Dioxygen-Derived Peroxo-Alkyl Complexes of Permethyltantalocene. Structural Characterization of $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}O_2)(CH_2C_6H_5)$ and Acid-Catalyzed Rearrangement to Oxo-Alkoxide Derivatives

Allan van Asselt, Mark S. Trimmer, Larry M. Henling, and John E. Bercaw*

Contribution No. 7803, Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Received June 27, 1988

The controlled transfer of oxygen to organic molecules is of fundamental importance in biology, in the synthesis of fine chemicals, and in the catalytic production of commodity chemicals. The most common (radical chain) pathway involves transition-metal-promoted autoxidation.[1] More controlled oxidations may be achieved where metal centers and their ligand environments serve as templates for the coordination of both substrate and dioxygen (e.g., cytochrome P450)[2] or the active oxidant (e.g., *tert*-butylhydroperoxide in allylic alcohol epoxidations).[3] The details of the actual oxygen-transfer step in controlled, metal-mediated oxidations are still poorly understood. Although organometallic compounds containing peroxide ligands are commonly invoked as intermediates,[4] very few have been isolated,[5] and examples of clean carbon–oxygen bond formation for well-characterized compounds are rarer still.[6] We report herein the synthesis, characterization, and some aspects of the reactivity of a series of alkyl-peroxo complexes of the general formula $Cp^*_2Ta(\eta^2\text{-}O_2)R$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, C_6H_5, $CH_2C_6H_5$).

As reported earlier alkylidene hydride, olefin hydride, or benzyne hydride derivatives of permethyltantalocene are in rapid equilibrium with the corresponding 16-electron alkyl or phenyl species.[7] Exposure of pentane solutions of $Cp^*_2Ta(=X)H$ (X = CH_2, CHC_6H_5, C_6H_4, $CH_2{=}CH_2$, $CH_2{=}CHCH_3$) to 1 atm of dry O_2 leads to precipitation of $Cp^*_2Ta(\eta^2\text{-}O_2)R$ as white solids upon warming from −80 °C to room temperature (eq 1–5).

$$Cp^*_2Ta(=CH_2)H \rightleftarrows [Cp^*_2TaCH_3] \xrightarrow{O_2} \underset{85\%}{Cp^*_2Ta(\eta^2\text{-}O_2)CH_3} + \underset{15\%}{Cp^*_2Ta(O)CH_3} \quad (1)$$

$$Cp^*_2Ta(=CHC_6H_5)H \rightleftarrows [Cp^*_2TaCH_2C_6H_5] \xrightarrow{O_2} Cp^*_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5 \quad (2)$$

$$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H \rightleftarrows [Cp^*_2TaC_6H_5] \xrightarrow{O_2} Cp^*_2Ta(\eta^2\text{-}O_2)C_6H_5 \quad (3)$$

$$Cp^*_2Ta(CH_2{=}CH_2)H \rightleftarrows [Cp^*_2TaCH_2CH_3] \xrightarrow{O_2} Cp^*_2Ta(\eta^2\text{-}O_2)CH_2CH_3 \quad (4)$$

$$Cp^*_2Ta(CH_2{=}CHCH_3)H \rightleftarrows [Cp^*_2TaCH_2CH_2CH_3] \xrightarrow{O_2} Cp^*_2Ta(\eta^2\text{-}O_2)CH_2CH_2CH_3 \quad (5)$$

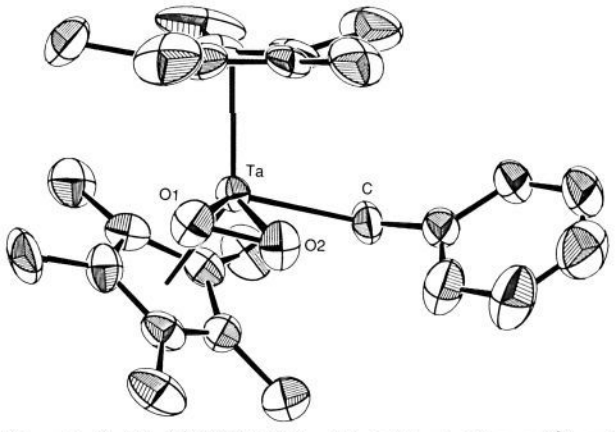
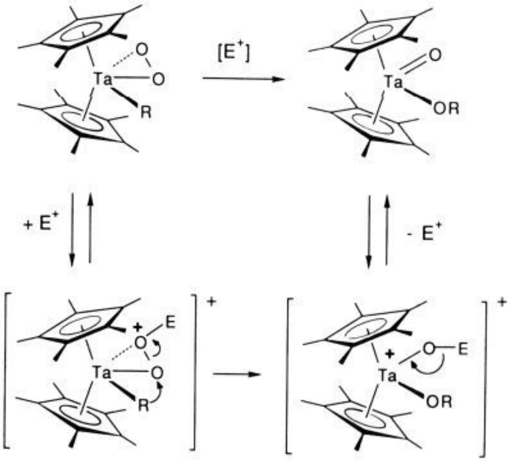


Figure 1. $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5$. Selected bond distances (Å) and angles (deg) are as follows: Ta–O1, 1.996 (6); Ta–O2, 1.955 (6); Ta–C, 2.323 (9); O1–O2, 1.477 (8); O2–Ta–O1, 43.9 (2); C–Ta–O1, 122.8 (3); C–Ta–O2, 78.9 (3); Cp*–Ta–Cp*, 134.6.

Scheme I



The products[8] are remarkably stable, especially in the solid state, remaining unchanged for several days at room temperature and indefinitely at −30 °C. Single crystals of the benzyl peroxide derivative were grown from pentane, and the structure (Figure 1) was determined by X-ray diffraction methods. The arrangement of peroxide and benzyl ligands in the equatorial plane of the bent sandwich structure is analogous to that for the ethylene and ethyl ligands of the isostructural and isoelectronic derivative $(\eta^5\text{-}C_5H_5)_2Nb(\eta^2\text{-}C_2H_4)(CH_2CH_3)$,[9] and the *d*(O–O) of 1.477 (8) Å is normal for an $\eta^2\text{-}O_2$ ligand.[8b]

$Cp^*_2Ta(\eta^2\text{-}O_2)CH_3$ will cleanly oxidize a limited number of substrates: SO_2 (immediate reaction at 25 °C)[10] > PMe_3 (days at 25 °C) > PPh_3 (1 day at 80 °C). Carbon monoxide (2 atm), $CNCH_3$ (≈5 equiv), $N(CH_2CH_3)_3$ (≈5 equiv), and styrene (≈5

---

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York 1981.

(2) Guengerich, F. P.; McDonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

(3) Finn, M. G.; Sharpless, K. B. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 247.

(4) Mimoun, H. *Comprehensive Coordination Chemistry*; Wilkinson, Gillard, McCleverty, Eds.; Pergamon Press: New York, 1987, p 318.

(5) (a) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C., in press. (b) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. (c) Drouin, M.; Harrod, J. F. *Can. J. Chem.* **1985**, *63*, 353. (d) Mason, M. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5153. (e) van der Ent, A.; Onderdelinden, A. L. *Inorg. Chim. Acta* **1973**, *7*, 203.

(6) van Asselt, A.; Santasiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 8291.

(7) (a) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. *Organometallics* **1986**, *5*, 976. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (c) Burger, B. J.; Santasiero, B. D.; Trimmer, M. S.; Bercaw, J. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

(8) $Cp^*_2Ta(\eta^2\text{-}O_2)CH_3$: ^{1}H NMR (benzene-$d_6$, 25 °C) s 1.68 δ (30 H); s 0.15 δ (3 H); IR ν(O–O) 858 cm^{-1}. Anal. Calcd for $C_{21}H_{33}O_2Ta$: C, 50.60; H, 6.69. Found: C, 50.99; H, 6.78. $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5$: ^{1}H NMR (benzene-$d_6$, 25 °C) s 1.67 δ (30 H); s 2.10 δ (2 H); m 6.95–7.75 δ; IR ν(O–O) 863 cm^{-1}. Anal. Calcd for $C_{27}H_{37}O_2Ta$: C, 56.44; H, 6.49. Found: C, 56.34; H, 6.46. $Cp^*_2Ta(\eta^2\text{-}O_2)C_6H_5$: ^{1}H NMR (benzene-$d_6$, 25 °C) s 1.54 δ (30 H), m 7.1–7.2 δ (2 H), td (7.4, 1.4 Hz), 7.29 δ (1 H), td (7.5, 1.4 Hz); 7.50 δ (1 H), d (7.7 Hz), 8.16 δ (1 H); IR ν(O–O) 872 cm^{-1}. Anal. Calcd for $C_{26}H_{35}O_2Ta$: C, 55.71; H, 6.29. Found: C, 55.39; H, 5.99. $Cp^*_2Ta(\delta^2\text{-}O_2)CH_2CH_3$; ^{1}H NMR (benzene-$d_6$, 25 °C) s 1.65 δ (30 H); q 0.08 δ (2 H); CH_2CH_3 ≈ 1.65 δ; IR ν(O–O) 863 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O_2Ta$: C, 51.56; H, 6.88. Found: C, 50.52; H, 6.79. $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2CH_2CH_3$: ^{1}H NMR (benzene-$d_6$, 25 °C) s 1.65 δ (30 H), m 0.70 δ (2 H), $CH_2\mathit{CH_2}CH_3$ ≈ 1.65 δ, t 1.35 (3 H); IR ν(O–O) 861 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O_2Ta$: C, 52.47; H, 7.08. Found: C, 52.83; H, 7.00.

(9) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

(10) The precipitate which immediately forms is likely $Cp^*_2Ta(\eta^2\text{-}SO_4)\text{-}CH_3$.

0002-7863/88/1510-8254$01.50/0

$$Cp^*_2Ta(\eta^2\text{-}O_2)CH_3 + P(C_6H_5)_3 \rightarrow Cp^*_2Ta(O)CH_3 + OP(C_6H_5)_3 \quad (6)$$

equiv) are not oxidized (days 80 °C). An interesting phenomenon was noted while carrying out these reactions. When heated to 80 °C in the presence of triethylamine $Cp^*_2Ta(\eta^2\text{-}O_2)CH_3$ does *not* decompose; isonitrile significantly slows its decomposition. In contrast, when $Cp^*_2Ta(\eta^2\text{-}O_2)CH_3$ is heated in solution alone, or in the presence of styrene or CO, a (non-first-order) rearrangement to $Cp^*_2Ta(O)OCH_3$ occurs. Trace amounts of acid, possibly on the surface of the glass NMR tube,[11] might serve to catalyze the observed rearrangement. Indeed, addition of even trace amounts of methanesulfonic acid greatly accelerates methyl migration to oxygen (eq 7).

$$Cp^*_2Ta(\eta^2\text{-}O_2)CH_3 \xrightarrow{[H^+],\ 80\ ^\circ C} Cp^*_2Ta(O)OCH_3 \quad (7)$$

The reactivity of the phenyl derivative is similar to that for the methyl, except that trace acid is required to oxidize triphenylphosphine.[12] Addition of 1 equiv of $R'SO_3H$ ($R' = CH_3$, $C_6H_4CH_3$) to $Cp^*_2Ta(\eta^2\text{-}O_2)R$ ($R = CH_3$, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2C_6H_5$) leads to the corresponding alcohol (ROH) and what appears to be $Cp^*_2Ta(O)OSO_2R'$ over a period of 3 days at 25 °C. Initial indications were that other Lewis acids, e.g., AlR_3,[13] will also promote the rearrangement shown in eq 7.

$$Cp^*_2Ta(O_2)R + R'SO_3H \rightarrow Cp^*_2Ta(O)OSO_2R' + ROH \quad (8)$$

Electrophilic attack at the exo-oxygen atom would enhance heterolysis of the O–O bond during migration of the alkyl (or phenyl) group (Scheme I). Similarly, nucleophilic attack at the endo-O by phosphines or sulfur dioxide would be enhanced when Lewis acids are coordinated to the exo-oxygen atom. This mechanism for the acid-catalyzed rearrangement of $Cp^*_2Ta(\eta^2\text{-}O_2)R$ to $Cp^*_2Ta(O)OR$ is reminiscent of the mechanism proposed for the rearrangement of the isoelectronic $Cp^*_2Hf(OOCMe_3)(R)$ to $Cp^*_2Hf(OCMe_3)(OR)$, where $[CMe_3]^+$ formally serves the role of the electrophile in Scheme I.[6]

The clean nature of these rearrangements as well as the promotion by Lewis acids indicates a *dipolar* character for intramolecular or bimolecular attack at $M(\eta^2\text{-}O_2)$ concurrent with O–O bond cleavage, which proceeds by interaction of the migrating (or in-coming) group's electron pair with the activated σ^* orbital of the [O–O] moiety. This dipolar reactivity reveals potentially very different reaction patterns for these metal peroxides as compared with free-radical autoxidations.

Acknowledgment. This work was supported by the National Science foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged. We also thank NSF (Grant No. CHE-8219039) for purchase of the diffractometer and Exxon Educational Foundation for financial support.

Supplementary Material Available: Experimental details describing the syntheses of $Cp^*_2Ta(=CHC_6H_5)H$, $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$, and $Cp^*_2Ta(\eta^2\text{-}O_2)R$ and tables of crystal structure parameters, final parameters, bond distances and angles, hydrogen parameters, and anisotropic displacement parameters (13 pages); tables of observed and calculated structure factors for $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2C_6H_5$ (20 pages). Ordering information is given on any current masthead page.

---

[11] Prior rinsing of the NMR tube with KOH/isopropyl alcohol results in a much slower rate of decomposition.

[12] Acid promotion in the transfer of oxygen from metal peroxides to triphenylphosphine has been noted previously: Mimoun, H.; Perez-Machirant, M. M.; Seree de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

[13] These reactions appear to be more complex due to alkyl/alkoxide exchange between aluminum and tantalum. For example, treatment of $Cp^*_2Ta(\eta^2\text{-}O_2)CH_2CH_2CH_3$ with $Al(CH_2CH_3)_3$ affords the adduct $Cp^*_2Ta(O)(CH_2CH_3)\cdot Al(CH_2CH_3)_2(OCH_2CH_2CH_3)$.

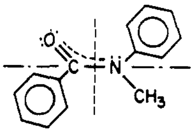
Intramolecular Charge-Transfer Transition in Benzanilides and Its Dielectric Medium Modulation

Jozef Heldt,† David Gormin, and Michael Kasha*

Institute of Molecular Biophysics and
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306-3015

Received July 1, 1988

The fluorescence spectrum of benzanilide exhibits the anomaly that its λ_{max} occurs at longer wavelengths than that of its phosphorescence emission.[1] Recently, Tang, MacInnis, and Kasha[2] interpreted this anomaly on the basis of a proton-transfer fluorescence $S_1' \rightarrow S_0'$ of the imidol tautomer transient. A test of a proton-transfer mechanism is the methylation of the molecule at the sensitive proton position. We have now studied the *N*-methylbenzanilide (I) and were surprised to observe a fluorescence in the 500-nm region, Figure 1 (curve 1, onset 450 nm, λ_{max} 510 nm, MCH, 298 K).



I

(trans)-N- METHYLBENZANILIDE

The UV absorption spectrum shows moderate to strong absorption starting at 310 nm. The weak fluorescence observed from 300 to 400 nm (Figure 1) must arise from a weak absorption band, corresponding to excitation in a locally excited moiety (structure I), buried in the stronger $S_1(\pi\pi^*) \leftarrow S_0$ absorption with $\lambda_{max} \sim 250$ nm, $\epsilon = 10\,000\ M^{-1}\ cm^{-1}$.[1] This is supported by the suggestive band contour (exceptional long wavelength tail), the strongly competitive excitation of the $T_1 \rightarrow S_0$ emission, and the resolved and discrete weak absorption observed[3] in benzamide (λ_{max} 270 nm, $\epsilon \sim 600\ M^{-1}\ cm^{-1}$).

The long wavelength fluorescence band at 510 nm must result from an intramolecular charge-transfer transition which involves the whole molecule. Such charge-transfer fluorescence bands with large wavelength shifts have been characterized as *twisted intramolecular charge-transfer* emissions in dimethylanilines and have been studied for many different molecular structures.[4] Such intramolecular CT transitions have not been suspected previously for benzanilides. The absence of a *direct absorption* to the charge-transfer state is an indication of the indirect relaxation mechanism by which the state is excited. This mechanism involves internal torsion (cf. structure I) and dielectric relaxation. One test of the charge-transfer nature of the fluorescence is the sensitivity of the band to dielectric medium effects. The 510-nm band for *N*-methylbenzanilide (and the corresponding one for benzanilide) does shift strongly with changes in dielectric constant, with $\Delta\bar{\nu} = 1080\ cm^{-1}$ for the change from *n*-heptane ($\epsilon = 1.92$) to tetrahydrofuran ($\epsilon = 7.39$); the comparable shift for anthracene π,π^* fluorescence is $118\ cm^{-1}$. Parallel behavior is observed with empirical solvent polarity indices, such as the E_T index,[5] although the values of E_T available are limited.

If a strongly dipolar solvent is used, e.g., ethyl alcohol or propylene oxide, the 510-nm fluorescence is quenched, and the normal short wavelength fluorescence is strengthened. A specific dipole–dipole complex can block the charge-transfer excitation by severely polarizing one end of the heteromolecule.

---

† On leave of absence from the Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland.

[1] O'Connell, E. J., Jr.; Delmauro, M.; Irwin, J. *Photochem. Photobiol.* **1971**, *14*, 189–195.

[2] Tang, G.-Q.; MacInnis, J. M.; Kasha, M. *J. Am. Chem. Soc.* **1987**, *109*, 2531–2533.

[3] Heldt, J.; Kasha, M., Unpublished Work, this Laboratory, June 1988.

[4] Cf. Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

[5] Reichert, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

0002-7863/88/1510-8255$01.50/0