Journal of Organometallic Chemistry, 264 (1984) 309–316
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FORMATION AND CHARACTERIZATION OF A HYDRIDO-TANTALACYCLOPROPANE COMPLEX FROM THE PHOTO-INDUCED β-HYDRIDE ELIMINATION OF DI-η^5-CYCLOPENTADIENYL-ETHYL(CARBONYL)TANTALUM

MANFRED E. EICHNER, HELMUT G. ALT*

Laboratorium für Anorganische Chemie der Universität Bayreuth, Universitätsstrasse 30, D-8580 Bayreuth (B.R.D.)

and MARVIN D. RAUSCH*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

(Received August 17th, 1983)

Summary

A reaction between Cp_2TaCl_2 and 2 equivalents of C_2H_5MgBr in refluxing dimethoxyethane has produced the hydrido-ethylene complex $Cp_2Ta(C_2H_4)H$ in 62% yield. Acid hydrolysis of $Cp_2Ta(C_2H_4)H$ yields Cp_2TaCl_2 and ethane, whereas the ethylene ligand can be displaced by PEt_3 under photochemical conditions to yield $Cp_2Ta(PEt_3)H$. A reaction between $Cp_2Ta(C_2H_4)H$ and carbon monoxide in toluene at 80°C results in CO-induced insertion of the ethylene ligand into the Ta–H bond, and formation of $Cp_2Ta(CO)C_2H_5$ in 56% yield. Photolysis of $Cp_2Ta(CO)C_2H_5$ in hydrocarbon solvents generates $Cp_2Ta(C_2H_4)H$ as well as $Cp_2Ta(CO)H$ by a process of CO dissociation and β-hydride elimination. ^1H NMR studies on $Cp_2Ta(C_2H_4)H$ demonstrate that the ethylene ligand does not rotate in solution up to 120°C. ^1H and ^{13}C NMR studies indicate a configuration for $Cp_2Ta(C_2H_4)H$ in which the ethylene C=C axis lies in the symmetry plane of the molecule, and together with the chemical degradation data are consistent with a tantalacyclopropane formulation for this molecule.

Introduction

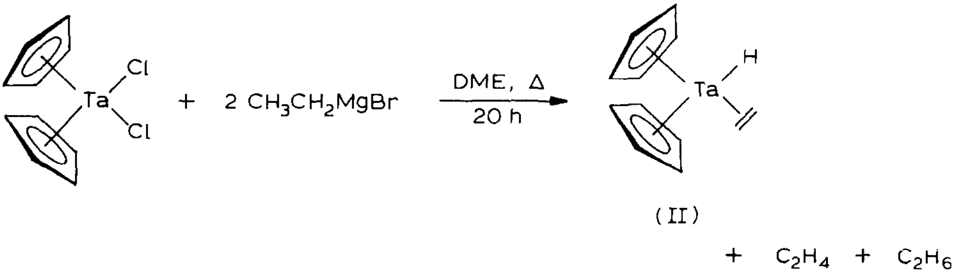
Recent studies in our laboratories have demonstrated that photolyses of Cp_2MH_3 or $Cp_2M(CO)H$ (M = Nb, Ta) in aromatic solvents lead to a common coordinatively unsaturated intermediate, Cp_2MH, that can react with carbon monoxide, hydrogen or triethylphosphine. These photogenerated species are also capable of inserting into the carbon–hydrogen bonds of benzene, and catalyzing the photoassisted H/D exchange between molecular hydrogen and benzene [1]. We have likewise recently

0022-328X/84/$03.00

demonstrated that photolysis of $CpW(CO)_3C_2H_5$ in solution leads to the intermediate complexes $CpW(CO)_2(C_2H_4)H$ and $CpW(CO)_3H$, products which are characteristic for β-hydride elimination [2]. We now report extensions of these investigations to include the photo-induced β-hydride elimination of $Cp_2Ta(CO)C_2H_5$ (I) to form $Cp_2Ta(C_2H_4)H$ (II) and $Cp_2Ta(CO)H$ (III). Also discussed are ^1H and ^{13}C NMR spectral studies which indicate a rigid conformation of the ethylene ligand in complex II.

Results and discussion

Teuben and Klazinga [3] have recently described the synthesis of a series of hydrido-olefin complexes of tantalocene of the type $Cp_2Ta(L)H$ ($L = C_3H_6$, C_4H_8, C_5H_{10}, and C_5H_8). We have now been able to extend this approach for the synthesis of the parent member of this series, complex II ($L = C_2H_4$) *. In contrast to the formation of the previously described higher homologues, an increased reaction temperature is necessary to promote the reaction between Cp_2TaCl_2 and two equivalents of C_2H_5MgBr. When this reaction was run in refluxing dimethoxyethane (DME) for 20 h, complex II was obtained in 62% yield, together with the formation of ethane and ethylene in nearly equal amounts. Presumably, the first step in this reaction involves reduction of Cp_2TaCl_2 to Cp_2TaCl, which can subsequently be alkylated to generate $Cp_2TaC_2H_5$. This intermediate, formally a 16-electron species, undergoes β-hydride elimination to generate the more stable, coordinatively saturated product II. The ethylene-hydrido complex II is a very air-sensitive, pale-yellow solid. Due to its low solubility in organic solvents, it is best purified by vacuum sublimation rather than extraction and crystallization as in the case of the higher homologues [3].



The structure of complex II was elucidated by both spectroscopic and chemical means. The mass spectrum of II exhibited a molecular ion at *m/e* 340, whereas the base peak at *m/e* 312 corresponded to the fragment ion (Cp_2TaH^+) resulting from loss of ethylene. The ^1H and ^{13}C NMR spectra of II are discussed in detail below.

Treatment of II with HCl-saturated toluene resulted in cleavage of the ethylene ligand and formation of both Cp_2TaCl_2 and ethane. This reduction of the ligand is in agreement with a metallacyclopropane structure for complex II, as is also indicated from NMR spectral considerations (vide infra). Similar acid hydrolysis of a dimethyl fumarate complex of titanocene likewise resulted in the formation of

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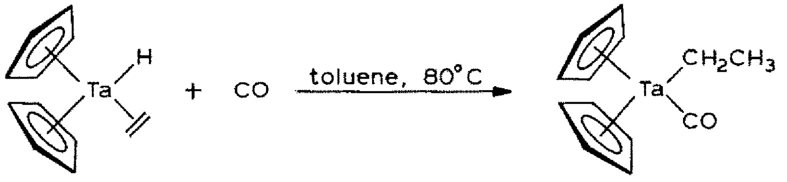
* Complex II has previously been briefly mentioned in the literature [4]. However, it was characterized only by a ^1H NMR spectrum, and was produced in very low overall yield involving a multi-step sequence of reactions.

Cp_2TiCl_2 and the reduction product dimethyl succinate [5]. Furthermore, photolysis of a pentane solution of II and triethylphosphine led to liberation of the ethylene ligand and formation of the known hydrido-phosphine complex $Cp_2Ta(PEt_3)H$ (IV) [6] (Scheme 1).

Klazinga and Teuben have shown that reactions of the hydrido-olefin complexes $Cp_2Ta(L)H$ ($L = C_3H_6$, C_4H_8, C_5H_{10} and C_5H_8) with carbon monoxide under mild conditions resulted in CO-induced insertion of the olefin into the Ta–H bond and formation of the respective tantalocene(carbonyl)alkyl complexes $Cp_2Ta(CO)R$ ($R = C_3H_7$, C_4H_9, C_5H_{11} and C_5H_9) [7]. In our studies, a reaction between complex II and carbon monoxide in toluene at 80°C for 12 h produced the carbonyl-ethyl complex $Cp_2Ta(CO)C_2H_5$ (I) in 56% yield. Complex I was obtained as air-sensitive blue-green crystals. The IR spectrum of I contained a terminal carbonyl stretching frequency at 1900 cm^{-1}. The mass spectrum of I exhibited a molecular ion at *m/e* 368. As in the case of the hydrido-ethylene complex II, the base peak corresponded to the fragment ion (Cp_2TaH^+).



(II) (I)

When complex I was photolyzed in toluene-d_8 solution in an NMR tube at −30°C, examination of the ^1H NMR spectrum of the reaction mixture indicated the presence of unreacted I as well as complexes II and III, in a molar ratio of approximately 2/2/1, respectively. The photo-degradation of I in pentane solution at −30°C was also investigated by IR techniques. While the carbonyl absorption for I at 1900 cm^{-1} decreased during the course of the photolysis, a new carbonyl band at 1890 cm^{-1} developed which is assignable to the hydrido-carbonyl complex $Cp_2Ta(CO)H$ (III) [8]. By means of sublimation of the reaction mixture, the dark purple hydrido-carbonyl complex III could be separated from the pale-yellow hydrido-ethylene complex II. Gas chromatographic analysis of gases evolved during the photolysis of complex I indicated the formation of both carbon monoxide and ethylene; neither ethane nor n-butane could be observed.

The photo-induced conversion of the carbonyl-ethyl complex I to form complexes II and III most likely proceeds via a mechanism similar to that which we have previously proposed for the photodegradations of $CpFe(CO)_2C_2H_5$ [9] and $CpW(CO)_3C_2H_5$ [2] (Scheme 1). The first step in the process involves photo-induced loss of carbon monoxide to generate the coordinatively unsaturated species $[Cp_2TaCH_2CH_3]$. β-Hydride elimination from this intermediate leads to II, a hydrido-ethylene complex of remarkably high thermal stability. As in the photolyses of $CpFe(CO)_2C_2H_5$ and $CpW(CO)_3C_2H_5$, substitution of the ethylene ligand in II by carbon monoxide in solution also occurs, leading in part to the hydrido-carbonyl complex III *. In addition to II and III, a very small amount of the trihydrido

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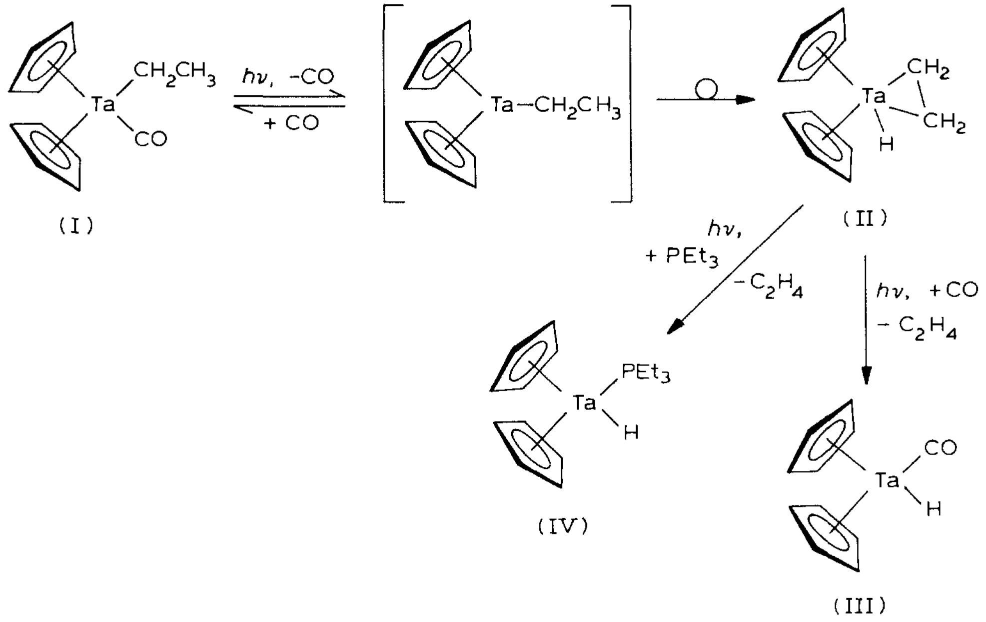
* In a separate experiment, photolysis of a toluene-d_8 solution of $Cp_2Ta(C_2H_4)H$ in the presence of carbon monoxide for ca. 30 min resulted in the formation of $Cp_2Ta(CO)H$, as identified by its ^1H NMR spectrum.



SCHEME 1

complex Cp_2TaH_3 was likewise detected from the photolysis of I. It was identified by means of its characteristic ^1H NMR spectrum [10]. In contrast to the photolysis of $CpFe(CO)_2C_2H_5$ and $CpW(CO)_3C_2H_5$, which generate both ethane and ethylene as evolved gases, photo-degradation of complex I under similar conditions led only to ethylene. Ethane formation has been proposed to result from reactions between the intermediate hydrido complexes $CpFe(CO)_2H$ and $CpW(CO)_3H$ with the ethyl derivatives $CpFe(CO)_2C_2H_5$ and $CpW(CO)_3C_2H_5$, respectively [2,9]. An analogous reaction to form ethane during the photolysis of $Cp_2Ta(CO)C_2H_5$ apparently does not occur, however.

NMR spectral results for $Cp_2Ta(C_2H_4)H$ (II)

^1H NMR spectrum

The 250 MHz ^1H NMR spectrum of $Cp_2Ta(C_2H_4)H$ (II) is presented in Fig. 1. We found by selective decoupling experiments that the doublet representing the cyclopentadienyl protons is derived from a ^3J-coupling of the protons of the two homotopic cyclopentadienyl rings with the terminal hydrido ligand (δ(Cp) 4.37, δ(Ta–H) -3.50 ppm, ^3J(H,H) 0.6 Hz). Upon selective decoupling, the multiplet due to the hydrido ligand is simplified to a triplet (^3J(H,H) 2.6 Hz). Simultaneously, the C_2H_4 protons can be identified as an AA′BB′ pattern, because the two sets of geminal protons are diastereotopic (δ 0.17 and 0.63 ppm) [11]. The ^3J(H,H) *cis*- and *trans*-coupling constants are 11 Hz. A similar NMR spectrum has been previously described for $Cp_2Nb(C_2H_4)H$ [12].

It is noteworthy that when a solution of complex II in toluene-d_8 was warmed to 120°C (slight overpressure), the resonance pattern for the C_2H_4 protons did not change; only slight line broadening could be observed at higher temperatures. We

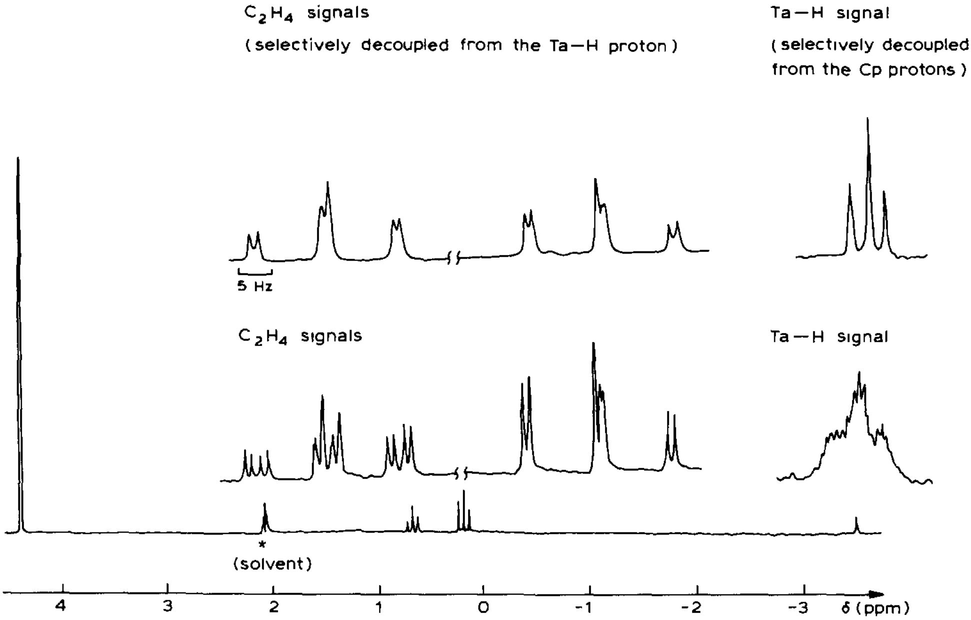


Fig. 1. 250 MHz ^{1}H NMR spectrum of the hydrido-ethylene complex $Cp_2Ta(C_2H_4)H$ (II) in toluene-d_8.

attribute this result to an extraordinarily high rotational barrier of the ethylene ligand about the metal–olefin axis ($\Delta G^{\neq} > 80$ kJ mol^{-1}) *. Such a finding is in striking contrast to the mobility of other C_2H_4 ligands in $CpMn(CO)_2(C_2H_4)$ [14], $CpFe(CO)(C_2H_4)CH_3$ [15], and $CpW(CO)_2(C_2H_4)H$ [2], in which the barrier to rotation ranges from 37 to 52 kJ mol^{-1}. These results suggest that there is an extremely high back donation from filled *d* orbitals of the metal to the π^* orbitals of the olefin carbon atoms, and are indicative of a formulation of complex II as a tantalacyclopropane derivative.

^{13}C NMR spectrum

The ^{13}C NMR spectrum of complex II in toluene-d_8 solution is summarized in Table 1. A single resonance for the cyclopentadienyl carbons and two resonances for the highly shielded carbons of the C_2H_4 ligand were observed for the temperature range from +20 to +90°C. This result is indicative of a configuration in which the ethylene C=C axis lies in the symmetry plane of the molecule (Fig. 2). Such a structure has previously been established crystallographically for the related ethylene complex $Cp_2Nb(C_2H_4)C_2H_5$ [12]. For other ethylene complexes including $CpW(CO)_2(C_2H_4)H$, however, low temperature ^{1}H NMR spectra suggest that the ethylene C=C axis is oriented preferably perpendicular to the symmetry plane of the molecule (Fig. 2) [2,14,15]. It is interesting that the isoelectronic cation $[Cp_2W(C_2H_4)H]^+$ [20] shows only a very small rotational barrier for the ethylene ligand compared to complex II. This difference may be attributable to the relatively

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* It is of interest that substituted alkyne ligands in $(MeCp)_2Ta(alkyne)I$ complexes also show high rotational barriers for the alkyne ligands [13].

TABLE 1

COMPARISON OF ^{13}C NMR DATA FOR $Cp_2Ta(C_2H_4)H$, $Cp_2Nb(C_2H_4)H$, $CpW(CO)_2(C_2H_4)H$, $CpFe(CO)(C_2H_4)CH_3$, CYCLOPROPANE AND ETHYLENE (δ in ppm, J in Hz)

Compound	δ(Cp)	J(C,H)	$\delta(H_2C{=})$	J(C,H)	$\delta({=}CH_2)$	J(C,H)
$Cp_2Ta(C_2H_4)H$ [a]	90.0	176	5.8	150	−1.1	155
$Cp_2Nb(C_2H_4)H$ [b,c]	91.1	176	13.4	153	8.0	156
Cyclopropane [d]					−3.5	161
Ethylene [e]			123.3	156	123.3	156
$CpW(CO)_2(C_2H_4)H$ [f,g]	90.6		21.1		21.1	
$CpFe(CO)(C_2H_4)CH_3$ [f,h]	86.1 86.1		43.3 [i] 48.3 [j]		43.3 [i] 37.2 [j]	

[a] In toluene-d_8. [b] In benzene-d_6. [c] Ref. 12. [d] Refs. 16, 17. [e] Refs. 18, 19. [f] In acetone-d_6. [g] Ref. 2. [h] Ref. 15. [i] Measured at −30°C. [j] Measured at −90°C.

lower electron density on the tungsten atom in $[Cp_2W(C_2H_4)H]^+$, a feature which would not allow strong back donation to the ethylene ligand as in the neutral complex II.

Experimental

All reactions and manipulations were conducted under a purified argon or nitrogen atmosphere using Schlenk techniques. Gases and solvents were purified as described previously [21]. Photolyses were conducted in Pyrex Schlenk tubes with a 450-W Hanovia photochemical lamp located in a quartz, water-cooled immersion well. The light source was placed 1–2 cm from the water-cooled tube to be irradiated. Cp_2TaCl_2 was prepared by a literature method [22]. IR spectra were obtained on either Perkin–Elmer 237-B or 297 infrared spectrophotometers. ^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q or a Bruker 250 MHz

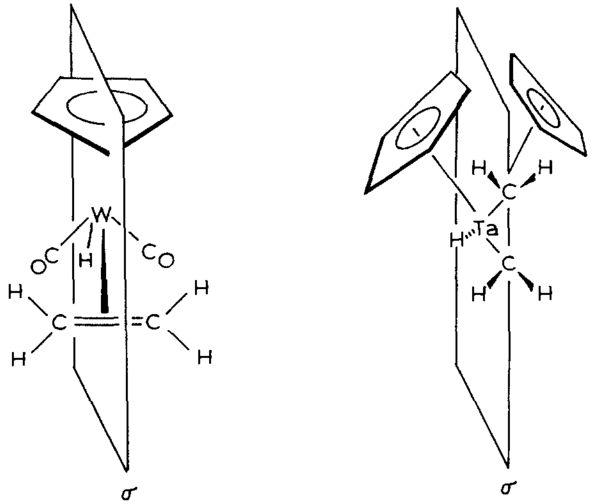

Fig. 2. Configurations of $Cp_2Ta(C_2H_4)H$ (II) and $CpW(CO)_2(C_2H_4)H$.

spectrometer. Mass spectra were determined on a Varian MAT CH7 mass spectrometer at 70 eV. Gas chromatographic analyses were performed on either Varian 2400 or Packard 427 gas chromatographs equipped with flame ionization and thermal conductivity detectors, respectively. Analyses were conducted on Porapac Q columns at ambient temperatures. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA.

Preparation of $Cp_2Ta(C_2H_4)H$ (II)

To a suspension of 3.30 g (8.64 mmol) of sublimed Cp_2TaCl_2 in 100 ml of dimethoxyethane was added dropwise 17.5 ml of 1.0 *M* C_2H_5MgBr in ethyl ether. The reaction mixture was subsequently stirred at reflux in an ethylene atmosphere for 20 h, during which time the color changed from green-black to yellow. While still hot, the reaction mixture was filtered through a Celite plug and the solvent removed from the filtrate under reduced pressure. From the air-sensitive residue, complex II was obtained via sublimation (100–110°C, 10^{-3} Torr) in the form of pale yellow crystals; 1.82 g (62%). MS *m/e* 340 (M^+), 312 ($M - C_2H_4{}^+$).

Preparation of $Cp_2Ta(CO)C_2H_5$ (I)

A solution of $Cp_2Ta(C_2H_4)H$ (340 mg, 1.0 mmol) in 10 ml of toluene was saturated with carbon monoxide. The solution was subsequently heated under carbon monoxide to 80°C for 12 h, during which time the color changed from yellow to green. The solvent was removed at reduced pressure, the residue was extracted with pentane, and the extracts filtered through a Celite plug. The filtrate was then cooled to -78°C to produce 206 mg (56%) of complex I as blue-green plates. (Found: C, 42.08; H, 4.34. $C_{13}H_{15}OTa$ calcd.: C, 42.40; H, 4.11%). IR (pentane) ν(CO) 1900 cm^{-1}; MS *m/e* 368 (M^+). ^1H NMR (toluene-d_8) δ 4.45 (s, 10H, Cp), 1.29 (vt, 3H, CH_3), 0.50 ppm (vq, 2H, CH_2, ^3J 7.4 Hz). ^{13}C NMR (toluene-d_8) δ 264.8 (CO), 89.1 (Cp), 23.3 (CH_3), -10.8 ppm (CH_2).

Chemical characterization of $Cp_2Ta(C_2H_4)H$ (II)

(a) Treatment with HCl. $Cp_2Ta(C_2H_4)H$ (100 mg) was dissolved in 5 ml of toluene and treated with 5 ml of HCl-saturated toluene. The solid which rapidly formed was identified by comparison of its ESR spectrum with that of an authentic sample. Gas chromatographic analysis of the gases evolved demonstrated the formation of ethane and only a trace of ethylene.

(b) Treatment with PEt_3. A concentrated solution of $Cp_2Ta(C_2H_4)H$ in benzene-d_6 was treated with an excess of PEt_3. The reaction mixture was photolyzed for 4.5 h, after which time the color had turned from yellow to red. A ^1H NMR spectrum indicated that the major product formed was $Cp_2Ta(PEt_3)H$ [6].

Photolysis of $Cp_2Ta(CO)C_2H_5$ (I) to form $Cp_2Ta(C_2H_4)H$ (II) and $Cp_2Ta(CO)H$ (III)

In a typical experiment, 0.70 g (1.9 mmol) of $Cp_2Ta(C_2H_4)H$ was dissolved in 120 ml of pentane and placed into a water-jacketed Pyrex Schlenk tube. Upon irradiation, ethylene was evolved and the solution turned yellow-green. After 5 h of photolysis, ^1H NMR analysis indicated the presence of unreacted I as well as $Cp_2Ta(C_2H_4)H$ and $Cp_2Ta(CO)H$ [1]; the molar ratio was approximately 2/2/1, respectively.

Acknowledgement

This research has been supported by a National Science Foundation – Deutschen Forschungsgemeinschaft International Cooperation Grant (NSF INT-8111979) to M.D.R. and H.G.A., in connection with the U.S.-Germany Cooperative Science Program, as well as by NSF and DFG research grants to M.D.R. and H.G.A., respectively. We gratefully acknowledge this support.

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