very similar to the superposition of the intermediate structure and its mirror image.

The cleavage of the Co–C bond in the mce complexes is considered to be easier than that in the cyanoethyl complexes, since the rate of the racemization of the mce group by visible light is faster than that of the cyanoethyl complexes in an aqueous methanol solution.[19] This suggests that the (methoxycarbonyl)ethyl radical would be formed in the present crystal by X-ray exposure at 293 K, but the rotation of the radical is prohibited. The crystal structure clearly distinguishes the difference between the rotation of the mce radical, as a whole, and that of the methoxycarbonyl group around the Co–C or C–C bond. Further study to clarify the details of this reaction is in progress.

Acknowledgment. We are grateful to Dr. N. Hirayama and Dr. K. Shirahata for measurement of NMR spectra and valuable discussion. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 56430005).

Registry No. *R*-mce-py·CH_3OH, 91328-25-5; *R*-mce-py, 80514-20-1; mce-py, 37824-56-9.

Supplementary Material Available: A table of the final atomic coordinates for non-H atoms of the initial stage at 293 K, a list of bond distances at the initial stage at 293 K and at the intermediate stage, and tables of the observed and calculated structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms at the initial stage at 223 and 293 K and at intermediate stage (57 pages). Ordering information is given on any current masthead page.

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[19] Ohgo, Y.; Baba, S.; Ohtera, C.; Wada, H.; Takeuchi, S.; Hirata, H. "Abstracts of Papers", Joint Meeting of CSJ and SPSJ, Niigata, Japan, 1981; p 41.

Communications to the Editor

Electrochemistry of Porphyrins Containing a Metal–Metal σ Bond. Reduction of (TPP)In(M(CO)$_3$Cp) Complexes where M = Mo and W

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Received May 3, 1984

The synthesis and characterization of a promising new class of porphyrin complexes with a bi- or trinuclear framework has recently been reported.[2-4] These compounds are of the form (P)M(M′L) where (P)M is a metalloporphyrin and M′L is an axial ligand of the type M(CO)$_X$(η^5-C_5H_5)$_Y$. No electrochemical data have ever been reported for metalloporphyrins containing a metal–metal bond but it was expected that the porphyrin ring would be able to stabilize the singly and possibly doubly reduced metal–metal bonded system. This, indeed, is the case as we wish to report in this communication.

We have selected two complexes for our initial electrochemical investigation. These are (TPP)In(Mo(CO)$_3$Cp) and (TPP)In(W(CO)$_3$Cp) where Cp = η^5-C_5H_5. For comparison, we have also included the electrochemistry of (TPP)InClO$_4$. The electrochemistry of this compound has never been reported.

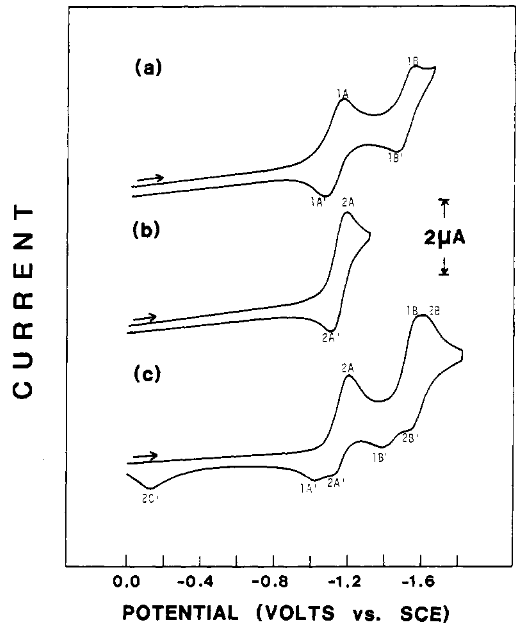

Figure 1. Cyclic voltammograms illustrating (a) two successive reductions of 1.2 × 10^{-3} M (TPP)InClO$_4$, (b) first reduction of 1.1 × 10^{-3} M (TPP)In(Mo(CO)$_3$Cp), and (c) two successive reductions of 1.1 × 10^{-3} M (TPP)In(Mo(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP. Scan rate = 100 mV/s. The numerical part of the peak notation indicates the investigated compound (**1**, **2**, or **3**) while A, B and A′,B′ indicate the first and second reduction and reoxidation peaks, respectively.

Table I. Half-Wave Potentials for Reduction of (TPP)InClO$_4$, (TPP)In(Mo(CO)$_3$Cp), and (TPP)In(W(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP

	$E_{1/2}$, V vs. SCE	
compd	1st redn	2nd redn
(TPP)InClO$_4$ (**1**)	−1.10	−1.48
(TPP)In(Mo(CO)$_3$Cp) (**2**)	−1.15	−1.54[a]
(TPP)In(W(CO)$_3$Cp) (**3**)	−1.21	−1.57[a]

[a] Potential quoted is at −74 °C.

(TPP)InClO$_4$ (**1**) was synthesized from (TPP)InCl[5] by metathesis of the axial ligand using a stoichiometric amount of AgClO$_4$ in boiling tetrahydrofuran. The obtained product showed characteristic IR stretching frequencies for a bound perchlorate group[6] at 1140, 1100, 1020, 890, and 625 cm^{-1}. (TPP)In(M(CO)$_3$Cp), where M = Mo, **2**, or M = W, **3**, was prepared by reaction of (TPP)InCl with the [M(CO)$_3$Cp]$^-$ anion according

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[1] (a) University of Houston. (b) Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au CNRS (LA 33). (c) On leave from the Ecole Supérieure de Chimie Industrielle de Lyon, France.

[2] Cocolios, P.; Moise, C.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C43.

[3] Onaka, S.; Konda, Y.; Toruimi, K.; Ito, T. *Chem. Lett.* **1980**, 1605.

[4] Barbe, J. M.; Guilard, R.; Lecomte, C.; Gerardin, R., *Polyhedron*, in press.

[5] Bhatti, M.; Bhatti, W.; Mast, E. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 133.

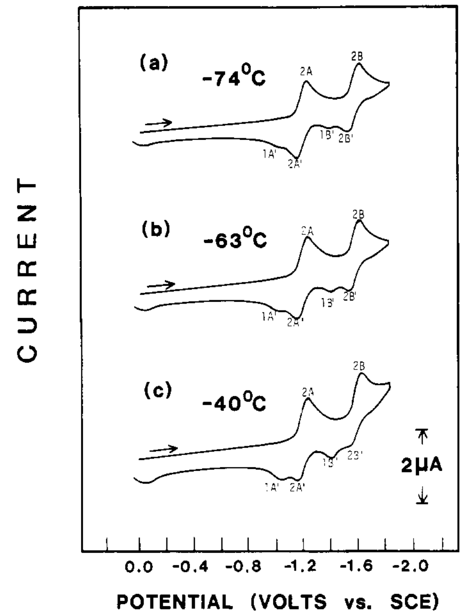

Figure 2. Temperature-resolved cyclic voltammograms of 0.9 × 10^{-3} M (TPP)In(Mo(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP. Scan rate = 100 mV/s. Temperature: (a) −74, (b) −63, and (c) −40 °C.

to a previous reported procedure.[2] Characterization was achieved by IR (ν_{CO} 1985, 1910, 1880 cm^{-1} for **2** and ν_{CO} 1990, 1900, 1870 cm^{-1} for **3**), ^{1}H NMR (δ_{Cp} 2.88 for **2**, 2.95 for **3**), and UV-vis spectra (398, 456 (Soret), 522, 586, 633 nm for **2**, and 368, 455 (Soret), 523, 589, 635 nm for **3**). All electrochemical measurements were carried out in methylene chloride (CH_2Cl_2) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte.

As shown in Figure 1a and Table I, the electrochemical reduction of **1** proceeds in two reversible steps (at $E_{1/2} = -1.10$ and −1.48 V vs. SCE) to yield the anion radical and dianion. The metal–metal σ-bonded (TPP)In(M(CO)$_3$Cp) derivatives also exhibit two one-electron reductions on the cyclic voltammetry time scale. The initially generated anion is extremely stable for the case of **3**, while for the case of **2** the stability extends only to the cyclic voltammetric time scale. This is illustrated in Figure 1b. The generated anion (at $E_{1/2} = -1.15$ V) and further reduced dianion (at $E_{1/2} = -1.54$ V) partially dissociate, giving rise to a mixture of [(TPP)In]$^{-1}$, [(TPP)In(Mo(CO)$_3$Cp)]$^{2-}$, and [Mo(CO)$_3$Cp]$^-$. Peaks **1**B, **1**B′, and **1**A′ in Figure 1c are at identical potentials with peaks present for the uncomplicated reduction and reoxidation of (TPP)InClO$_4$ (Figure 1a). Furthermore, cleavage of the metal–metal bond leads to an oxidation peak at −0.10 V (peak 2C′, Figure 1c). This peak has been assigned as the oxidation of the electrogenerated [M(CO)$_3$Cp]$^-$ to give the corresponding [M(CO)$_3$Cp]· radical.[7] The one-electron reduction product is much more stable for the case of (TPP)In(W(CO)$_3$Cp), and cleavage of the indium–tungsten bond occurs only after addition of a second electron.

Attempts were made to stabilize the reduced metal–metal bonded species by lowering the temperature. This is illustrated in Figure 2a–c for complex **2**. At −74 °C only a small amount of decomposition occurs after reduction by two electrons. The obtained voltammogram does not show any reduction wave attributable to (TPP)InClO$_4$. On the other hand, very weak peaks are observed for the reoxidation of [(TPP)In]$^-$ (peaks **1**B′ and **1**A′). The better stabilization of the indium–tungsten complex compared to its indium–molybdenum analogue is also confirmed by the two diffusion-controlled waves ($E_{pa} - E_{pc} = 60 \pm 5$ mV) at −1.21 and −1.57 V for complex **3** at −50 °C.

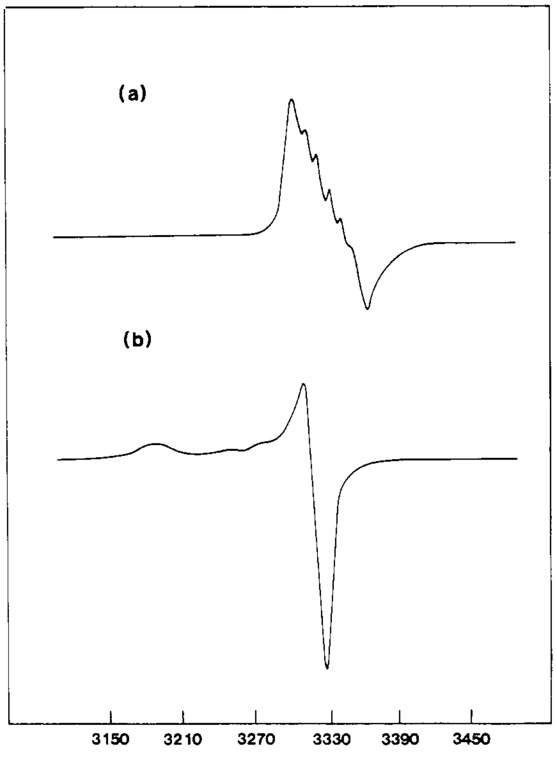

Figure 3. Frozen ESR spectra recorded after exhaustive bulk electrolysis at −1.30 V of solutions containing (a) 1.0 × 10^{-3} M (TPP)InClO$_4$ and (b) 1.0 × 10^{-3} M (TPP)In(W(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP.

ESR spectra were recorded after bulk electrolysis of the three investigated compounds at −1.30 V. The one-electron reduction of (TPP)InClO$_4$ produced the spectrum shown in Figure 3a. This spectrum, centered at $g = 1.999$, suggests a ring-centered reaction involving a weak interaction with the orbitals of the indium atom.[9-12] An identical spectrum was obtained when (TPP)In(Mo(CO)$_3$Cp) was reduced indicating cleavage of the Mo(CO)$_3$Cp unit and reduction of [(TPP)In]$^+$. In contrast, the electrogenerated [(TPP)In(W(CO)$_3$Cp)]$^-$· species was quite stable and gave rise to the ESR spectrum shown in Figure 3b. The shape and *g* values of this spectrum ($g_\parallel = 2.090$, $g_\perp = 2.006$) suggest reduction at the W(CO)$_3$Cp ligand leading to a species with axial symmetry. If this is the case. the electron addition would most likely occur at the tungsten atom, producing W(−I) which would have a d^7 electron configuration. Finally, at longer electrolysis times the metal-metal bond was cleaved and an identical spectrum to that outlined in Figure 3a for reduced (TPP)InClO$_4$ was observed.

The oxidation state assignment of the neutral or the reduced metal–metal σ-bonded complexes is not clear-cut. One may consider the neutral complexes as consisting of formal (P)In^{III}(M^0(CO)$_3$Cp) units. In this way M(CO)$_3$Cp can be considered as an axial ligand bound to the In(III) porphyrin by means of an ionic bond. On the other hand, spectral data[2] indicate that substantial charge is transferred from the Mo or the W atom to the In(III) center so that an alternative formulation would be (P)In^I(M^{II}(CO)$_3$Cp). This formulation is in good agreement with

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[6] (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 242. (b) Buisson, G.; Deronzier, A.; Duée, E.; Gans, P.; Marchon, J. C.; Regnard, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6793.

[7] Reduction of [M(CO)$_3$Cp]$_2$ gives rise to [M(CO)$_3$Cp]$^-$ via a two-electron reduction and a rapid cleavage of the dimer.[8] This anionic product may then be reoxidized (at −0.10 V) to yield [M(CO)$_3$Cp]·, which rapidly couples to reform the dimer.

[8] (a) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117. (b) Giraudeau, A.; Lemoine, P.; Gross, M.; Braunstein, P. *J. Organomet. Chem.* **1980**, *202*, 455.

[9] Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.

[10] Halpern, J.; Topich, J.; Zamarev, K. I. *Inorg. Chim. Acta* **1976**, *20*, L21.

[11] Yamamoto, K.; Kohno, M.; Ohya-Nishiguchi, H. *Chem. Lett.* **1981**, 255.

[12] Mengersen, Chr.; Subramanian, J.; Fuhrhop, J.-H.; Smith, K. M. *Z. Naturforsch., A* **1974**, *29A*, 1827.

the theoretical calculations of the electronic absorption spectra for group 3A metalloporphyrins.[13] In addition, this formulation is consistent with the ESR data of **3** which indicate that the initial reduction site occurs at the ligand and specifically at the tungsten atom. This formulation is also consistent with a shift of the potential for π radical formation to more negative values and would also suggest the formation of a transient $[(P)In^{I}(M^{0}(CO)_3Cp)]^{2-}$ species after the second reduction and before cleavage of the metal-metal bond. Unfortunately, this dianion has not been isolated but is postulated to be a transient species by cyclic voltammetry.

Acknowledgment. The support of the National Science Foundation (Grant CHE 8215507) is gratefully acknowledged. We also thank Jean-Luc Cornillon for help in obtaining the ESR spectra of reduced $(TPP)InClO_4$.

Registry No. 1, 91312-86-6; **2**, 91312-84-4; **3**, 91312-85-5.

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[13] Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter I, and references therein.

Steric Compression Control of Photochemical Reactions in the Solid State

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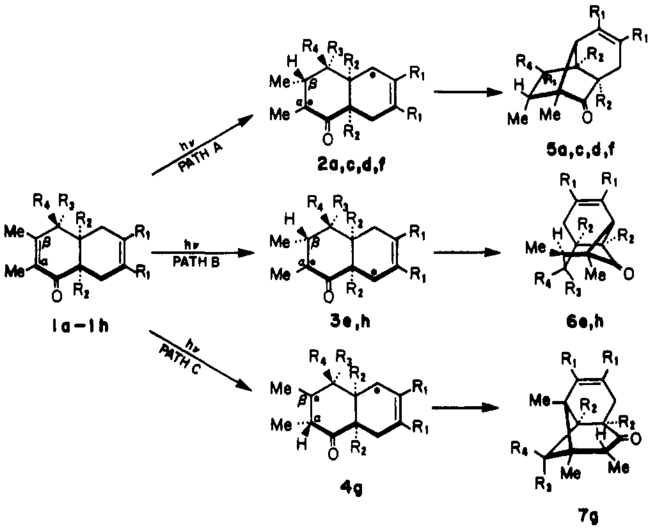
Received May 9, 1984

There is considerable current interest concerning the question of what factors govern the α vs. β regioselectivity of hydrogen atom abstraction by the carbon-carbon double bonds of photoexcited α,β-unsaturated ketones.[1] Recent work from our laboratory[2] has shown that enones of general structure **1**, when irradiated in the crystalline phase, undergo one of two possible photorearrangements (path A or path B, Scheme I), both of which are initiated by intramolecular allylic hydrogen atom transfer to the β-carbon atom of the enone moiety.[3] In one instance, however, that of enone **1g**, irradiation in the solid state led exclusively to the product resulting from initial hydrogen atom abstraction by the α-carbon atom of the enone chromophore (path C).[4]

In this communication we demonstrate with the aid of X-ray crystallography that in all likelihood, this change in reactivity is caused by specific crystal lattice packing effects near the reaction site that are unique to enone **1g**. We suggest the term "steric compression control" for this effect and show that it can also be applied to bimolecular reactions (e.g., [2 + 2] photocycloadditions) in the solid state.

One possible explanation for the anomalous behavior of compound **1g** is that the allylic hydrogen atom being abstracted in this case is much closer to the enone α-carbon atom than to the β-carbon. That this is not so is evident from the carbon-hydrogen distances summarized in Table I. These values, which are taken from the X-ray work,[5] show no trend between ground-state abstraction distance and preferred reactivity.

Scheme I. Reactants and Products in Solid-State Photorearrangements[a]



[a] Refer to Table I for list of substituents.

A second possible explanation is that the acetate group (R_4) of enone **1g** favors the formation of biradical **4** (path C) through interaction with the radical center produced on the adjacent β-carbon atom.[6] This is rendered unlikely by the observation that enone **1h** (R_3 = OAc) as well as enone **1i** ($R_1 = CH_3$, $R_2 = R_3$ = H, and R_4 = OAc)[7] behave normally, i.e., react via initial β-carbon abstraction, when photolyzed in the solid state. Using similar logic, other explanations that utilize the difference between acetate and hydroxyl (e.g., hydrogen bonding capability) can be discounted.

A clue to the explanation we favor came from an inspection of the crystal packing diagrams for enones **1a**–**1h**. It appeared that the change in hybridization of C_α or C_β from sp^2 to sp^3, which necessarily accompanies hydrogen transfer to these atoms, would force the methyl groups at these centers into close contacts with certain hydrogen atoms on neighboring molecules and thus sterically impede the reaction. The only exceptions to this were the C_α methyl group of compound **1g** and the C_β methyl group of enone **1d** whose pyramidalizations appeared to be totally unimpeded. This formed the basis of our working hypothesis, namely, that *it is the void space surrounding the methyl group at the α-carbon atom of enone **1g** that allows reaction and pyramidalization at this center in contrast to the steric compression which would attend reaction and pyramidalization at the β-carbon atom.*

This hypothesis was tested by simulating pyramidalization at C_α and C_β by computer and determining the new intermolecular hydrogen-hydrogen contacts which develop. With the X-ray crystal structure derived coordinates of enones **1a**–**1h** as a starting point, the methyl groups attached to C_α and C_β were rotated downward by intervals of 11°, 22°, 33°, 44°, and 55° (fully pyramidalized) keeping all other coordinates unchanged (Figure 1). The results supported the hypothesis: Pyramidalization at

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[1] (a) Byrne, B.; Wilson, C. A., II; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1550-1560. (b) Schuster, D. I. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 199-204. (c) Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928-2929.

[2] Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354-5363.

[3] Preferential hydrogen abstraction by the β-carbon atom of α,β-unsaturated ketones is normally observed in solution as well.[1] For enones **1a**–**h**, however, irradiation in solution leads exclusively to intramolecular [2 + 2] photocycloaddition.[2] The reasons for these solution-phase/solid-state reactivity differences have been discussed.[2]

[4] The photochemistry of enones **1g** and **1h** has not been reported previously. The synthesis of these compounds as well as the characterization of their solid-state photoproducts **7g** and **6h**, respectively, will be detailed in a subsequent full paper. All four compounds gave satisfactory elemental analyses and exhibited spectra completely in accord with their assigned structures.

[5] Compounds **1a** and **1b**: Greenhough, T. J.; Trotter, J. *Acta Crystallogr. Sect. B*, **1980**, *B36*, 1831-1835. Compound **1c**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *B38*, 2190-2196. Compound **1d**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *B36*, 2843-2846. Compound **1e**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *B36*, 1835-1839. Compound **1f**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *B38*, 1233-1237. Compounds **1g** and **1h**: Ariel, S.; Trotter, J. *Ibid.*, submitted for publication.

[6] For a discussion of the interaction of acyloxy groups with adjacent radical centers (1,3-dioxolan-2-yl radical formation), see: Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 242-244. See also: Barclay, L. R. C.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 1793-1796.

[7] The crystal structure of enone **1i** has not been determined. Photolysis of **1i** in the solid state gives **5i**. Scheffer, J. R.; Walsh, L., unpublished results.

0002-7863/84/1506-5726$01.50/0