



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 688 (2003) 1–4

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

Short communication

Unusual behavior in the 308 nm flash photolysis of Vaska's complex

Richard H. Schultz*

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

Received 19 May 2003; received in revised form 21 August 2003; accepted 27 August 2003

Abstract

Time-resolved IR absorption spectroscopy was used to investigate the photolysis of Vaska's Complex (VC), *trans*-(PPh₃)₂Ir(CO)(Cl). Upon 308 nm photolysis, an intermediate was formed that regenerated VC on a millisecond timescale. This intermediate was not formed at the laser flash, but was generated over the course of ~ 10 μs. Most unusually, there was no evidence for prompt bleach of the C–O stretch of VC upon photolysis. Evidence was presented that the intermediate from which regeneration of VC occurred was a dimeric species. Possible pathways for the generation of the dimeric intermediate are discussed.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Vaska's complex; Photolysis; Infrared spectroscopy; kinetics

1. Introduction

Vaska's complex, *trans*-(PPh₃)₂Ir(CO)(Cl) [1], (VC) is the textbook example [2] of an organometallic complex that readily reacts via oxidative addition. While the thermal oxidative addition reactions of VC are well-known, considerably less attention has been paid to its photochemistry. Initial studies reported that UV irradiation of VC led to increased activity as a catalyst for alkene isomerization [3] and hydrogenation [4], presumably due to formation of coordinatively unsaturated species via ligand dissociation. Shortly thereafter, however, it was reported that 366 nm photolysis of VC does not lead to any net reaction [5]. The only experiments to appear in the literature to observe the short-lived species present following photolysis of VC were performed by Wink and Ford (WF) in the 1980's [6]. WF used a Xe flashlamp ($\lambda_{\text{irr}} > 295$ nm) to photolyze a solution of VC, and probed the subsequent behavior of the system by using time-resolved UV–vis absorption spectroscopy (TRUVVIS). They observed that within 20 μs of the photolysis, a new species appeared, the electronic spectrum of which returned to that of the parent over the course of several ms. From the observation that the rate of recovery of parent increases with increasing CO

pressure, WF concluded that photolysis produces a three-coordinate 'IrCl(PPh₃)₂' complex that reacts with dissolved CO to regenerate VC.

Several factors motivated the present reexamination of the 'fast' photochemistry of VC. First, the photolysis system in our laboratory has a response time < 100 ns, enabling us to observe reactions that might occur during the first 20 μs following photolysis. In addition, we use a laser rather than a flashlamp as our photolysis source. Since VC has four electronic absorption bands between 270 and 400 nm [7], the use of a monochromatic photolysis source can eliminate complications from the possibility that the photochemistry of VC might vary depending on which electronic transition is excited. For example, changing the photolysis wavelength appears to alter the intermediates formed by photolysis of *trans*-RhCl(PMe₃)₂(CO) both in solution [8,9] and in low-temperature glasses [10].

In the present experiment, time-resolved infrared spectroscopy (TRIR) rather than TRUVVIS is used to monitor the kinetics. The primary advantage of TRIR over TRUVVIS in the present case is its greater ability to tell whether or not a given intermediate contains a carbonyl ligand, which can be useful for structure determination. In typical fast kinetics experiments, the parent complex is a homoleptic carbonyl, so there cannot be any question of which ligand has dissociated. In the case of a compound such as VC, photolysis could

* Tel.: +972-3-531-8065; fax: +972-3-535-1250.

E-mail address: schultr@mail.biu.ac.il (R.H. Schultz).

in principle remove either the CO ligand or one of the PPh₃ ligands—or none of them.

2. Experimental

The TRIR apparatus used in these experiments has been described in detail elsewhere [11]. Reaction takes place in a CaF₂ cell (0.5–1.0 mm pathlength), where it is initiated by the pulsed output (ca. 20 ns) of a XeCl excimer laser (308 nm, typically 110–150 mJ/pulse, repetition rate 3–6 Hz). The experiments discussed in this report were performed at room temperature (ca. 20 °C) under an Ar atmosphere. Time-dependent IR spectra following the photolysis are obtained by using a Bruker Equinox 55 S²FTIR spectrometer, typically at 200 ns time resolution; additional TRIR information is obtained by measuring the time dependence of the absorption of the output of a CW diode laser tuned to 1966 cm⁻¹. Because of the expense of the C₆D₆ solvent, and because VC is regenerated following photolysis, the solution is recirculated through the system.

VC was obtained from Pressure Chemicals Inc. and used without further purification except for overnight heating at ~110 °C in a vacuum oven to drive off any complexed O₂. Prior to each experiment, the IR spectrum of the complex was checked to make sure that the O₂ adduct, which has a distinctive C–O stretch at $\nu_{\text{CO}} \approx 2000 \text{ cm}^{-1}$ [12], was absent. C₆D₆ was obtained from Cambridge Isotopes Laboratories, and distilled from Na and degassed with Ar prior to use.

3. Results and discussion

Fig. 1 shows results for photolysis of C₆D₆ solutions of VC. Following the laser flash, a new C–O stretch at $\nu_{\text{CO}} = 1924 \text{ cm}^{-1}$ grows in over the course of ~10 μs , Fig. 1a. On a timescale of several ms, we observe regeneration of VC, Fig. 1b, consistent with the results of WF [13]. Kinetic measurements made at several VC concentrations over the range of $1.1\text{--}4.3 \times 10^{-3} \text{ mol l}^{-1}$ revealed a linear [VC] dependence for the rate of formation of the intermediate that absorbs at 1924 cm⁻¹. Preliminary measurements imply a second-order rate constant for its formation of $\sim 6 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, of similar magnitude to those determined by WF for reaction of CO and PPh₃ with the intermediate formed in their experiment, $(2.7 \pm 0.7) \times 10^8$ and $(1.3 \pm 0.4) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively. Attempts to determine whether or not the rate of formation of the intermediate that absorbs 1924 cm⁻¹ depends on [CO] were unsuccessful because VC reacts thermally with CO to form IrCl(PPh₃)₂(CO)₂, photolysis of which regenerates VC.

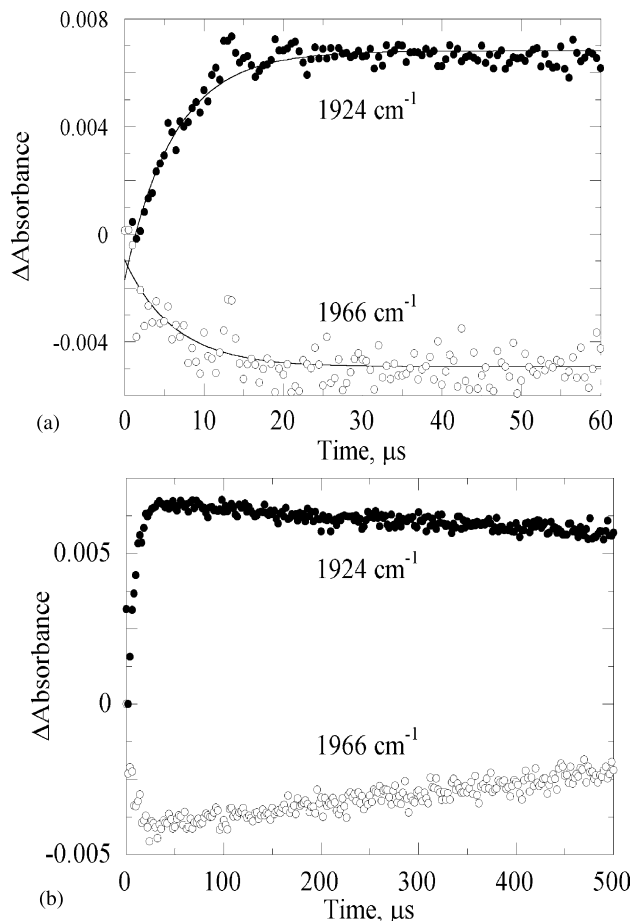


Fig. 1. Time-dependent changes in the absorbance at 1966 cm⁻¹ (open circles) and 1924 cm⁻¹ (closed circles) of C₆D₆ solutions of Vaska's complex. Part a shows the absorbance changes of a 3.8 mmol l⁻¹ solution during the first 60 μs following photolysis; the solid lines are single-exponential fits to the data with $k_{\text{obs}} = 1.6 \times 10^5 \text{ s}^{-1}$. Part b shows the absorbance changes of a 2.3 mmol l⁻¹ solution during the first 0.5 ms following photolysis.

A bleach of the parent absorbance at $\nu_{\text{CO}} = 1966 \text{ cm}^{-1}$ occurs with a single exponential time dependence that is the same to within experimental error of that of the growth of the intermediate. This result is most unexpected, since in flash photolysis experiments involving transition metal carbonyl compounds, photolysis typically leads to the formation of an intermediate (e.g. via carbonyl loss and solvation of the resulting coordinatively unsaturated fragment) on the timescale of tens of ps [14]. In the present experiment, no evidence was found for a 'rapid' bleach of the parent C–O stretch or for the presence of any other species with an IR absorption between 1820 cm⁻¹ and 2200 cm⁻¹.

Although some ambiguities remain in the details of the mechanism of the reaction, we can reach some definite conclusions based on the present results (Fig. 1). Any mechanism for the reaction observed here must account for the following observations: (1) the rate of formation of the absorption at 1924 cm⁻¹ depends on

[VC]; (2) the rate of the formation of the intermediate is identical to that of disappearance of the absorption corresponding to VC; (3) the intermediate from which VC is regenerated contains a CO ligand; and (4) the parent absorption at 1966 cm^{-1} does not show any kind of ‘instantaneous’ bleach at the flash.

The most likely explanation for the first three observations is that the intermediate from which VC is regenerated is a dimer, $\text{Ir}_2(\text{PPh}_3)_m\text{Cl}_2(\text{CO})_n$. The presence of a single CO stretch implies that $n = 1$, but the possibilities of bridging CO ligands with lower than usual ν_{CO} , or of a symmetrical dimer with a particularly weak symmetric CO stretch, are not excluded.

What is more difficult to explain is the observation that the absorbance at 1966 cm^{-1} does not decrease immediately upon photolysis. We can imagine several plausible pathways to a dimeric intermediate. The most intuitive ones are those in which photolysis causes prompt loss of a ligand (CO or PPh_3) to form a formally three-coordinate intermediate that reacts with unphotolyzed VC to form a dimer. Such pathways are difficult to reconcile with the experimental results shown in Fig. 1. While ‘ $\text{IrCl}(\text{PPh}_3)_2$ ’ would be invisible in our experiment, if it were formed promptly, its presence would be revealed by a decrease *at the laser flash* of the absorbance at 1966 cm^{-1} equal to half of the total bleach. The exponential decrease in the absorbance at 1966 cm^{-1} appears to begin from the initial baseline without any prompt absorbance changes, however. This result implies that the laser flash does not cause prompt ligand loss. Similar considerations appear to rule out elimination of PPh_3 to yield ‘ $\text{IrCl}(\text{PPh}_3)(\text{CO})$ ’ as well. Not only is there no prompt decrease of absorption at 1966 cm^{-1} , but there is no evidence for $\text{IrCl}(\text{PPh}_3)(\text{CO})$, which should be observable in our experiment and whose rate of formation should be independent of the original concentration of VC. Nor do we see any evidence for a second C–O stretching absorption expected from an $\text{Ir}_2\text{Cl}_2(\text{PPh}_3)_3(\text{CO})_2$ intermediate. Furthermore, an intermediate formed by loss of phosphine would not be expected to regenerate VC upon reaction with CO as was observed by WF. Neither does it seem likely that the intermediate absorbing at 1924 cm^{-1} is an unstable oxidative addition product of orthometallation or solvent C–D bond activation, since such an intermediate would be expected to have a ν_{CO} at a *higher* frequency than that of VC. Our results do not exclude the possibility that WF did observe a three-coordinate intermediate; their broadband photolysis included excitation of electronic bands that have been attributed to MLCT transitions [7], which can plausibly be expected to lead to loss of a ligand.

Thus, the lack of a prompt decrease in the absorbance at 1966 cm^{-1} seems to indicate that the dimeric intermediate from which VC is regenerated is itself formed from a species that has not yet lost any ligands.

It is true that upon excitation of MLCT states in transition metal carbonyls, which are the ones typically involved in UV photolysis experiments, ν_{CO} are normally shifted significantly ($10\text{--}90\text{ cm}^{-1}$) from their frequencies in the ground state because formal oxidation of the metal atom lessens its back donation ability [15,16]. Other transitions need not affect ν_{CO} significantly, however. For example, the dppz ligand-based $\pi\pi^*$ transition in *fac*- $[\text{Re}(\text{dppz})(\text{CO})_3(\text{PPh}_3)]^+$ (dppz = dipyrrodo[3,2-*a*:2',2'-*c*]phenazine) hardly shifts ν_{CO} from those found in the ground state [17]. In the case of VC, bands in the electronic spectrum of VC at $\lambda = 339, 387,$ and 439 nm have been assigned to MLCT transitions [7], but to our knowledge, the origin of the electronic absorption by VC at $\sim 300\text{ nm}$ has not been identified. If this band, into which 308 nm irradiation excites VC, is not an MLCT transition, but rather a ligand-based or perhaps an Ir d–p transition, then its excitation would not be expected to affect ν_{CO} very much. Furthermore, the failure to observe ligand dissociation following the photolysis is also consistent with this electronic absorption not being an MLCT transition. Another possibility is that this absorption is to a relatively long-lived excited triplet state of VC [18]. Excited triplet states of the coordinatively unsaturated complexes $\text{CpCo}(\text{CO})$ [19] and $\text{Fe}(\text{CO})_4$ [20] do not appear to solvate, and the IR spectrum of solvated singlet $\text{Fe}(\text{CO})_4$ has C–O stretches that are coincident or near-coincident with those of the unsolvated triplet [20].

While we cannot yet definitively identify the precise nature of the electronic state involved, it seems that the most reasonable explanation for the present results is that 308 nm photolysis of VC leads to formation of an electronically excited state with ν_{CO} similar to that of the ground state. This excited complex then reacts with an unphotolyzed molecule of VC, losing CO to form a dimeric species, presumably $\text{Ir}_2\text{Cl}_2(\text{PPh}_3)_4(\text{CO})$. It is this dimer, and not a formally tricoordinate species formed upon ligand dissociation, that reacts with CO to regenerate VC. These results are to our knowledge the first example of solution photochemistry of a transition metal carbonyl complex in which the parent bleach occurs on a timescale of microseconds.

Acknowledgements

This work was funded by the Israel Science Foundation, founded by the Israel Academy of Arts and Sciences, and by the Bar-Ilan University Research Authority. The author would like to thank Eli Perel of the Bar-Ilan University Electronics Shop for technical assistance, and all-around nice guy Dave Wink for useful discussions.

References

- [1] (a) L. Vaska, J.W. Diluzio, *J. Am. Chem. Soc.* 84 (1962) 679;
(b) L. Vaska, *Acc. Chem. Res.* 1 (1968) 335.
- [2] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, Ch. 5, 2d ed., University Science Books, Mill Valley, CA, 1987;
(b) R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Ch. 6, 3d ed., Wiley, New York, 2001.
- [3] W. Strohmeier, *J. Organomet. Chem.* 60 (1973) C60.
- [4] W. Strohmeier, G. Csontos, *J. Organomet. Chem.* 72 (1974) 277.
- [5] G.L. Geoffroy, G.S. Hammond, H.B. Gray, *J. Am. Chem. Soc.* 97 (1975) 3933.
- [6] (a) D.A. Wink, P.C. Ford, *J. Am. Chem. Soc.* 105 (1985) 1974;
(b) D.A. Wink, P.C. Ford, *J. Am. Chem. Soc.* 105 (1985) 5566;
(c) D.A. Wink, P.C. Ford, *J. Am. Chem. Soc.* 109 (1987) 436.
- [7] (a) R. Brady, B.R. Flynn, G.L. Geoffroy, H.B. Gray, J. Peone, Jr, L. Vaska, *Inorg. Chem.* 15 (1976) 1485;
(b) G.L. Geoffroy, H. Isci, J. Litrenti, W.R. Mason, *Inorg. Chem.* 16 (1977) 1950.
- [8] R. Krishnan, R.H. Schultz, in preparation.
- [9] (a) J.S. Bridgewater, B. Lee, S. Bernhard, J.R. Schoonover, P.C. Ford, *Organometallics* 16 (1997) 5592;
(b) J.S. Bridgewater, T.L. Netzel, J.R. Schoonover, S.M. Massick, P.C. Ford, *Inorg. Chem.* 40 (2001) 1466.
- [10] T.E. Bitterwolf, W.B. Scallorn, J.T. Bays, C.A. Weiss, J.C. Linehan, J. Franz, R. Poli, *J. Organomet. Chem.* 652 (2002) 95.
- [11] R. Paur-Afshari, J. Lin, R.H. Schultz, *Organometallics* 19 (2000) 1682.
- [12] J.P. Collman, C.T. Sears, Jr, M. Kubota, *Inorg. Synth.* 28 (1990) 92.
- [13] We have found that because of the AC time constant of our system, our S²FTIR spectrometer cannot measure accurately the time dependence of any process occurring on a ms time scale.
- [14] (a) J.A. Welch, K.S. Peters, V. Vaida, *J. Phys. Chem.* 86 (1982) 1941;
(b) J. Simon, K.S. Peters, *Chem. Phys. Lett.* 98 (1983) 53;
(c) L. Wang, X. Zhu, K.G. Spears, *J. Am. Chem. Soc.* 110 (1988) 8695;
(d) M. Lee, C.B. Harris, *J. Am. Chem. Soc.* 111 (1989) 8963;
(e) X. Xie, J.D. Simon, *J. Phys. Chem.* 93 (1989) 4401;
(f) A.G. Joly, K.A. Nelson, *Chem. Phys.* 152 (1991) 69.
- [15] (a) F.P.A. Johnson, J.J. Turner, M.W. George, *Inorg. Chem.* 32 (1993) 4226;
(b) J.J. Turner, M.W. George, F.P.A. Johnson, J.R. Westwell, *Coord. Chem. Rev.* 125 (1993) 101;
(c) P. Chen, K.M. Omberg, D.A. Kavaliunas, J.A. Treadway, R.A. Palmer, T.J. Meyer, *Inorg. Chem.* 36 (1997) 954;
(d) P. Chen, R.A. Palmer, T.J. Meyer, *J. Phys. Chem. A* 102 (1998) 3042.
- [16] While formation of a five-coordinate solvate complex is not ruled out by the present experimental results, it is difficult to explain why such a species should only form over a period of μ s rather than ps unless it is produced via a long-lived excited electronic state. Such a species might also be expected to have a significantly different ν_{CO} from that of VC.
- [17] J.R. Schoonover, G.F. Strouse, R.B. Dyer, W.D. Bates, P. Chen, T.J. Meyer, *Inorg. Chem.* 35 (1996) 273.
- [18] While the large molar absorptivity of this transition ($\epsilon > 5000 \text{ l mol}^{-1} \text{ cm}^{-1}$) may mitigate against its being to a triplet excited state, significant effects of spin-orbit coupling have been observed in the spectra of square-planer Ir complexes [7].
- [19] A.A. Bengali, R.G. Bergman, C.B. Moore, *J. Am. Chem. Soc.* 117 (1995) 3879.
- [20] M. Poliakoff, J.J. Turner, *Angew. Chem. Int. Ed. Engl.* 40 (2001) 2809 (and references therein).