h TMEDA (2 mL) was distilled into the reaction flask. All but ~3 mL of THF was removed under vacuum, and 30 mL of diethyl ether was distilled into the reaction flask. The solution was filtered, and the solvent was removed by vacuum distillation. The solid product (red-orange) was washed with 40 mL of hexane, and solvent was removed under vacuum, giving a 91% yield of 2·2TMEDA. Slow evaporation of a Et_2O solution of 2·2TMEDA yielded crystals suitable for X-ray diffraction. ^1H NMR (200 MHz, C_6D_6): δ 0.90 (s, 8 H, CH_2 TMEDA), 1.10 (s, 24 H, CH_3 TMEDA), 7.30–7.33 (m, 6 H), 7.55 (dd, J_1 = 3.3 Hz, J_2 = 6 Hz, 2 H), 8.05–8.11 (m, 2 H), 8.69 (dd, J_1 = 3.3 Hz, J_2 = 6 Hz, 2 H), 9.40–9.46 (m, 2 H). IR: ν(C=C) 1611 cm^{-1}.

3. To a toluene (20 mL) solution of 2·2TMEDA (0.1 g) under argon was added 1 mL of degassed CH_3OH via syringe. The color changed from red to yellow-brown. Crystallization from toluene gave crystals suitable for X-ray diffraction. ^1H NMR (200 MHz, $CDCl_3$): δ 4.22 (s, 4 H), 7.26–7.54 (m, 6 H), 7.68 (d, J = 7.3 Hz, 2 H), 8.03 (dd, J_1 = 3.3 Hz, J_2 = 4.8 Hz, 2 H), 8.52 (d, J = 7.3 Hz, 2 H).

Acknowledgment. This research has been supported by the National Science Foundation. A.D. was supported by a Fellowship from the Algerian Government.

Supplementary Material Available: Tables of crystal data and structure solution and data collection details, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances and angles, and hydrogen atom atomic coordinates and labeling diagrams for 2 and 3 (18 pages); tables of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

Photochemistry of Methyltrioxorhenium(VII)

Horst Kunkely,[1a] Thomas Türk,[1a] Clementina Teixeira,[1a] Claude de Meriĉ de Bellefon,[1b] Wolfgang Anton Herrmann,[1b] and Arnd Vogler*,[1a]

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, Germany, and Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching, Germany

Received March 11, 1991

Summary: Ligand-to-metal charge transfer excitation of CH_3ReO_3 leads to a homolysis of the CH_3–Re bond. Product formation takes place by outer-sphere back electron transfer or atom abstraction by the methyl radical.

The photochemistry of organometallic compounds,[2] including alkyl complexes,[3] has been investigated extensively during the last 15 years. Potential applications in photocatalysis stimulated many studies in this field. However, organometallic photochemistry has been largely restricted to compounds with transition metals in low oxidation states. In recent years the chemistry of organometallics with metals in high oxidation states[4,5] has gained increased attention. This interest, particularly in organometallic oxides,[4,6] is related to the idea that such compounds might serve as molecular models for heterogeneous catalysis at metal oxide surfaces. In this context it is remarkable that metal oxides or solid oxometalates with d^0 metals in high oxidation states (e.g. V_2O_5, MoO_4^{2-}) have been shown to be promising photocatalysts for the transformation of organic compounds.[7] Similarly, polyoxometalates were found to selectively photoactivate C–H bonds.[8] It follows from these considerations that the study of the photochemistry of a simple organometallic oxide should be of general importance. We explored this possibility and selected the compound CH_3ReO_3[4,9] for the present study.

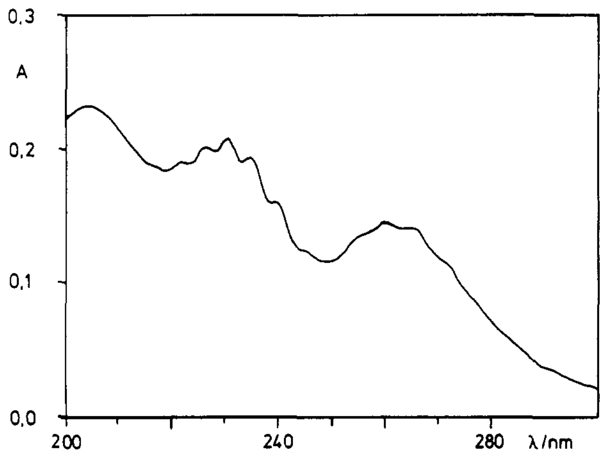

Figure 1. Electronic absorption spectrum of 1.42 × 10^{-4} M CH_3ReO_3 in n-hexane at room temperature (1-cm cell).

The electronic spectrum of CH_3ReO_3 consists of three absorption bands. The band maxima were slightly dependent on the solvent. In organic solvents such as hexane (Figure 1) the two longest wavelength bands at λ_{max} = 231 nm (ϵ = 1500) and λ_{max} = 260 nm (ϵ = 1020) show a clear vibrational progression with 850 cm^{-1} while the third band at λ_{max} = 205 nm (ϵ = 1600) is structureless. In aqueous solutions of CH_3ReO_3 (λ_{max} = 270 nm, ϵ = 1300; λ_{max} = 239 nm, ϵ = 1900) this vibrational structure is much less pronounced (Figure 2).

In low-temperature glasses (77 K) of ethanol that contains some water (5%) CH_3ReO_3 emitted a red luminescence at λ_{max} = 640 nm. This emission, which was inde-

(1) (a) Universität Regensburg. (b) Technische Universität München.
(2) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.
(3) (a) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766. (b) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249.
(4) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.
(5) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.
(6) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.
(7) Anpo, M.; Kondo, M.; Colluccia, S.; Louis, C.; Che, M. *J. Am. Chem. Soc.* **1989**, *111*, 8791 and references cited therein.
(8) Chambers, R. C.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 8427 and references cited therein.
(9) (a) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394. (b) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351.

0276-7333/91/2310-2090$02.50/0

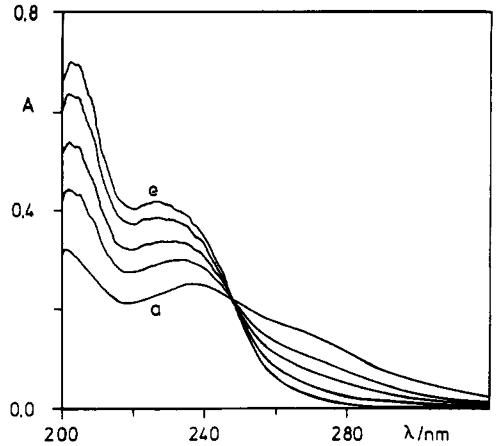

Figure 2. Spectral changes during the photolysis of 1.69×10^{-4} M CH_3ReO_3 in water at (a) 0, 0.5, 1, 2, and (e) 5 min irradiation time, with white-light irradiation (Osram HBO 100 W/2 lamp) and a 1-cm cell.

pendent of the exciting wavelength between 250 and 320 nm, was not detected if the ethanol was completely dry. The IR spectrum of CH_3ReO_3 in KBr shows Re–O stretching vibrations at ν(asym) = 958 cm^{-1} (vs, br) and ν(sym) = 1005 cm^{-1} (w).[10]

Solutions of CH_3ReO_3 were *very sensitive to UV light*. At low concentrations ($<7 \times 10^{-4}$ M) the aqueous complex photolyzed according to the simple stoichiometry

$$CH_3ReO_3 + H_2O \rightarrow CH_4 + H^+ReO_4^-$$

The photolysis was not effected by deaeration. The photoreaction could be driven to completion. The final absorption spectrum (Figure 2) was identical with that of ReO_4^-. A concomitant pH decrease took also place. Methane, which was determined by GC methods, was formed in *stoichiometric* amounts. Ethane was not detected even in traces. The quantum yield of the photolysis, which was measured for less than 10% conversion, was ϕ = 0.58 at λ_{irr} = 254 nm.

At higher concentrations ($c > 10^{-3}$ M) the photolysis of aqueous CH_3ReO_3 wa accompanied by the formation of a brownish precipitate, which was apparently ReO_3. The reflectance spectrum of this precipitate showed features (λ_{max} = 516 nm, with a shoulder at 370 nm) that were similar to those of an authentic sample of ReO_3.[11] In addition, ReO_4^- and methane but not ethane were identified as photoproducts. In nonaqueous solutions, the photolysis led to the formation of ReO_3 independent of the concentration of CH_3ReO_3. In solutions of CH_3CN methane was also released. In solutions of CCl_4, CH_3Cl, not methane, was formed.

In the complex CH_3ReO_3, the d^0 metal is coordinated pseudotetrahedrally (C_{3v}). All electronic transitions are of the ligand-to-metal charge-transfer (LMCT) type. A detailed assignment follows from a MO diagram that was developed for the isoelectronic molecule CH_3TiCl_3.[12] This MO scheme was modified according to the spectral and photochemical properties of CH_3ReO_3.[13] The diagram (Figure 3) includes only those MO's that are involved in low-energy transitions. The a_1 orbital (HOMO) represents

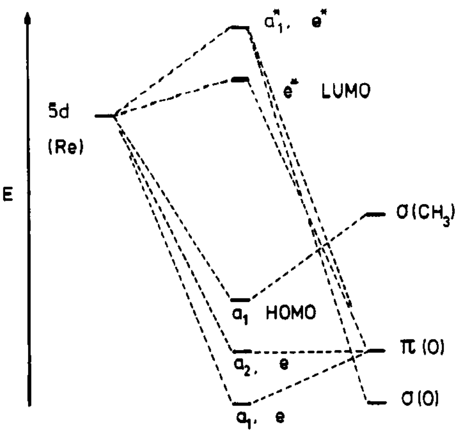

Figure 3. Qualitative MO diagram of CH_3ReO_3.

the Re–CH_3 σ-bond, which can be split photochemically (see below). The e* orbital (LUMO) is π-antibonding with regard to the Re–O interaction. The lowest energy $a_1 \rightarrow$ e* LMCT transition leads not only to the homolysis of the Re–CH_3 bond but also to a weakening of Re–O bonds. This assumption is confirmed by the vibrational progression of the longest wavelength absorption (Figure 1). The Re–O stretching vibration in the a_1e^* excited state occurs clearly at frequencies lower ($\nu \approx 850$ cm^{-1}) than that in the ground state (ν = 958 and 1005 cm^{-1}). Such a change by about 10% seems to be typical for d^0 oxometalates.[14-17]

The assignments of the other two absorption bands of CH_3ReO_3 at shorter wavelengths (Figure 1) are less clear. The second absorption at λ_{max} = 231 nm (in hexane) can be assigned to the a_2(e) $\rightarrow$ e*(LUMO) transition, since this band shows the same vibrational progression as the first band. The third band at λ_{max} = 205 nm (Figure 1) is structureless. The corresponding electronic transition should then not terminate at the π-antibonding LUMO e*[16] and may involve the promotion of electron from a filled MO (e.g. a_1, a_2, e) to an empty one at higher energies.

In aqueous solution the vibrational structure is much less pronounced (Figure 2). This is an indication of a strong interaction of water with CH_3ReO_3.[9b] Such an interaction accounts also for the high solubility of the complex in water.

The observation of luminescence from CH_3ReO_3 is quite remarkable, since organometallic alkyl complexes have not been observed to emit.[18] In addition, d^0 oxometalates are known to luminesce only in the solid state.[7,19] The emission of CH_3ReO_3 is assigned to the e*(LUMO) $\rightarrow$ a_1(HOMO) transition. The luminescence was only observed in low-temperature glasses of water-containing ethanol. The large red shift from absorption to emission ($\Delta\nu$ = 21 400 cm^{-1}) is indicative of a large structural rearrangement, probably an extension of the metal–ligand bonds, in the excited state. The absence of an emission in glasses of dry ethanol may be related to the large reactivity of the LMCT excited state toward hydrogen abstraction from organic compounds even at low temperatures (see below).

The lowest energy $a_1 \rightarrow$ e* LMCT excitation of CH_3-ReO_3 involves the removal of an electron from the CH_3–Re

(10) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.*, in press.
(11) Nechamkin, H.; Hiskey, C. F. *Inorg. Synth.* **1950**, *3*, 186.
(12) Dijkgraaf, C.; Rousseau, J. P. G. *Spectrochim. Acta* **1969**, *25A*, 1455.
(13) A theoretical evaluation of the thermal stability of CH_3ReO_3 was published recently: Szyperski, T.; Schwerdtfeger, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1288.
(14) Jeans, D. B.; Penfield, J. D.; Day, P. *J. Chem. Soc., Dalton Trans.* **1974**, 1777.
(15) Clark, R. J. H.; Stewart, B. *J. Am. Chem. Soc.* **1981**, *103*, 6593.
(16) Homborg, H. *Z. Anorg. Allg. Chem.* **1983**, *498*, 25.
(17) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 320.
(18) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.
(19) (a) Blasse, G. *Struct. Bonding* **1980**, *42*, 1. (b) Blasse, G. *Prog. Solid State Chem.* **1988**, *18*, 79.

σ-bond, which eventually is split homolytically:

$$CH_3ReO_3 \rightarrow CH_3 + ReO_3$$

The fate of the primary radical pair depends on the medium. The strong interaction of CH_3ReO_3 with water may facilitate an aquation of the ReO_3 fragment. Since the coupling of two methyl radicals is apparently not favored,[20] product formation occurs only by back electron transfer:

$$CH_3 + H_2OReO_3 \rightarrow CH_4 + H^+ReO_4^-$$

Such an outer-sphere electron transfer applies also to the oxidation of certain Co(II) complexes by methyl radicals.[22] While at low complex concentrations the photolysis of CH_3ReO_3 in water proceeds only by this mechanism, another process competes at higher concentrations. Methyl radicals have an extremely strong tendency to abstract hydrogen atoms.[21] Suitable hydrogen donors apparently include CH_3ReO_3.[23] Among other products, methane and ReO_3, which is insoluble and not very reactive,[11] are formed by irradiation of CH_3ReO_3 at higher concentrations.

In nonaqueous solvents the methyl radicals prefer to attack the solvent[3] and ReO_3 is formed upon photolysis of CH_3ReO_3 at any concentration. Acetonitrile is a very efficient hydrogen donor for methyl radicals, while chlorine atoms are easily abstracted from CCl_4.[22] Accordingly, the formation of methane was observed if CH_3ReO_3 was photolyzed in CH_3CN, while CH_3Cl was released when the irradiation was carried out in CCl_4.

It is quite interesting that a related Re(VII) complex apparently also undergoes a homolytic Re–C bond splitting in the primary photochemical step. The photolysis of $(Me_3SiCH_2)_3ReO_2$ yields $(Me_3SiCH_2)_4Re_2O_4$,[24] which should arise from dimerization of $(Me_3SiCH_2)_2ReO_2$ radicals. The product formation certainly depends on the reactivity of the Me_3SiCH_2 radical, which may abstract a hydrogen atom from the solvent or another complex molecule. Finally, thermolytic scission of the carbon–rhenium bonds even *in the dark* is a major decomposition route of higher alkylrhenium oxides of formula $RReO_3$. Thus, the instability of $(^tC_4H_9)ReO_3$ and $(Me_3CCH_2)ReO_3$ are due to the radical stability of *tert*-butyl and neopentyl, respectively, while $C_2H_5ReO_3$ can be isolated in a pure state.[25] On the basis of our present findings, both thermal and photolytic reactions, including radical pathways, are expected to yield catalytically active species resulting from compounds $RReO_3$.[26] Photochemical activation of this class of compounds should therefore be exploited in future catalytic applications.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(20) Although the coupling of methyl radicals is a rapid process,[21] their stationary concentration is apparently too small for an efficient dimerization.

(21) Lazár, M.; Rychlý, J.; Klimo, V.; Pelián, P.; Valko, L. *Free Radicals in Chemistry and Biology*; CRC Press: Boca Raton, FL, 1989.

(22) Roche, T. S.; Endicott, J. F. *Inorg. Chem.* **1974**, *13*, 1575.

(23) Generally, the photochemical dealkylation of methyl complexes almost exclusively yields methane.[3]

(24) Cai, S.; Hoffmann, D. M.; Lappas, D.; Woo, H.-G. *Organometallics* **1987**, *6*, 2273.

(25) Herrmann, W. A.; de Meric̆ de Bellefon, C.; Fischer, R. W.; Kiprof, P.; Romao, C. C. *Angew. Chem., Int. Ed. Engl.*, in press.

(26) For an updated review, cf.: Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1.

Preparation, Reactivity, and X-ray Structure of a Cationic Alkoxyzirconocene Complex

Scott Collins,* Bryan E. Koene, Ravindranath Ramachandran, and Nicholas J. Taylor

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received March 22, 1991

Summary: The tetrahydrofuran adduct of bis(cyclopentadienyl)-*tert*-butoxyzirconium(1+) tetraphenylborate (**2**) was prepared, in high yield, by reaction of *tert*-butanol with bis(cyclopentadienyl)(methyl)zirconium(1+) tetraphenylborate (**1**). Analogous reactions of compound **1** with less hindered alcohols were complicated by the formation of several compounds of undetermined structure. The structure of compound **2** was determined by X-ray diffraction: triclinic, space group $P\bar{1}$, a = 15.564 (2) Å, b = 17.253 (4) Å, c = 21.647 (3) Å, α = 106.12 (1)°, β = 94.71 (1)°, γ = 101.76 (1)°, V = 5407.3 (17) Å^3, Z = 6 with three independent molecules of **2** in the asymmetric unit, R = 0.0483, and R_w = 0.0652, for 9608 observed reflections with $F > 6\sigma(F)$. In this structure, the lone pairs on the oxygen atom of the *tert*-butoxy ligand are involved in significant back-donation to the electron deficient metal center, as revealed by the short Zr–O bonds and near-linear angles at oxygen in the three independent molecules. The exchange of bound and free THF is a higher energy process in solution as compared to that observed for compound **1**. Complex **2** catalyzes the Diels–Alder reaction between methyl acrylate and dienes in CH_2Cl_2 solution under mild conditions.

Introduction. There is considerable interest in the structure and chemistry of cationic zirconocene compounds of the group 4 transition elements; in particular, alkyl derivatives **1** serve as useful models for the catalytic intermediates implicated in olefin polymerization and hydrogenation processes.[1] Moreover, these compounds are active in a number of other catalytic and stoichiometric processes that should prove useful in organic chemistry.[2]

Quite surprisingly, very little attention has been devoted to the preparation and chemistry of heteroatom derivatives of these d^0, $14e^-$ zirconocene compounds.[3] We report here

(1) For leading references see: (a) Jordan, R. F.; Bajgur, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (e) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (h) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Ibid.* **1990**, *9*, 1539. (i) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Ibid*, **1990**, *9*, 1650.

(2) (a) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546 and references cited therein. (b) Jordan, R. F. Personal communication.

0276-7333/91/2310-2092$02.50/0