13}$CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$ | ($C_{3v}$) | $A_1$ | 1 954.4 | 1 954.8 |
| | | $E$ | 1 855.5 | 1 856.4 |

[a] Refined energy-factored force constants for [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)]: $K_1$ = 1 559.3, $K_2$ = 1 574.1, $k_{12}$ = 43.9, and $k_{23}$ = 51.9 N m$^{-1}$ as defined by the numbering $1-\underset{\substack{|\\3}}{\overset{\substack{2\\|}}{W}}-H$ ($1 \neq 2 = 3$). [b] $^{13}$CO in position 1. [c] Band obscured by parent molecule band at 1 942.0 cm$^{-1}$. [d] $^{13}$CO in position 2. [e] $^{12}$CO in position 2. [f] $^{12}$CO in position 1. [g] Band obscured by band of $^{13}$CO-enriched [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] at 1 920.8 cm$^{-1}$. [h] Refined energy-factored force constants for [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)]: $K$ = 1 494.5 and $k_i$ = 67.0 N m$^{-1}$. [i] Refined energy-factored force constants for *trans*-[WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)]: $K$ = 1 523.0 and $k_i$ = 49.2 N m$^{-1}$. For Mo complex: $K$ = 1 527.9 and $k_i$ = 49.7 N m$^{-1}$. [j] Refined energy-factored force constants for [W(CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$: $K$ = 1 509.2 and $k_i$ = 52.8 N m$^{-1}$ in a mixed $^{13}$CO–$^{12}$CO (25 : 75) matrix. [k] Band obscured by the band of [W($^{13}$CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$ at 1 855.5 cm$^{-1}$.

action force constant ($k_i$ = 49.7 N m$^{-1}$) confirmed the structure as *trans*-[MoH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] (see above). Spectroscopic data for the new dinitrogen complexes are given in Table 2.

The position of the NN stretching band for *trans*-[WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] is similar to that for [Mn(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)], which, as well as being formed in a N$_2$ matrix,[35] has been obtained by conventional preparative techniques.[36] It seems possible that *trans*-[WH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] might exist as a stable complex at ambient temperatures. The band for *trans*-[MoH(CO)$_2$(N$_2$)($\eta^5$-C$_5$H$_5$)] (2 192.0 cm$^{-1}$), however, is at much higher wavenumber, *cf.* [Fe(N$_2$)(CO)$_2$($\eta^4$-C$_4$H$_4$)] [$\nu$(NN) at 2 206.8 cm$^{-1}$],[35] which is indicative of a weaker Mo–N bond than for W. An attempt [40] to prepare [Fe(CO)$_2$(N$_2$)($\eta^4$-C$_4$H$_4$)], following the successful matrix isolation experiments, led to the isolation of the novel iron dimer (III). For the [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] complexes (M = Mo or W) although a reaction took place in the presence of N$_2$, no new N$_2$ complexes could be isolated (see above).



(III)

*Photolysis of* [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] (M = Mo *or* W) *in* CO *matrices at* 12 K. The i.r. spectrum of [MoH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a CO matrix is shown in Figure 5(*a*). Irradiation of the matrix with u.v. light ($230 < \lambda < 390$ nm) resulted in the growth of four new bands at 2 008.9, 1 915.5, 1 908.4, and 1 859.1 cm$^{-1}$ [Figure 5(*b*)]. Longer times of irradiation with u.v. light caused the four bands to grow, together with an additional band at 1 985.1 cm$^{-1}$ [Figure 5(*c*), (*d*)]. Photolysis with long-wavelength radiation ($\lambda > 430$ nm) produced a decrease in the bands at 2 008.9, 1 915.5, 1 908.4, and 1 859.1 cm$^{-1}$ and an increase in the bands of [MoH(CO)$_3$($\eta^5$-C$_5$H$_5$)] [Figure 5(*e*)]. The band at 1 985.1 cm$^{-1}$, however, did not show a change in relative intensity on long-wavelength irradiation.

By analogy with the hydrides [CoH(CO)$_4$] [20] and [MH(CO)$_5$] (M = Mn or Re) [19] which give the radicals HCO$^\bullet$ and [Co(CO)$_4$]$^\bullet$ and HCO$^\bullet$ and [M(CO)$_5$]$^\bullet$ respectively on photolysis at 4—20 K, it might be expected that [MoH(CO)$_3$($\eta^5$-C$_5$H$_5$)] would give HCO$^\bullet$ and [Mo(CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$. Indeed, the band at 1 859.1 cm$^{-1}$, which shows the appropriate $^{13}$C shift in $^{13}$CO-doped matrices, corresponds to the band position for HCO$^\bullet$ reported previously (1 860 cm$^{-1}$).[19,20] The bands at 2 008.9, 1 915.5, and 1 908.4 cm$^{-1}$ may then be assigned to [Mo(CO)$_3$($\eta^5$-C$_5$H$_5$)]$^\bullet$ with $C_{3v}$ local symmetry for the Mo(CO)$_3$ fragment. This was confirmed by a study of [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] (M = Mo or W) in mixed $^{12}$CO–$^{13}$CO matrices. The resulting band patterns were subjected to an energy-factored force-field fitting procedure (see above) and satisfactory agreement between observed and calculated bands for a $C_{3v}$ symmetry M(CO)$_3$ fragment was obtained (Table 3), *i.e.* [M($^{12}$CO)$_{3-n}$($^{13}$CO)$_n$($\eta^5$-C$_5$H$_5$)]$^\bullet$ ($n$ = 0—3).[41]

The remaining band at 1 985.1 cm$^{-1}$ corresponds exactly with the band position of [Mo(CO)$_6$] isolated at high dilution in a CO matrix, *i.e.* long irradiation times with u.v. light result in dissociation of the $\eta^5$-C$_5$H$_5$ ligand. A precedent for this is the conversion of [Ni(NO)($\eta^5$-C$_5$H$_5$)] to [Ni(CO)$_4$] by photolysis in a CO matrix at 20 K.[42]

Similar results were obtained with [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in CO matrices. Interestingly, neither the Mo nor W complexes gave any indication of the formation of [MH(CO)$_2$($\eta^5$-C$_5$H$_5$)] species as was found in CH$_4$ and Ar matrices. Spectroscopic data for the new species formed in CO matrices are given in Table 2.

*Photolysis of* [MH(CO)$_3$($\eta^5$-C$_5$H$_5$)] (M = Mo *or* W) *in* 5% C$_2$H$_4$-*doped* CH$_4$ *matrices at* 12 K. Infrared spectra from an experiment with [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a 5% C$_2$H$_4$–CH$_4$ matrix are shown in Figure 6. Before photolysis the spectrum shows two broadened bands (2 024.0 and 1 932.5 cm$^{-1}$) [Figure 6(*a*)] whereas in pure Ar,

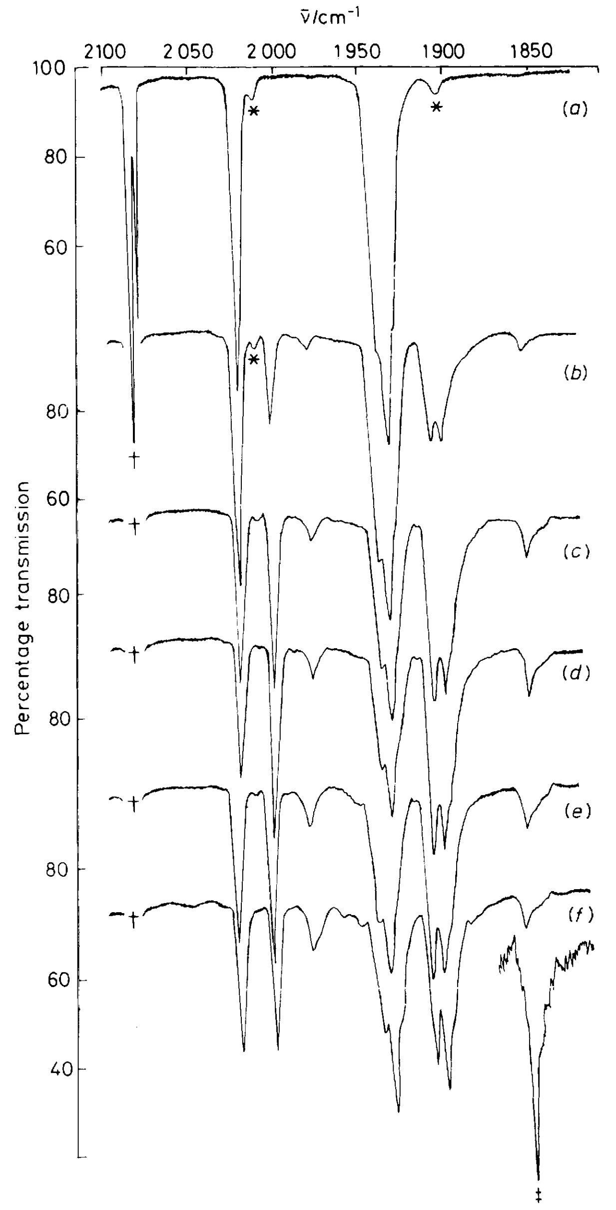


**Figure 5.** Infrared spectra from an experiment with [MoH(CO)$_3$-($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition, (*b*) after 15 min photolysis using 230 $< \lambda <$ 390 nm radiation, (*c*) after 30 min further photolysis using the same source, (*d*) after further 30 min further photolysis using the same source, (*e*) after 30 min reversal using $\lambda >$ 430 nm radiation, and (*f*) after annealing to *ca.* 30 K for 2 min. Bands marked (*) are due to [MoH($^{12}$CO)$_2$($^{13}$CO)($\eta^5$-C$_5$H$_5$)] present in natural abundance, those marked (†) to $^{13}$CO, and that marked (‡) is assigned to the HCO· radical and is expanded × 5

N$_2$, and CO matrices sharper bands are observed together with a splitting of the lower wavenumber band [Figures 1(*a*), 4(*a*), and 5(*a*)]. This band broadening is commonly experienced with ' mixed ' matrices and does not imply a lack of solute molecule isolation.

Irradiation of the matrices with medium-energy u.v. radiation (290 $< \lambda <$ 370 nm) produced new terminal CO stretching i.r. bands at 1 956.0 and 1 874.5 cm$^{-1}$ [Figure 6(*b*)]. Longer irradiation times with the same radiation resulted in the appearance and growth of bands at 1 986.2, 1 974.0, 1 945.3, 1 927.8, 1 897.5, and 1 859.3 cm$^{-1}$ [Figure 6(*c*)].

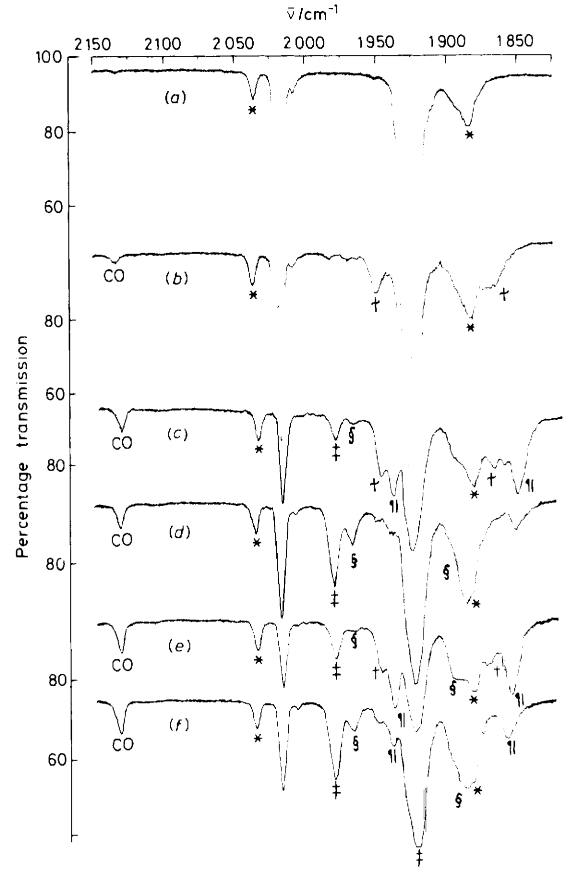


**Figure 6.** Infrared spectra from an experiment with [WH(CO)$_3$-($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a 5% C$_2$H$_4$-doped CH$_4$ matrix at 12 K: (*a*) after deposition, (*b*) after 3 min photolysis using 290 $< \lambda <$ 370 nm radiation, (*c*) after further 15 min photolysis using the same source, (*d*) after 90 min photolysis using $\lambda >$ 430 nm radiation, (*e*) after 15 min further photolysis using u.v. radiation (290 $< \lambda <$ 370 nm), and (*f*) after further 30 min photolysis using visible light ($\lambda >$ 430 nm). Bands marked (*) are due to C$_2$H$_4$ in the matrix, those marked (†) to [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)], those marked (‡) to *cis*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)], those marked (§) to *trans*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)], and those marked (¶) to [W(CO)$_2$(C$_2$H$_5$)($\eta^5$-C$_5$H$_5$)] (see text)

Prolonged photolysis with the same energy showed that the bands at 1 956.0, 1 945.3, 1 874.5, and 1 859.3 cm$^{-1}$ increase more markedly than the other new bands while the bands of [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] continue to decrease. Irradiation with long-wavelength radiation ($\lambda >$ 430 nm) caused the bands at 1 986.2, 1 974.0, 1 927.8, and 1 897.5 cm$^{-1}$ to increase dramatically while other bands decreased [Figure 6(*d*)]. In these photolyses it was found that the lower band of [WH(CO)$_3$-($\eta^5$-C$_5$H$_5$)] decreased more slowly than the upper band, indicating the overlapping growth of a new product band with the lower band.

Comparison of the band positions with those observed on photolysis of [WH(CO)$_3$($\eta^5$-C$_5$H$_5$)] in CH$_4$ matrices (see above), on photolysis of [W(CO)$_3$(C$_2$H$_5$)($\eta^5$-C$_5$H$_5$)] in CH$_4$ matrices,[5] and deposition of an authentic sample of [WH-(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] in a CH$_4$ matrix (see below), enabled a complete assignment to be made for all the new bands. The species observed were [WH(CO)$_2$($\eta^5$-C$_5$H$_5$)] (1 956.0 and 1 874.5 cm$^{-1}$), [W(CO)$_2$(C$_2$H$_5$)($\eta^5$-C$_5$H$_5$)] (1 945.3 and 1 859.3 cm$^{-1}$), *cis*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] (1 986.2 and 1 927.8 cm$^{-1}$), and *trans*-[WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] (1 974.0 and 1 897.5 cm$^{-1}$). It is notable that the rate of formation of the *cis* and *trans* isomers of [WH(CO)$_2$(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] depends on the rate of formation of the 16-electron species $[WH(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$ and these in turn are formed at a rate which is a function of the radiation used. This is illustrated in Figure 6(*e*) and (*f*), where photolysis with visible light ($\lambda > 430$ nm) causes the bands for $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ and for the ethylene complexes $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ to grow whereas irradiation with u.v. light results in the formation of the 16-electron species $[WH(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$.

Ultimately, prolonged photolysis produces a single new band at 1 904.3 cm$^{-1}$ which was also observed on photolysis of $[W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ and *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ (see below). This band is tentatively assigned to the 16-electron $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$ species.

Analogous results were obtained with $[MoH(CO)_3(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in 5% $C_2H_4$–$CH_4$ doped matrices with the exception that only the *trans* isomer was observed for Mo whereas both *cis*- and *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ were observed for W. Spectroscopic data for the new species are presented in Table 2. It is important to note that all the intermediates in this photoreaction are also generated when the ethyl derivatives $[M(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) are photolysed in $CH_4$ and CO matrices at 12 K.[5]

*Photolysis of trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ *in* $CH_4$ *and* CO *matrices at* 12 K. The i.r. spectrum produced on co-condensing $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ with an excess of $CH_4$ at 12 K shows *two* bands at 1 974.3 and 1 897.2 cm$^{-1}$ in addition to bands arising from $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ and $[W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ present as impurities [Figure 7(*a*)]. The bands at 1 974.3 and 1 897.2 cm$^{-1}$ correspond well with the i.r. bands in solution where a *trans* structure has been deduced on the basis of i.r. and n.m.r. spectroscopy (Table 1). Tracing and weighing the terminal CO stretching bands, from spectra recorded in absorbance mode, gave[33] a OC–W–CO bond angle ($\theta$) of *ca.* 112° (see above).

Photolysis with medium-energy radiation ($310 < \lambda < 370$ nm) resulted in the formation of new bands at 1 987.6, 1 947.8, 1 928.5, and 1 861.1 cm$^{-1}$ [Figure 7(*b*)]. Irradiation with visible light ($\lambda > 430$ nm) caused the bands at 1 947.8 and 1 861.1 cm$^{-1}$ to decrease while the other two bands at 1 987.6 and 1 928.5 cm$^{-1}$ increased [Figure 7(*c*)]. Irradiation for a longer time with medium-energy radiation ($310 < \lambda < 370$ nm) produced a significant increase in the bands at 1 947.8 and 1 861.1 cm$^{-1}$ at the expense of the parent molecule bands [Figure 7(*d*)]. Irradiation with visible light ($\lambda > 430$ nm) confirmed that the two sets of bands at (*i*) 1 947.8 and 1 861.1 and (*ii*) 1 987.6 and 1 928.5 cm$^{-1}$ are due to *two* different species [Figure 7(*e*)] which are linked together in a reversible process (*i*) $\rightleftharpoons$ (*ii*). Longer photolysis times with higher energy radiation ($290 < \lambda < 370$ nm) produced a single new intense band at 1 904.0 cm$^{-1}$ together with a band due to free CO at 2 138 cm$^{-1}$.

By comparison with the species produced on photolysis of $[W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$[5] the bands at 1 947.8 and 1 861.1 cm$^{-1}$ may be assigned to $[W(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$ and those at 1 987.6 and 1 928.5 cm$^{-1}$ may be assigned to *cis*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$. Two possibilities exist for the band at 1 904.0 cm$^{-1}$: the 14-electron species $[W(CO)(C_2H_5)(\eta^5\text{-}C_5H_5)]$ or 16-electron species $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$. The former contains an ethyl group which might be expected to undergo $\beta$-elimination to relieve the electronic unsaturation. Therefore, the band at 1 904.0 cm$^{-1}$ is assigned to the 16-electron species $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$.

In CO matrices analogous products were observed with the differences that on extended photolysis the final product was $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$; no band was seen for $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$.

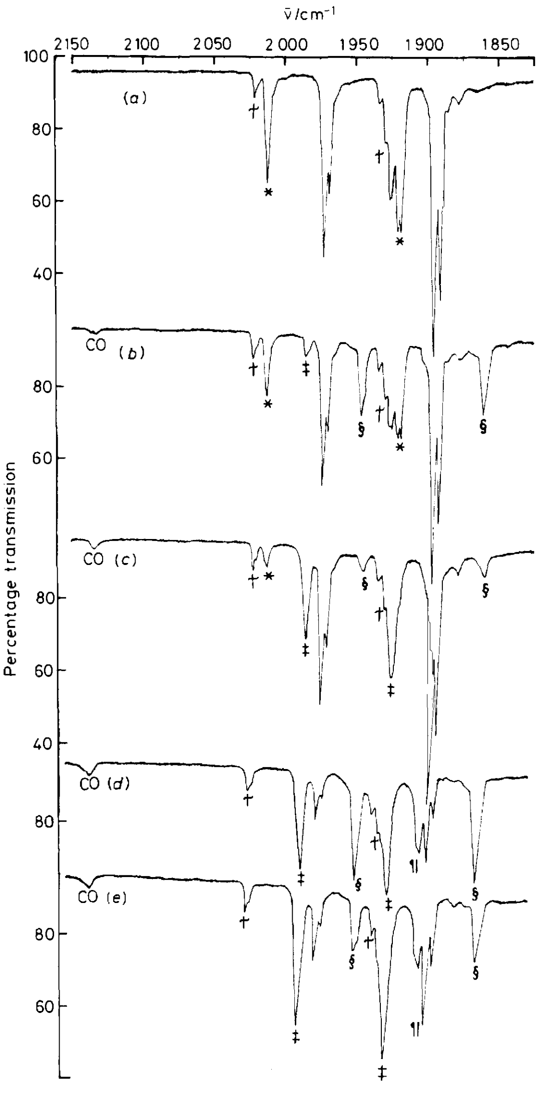
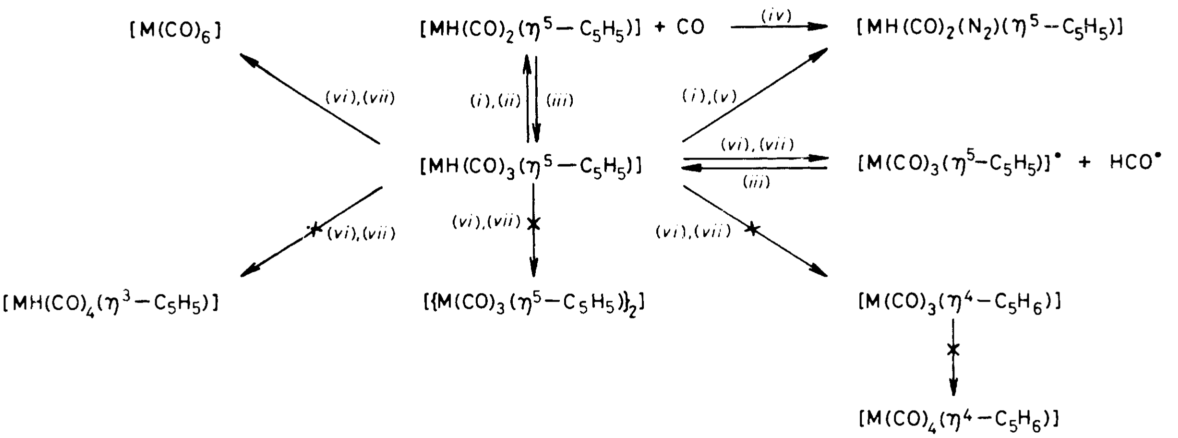


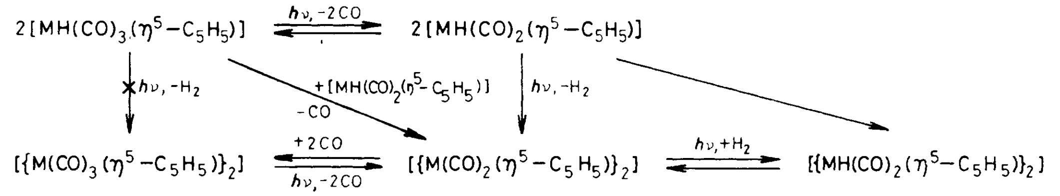
Figure 7. Infrared spectra from an experiment with *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a $CH_4$ matrix at 12 K: (*a*) after deposition, (*b*) after 10 min photolysis using $310 < \lambda < 370$ nm radiation, (*c*) after 90 min photolysis using visible light ($\lambda > 430$ nm), (*d*) after further 60 min photolysis using $310 < \lambda < 370$ nm radiation, and (*e*) after further 30 min photolysis using visible light ($\lambda > 430$ nm). Bands marked (*) are due to $[W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ and those marked (†) are due to $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ present as decomposition impurities. Product bands marked (‡) are due to *cis*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$, those marked (§) to $[W(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$, and that marked (¶) to $[WH(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)]$ (see text)

## Discussion

The combined investigation of photolysis studies in the matrix and in solution represents an excellent approach to identify reaction pathways for transition metal carbonyl complexes because the patterns of the CO bands in the i.r. spectra can provide detailed information about the number, the nature, and the relative orientation of carbonyl ligands in the various products. Since the pioneering work of Strohmeier[43] it is well known[14] that photo-excited carbonyl complexes can lose one or even more CO ligands, generating highly reactive unsaturated fragments. The carbonyl–hydrido-complexes $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) and $[WH(CO)_2(C_2H_4)(\eta^5\text{-}$



**Scheme 1.** (*i*) $CH_4$, Ar; (*ii*) $h\nu$ ($230 < \lambda < 420$ nm); (*iii*) $h\nu$ ($430 < \lambda < 460$ nm); (*iv*) $N_2$; (*v*) $h\nu$ ($290 < \lambda < 370$ nm); (*vi*) CO; (*vii*) $h\nu$ ($230 < \lambda < 390$ nm)



**Scheme 2.**

$C_5H_5)]$ represent attractive models for photochemical studies because not only the carbonyl ligands but also the hydrido-ligands can be considered to be photolabile. The photoreactions of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ in frozen gas matrices (Ar, $CH_4$, $N_2$, and CO) are summarised in Scheme 1.

The primary process in the photolysis reaction of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ in different gas matrices (Ar, $CH_4$, and $N_2$) is the dissociative loss of one CO ligand and the formation of the unsaturated fragment $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$. This highly reactive species can be characterised by i.r. spectroscopy in $CH_4$ and Ar matrices. Rapid $^{13}CO$ exchange during the photolysis of $[MH(^{12}CO)_3(\eta^5\text{-}C_5H_5)]$ complexes (M = Mo or W) in $^{13}CO$-doped matrices at 12 K, leading to $[MH(^{12}CO)_{3-n}(^{13}CO)_n(\eta^5\text{-}C_5H_5)]$ (*n* = 1, 2, and ultimately 3), confirms that photo-induced dissociation and exchange of CO ligands is taking place in matrices at low temperature and will also be taking place during irradiations in solution. In matrices with donor capability, *e.g.* $N_2$ and $C_2H_4$, the 16-electron species $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) react very efficiently to give the corresponding 1 : 1 adducts (see below). However, this does not mean that all these derivatives can be isolated from solution. The solution studies, especially the results from the photolysis of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$, suggest that $[\{MH(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ complexes are either formed by direct dimerisation of photochemically generated 16-electron species $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ or by the reaction of these fragments with the starting material with the ejection of one CO ligand. The dimeric hydrido-complexes $[\{MH(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ can lose $H_2$ reversibly upon u.v. irradiation, forming $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$. This reaction pathway has been clearly demonstrated for $[\{MoH(CO)_2(\eta^5\text{-}C_5Me_5)\}_2]$ [reaction (1)]. Depending on

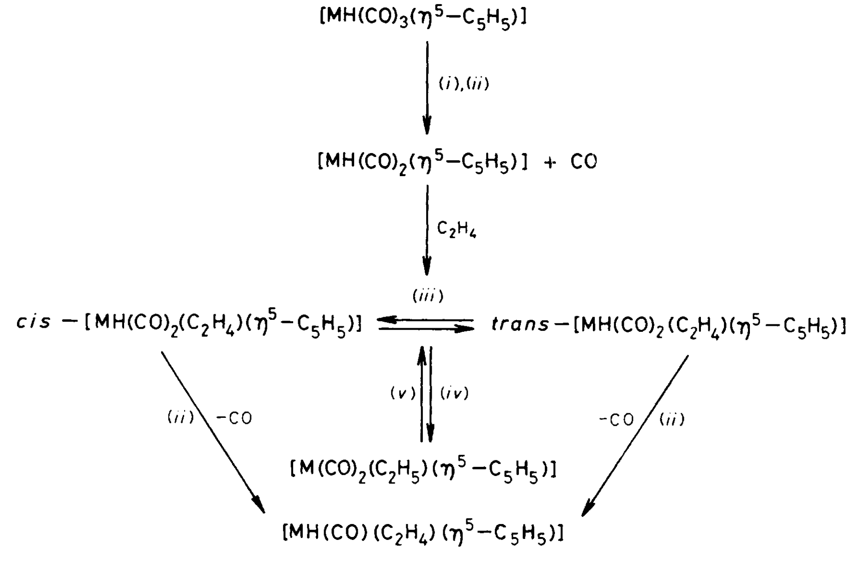
$$[\{MoH(CO)_2(\eta^5\text{-}C_5Me_5)\}_2] \overset{h\nu}{\rightleftharpoons} [\{Mo(CO)_2(\eta^5\text{-}C_5Me_5)\}_2] + H_2 \qquad (1)$$

the concentration of free $H_2$ the equilibrium can be pushed to the right or left in a few minutes.[29b] The complexes $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (M = Mo or W) are known to add carbon monoxide in a dark reaction, forming $[\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ (Scheme 2; M = Mo or W).

An alternative reaction path to CO ejection is M–H bond cleavage to give H atoms and the radicals $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\bullet}$ (M = Mo or W). Hoffman and Brown [25] have postulated that the facile thermal and photo-induced reactions of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PBu^n_3$ both proceed *via* radical intermediates. Some further evidence for this path could be derived from the observation that the final product, when $[MoH(CO)_3(\eta^5\text{-}C_5H_5)]$ is photolysed alone in n-pentane, is the dimer $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$. No evidence for radicals was found in $CH_4$ and Ar matrices but in CO matrices a band clearly assignable to the formyl radical ($HCO^{\bullet}$, 1 860 $cm^{-1}$ [20]) was observed together with terminal CO stretching bands which we assign to the radicals $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\bullet}$ (M = Mo or W). This observation is analogous to the detection of the radicals $[Mn(CO)_5]^{\bullet}$ and $[Co(CO)_4]^{\bullet}$ on photolysis of $[MnH(CO)_5]$ [20] and $[CoH(CO)_4]$ [21] respectively in CO matrices at 4—20 K. In the latter case, e.s.r. was able to detect H atoms and the radical $[Co(CO)_4]^{\bullet}$ in noble gas matrices. It is interesting that reaction (2) should be reversed by visible radiation.

$$[MH(CO)_3(\eta^5\text{-}C_5H_5)] \overset{CO}{\rightleftharpoons} [M(CO)_3(\eta^5\text{-}C_5H_5)]^{\bullet} + HCO^{\bullet} \qquad (2)$$

Such radiation is known to photodissociate HCO to give H atoms [44] and these could diffuse through the matrix and recombine with the $[M(CO)_3(\eta^5\text{-}C_5H_5)]^{\bullet}$ radicals. It is not clear from the above experiments whether the first step to produce radicals consists of the photo-induced formation of the 16-electron species $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ that could undergo subsequent photo-induced M–H bond homolysis followed by fast uptake of one CO and formation of the radicals $[M(CO)_3$-



**Scheme 3.** (*i*) 5% $C_2H_4$ in $CH_4$; (*ii*) *h*ν, $290 < \lambda < 370$ nm; (*iii*) *h*ν, $\lambda > 370$ nm; (*iv*) *h*ν, $310 < \lambda < 370$ nm; (*v*) *h*ν, $\lambda > 430$ nm

$(\eta^5\text{-}C_5H_5)]^\bullet$ (M = Mo or W), or whether the M–H bond fission occurs directly in the starting material. Both processes seem possible but certainly no evidence could be found for the presence of $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ species in CO matrices.

An alternative pathway involving the hydride ligand could be migration to the $\eta^5\text{-}C_5H_5$ ring to produce the 16-electron species $[M(CO)_3(\eta^4\text{-}C_5H_6)]$ (M = Mo or W) which could add a CO ligand from the matrix to give $[M(CO)_4(\eta^4\text{-}C_5H_6)]$ complexes. A precedent for hydride migration from a metal to a ring is the observation that photolysis of $[ReH(\eta^5\text{-}C_5H_5)_2]$ in a CO matrix at 12 K and in solution leads to the formation of $[Re(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)]$.[15,45] This complex is formed in a CO matrix *via* $[ReH(CO)(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$ and $[ReH(CO)_2(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)]$. If $[M(CO)_4(\eta^4\text{-}C_5H_6)]$ complexes had been formed from $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ complexes (M = Mo or W) in CO matrices, bands would be expected to appear at higher wavenumbers than those of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$. This is by analogy with the formation of $[Fe(CO)_3(CH_3)(\eta^3\text{-}C_5H_5)]$ [46] and $[Co(CO)_3(\eta^3\text{-}C_5H_5)]$ [34] from $[Fe(CO)_2(CH_3)(\eta^5\text{-}C_5H_5)]$ and $[Co(CO)_2(\eta^5\text{-}C_5H_5)]$ respectively in CO matrices at 12 K and reflects the fact that increasing the number of CO ligands reduces the back-bonding for each CO ligand and this in turn strengthens the C–O bonds so that the bands are at higher wavenumbers. No such higher bands were observed but instead bands at lower wavenumbers assigned to the radicals $[M(CO)_3(\eta^5\text{-}C_5H_5)]^\bullet$ (M = Mo or W) were produced. That changes may occur in the ring–metal binding is evident from the observation of bands assigned to $[M(CO)_6]$ complexes (M = Mo or W) {*cf.* the conversion of $[Ni(NO)(\eta^5\text{-}C_5H_5)]$ to $[Ni(CO)_4]$}.[42] The conversion of $[M(CO)_3(\eta^5\text{-}C_5H_5)]^\bullet$ to $[M(CO)_6]$ is hardly likely to be a one-step process but no intermediate stages could be seen.

The N–N stretching band for $[WH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$ (2 163.5 cm$^{-1}$) occurs at a very similar wavenumber to those for $[Mn(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$ (2 169 cm$^{-1}$) [35,36] and $[Cr(CO)_2(N_2)(\eta^6\text{-}C_6H_6)]$ (2 148 cm$^{-1}$) [47] which have been prepared by conventional techniques as well as in $N_2$ matrices. The comparability of ν(NN) suggests a similar metal–dinitrogen bond strength, *i.e.* that $[WH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$ might exist as a stable complex. Attempts to isolate $[WH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$, by bubbling $N_2$ through n-pentane solutions of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ and $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ while photolysing them, were unsuccessful. A rapid decrease in intensity of the parent terminal CO stretching bands occurred but no new terminal CO stretching bands appeared. On the basis of the higher wavenumber for ν(NN) of $[MoH(CO)_2(N_2)(\eta^5\text{-}C_5H_5)]$ (2 197.0 cm$^{-1}$) the N–N bond is stronger in this complex than in the W complex and, therefore, the metal–dinitrogen bond is predicted to be weaker.[48] An interesting feature of both Mo and W dinitrogen complexes is their *trans* stereochemistry deduced on the basis of OC–M–CO bond angles and energy-factored CO interaction force constants (see above). The stereochemistry is analogous to *trans*-$[MoH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ in the case of Mo but not for W, where both *cis* and *trans* isomers are known in matrices at 12 K although only *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ exists as a stable solid or in solution at low temperatures.

The photolysis of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) in a 5% $C_2H_4$-doped $CH_4$ matrix led to the formation of $[MH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ complexes *via* $[MH(CO)_2(\eta^5\text{-}C_5H_5)]$ species. Interestingly, even this route failed to produce any *cis* isomer for Mo whereas both *cis* and *trans* isomers were observed for W. It is noteworthy that reversible *cis* $\rightleftharpoons$ *trans* isomerisation occurs for $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ in matrices at 12 K (Scheme 3). At 77 K Kazlauskas and Wrighton [11] were only able to observe the *trans* isomer of $[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ by photolysis of $[W(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ whereas at 12 K similar photolysis [5] produced again *cis* and *trans* isomers. Photolysis of $[Mo(CO)_3(C_2H_5)(\eta^5\text{-}C_5H_5)]$ gave the *trans* isomer at 12 and 77 K. Trimethylphosphine reacts instantly with *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ in pentane solution forming a mixture of *cis* and *trans*-$[WH(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)]$.[28] It is striking that only the olefin ligand is substituted by $PMe_3$ and not a carbonyl ligand. The photo-induced reaction of *trans*-$[WH(CO)_2(C_2H_4)(\eta^5\text{-}C_5H_5)]$ with the σ-donor thf gives only the corresponding *trans*-$[WH(CO)_2(thf)(\eta^5\text{-}C_5H_5)]$, indicating selective substitution of the olefin ligand without any change of the configuration. This is in striking contrast to the photolysis of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ in thf solution where both *cis* and *trans* isomers are formed; $[WH(CO)_2(thf)(\eta^5\text{-}C_5H_5)]$ can be isolated and is stable at temperatures not higher than −20 °C.

It is noteworthy that prolonged photolysis of $[MH(CO)_3(\eta^5\text{-}C_5H_5)]$ in 5% $C_2H_4$-doped $CH_4$ matrices leads to the production of the 16-electron co-ordinatively unsaturated species $[M(CO)_2(C_2H_5)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; Scheme 3). This entails substitution of a CO by $C_2H_4$ and then insertion of the co-ordinated $C_2H_4$ into a M–H bond. Exactly these steps are proposed in the mechanism of the hydroformylation reaction.[6,49] This is the *first time* intermediates corresponding to proposed insertion processes have been observed.[50]

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