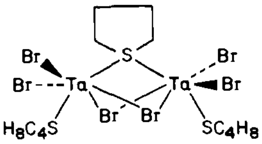
J. Am. Chem. Soc. **1980,** *102,* 7111-7113

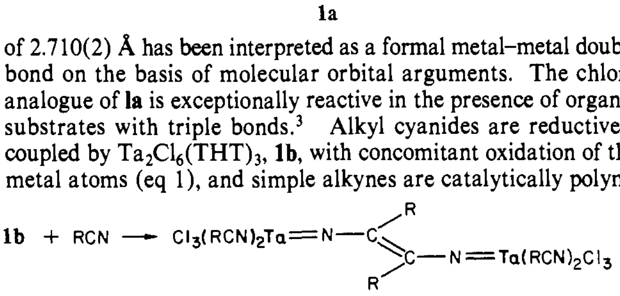
Metal-Metal Bonded Complexes of the Early Transition Metals: Synthesis of a Binuclear Tantalum(III) Trimethylphosphine Complex and Its Reactions with Hydrogen and Ethylene

Sir:

Binuclear complexes of tantalum(III) are very rare, and the only well-characterized dimers are the tantalum(III) halide adducts with tetrahydrothiophene (THT).[1] An X-ray crystallographic study of $Ta_2Br_6(THT)_3$, **1a**, revealed the metal-metal bonded confacial bioctahedral structure.[2] The Ta-Ta separation of 2.710(2) Å has been interpreted as a formal metal-metal double bond on the basis of molecular orbital arguments. The chloro analogue of **1a** is exceptionally reactive in the presence of organic substrates with triple bonds.[3] Alkyl cyanides are reductively coupled by $Ta_2Cl_6(THT)_3$, **1b**, with concomitant oxidation of the metal atoms (eq 1), and simple alkynes are catalytically polymerized to substituted arenes by **1b**. We report here a further elaboration of the noncyclopentadienyl chemistry of tantalum(III) which has led to the structural characterization of two interesting binuclear tantalum complexes.



1a



$$\mathbf{1b} + \mathrm{RCN} \longrightarrow \mathrm{Cl_3(RCN)_2Ta{=}N{-}C(R){=}C(R){-}N{=}Ta(RCN)_2Cl_3} \qquad (1)$$

Reduction of tantalum pentachloride in the presence of 2-2.5 equiv of trimethylphosphine (eq 2) provides an air-sensitive burgundy red diamagnetic solid, **3**, in ~75% yield. One recrystallization from toluene at -40 °C provided an analytically pure sample.[4] **2** is dimeric in toluene, and its $^{31}P\{^1H\}$ NMR spectrum[5] shows two singlets (each of area one) at δ -31.0 and -57.1. These data led us to postulate an edge-sharing bioctahedral structure wherein two PMe_3 ligands adopt axial positions on one tantalum with the remaining phosphines in terminal equatorial positions on the second tantalum. This was confirmed in a single-crystal X-ray structure determination (vide infra). Further reduction of the isolated **3** with sodium amalgam in toluene or THF has been attempted. Reduction, as evidenced by the formation of sodium chloride, does take place, but a mixture of products is formed (by ^{31}P NMR) which we have not, as yet, been able to separate.[6]

$$TaCl_5 + 2Na/Hg + PMe_3 \xrightarrow{PhCH_3} Ta_2Cl_6(PMe_3)_4 + 2NaCl \qquad (2)$$

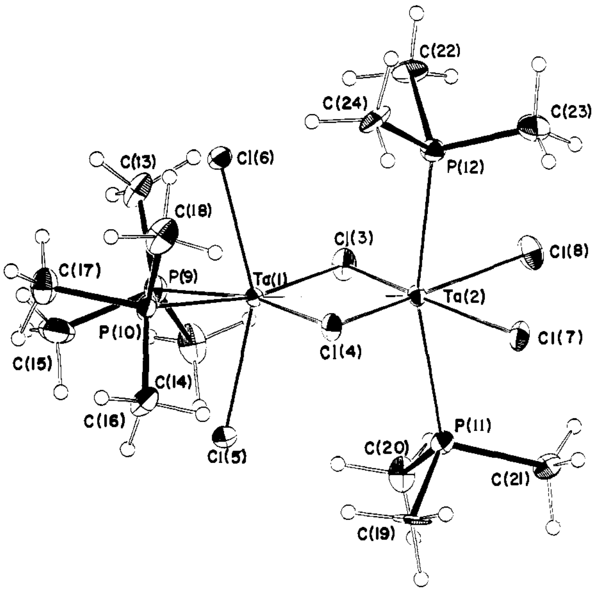


Figure 1. ORTEP drawing of the structure of $Ta_2Cl_6(PMe_3)_4$. Selected data not presented in the text: Ta(1)-Cl(3), 2.477 (3) Å; Ta(1)-Cl(5), 2.398 (3) Å; Ta(1)-P(9), 2.666 (4) Å; Ta(2)-Cl(3), 2.427 (3) Å; Ta(2)-Cl(7), 2.472 (3) Å; Ta(2)-P(11), 2.598 (4) Å; P(9)-Ta(1)-P(10), 98.9 (1)°; Cl(7)-Ta(2)-Cl(8), 86.6 (1)°; Cl(3)-Ta(1)-Cl(4), 111.1 (1)°; and Cl(3)-Ta(2)-Cl(4), 114.1 (1)°.

Crystals of **2** were grown from concentrated toluene solutions, carefully layered with methylcyclohexane at -40 °C, and its structure was determined from diffraction data collected at -170 °C.[7] The molecular geometry with selected bond distances and angles is shown in Figure 1. The molecule consists of two somewhat distorted octahedra sharing a common edge. The M-M separation in this d^2-d^2 dimer is 2.721 (1) (1) Å, only slightly longer than that found in **1a**. The only other structurally characterized metal complex with an overall geometry *and* ligand stereochemistry similar to **2** is the d^3-d^3 dimer, $W_2Cl_6(\text{pyridine})_4$ (**3**).[9] Comparison of these two structures is pertinent (vide infra) and reveals the following trends (tantalum data given first): (1) the metal-bridge chlorine-metal angle, θ_b, increases from 67.4 (1)° to 69.8 (2)°; (2) the M-M separation increases from 2.721 (1) Å to 2.737 (3) Å; (3) the $M(1)$-$M(2)$-L_{axial} ($L = PMe_3$, C_5H_5N) angle decreases from 97.6 (1)° to 94.1 (7)°, and the $M(2)$-$M(1)$-Cl_{axial} angle decreases from 103.2 (1)° to 96.2 (2)°. Taken as a whole these data suggest the metal-metal interaction in the tantalum(III) dimer is stronger than in the tungsten(III) dimer. Recent extended Hückel molecular orbital calculations on edge-sharing bioctahedral 5d metal complexes by Hoffmann and co-workers provide a possible explanation for this observation.[10] In the region of θ_b values near 70°, the calculated ordering of valence MO's is $\sigma < \pi < \delta^*$. These MO's are primarily metal 5d in character and originate from the σ, π, and δ overlap of metal $d_{z^2-y^2}$, d_{xz}, and d_{xy} atomic orbitals, respectively. The four available 5d metal electrons in **2** fill the σ and π levels and the M-M bond order is two. In the tungsten dimer, two additional electrons fill

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[1] Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

[2] Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.

[3] Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

[4] Elemental analyses and molecular weight measurements were performed by Galbraith Laboratories, Knoxville, Tn. Anal. Calcd for $Ta_2Cl_6P_4C_{12}H_{36}$: C, 16.40; H, 4.13; Cl, 24.20; mol wt, 879. Found: C, 16.53; H, 4.12; Cl, 24.42; mol wt, 876.

[5] These ^{31}P NMR measurements were recorded at 36.20 MHz on a JEOL FX90Q. Chemical shifts (δ) are in ppm from external H_3PO_4. Shifts are negative for lines upfield of H_3PO_4. Free PMe_3 in benzene-d_6 appears at δ -63.3.

[6] (a) It is interesting to note that sodium amalgam reductions[6b] of $TaCl_5$ in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) do *not* provide Ta(III) complexes. Only paramagnetic $TaCl_4(\text{dmpe})$ or $TaCl_2(\text{dmpe})_2$ can be isolated from the reaction mixtures. (b) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134.

[7] $Ta_2Cl_6(PMe_3)_4$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ with $a = 11.681$ (3), $b = 11.834$ (3), $c = 20.257$ (7) Å; $V = 2800.18$ Å^3 and ρ(calcd) = 2.085 g cm^{-3} for mol wt 878.9 and $z = 4$. Diffraction data were collected at -170 °C by a θ-2θ scan technique with equipment described in detail elsewhere.[8] Data were corrected for absorption ($\mu = 85.2$ cm^{-1}) and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, including all hydrogen atoms, were located and their positional and thermal parameters (anisotropic for Ta, Cl, P and C; isotropic for H) refined. The resulting descrepancy indices are $R_F = 3.65\%$ and $R_{wF} = 3.45\%$ for those 2610 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $5° < 2\theta < 50°$ (Mo Kα radiation).

[8] Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

[9] Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

[10] (a) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555. (b) This article actually predicts that **2** and **3** ($M_2D_8(\mu\text{-}D)_2$ complexes, where D represents a donor ligand) should have θ_b values closer to 100° and nonbonded M-M separations. Evidently, these molecules, through a combination of small deformations, find their way into a region of the potential-energy surface closer to $\theta_b = 70°$.[10c] The level ordering of valence MOs given in the text is appropriate to this region (±10°) only. (c) Roald Hoffmann, private communication.

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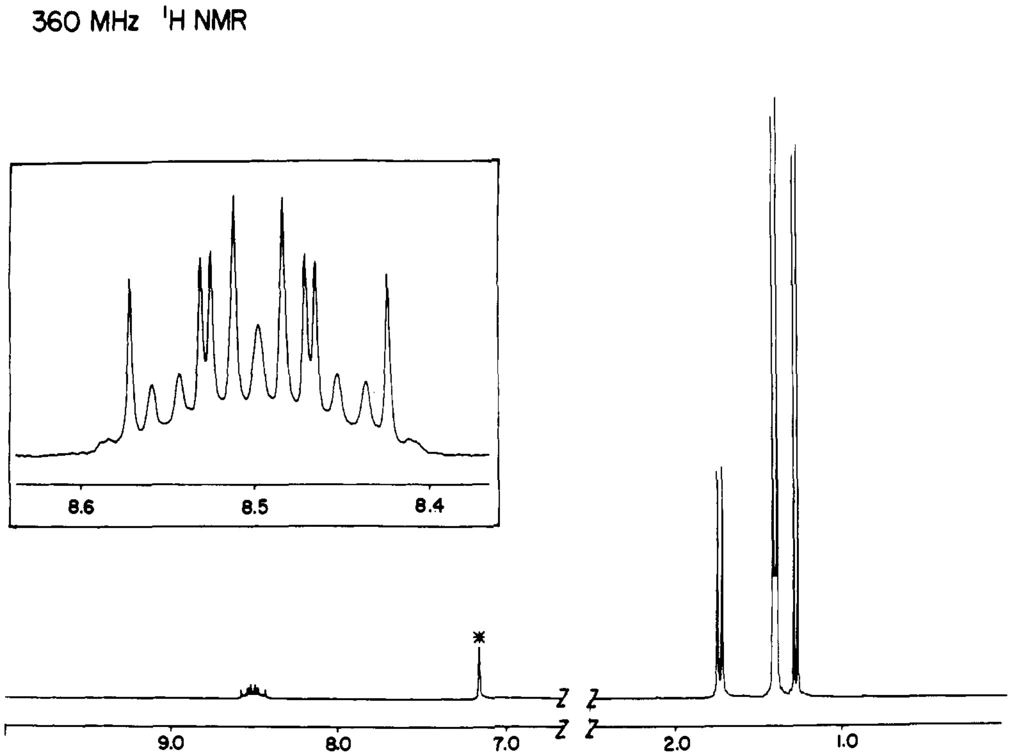

Figure 2. 360-MHz ^1H NMR spectrum of **4** at 25 °C, C_6D_6 solvent (*). Chemical shifts (δ) are in ppm downfield from Me_4Si. The insert is an enlargement of the resonance at δ 8.5.

the δ antibonding level to give a $\sigma^2\pi_2\delta^{*2}$ ground-state electronic configuration and a formal bond order of one. Since π bonding should be worth considerably more than δ antibonding, the small increases in θ_b and M–M separation going from **2** to **3** seem quite reasonable.

Compound **2** dissolved in toluene reacts readily and cleanly with molecular hydrogen (1 atm) at 25 °C (eq 3) to give an emerald

$$Ta_2Cl_6(PMe_3)_4 + H_2 \xrightarrow{PhCH_3} \underset{\mathbf{4}}{Ta_2Cl_6(PMe_3)_4H_2} \quad (3)$$

green diamagnetic crystalline solid, **4**. Elemental analyses and molecular weight measurement[11] were very similar to those obtained for **2**. Solid **4** is stable in air for months and only moderately sensitive in solution.[12] To our knowledge, this is the first time that hydrogen has added to a metal–metal multiple bond (vide infra). The hydrogen is firmly bound, and we have not succeeded in removing it thermally or photochemically. The 360-MHz proton NMR spectrum[13] of **4** is shown in Figure 2. We assign the complex multiplet centered at δ 8.5 to a pair of chemically equivalent bridging hydride ligands.[14] Integration of the hydride resonance vs. the three observed phosphine methyl resonances at δ 1.72, 1.39, and 1.27, respectively, gives the following ratios: 1:4.32:8.76:4.47 (theory 1:4.5:9.0:4.5). The 1:2:1 ^1H NMR pattern for the phosphine methyl groups is mimicked in the $^{31}P\{^1H\}$ NMR[13] spectrum of **4** where we find two AX doublets (each of area one) and a singlet (area two). The data suggested that the basic phosphine stereochemistry found earlier in **2** (two axial, two equatorial) was maintained in **4**. Puckering of the inner rhomboid of **2** to accommodate the two bridging hydrides destroys the chemical equivalence of the axial phosphines while maintaining the equivalence of the equatorial phosphines. ^{31}P NMR experiments,[13] with selective spin decoupling of the methyl protons, establish the axial phosphines and bridging hydrides as an A_2MX spin system and the equatorial phosphines and bridging hydrides as an AA′XX′ spin system. The complexity of the hydride resonance in Figure 2 is now understood. Full details of the NMR spectra and computer simulations will be reported elsewhere. The data presented here led us to postulate a structure for **4** which included a metal–metal bond bridged by four ligands (2H, 2Cl). Such complexes are rare,[15] so an X-ray

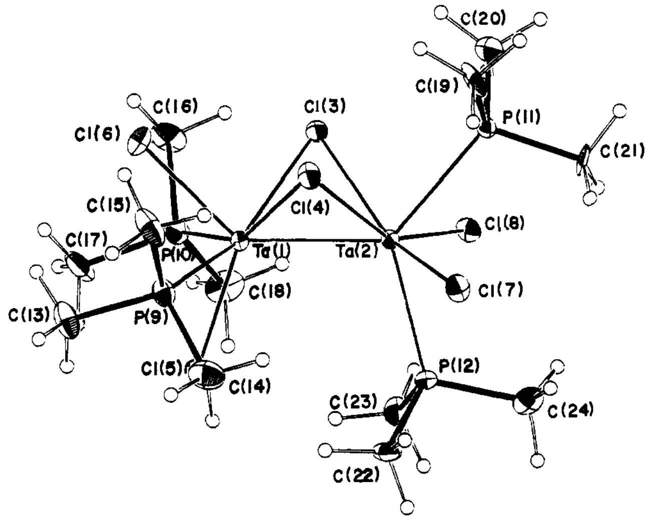

Figure 3. ORTEP drawing of the structure of $Ta_2Cl_6(PMe_3)_4H_2$. Selected data not presented in the text: Ta(1)–Cl(3), 2.554 (3) Å; Ta(1)–Cl(5), 2.475 (3) Å; Ta(1)–Cl(6), 2.492 (3) Å; Ta(2)–Cl(3), 2.559 (3) Å; Ta(2)–Cl(7), 2.466 (3) Å; Ta(2)–Ta(1)–Cl(6), 133.7 (1)°; Ta(2)–Ta(1)–Cl(5), 108.3 (1)°, and Cl(7)–Ta(2)–Cl(8), 114.9 (1)°.

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[11] Anal. Calcd for $Ta_2Cl_6P_4C_{12}H_{38}$: C, 16.36; H, 4.35; Cl, 24.14; mol wt, 881. Found: C, 16.20; H, 4.10; Cl, 24.31; mol wt, 896.

[12] Toluene solutions of **4** do not react with carbon monoxide under modest conditions (40 psi, 50 °C, 24 h).

[13] These proton and ^{31}P NMR spectra were recorded at 360.1 and 145.8 MHz, respectively, on a Brucker 360. ^1H NMR (ppm, C_6D_6) 8.5 (m, 2, H_b), 1.72 (d, 9, J_{PH} = 9.8 Hz, P_{ax} 1.39 (m, 18, P_{eq}–CH_3), 1.27 (d, 9, J_{PH} = 8.9 Hz, P'_{ax}–CH_3); ^{31}P NMR (ppm, C_6D_6, ^1H decoupled) 3.55 (d, 1, $J_{PP'}$ = 7.25 Hz, P_{ax}), –14.54 (s, 2, P_{eq}), –29.92 (d, 1, $J_{PP'}$ = 7.25 Hz, P'_{ax}); ^{31}P NMR (ppm, ppm, C_6D_6, selective ^1H decoupling of P–CH_3) 3.55 (t of d, 1, $J_{PP'}$ = 7.25 Hz, J_{PH} = 19.46 Hz, P_{ax}), –14.54 [m(AA′XX′), 2, P_{eq}], –29.92 (t of d, 1, $J_{PP'}$ = 7.25 Hz, J_{PH} = 15.26 Hz, P'_{ax}).

[14] The IR spectrum of **4** (KBr disk) at ambient temperature is featureless from 1420 cm^{-1} [$\delta_d(CH_3)$] to 2915 cm^{-1} [$\nu_s(CH_3)$]. Lowering the temperature to –196 °C did not reveal any new bands in this region. The Ta–H–Ta vibrations are either hidden under the low-energy phosphine vibrations or are too weak to observe under our experimental conditions.

diffraction analysis was performed.

Crystals of **4** were grown from concentrated toluene solutions, carefully layered with methylcyclohexane at −40 °C, and its structure was determined from diffraction data collected at −170 °C.[16] The molecular geometry with selected distances and angles is shown in Figure 3. The bridging hydrogens did *not* appear in the final difference Fourier but must be located in the cavity below the bridging chlorides. **4** may be described as a quadruply bridged tantalum(IV) dimer with a metal–metal single bond of 2.621 (1) Å. The terminal Cl_2P_2 units and the bridging ligands are in a mutually staggered arrangement so that the coordination about each tantalum is roughly square antiprismatic. The molecular symmetry is very close to C_s (mirror symmetry), although this is not imposed by the space group. The solid-state phosphine stereochemistry agrees very well with that predicted on the basis of solution NMR measurements. The two angles, Ta(2)–Ta(1)–P(9) and Ta(2)–Ta(1)–P(10), are equal [117.6 (1)°], as are the two Ta(1)–P_{eq} distances [2.635 (3) and 2.646 (3) Å]. The axial phosphines are clearly nonequivalent. The Ta(1)–Ta(2)–P(11) and Ta(1)–Ta(2)–P(12) angles are 130.6 (1) and 103.2 (1)°, respectively. P(11), which is adjacent to the chloride bridges and trans to the bridging hydrides, is 2.665 (3) Å from Ta(2) while the Ta(2)–P(12) distance is significantly shorter, 2.610 (3) Å. The bridging chlorine angles, Ta(1)–Cl(3,4)–Ta(2), are very acute and average 61.8°. There is one exceptionally short nonbonded intramolecular contact. The two bridging chlorines are separated by 3.072 Å, well below the van der Waals limit. Full details of the two structures described here will be reported in a future publication.

Finally, we note that **2**, dissolved in toluene, reacts readily and cleanly with ethylene (20 psi) at 25 °C (eq 4) to give a royal blue

$$Ta_2Cl_6(PMe_3)_4 + C_2H_4 \xrightarrow{PhCH_3} 2TaCl_3(PMe_3)_2(C_2H_4) \quad (4)$$

diamagnetic crystalline solid, **5**. Elemental analyses and a mass spectrum[17] of this volatile compound establish it as the monomeric tantalum(III) ethylene complex, $TaCl_3(PMe_3)_2(C_2H_4)$. A trans,mer geometry is indicated by ^{31}P, ^{13}C, and ^1H NMR measurements.[18] **5** has been reported previously by Schrock and co-workers[19] from the reaction of the tantalum alkylidene complex, *trans,mer*-$Ta(CHCMe_3)Cl_3(PMe_3)_2$, with ethylene. It is not obvious why only one isomer should form in eq 4. Low-temperature reactions of **2** with C_2H_4 which may bear on this question are in progress.

Acknowledgment. The authors thank Professor Roald Hoffmann for this comments concerning M_2L_{10} complexes. The Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for support of this work. We also thank the Marshall H. Wrubel Computing Center, Indiana University, for a generous gift of computing time. The Brucker 360 NMR spectrometer was purchased, in part, by funds provided by the National Science Foundation.

Supplementary Material Available: Fractional coordinates and thermal parameters for $Ta_2Cl_6[P(CH_3)_3]_4$ and $Ta_2Cl_6[P(CH_3)_3]_4H_2$ (6 pages). Ordering information is given on any current masthead page.

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Received July 28, 1980

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(15) (a) The only structural report we are aware of is the neutron diffraction analysis[15b] of $H_8Re_2(PEt_2Ph)_4$, a complex with four bridging hydrides. (b) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(16) $Ta_2Cl_6(PMe_3)_4H_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.650$ (4), $b = 11.285$ (3), $c = 22.479$ (8) Å, $\beta = 125.45$ (1)°; $V = 2820.95$ Å^3 and ρ(calcd) = 2.074 g cm^{-3} for mol wt 880.9 and $z = 4$. Diffraction data were collected at −170 °C by a θ–2θ scan technique using equipment described elsewhere.[8] Data were corrected for absorption ($\mu = 84.6$ cm^{-1}) and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, with the exception of the bridging hydrogens, were located and their positional and thermal parameters (anisotropic for Ta, Cl, P and C; isotropic for H) refined. The resulting discrepancy indices are $R_F = 6.21\%$ and $R_{wF} = 4.83\%$ for those 5153 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $5° < 2\theta < 55°$ (Mo Kα radiation).

(17) Anal. Calcd for $TaCl_3P_2C_8H_{22}$: C, 20.55; H, 4.74; Cl, 22.75. Found: C, 20.40; H, 4.78; Cl, 22.67. The mass spectrum of **5** (electron impact, 45 eV) did not show the parent ion (P) but P minus C_2H_4 and P minus (C_2H_4 + PMe_3) were observed with the correct isotope patterns expected for $TaCl_3(PMe_3)_2$ and $TaCl_3(PMe_3)$, respectively.

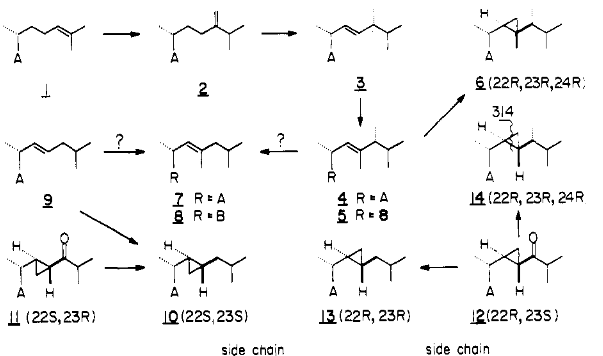
(18) JEOL FX90Q data. ^1H NMR (ppm, C_6D_6, 89.56 MHz) 2.84 (t, 4, C_2H_4, $J_{PH} = 2.0$ Hz), 1.45 ("virtual triplet", 18, P–CH_3, J_{PH}(apparent) = 4.0 Hz). $^{13}C\{^1H\}$ NMR (ppm from Me_4Si, C_6D_6, 22.50 MHz) 59.09 (poor t, C_2H_4, $J_{PC} \sim 3.9$ Hz), 14.45 ("virtual triplet", P–CH_3, J_{PC} (apparent) = 13.7 Hz). $^{31}P\{^1H\}$ NMR (ppm from H_3PO_4, C_6D_6, 36.20 MHz) −10.1 (s, P–CH_3).

(19) Fellmann, J. D.; Rupprecht, G. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099.

Isolation and Structure Elucidation of 22(*S*),23(*S*)-Methylenecholesterol. Evidence for Direct Bioalkylation of 22-Dehydrocholesterol[1]

Sir:

A unique feature of certain marine sterols—never encountered among terrestrial counterparts—is the occurrence of bioalkylation of the cholesterol side chain at positions 22 and 23. Gorgosterol (**6**)[2] is the first recorded example, and we hypothesized[2,3] that its biosynthetic precursor is brassicasterol (**3**), itself derived by the conventional C-24 bioalkylation from desmosterol (**1**).[4,5] This implied the existence of an intermediate 23,24-dimethyl-Δ^{22}-sterol whose subsequent isolation[6,7] (e.g., **5** and **4**) added plausibility



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(1) Minor and Trace Sterols in Marine Invertebrates. 21. For the preceding paper see L. Bohlin, U. Sjöstrand, B. W. Sullivan, and C. Djerassi, *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) N. C. Ling, R. L. Hale, and C. Djerassi, *J. Am. Chem. Soc.*, **92**, 5281-5282 (1970).

(3) C. Djerassi, N. Theobald, W. C. M. C. Kokke, C. S. Pak, and R. M. K. Carlson, *Pure Appl. Chem.*, **51**, 1815-1828 (1979).

(4) E Lederer, *Q. Rev., Chem. Soc.*, **23**, 453-481. See also W. R. Nes and M. L. McKean, "Biochemistry of Steroids and other Isopentenoids", University Park Press, Baltimore, MD, 1977.

(5) For recent review see L. J. Goad in "Marine Natural Products", Vol. II, P. J. Scheuer, Ed., Academic Press, New York, 1978, pp 75-172.

(6) Y. Shimizu, M. Alam, and A. Kobayashi, *J. Am. Chem. Soc.*, **98**, 1059-60 (1976). J. Finer, K. Hirotsu, and J. Clardy in "Marine Natural Products Chemistry" NATO Conf. [Ser.] 4, Plenum Press, New York, 1977, 147-148 (1977).

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