spectrophotometer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

Carbon-13 labeled carbon monoxide (90% enriched) was obtained from Prochem, tetrafluoroethylene was supplied by PCR Research Chemicals Inc., and tetracyanoethylene was obtained from Aldrich.

The complex *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was prepared by treating *trans*-$[PtHCl(P\text{-}c\text{-}Hx_3)_2]$ with $NaBH_4$ in ethanol.[32]

Reaction of *trans*-$[PtH_2(Pt\text{-}c\text{-}Hx_3)_2]$ with Carbon Monoxide. *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was dissolved in toluene and the solution was cooled to 213 K. Carbon monoxide was passed through the solution for 1 h (or, where ^{13}CO was used, the solution was stirred under 1 atm of the gas for 3 h), resulting in quantitative conversion to the complex $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 20.2 (^1J(Pt–P) = 3123 Hz); δ(C) 185.0 (^1J(Pt–C) = 1809 Hz, ^2J(P–C) 12 Hz)). When excess CO was removed by purging the solution with nitrogen, the major species present after standing for 24 h at ambient temperature was still $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$, but when the solution was allowed to warm in the presence of free CO, it rapidly became red and its $^{31}P\{^1H\}$ NMR spectrum indicated the presence of free P-c-Hx_3 (δ(P) 7.0) and $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$ (δ(P) 71.0 (^1J(Pt–P) = 4409 Hz, ^2J(Pt–P) = 409 Hz, ^3J(P–P) = 55 Hz, ^1J(Pt–Pt) = 1633 Hz)), when the spectrum was recorded at 213 K.

Thermal Decomposition of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$. A toluene-$d_8$ solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was sealed in a NMR tube under vacuum and heated to 423 K. After 4 days the signal at δ(H) –3.35 in the ^1H NMR spectrum had diminished in intensity, and after 11 days it had disappeared completely. In the $^{31}P\{^1H\}$ NMR spectrum the resonance due to *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was replaced by one associated with $[Pt(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 61.1 (^1J(Pt–P) = 4180 Hz)). When the solution was heated in air, the complex $[PtO_2(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 25.0 (^1J(Pt–P) = 3940 Hz)) was produced.

Reaction of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ with Tri-*n*-butylphosphine. To a solution of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$, prepared by treatment of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with carbon monoxide in toluene at 213 K, was added 1 mol equiv of P-*n*-Bu_3. The $^{31}P\{^1H\}$ NMR spectrum at 213 K indicated the formation of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)(P\text{-}n\text{-}Bu_3)]$ (δ(P-c-Hx_3) 24.2 (^1J(Pt–P) = 3064 Hz); δ(P-*n*-Bu_3) –24.4 (^1J(Pt–P) = 3230 Hz, ^2J(P–P) = 15 Hz)) and free P-c-Hx_3 (δ(P) 7.0). Addition of further P-*n*-Bu_3 resulted in some formation of $[Pt(CO)_2(P\text{-}n\text{-}Bu_3)_2]$ (δ(P) –19.3 (^1J(Pt–P) = 3191 Hz)).

(32) Leviston, P. G.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1976**, *110*, 271.

Similar treatment of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ with CN-*t*-Bu (1 mol equiv), Me_2S, or pyridine (excess) caused no reaction at 213 K, while displacement of P-c-Hx_3 (δ(P) 7.0) occurred at ambient temperature, accompanied by extensive decomposition.

Reaction of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ with Iodine. Excess iodine was added to a toluene solution of $[Pt(^{13}CO)_2(P\text{-}c\text{-}Hx_3)_2]$ at 213 K and, after the solution was left standing at this temperature for 2 h, the $^{31}P\{^1H\}$ NMR spectrum contained resonances due to *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 9.3 (^1J(Pt–P) = 2253 Hz)) and a very minor amount of *cis*-$[PtI_2(^{13}CO)(P\text{-}c\text{-}Hx_3)]$ (δ(P) 33.6 (^1J(Pt–P) = 2788 Hz, ^2J(P–C) 5 Hz)).

Reaction of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with Tetrafluoroethylene. A benzene solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was stirred under 1 atm of C_2F_4 for 2 days, which resulted in complete reaction to give *trans*-$[PtH(CF_2CF_2H)(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 36.9 (^1J(Pt–P) = 2905 Hz, ^3J(P–F) 15 Hz); δ(H) –9.95 (^1J(Pt–H) = 520 Hz, ^2J(P–H) = 16 Hz, ^3J(F–H) = 3 Hz)). Slow evaporation of the solvent allowed isolation of colorless crystals. (Anal. Calcd for $C_{38}H_{68}F_4P_2Pt$: C, 53.21; H, 8.00; F, 8.87. Found: C, 53.11; H, 8.13; F, 8.96.)

Reaction of *trans*-$(PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with Tetracyanoethylene. Tetracyanoethylene (1 mol equiv) was added to a toluene solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ at 213 K, giving a pale green solution, and quantitative formation of a new species (δ(P) 34.5 (^1J(Pt–P) = 2695 Hz); δ(H) –18.06 (^1J(Pt–H) = 1146 Hz, ^2J(P–H) 12 Hz)) resulted. Heating to 348 K for 1 h caused complete conversion to *trans*-$[PtH\{C(CN)=C(CN)_2\}(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 37.5 (^1J(Pt–P) = 2603 Hz); δ(H) –8.41 (^1J(Pt–H) = 777 Hz, ^2J(P–H) = 14 Hz)) and, after treatment with charcoal and filtration, slow evaporation of the solvent produced yellow crystals. (Anal. Calcd for $C_{41}H_{67}N_3P_2Pt$: C, 57.34; H, 7.87; N, 4.90. Found: C, 56.64; H, 8.08; N, 4.68. IR data: ν(C=C) 1595 cm^{-1}, ν(Pt—dH) and ν(C≡N) 2192, 2168, and 2144 cm^{-1}.)

Acknowledgment. Thanks are expressed to Johnson-Matthey Ltd for a generous loan of platinum salts and the continued financial support of the Natural Sciences and Engineering Research Council of Canada (H.C.C.) is gratefully acknowledged.

Registry No. *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$, 42764-83-0; $Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2$, 79769-84-9; $Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3$, 62987-80-8; $Pt(CO)_2(P\text{-}c\text{-}Hx_3)(P\text{-}n\text{-}Bu_3)$, 79769-85-0; $Pt(CO)_2(P\text{-}n\text{-}Bu_3)_2$, 79769-86-1; *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$, 53856-43-2; *cis*-$[PtI_2(Co)(P\text{-}c\text{-}Hx_3)$, 79813-73-3; *trans*-$[PtH(CF_2CF_2H)(P\text{-}c\text{-}Hx_3)_2]$, 79769-87-2; *trans*-$[PtH\{C(CN)=C(CN)_2\}(P\text{-}c\text{-}Hx_3)_2]$, 79769-88-3; C_2F_4, 116-14-3; $(NC)_2C=C(CN)_2$, 670-54-2; $PtH_2(P\text{-}c\text{-}Hx_3)_2\{(NC)_2C=C(CN)_2\}$, 79769-89-4.

Silicon in Synthesis. 14. (Methoxy(trimethylsilyl)methyl)lithium. A New Reagent for Carbonyl Homologation

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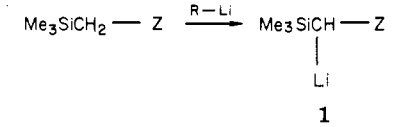
Received September 22, 1981

(Methoxy(trimethylsilyl)methyl)lithium (8) is generated by treatment of (methoxymethyl)trimethylsilane with *sec*-butyllithium. The reagent 8 reacts with aldehydes and ketones to give 1:1 adducts that are readily transformed into enol ethers, aldehydes, methoxymethyl alcohols, and methoxymethyl ketones.

Introduction

During the past decade or so a wide range of organosilicon reagents has been developed for use in organic synthesis.[2] Many of these reagents utilize the ability of the trimethylsilyl group to stabilize an adjacent carbon–metal bond. In general, for convenience, the choice of the

Scheme I



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(2) For recent reviews see: Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; p 761. Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.

0276-7333/82/2301-0553$01.25/0

Table I

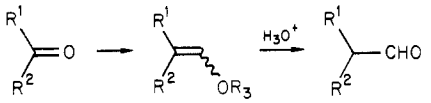
$$Me_3SiCH_2Cl^a + RONa \xrightarrow{ROH} Me_3SiOR + Me_3SiCH_2OR$$

R = Me	0%	75%
R = Et	11%	70%
R = *n*-Bu	31%	19%

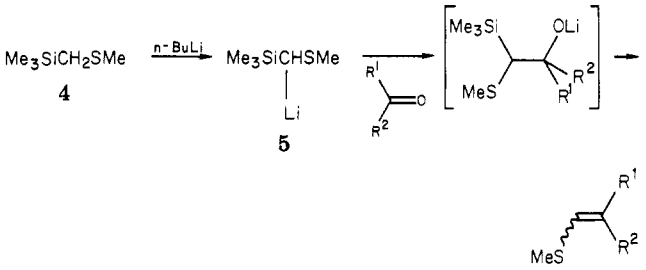
$$PhMe_2SiCH_2Cl \xrightarrow[EtOH]{EtONa} \underset{32\%}{Me_2Si(OEt)CH_2Ph} + \underset{42\%}{PhMe_2SiCH_2OEt} + \underset{16\%}{PhMe_2SiOEt}^{12}$$

[a] Me_3SiCH_2Br gives more cleavage products; aprotic solvents give more cleavage products.

Scheme II

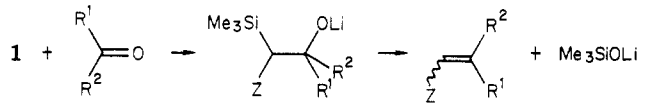


Scheme III



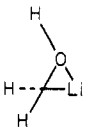
metal is lithium, since the synthesis of these reagents most frequently involves hydrogen–metal exchange using an alkyllithium as the base (Scheme I).

A comprehensive range of variations of this metalation process has been described, where the resulting species **1** usually is treated with either an aldehyde or a ketone to give a β-alkoxysilane **2**.[3] The adduct **2** either undergoes in situ syn elimination of the elements of lithium trimethylsilanolate to give an alkene or is reasonably stable and is eliminated to an alkene in a subsequent step. As such, this reaction, most frequently known as the Peterson reaction, may be viewed as a silicon version of the Wittig olefin synthesis. The exceptionally wide range of substituents Z make this an extremely flexible method of preparing functionalized alkenes. Furthermore, the lithium species **1** appear to be considerably more nucleophilic



than their phosphorane counterparts. Unfortunately, the overall method is not stereospecific, even though the elimination of trimethylsilanolate is known to be a syn process,[4] since the initial diastereomeric adducts are not formed with any overwhelming stereoselectivity. Consequently, if the stereochemical outcome of an olefination reaction is not a prime consideration, then the ((trimethylsilyl)methyl)lithium system **1** offers high nucleophilicity and large variations in Z.

While, as already alluded to above, the wide range of Z is a very commendable feature of the Peterson reaction, it is noticeable that Z = OR is absent from the list. Many lithio species adjacent to oxygen have been described,[5] and recently a theoretical description of *C*-lithiomethanol as a model for α-lithio ethers suggests that these compounds have an energy minimum as the bridged structure **3**.[6] A



large number of reagents has been studied where the carbon–lithium bond is adjacent to phosphorus (3 or 5 oxidation states) as well as an alkoxy group. These modified Wittig reagents convert aldehydes or ketones into their respective enol ether derivatives (Scheme II).[7] This important transformation forms the basis of a useful sequence that converts an aldehyde or a ketone into the homologous aldehyde or ketone. In purely descriptive terms, such a process is called *reductive nucleophilic*

(3) A wide range of reagents of the general type Me_3SiCH_2Z have been described, representative examples are Z = H, Ph, $SiMe_3$, PPh_2, $P(S)Ph_2$, SMe, $P(O)(EtO)_2$, SPh, SOPh, SePh, CN, CO_2H, CO_2Et, and Cl. For a more complete list consult the last citation in ref 2.

(4) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 133. Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

(5) $MeOCH_2Li$: Schollkopf, U. "Methoden der Organischen Chemie"; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart. 1970; Vol. 13, pp 87, 253. Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1482. Still, W. C.; Sreekumar, C. *Ibid.* **1980**, *102*, 1201. [2.3] sigmatropic rearrangement of α-alkoxy anions: Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, 1927. Oxyallyl anions: Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. Still, W. C.; MacDonald, T. L. *Ibid.* **1974**, *96*, 5561. Burke, S. D. *Tetrahedron Lett.* **1980**, 1285. Dipole-stabilized anions: Beak, P.; Baillargeon, M.; Carter, L. *J. Org. Chem.* **1978**, *43*, 4255. Beak, P.; McKinnie, B. G. *J. Am. Chem. Soc.* **1977**, *99*, 5213. Reitz, D. B.; Beak, P.; Farney, R. F.; Heimick, L. S. *Ibid.* **1978**, *100*, 5428. Beak, P.; McKinnie, B. G.; Reitz, D. B. *Tetrahedron Lett.* **1977**, 1839. Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. Schecker, R.; Seebach, D.; Lubosch, W. *Helv. Chim. Acta* **1978**, *61*, 512. Beak, P.; Carter, L. G. *J. Org. Chem.* **1981**, *46*, 2363. $LiOCH_2Li$: Seebach, D.; Meyer, N. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 438. Seebach, D.; Meyer, N. *Chem. Ber.* **1980**, *113*, 1290. α-Halo ethers as precursors to α-metallo ethers: Schollkopf, U.; Kuppers, H. *Tetrahedron Lett.* **1964**, 1503. Runge, F.; Taeger, E.; Fiedler, C.; Kahlert, E. *J. Prakt. Chem.* **1963**, *291*, 37. Welge, P. M.; Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 3144. α-Phenylthiohemiacetals as precursors to α-lithio ethers: Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6902. α-Lithio tetrahydrofuran fragmentation: Maercker, A.; Theasohn, W. *Justus Liebigs Ann. Chem.* **1971**, *747*, 70. Carbenoids from α-halo ethers: Olofson, R. A.; Lotts, K. D.; Barber, G. *Tetrahedron Lett.* **1976**, 3779. Wittig rearrangement of α-metallo ethers: Schollkopf, U.; Eisert, M. *Justus Liebigs Ann. Chem.* **1963**, *664*, 76. Dalrymple, D. L.; Kruger, T. L.; White, W. N. In "The Chemistry of the Ether Linkage"; Patai, S., Ed.; wiley: New York, 1967; p 618. Brook rearrangement: Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. For recent general reviews of α-heterosubstituted organometallics see: Krief, A. *Tetrahedron* 1980, **36**, 2531. Peterson, D. J. *Organomet. Chem. Rev., Sect. A* **1972**, *7*, 295.

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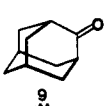
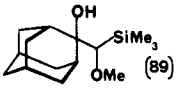
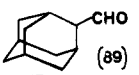
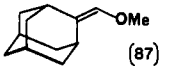
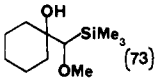
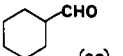
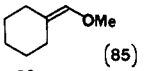
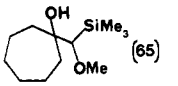
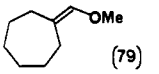
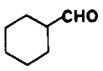
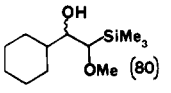
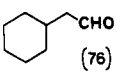
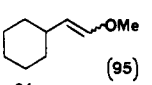
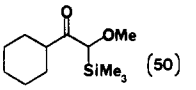
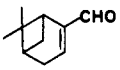
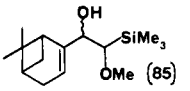
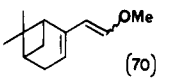
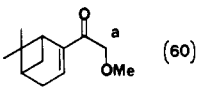
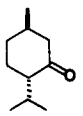
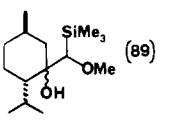
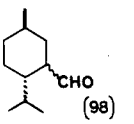
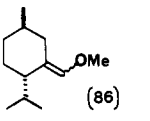
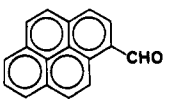
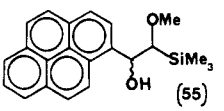
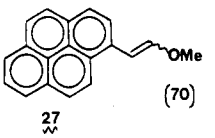
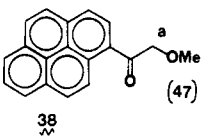
Table II[a]

substrate	adduct (%)	aldehyde (%)	enol ether (%)	methoxy ketone (%)
 9	 10	 17	 21	
	 11	 18	 22	
	 12	——	 23	
	 13	 19	 24	 36
	 14	——	 25	 37
	 15	 20	 26	
	 16	——	 27	 38

[a] These desilylated products resulted from chromatography over silica gel.

acylation. The original electrophilic carbonyl group in the substrate has become reduced in the homologous carbonyl compound.[8] Peterson[9] has reported that the reagent, ((methylthio)methyl)trimethylsilane **4**, is readily deprotonated by using *n*-butyllithium, and the resulting lithio species **5** on treatment with aldehydes or ketones gives thiomethyl enol ethers directly (Scheme III).

Reported attempts to deprotonate (methoxymethyl)trimethylsilane **6** using *n*-butyllithium resulted in nucleophilic attack at silicon and subsequent cleavage of the $-CH_2OMe$ group, giving trimethyl-*n*-butylsilane as an isolable product.[9] Treatment of **6** with *tert*-butyllithium gave the α-lithio species **7**, which could be regarded as a kinetic product.[9] Eisch has reported the lithiation of epoxyethylsilanes where lithium is adjacent to a triphenylsilyl group and an epoxy oxygen atom.[10]

Me_3SiCH_2OMe **6** $LiCH_2SiMe_2CH_2OMe$ **7** $Me_3SiCHOMe$ (Li) **8**

Results[11]

(Methoxymethyl)trimethylsilane **6** is readily prepared by treatment of (chloromethyl)trimethylsilane with sodium methoxide in methanol heated at reflux.[12] It is interesting

(8) For examples of methods used to conduct reductive nucleophilic acylation sequences see: Cooke, F.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 513. Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536. Seebach, D.; Grobel, G.-Th.; Beck, A. K.; Braun, M.; Geiss, K.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 443; Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 1926. Carey, F. A.; Neergaard, J. R. *Ibid.* **1971**, *36*, 2731. Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777. Corey, E. J.; Shulman, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 5522. Jones, P. F.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 526. Ferwanah, A.; Pressler, W.; Reichardt, C. *Tetrahedron Lett.* **1973**, 3979. Pettit, G. R.; Green, G.; Dunn, G. L.; Sunder-Plassmann, P. *J. Org. Chem.* **1970**, *35*, 1385. Reichardt, C.; Wurtheim, E.-U. *Synthesis* **1973**, 604. Blanchard, E. P.; Buchi, G. *J. Am. Chem. Soc.* **1963**, *85*, 995. Matteson, D. S.; Moody, R. J.; Jesthi, P. K. *Ibid.* **1975**, *97*, 5608. For an interesting method, particularly applicable to hindered ketones see: Corey, E. J.; Tius, M. A.; Das, J. *J. Am. Chem. Soc.* **1980**, *102*, 1742. For general references to nucleophilic acylation see: Lever, O. W. Jr. *Tetrahedron* **1976**, 1943. ApSimon, J.; Holmes, A. *Heterocycles* **1977**, *6*, 731. Martin, S. F. *Synthesis* **1979**, 633. Reference 7 describes phosphorus-based reagents that accomplish the conversion shown in Scheme II.

(9) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. Carey, F. A.; Court, A. S. *Ibid.* **1972**, *37*, 939.

(10) Eisch, J.; Galle, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4646.

(11) A preliminary account of this work has been reported. Magnus, P.; Roy, G. *J. Chem. Soc., Chem. Commun.* **1979**, 822. Part 13: Schwindeman, J. A.; Magnus, P. *Tetrahedron Lett.* **1981**, 4925.

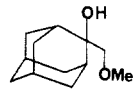
to note that use of higher alcohols and replacement of the trimethylsilyl group by a dimethylphenylsilyl group lead to increasing amounts of alkoxide attack at silicon and subsequent rearrangement. Table I shows this trend and demonstrates that it is by no means a foregone conclusion that treatment of alkoxides with (α-haloalkyl)silanes will give useful yields of the corresponding ethers.

Treatment of (methoxymethyl)trimethylsilane (**6**) in tetrahydrofuran at −78 °C with *sec*-butyllithium (1.4 M in cyclohexane) followed by warming the mixture to −30 °C gave solutions of (methoxy(trimethylsilyl)methyl)lithium (**8**) in >95% yield, as judged by its subsequent reactions with aldehydes and ketones. It is essential to bring the reaction mixture to −30 °C to ensure formation of **8**; at lower temperatures very little hydrogenmetal exchange occurs. Once **8** has been formed, it can be used at a variety of temperatures, usually between −78 and +25 °C is convenient.

Table II shows that **8** adds efficiently to a number of aldehydes and ketones to give 1:1 adducts, and, most notably, the elimination of lithium trimethylsilanolate (Me_3SiOLi) did not take place. This is in marked contrast to the thioanalogue of **8**, namely, **5**, where the reaction proceeds directly to the thio enol ether. The reagent **8** shows no marked stereoselectivity since the adducts **13**, **14**, **15**, and **16** were formed in the ratios 3:1, 1.6:1, 2:1, and 1:1, respectively as diastereomeric mixtures (NMR, VPC). The (β-hydroxyalkyl)silane adducts are labile to acidic conditions. When they are treated with 90% formic acid at room temperature, they are converted into aldehydes (Table II). For very sensitive aldehydes, acid-catalyzed elimination of trimethylsilanol is competitive with the destruction of the product aldehyde. This is the case with 1-pyrenylacetaldehyde.

Exposure of the β-hydroxysilanes **10**, **11**, **12**, **13**, **14**, and **15** to potassium hydride in tetrahydrofuran at 60 °C resulted in the elimination of potassium trimethylsilanolate to give the enol ethers **21**, **22**, **23**, **24**, **25**, **26**, and **27**, respectively.[16]

When the adamantane adduct **10** was treated with dry cesium fluoride in dimethyl sulfoxide at 80 °C, it was cleanly transformed into the desilylated product **28**. No



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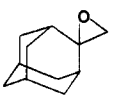

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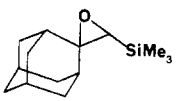

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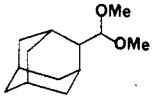

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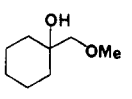

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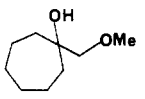

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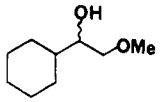
trace of elimination to give the enol ether **21** was detected. To verify this unusual result, adamantanone was converted into the epoxide **29** by treatment with dimethylsulfonium methylide and exposed to potassium methoxide in methanol to give **28**. In an attempt to prepare **10** by an alternative route, the epoxysilane **30** was treated with methanol containing a catalytic amount of trifluoroacetic acid at 0 °C.[17] The only product formed was adamantane-2-carboxaldehyde dimethyl acetal **31** (70%).[18] Exposure of a number of adducts to cesium fluoride in dimethyl sulfoxide resulted in desilylation. The substrates **11** and **12** gave **32** and **33**, respectively, but competitive elimination also took place resulting in **22** and **23**, whereas the adducts **13** and **15** were cleanly desilylated to give **34** and **35**, respectively.



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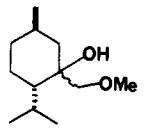

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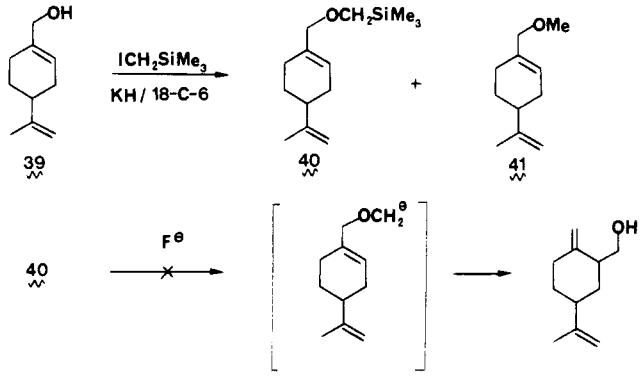
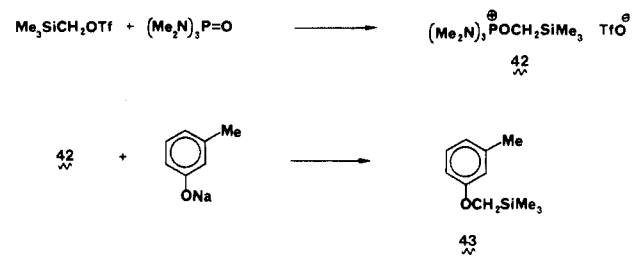
Oxidation of the adducts derived from aldehydes **13**, **14**, and **16** with pyridinium chlorochromate leads initially to the (α-trimethylsilyl)alkyl ketones, which on chromatography undergo desilylation to give α-methoxyalkyl ketones (Table II).

In an effort to use (trimethylsilyl)methyl ethers of allylic alcohols in [2.3] sigmatropic rearrangements, analogous to the tin system described by Still,[5] we treated perillyl alcohol **39** with (iodomethyl)trimethylsilane in the presence



of potassium hydride/18-crown-6 to give the ethers **40** and **41** (1:1). Exposure of **40** to cesium fluoride resulted only in conversion to the starting alcohol **39** and the methyl ether **41**. No rearrangement was detected.

As alluded to in the Introduction, (trimethylsilyl)methyl ethers can be difficult to prepare. In connection with another study we required the trimethylsilylmethyl ether of a phenol. It was found that trimethylsilyl trifluoromethanesulfonate[13] reacts with hexamethylphosphorus triamide to give the salt **42**. Treatment of this salt with *m*-cresol in the presence of sodium hydride gave a clean transformation, and the ether **43** was isolated in 72% yield.



(12) Speier, J. L. *J. Am. Chem. Soc.* **1948**, *70*, 4142. Speier, J. L.; Daubert, B. F.; McGregor, R. R. *Ibid.* **1948**, *70*, 1117. Earborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1957**, 137.
(13) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *107*, 6452.
(14) Kende, A. S.; Blacklock, T. *J. Tetrahedron Lett.* **1980**, 3119.
(15) Farcasiu, D. *Synthesis* **1972**, 615.
(16) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.
(17) Robbins, C. M.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 697.
(18) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

Finally, all attempts to make a cuprate species of 8 were unsuccessful.

Conclusions

(Methoxy(trimethylsilyl)methyl)lithium 8 converts ketones and aldehydes into (β-hydroxy-α-methoxyalkyl)trimethylsilane adducts (Table II). These adducts are readily transformed into enol ethers, aldehydes, methoxymethyl alcohols, and methoxymethyl ketones. The major advantage the reagent 8 offers over modified Wittig reagents is higher nucleophilicity and less steric encumbrance. The conversion of menthone into 15 is exemplary.

Kende[14] has recently reported a successful application of this new homologation sequence to the synthesis of a warburganal, where other methods (including Wittig reagents) to convert a ketone into the homologous aldehyde failed.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer grating spectrometer. ^1H NMR spectra were recorded on either a Varian A-60A or Varian EM-360 (90-MHz) spectrometer. For compounds containing a trimethylsilyl group, spectra were recorded in the stated solvents containing approximately 2% benzene as an internal standard. Mass spectra were recorded on a Consolidated Electronic MS-9 double-focusing mass spectrometer. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. Gas chromatographic analyses were done on a Perkin-Elmer 3920B instrument with 10% OV101 on Chrom WHP (80-100) or 10% SE-30 on Chrom DAW (100-120). Plate layer chromatography (PLC) was done by eluting with petroleum ether (bp 60–90 °C) and ethyl acetate (4:1) unless otherwise specified. Column chromatography was carried out by using silica gel (nominal grade 923). All solvents were dried and purified by standard techniques prior to use. Reactions involving alkyllithiums were run under argon or nitrogen.

(Methoxymethyl)trimethylsilane (6)[12] was prepared as described in the literature:[12] bp 83 °C (760mm); NMR (CCl_4) δ 0.2 (9 H, s), 3.1 (2 H, s), 3.4 (3 H, s).

2-(Methoxy(trimethylsilyl)methyl)-2-adamantanol (10). (Methoxymethyl)trimethylsilane (6) (0.66 mL, 4.23 mmol) in dry tetrahydrofuran (6.0 mL) was cooled to −78 °C and *sec*-butyllithium (3.0 mL, 4.23 mmol, 1.4 M in cyclohexane) slowly added via syringe. The mixture was warmed to −25 °C and held at this temperature for 0.5 h to ensure complete formation of (methoxy(trimethylsilyl)methyl)lithium (8). The above pale yellow solution was cooled to −35 °C and adamantanone (9) (0.57 g, 3.8 mmol) added. The mixture was slowly allowed to warm to 25 °C over 1.5 h and then quenched with saturated aqueous ammonium chloride solution (30 mL) and the solution extracted with ether (2 × 30 mL). The ether layer was washed with water (2 × 20 mL) and saturated aqueous sodium chloride solution (10 mL), dried ($MgSO_4$), and evaporated in vacuo to give 10 (0.91 g, 89%): mp 65–67 °C (from petroleum ether (bp 30–40 °C)/ethyl acetate); IR (Nujol) 3500, 2900, 2850, 1450, 1375, 1320, 1250, 1170, 1050, 990, 930, 910, 870, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.1 (9 H, s), 1.65 (10 H, b s), 1.7(4 H, b s), 2.2 (1 H, b s), 3.4 (3 H, s); mass spectrum *m/e* ($M^+ - H_2O$) 250 (87.5), 236 (60), 223 (40), 205 (70), 178 (100). Anal. Calcd for $C_{15}H_{28}SiO_2$ requires: C, 67.16; H, 10.45. Found: C, 67.04; H, 10.30.

2-(Methoxymethyl)-2-adamantanol (28). The adduct 10 (50 mg, 0.186 mmol) in dry dimethyl sulfoxide (3 mL) containing anhydrous cesium fluoride (0.04 g, 0.2 mmol) was heated at 80 °C for 1 h. The mixture was cooled to room temperature and quenched with water (10 mL) and the solution extracted with ether (2 × 10 mL). Drying ($MgSO_4$) and evaporation of the extract gave 26 (36 mg, 98%): mp 86–87 °C (sublimation at 32 °C (0.1 mmHg)); IR (Nujol) 3520, 2900, 1485, 1470, 1460, 1350, 1340, 1195, 1170, 1100, 1050, 1035, 965, 955, 935, 875, 880, 810 cm^{-1}; NMR ($CDCl_3$) δ 1.2 (4 H, b s), 1.7 (10 H, b s), 3.4 (3 H, s), 3.5 (2 H, s); mass spectrum, *m/e* 196 (0.26), 178 (3), 164 (2), 152 (10), 151 (100), 150 (3.6), 148 (3.1), 135 (2), 109 (2.3), 107 (5), 105 (2.9), 95 (3), 93 (6.3), 92 (13.3), 81 (7). Anal. Calcd for $C_{12}H_{20}O_2$ requires: C, 73.47; H, 10.20. Found: C, 73.66; H, 10.38.

Adamantylidene oxide (29), prepared by the literature method[15] (trimethylsulfonium iodide/sodium hydride/tetrahydrofuran, mp 40 °C; NMR ($CDCl_3$) δ 1.4 (2 H), 1.9 (12 H, b s), 2.6 (2 H)), on treatment with potassium methoxide in methanol for 4 days at 55 °C gave 28 (85%), whose NMR, IR, and mass spectra, melting point, and mixed melting point were identical with those of the compound described above.

2-(Dimethoxymethyl)-2-adamantane (31). The epoxysilane 30 (230 mg, 0.97 mmol; from 2-adamantanone and (chloro(trimethylsilyl)methyl)lithium),[8] in methanol (2 mL) at 0 °C was treated with trifluoroacetic acid (0.1 mL). After 1 h the mixture was quenched with saturated aqueous sodium bicarbonate (30 mL) and the solution extracted with ether (2 × 30 mL), dried ($MgSO_4$), and evaporated to give 31 (70%), purified by PLC IR (neat liquid) 2900, 2850, 2650, 1450, 1385, 1360, 1350, 1310, 1260, 1250, 1190, 1135, 1100, 1065, 1045, 1040, 985, 970, 960, 940, 910, 880, 840, 820 cm^{-1}; NMR (CCl_4) δ 1.6–2.0 (14 H, b m), 3.15 (1 H, b s), 3.40 (6 H, s), 3.70 (1 H, b s); mass spectrum, *m/e* 210 (1.6), 194 (1.6), 179 (38), 178 (100), 165 (89), 164 (20); M^+ corresponding to $C_{13}H_{22}O_2$.

Adamantane-2-carboxaldehyde (17). The adduct 10 (50 mg, 0.186 mmol) in 90% formic acid (1 mL) was stirred at 0 °C to 25 °C over 0.5 h and the mixture evaporated under reduced pressure (0.1 mm) to give 17 (30 mg, 89%): mp 99–102 °C; IR (Nujol) 2900, 2850, 2700, 1725, 1450, 1100, 935, 875 cm^{-1}; NMR ($CDCl_3$) δ 1.75–2.00 (10 H, b), 2.10 (2 H, b s), 2.20 (1 H, b s), 2.45 (2 H, b s), 9.7 (1 H); mass spectrum (*m/e*) calcd for $C_{11}H_{16}O$ 164.120, obsd 164.120; mass spectrum, *m/e* 164 (62), 162 (31), 150 (14), 136 (35), 135 (100), 134 (55).

2-Methoxy-2-adamantylidene (21). The adduct 10 (50 mg, 0.18 mmol) in dry tetrahydrofuran (4 mL) under argon was treated with potassium hydride (0.2 g, 0.8 mmol, 20% dispersion in oil, washed with pentane and decanted). The mixture was heated at 60 °C for 1 h and then quenched with saturated aqueous ammonium chloride (10 mL) and the solution extracted with ether (2 × 20 mL). The extract was eashed with water (2 × 10 mL) and saturated aqueous sodium chloride (10 mL), dried ($MgSO_4$), and evaporated in vacuo to give 21 (28 mg, 87%), purified by PLC: IR (thin film) 2920, 2860, 1460, 1370, 1300, 1200, 1150, 1120, 1030, 970, 930 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.2(14 H, b), 3.6 (3 H), 5.8 (1 H); mass spectrum calcd for $C_{12}H_{18}O$ 178.136, obsd 178.136; mass spectrum, *m/e* 178 (100), 163 (11), 151 (3), 135 (5), 131 (6), 121 (24).

1-(Methoxy(trimethylsilyl)methyl)cyclohexanol (11). (Methoxy(trimethylsilyl)methyl)lithium 8 (prepared as described from (methoxymethyl)trimethylsilane (0.66 mL 4.2 mmol) was treated at −35 °C with cyclohexanone (0.4 mL, 3.8 mmol). After 1.5 h the above mixture was worked up in the usual way to give the adduct 11 (0.6 g, 73%): bp 60 °C (0.05mmHg); IR (thin film) 3450, 2940, 2850, 2820, 1450, 1375, 1350, 1310, 1300, 1260, 1250, 1175, 1150, 1090, 1050, 980, 960, 940, 890, 870, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.0 (9 H), 1.35 (10 H, b s), 2.15 (1 H, –OH), 2.45 (1 H), 3.30 (3 H); mass spectrum (*m/e*) calcd for $C_{11}H_{24}SiO_2$ 216.156, obsd 216.155.

The adduct 11 (200 mg) was dissolved in 90% formic acid (2 mL) and this solution stirred at 25 °C for 2 h. Workup as described gave cyclohexane-carboxaldehyde 18 (90%): IR ν(max) (thin film) 2920, 2850, 2700, 1725, 1450, 1440, 1410, 1375, 1340, 1250, 1120, 1050, 940, 830, 750 cm^{-1}; NMR (CCl_4) δ 1.5 (10 H, b s), 2.3 (1 H, b m), 9.7 (1 H, d, J = 2 Hz).

The adduct 11 (150 mg, 0.69 mmol) was treated with potassium hydride (0.2 g) in dry tetrahydrofuran (3 mL) at reflux for 3 h. Workup as described gave the enol ether 22 (77 mg, 85%) which was identical with an authentic sample.[19]

The adduct 11 (150 mg) in dimethyl sulfoxide (2 mL) containing cesium fluoride (117 mg) was heated at 80 °C for 1 h. The mixture was worked up in the usual way to give a mixture (70 mg, 69%) of 22 and 32 in approximately 1:1 ratio.

1-(Methoxy(trimethylsilyl)methyl)cycloheptanol (12). (Methoxy(trimethylsilyl)methyl)lithium (8) (prepared as described from (methoxymethyl)trimethylsilane (2.1 mL, 13.37 mmol)) was treated at −30 °C with freshly distilled cycloheptanone (1 mL,

(19) Wittig, G.; Boell, W.; Krueck, K. H. *Chem. Ber.* **1962**, *95*, 2514.

8.9 mmol). The mixture was stirred at −30 °C for 0.5 h and then slowly warmed to 0 °C over 1 h. Workup, in the usual way, gave an oil that was distilled to give **12** (1.3 g, 65%): bp 103 °C (2.2mmHg); IR (thin film) 3450, 2920, 2840, 2800, 1460, 1440, 1250, 1080, 1050, 1020, 920, 900, 860, 840, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.1 (9 H), 1.5 (12 H, b s), 2.6 (1 H), 3.2 (1 H), 3.4 (3 H). Anal. Calcd for $C_{12}H_{26}SiO_2$ requires: C, 62.61; H, 11.30. Found: C, 62.42; H, 11.18.

The adduct **12** (250 mg, 1.08 mmol) was treated with potassium hydride (260 mg) in dry tetrahydrofuran (10 mL) at reflux for 10 h. Workup as described gave the enol ether **23** (120 mg, 79%): bp 80 °C (1.5mmHg); IR (thin film) 2920, 2850, 1670, 1460, 1440, 1370, 1340, 1250, 1210, 1190, 1150, 1120, 1050, 1000, 960, 890, 830, 800, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.5 (8 H, b s), 2.0–2.4 (4 H, b m), 3.3 (1 H, s), 3.5 (2 H, s), 3.6 (3 H, s). Desilylation of **12** in the described manner (CsF/Me_2SO) gave a mixture of the enol ether **23** and the alcohol **33** (3:1 ratio, 70% yield).

(Methoxy(trimethylsilyl)methyl)-1-cyclohexylcarbinol (13). (Methoxy(trimethylsilyl)methyl)lithium **8** (prepared as described from (methoxymethyl)trimethylsilane (1.0 mL 6.68 mmol)) was treated at −35 °C with cyclohexane carboxaldehyde (0.54 mL, 4.4 mmol) and the mixture warmed to 25 °C over 1.5 h. Workup, in the usual way, gave a mixture of diastereomeric adducts **13** (0.8 g, 80%): bp 69 °C (0.2mmHg); IR (thin film) 3450, 2920, 2860, 1450, 1250, 1100, 1080, 1060, 1040, 980, 940, 890, 845, 760 cm^{-1}; NMR ($CDCl_3$) δ 0.2 (9 H), 1.1–1.9 (11 H, b), 2.4 (1 H, m) 3.1–3.2 (1 H, d, J = 2.5 Hz), 3.5–3.6 (3 H, d, 3:1 ratio for the two adducts). No mass ion could be obtained for this adduct. $M^+ - 15$ corresponds to $C_{12}H_{26}O_2Si$. Anal. Calcd for $C_{12}H_{26}O_2Si$ requires: C, 62.60; H, 11.30. Found: C, 62.36; H, 11.14.

The adduct **13** (50 mg) was dissolved in 90% formic acid (1 mL) and the mixture stirred at 25 °C for 0.5 h. Workup as described gave cyclohexylacetaldehyde **19** (21 mg 76%): IR ν(max) (thin film) 2720, 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.8 (11 H, b m), 2.0–2.2 (2 H, m), 9.6 (1 H, t, J = 2 Hz).

The adduct **13** (0.5 g, 2.1 mmol) was treated with potassium hydride (1.0 g) in dry tetrahydrofuran (8 mL) at reflux for 3 h. Workup as described gave the enol ether **24** (0.29 g, 95%): IR (thin film) 2920, 2840, 1660, 1440, 1375, 1280, 1250, 1225, 1200, 1160, 1100, 1080, 970, 940, 880, 830 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.9 (10 H, b m), 2.1 (1 H, b s), 3.6 (3 H, two singlets), 4.2–4.9 (2 H, m), 5.8–5.9 (1 H, d, J = 6 Hz), 6.2–6.5 (1 H, d, J = 12 Hz) for E and Z isomers; mass spectrum (m/e) calcd for $C_9H_{16}O$ 140.120, obsd 140.120.

The adduct **13** (150 mg) in dimethyl sulfoxide (5 mL) containing cesium fluoride (117 mg) was heated at 80 °C for 1 h. The mixture was worked up in the usual way to give **34** (60%): IR (thin film) 3450, 2920, 2860, 1450, 1100, 1080, 1060, 1040, 980, 890, 810, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.9 (11 H, b s), 2.4 (1 H, b s), 3.1–3.2 (1 H, m), 3.5–3.6 (3 H, two singlets, diastereomers), 3.7 (2 H, d, J = 3 Hz); mass spectrum (m/e) ($M^+ - H_2O$) calcd for $C_9H_{16}O$ 140.120, obsd 140.120.

Methoxy(trimethylsilyl)methyl Cyclohexyl Ketone (36). Pyridinium chlorochromate (70 mg, 0.325 mmol), slurried in dichloromethane (1 mL) at 0 °C, was treated with the adduct **13** (50 mg, 0.217 mmol) in dichloromethane (1.0 mL). After 1 h the mixture was diluted with ether (15 mL) and filtered through Celite. Evaporation and plate layer chromatography of the residue gave **36** (31 mg 50%); IR (thin film) 2920, 2860, 1725, 1450, 1375, 1310, 1250, 1100, 890, 845, 750 cm^{-1}; NMR (CCl_4) δ 0.0 (9 H), 1.0–1.8 (10 H, b s), 2.1 (1 H, b s), 3.3 (3 H), 3.8 (1 H); mass spectrum (m/e) calcd for $C_{12}H_{24}O_2Si$ 228.156, obsd 228.155.

1-(Methoxy(trimethylsilyl)methyl)myrtenol (14). (Methoxy(trimethylsilyl)methyl)lithium (8) (prepared as described from (methoxymethyl)trimethylsilane (2.55 mL, 9.9 mmol)) was treated with freshly distilled myrtenal (1 g, 6.6 mmol) in tetrahydrofuran (1 mL) and the mixture stirred at −30 °C for 1 h and then warmed to 25 °C over 1.5 h. Workup, in the usual way, gave **14** (1.5 g, 85%): bp 120 °C (0.2mmHg); NMR (CCl_4) δ 0.1 (9 H, two singlets, diastereomers), 0.8 (6 H, d), 1.3 (4 H, b s), 2.3 (3 H, b m), 2.8 (1 H, m), 3.3 (3 H, two singlets, diastereomers), 3.85 (1 H, m), 5.4 (1 H, b s). ($M^+ - H_2O$) mass spectrum (m/e) calcd for $C_{15}H_{26}OSi$ 250.175, obsd 250.175. Anal. Calcd for $C_{15}H_{28}O_2Si$ requires: C, 67.16; H, 10.44. Found: C, 66.90; H, 10.40.

Methoxymethyl Myrtenyl Ketone (37). The adduct **14** (250 mg, 0.93 mmol) in dichloromethane (6 mL) at 0 °C was treated with pyridinium chlorochromate (301 mg, 1.4 mmol). Workup, as before, followed by chromatography over silica gel gave **37** (110 mg, 60%): IR 3010, 2920, 2860, 2820, 1670, 1610, 1460, 1370, 1360, 1240, 1100, 1050, 830, 780, 750, 700 cm^{-1}; NMR (CCl_4) δ 0.8 (3 H), 1.3 (3 H), 1.6–2.5 (6 H, b m), 3.3 (3 H), 3.9 (2 H, s), 6.5 (1 H, b s). Anal. Calcd for $C_{12}H_{18}O_2$ requires: C, 74.23; H, 9.28. Found: C, 74.01; H, 9.18.

1-Methoxymyrta-1,3-diene (25). The adduct **14** (210 mg, 0.78 mmol) was added dropwise in tetrahydrofuran (1 mL) to potassium hydride (250 mg) in tetrahydrofuran (6 mL). The mixture was heated at 60 °C for 1 h and worked up in the usual way to give **25** (70%): bp 100 °C (1mmHg); IR (thin film) 3030, 2920, 2880, 2840, 1670, 1640, 1600, 1460, 1375, 1360, 1270, 1190, 1100, 1050, 960, 890, 830, 800, 780 cm^{-1}; NMR (CCl_4) δ 0.9 (3 H, b s), 1.1 (2 H, b s), 1.3 (3 H, b s), 1.7 (2 H, bs), 2.0–2.6 (2 H, b m), 3.3 and 3.6 (3 H, two singlets, 1.6:1 ratio for E and Z isomers), 5.2–5.8 (4 H, b m); mass spectrum (m/e) calcd for $C_{12}H_{18}O$ 178.135, obsd 178.136.

1-(Methoxy(trimethylsilyl)methyl)menthol (15). (Methoxy(trimethylsilyl)methyl)lithium (8) (prepared as described from (methoxymethyl)trimethylsilane (1.55 mL, 9.9 mmol)) was treated with freshly distilled L-menthone (1 mL, 6.65 mmol) in dry tetrahydrofuran (2 mL). The mixture was stirred at −30 °C for 0.5 h and then warmed to 25 °C over 1.5 h. Workup in the usual way gave **15** (1.6 g, 89%): bp 83 °C (1.5mmHg); IR (thin film) 3500, 2940, 2920, 1450, 1380, 1360, 1320, 1260, 1250, 1175, 1150, 1080, 1070, 1000, 980, 940, 930, 910, 880, 860, 840, 780, 760, 750 cm^{-1}; NMR (CCl_4) δ 0.1 (9 H, d), 0.6–0.9 (9 H, b m), 1.1–1.9 (9 H, b m), 3.0 (1 H, b s), 3.2 (1 H, d), 3.4 (3 H, s); mass spectrum ($M^+ - H_2O$) m/e calcd for $C_{15}H_{30}OSi$ 253.972, obsd 253.972. Anal. Calcd for $C_{15}H_{32}O_2Si$ requires: C, 66.17; H, 11.76. Found: C, 65.98; H, 11.66.

The adduct **15** (250 mg, 0.9 mmol) was stirred with 88% formic acid (2 mL) at 25 °C for 1 h. The mixture was poured into saturated aqueous sodium bicarbonate solution (20 mL) and extracted with ether (3 × 10 mL). Evaporation and distillation of the residue gave menthyl carboxaldehyde **20** (150 mg, 98%): bp 80 °C (0.4mmHg); IR (thin film) 2960, 2920, 2880, 2700, 1720, 1450, 1380, 1370, 1250, 1220, 1180, 1110, 1050, 1030, 930, 840, 780, 750, 700 cm^{-1}; NMR (CCl_4) δ 0.7–1.0 (9 H, b m), 1.0–2.2 (10 H, b m), 9.3 and 9.7 (1 H, two singlets for epimers of the aldehyde, 1:1); mass spectrum (m/e) calcd for $C_{11}H_{20}O$ 168.151, obsd 168.150.

The adduct **15** (400 mg, 1.47 mmol) in tetrahydrofuran (10 mL) was treated with potassium hydride (440 mg) and the mixture heated at 60 °C for 1 h. Workup in the usual way gave **26** (230 mg, 86%): bp 95 °C (0.4mmHg); IR (thin film) 2940, 2920, 2860, 1670, 1460, 1450, 1370, 1360, 1280, 1250, 1230, 1220, 1200, 1180, 1120, 1110, 1060, 1050, 1010, 980, 960, 890, 870, 830, 750 cm^{-1}; NMR (CCl_4) δ 0.8 (3 H, d, J = 3 Hz), 0.9 (6 H, d, J = 3 Hz), 1.2 (2 H, s), 1.5–1.9 (5 H, b m), 2.1–2.4 (2 H, b m), 3.5 (3 H, s), 5.7 (1 H, s); mass spectrum (m/e) calcd for $C_{12}H_{22}O$ 182.167, obsd 182.167.

The adduct **15** (200 mg, 0.74 mmol) in dimethyl sulfoxide (3 mL) containing cesium fluoride (123 mg) was heated at 70 °C for 24 h. The mixture was worked up in the usual way to give **35** (100 mg, 67%): IR (thin film) 3400, 2940, 2860, 1460, 1450, 1190, 1110, 1050, 1030, 950 cm^{-1}; NMR (CCl_4) δ 0.6 (3 H, d, J = 3.5 Hz), 0.8 (6 H, d, J = 4 Hz), 1.0–1.8 (9 H, b m), 3.0 (2 H, d, epimers), 3.1 (3 H, s). Mass spectrum (m/e) calcd for $C_{12}H_{24}O_2$ 200.177, obsd 200.177.

(Methoxy(trimethylsilyl)methyl)-1-pyrenylcarbinol (16). (Methoxy(trimethylsilyl)methyl)lithium (8) (prepared as described from (methoxymethyl)trimethylsilane (2.1 mL, 13.37 mmol)) was treated with 1-pyrenecarboxaldehyde (1.0 g, 4.34 mmol) dissolved in tetrahydrofuran (5 mL). The mixture was stirred at −30 °C for 0.5 h and then warmed to 25 °C over 1 h. Workup in the usual way gave **16** (0.80 g, 55%) purified by plate layer chromatography: IR (thin film) 3400, 3040, 2960, 2920, 2890, 2800, 1600, 1590, 1580, 1450, 1410, 1370, 1250, 1180, 1060, 1040, 920, 860, 750, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.1 (9 H, s), 3.5 (3 H, s), 3.8 (1 H, b m), 6.2 (1 H, d, J = 6 Hz), 8.0–8.6 (9 H, b m); mass spectrum (m/e) calcd for $C_{22}H_{24}O_2Si$ 348.154, obsd 348.154. Anal. Calcd for $C_{22}H_{24}O_2Si$ requires: C, 75.86; H, 6.90. Found: C, 75.66; H, 6.68.

Methoxymethyl 1-Pyrenyl Ketone (38). The adduct **16** (130 mg, 0.37 mmol) in dry dichloromethane (5 mL) at 0 °C was treated with pyridinium chlorochromate (120 mg). After 1 h at 25 °C, the mixture was worked up and chromatographed over silica gel

to give **38** (47%, 48 mg): mp 45 °C; IR 3040, 2920, 1670, 1590, 1460, 1370, 1200, 900, 840 cm^{-1}; NMR ($CDCl_3$) δ 3.70 (3 H, s), 4.35 (2 H, s), 7.9–8.3 (9 H, m); mass spectrum (*m/e*) calcd for $C_{19}H_{14}O_2$ 274.099, obsd 274.100.

The adduct **16** (100 mg, 0.28 mmol) in dry tetrahydrofuran (5 mL) was treated with potassium hydride (35 mg) and the mixture heated at 60 °C for 12 h. Workup in the usual way gave **27** (70%, 78 mg purified by plate layer chromatography): IR (thin film) 3040, 2940, 2920, 2850, 1630, 1460, 1410, 1330, 1220, 1210, 1150, 840, 710 cm^{-1}; NMR ($CDCl_3$) δ 3.9 (3 H, s), 7.05 (2 H, ABq., *J* = 14 Hz), 8.0–8.5 (9 H, b m); mass spectrum (*m/e*) calcd for $C_{19}H_{14}O$ 258.104, obsd 258.104.

Perilla Alcohol (Trimethylsilyl)methyl Ether (40). Perilla alcohol (**39**) (1.8 g, 0.118 mmol) in dry THF (12 mL) and sodium hydride (370 mg) were heated at reflux for 2 h. (Iodomethyl)-trimethylsilane (3.2 g, 0.15 mmol) was added to the above mixture and the solution maintained at reflux for 15 h. The mixture was poured into saturated aqueous sodium bicarbonate (100 mL) and the solution extracted with ether (2 × 30 mL), dried ($MgSO_4$), and evaporated to give an oil (2.86 g). Plate layer chromatography of this oil gave two products. **40** (0.86 g): IR (thin film) 3080, 2960, 2920, 1640, 1250, 1070, 860, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.1 (9 H, s), 1.0 (2 H, s), 1.8 (3 H, s), 2.0–2.2 (7 H, b m), 4.0 (2 H, t, *J* = 10 Hz), 4.7 (2 H, s), 5.7 (1 H, b s); mass spectrum (*m/e*) calcd for $C_{14}H_{26}SiO$ 238.175, obsd 238.176. **41** (0.58 g): NMR ($CDll_3$) δ 3.3 (3 H, s, –OMe); mass spectrum (*m/e*) calcd for $C_{11}H_{18}O$ 166.136, obsd 166.136. The ratio of **40** to **41** is ca. 1:1 (VPC) in a yield of 30% for each product.

((Trimethylsilyl)methoxy)tris(dimethylamino)-phosphonium Trifluorosulfonate (42). To a solution of (trimethylsilyl)methyl trifluoromethanesulfonate (519 mg, 2.2 mmol) in dry THF (5 mL) was added HMPA (447 mg, 2.5 mmol). A colorless crystalline precipitate formed immediately. Filtration gave the salt **42** (660 mg, 69%): mp 150–152 °C; NMR (Me_2SO-d_6) δ 3.88 (1 H, s), 3.82 (1 H, s), 2.68 (9 H, s), 2.54 (9 H, s), 0.09 (9 H, s). The salt did not give satisfactory mass spectrum or microanalytical data.

***O*-((Trimethylsilyl)methyl)-*m*-cresol (43).** *m*-Cresol (108 mg, 1 mmol) in THF (5 mL) was treated with NaH (26 mg) and the mixture stirred 4 h at 20 °C. The salt **42** (410 mg, 1 mmol) was added to the above solution and the mixture stirred for 48 h at 20 °C. Water (10 mL) was added to the above mixture and the solution extracted with ether (2 × 20 mL), dried ($MgSO_4$), and evaporated to give **43** (140 mg, 72%): IR (thin film) 2950, 1600, 1490, 1250, 1154, 860, 840 cm^{-1}; NMR ($CDCl_3$) δ 7.30–6.80 (4 H, m), 3.53 (2 H, s), 2.70 (3 H, s), 0.1 (9 H, s). This compound did not give satisfactory mass spectrum ($M^+ - 15$) or microanalytical data, although the above spectra, because of their simplicity, confirm the structure.

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Registry No. **6**, 14704-14-4; *8*, 73061-27-5; **9**, 700-58-3; **10**, 73061-29-7; **11**, 73061-28-6; **12**, 80434-53-3; **13** isomer 1, 80434-54-4; **13** isomer 2, 80434-66-8; **14**, 80434-55-5; **15**, 80434-56-6; **16** isomer 1, 80434-57-7; **16** isomer 2, 80434-58-8; **17**, 39750-93-1; **18**, 2043-61-0; **19**, 5664-21-1; **20** isomer 1, 80434-59-9; **20** isomer 2, 80482-64-0; **21**, 72590-63-7; **22**, 19096-89-0; **23**, 66051-09-0; (*E*)-**24**, 80434-60-2; (*Z*)-**24**, 80434-61-3; (*E*)-**25**, 80434-62-4; (*Z*)-**25**, 80447-42-3; **26**, 80447-43-4; **27**, 80434-63-5; **28**, 73061-33-3; **29**, 24759-97-5; **30**, 63830-94-4; **31**, 80434-64-6; **32**, 73061-32-2; **33**, 80434-65-7; **34**, 73061-34-4; **35** isomer 1, 80434-67-9; **35** isomer 2, 80434-68-0; **36**, 73061-35-5; **37**, 80441-10-7; **38**, 80434-69-1; **39**, 536-59-4; **40**, 80434-70-4; **41**, 80434-71-5; **42**, 80434-73-7; **43**, 80434-74-8; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; myrtenal, 23727-16-4; L-menthone, 14073-97-3; 1-pyrenecarboxaldehyde, 3029-19-4.

Communications

Reduction of Nitriles by a Binuclear Tantalum Hydride Complex. Structural Study of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2](\mu\text{-}\eta^1\text{-}N, \eta^2\text{-}C,N\text{-}NCHMe)(\mu\text{-}Cl)(\mu\text{-}H)[(\eta^5\text{-}C_5Me_4Et)TaCl]$

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Summary: $[TaCp'Cl_2H]_2$ (Cp′ = η^5-C_5Me_4Et) reacts with acetonitrile to give $Ta_2Cp'_2Cl_4(H)(NCHMe)$. A single-crystal X-ray structure shows that $Ta_2Cp'_2Cl_4(H)(NCHMe)$ has a structure related to that of $Ta_2Cp'_2Cl_4(H)(CHO)$ and $Ta_2Cp'_2Cl_4(H)(Me_3PCH)(O)$ in which the three bridging positions between the two tantalum atoms are occupied by the nitrogen of the NCHMe ligand, a chloride, and a hydride. Addition of ethylene to $Ta_2Cp'_2Cl_4(H)(NCHMe)$ yields $Cp'Cl_2TaCH_2CH_2CH_2CH_2$ and $TaCp'Cl_2(NEt)$ by a proposed ethylene-induced formation of a C–H bond on one tantalum center.

We have been exploring the reactions of $[TaCp'Cl_2H]_2$[1] (Cp′ = η^5-C_5Me_4Et) with reducible substrates in order to probe the question concerning the role of more than one metal in such reactions. For example, we have shown that carbon monoxide is reduced to give a dimeric formyl hydride complex in which the formyl and hydride are trapped between the two metal centers.[2,3] Here we show that nitriles are also reduced to give dimeric species whose structures are related to that of the formyl hydride product.

$[TaCp'Cl_2H]_2$ reacts rapidly with one and only one equivalent of acetonitrile at 25 °C to give dimeric, orange-red $Ta_2Cp'_2Cl_4(H)(NCHMe)$.[4] The analogous reaction between $[TaCp'Cl_2H]_2$ and CD_3CN gives $Ta_2Cp'_2Cl_4(H)[NCH(CD_3)]$, between $[TaCp'Cl_2D]_2$ and CH_3CN gives $Ta_2Cp'_2Cl_4(D)(NCDMe)$, and between [Ta-

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