

- rings), 6.98 (m, 2.9, remaining H on nonspirobicyclic ring), 3.11 (s, 12.4,  $^+NMe_4$ ).  $^{19}F$  NMR for **3b** ( $Me_2SO-d_6$ , 84.6 MHz) shows two quartets, at 72.9 and 74.3 ppm upfield from  $CFCl_3$ ,  $J_{FF} = 8.5$  Hz. The  $^1H$  and  $^{19}F$  NMR data for **2a** and **3a** are very similar to those given above.
- (22) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 4390 (1977).
- (23) R. L. Amey and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 300 (1978).
- (24)  $^1H$  NMR ( $Me_2SO-d_6$ ):  $\delta$  7.93 (m, 2.0, H ortho to Si), 7.27 (m, 6.3 ArH).  $^{19}F$  NMR:  $\phi$  74.2 and 74.6 (q,  $J_{FF} = 8.5$  Hz). Mass spectrum:  $m/e$  512 ( $M^+ - LiH$ ). Anal. Calcd for  $C_{18}H_{16}F_{12}LiO_2Si \cdot 0.4994LiCl$ : C, 39.93; H, 1.68; Li, 1.92; Cl, 3.27. Found: C, 40.77; H, 2.01; Li, 1.48; Cl, 3.27.
- (25) Anal. Calcd for **10**,  $C_{25}H_{18}F_{12}N_2O_2Si$ : C, 47.32; H, 2.86; N, 4.42. Found: C, 46.83; H, 3.05; N, 4.20. All other analyses are within 0.4% of the calculated values unless otherwise reported.

Edmund F. Perozzi, J. C. Martin\*

Roger Adams Laboratory, Department of Chemistry  
University of Illinois, Urbana, Illinois 61801

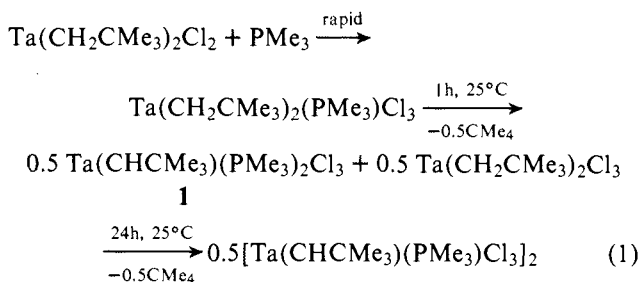
Received October 31, 1978

### Interaction of Hydrogen and Hydrocarbons with Transition Metals. Neutron Diffraction Evidence for an Activated C-H Bond in an Electron-Deficient Tantalum-Neopentylidene Complex

Sir:

For some time we have observed two peculiarities in the  $^{13}C$  NMR and IR spectra of electron-deficient niobium- and tantalum-benzylidene and -neopentylidene complexes: both  $^1J_{CH_{\alpha}}$  (75–100 Hz) and  $\nu_{CH_{\alpha}}$  (2400–2600  $cm^{-1}$ ) are unexpectedly low.<sup>1</sup> In the more sterically crowded 18-electron complexes  $TaCp_2(CHR)X$  ( $R = H, Ph$ , or  $CMe_3$  and  $X = CH_3, CH_2Ph$ , or  $Cl$ , respectively), whose structures are known,  $^1J_{CH_{\alpha}} = 135, 127$ , and  $121$  Hz, respectively. Interestingly, the  $M-C_{\alpha}-R$  angle varies *inversely* with  $^1J_{CH_{\alpha}}$ , from  $126$  ( $4^\circ$ ) when  $R = H$ ,<sup>5a</sup> to  $135.2$  ( $7^\circ$ ) when  $R = Ph$ ,<sup>5b</sup> to  $150.4$  ( $5^\circ$ ) when  $R = CMe_3$ .<sup>5c,d</sup> Therefore, it seems likely that the even lower values for  $^1J_{CH_{\alpha}}$  and  $\nu_{CH_{\alpha}}$  in the electron-deficient complexes are characteristic of even larger  $M-C_{\alpha}-R$  angles and, consequently, smaller  $M-C_{\alpha}-H_{\alpha}$  angles. The previous structural studies were all determined by X-ray diffraction methods, from which the location of the  $\alpha$ -hydrogen atom cannot be accurately obtained. In order to characterize precisely the molecular structure of an alkylidene complex, we have determined the structure of  $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$  by neutron diffraction.

$Ta(CH_2CMe_3)_2Cl_3$  in toluene reacts with 1 mol of  $PMe_3$  to give  $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ , which then disproportionates to **1** and starting material (eq 1). All **1** and starting material are converted to **2**, the final product, which slowly crystallizes as large red nuggets, in 24 h.<sup>6,7</sup> In electron-deficient **2** (14 electrons per Ta assuming bridging Cl ligands),  $^1J_{CH_{\alpha}} = 101$  Hz and  $\nu_{CH_{\alpha}} = 2605$   $cm^{-1}$ .



The compound crystallizes in the monoclinic space group  $P2_1/n$  with refined cell dimensions at 110 K of  $a = 10.920$  (6)  $\text{\AA}$ ,  $b = 12.827$  (7)  $\text{\AA}$ ,  $c = 10.553$  (6)  $\text{\AA}$ ,  $\beta = 91.05$  ( $2^\circ$ ), and  $Z = 2$ , which imposes a crystallographic center of inversion on the molecule. A 30-mg crystal of **2** was sealed in a lead-glass capillary under a nitrogen atmosphere and transferred to the computer-controlled diffractometer at the CP-5 reactor.<sup>9</sup> The crystal was cooled by a cold stream of nitrogen gas<sup>10</sup> and all

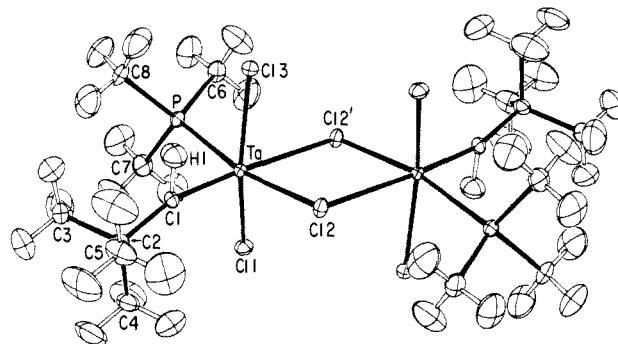


Figure 1. Drawing of the molecular structure of  $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$  determined by neutron diffraction at 110 K. A crystallographic inversion center is located midway between the two Ta atoms. The ellipsoids of thermal motion for all atoms are scaled to enclose 50% probability.

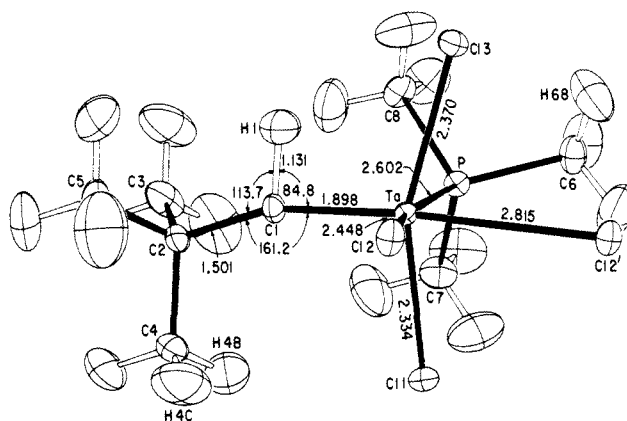


Figure 2. A view of the pseudooctahedral coordination geometry of one Ta atom with emphasis on the configuration of the neopentylidene ligand. The  $C(1)-H(1)$  distance of  $1.131$  ( $3$ )  $\text{\AA}$  may be compared with the average methyl C-H distance of  $1.083$  ( $2$ )  $\text{\AA}$  (see text).

data were measured at 110 K. Data were measured out to  $(\sin \theta)/\lambda = 0.62$   $\text{\AA}^{-1}$  ( $\lambda$  1.142 (1)  $\text{\AA}$ ) using the  $\theta-2\theta$  step scan mode with  $0.1^\circ$  steps. Each of the data was corrected for its Lorentz factor and absorption ( $\mu = 2.37$   $cm^{-1}$ ) to yield a set of 2930  $F_o^2$  values. The initial positions of all independent nonhydrogen atoms were obtained by direct methods using the program MULTAN.<sup>11</sup> The 19 hydrogen atoms were located on a Fourier map with phases calculated from the refined coordinates of the nonhydrogen atoms. In the final stages of full-matrix least-squares refinement, the thermal motion of all atoms was treated anisotropically and the data were corrected for secondary extinction<sup>12</sup> ( $g = 0.56$  ( $3$ )  $\times 10^{-4}$ ). The final discrepancy indices for all 2930 reflections are  $R(F_o^2) = 0.079$  and  $R_w(F_o^2) = 0.095$ .

As illustrated in Figure 1, each Ta atom possesses distorted octahedral geometry and forms an edge-sharing dimer with a center of inversion located midway between the two Ta atoms. The Ta-Ta distance ( $4.061$  ( $2$ )  $\text{\AA}$ ) is much greater than that in Ta metal ( $2.86$   $\text{\AA}$ ) and precludes any direct metal-metal interaction. The distance and angles associated with the  $PMe_3$  ligand are within normal ranges. Figure 2 is a view of half of the dimer molecule which emphasizes several important features of the neopentylidene ligand.

In the neopentylidene ligand,  $C(2)$ ,  $C(1)$ ,  $H(1)$ , and Ta form a plane which is oriented perpendicular to the  $C(1)-Ta-P$  plane (dihedral angle =  $89.8$  ( $2^\circ$ )). The short hydrogen-chlorine contacts ( $H(1)\cdots Cl(3) = 2.657$  ( $4$ ),  $H(4B)\cdots Cl(1) = 3.061$  ( $5$ ), and  $H(4C)\cdots Cl(1) = 3.291$  ( $5$ )  $\text{\AA}$ ) and the bending of the chloride ligands away from the alkylidene coordination site ( $C(1)-Ta-Cl(3) = 104.01$  ( $7$ ) and  $C(1)-Ta-Cl(1) = 95.13$  ( $7^\circ$ )) provide evidence that the alkylidene ligand is coordinated in this position by multiple bonding between Ta

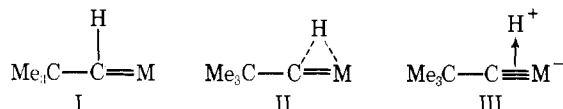
and C(1) and that steric interaction between the neopentylidene ligand, Cl(1), and Cl(3) is significant. Additional evidence of multiple bonding is the very large trans influence exhibited by the alkylidene ligand, such that the Ta-Cl (bridging) distances of 2.448 (2) (cis) and 2.815 (2) Å (trans) differ by 0.367 (2) Å.

Steric crowding between the CMe<sub>3</sub> group and Cl(1) must be *in part* responsible for the large Ta-C(1)-C(2) angle. However, if this were the *only* determining factor, then Cl(1) should be bent *further* from its ideal octahedral position than Cl(3), and the H(1)··Cl(3) distance should be *greater* than the H(4B,4C)··Cl(1) distances. The opposite, in fact, is the case. The Ta-C(1)-C(2) (Ta-C<sub>α</sub>-C<sub>β</sub>) angle of 161.2 (1)° is significantly larger than that found in TaCp<sub>2</sub>(CHCMe<sub>3</sub>)Cl (150.4 (5)°), but smaller than the Ta-C<sub>α</sub>-C<sub>β</sub> angle of 171.8 (6)° found in the tantalum-benzylidene complex.<sup>8a</sup> The Ta-C<sub>α</sub>-H<sub>α</sub> angle of 84.8 (2)° is consequently significantly smaller than that in TaCp<sub>2</sub>(CHCMe<sub>3</sub>)Cl of 111 (4)°. The Ta··H(1) distance (2.119 (4) Å), in fact, is less than the sum of van der Waals radii and only ~0.35 Å longer than the average terminal Ta-H distance (1.774 (3) Å) in Ta(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>H<sub>3</sub> (by neutron diffraction<sup>13</sup>). Note that M-H distances for bridging hydrides, M-H-M, are generally ~0.2 Å longer than those for terminal hydrides.<sup>14</sup> Thus, the Ta··H(1) distance is only ~0.15 Å longer than that expected for a bridging Ta-H-Ta bond. Finally, the C(2)-C(1)-H(1) angle (113.7 (2)°) is considerably larger than that in TaCp<sub>2</sub>(CHCMe<sub>3</sub>)Cl (99 (4)°).<sup>5c,d</sup>

The Ta-C(1) bond distance (1.898 (2) Å) is much shorter than the "double bonds" found in the three TaCp<sub>2</sub>(CHR)X complexes mentioned earlier<sup>5</sup> (M=C<sub>α</sub> = 2.026 (10), 2.07 (1), and 2.030 (6) Å; average, 2.04 Å). In fact, it is only slightly longer than the Ta-carbon triple-bond length (1.849 (8) Å) recently found in the benzylidene complex Ta(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(Cl)(CC<sub>6</sub>H<sub>5</sub>).<sup>8a</sup> A normal Ta-C (alkyl) single-bond length is ~2.25 Å.<sup>5a,b</sup>

The C(1)-H(1) bond distance of 1.131 (3) Å is possibly the longest C-H bond distance of high precision ever observed in a crystal structure. The 18 independent methyl C-H distances range from 1.065 (5) to 1.094 (5) Å, with an average value of 1.083 (2) Å, which is normal for C(sp<sup>3</sup>)-H(s) bonds.<sup>15</sup> It is slightly longer than that (1.120 Å) predicted for a bond between a carbon pure p orbital and a hydrogen 1s orbital.<sup>15</sup> If viewed in this way we can easily rationalize the extraordinarily low values of <sup>1</sup>J<sub>CH<sub>α</sub><sup>16a</sup> and ν<sub>CH<sub>α</sub></sub>.<sup>16b</sup></sub>

The valence bond description (I) is consistent with all the above data. Since steric interaction between the *tert*-butyl group and Cl(1) cannot alone account for the large Ta-C(1)-C(2) angle, we postulate that the electron-deficient metal attracts electron density from the C(1)-H(1) bond, thus further lengthening that bond and shortening the Ta-C(1) bond. Therefore, alternative descriptions (II, an unsymmetrical bridging hydride in a three-center, two- (or six-) electron bond, and III, a "protonated triple bond") are valid to some extent.



(It is interesting to compare the latter description with the "lithiated neopentylidene complex", Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>-(CCMe<sub>3</sub>)[Li·N,N'-dimethylpiperazine], in which Ta≡C = 1.76 (2) Å and Ta≡C<sub>α</sub>-C<sub>β</sub> = 165 (1)°.<sup>18a</sup>) This *electronic* effect must operate synergistically with the *steric* effect, and one would expect it to become more important (all else being equal) as the metal becomes more electron deficient. Irrespective of which of the above descriptions is more appealing, we can begin to understand why (if not exactly how) an alkyl ligand can remove H<sub>α</sub> to give an alkane and an alkylidyne complex;<sup>8a</sup> the C(2p)-H(1s) bond energy is lower<sup>15</sup> or, alter-

natively, bridging hydrides are more acidic than terminal hydrides.<sup>19</sup> Therefore, we can postulate either that R· removes H· or that R<sup>-</sup> removes H<sup>+</sup>. The difference between these two processes, however, may be more formal than real.

We can go one step further and suggest that similar steric and electronic effects also increase the M-C<sub>α</sub>-C<sub>β</sub> angle in Nb(V) and Ta(V) *alkyl* complexes and set the stage for H<sub>α</sub> to be abstracted by another alkyl ligand. We can, in fact, see evidence for this in certain crowded neopentyl complexes, such as Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>Cl,<sup>2</sup> in the form of a low value for <sup>1</sup>J<sub>CH<sub>α</sub></sub> (105–110 Hz). However, these steric and electronic factors will be least important in a methyl complex where "M-C<sub>α</sub>-C<sub>β</sub>" = M-C<sub>α</sub>-H<sub>α</sub> ≈ 110°. Indeed, facile α-hydrogen abstraction in a methyl complex to give methane and a *stable* methylene complex<sup>18b</sup> is as yet unknown,<sup>20,21</sup> whereas many neopentylidene complexes and benzylidene complexes have been prepared in this manner.

The phenomenon described here should be compared with other confirmed examples of C-H···M interactions.<sup>23,24</sup> It could be regarded as a type of electrophilic C-H bond activation,<sup>26</sup> the analogue of which in electron-deficient alkyl complexes may be more common than heretofore suspected, but is usually unobservable unless the alkylidene product is stable or can be trapped.<sup>21</sup>

**Acknowledgments.** Work at Argonne National Laboratory is performed under the auspices of the Division of Basic Energy Science of the U.S. Department of Energy. Support of the neutron diffraction research by the National Science Foundation under Grant NSF CHE 77-22650 is gratefully acknowledged (J.M.W.). Work at MIT was supported by NSF Grant CHE 76-07410 (R.R.S.).

## References and Notes

- (1) A low <sup>1</sup>J<sub>CH<sub>α</sub></sub> value (90 Hz) was noticed in the first tantalum-alkylidene complex, Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(CHCMe<sub>3</sub>).<sup>2</sup> The first, and most obvious, anomalous ν<sub>CH<sub>α</sub></sub> stretch was observed in TaCp(CHCMe<sub>3</sub>)Cl<sub>2</sub><sup>3</sup> as a weak, fairly sharp peak at 2510 cm<sup>-1</sup> (ν<sub>CO<sub>α</sub></sub> = 1855 cm<sup>-1</sup>). In Ta(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CHCMe<sub>3</sub>)Br<sub>2</sub><sup>4</sup> it is a medium strength peak at 2420 cm<sup>-1</sup>.
- (2) R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, **100**, 3359 (1978).
- (3) S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977).
- (4) Full details of all members of this class of complexes will appear shortly: C. D. Wood, S. J. McLain, and R. R. Schrock, *J. Am. Chem. Soc.*, submitted for publication.
- (5) (a) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975); (b) R. R. Schrock, C. D. Wood, L. W. Messerle, and L. J. Guggenberger, *ibid.*, **100**, 3793 (1978); (c) M. R. Churchill, F. J. Hollander, and R. R. Schrock, *ibid.*, **100**, 647 (1978); (d) M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **17**, 1957 (1978).
- (6) Anal. Calcd for TaC<sub>8</sub>H<sub>19</sub>Cl<sub>3</sub>P: C, 22.17; H, 4.41. Found: C, 22.68; H, 4.28. <sup>1</sup>H NMR (τ, C<sub>6</sub>D<sub>6</sub>): 4.70 (br s, 1, CHCMe<sub>3</sub>), 8.86 (d, 9, <sup>2</sup>J<sub>HP</sub> = 9.6 Hz, PMe<sub>3</sub>), 8.90 (s, 9, CHCMe<sub>3</sub>). <sup>13</sup>C NMR (ppm, C<sub>6</sub>D<sub>6</sub>): 276.0 (CHCMe<sub>3</sub>, <sup>2</sup>J<sub>CP</sub> = 7.3, <sup>1</sup>J<sub>CH</sub> = 101 Hz), 35.5 (CHCMe<sub>3</sub>), 33.5 (CHCMe<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> = 126 Hz), 15.8 (PMe<sub>3</sub>, <sup>1</sup>J<sub>CP</sub> = 29, <sup>1</sup>J<sub>CH</sub> = 132 Hz).
- (7) This reaction is an example of a PMe<sub>3</sub> accelerated α abstraction from an *alkyl* ligand which is analogous to the recently reported PMe<sub>3</sub> accelerated α abstraction from an *alkylidene* ligand to give an alkylidyne complex<sup>8a</sup> and related reactions which give niobium- and tantalum-bis(alkylidene) complexes<sup>8b</sup> and molybdenum- and tungsten-alkylidyne and tungsten-alkylidene complexes.<sup>8c</sup> It is successful using PMe<sub>2</sub>Ph, PPhMe<sub>2</sub>, Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>, or Me<sub>2</sub>AsC<sub>6</sub>H<sub>4</sub>AsMe<sub>2</sub> instead of PMe<sub>3</sub>, and for Nb as well as Ta.
- (8) (a) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *J. Am. Chem. Soc.*, **100**, 5962 (1978); (b) J. D. Fellmann, G. A. Rupprecht, C. D. Wood, and R. R. Schrock, *ibid.*, **100**, 5964 (1978); (c) D. N. Clark and R. R. Schrock, *ibid.*, **100**, 6774 (1978).
- (9) The instrumentation and data collection technique have been described in detail previously: J. M. Williams, P. L. Johnson, A. J. Schultz, and C. C. Coffey, *Inorg. Chem.*, **17**, 834 (1978).
- (10) We thank Drs. C. E. Strouse and J. Strouse for designing and assembling the low temperature apparatus at the CP-5 reactor: C. E. Strouse, *Rev. Sci. Instrum.*, **47**, 871 (1976).
- (11) J. P. Declercq, G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **29**, 231 (1973).
- (12) (a) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); (b) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **28**, 71 (1970).
- (13) R. D. Wilson, T. F. Koetzle, D. W. Hart, A. Kwick, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1775 (1977).
- (14) For a review of metal-hydride distances determined by single-crystal neutron diffraction, see R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle,

- Acc. Chem. Res., in press.
- (15) C. A. Coulson, "Valence", 2nd Ed., Oxford University Press, London, 1961, pp 208-211.
- (16) (a)  $^1J_{CH}$  correlates fairly well with the percent s character in the carbon orbital in hydrocarbons.<sup>17a,b</sup> In other cases (e.g., the  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$  series) it correlates linearly with bond length.<sup>17c</sup> In the latter series, if a bond length were 1.13 Å,  $^1J_{CH}$  would be ~95 Hz. (b) Coulson<sup>15</sup> predicts  $k = 4.490 \times 10^{-5}$  dyn  $cm^{-1}$  for a pure C(p)-H(s) bond; for a C(sp<sup>3</sup>)-H(s) bond  $k = 5.387 \times 10^{-5}$  dyn  $cm^{-1}$ .
- (17) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York and London, 1972; (b) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959); (c) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).
- (18) (a) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975); (b) R. R. Schrock and P. R. Sharp, *ibid.*, **100**, 2389 (1978).
- (19) (a) K. Wade, "Electron Deficient Compounds", Appleton-Century-Crofts, New York, 1971; (b) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963, p 172.
- (20) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).
- (21) Green<sup>22</sup> has "trapped" a methylene hydride complex with a tertiary phosphine. It now seems possible, however, that  $H_a$  may never transfer "completely" from a methyl ligand to an electron-deficient metal to give an observable, *cis*-alkylidene-hydride complex.
- (22) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 208, 761 (1974).
- (23) (a) F. A. Cotton and A. G. Stanislawski, *J. Am. Chem. Soc.*, **96**, 5074 (1974); (b) M. Brookhart, T. H. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976); (c) S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 1317 (1978); (d) R. B. Calvert and J. R. Shapley, *ibid.*, **99**, 5225 (1977); (e) G. A. Olah, G. Liang, and S. H. Yu, *J. Org. Chem.*, **41**, 2227 (1976).
- (24) In the neutron diffraction study<sup>25</sup> of  $[Fe[P(OMe)_3]_3(\eta^3-C_6H_5)]^+BF_4^-$ ,<sup>23c</sup> the Fe...H distance is 1.879 (9) Å. In  $[Fe(CO)_3(\eta^3-C_4H_7)]^+$  the  $J_{CH}$  value in the suggested<sup>23b</sup> three-center, four-electron Fe...H...C bond was shown to be 74 Hz.<sup>23e</sup>
- (25) J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100**, 7407 (1978).
- (26) (a) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975), and references therein; (b) D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977).
- (27) (a) Camille and Henry Dreyfus Teacher-Scholar, 1978. (b) PRF Predoctoral Fellow; (c) Halcon Fellow, 1978.

A. J. Schultz,\* Jack M. Williams

Chemistry Division, Argonne National Laboratory  
Argonne, Illinois 60439

R. R. Schrock,\*<sup>27a</sup> G. A. Rupprecht,<sup>27b</sup> J. D. Fellmann<sup>27c</sup>

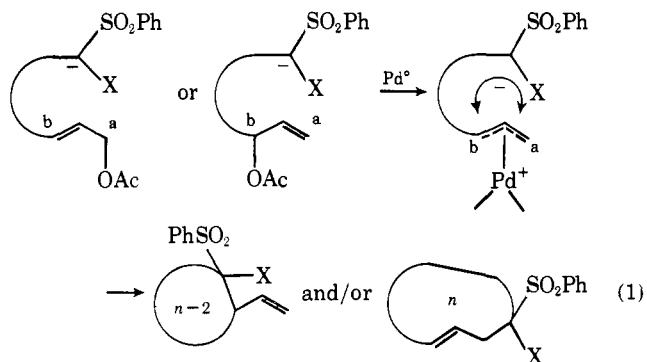
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received August 13, 1978

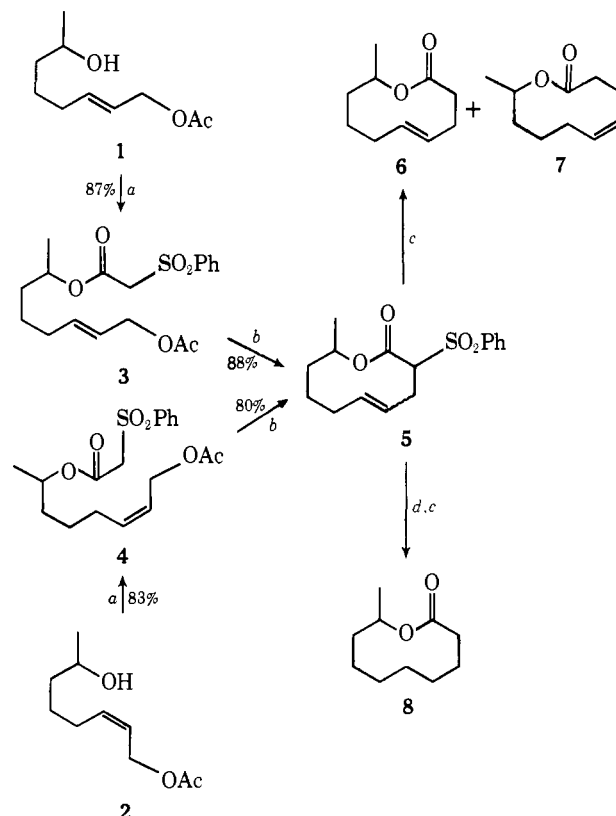
### Influence of a Transition Metal on the Regiochemistry of Ring Closures. An Approach to Medium-Ring Compounds

Sir:

A basic tenet of cyclization is the great preference for formation of three-, five-, six-, and seven-membered rings over four-, eight-, nine-, and ten-membered rings. For example, a six-membered ring forms  $>10^4$  faster than an eight-membered ring.<sup>1</sup> We report an unusual effect of palladium<sup>2</sup> on the rules for ring closure<sup>3</sup> and the first examples of the preference for formation of eight- and nine-membered rings over competing six- and seven-membered rings. Growing interest in the syn-



Scheme I. Eight vs. Ten. Synthesis of Phoracantholides



<sup>a</sup>  $PhSO_2CH_2CO_2H$ ,  $Ph_3P$ ,  $C_2H_5O_2CN \equiv NCO_2C_2H_5$ ,  $PhCH_3$ , RT.

<sup>b</sup>  $NaH$ , THF, 6 mol %  $(Ph_3P)_4Pd$ , 12 mol % diphos, reflux. <sup>c</sup> 6% Na (Hg),  $Na_2HPO_4$ ,  $C_2H_5OH$ ,  $-20^\circ C$ . <sup>d</sup> 5%  $Pd/BaCO_3$ ,  $H_2$ , 2 atm,  $C_2H_5OH$ .

thesis of medium rings and the fact that medium-ring lactones are generally not accessible by lactonization<sup>4-6</sup> methods highlight the potential importance of these observations.

Equation 1 represents the general class of reaction that we have examined.<sup>2,3</sup> The importance of ten-membered ring compounds in natural products and the fact that eight- and ten-membered ring formation occurs with almost equal facility<sup>1</sup> led us to compete an eight vs. ten (i.e.,  $n = 10$ ) directed to the phoracantholides as summarized in Scheme I. The hydroxyacetates **1**<sup>8</sup> and **2**,<sup>8</sup> whose olefin stereochemistry is established by the mode of synthesis<sup>7</sup> and the 270-MHz NMR spectrum (**1**,  $\delta$  5.77 (dtt,  $J = 15.3, 6.3, 1$  Hz, 1 H), 5.56 (dtt,  $J = 15.3, 6.3, 1$  Hz, 1 H); **2**,  $\delta$  5.65 (dtt,  $J = 11, 7.3, 1.5$  Hz, 1 H), 5.53 (dtt,  $J = 11, 6.8, 1.5$  Hz, 1 H)), were esterified with benzenesulfonylacetic acid by the reverse activation procedure<sup>9</sup> to give the cyclization substrates **3**<sup>8</sup> and **4**.<sup>8</sup> In both cases, treatment of the corresponding anions with a Pd(0) catalyst in the presence of diphos led to an isomeric mixture (*E,Z* and *R\*,R\**, and *R\*,S\**) of cyclization products **5**. The absence of absorptions at  $\delta$  5-5.5 for a monosubstituted olefin suggested the absence of eight-membered rings. Desulfonylation gave a mixture of *E* and *Z* ten-membered-ring lactones **6**<sup>8</sup> and **7**,<sup>8</sup> which were separated by VPC (20% DC710 on 60/80 Chromosorb W at 170 °C), the latter (phoracantholide J) isolated from the metasternal gland secretion of *Phoracantha synonyma*.<sup>6,10,11</sup> NMR allows assignment of double-bond stereochemistry (**6**,  $\delta$  5.42 (ddd,  $J = 15, 9.5, 4.5$  Hz), 5.28 (ddd,  $J = 15, 10.5, 4$  Hz); **7**, 5.46 (tdd,  $J = 11, 5.5, 2$  Hz), 5.35 (td,  $J = 11, 4$  Hz)). The ratio of **6**:**7** was 85:15 from **3** and 65:35 from **4**. Thus, in contrast to the 12-membered-ring case, substantial loss of olefin geometry accompanied this cyclization. Further confirmation that the isomeric nature of **5** does not result from regioisomers arose in the catalytic hydrogenation