Journal of Organometallic Chemistry, *444* (1993) 75–81

JOM 23068

Photochemistry of $Cp_2Ti(CO)_2$ and $Cp_2Ti(N_3)_2$ in solid matrices and in solution at low temperatures

M. Tacke [1], Ch. Klein [1], D.J. Stufkens and A. Oskam

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (Netherlands)

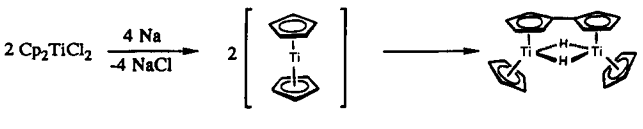
(Received December 10, 1991; in revised form July 8, 1992)

Abstract

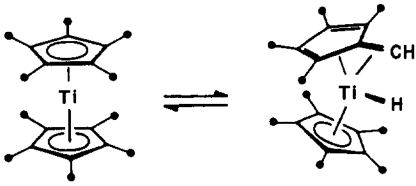
Photolysis of $Cp_2Ti(CO)_2$ in various solid matrices (Ar, CH_4, CO, 2-MeTHF) at temperatures below 120 K generated (the previously unknown) Cp_2TiCO. The 16-valence electron species was characterized by IR spectroscopy and the back-reaction with CO was studied. The CO stretching frequency of the product was shown to depend on the donor strength of the matrix material used. $Cp_2Ti(N_3)_2$ was photolysed in a CO-doped Ar matrix at 12 K. Four photoproducts (Cp_2TiCO, $Cp_2Ti(CO)_2$, $Cp_2Ti(NCO)_2$, $Cp_2Ti(N_2)_2$) were identified by IR spectroscopy. A plausible mechanism for the photodecomposition of $Cp_2Ti(N_3)_2$ via $Cp_2Ti(N)(N_3)$ and Cp_2Ti is suggested. The reaction with CO was also monitored in liquid xenon (LXe) at 243 K and in toluene at room temperature under CO pressure; $Cp_2Ti(NCO)_2$ was produced in both cases.

1. Introduction

The experiments reported in this paper were carried out to elucidate the complicated chemistry of the 14-valence electron (VE) species of Cp_2Ti [1]. Previous reports revealed that this complex could not be isolated, and the product formed by reduction of, *e.g.* Cp_2TiCl_2 turned out to be a hydrogen-bridged fulvene complex [2].



Introduction of permethylated Cp-rings (Cp*) will of course increase the stability of this compound. However, Cp^*_2Ti is still coordinatively unsaturated and it is believed that in the decamethyl derivative there is reversible activation of an intramolecular C–H bond [3].



Initially, $Cp_2Ti(CO)_2$ (**I**) and $Cp_2Ti(N_3)_2$ (**II**) seemed to be possible precursors for the titanocene system. The last system is electron deficient. The first compound has titanium in the right oxidation state and the complex is known to be photochemically active [4]. The second compound is also a possible titanocene precursor, since azide groups normally give dinitrogen ligands to form $Cp_2Ti(N)_2$ in the first instance [5] and finally open sites at the metal centre [6,7]. Vogler *et al.* [7] have studied the fate of the azide groups after irradiation but without obtaining definite evidence. With W as the metal centre, Rest revealed the presence of

---

Correspondence to: Dr. M. Tacke or Professor A. Oskam.

[1] Present address: Anorganisch Chemisches Institut der Universität München, Meiserstrasse 1, W-8000 München 2, Deutschland.

0022-328X/93/$6.00

© 1993 – Elsevier Sequoia S.A. All rights reserved

NCO as a ligand in the final product from $CpW(CO)_2(N)$ after irradiation in a CO matrix [5]. In considering the reaction mechanisms and the possible reactions, ring-slippage must be taken into account [8]. In order to monitor the reactions under very mild reaction conditions, frozen matrices and cold inert solvents were used as media.

2. Experimental details

The starting materials $Cp_2Ti(CO)_2$ and $Cp_2Ti(N_3)_2$ were prepared by published methods [9,10]. The synthesis of $Cp_2Ti(N_3)_2$ involved a stepwise substitution via $Cp_2Ti(Cl)(N_3)$ as an intermediate; the latter had $\nu_{as}(N_3)$ at 2063 cm^{-1} (eqn. (1)).

$$Cp_2TiCl_2 \xrightarrow[-NaCl]{+NaN_3} Cp_2Ti(Cl)(N_3) \xrightarrow[-NaCl]{+NaN_3} Cp_2Ti(N_3)_2 \qquad (1)$$

High purity gases Ar (4.0; AGA), N_2 (5.2; AGA), CH_4 (5.0; AGA), CO (4.7; AGA), ^{13}CO (99.8% ^{13}C, 14.8% ^{18}O) (Matheson), Xe (4.5; Air Products) were used as purchased. Solvents were dried by conventional means and stored under nitrogen.

Matrix isolation studies were performed with a Displex Air Products and Chemicals closed cycle cryostat that cooled a CaF_2 plate to 12 K. The parent compounds were sublimed from a Knudsen cell at 80°C ($Cp_2Ti(CO)_2$) or 100°C ($Cp_2Ti(N_3)_2$) and cocondensed with a large excess of matrix gas (ratio 1 : 1000–5000) at 12 K for 2 h.

Solid 2-MeTHF matrices were prepared in a low temperature IR cell. The solution (0.1–0.01 M) was injected between two CaF_2 plates (0.3 mm spacer) and cooled down rapidly in an Oxford Instruments XL-500 Cryostat to avoid crystallization.

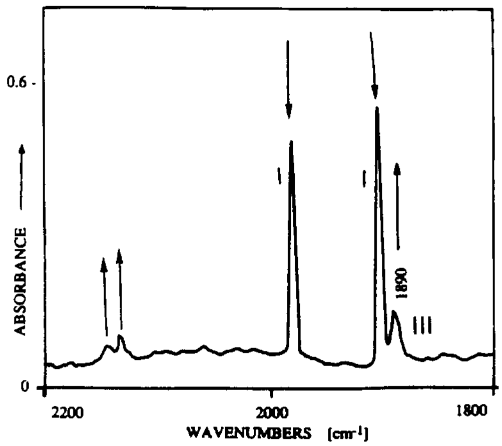


Fig. 1. IR spectral changes in the ν(CO) stretching region upon photolysis of $Cp_2Ti(CO)_2$(I) in an Ar matrix at 12 K. I = $Cp_2Ti(CO)_2$; III = $Cp_2Ti(CO)$; small amounts of CO are always deposited in the matrix as a result of decomposition of I and oxidation of the diffusion pump oil.

Unless stated otherwise the irradiation source was a 200 W Hg-arc (Oriel Corporation), with a water-filled 50 mm quartz cell filter followed by an interference filter (313 nm). IR spectra were recorded on a Nicolet 7199 B FT-IR spectrometer (4000–1200 cm^{-1}, 32 scans, resolution 1 cm^{-1}), UV–VIS spectra on a Perkin–Elmer Lambda 5 spectrophotometer (900–190 nm, 1 scan, resolution 2 nm).

Solution reactions under CO pressure were either studied in a UV–VIS transparent autoclave made from a 10 cm sapphire tube or in a pressure-resistant LXe IR cell connected to a Bio-Rad FTS-7 FT-IR spectrometer (4000–1000 cm^{-1}, 32 scans, resolution 2 cm^{-1}). Details of the autoclave [11] and LXe IR cell [12] have been described previously.

TABLE 1. Spectroscopic data

	Compound	Matrix	IR frequencies (cm^{-1})	Electronic absorptions (nm)
I	$Cp_2Ti(CO)_2$	Argon	1982 and 1903	308 and 379
II	$Cp_2Ti(N_3)_2$	Argon/CO	2081 and 2056	291 and 413
		N_2	2084 and 2059	
		LXe	2078 and 2050	
III	$Cp_2Ti(CO)$	Argon	1890	
		CH_4	1875	
IV	$Cp_2Ti(CO)(2MeTHF)$	2MeTHF	1822	403
V	$Cp_2Ti(NCO)_2$	Argon/CO	2218 and 2205	
		LXe	2216	
VI	$Cp_2Ti(N_2)_2$	Argon/CO	2080	
		LXe	2140 and 2080	

3. Results

3.1. Investigations in $Cp_2Ti(CO)_2$

3.1.1. Matrix studies

The first experiments were carried out with frozen gas matrices. The IR spectrum of $Cp_2Ti(CO)_2$ (**I**) isolated in solid Ar at 12 K showed two terminal CO-stretching vibrations at 1982 and 1903 cm^{-1} respectively (Fig. 1). The UV–VIS spectrum of **1** measured in C_6H_{14} showed a band at 308 nm ($\epsilon = 8000$ mol^{-1} cm^{-1}) [13] with a shoulder at 379 nm, probably because of its lower intensity, belonging to a ligand field transition. Upon UV irradiation, the parent CO bands decreased in intensity while a new CO vibration appeared at 1890 cm^{-1}. In addition, bands belonging to free and matrix-cage isolated CO appeared at 2136 and 2145 cm^{-1}, respectively. However, the possibility that the band at 2145 cm^{-1} is due to $CO\ldots H_2O$ [14] cannot be excluded.

The 1890 cm^{-1} band is assigned to the photoproduct titanocene monocarbonyl **III**, formed by the CO-loss reaction (eqn. (2)).

$$\mathbf{I} \xrightarrow[\text{Ar matrix/12K}]{\lambda = 313\ \text{nm/4 h}} \underset{(\mathbf{III})}{Cp_2TiCO} + CO \qquad (2)$$

The CO abstraction proved to be reversible under matrix conditions, and a nearly complete back reaction took place during three annealing cycles to 30 K. This shows that **III** is a short-lived intermediate in the presence of CO. No evidence was found for a secondary photochemical reaction when the irradiation time was prolonged to 24 h. This means that 'Cp_2Ti' could not be produced in this way. It was not even possible to achieve a complete conversion of **I** into **III**, probably because of the thermal back reaction of **III** at higher CO concentrations.

To confirm the above reaction, the photolysis was repeated under similar conditions in a methane matrix. Figure 2 shows the IR spectrum of **I**, isolated in a methane matrix. The two CO fundamentals now have a matrix splitting of 4 cm^{-1}, probably due to slightly different environments (ν(CO) 1971/1975 cm^{-1} and 1894/1890 cm^{-1}).

Irradiation induced a major reaction of the species having higher frequencies for both doublets to give titanocenemonocarbonyl (**III**) (eqn. (3)) having ν(CO) at 1875 cm^{-1} (Fig. 2). This difference in photochemical rates can be attributed to reaction at two sites in different environments.

$$\mathbf{I} \xrightarrow[CH_4\ \text{matrix/12 K}]{\lambda = 313\ \text{nm/4h}} \underset{(\mathbf{III})}{Cp_2TiCO} + CO \qquad (3)$$

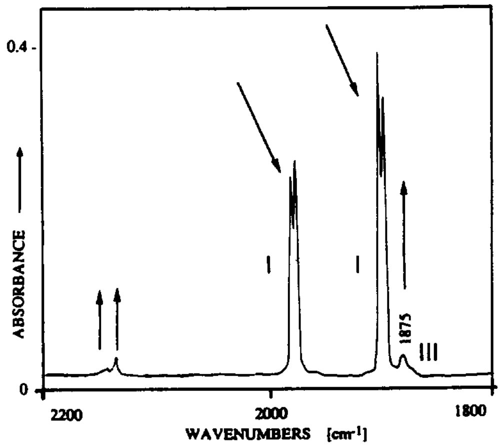


Fig. 2. IR spectral changes in the ν(CO) stretching region upon photolysis of $Cp_2Ti(CO)_2$ (**I**) in a methane matrix at 12 K (**I** = $Cp_2Ti(CO)_2$; **III** = $Cp_2Ti(CO)$).

There is a matrix shift of about 15 wavenumbers between **III** in Ar and CH_4, indicating a significant interaction between **III** and the matrix molecules, but there is no spectroscopic evidence for C–H activation of methane by **III**.

Back reaction occurred at 30 K in the dark, again confirming the poor stability of **III** in the presence of CO. Just as in the Ar matrix, free and matrix-cage isolated CO absorb at 2136 and 2145 cm^{-1}, respectively. Prolonged irradiation did not give rise to titanocene formation via **III**.

In a further experiment, **I** was isolated in a pure CO matrix in order to study the coordination of a third CO-ligand under "ring-slippage" [8]. The two CO fundamentals of **I** found at 1975 and 1894 cm^{-1}, respectively, are broader than in Ar because of stronger matrix interactions. Although irradiations were carried out at different wavelengths no association of CO by ring-slippage [8] was observed (eqn. (4)).

$$\mathbf{I} \underset{\text{CO matrix/12 K}}{\overset{h\nu}{-\!\!\!-\!\!\!\times\!\!\!-\!\!\!\longrightarrow}} (\eta^3-Cp)(\eta^5-Cp)Ti(CO)_3 \qquad (4)$$

The final matrix material used was a 2-MeTHF glass. A 0.1 M solution of **I** was placed in an IR liquid cell and cooled down to 120 K. Two CO frequencies were then observed, at 1962 and 1876 cm^{-1}, respectively. The frozen solution was irradiated for 2 min with unfiltered light from the Hg-lamp. A substantial amount of **I** had then been converted into the monocarbonyl-2-MeTHF adduct (**IV**) (eqn. (5)), absorbing at 1822 cm^{-1}, and free CO (ν(CO) 2132 cm^{-1}) (Fig. 3). Because of the high yield of the reaction the UV-vis spectrum of **IV** could be recorded, and showed a well resolved band at 403 nm. This band probably belongs to the lowest LF transition, since it is shifted to lower

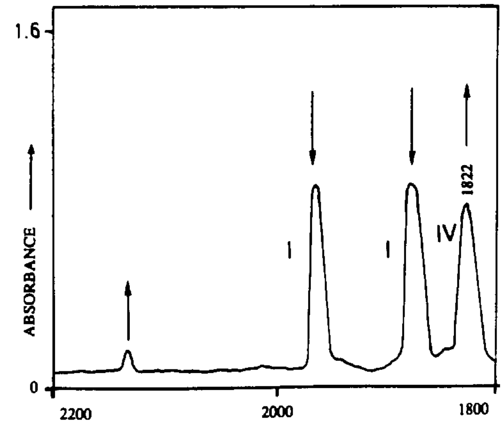


Fig. 3. IR spectral changes in the ν(CO) stretching region upon photolysis of $Cp_2Ti(CO)_2$ (I) in a 2-MeTHF glass at 120 K. (I = $Cp_2Ti(CO)_2$; IV = $Cp_2Ti(CO)(2\text{-MeTHF})$).

energy (379 → 403 nm) when CO in I is replaced by 2-MeTHF to give IV.

$$\text{I} \xrightarrow[\text{2-MeTHF/120 K}]{h\nu/2\ \text{min}} \underset{(\text{IV})}{Cp_2Ti(CO)(2\text{-MeTHF})} + CO \qquad (5)$$

After generation of IV the matrix was allowed to warm up smoothly. At 170 K, the back reaction with CO took place. The lifetime of IV ($t_{1/2}$) was found to be 2 min at this temperature.

3.2. *Investigations in $Cp_2Ti(N_3)_2$*

3.2.1. *Matrix studies*

The next precursor molecule, $Cp_2Ti(N_3)_2$ (II), was matrix-isolated in a 2% CO-doped Ar matrix. In addition to a band at 2139 cm^{-1} belonging to frozen CO, a split absorption of $\nu_{as}(N_3)$ at 2081 and 2056 cm^{-1}, respectively, was observed in the IR spectrum, but there was no evidence for formation of $Cp_2Ti(N_3)_2(CO)$. The UV-VIS spectrum of this orange compound (II) showed two absorption bands at 291 and 413 nm, respectively, belonging to LMCT transitions [15]. Wavelength-dependent photolysis (313 or 450 nm) resulted in the formation of four identified photoproducts: $Cp_2Ti(CO)$ (III) (ν(CO) 1878 cm^{-1}), $Cp_2Ti(CO)_2$ (I) (ν(CO) 1979/1898 cm^{-1}) and a larger amount of the N-bonded [16] $Cp_2Ti(NCO)_2$) (V). Complex V was identified from its characteristic ν_{as}(NCO) bands at

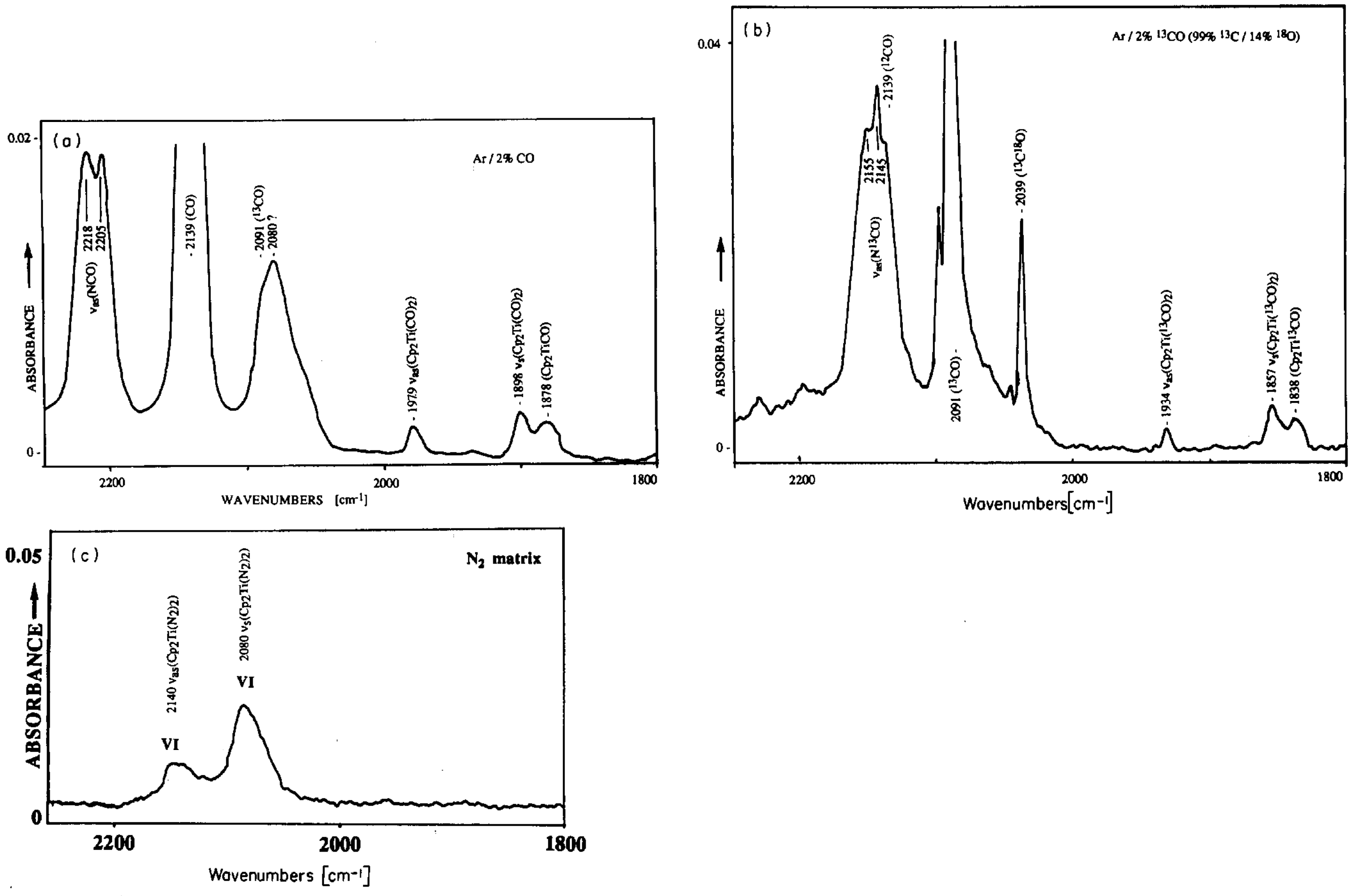


Fig. 4. Infrared spectra in the 2250–1800 cm^{-1} region after irradiation of $Cp_2Ti(N_3)_2$ (II) in a ^{12}CO doped Ar matrix at 12 K (a) and after irradiation of II in a ^{13}CO doped Ar matrix at 12 K (b). (c) Infrared spectrum in the 2250–1800 region after irradiation of II in a N_2 matrix at 12 K (I = $Cp_2Ti(CO)_2$; III = $Cp_2Ti(CO)$; V = $Cp_2Ti(NCO)_2$; VI = $Cp_2Ti(N_2)_2$).

2218 and 2205 cm^{-1}, respectively [17] (Fig. 4a). Another photoproduct (**VI**) had an absorption band at 2080 cm^{-1} (eqn. (6)). To confirm the formation of these photoproducts, the experiment was repeated with ^{13}C-enriched CO (99.8 % ^{13}C; 14.8 % ^{18}O). The $\nu_{as}(NCO)$ bands were then shifted by about 60 cm^{-1} to lower frequencies ($\nu_{as}(N^{13}CO)$ 2155/2145 cm^{-1}) and the CO stretching vibrations of **I** ($\nu(^{13}CO)$ 1934/1857 cm^{-1}) and **III** ($\nu(^{13}CO)$ 1838 cm^{-1}) by about 40 cm^{-1}, in agreement with earlier data [18] (Fig. 4b). Because no shift for the band at 2080 cm^{-1} was observed in the ^{13}CO-doped Ar matrix experiment, this band was attributed to a dinitrogen vibration.

To prove that such a dinitrogen complex was formed, the experiment was repeated in a pure dinitrogen matrix. The two azide bands of **II** then appeared at 2084 and 2059 cm^{-1}, respectively, slightly different in frequencies from those observed in the CO-doped Ar matrix. Photolysis resulted in complete decomposition of **II** and the appearance of two new IR bands, at 2140 and 2080 cm^{-1}, respectively (Fig. 4c). The weak absorption at 2140 cm^{-1} was hidden in the earlier CO experiments. We attribute these bands to the antisymmetric and symmetric dinitrogen-stretching vibrations of the titanocene-bis-dinitrogen complex $Cp_2Ti(N_2)_2$ (**VI**) (eqn. (6)), but definite proof could only be obtained by $^{15}N_2$ experiments.

$$\mathrm{II}\ \xrightarrow{h\nu}\ \begin{cases} \xrightarrow[\text{Ar matrix/12 K}]{+\mathrm{CO}\ \times} & Cp_2Ti(N_3)_2(CO) \\ \xrightarrow[\text{Ar matrix/12 K}]{+\mathrm{CO}} & \mathrm{I}+\mathrm{III}+\mathrm{V}+\mathrm{VI} \end{cases} \qquad (6)$$

3.2.2. *Solution studies*

In order to obtain more information about the photochemical reactivity of **II** in solution, we investigated the reaction with CO in LXe. This solvent is an excellent medium in which highly reactive intermediates can be stabilized and detected [12,19], since it is nearly inert to chemical reactions. Moreover, it is transparent in the UV–VIS and IR region and it can be cooled down to 170 K.

The IR spectrum of **II** in LXe (19 bar Xe + 1 bar CO) at 243 K shows the absorptions of $\nu_{as}(N_3)$ at 2078 and 2050 cm^{-1}, respectively. Unfortunately this maximum temperature of the LXe cell had to be used because of the low solubility of the parent compound at lower temperatures. Irradiation for 10 min eliminated the small amount of **II** and produced **V** as the only detectable photoproduct ($\nu_{as}(NCO)$ 2216 cm^{-1}, br) (eqn. (7)).

$$\mathrm{II}\ \xrightarrow[\text{LXe + CO/243 K}]{\lambda = 313\ \text{nm/10 min}}\ \underset{(\mathrm{V})}{Cp_2Ti(NCO)_2} \qquad (7)$$

V was also synthesized in a conventional solvent at room temperature. A 0.1 M solution of **II** in toluene was transferred under CO into a sapphire autoclave and the pressure was increased to 50 bar. After 10 min irradiation, the pressure was released and all volatiles were evaporated. At least two compounds had been formed: **V**, identified from its IR spectrum in Nujol, and a species absorbing at 2082 cm^{-1}, probably a titanium dinitrogen complex, with an unknown structure. This reaction did not produce **I** or **VI** (eqn. (8)).

$$\mathrm{III}\ \xrightarrow[\text{toluene/50 bar CO/RT}]{\lambda = 313\ \text{nm/10 min}}$$

$$\underset{(\mathrm{V})}{Cp_2Ti(NCO)_2} + \text{titanium–dinitrogen complex} \qquad (8)$$

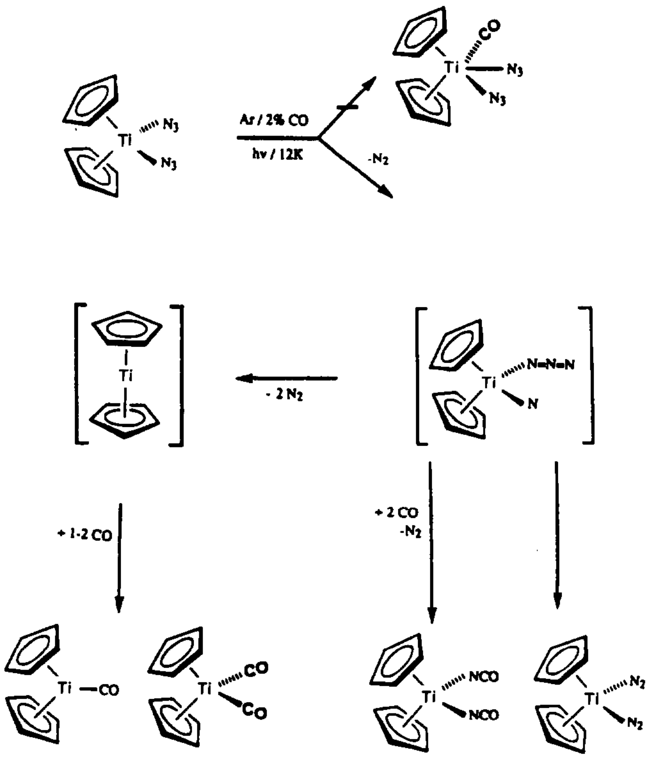
4. Discussion

Unsubstituted titanocene was not produced by photolysis of **I** in an Ar or CH_4 matrix at 12 K nor in a 2-MeTHF glass at 120 K. The photolysis resulted in the formation of the 16 VE complex titanocenemonocarbonyl (**III**) in the former case and the 18 VE species $Cp_2Ti(CO)(2\text{-MeTHF})$ (**IV**) in the latter.

Complex **III** is a very reactive, coordinatively saturated species, which incorporates CO rapidly at 30 K nearly without any activation energy, just at the point when the frozen gas matrix allows some diffusion. However, **III** does not activate methane from the matrix by an oxidative addition process.

In the less rigid medium 2-MeTHF, which has larger 'matrix holes' compared with solid Ar or CH_4, the yield of **IV** can reach a value of 50% after a markedly short irradiation time. In contrast to **III**, **IV** is more stable because of its 18 VE structure. However, since 2-MeTHF is only a σ-donor, without the possibility of π back-bonding, it is readily replaced by CO at 170 K in the solid state. The CO-stretching vibrations of **I**, **III** and **IV** give some information about the electronic structure of these carbonyls. In **I**, the average value of the carbonyl frequencies is 1940 cm^{-1}. Thus we start with a relatively strong π-back bonded system (compare, *e.g.* $Cr(CO)_6$ $\nu(C)$ $\approx$ 2000 cm^{-1}). The low-coordinate, 16 VE complex **III** gives a CO frequency of 1890 or 1875 cm^{-1}, depending on the matrix material. Due to the strong σ-donation of 2-MeTHF, complex **IV** shows more π back-bonding to CO. As a result, $\nu(CO)$ is observed at a much lower frequency ($\nu(CO)$ 1822 cm^{-1}).

Finally, these frequencies can be compared with those for the known complex $Cp_2Ti(CO)(PMe_3)$. In this 18 VE complex, CO and PMe_3 interact as good π-acceptor ligands, and PMe_3 is also a valuable donor.



Scheme 1.

The CO band appears at 1863 cm^{-1} [4], between the values of $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(2\text{-}MeTHF)$. The photolysis of **I** was always performed at the 313 nm line of the Hg-arc. This means that the Ti–C bond energy must be lower than 383 kJ mol^{-1}.

Photodecomposition of **II** ends up closer to titanocene. In a CO-doped Ar matrix there is some circumstantial evidence for formation of a titanocene intermediate (a 14 VE species) that adds one or two molecules of CO to end up as titanocene carbonyl (**I** or **III**). Surprisingly there is no hint of the formation of the mixed 18 VE complex $Cp_2Ti(CO)(N_2)$. Instead the preferred reaction is the stepwise loss of dinitrogen to give a titanocene-azidenitride intermediate that reacts with CO to give titanocene-diisocyanate (**V**) (Scheme 1). The NCO ligand may be formed via a metal nitride complex that captures CO in the outer sphere, rather than by preliminary coordination of CO to the parent compound **II** [5]. This product can also be formed in toluene solution at room temperature and in cold LXe under CO pressure.

Under matrix conditions (pure N_2 and CO doped Ar matrices) there are also bands in the 2000 cm^{-1} region, which indicate the formation of $Cp_2Ti(N_2)_2$ (**VI**). A titanium–dinitrogen complex is also formed in solution studies (eqn. (8)), but with an unknown structure, probably with less nitrogen per titanium than **VII**, owing to the higher reaction temperature and lower nitrogen concentration.

However, even under matrix conditions titanocene is a reactive intermediate which tries to complete its coordination sphere. Photolysis of **II** seems to be a suitable way of initiating reactions of this low-coordinate organotitanium substrate. The photo-products of **II** formed in Ar/CO or dinitrogen matrices provide evidence for the loss of dinitrogen, either stepwise to form $Cp_2Ti(N)(N_3)$, or complete to form Cp_2Ti as intermediate. A third possible route, via $Cp_2Ti(N_3)$, was not observed.

In the near future we plan to investigate reactions with decamethyltitanocene compounds in cold LXe [20].

Acknowledgements

The authors are grateful to Professor J.H. Teuben for his gift of purified $Cp_2Ti(CO)_2$ and G. Schoemaker for his assistance with the matrix investigations. M. Tacke thanks "Deutsche Forschungsgemeinschaft" for a post-doctoral scholarship.

References

1 G. P. Pez and J. N. Armor, *Adv. Organomet. Chem.*, 21 (1981) 1.
2 L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 98 (1976) 4137;
A. Davison and S. S. Wreford, *J. Am. Chem. Soc.*, *96* (1974) 3017;
H. H. Brintzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, *92* (1970) 6182.
3 R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh and J. E. Bercaw, *J. Am. Chem. Soc.*, *98* (1976) 8358;
J. E. Bercaw, *J. Am. Chem. Soc.*, *96* (1974) 5087;
J. E. Bercaw, R. H. Marvich, L. J. Bell and H. H. Brintzinger, *J. Am. Chem. Soc.*, *94* (1972) 1219.
4 B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organomet. Chem.*, *93* (1975) 199;
L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, B. Wolf and U. Thewalt, *J. Organomet. Chem.*, *297* (1985) 159.
5 R. B. Hitam, A. J. Rest, M. Herberhold and W. Kremnitz, *J. Chem. Soc., Chem. Commun.*, (1984) 471.
6 D. A. Freedman and K. R. Mann, *Inorg. Chem.*, *30* (1991) 836;
H. Knoll, R. Stich, H. Henning and D. J. Stufkens, *Inorg. Chim. Acta*, *178* (1990) 71;
W. Beck, W. P. Fehlhammer, P. Pöllmann and H. Schächl, *Chem. Ber.*, *102* (1969) 1976;
H. Werner, W. Beck and H. Engelmann, *Inorg. Chim. Acta*, *3* (1969) 331;
A. T. McPhail, P. M. Gross, G. R. Knox, C. G. Robertson and G.A. Sim, *J. Chem. Soc. A*, (1971) 205.
7 A. Vogler, R. E. Wright and H. Kunkely, *Angew. Chem.*, *92* (1980) 745;
A. Vogler and J. Hlavatsch, *Angew. Chem.*, *95* (1983) 153.
8 R. B. Hitam, A. Mahmoud and A. J. Rest, *Coord. Chem. Rev.* *551*, (1984) 1;
P. E. Bloyce, A. J. Rest and L. Whitwell, *J. Chem. Soc., Dalton Trans.*, (1990) 813;

D. J. Fetters, R. Narayanaswamy and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, (1981) 2311.

9 F. Calderazzo, J.J. Salzmann and P. Mosimann, *Inorg. Chim. Acta, 1* (1967) 65;
B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organomet. Chem., 101* (1975) C24.

10 R. S. P. Coutts and P. C. Wailes, *Aust. J. Chem., 24* (1971) 1075.

11 D. C. Roe, *J. Magn. Reson., 63* (1985) 388.

12 R. R. Andrea, H. Luyten, M. A. Vuurman, D. J. Stufkens and A. Oskam, *Appl. Spectrosc., 40* (1986) 1184.

13 E. O. Fischer and R. Amtmann, *J. Organomet. Chem., 9* (1967) P15.

14 R. N. Perutz and J. J. Turner, *J. Chem. Soc., Faraday Trans. 2, 69* (1973) 452.

15 R. W. Harrigan, G. S. Hammond and H. B. Gray, *J. Organomet. Chem., 81* (1974) 79;
G. L. Geoffroy and M.S. Wrighton, *Organometallic Photochemistry,* Academic Press, New York, 1979, 230–237 and references cited therein.

16 S. J. Anderson, D. S. Brown and A. H. Norbury, *J. Chem. Soc., Chem. Commun.*, (1974) 996.

17 J. L. Burmeister, E. A. Deardorff and C. E. van Dyke, *Inorg. Chem., 8* (1969) 170;
J. L. Burmeister, E. A. Deardorff, A. Jensen and V. H. Christiansen, *Inorg. Chem., 9* (1970) 58.

18 A. Maki and J. C. Decius, *J. Chem. Phys., 31* (1959) 772.

19 S. A. Jackson, P. N. Hodges, N. Poliakoff, J. J. Turner and F. W. Grevels, *J. Am. Chem. Soc., 112* (1990) 1221 and references cited therein.

20 M. Tacke, Ch. Klein, D. J. Stufkens, A. Oskam and J. H. Teuben, unpublished results.