brane feature would be a specified arrangement of different substrates in different binding sites depending on their properties. We can also envisage a wider scope of other applications, in both mechanistic and practical senses, to barrier-dependent phenomena such as encapsulation and transport of various substrates.

Quadruply Bonded Tetramethyltetrakis(trialkylphosphine)dimolybdenum Compounds: Phosphine Exchange Kinetics, Acetone Formation with Carbon Monoxide, and Crystal Structure of Mo2Me4(PMe3)4

Gregory S. Girolami, Vera V. Mainz, and
Richard A. Andersen*

*Department of Chemistry, University of California
Berkeley, California 94720*

Sara H. Vollmer[†] and Victor W. Day*

*Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
and Crystalytics Company
Lincoln, Nebraska 68501*

Creation of coordinative unsaturation about a metal center is crucial for the generation of a catalytic cycle.[1] One of the most general methods for achieving such unsaturation is reversible dissociation of neutral ligands, such as phosphines. A reasonable amount is known concerning the energetics of phosphine exchange in mononuclear transition-metal systems,[2] but relatively little is known about polynuclear ones.[3] The quadruply bonded Mo(II) dimers are interesting candidates for such a study, since generation of vacant coordination sites about two metal atoms ca. 2 Å apart may allow them to cooperate in promoting reactions which are not otherwise possible. Unfortunately, little is known about the intimate reaction mechanisms which govern this class of molecules.[4] As part of our efforts to explore the reactivity of quadruply bonded dimers,[5–7] we have examined phosphine exchange kinetics and reductive cleavage by carbon monoxide in the alkyl compounds Mo2Me4(PR3)4.

Blue Mo2Me4(PEt3)4[8] was prepared from Mo2(O2CCMe3)4, MgMeCl, and PEt3 in diethyl ether, followed by crystallization from diethyl ether at −10 °C. This complex undergoes ligand exchange with excess PMe2Ph or PMe3 in toluene solution within minutes at room temperature to give the known Mo2Me4-
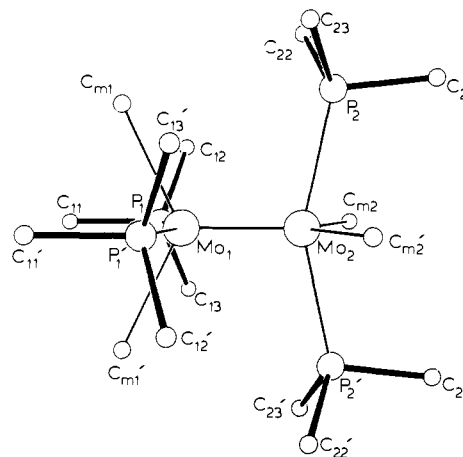

Figure 1. Perspective ORTEP drawing of the nonhydrogen atoms of Mo2Me4(PMe3)4. All atoms are represented by arbitrary-sized open circles for purposes of clarity. Atoms labeled with a prime are related to those labeled without a prime by the crystallographic twofold axis which passes through Mo1 and Mo2.

(PMe2Ph)4 or Mo2Me4(PMe3)4, respectively.[9] The NMR parameters of all three complexes are similar, and they are doubtless isostructural. An X-ray crystal structure analysis of Mo2Me4-(PMe3)4 has been performed,[10] and the molecular geometry (Figure 1) is in accord with that previously deduced spectroscopically.[9] The structure analysis reveals that the single crystals are composed of discrete binuclear molecules (Figure 1) which presumably contain a Mo–Mo quadruple bond.[10a] These crystals are essentially isomorphous with those of W2Cl4(PMe3)4[11] and have a solid-state packing arrangement which is quite similar to Mo2Cl4(SEt2)4.[12] Although the rigorous solid-state crystallographic symmetry of Mo2Me4(PMe3)4 is only C_2, it approximates rather closely to full D_{2d} symmetry with the two MoL2L′2 units having a nearly eclipsed (to within 0.8°) conformation. Relevant bond lengths and angles include Mo1–Mo2, 2.153 (1)Å; Mo–P, 2.513 (2,0,0,2) Å; Mo–C, 2.439 (5,18,18,2) Å; Mo–Mo–P, 102.5 (5,9,9,2)°; Mo–Mo–C, 115.3 (1,4,4,2)°.[10b]

It is of interest to determine the kinetics and mechanisms of phosphine exchange in these binuclear clusters. But before an examination of the kinetic parameters is possible, the stoichiometry of the reaction and stereochemistry of the products must be established. This is accomplished conveniently by monitoring the $^{31}P\{^1H\}$ NMR spectra as a function of temperature during the progress of the reactions.

A toluene-d_8 solution of Mo2Me4(PEt3)4 (0.036 M) and PMe2Ph (0.75 M) at −80 °C gives a spectrum that consists of two singlets due to these two species. Warming the sample to −50 °C gives free PEt3, which eventually accounts for 25 ± 3%

† University of Nebraska.

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(4) Hynes, M. J. *J. Inorg. Nucl. Chem.* **1972**, *34*, 366–369. Webb, T. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 6289–6294. Mureinik, R. J. *Inorg. Chim. Acta* **1977**, *23*, 103–110. Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 446–451.

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(6) Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 2165–2169.

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(8) Anal. Calcd: C, 46.4; H, 10.0. Found: C, 46.1; H, 9.78. ^1H NMR (PhMe-d_8, −50 °C): δ 0.32 (Mo–*Me* br), 2.18 (P(C*H*2CH3)3, br), 1.11 (P(CH2C*H*3)3 br); $^{13}C\{^1H\}$ NMR (PhMe-d_8, −50 °C): δ 3.86 (Mo–*Me* t, J_{pc} = 9 Hz), 16.29 (P (C*H*2CH3)3 t, J_{pc} = 7 Hz), 9.46 (P(CH2C*H*3)3, s; $^{31}P\{^1H\}$ NMR (PhMe-d_8, −50 °C): δ 19.9 (s). Positive chemical shifts are downfield of Me4Si or 30% H3PO4.

(9) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446–453.

(10) (a) Single crystals of Mo2Me4(PMe3)4 are monoclinic, space group $C_{2/c}$–C_{2h}^6 (No. 15) with *a* = 18.507 (5), *b* = 9.462 (3), *c* = 17.513 (4) Å; *β* = 116.18 (2)°; *Z* = 4 (dimeric units). Three-dimensional X-ray diffraction data were collected for 3172 independent reflections having $2\theta_{MoK\alpha}$ < 55° on a Nicolet P1 autodiffractometer by using graphite-monochromated Mo Kα radiation and full (1° wide) ω scans. The solid-state structure was solved by using the "heavy-atom" technique, and the resulting structural parameters for all nonhydrogen atoms have been refined anisotropically to convergence [R-(unweighted, based on F) = 0.044 for 2372 independent reflections having $2\theta_{MoK\alpha}$ < 55° and $I > 3\sigma(I)$] by empirically weighted full-matrix least-squares techniques on a Data General Eclipse S-200 computer using locally modified versions of the Nicolet E-XTL interactive crystallographic software system. (b) The first number in parenthesis following an averaged value of a bond length or angle is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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3954 *J. Am. Chem. Soc., Vol. 103, No. 13, 1981*
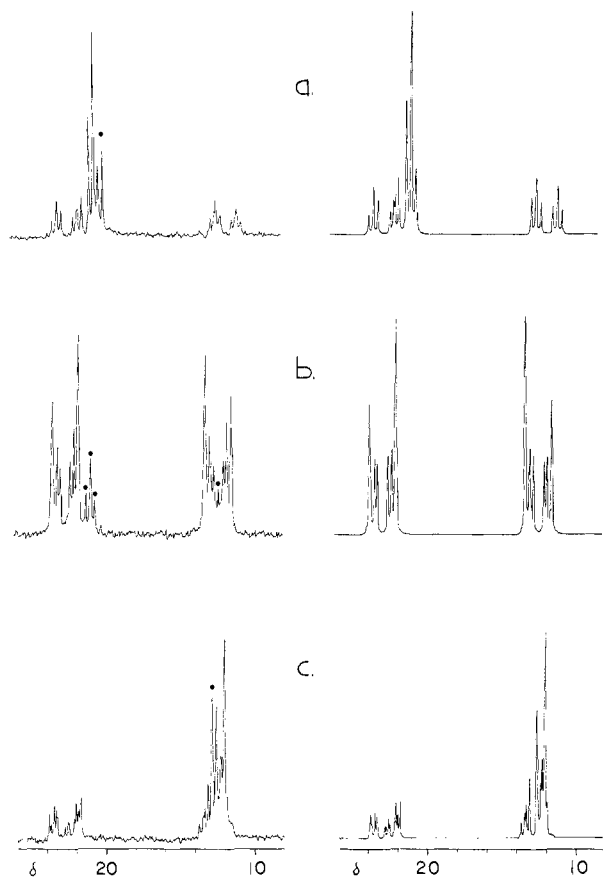
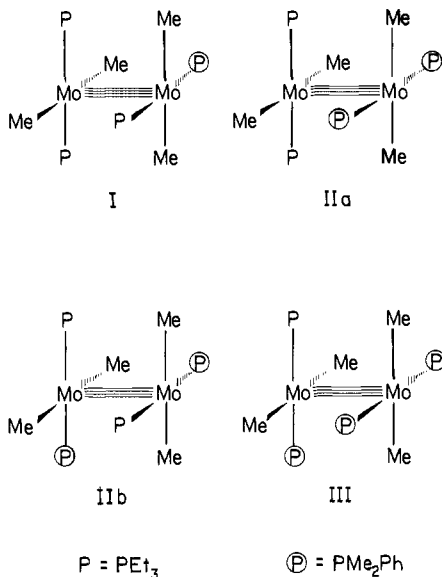*Communications to the Editor*

Figure 2. Observed (left-hand side) and calculated (right-hand side) spectra; A = I, B = IIb, and C = III. Solid circles indicate previous or subsequent substitution products.

of the total PEt_3 that is present initially.[13] Simultaneously, the resonance due to $Mo_2Me_4(PEt_3)_4$ gradually disappears and is replaced by new multiplets due to coordinated PEt_3 and PMe_2Ph. These new resonances comprise an A_2BC spin system[14] and correspond to the monosubstitution product $Mo_2Me_4(PEt_3)_3$-(PMe_2Ph) (I) (see Figure 2a). At -50 °C, no further changes

P = PEt₃   Ⓟ = PMe₂Ph

in the spectrum are evident, but warming to -30 °C causes liberation of a further molar equivalent of PEt_3. Concurrently, the A_2BC resonances diminish and new multiplets appear which correspond to the disubstitution product $Mo_2Me_4(PEt_3)_2$-$(PMe_2Ph)_2$. Two isomers of this mixed phosphine complex are possible, IIa and IIb, and these possibilities are distinguishable, since the former is an A_2B_2 spin system, while the latter is $AA'BB'$. The observed spectrum[15] (Figure 2b) is consistent with isomer IIb only, and thus, the second phosphine substitution does *not* occur on the same molybdenum atom as did the first substitution. Replacement of a third equivalent of phosphine occurs at a temperature of ca. -10 °C, and the product formed, Mo_2Me_4-$(PEt_3)(PMe_2Ph)_3$ (III), is another example of an A_2BC spin system[16] (figure 2c). Finally, at 0 °C, the last PEt_3 group is replaced by PMe_2Ph, giving $Mo_2Me_4(PMe_2Ph)_4$. The only other resonances remaining are those due to free PEt_3 and free PMe_2Ph.

It is apparent that the phosphine exchange process in these molecules is stepwise. Having established the stoichiometry of the individual steps and the stereochemistries of the respective products, it becomes possible to measure kinetic parameters, viz., the rate of substitution of the first PEt_3 group in Mo_2Me_4 $(PEt_3)_4$ by PMe_2Ph. At -50 °C, the rate of disappearance of Mo_2Me_4-$(PEt_3)_4$ is first order in $[Mo_2Me_4(PEt_3)_4]$ and zero order in $[PMe_2Ph]$, when the latter is in excess. Further, the rate is invariant on $[PMe_2Ph]$, when the latter is varied over a 10- to 30-fold excess. Under these conditions, the first-order rate constant is $k_{obs} = (5.5 \pm 0.1) \times 10^{-4}$ s^{-1} over three half-lives. An Arrhenius plot of ln $(k_{obs}h/k_BT)$ vs. $1/T$ yields the activation parameters, $\Delta H^{\ddagger} = 20.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 19.7$ eu. Further, replacement of PEt_3 in $Mo_2Me_4(PEt_3)_4$ by PMe_3 proceeds via the same stepwise reaction path as did the PMe_2Ph experiment and follows identical kinetics within experimental error: $k_{obs} = (5.3 \pm 0.3) \times 10^{-4}$ s^{-1} at -50 °C.

The invariance of the reaction rates on the nature of the incoming group and the positive $\Delta S^{\ddagger}$ both are indicative of a *dissociative* mechanism. Surprisingly, associative attack by phosphine does *not* occur, even though these complexes possess vacant axial sites. However, previous studies suggest that axial ligation is weak at best and does not involve covalent interaction.[5,17] The driving force for these dissociative reactions is most reasonably ascribed to relief of steric congestion, as PEt_3 is replaced by the smaller PMe_2Ph or PMe_3 ligands.[5] Consistent with this, Mo_2Me_4-$(PMe_2Ph)_4$ does not react at all with excess PMe_3 until a temperature of 0 °C is reached. Further, neither $Mo_2Me_4(PMe_3)_4$ nor $Mo_2Me_4(PMe_2Ph)_4$ react with excess PEt_3 at 25 °C, as shown by $^{31}P\{^1H\}$ NMR spectroscopy.

The $Mo_2Me_4(PR_3)_4$ compounds (PR_3 = PEt_3, PMe_2Ph, PMe_3) also react with carbon monoxide under 18 atm at room temperature in benzene. NMR spectroscopy shows the formation of acetone and $Mo[O]$ compounds of the type $Mo(CO)_{6-x}(PR_3)_x$ where x = 0–3.[18] Qualitatively, the rates of reaction at room temperature of CO with $Mo_2Me_4(PR_3)_4$ depend on the coordinated phosphine: $PEt_3 \gg PMe_2Ph > PMe_3$. This suggests that the rate-determining step involves phosphine dissociation by analogy with the results described above. On the basis of studies of the reaction of quadruply bonded dimers with isoelectronic *tert*-butyl isocyanide, it is possible that reductive elimination of acetone may not occur from the intact binuclear alkyl, but from a mononuclear one.[7] Further studies are under way in an attempt to resolve this question.[19,20]

(13) The values are corrected for differing NOE's. Spectra were acquired at 72.9 MHz.

(14) $\delta_A = 19.7$, $\delta_B = 21.4$, $\delta_C = 10.9$; $J_{AB} = 21.5$, $J_{AC} = 21.2$, $J_{BC} = 102.9$ Hz. Simulations were performed by using the program ITRCAL, written by Nicolet Technology Corp. Note that this is the first time P–P coupling across a M–M quadruple bond has been directly observed.

(15) $\delta_A = 22.5$, $\delta_B = 12.3$; $J_{AA'} = 20.0$, $J_{AB} = 104.1$, $J_{AB'} = 23.0$, $J_{BB'} = 19.2$ Hz.

(16) $\delta_A = 12.3$, $\delta_B = 12.7$, $\delta_C = 22.7$; $J_{AB} = 23.0$, $J_{AC} = 23.0$, $J_{BC} = 106.8$ Hz.

(17) Cotton, F. A.; Norman, J. G. *J. Am. Chem. Soc.* **1972**, *94*, 5697–5702. Garner, C. D.; Senior, R. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1171–1174.

(18) The 18-atm reactions do not represent the minimum pressure for reaction but is a convenient pressure that gives satisfactory rates of reaction at room temperature. Some of the phosphine carbonyls may arise from scrambling after acetone has been eliminated.

(19) For kinetic studies of acetone formation in other systems, see: Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113–120.

(20) *trans*-Mo(CO)₄(PMe₃)₂ and other products have been observed in the reaction of Mo₂Me₄(PMe₃)₄ with CO in refluxing toluene. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. Southwest–Southeast American Chemical Society Regional Meeting, New Orleans, L.A., Dec 10–13, 1980; INOR 235.

Sulfenium Ion Addition to Hexamethyl(Dewar benzene). A Case for a Hypervalent Sulfonium Ion Intermediate

John M. Bolster, Hepke Hogeveen,* Richard M. Kellogg,* and Lourens Zwart

Department of Organic Chemistry, University of Groningen Nijenborgh 16, 9747 AG Groningen, The Netherlands

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The addition of electrophiles to hexamethyl(Dewar benzene) (1) induces its transformation to reactive intermediates that provide a rich array of rearrangement products.[1] In the addition of hetero atom derived electrophiles, i.e., halonium ions, the pivotal intermediate is the bicyclo[2.2.1.]hexenyl cation (2), the formation of which is initiated by addition to a double bond from the endo face of 1 followed by rearrangement (eq 1).[1,2] We find now that
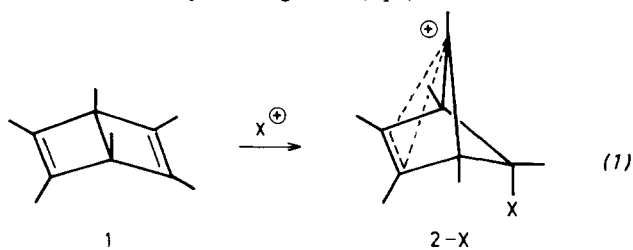
reaction of 1 with sulfenium ion (RS⁺) equivalents involves a significant deviation from this course of reaction.

Phenylsulfenyl chloride (3) and 1 were mixed in equimolar amounts at –120 °C in CH₂Cl₂ under an N₂ atmosphere. The solution became homogeneous at –70 °C and the ¹H NMR spectrum taken immediately revealed in the methyl region three new singlets of equal intensity at δ 1.49, 1.57, and 1.67 (the absorptions for 1 are found at δ 1.55 and 1.05).[3] Within 10 min the ¹H NMR spectrum becomes complex, but after warming to room temperature a clean spectrum is obtained which arises from 1 (48% yield) and dichloride 5, formed in 31% yield. The latter is known to be the end product of the chlorination of 1.[2b] Diphenyl disulfide is also formed.
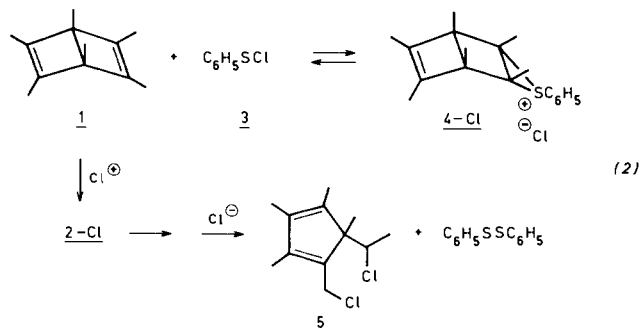
An abbreviated scheme consistent with these observations is given in eq 2. The intermediate immediately formed at low temperature is assigned structure 4-Cl (endo attack, exo orientation of phenyl substituent) consistent with the normal reaction course of sulfenyl halides.[4] The complicated spectrum that soon appears is probably the consequence of subsequent formation of covalent adducts. However, the formation of 4, as well as any adducts, must be reversible. This is indicated by the failure to obtain sulfur

(2)

containing stable adducts as well as by the recovery of 48% of the starting material 1. The other half of the starting material (1) is ultimately irreversibly consumed by chlorination via a chloronium ion from 3.[5] Reversible thiiranium ion formation has been previously demonstrated by us.[6]

The chloride counterion in 4 is clearly too nucleophilic. Phenylbis(thiophenyl)sulfonium hexachloroantimonate (6) has the less nucleophilic diphenyl disulfide as the leaving group.[7] On treatment of 1 with 6 in CH₂Cl₂ (this was the only suitable solvent found) a solid formed at low temperatures, but at –60 °C the solution became homogeneous. In the methyl region four new singlets were observed in the ¹H NMR spectrum (60 MHz) at δ 1.10 (3 H), 1.37 (6 H), 1.43 (6 H), and 1.51 (3 H). A small and variable amount of 1 remained; the phenyl absorptions were obscured by diphenyl disulfide. On warming the three absorptions at δ 1.37, 1.43, and 1.51 broaden and coalesce at –43 °C. At –30 °C the spectrum consists of two sharp singlets at δ 1.43 (15 H) and 1.10 (3 H). These spectra are shown in Figure 1. Owing to the limited solubility and stability we have been unable to obtain ¹³C NMR spectra. Above –20 °C the spectrum broadens irreversibly, but after standing for some hours the sharp absorption for hexamethylbenzene appears. A rationalization for these observations is given in eq 3.

At low temperatures 4-SbCl₆ is formed as a solid that at –60 °C rearranges to 7, which is a single geometrical isomer with the phenyl group oriented toward the five-membered ring.[8] That the structure of the ion is 7 and not 2-SC₆H₅, which has the same symmetry, is shown by the high field positions of the methyl groups in the ¹H NMR spectrum.[9] Moreover, this structural assignment is in agreement with the observation that quenching with (C₂H₅)₃N gives in 45% yield tricyclic alkene 9[10] as shown in eq 3. This is

(1) Review: Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413 and references cited therein.

(2) (a) Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 385, 1042; **1969**, *88*, 353. (b) Hogeveen, H.; Kwant, P. W.; Schudde, E. P.; Wade, P. A. *J. Am. Chem. Soc.* **1974**, *96*, 7518. (c) Paquette, L.; Krow, G. *Ibid.* **1969**, *91*, 6107.

(3) For comparison purposes in 2-Cl the methyl absorptions are found at δ 1.64 (3 H), 1.71 (6 H), 1.97 (3 H), and 2.30 (6 H). See: Schaefer, W.; Hellmann, H. *Angew. Chem.* **1967**, *79*, 566.

(4) See, for example: Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. These authors also discuss the problem whether thiiranium salts have a covalent sulfurane structure or an ionic structure as drawn for 4-Cl.

(5) With 2 equiv of 3, addition to both double bonds of 1 occurs to give a product: ¹H NMR δ 1.46 (s, 12 H), 1.60 (s, 6 H), and 7.25–7.50 (br abs, 10 H). This is apparently a dithiiranium salt derived from addition of phenylsulfenium ion to both double bonds of 1. The C₂ᵥ symmetry apparent from the ¹H NMR spectrum is consistent with endo–endo or exo–exo addition.

(6) Bolster, J. M.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630.

(7) Gybin, A. S.; Smit, W. A.; Bogdanov, V. S.; Krimer, M. Z.; Kakyarov, J. B. *Tetrahedron Lett.* **1980**, 383.

(8) No indication for a second isomer could be found from the 360-MHz ¹H NMR spectrum. Examination of models indicates that the isomer drawn has the phenyl group in the least hindered position. The formation of only one of two possible isomers of a thiiranium ion has been observed previously. See, for example: Raynolds, P.; Zonnebelt, S.; Bakker, S.; Kellogg, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 3146. Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.

(9) The carbon bound methyl groups in the methyl sulfonium salt of *cis*-2,4-dimethylthietane absorb at δ 1.64 (Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. *J. Am. Chem. Soc.* **1971**, *93*, 676), which value should be compared with the chemical shifts for 2-Cl cited in ref 3.

(10) As has been shown (Hogeveen, H.; Zwart, L. *Israel. J. Chem.*, in press) ¹³C NMR spectroscopy provides a powerful tool for structural assignments of these types of compounds. The characteristic chemical shifts are sp² carbon atoms 135–165 ppm; cyclopropane quaternary atoms 29–36 ppm; cyclobutane quaternary atoms 48–60 ppm; bicyclobutane quaternary atoms 19–32 (bridgehead) and 37–47 ppm (bridgehead atoms) and the methyl groups 1.5–4 ppm (nonbridgehead connected methyl groups) and 4–9 ppm (bridgehead connected methyl groups). Spectra for 9: ¹H NMR (CDCl₃) δ 0.91 (s, 3 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 1.22 (s, 3 H), 1.34 (s, 3 H), 4.32 (s, 1 H), 4.35 (s, 1 H), 7.1–7.5 (m, 5 H); ¹³C NMR (CDCl₃) δ 4.2 (CH₃), 6.1 (CH₃), 6.4 (CH₃), 7.4 (CH₃), 20.4 (CH₃), 40.0 (C), 44.6 (C), 48.7 (C), 60.2 (C), 62.1 (C), 85.2 (sp² CH₂), 126.2 (aromatic CH, 2×) 127.6 (aromatic C), 128.0 (aromatic CH, 2×), 136.1 (aromatic CH), 158.1 (sp² C).