terpenoid, and (hydronaphthalene) sesquiterpene type.

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Supplementary Material Available: Tables of the atomic positional and thermal parameters, bond distances, bond angles and structural figure for **10**, and the physical and spectral data for compounds **1**, **5**, **6b**, **7**, **8**, **9**, **10**, and entries 1-5 of Table I (11 pages). Ordering information is given on any current masthead page.

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[16] Wollenberg, R. H.; Goldstein, J. E. *Synthesis*, **1980**, 757.

Photochemical α-Hydride Abstraction

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The abstraction of α-hydrogens from transition-metal alkyl groups is an important process in organo-transition-metal chemistry, especially in view of the proven and implied activity of the generated alkylidene and alkylidyne functions in a number of catalytic and stoichiometric reactions.[1-5] We wish to communicate here our initial observations on the high yield and efficient photochemical generation of alkylidene groups in tantalum systems.[6,7] These results are important in that they represent the first unequivocal demonstration of photochemically induced α-hydride abstraction generating alkylidene groups that are thermally inaccessible. Furthermore the results also demonstrate the high activity of alkylidene functions for the activation of aliphatic CH bonds, an area of intense current interest.[8]

We recently reported the metalation behavior of the compound $Ta(OAr')_2Me_3$ (I) (OAr′ = 2,6-di-*tert*-butylphenoxide) in which on thermolysis at 120 °C loss of 2 equiv of methane and cyclometalation of a *tert*-butyl group in each aryl oxide ligand takes place.[9] Mild thermolysis of I (75 °C, 7 days in toluene) allows the isolation of the intermediate, monometalated compound III (Scheme I).[10] However, on photolysis, I undergoes the smooth loss of 1 equiv of methane (as monitored by ^1H NMR) and the formation of a new compound (II).[11] Spectroscopic data are consistent with II being the methyl, methylidene compound $Ta(OAr')_2(=CH_2)(CH_3)$.[12] When allowed to stand at 25 °C, II smoothly converts to the monometalated compound III. Both the photochemical conversion of I to II and the isomerization of II to III are essentially quantitative as determined by ^1H NMR. In order to prove that the thermal and photochemical routes to III are different, we performed a labeling study, the results of which

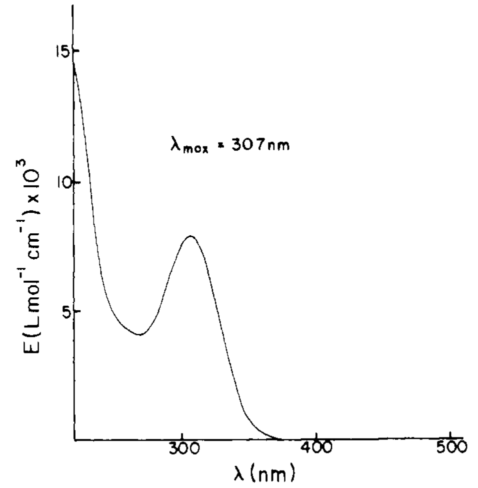
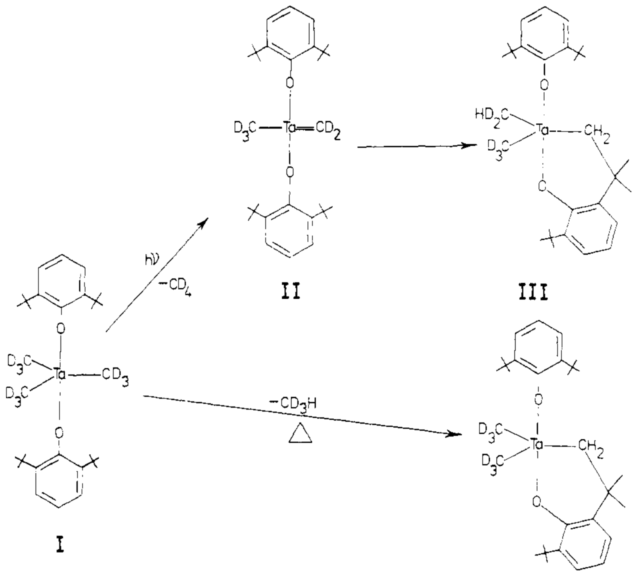


Figure 1. Absorption spectrum of $Ta(OAr')_2Me_3$ in cyclohexane solvent.

Scheme I



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[1] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[2] Schrock, R. R. In "Reactions of Coordinated Ligands"; Bratermann, P. S., Eds.; Plenum Press: New York, 1982.

[3] Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

[4] (a) Ivin, K. J.; Rooney, J. J.; Stewart, D.; Green, M. L. H.; Mahtab, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 604. (b) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331. (c) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1011.

[5] Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.*, **1981**, *103*, 4648.

[6] It has been mentioned that photolysis of Cp_2TaMe_3 can lead to the formation of $Cp_2Ta(=CH_2)(CH_3)$, but experimental details were not reported.[2] The photochemistry of a number of group 4 and 5 (cyclopentadienyl) alkyl compounds has been extensively studied. No alkylidene compounds, however, were isolated. See: (a) Emad, A.; Rausch, M. D., *J. Organomet. Chem.* **1980**, *191*, 313. (b) Leeuwen, P. W. N. M.; Van der Heigden, H.,; Roobeck, C. F.; Frijns, J. H. G. *Ibid.* **1981**, *209*, 169. (c) Mintz, E. A.; Rausch, M. D. *Ibid.* **1979**, *171*, 345. (d) Rausch, M. D.; Boon, W. H.; Alt, H. G. *Ibid.* **1977**, *141*, 299.

[7] Photoinduced β-hydride abstraction has been documented. See: (a) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1860. (b) Kazlauskas, R. J.; Wrighton, M. S. *Ibid.* **1982**, *104*, 6005. (c) Alt, H. G.; Eichner, M. E. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 78.

[8] (a) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (b) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (c) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (d)Brookhart, M., Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein.

[9] Chamberlain, L.; Keddington, J.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1538.

[10] ^1H NMR (30 °C, toluene-d_8) δ 1.11 (s, Me_2), 1.38 (s, $OC_6H_3\text{-}\mathit{t\text{-}Bu_2}$), 1.61 (s, $OC_6H_3\text{-}t\text{-}\mathit{Bu}CMe_2CH_2$), 1.20 (s, $OC_6H_3\text{-}t\text{-}BuC\mathit{Me_2}CH_2$), 2.07 (s, $OC_6H_3\text{-}t\text{-}BuCMe_2\mathit{CH_2}$), 6.5-7.5 (m, OC_6H_3). The signal due to the TaMe groups was assigned by comparison with the deuterated compound.

[11] Photolysis was achieved by the use of a 450-W Ace-Hanovia medium-pressure Hg lamp housed in a cooled quartz jacket. Samples to be photolyzed (either ^1H NMR tube samples or bulk samples in Pyrex tubing) were immersed in cold, running water between 3 and 10 cm from the lamp. The 313-nm line of the Hg spectrum was isolated by the use of an interference filter purchased from Oriel Corp. Quantum efficiencies were determined in benzene by using the known *trans*-cis isomerization of stilbene; see ref 6e and: Lewis, F. D.; Johnson, D. E. *J. Photochem.* **1977**, *7*, 421.

[12] ^1H NMR (30 °C, C_6D_6) δ 1.20 (s, $TaCH_3$), 9.41 (s, $Ta{=}CH_2$), 1.47 (s, $OC_6H_3\text{-}\mathit{t\text{-}Bu}$); ^{13}C NMR δ -288 ($Ta{=}CH_2$).

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are outlined in Scheme I.[13] Mass spectroscopic analysis clearly shows that the product of thermolysis of $Ta(OAr')_2(CD_3)_3$ is $Ta(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr')(CD_3)_2$ whereas photolysis followed by room-temperature metalation leads to $Ta(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr')(CD_3)(CD_2H)$, the proton being incorporated from the *tert*-butyl group.

These results prove that the methylidene compound is not generated during the thermal reaction, and the thermal metalation step probably proceeds in a four-center pathway.[14] The structure of the methylidene compound is at present unknown although it should be very similar to that of the related compound $Ta(OAr')_2({=}CHSiMe_3)(CH_2SiMe_3)$.[15] This latter compound also undergoes cyclometalation on thermolysis (80 °C), but a number of pathways are possible.[15] The fact that II converts directly to III at room temperature indicates that methylidene functions have a higher activity for aliphatic CH bond activation (at least intramolecularly) than simple alkyl groups. This metalation step can be thought of as an intramolecular reverse of the α-hydride abstraction process, the aliphatic CH bond adding to the tantalum-carbon double bond.

The question arises as to the pathway of the photochemical α-hydride abstraction itself. Figure 1 shows that the electronic spectrum of I contains a strong absorption in the ultraviolet with $\lambda_{max} = 307$ nm and a molar extinction coefficient $\epsilon_{max} = 7300$ L mol^{-1} cm^{-1}. This band we assign as a ligand to metal charge-transfer process from the aryl oxide oxygen atoms to tantalum,[16] being neither in the right position or of the correct shape or intensity to be due to the lowest lying π–π^* transition (A_{1g}–B_{2u}) of the aromatic ring of the OAr' ligands. Irradiation into this bond at 313 nm results in the generation of II with a high quantum efficiency of 0.95 ± 0.1.[11] Further evidence for the assignment of this band comes from the spectrum of the yellow compound $TaCl_2(CH_2SiMe_3)_3$. Here the band is of comparable intensity but is red shifted to $\lambda_{max} = 344$ nm, as would be expected for this less electronegative donor atom.

Evidence for the possible generality of this process comes from a study of the compound $Ta(OAr'')_2(CH_2SiMe_3)_3$ (OAr'' = 2,6-di-isopropylphenoxide). Thermolysis of this compound at 120 °C (toluene-d_8/sealed ^1H NMR tube) for 7 days causes little change in the spectrum, approximately 5% Me_4Si being generated with no other identifiable products. In contrast photolysis leads to the rapid formation of 1 equiv of Me_4Si and the alkylidene $Ta(OAr'')_2({=}CHSiMe_3)(CH_2SiMe_3)$.[17] Further work is in progress to more fully study the possible generality of this process in compounds of this type and to try and ascertain the mechanism of this photoreaction.[18]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8219206 to I.P.R.), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corp. for support of this work. We thank Drs. C. P. Kubiak, D. R. McMillin, and W. G. Klemperer for helpful discussion.

Registry No. I, 82182-23-8; II, 88915-83-7; III, 88915-84-8; $Ta(OAr'')_2(CH_2SiMe_3)_3$, 88915-85-9.

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[13] $Ta(OAr')_2(CD_3)_3$ was prepared as described previously.[13] Analysis of samples of III generated from $Ta(OAr')_2(CH_3)_3$ either by thermolysis[8] or photolysis followed by room-temperature metalation showed identical mass spectral patterns. A parent molecular ion peak at 620 (100%) was accompanied by peaks at 621 (35%) and 622 (≈5%) due to the ^{13}C natural abundances in this C_{30} molecule. In contrast, the thermolysis of $Ta(OAr')_2(CD_3)_3$ led to a sample of III with a base peak at 626 (i.e., III-d_6) with less than 4% 625, whereas the sample of III from photolysis of $Ta(OAr')_2(CD_3)_3$ gave a base peak of 625 (i.e., III-d_5) and approximately 40% 626 (as expected from ^{13}C natural abundance). In the ^1H NMR of III generated via the photochemical route from $Ta(OAr')_2(CD_3)_3$, a broad, weak multiplet at δ 1.05 was observed and assigned to the $TaCD_2\mathit{H}$ group. No such multiplet could be resolved for the thermally generated compound.

[14] (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (b) Tulip, T. H.; Thorn, D. L. *Ibid.* **1981**, *103*, 2448. (c) Gell, K. I., Posin, B.; Schwartz, J.; Williams, G. M. *Ibid.* **1982**, *104*, 1846.

[15] Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.

[16] Fowler, G. W. A.; Tidmarsh, D. j.; Walton, R. A. *Spectrochim. Acta* **1969**, *25*, 999.

[17] The compound $Ta(OAr'')_2(CH_2SiMe_3)_3$ was prepared either by treatment of $Ta(OAr'')_2Cl_3$ with $LiCH_2SiMe_3$ or by reacting $TaCl_2(CH_2SiMe_3)_3$ with excess LiOAr'', both in hydrocarbon solvents. The product is a white solid extremely soluble in hexane. ^1H NMR (30 °C, C_6D_6) δ 1.11 (s, CH_2SiMe_3), 0.11 (s, $SiMe_3$), 3.84 (septet, $C\mathit{H}Me_2$), 1.36 (d, $CH\mathit{Me}_2$), 6.8–7.3 (m, OC_6H_3). The electronic spectrum shows a band with $\lambda_{max} = 302$ nm and $\epsilon = 9900$ L mol^{-1} cm^{-1}. On photolysis Me_4Si was rapidly generated along with a solution of $Ta(OAr'')_2({=}CHSiMe_3)(CH_2SiMe_3)$. ^1H NMR (30 °C, $C_6D_5CD_3$) δ 8.68 (s, $Ta{=}\mathit{CH}SiMe_3$), 0.24 and (s) 0.29 (s, $CHSi\mathit{Me}_3$ and $CH_2Si\mathit{Me}_3$), 3.47 (septet, $C\mathit{H}Me_2$), 1.17 (d) and 1.20 (d, $CH\mathit{Me}_2$), 6.7–7.2 (m, OC_6H_3). The CH_2SiMe_3 signals could not be resolved.

[18] Since the submission of this manuscript, experimental details of the photochemical generation of $Re(N\text{-}t\text{-}Bu)_2({=}CHSiMe_3)(CH_2SiMe_3)$ from $Re(N\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_3$ have appeared, see: Edwards, D. S.; Blondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

Alignment of a Nonaqueous Lyotropic Liquid Crystalline Phase with Lecithin

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The aqueous lyotropic liquid crystalline phases based on phosphatidyl cholines (lecithins) have been widely studied by NMR in recent years. The important NMR parameters can be obtained most easily from oriented samples. For example, following the discovery that the aqueous phase can be aligned on glass plates, it was relatively straightforward to show that the proton broadening is orientation dependent.[1] Surface orientation of samples is now the normal technique used in preparing samples prior to study by NMR.[2] To our knowledge, spontaneous magnetic alignment for lyotropic phases based on lecithin has not been observed.

We are currently conducting studies on the nonaqueous lamellar liquid crystalline phase composed of lecithin and various organic diols.[3-6,10] In the course of these studies, we have observed ^{31}P NMR line shapes that exhibit effects consistent with the sample being aligned under certain conditions. Figure 1 shows several ^{31}P NMR spectra for a lamellar sample 70/30 (w/w) soy lecithin/ethylene glycol (I). Proton decoupled and nondecoupled spectra are presented for two Zeeman field strengths. In the case of $B_o = 2.35$ T (Figure 1A), the sample yields a spectrum that is roughly a randomly oriented (three-dimensional) powder pattern[7] for a spin $^1/_2$ nucleus. There is no evidence for alignment under these conditions. A distinctly different spectrum is observed for $B_o = 4.70$ T (Figure 1C). This spectrum has the qualitative appearance of a 2-dimensional spin $^1/_2$ powder pattern.[7] This type spectrum is derived from a random distribution of directors in a plane passing through B_o; however, the only definite conclusion

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[1] de Vries, J. J.; Berendsen, H. J. C. *Nature (London)* **1969**, *221*, 1139–1140.

[2] Seelig, J. *Biochim. Biophys. Acta* **1978**, *515*, 105–140.

[3] Moucharafieh, N.; Friberg, S. E. *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 231–238.

[4] Gan-Zuo, L.; El-Nokaly, M.; Friberg, S. E. *Mol. Cryst. Liq. Cryst.* **1982**, *72*, 183–188.

[5] Larsen, D. W.; Friberg, S. E.; Christenson, H. *J. Am. Chem. Soc.* **1980**, *102*, 6565–6566.

[6] Larsen, D. W.; Rananavare, S. B.; El-Nokaly, M.; Friberg, S. E. *Finn. Chem. Lett.* **1982**, *6-8*, 96–104.

[7] Forrest, B. J.; Reeves, L. W. *Chem. Rev.* **1981**, *81*, 1–14.

0002-7863/84/1506-1848$01.50/0