Photochemistry of $[(\eta\text{-}C_5H_5)_2ReH]$ and $[(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)Re(CO)_2]$ in Low Temperature Matrices: Hydrogen Loss and Hydrogen Migration

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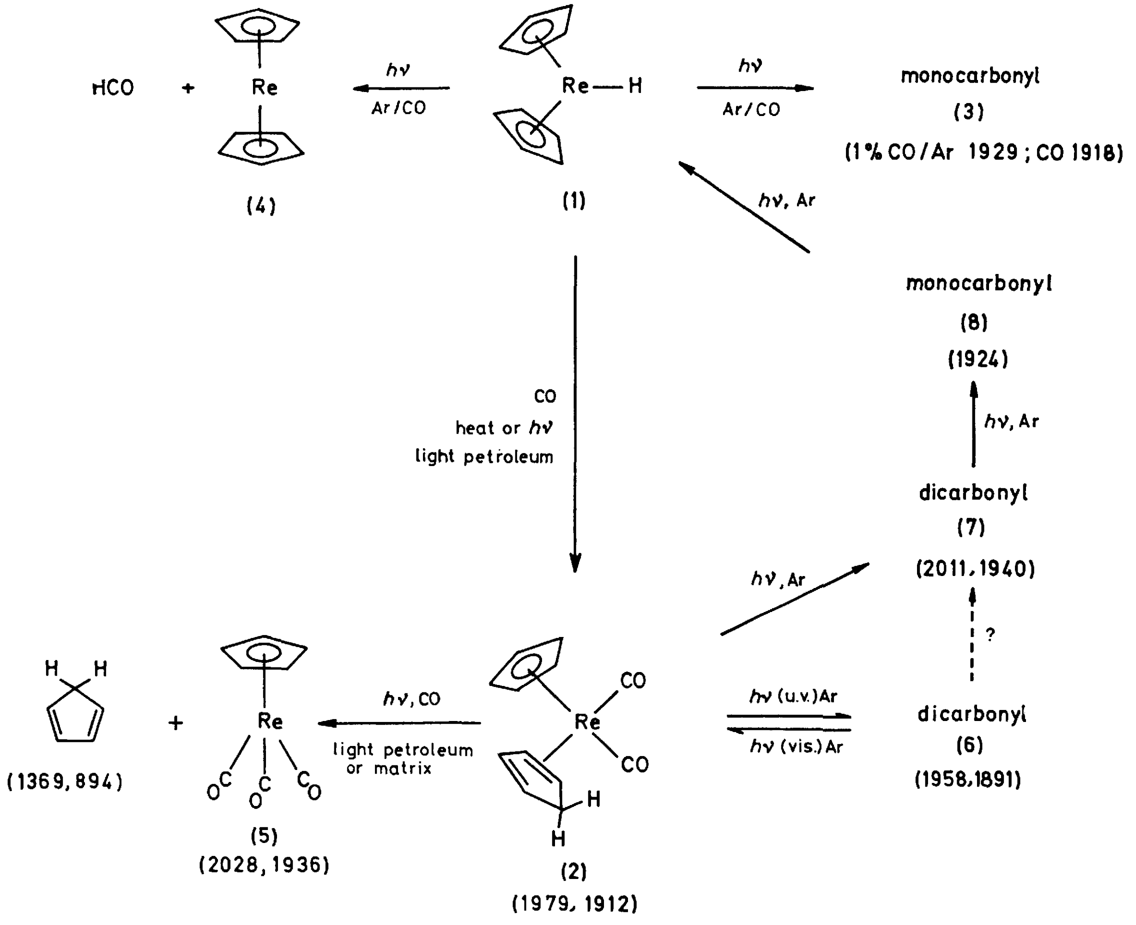
Summary On photolysis of $[(\eta\text{-}C_5H_5)_2ReH]$ (**1**) in Ar/CO matrices $[(\eta\text{-}C_5H_5)_2Re]$, HCO, and a monocarbonyl are generated; photolysis of $[(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)Re(CO)_2]$ in Ar matrices produces three carbonyl intermediates followed by (**1**).

THE reaction of $[(\eta\text{-}C_5H_5)_2ReH]$ (**1**) with CO to form $[(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)Re(CO)_2]$ (**2**) forms one of the best examples of metal-to-ring hydrogen transfer.[1] Such a migration and its reversal are postulated steps in many reactions, *e.g.* the H/D exchange of $[(\eta\text{-}C_5H_5)Fe(triphos)D]$,[2] (triphos = $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$) or the formation of



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$[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ from $[(\eta\text{-}C_5H_6)Ru(CO)_3]$,[3] but have only been observed directly in the fluxional behaviour of $[(\eta\text{-}1,3\text{-}C_6H_8)(\eta\text{-}1,5\text{-}C_8H_{12})IrH]$.[4] We report the stepwise photochemical conversion of (**2**) into (**1**) in an Ar matrix at 14 K, so providing an example of hydrogen transfer in which both the olefin and metal hydride complexes are characterised. Although photochemical loss of H_2 is a frequent feature of *cis*-dihydrides,[5] photochemical homolysis of M–H bonds in monohydrides has been reported only recently.[6] In a previous paper we demonstrated the photochemical expulsion of H_2 from $[(\eta\text{-}C_5H_5)_2WH_2]$ in a single step.[7] The matrix reactions of (**1**) reported here show that this isoelectronic monohydride is also photosensitive. However, solution experiments show important differences between the photochemical pathways of (**1**) in matrices and in solution.

$[(\eta\text{-}C_5H_5)_2ReH]$ (**1**) proves to be photostable in pure Ar matrices but u.v. photolysis ($220 < \lambda < 350$ nm) of (**1**) in CO or CO/Ar matrices results in three products detected by i.r. absorption in proportions dependent on the CO/Ar ratio (Figure 1). A metal carbonyl (**3**) [ν(CO) 1918 cm^{-1}] is detected with concentrations of CO $\geqslant 1\%$. HCO (2488, 1860, and 1090 cm^{-1})[8] and a third non-carbonyl product (**4**) with five absorption bands between 1100 and 250 cm^{-1} are detected with CO concentrations $\geqslant 50\%$. Use of a $^{13}CO/^{12}CO$ (1 : 1) matrix showed bands of (**3**) at 1918 and 1873 cm^{-1} in the CO stretching region but none between them. The absence of bands assignable to a mixed $^{13}CO/^{12}CO$ species indicates that (**3**) is a monocarbonyl of rhenium. Photolysis of $[(\eta\text{-}C_5D_5)_2ReH]$ (*ca.* 90 atom % D) yields HCO and isotopic shifts for (**4**) consistent with a metallocene (see the Table). On photolysis of $[(\eta\text{-}C_5H_5)_2ReD]$, both DCO (1935?, 1799 cm^{-1})[8] and HCO are observed. The HCO may be generated from $[(\eta\text{-}C_5H_5)_2ReD]$ by a photodissociation/recombination exchange process.† The behaviour of (**4**) on isotopic substitution of (**1**), the production of HCO, and the similarity of the i.r. spectrum to those of $[(\eta\text{-}C_5H_5)_2Mo]$ and $[(\eta\text{-}C_5H_5)_2Ru]$ (Table) lead us to conclude that the Re–H bond has cleaved homolytically to yield the previously unknown metallocene $[(\eta\text{-}C_5H_5)_2Re]$

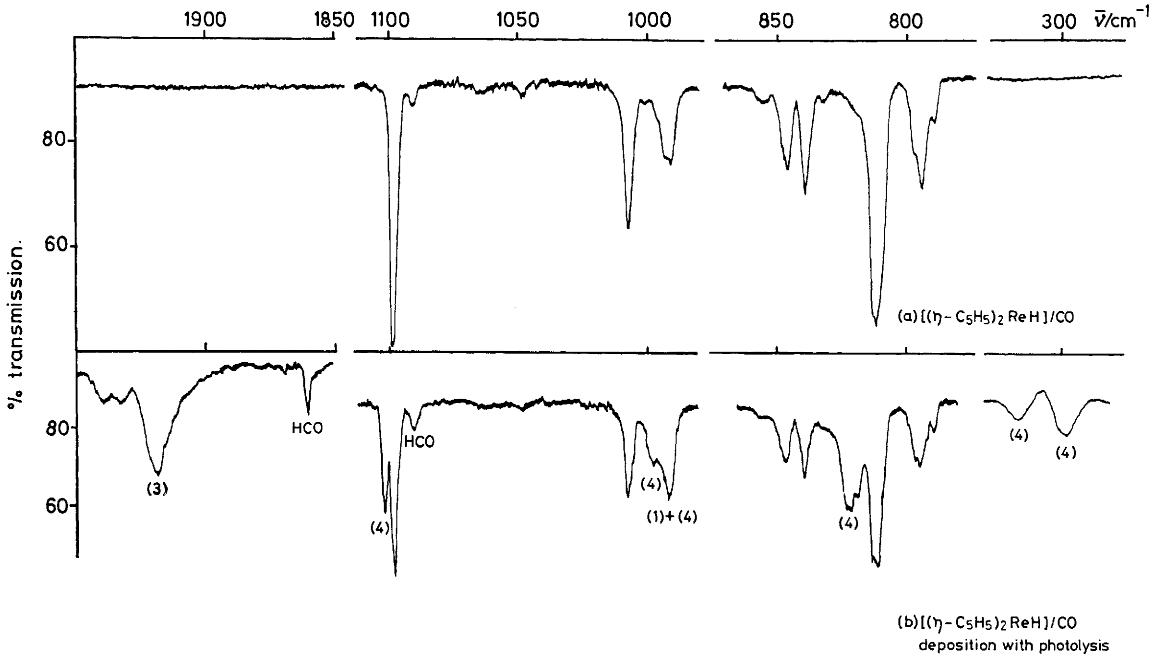

Figure 1. (a) I.r. spectrum of $[(\eta\text{-}C_5H_5)_2ReH]$ in 3 mmol of CO at 14 K prepared by slow deposition (3 h spray on: sublimation temperature 313 K); (b) I.r. spectrum of similar deposit photolysed with water-filtered Hanovia 250 W high-pressure Hg arc during deposition, showing HCO, a monocarbonyl (**3**), and $[(\eta\text{-}C_5H_5)_2Re]$ (**4**).

Table. I.r. wavenumbers of matrix-isolated metallocenes (cm^{-1}).

$[(\eta\text{-}C_5H_5)_2Re]^a$	$[(\eta\text{-}C_5H_5)_2Mo]^{b,c}$	$[(\eta\text{-}C_5H_5)_2Ru]^b$	$[(\eta\text{-}C_5D_5)_2Re]^a$	$[(\eta\text{-}C_5D_5)_2Mo]^b$
1101	1094	1105	1054	1051
997, 991	991, 985	1004	1045	1038
—	970	—	772	762
832	778	812	616	610
317	350	458	305	568
299	—	357	289	—

^{a} CO matrix. ^{b} Ar matrix. ^{c} Data from ref. 6.

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† Jacox reports the ready photodissociation of HCO with visible light in Ar matrices: M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, 1973, **47**, 148.

(**4**). The effect of CO concentration on the yields of (**3**), (**4**), and HCO suggests that there are two independent pathways, an H loss pathway requiring CO to trap released H atoms and a CO gain pathway, not involving H loss. Subsequent photochemical reaction of (**1**) with CO at 300 K in solution showed production of (**2**) and $[(\eta\text{-}C_5H_5)Re(CO)_3]$ (**5**) (Scheme). In contrast with the matrix experiments no monocarbonyl was detected and the CO gain pathway predominated.

U.v. photolysis of (**2**) in Ar or CH_4 matrices, undertaken originally to investigate the nature of (**3**), led to three new carbonyl species, (**6**), (**7**), and (**8**), (Figure 2) followed by almost quantitative conversion into (**1**) (Scheme) which was identified by the coincidence of 12 bands with those observed by direct sublimation. U.v. photolysis of (**2**) in CO matrices led to cyclopentadiene and $[(\eta\text{-}C_5H_5)Re(CO)_3]$ (**5**) as the major carbonyl product; (**1**) and its photoproducts were also generated. Cyclopentadiene and (**5**) were identified by direct matrix-isolation experiments. The assignment of (**6**), (**7**), and (**8**) to three different carbonyl species was dictated by the changes in relative intensity of their absorptions during photolysis (Figure 2). The dicarbonyl (**6**) may be a conformational isomer of (**2**) or, more likely, $[(\eta\text{-}C_5H_5)Re(CO)_2]$ perturbed by expelled cyclopentadiene (*cf.* cyclopentadiene loss using CO matrices). Photolysis experiments on $[(\eta\text{-}C_5H_5)Re(CO)_3]$, similar to those of Rest *et al.* on the Mn system,[9] show that $[(\eta\text{-}C_5H_5)Re(CO)_2]$ absorbs at 1964 and 1896 cm^{-1} in Ar matrices. Dicarbonyl (**7**), which shows a large high-frequency shift relative to (**2**), may be an isomer related to (**2**) by hydrogen migration to the metal and alteration of the hapticity of the rings. The monocarbonyl (**3**) generated from (**1**) has its CO stretching band very close to (**8**), suggesting that it may be another conformer of the same molecule. In further experiments we will try to distinguish whether (**6**) and (**7**) are essential intermediates in the formation of (**8**) from (**2**), and whether hydrogen migration precedes or succeeds loss of the first carbon monoxide.

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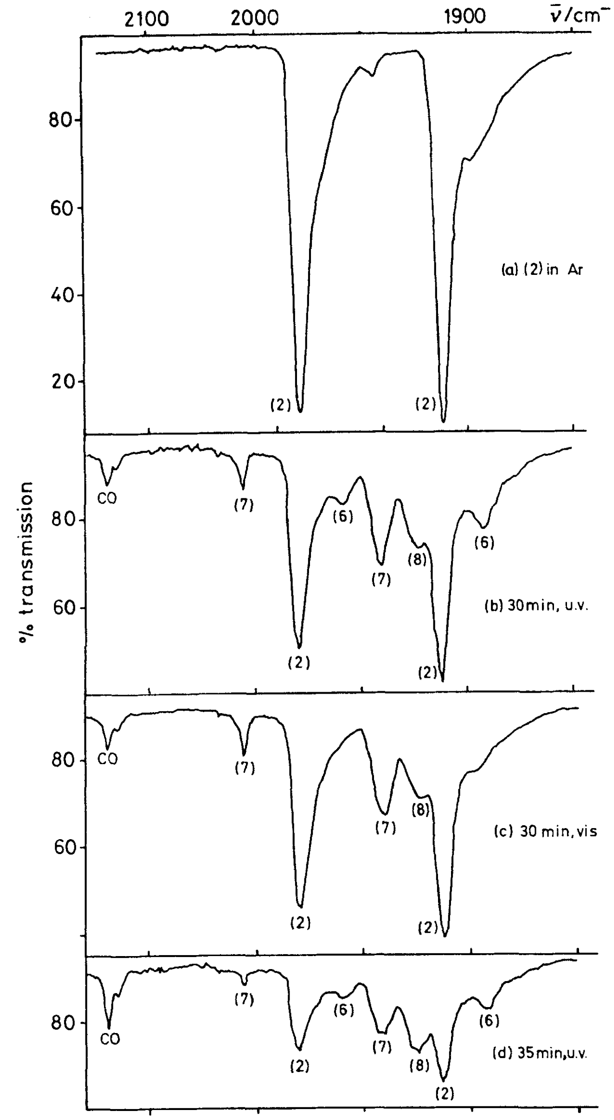

FIGURE 2. (a) I.r. spectrum of $[(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)Re(CO)_2]$ (**2**) in 1·5 mmol of Ar at 14 K prepared by slow deposition (2 h spray on: sublimation temperature 322 K) showing the C=O stretching region; (b) after 30 min photolysis with filtered Philips HPK 125 W Hg arc ($220 < \lambda < 350$ nm); (c) after 30 min photolysis with filtered Hg arc ($\lambda > 375$ nm); (d) after 35 min further photolysis as in (b). The products are labelled as in the text.

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