Journal of Organometallic Chemistry, 284 (1985) 229–242
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOCHEMISTRY OF M(η^5-C_5H_5)$_2$(H)CO AND M(η^5-C_5H_5)$_2H_3$ (M = Nb, Ta) IN LOW-TEMPERATURE MATRICES

ROBIN F.G. BAYNHAM, JENNIFER CHETWYND-TALBOT, PETER GREBENIK *,
ROBIN N. PERUTZ ** and MARK H.A. POWELL

Inorganic Chemistry Laboratory, South Parks Road, Oxford (Great Britain)

(Received August 17th, 1984)

Summary

Photolysis of MCp_2H_3 (M = Nb, Ta; Cp = η^5-C_5H_5) in argon and nitrogen matrices yields the 16-electron complexes MCp_2H, previously postulated as intermediates in the catalytic activation of aryl C–H bonds. The same complexes are generated by photolysis of MCp_2(H)CO, together with small amounts of the 17-electron MCp_2CO. In CO matrices MCp_2H_3 is converted to MCp_2(H)CO while further reaction of MCp_2(H)CO yields MCp_2CO and dicarbonyl products. The reactions were followed by IR and UV/VIS spectroscopy. The UV data on $TaCp_2H_3$ conflict with previously published solution spectra.

Introduction

The prospect of homogeneous catalysis of C–H activation reactions by organotransition metal complexes has been given renewed impetus by the discoveries of reactions of saturated hydrocarbons with iridium, rhodium and rhenium complexes [1–5]. However, none of the reaction intermediates involved in the C–H activation step had been detected until our recent characterization of tungstenocene [6,7]. Two activators of aryl C–H bonds discovered considerably earlier are $NbCp_2H_3$ and $TaCp_2H_3$ (Cp = η-C_5H_5) [8,9]. These complexes catalyse H/D exchange between D_2 and aromatics at 80–110°C. The C–H activation process is postulated to occur via successive coordination, oxidative addition and reductive elimination of the arene. The crucial intermediates are thought to be MCp_2H and MCp_2D [10]. Evidence for these monohydride intermediates has been obtained by the isolation of the adducts MCp_2(H)L (L = CO, PR_3, C_2H_4) [8] on heating the trihydrides with the appropriate ligands. Alternative thermal sources of the $NbCp_2H$ moiety are

---

* Present address: Department of Physical Sciences, Oxford Polytechnic, Oxford (Great Britain).

** Address correspondence to RNP at Department of Chemistry, University of York, York Y01 5DD (Great Britain).

0022-328X/85/$03.30

$NbCp_2(\mu\text{-}H)_2BH_2$ [11] and $NbCp_2H$(carbene) complexes [12]. Evidence for η^2-coordination of arenes prior to oxidative addition has been obtained in analogous reactions of rhodium complexes [5].

Until recently MCp_2H_3 complexes were not reported to participate in photochemical reactions except with highly photosensitive substrates such as $NbCp(CO)_4$, $Mn_2(CO)_{10}$, CH_3SSCH_3, or Bu^tOOBu^t [13–16]. In these cases the major absorber must have been the substrate rather than MCp_2H_3. When our work was nearing completion, Foust et al. reported that photolysis of MCp_2H_3 (M = Nb, Ta) in C_6D_6 resulted in H/D exchange with benzene [17]. They also showed that photolysis of toluene solutions of MCp_2H_3 in the presence of ligands yielded $MCp_2(H)L$ (L = CO, PEt_3). The $MCp_2(H)CO$ complexes reacted photochemically with H_2 or PEt_3 to yield MCp_2H_3 and $MCp_2(H)PEt_3$ respectively. These reactions were interpreted in terms of photochemical generation of common MCp_2H intermediates from MCp_2H_3 and $MCp_2(H)CO$.

We have recently reported that matrix isolation in conjunction with IR and UV/VIS spectroscopy can be used to characterize the reactive intermediates MCp_2 (M = Mo, W) generated by photolysis of MCp_2H_2 and related precursors [6,7]. The magnetic circular dichroism (MCD) of these metallocenes is indicative of paramagnetic $^3E_2$ ground states. The related monohydride $ReCp_2H$ is also photosensitive in matrices and reacts via two competing pathways involving either H loss or addition of L (L = N_2, CO) [18,19]. In this paper we report that photochemical reactions of MCp_2H_3 and $MCp_2(H)CO$ in matrices yield the monohydrides MCp_2H (M = Nb, Ta). Evidence is also presented for dissociation of H atoms from $MCp_2(H)CO$.

Results and discussion

Photolysis of $TaCp_2H_3$

The IR spectrum of a sample of $TaCp_2H_3$ in an argon matrix shows a complex group of broad bands in the 1700–1800 cm^{-1} region corresponding to Ta–H stretching vibrations, together with numerous bands below 1130 cm^{-1}. (The IR spectra of the precursors will be discussed in more detail elsewhere). After 15 min unfiltered UV photolysis, the bands of the starting material decreased by 25%; the conversion increased to ~ 60% after 165 min photolysis. Several sharp product bands (Table 1) were conspicuous between 700 and 1000 cm^{-1} together with a broad band at 1746 cm^{-1} (Table 1). There were no product bands between 300 and 700 cm^{-1}.

In contrast to the solution measurements of Foust et al. [17], the UV/VIS spectrum of $TaCp_2H_3$ in Ar showed no absorption maxima but a steeply rising absorption from 300 to 200 nm (Fig. 1a). On photolysis an intense product band was observed at 267 nm together with a shoulder at 314 nm (Fig. 1b, c). On account of their continuous growth with photolysis, both the IR and UV product peaks are assigned to a single species, I.

On isolating $TaCp_2H_3$ in a N_2 matrix using very dilute conditions a much sharper IR spectrum was obtained (about seven-fold dilution with respect to argon experiments; fullwidth at half-maximum (fwhm) of bands 2–3 cm^{-1}). On 2 h photolysis, there was 60% conversion to product (Fig. 2). With the exception of one band at 893 cm^{-1}, unobserved in argon, the product bands were within 5 cm^{-1} of

TABLE 1. IR AND UV ABSORPTIONS OF THE PHOTOPRODUCTS OF MCp_2H_3 AND $MCp_2(H)CO$ (M = Nb, Ta) IN Ar AND N_2 MATRICES ($\bar{\nu}$ in cm^{-1})

	Precursor complex					
	$TaCp_2H_3$		$TaCp_2(H)CO$		$NbCp_2H_3$	$NbCp_2(H)CO$
	Photoproduct					
	$TaCp_2H$ (I)		$TaCp_2H$ (I)		$NbCp_2H$ (VI)	$NbCp_2H$ (VI)
	Ar	N_2	Ar	N_2	Ar	Ar ^{c}
Infrared	1746	1744	1744	1744	1710	–
	1741	1740	1741	1741	1692	–
	1736	1735	1735	1735	1673	–
	1106	1106	1106	1105	1110	1110 ^{a}
	1010 ^{a}	1009 ^{a}	1009	1009	1014	1014 ^{a}
	1002	1003	1001	1003	1005	1006
	893	–	892	–	886	–
	840	840	840?	^{b}	838	–
	^{b}	798	^{b}	799	830	–
	793	^{b}	792	ca. 792	807	–
	785 ^{a}	^{b}	786	^{b}	800sh	–
	780	–	780	^{b}	794	794
	777	775	–	778	788	–
	767	768	766	–	750	748
Ultraviolet	37450		ca. 37700			38310
	31850sh	–	–			30860

^{a} Overlaps with precursor absorption. ^{b} Obscured by precursor absorption. ^{c} Low yield – only the most intense absorptions detectable.

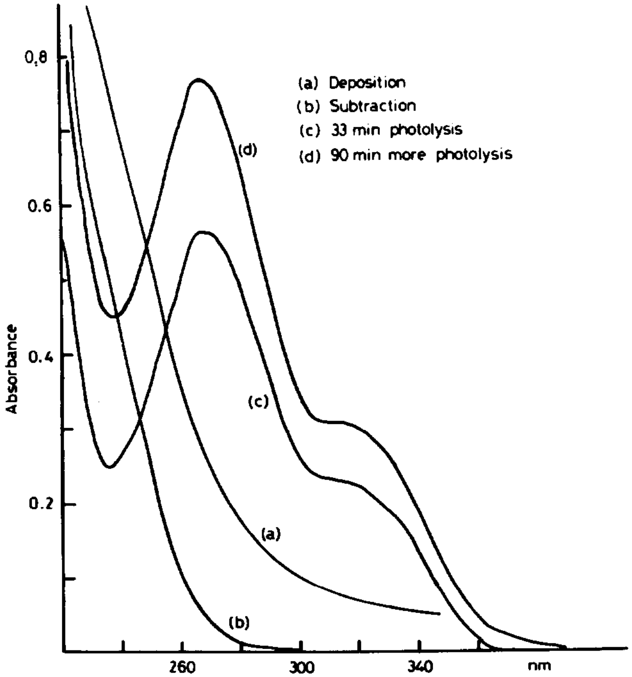


Fig. 1. Ultraviolet spectra of $TaCp_2H_3$ in argon at 20 K (a) following deposition for 144 min (sublimation temperature 62°C, 4.7 mmol Ar deposited); (b) after subsequent background subtraction; (c) after 33 min UV photolysis with filtered mercury arc ($220 < \lambda < 340$ nm); (d) after 90 min further photolysis. The product peaks are assigned to I.

the positions of I Ar and had similar intensity ratios. They are therefore assigned to the same product, I. There was no evidence for formation of a dinitrogen complex.

Photolysis of $TaCp_2H_3$ in a CO matrix generated a significantly different IR spectrum from I. The most intense product band lay at 1904 cm^{-1} in the CO stretching region and new bands were observed between 300 and 500 cm^{-1}. The product was identified as $TaCp_2(H)CO$ by comparison with a spectrum obtained by condensation of an authentic sample with CO. The spectrum of $TaCp_2(H)CO$ generated in situ showed 15 bands within 2 cm^{-1} of those observed in the sample sublimed directly (Table 2). Of the remaining bands in the spectrum of the sample deposited directly, only that at 809 cm^{-1} was sufficiently intense to have been observed in the photolysis experiment. Three further bands, observed to grow on prolonged photolysis of $TaCp_2H_3$ in a CO matrix (1980, 1928, 1889 and 1790 cm^{-1}) may be assigned to secondary carbonyl products. More evidence for their identity was obtained by direct photolysis of $TaCp_2(H)CO$ (see below). Finally, a weak product band at 1860 cm^{-1} observed on initial photolysis, is found to grow at a different rate from $TaCp_2(H)CO$ and from the secondary products. The intensities suggest a contribution to this feature from HCO in addition to $TaCp_2(^{13}CO)H$ in natural abundance [20].

The UV spectrum observed after photolysis of $TaCp_2H_3$ in CO showed a peak at 281 nm with a tail extending to 400 nm, comparing well with the spectrum of a directly sublimed sample of $TaCp_2(H)CO$ in an argon matrix (maximum at 276 nm with a similar tail). These UV spectra showed conclusively that photolysis of

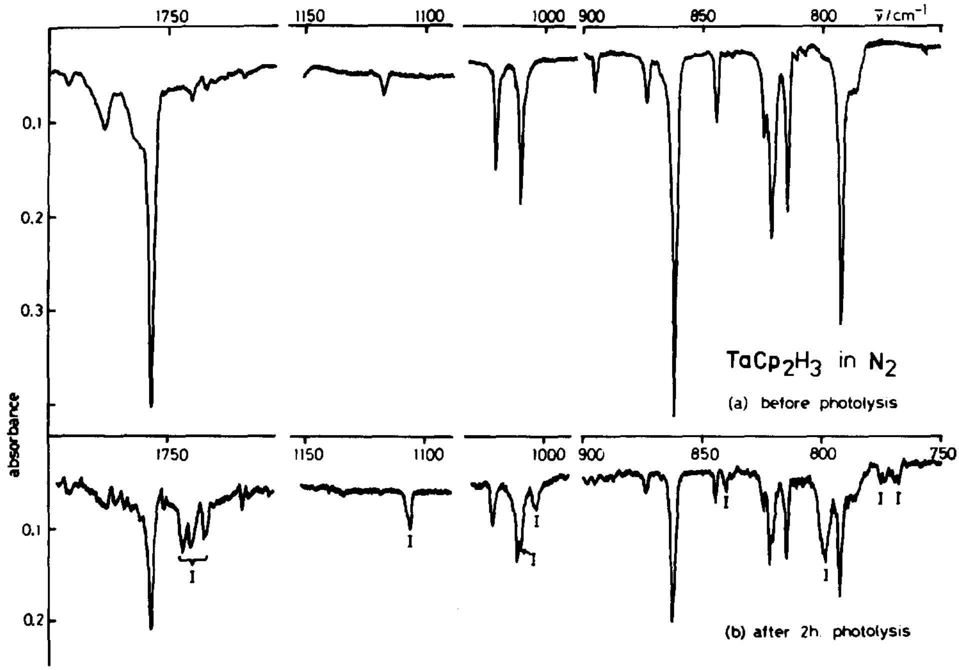


Fig. 2. Infrared spectra of $TaCp_2H_3$ in nitrogen at 20 K (a) following deposition for 720 min (sublimation temperature 65–80°C, 11.6 mmol N_2 deposited); (b) after 120 min photolysis with water-filtered mercury arc. The product peaks are assigned to complex I.

$TaCp_2H_3$ in a CO matrix did not generate a significant yield of I. (The IR evidence is equivocal on this point, because of the similarity of the IR spectrum of I in the 700–1100 cm^{-1} region to $TaCp_2(H)CO$.)

Photolysis of $TaCp_2(H)CO$

The IR spectrum of $TaCp_2(H)CO$ in Ar matrices in the CO stretching region is dominated by the intense ν(CO) band at 1913 cm^{-1}. However, the presence of a

TABLE 2

IR ABSORPTIONS OF $MCp_2(H)CO$ ($\bar{\nu}$ in cm^{-1}) IN MATRICES

$TaCp_2(H)CO$			$NbCp_2(H)CO$		
Ar Direct deposition	CO Direct deposition	CO Photolysis of $TaCp_2H_3$	Ar Direct deposition	CO Direct deposition	CO Photolysis of $NbCp_2H_3$
	1910m, sh			1922sh	
1913vs, br	1902.5s	1904	1924vs, br	1916vs	1917
1870w	1859w	1860	1882m	1872m	1874
1775m, br			1940w, br	–	
1750m, br	1756m	1757[a]	1716m	–	
			1700m	1696m, br	ca. 1706
				1680sh	
1438w			1437m	1435m	
1431w				1420m	
1420w					
1369m	1368w	1368		1369w	1369
1352w			1354w	1352w	1352
1106m	1105m	1105	1107m	1107m	1107
1070w			1069w		
1012m	1014m	1012[a]	1014s	1016m	1015
	1011sh				
997m	997m	999	998s	998m	998
994sh	994m	993sh			
	877w		895w	895w	
869w	854w		871w	879w	
	851w		841m	845m	846
846w	847w		831s	836s	836
837m	839m	839	828s	821m	821
817m	826m	824[a]	825m		
815sh	817m	818[a]	812m	812w	815
798m	809m	801[a]	806m	802w	
782sh	803w		788m	798w	798
776m	786m	785[a]	778sh	780s	
			769s	778s	778
			673m, br	673m	669?[a]
611w			611w	613w	
			602w	604w	
468w	467w	468	477m	478m	478
452m	451w	453	451m	454m	452
			428w, br	430w, br	
370w	352w, br		381m	376w	376
333m	335m	335	350w, br	353w	
			335m	341m	340

[a] Overlaps with absorptions of precursor.

weak band at 2138 cm^{-1} due to matrix-isolated CO indicates some thermal decomposition during sublimation. The IR spectrum of $TaCp_2(H)CO$ proved surprisingly dependent on the matrix material. Not only were the Ta–H stretching modes sharper in CO and N_2 matrices than in Ar, but there were also substantial differences in the 750–950 cm^{-1} region (Table 2). These changes may be associated with the extreme sensitivity of Ta–H stretching and deformation modes to conformation and trapping site.

The complex $TaCp_2(H)CO$ proved much less photosensitive than $TaCp_2H_3$ requiring 65 min photolysis ($220 < \lambda < 340$ nm) to reach 30% conversion to products, or 50% conversion after 250 min photolysis. The most intense product band in the ν(CO) region was at 2138 cm^{-1} indicating loss of CO as the dominant process. Nine product bands in the ν(TaH) and 750–1150 cm^{-1} regions were found within 2 cm^{-1} of those of I in the same matrix (Table 1). Photolysis of $TaCp_2(H)CO$ in a N_2 matrix also causes loss of CO as the major pathway, again giving a product with an IR spectrum almost identical to that for I. Because of the common products on photolysis of $TaCp_2H_3$ and $TaCp_2(H)CO$ in inert matrices, we conclude that I may be assigned as $TaCp_2H$. The presence of bands in the ν(TaH) region (ca. 1740 cm^{-1}) and the complexity of the 750–1150 cm^{-1} region allows us to exclude $TaCp_2$ as a possible product.

$$\mathrm{TaCp_2H_3} \xrightarrow{h\nu,\ \mathrm{Ar\ or\ N_2}} \mathrm{TaCp_2H + H_2}$$

$$\mathrm{TaCp_2H(CO)} \xrightarrow{h\nu,\ \mathrm{Ar\ or\ N_2}} \underset{(\mathrm{I})}{\mathrm{TaCp_2H}} + \mathrm{CO}$$

In addition to $TaCp_2H$ very weak carbonyl products were observed on photolysis of $TaCp_2(H)CO$ in Ar and N_2 matrices (Table 3). The bands to higher wavenumbers than $TaCp_2(H)CO$ are assigned to polycarbonyl species formed because of the slight excess of CO in the matrix. However, a further species, II, is observed with ν(CO) bands at ca. 1890 cm^{-1} which becomes the most prominent photoproduct in CO matrices (Table 3).

After 1 h photolysis ($220 < \lambda < 340$ nm) of $TaCp_2(H)CO$ in CO matrices several new CO stretching bands were observed (Table 3, Fig. 3). Prolonged visible irradiation ($\lambda > 325$ nm) reduced their intensities slightly but prior visible photolysis did not induce any reaction. The absence of product bands between 775 and 780 cm^{-1} indicated that no $TaCp_2H$ was formed, probably because of in-cage recombination with CO. This postulate was confirmed by irradiation of $TaCp_2(^{12}CO)H$ in a $^{13}CO/^{12}CO$ (1/1.2) matrix. Rapid exchange with ^{13}CO was revealed by the growth of an intense product band at 1860 cm^{-1} in the position anticipated for $TaCp_2(^{13}CO)H$.

The nature of II can be defined further from the presence of HCO on photolysis of $TaCp_2(H)CO$ in ^{12}CO matrices (1860, 1092 cm^{-1}), [20] suggesting loss of H atoms. The prominence of II and the presence of analogous bands in Ar and N_2 allows us to identify II as $TaCp_2CO$. The results in the $^{13}CO/^{12}CO$ matrix are consistent with this interpretation, although the band of $TaCp_2(^{13}CO)H$ could mask bands of alternative products. The reversibility of the production of II with long-wavelength irradiation probably involves photodissociation of HCO which is stimu-

TABLE 3

IR ABSORPTIONS OF THE PHOTOPRODUCTS OF MCp$_2$(H)CO AND MCp$_2$H$_3$ IN THE CO AND MH STRETCHING REGIONS ($\bar{\nu}$ in cm^{-1}, M = Nb, Ta)

Precursor complex					Assignment
TaCp$_2$(H)CO				TaCp$_2$H$_3$ ^{12}CO	
Ar	N$_2$	^{12}CO	^{12}CO/^{13}CO		
1968	–	1982	1982, 1959, 1944	1980	III, IV, V
1951	–	1972	1970, 1928	–	
1934	–	1929	1928, 1884sh	1928	
1913	1906	1910, 1903	1903	1904	TaCp$_2$(H)^{12}CO
1897	1891, 1888	1888	1888	1889	III (^{12}CO)
1869	1862	1860	1860	1860	TaCp$_2$(H)^{13}CO
–	–	1860	1860	1860	H^{12}CO
–	–	–	1845		III (^{13}CO)
–	–	–	1818		H^{13}CO
		1790	1789	1790	IV: ν(TaH)

Precursor complex			Assignment
NbCp$_2$(H)CO		NbCp$_2$H$_3$ CO	
Ar	CO		
	1980	1979	Dicarbonyl products
	1942	1940	Dicarbonyl products
1924	1916	1917	NbCp$_2$(H)CO
	1897	1897	VII
1882	1872	1874	NbCp$_2$(H)^{13}CO
	1860	1860	HCO
	1822	1821	?

lated by visible irradiation [21]:

$$\mathrm{TaCp_2(H)CO} \underset{\mathrm{VIS}}{\overset{\mathrm{UV/CO}}{\rightleftarrows}} \mathrm{TaCp_2CO + HCO}$$

The remaining product bands in the ν(CO) region which lie to higher wavenumbers than TaCp$_2$(H)CO, are assigned provisionally to Ta(η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)(CO)$_2$H (III), Ta(η^5-C$_5$H$_5$)(η^4-C$_5$H$_6$)(CO)$_2$ (IV) and perhaps Ta(η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)(CO)$_2$ (V). In keeping with the assignment to III, a product band is also observed in the ν(TaH) region which exhibits the same intensity behaviour (Table 3, Fig. 3). The same group of products is formed by prolonged photolysis of TaCp$_2$H$_3$ in CO, presumably via secondary reaction of TaCp$_2$(H)CO. The experiments using visible irradiation demonstrate that redistribution reactions between III, IV, V and TaCp$_2$(H)CO also occur. Comparison with published spectra shows that no TaCp(CO)$_4$ was generated in these CO addition reactions [22]. When using argon matrices some similar species were observed probably via reaction with excess CO in the matrix. However, no analogous polycarbonyls or dinitrogen complexes were observed in N$_2$ matrices.

Photolysis of NbCp$_2$H$_3$

The matrix IR spectrum of NbCp$_2$H$_3$ in Ar showed similar broad bands in the metal–hydride stretching region (1710–1740 cm^{-1}) to those observed for its tanta-

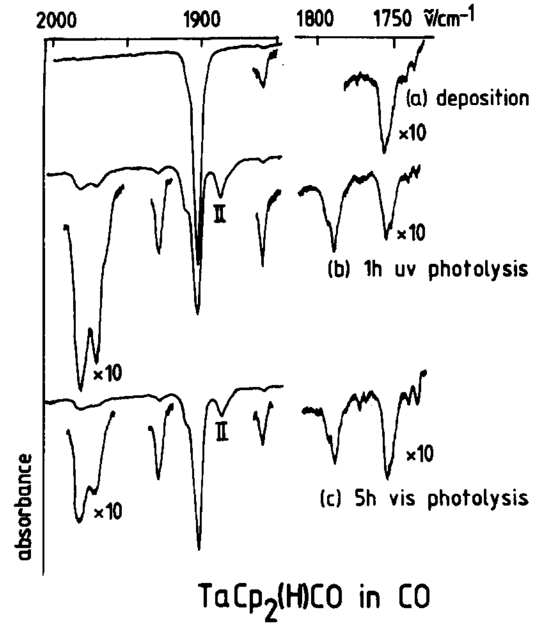


Fig. 3. Infrared spectra of $TaCp_2(H)CO$ in carbon monoxide at 20 K (a) following deposition for 240 min (sublimation temperature 52°C, 6.9 mmol CO deposited); (b) after 60 min UV photolysis with filtered mercury arc ($220 < \lambda < 340$ nm); (c) after 310 min visible photolysis with filtered arc (variously $\lambda > 285$ nm, $\lambda > 375$ nm, $\lambda > 325$ nm). Notice that some bands are shown with 10× ordinate expansion.

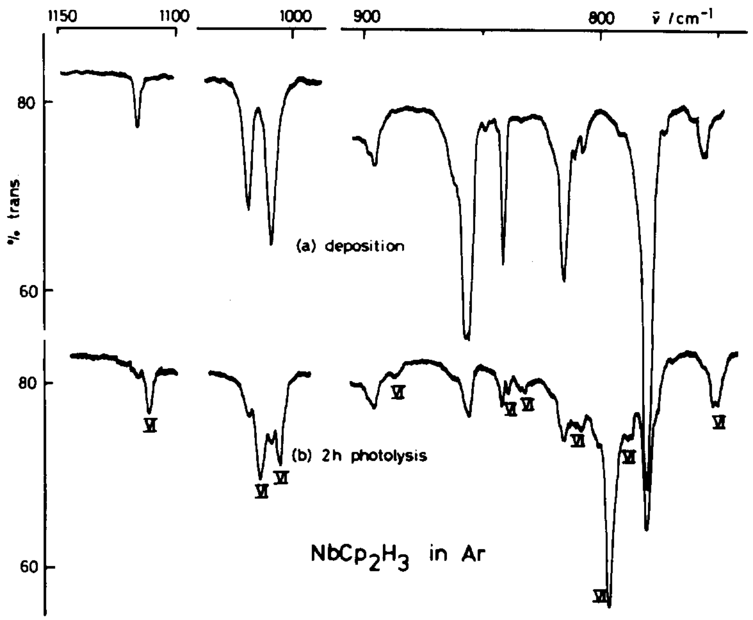


Fig. 4. Infrared spectra of $NbCp_2H_3$ in argon at 19 K (a) following deposition for 300 min (sublimation temperature 40°C, 3.4 mmol Ar deposited); (b) after 120 min UV photolysis with filtered mercury arc ($220 < \lambda < 340$ nm).

lum analogue. Again, the bands below 1400 cm^{-1} were considerably sharper. On 2 h photolysis ($220 < \lambda < 340$ nm) 75% of the $NbCp_2H_3$ reacted, yielding a group of product bands very reminiscent of the tantalum compound, assigned to product VI (Table 1, Fig. 4). The positions of the NbH stretching modes are tentative, because of their width, low intensity and because they occur in the water vapour region.

On photolysis in a CO matrix for 1 h ($220 < \lambda < 340$ nm) the absorptions of $NbCp_2H_3$ were reduced by ~ 70%. The major product was readily identified as $NbCp_2(H)CO$ by comparison with an authentic sample in a CO matrix (Fig. 5 and Table 2). The dominant ν(CO) band (1917 cm^{-1}) and all but one of the medium intensity and strong bands of $NbCp_2(H)CO$ were observed within 2 cm^{-1} of the positions found by direct deposition in CO. As in the corresponding tantalum experiments, a very small amount of HCO was detected (1860, 1090 cm^{-1}) and some weak peaks attributable to other carbonyl products (Table 3) which grew on prolonged photolysis. These peaks were also observed on photolysis of $NbCp_2(H)CO$ in CO matrices and are assigned to secondary photolysis products (see below).

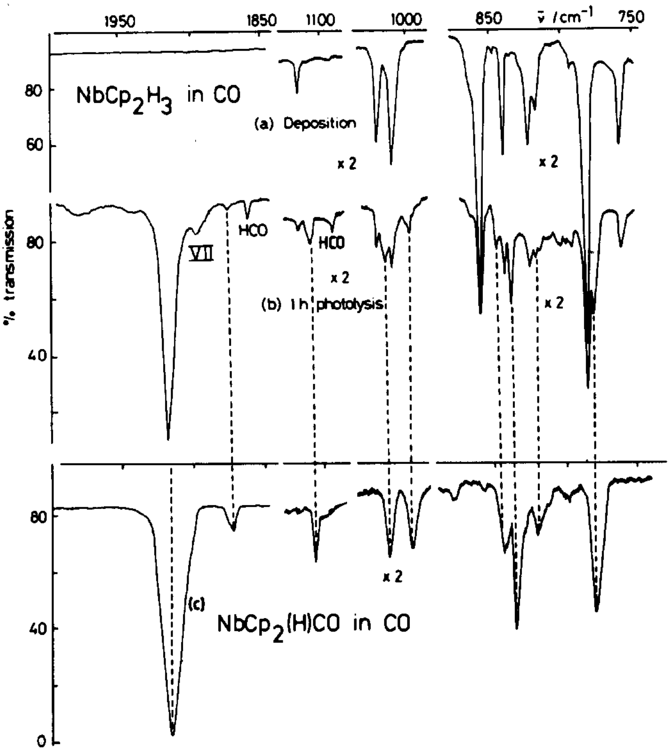


Fig. 5. Infrared spectra (a) of $NbCp_2H_3$ in carbon monoxide at 20 K following deposition for 270 min (sublimation temperature 40°C, 4.1 mmol CO deposited); (b) after 60 min filtered UV photolysis ($220 < \lambda < 340$ nm); (c) comparative spectrum of $NbCp_2(H)CO$ in carbon monoxide at 19 K following deposition for 120 min (sublimation temperature 45°C, 5.3 mmol CO deposited). The broken lines connect the bands of $NbCp_2(H)CO$. Notice that the bands below 1150 cm^{-1} are shown with 2× ordinate expansion.

Photolysis of $NbCp_2(H)CO$

The IR spectra of argon matrices containing $NbCp_2(H)CO$ showed small amounts of free CO (2138 cm^{-1}) before photolysis, indicating some thermal decomposition during deposition. On 2 h photolysis ($220 < \lambda < 340$ nm), about 15% of the starting material reacted releasing CO (2138 cm^{-1}) and forming VI with IR bands in almost identical positions to those observed on photolysis of $NbCp_2H_3$ (Table 1). The UV spectrum of $NbCp_2(H)CO$ in Ar showed intense bands at 205, 222 (sh) and 279 nm together with weaker features at 313, 360 (sh) and 374 nm (Fig. 6). On photolysis ($220 < \lambda < 340$ nm, 2 h), they were replaced by bands at 261 nm (strong) and 324 nm (medium, Fig. 6c). In contrast to the IR experiment the conversion after 5 h photolysis exceeded 37%, probably because UV spectra require a smaller quantity of material. The new IR and UV features are assigned to VI which may be identified as $NbCp_2H$, using similar arguments to those applied to the tantalum analogues:

$$NbCp_2H_3 \xrightarrow{h\nu,Ar} NbCp_2H + H_2$$

$$NbCp_2(H)CO \xrightarrow{h\nu,Ar} \underset{(VI)}{NbCp_2H} + CO$$

On photolysis of $NbCp_2(H)CO$ in a CO matrix, very slight conversion was observed to new carbonyl products and HCO. They are assigned as for their tantalum analogues to $NbCp_2CO$ (VII) and dicarbonyl species (Table 3). However, reductions in their intensity on dilution make it difficult to exclude dimeric products entirely. In a CO matrix, there was no evidence for formation of VI.

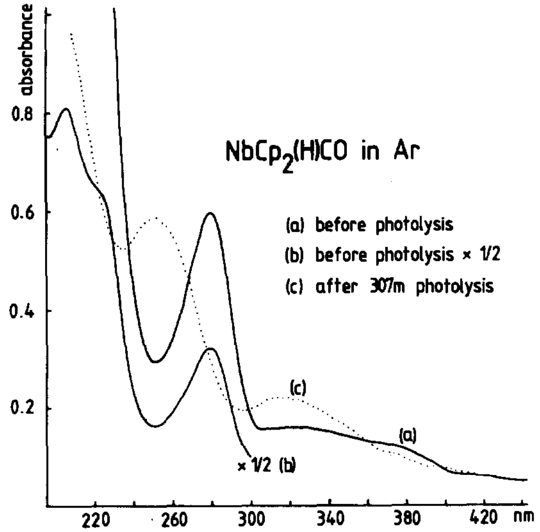
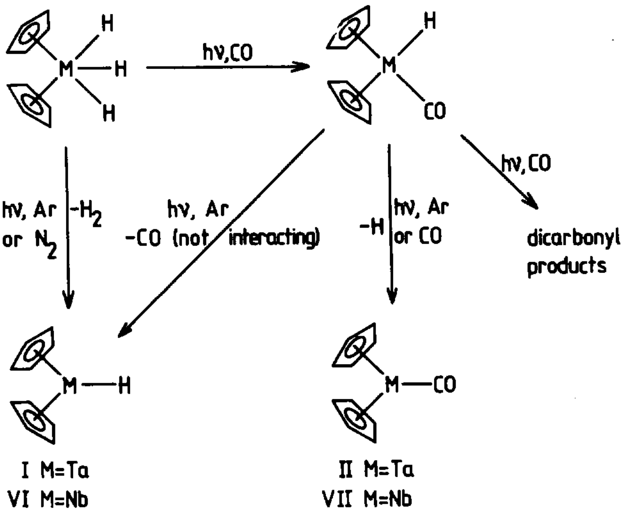


Fig. 6. Ultraviolet spectra of $NbCp_2(H)CO$ in argon at 20 K (a) following deposition for 71 min (sublimation temperature 40°C, 2.4 mmol Ar deposited); (b) the same spectrum with ordinate ×1/2; (c)... after 307 min filtered UV photolysis ($220 < \lambda < 340$ nm).

Photochemical pathways for MCp_2H_3

The matrix-isolation experiments described above establish conclusively the photosensitivity of $TaCp_2H_3$ and $NbCp_2H_3$. Taken together with earlier results on MCp_2H_2 (M = Mo, W) and $ReCp_2H$, it is evident that the entire family of 18-electron hydrides, MCp_2H_n is photosensitive, yielding H_2 or, for $ReCp_2H$, H atoms on photolysis. Considering that the Group V hydrides photolyse relatively rapidly despite a poor match of the absorption spectrum to the output of the mercury arc, they must have a quantum yield comparable to $MoCp_2H_2$ ($\phi \simeq 0.1$) [23] and considerably greater than WCp_2H_2 or $ReCp_2H$. As indicated above, our UV/VIS spectral data conflict with those measured by Foust et al. in heptane solution for $TaCp_2H_3$: we found no evidence for the intense absorption maxima at 280 and 273 nm. Indeed, according to our measurements, any solutions of these hydrides in toluene or benzene would be dominated by solvent absorptions. We therefore consider it possible that Foust et al. observed photosensitization by the aromatic solvent, rather than photochemistry following direct absorption by the hydrides.

The photochemical reactions observed in our matrix experiments are summarized in Scheme 1. The dominant photoprocess of MCp_2H_3 is loss of H_2 to form MCp_2H in inert matrices and $MCp_2(H)CO$ in CO matrices. The photolysis in CO matrices also acts as a test for production of H atoms via their reaction to form HCO. The formyl radical was present only in very small amounts which could be ascribed to secondary photolysis of $MCp_2(H)CO$. Intriguingly, there is no evidence for reaction of MCp_2H with N_2.



SCHEME 1

Photochemical pathways of $MCp_2(H)CO$

Loss of CO to form the 16-electron MCp_2H proved to be the major photoprocess observed for $MCp_2(H)CO$. Even this reaction occurred only in very low yield, although the absorptions match the lamp output well. For comparison, the photolysis of WCp_2CO occurs in higher yield than WCp_2H_2. The rapid exchange observed on photolysis in a ^{13}CO matrix suggests that the low yield is a consequence of rapid recombination within the matrix cage.

This is supported by the spectrum of expelled CO observed on photolysis of $MCp_2(H)CO$ in argon matrices which shows a single band at 2138 cm^{-1} with no evidence for CO interacting with MCp_2H. In contrast, the analogous spectra [6] observed on photolysis of $M'Cp_2CO$ (M' = Mo, W) show a band to lower frequency due to CO interacting with $M'Cp_2$ in addition to the band of isolated CO. This evidence suggests that in-cage recombination of MCp_2H with CO will occur unless the expelled CO molecule escapes the cage. We surmise that the bent structure of MCp_2H imposes no barrier to recombination, whereas the change in structure from parallel to bent rings on reaction of $M'Cp_2$ (M' = Mo, W) with CO is sufficient to suppress in-cage recombination.

Loss of H atoms from $MCp_2(H)CO$ to form the 17-electron molecule MCp_2CO was most conspicuous in CO matrices (cf. the analogous reactions of $ReCp_2H$, $Co(CO)_4H$, $Mn(CO)_5H$ [18,24]). In the presence of CO the H atoms were trapped as HCO, but $TaCp_2CO$ was also observed in Ar and N_2 matrices in the absence of a trap for H atoms. Further polycarbonyl species were observed in CO matrices which are assigned tentatively to the products of η^5–η^3 ring slip and metal–ring hydrogen migration, in each case followed by CO addition. Such photoprocesses have been observed previously for $ReCp_2H$ [18].

Spectrum and structure of MCp_2H

The experiments reported in this paper provide IR and UV spectroscopic data on the 16-electron complexes, MCp_2H (M = Nb, Ta) (Table 1). The IR spectra show bands in the 1670–1750 cm^{-1} region which may be assigned to M–H stretching modes. The presence of several bands in this region can be explained by multiple trapping and conformational effects. The M–H stretching bands of the stable MCp_2H_n complexes of Nb, Ta, Mo, W and Re have also proved either to be very broad or to be split into several components [6,18,25]. The remainder of the IR spectrum is consistent with those of $ReCp_2H$ [25] and $MCp_2(H)CO$ in argon matrices, although it is .surprising that no intense low frequency modes were observed for MCp_2H (M = Nb, Ta) to compare with the 356 cm^{-1} band of $ReCp_2H$. More detailed analysis must await selective deuteriation of MCp_2H_3.

The electron configuration of MCp_2H in the ground state could be $a_1^2a_1^2$ or $a_1^2a_1^1b_2^1$ yielding either $^1A_1$ or $^3B_2$ ground terms. (We are considering the metal *d* and the hydride orbitals [26]). For comparison, the isoelectronic metallocenes $M'Cp_2$ (M' = Mo, W) and VCp_2Me have triplet ground states [6,7,27] but $TaCp_2Cl$ has a singlet ground state [28]. We are currently attempting to establish the spin multiplicity using magnetic circular dichroism. Until then it would be inadvisable to attempt any analysis of the UV spectrum.

Experimental

Preparation of $TaCp_2H_3$ and $TaCp_2(H)CO$

Samples of $TaCp_2Cl_2$, prepared by reaction of MCl_5 with $CpSnBu^n_3$, were reacted with $NaAlH_2(OCH_2CH_2OCH_3)_2$ yielding $TaCp_2H_3$ [29]. This product was converted to $TaCp_2(H)CO$ by dissolving in the minimum volume of toluene in an ampoule with a teflon stopcock. The colourless solution was degassed and pressurized with CO (1.5 atm). After 6 h at ca. 150°C (with suitable protection against explosion) the solvent was removed in vacuo from the purple solution. Unreacted $TaCp_2H_3$ was removed by repeated washing with cold petroleum (0°C). The purple solid was purified by sublimation (75°C/10^{-3} torr) and recrystallization from toluene; it was identified by NMR [17].

Preparation of $NbCp_2H_3$ and $NbCp_2(H)CO$

Niobium pentachloride was converted to $NbCp_2Cl_2$ as in [29] and reacted with $LiAlH_4$ using Labinger's method [30] to form $NbCp_2H_3$. Reaction with CO by the method described above but using milder conditions (80°C for 70 min) yielded $NbCp_2(H)CO$. Attempts to prepare selectively labelled $NbCp_2D_3$ using $LiAlD_4$ were not successful.

Matrix isolation

Matrix isolation experiments were performed as described previously [6,18]. IR and UV spectra were recorded on Perkin–Elmer 580 and 552 spectrophotometers, respectively. Matrices were deposited with a window temperature of 20 K using CsI or LiF substrates for IR and UV spectroscopy respectively. The complexes were sublimed from a heated glass sidearm with a stopcock lubricated with Apezon T grease. Typical sublimation temperatures were as follows: $TaCp_2H_3$ 62–80°C, $TaCp_2(H)CO$ 45–55°C, $NbCp_2H_3$ 40°C, $NbCp_2(H)CO$ 40–45°C.

Acknowledgements

We thank S.E.R.C. for financial support.

References

1 M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac and R.G. Bergman, J. Amer. Chem. Soc., 106 (1984) 1121; A.H. Janowicz and R.G. Bergman, ibid., 104 (1982) 352.

2 J.K. Hoyano, A.D. McMaster and W.A.G. Graham, J. Amer. Chem. Soc., 105 (1983) 7190; A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano and A.D. McMaster, J. Chem. Soc., Chem. Commun., (1984) 624; J.K. Hoyano and W.A.G. Graham, J. Amer. Chem. Soc., 104 (1982) 3724.

3 R.H. Crabtree, M.F. Mellea, J.M. Mihelcic and J.M. Quirk, J. Amer. Chem. Soc., 104 (1982) 106; R.H. Crabtree, P.C. Demon, D. Eden, J.M. Mihelcic, C.A. Parnell, J.M. Quirk and G.E. Morris, ibid., 104 (1982) 6994.

4 D. Baudry, M. Ephritikine and H. Felkin, J. Chem. Soc., Chem. Commun., (1982) 606; D. Baudry, M. Ephritikine, H. Felkin, R. Holmes-Smith, ibid., (1983) 788; D. Baudry, M. Ephritikine, H. Felkin and J. Zakrzewski, ibid., (1982) 1235.

5 W.D. Jones and F.J. Feher, J. Amer. Chem. Soc., 106 (1984) 1650.

6 J. Chetwynd-Talbot, P. Grebenik and R.N. Perutz, Inorg. Chem., 21 (1982) 3647.

7 P.A. Cox, P. Grebenik, R.N. Perutz, M.D. Robinson, R. Grinter and D.R. Stern, Inorg. Chem., 22 (1983) 3614.

8 E.K. Barefield, G.W. Parshall and F.N. Tebbe, J. Amer. Chem. Soc., 92 (1970) 5234.

9 F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 93 (1971) 3793.

10 U. Klabunde and G.W. Parshall, J. Amer. Chem. Soc., 94 (1972) 9081.

11 A.A. Pasynskii, Yu.V. Skripkin, V.T. Kalinnikov, M.A. Porai-Koshits, A.S. Antskyshkina, G.G. Sadikov and V.N. Ostrikova, J. Organomet. Chem., 201 (1980) 269.

12 R.S. Threlkel and J.E. Bercaw, J. Amer. Chem. Soc., 103 (1981) 2650.

13 W.A. Herrmann, H. Biersack, M.L. Ziegler and P. Wülknitz, Angew. Chem. Int. Ed. Engl., 20 (1981) 388.

14 S. Baral, J.A. Labinger, W.R. Scheidt and F.J. Timmers, J. Organomet. Chem., 215 (1981) C53; F.J. Timmers, W.R. Scheidt, J.A. Labinger and S. Baral, ibid., 240 (1982) 153.

15 J.L. Le Quere, F.Y. Petillon, J.E. Guerchais and J. Sala-Pala, Inorg. Chim. Acta, 43 (1980) 5.

16 I.H. Elson, J.K. Kochi, V. Klabunde, L.E. Manzer, G.W. Parshall and F.N. Tebbe, J. Amer. Chem. Soc., 96 (1974) 7374. I.H. Elson and J.K. Kochi, ibid., 97 (1975) 1263.

17 D.F. Foust, R.D. Rogers, M.D. Rausch and J.L. Atwood, J. Amer. Chem. Soc., 104 (1982) 5646.

18 J. Chetwynd-Talbot, P. Grebenik, R.N. Perutz and M. Powell, Inorg. Chem., 21 (1983) 1675.

19 P.A. Cox, P. Grebenik, R.N. Perutz, R.G. Graham and R. Grinter, Chem. Phys. Lett., 108 (1984) 415.

20 D.E. Milligan and M.E. Jacox, J. Chem. Phys., 41 (1964) 3032; 51 (1969) 277.

21 M.E. Jacox, J. Mol. Spectrosc., 47 (1973) 1418; L.J. van Ijzendoorn, L.J. Allamandola, F. Baas and J.M. Greenberg, J. Chem. Phys., 78 (1983) 7019.

22 R.P.M. Werner, A.H. Filbey and S.A. Manastyrskyj, Inorg. Chem., 3 (1964) 298.

23 G.L. Geoffroy and M.G. Bradley, Inorg. Chem., 17 (1978) 2410.

24 R.L. Sweany, Inorg. Chem., 19 (1980) 3512; S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, J. Amer. Chem. Soc., 103 (1981) 7515; Inorg. Chem., 23 (1983) 3259; M.C.R. Symons and R.L. Sweany, Organometallics, 1 (1982) 834.

25 P. Grebenik, D. Phil. Thesis, University of Oxford, 1981.

26 J.W. Lauher and R. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 1729.

27 F.H. Köhler, P. Hofmann and W. Prössdorf, J. Amer. Chem. Soc., 103 (1981) 6359.

28 A. Antiñolo, M. Fajardo, A. Otero and P. Royo, J. Organomet. Chem., 246 (1983) 269.

29 M.J. Bunker, A. DeCian, M.L.H. Green, J.E. Moreau and N. Siganporia, J. Chem. Soc., Dalton Trans, (1980) 2155.

30 J.A. Labinger, Adv. Chem. Ser., 167 (1978) 149.