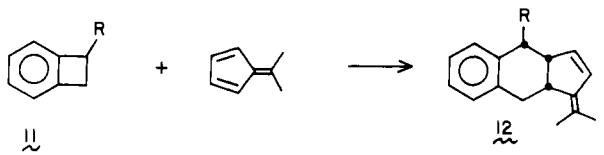
only endo [4 + 2] adducts **12a** and **12b**, respectively,[14] as are



observed for other Diels–Alder reactions of this *o*-xylylene.[17] This alteration in periselectivity may be rationalized primarily on the basis of conformational requirements in the ring, which is formed from the connecting side chain. As shown in Figure 1, the endo [6 + 4] cycloaddition can occur with the forming five-membered ring in a favorable envelope conformation. This transition state can also benefit from favorable secondary orbital interactions. The exo-cis transition structure must have a more strained developing five-membered ring. The spiro-[4 + 2] transition structure has a slightly less favorable conformation of the forming cyclopentane ring than the endo-[6 + 4]. In Figure 1, we have shown the spiro-[4 + 2] transition structure leading to the cis product, although the trans transition state is quite similar with respect to side-chain conformation. In the four possible transition structures that can give [4 + 2] adducts on a fulvene ring double bond, a cycloheptene is formed from the side chain. The most reasonable of these, a endo-cis transition structure, is disfavored by the partial eclipsing interactions that must develop in the forming cycloheptene ring.

These side-chain conformational effects make the [6 + 4] adduct preferable to the spiro-[4 + 2] and disfavor the ring-[4 + 2], whereas the intermolecular case (**11**, R = Me) produces these three adducts in 18%, 9%, and 50% yield, respectively.[14] The parent, **11a**, and cyano derivative, **11b**, give only the ring-[4 + 2] adducts, **12**. The [6 + 4] and spiro-[4 + 2] adducts are favored by xylylene HOMO–fulvene LUMO interactions, while the ring-[4 + 2] adduct is favored by xylylene LUMO–fulvene HOMO interactions,[18] which dominate for fulvenes and simple dienes in intermolecular cases.[18]

The cyano substituent shifts the reaction to [6 + 4] exclusively. This contrasts to the intermolecular case, which produces the endo-[4 + 2] adduct, **12b**, from the transition structure shown in Figure 1, as expected from maximization of the xylylene LUMO–fulvene HOMO overlap. The relevant frontier molecular orbitals are shown at the bottom of Figure 1. In the intramolecular reaction, the stabilizing interaction between C-4 of the diene and C-1 of the fulvene cannot be attained in any sterically feasible [4 + 2] transition state, and only the [6 + 4] cycloaddition is observed, in spite of the node through C-6 in the fulvene HOMO. Thus, intramolecular [6 + 4] cycloadditions of dienylfulvenes, joined at C-1 of the diene and C-6 of the fulvene, compete favorably with [4 + 2] cycloadditions. This tendency is accentuated when the diene is substituted by an acceptor substituent at C-1, as found here, and should also be favored by a donor at C-4, as found in intermolecular cases.[19]

We are exploring the generality of intramolecular 10 π electron cycloadditions for the synthesis of natural products containing a hydroazulene fused to an additional ring.

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Registry No. 1, 6809-91-2; **2**, 83692-94-8; **3**, 83692-95-9; **4a**, 83692-96-0; **4b**, 83692-97-1; **4c**, 83692-98-2; **5**, 83692-99-3; **6**, 3469-06-5; **7**, 83693-00-9; **8**, 83693-01-0; **9**, 83693-02-1; **10** (isomer 1), 83693-03-2; **10** (isomer 2), 83693-04-3; 5-chloro-2-pentanone ethylene ketal, 5978-08-5.

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Intramolecular Addition of an Aliphatic C–H Bond to a Tantalum–Carbon Double Bond

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The high valent, Early transition metal to carbon double bond (alkylidene), despite being a relatively new functionality is nevertheless an important group.[1] It has been shown to be the active species in olefin metathesis[2] and implied as a key intermediate in olefin polymerization.[3] Other, stoichiometric reactions of this group include Wittig-type functionalizations of ketones and imines,[4] insertion of carbon monoxide to yield ketenes,[1] and hydrogenation under mild conditions to alkane.[1] Recently, the migratory insertion of a number of groups to alkylidene ligands have been characterized.[5,6] We report here our observation that intramolecular addition of an aliphatic CH bond to a tantalum alkyidene can be facile, implying a possible potential of this function for CH bond activation.

We recently reported the synthesis of the alkylidene compound $Ta(OAr')_2(=CHSiMe_3)(CH_2SiMe_3)$ (I) from the reaction of $Ta(OAr')_2Cl_3$ (OAr' = 2,6-di-*tert*-butylphenoxide) with 3 equiv of $LiCH_2SiMe_3$.[7] A single-crystal X-ray diffraction study of I has been carried out, and the resulting structure along with the atom numbering scheme and some pertinent bond distances and angles are shown in Figure 1.[8] The molecule can be seen to possess an approximately tetrahedral geometry about the metal, but with some distortions. The angle between the sterically demanding aryl oxide ligands has opened up to 127°, while that between the two organic functions has been compressed. The Ta–OAr' distances are short (Figure 1), implying that a considerable amount of oxygen to tantalum π bonding is taking place. The tantalum–alkylidene distance is consistent with previously characterized alkylidene complexes of this type.[1] The orientation

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(8) Crystal data for $Ta(OC_{14}H_{21})_2(=CHSiMe_3)(CH_2SiMe_3)$ at −162 °C: space group = $P2_1/c$; a = 11.037 (4), b = 25.402 (15), c = 17.113 (7) Å; β = 126.69 (2)°; Z = 4; d_c = 1.321 g·cm^{-3}. Of the 3605 unique reflections collected with use of Mo Kα radiation ($6° \le 2\theta \le 40°$), the 2450 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are R_F = 0.0802 and R_{wF} = 0.0677.

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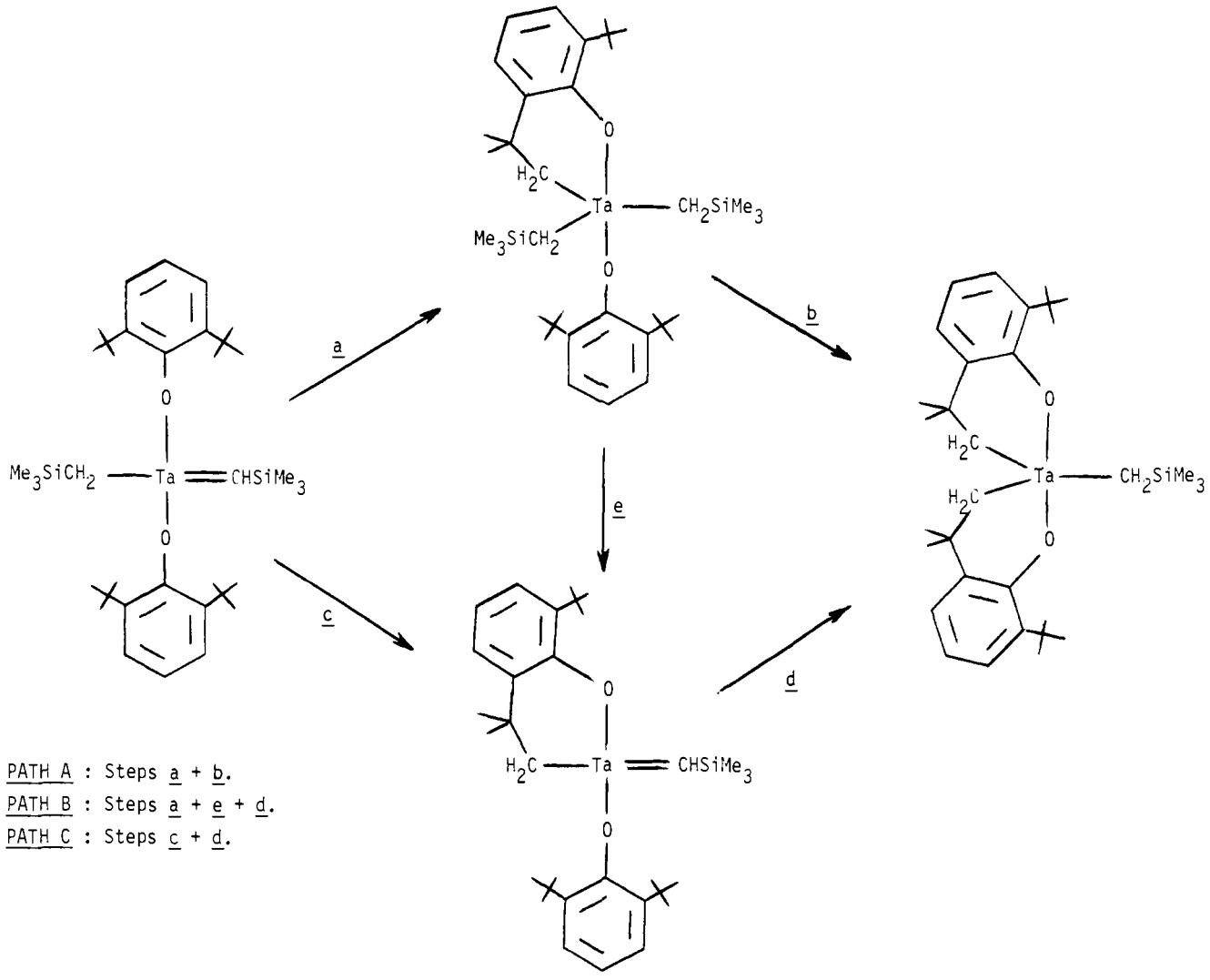
Scheme I



of the Ta=CHSiMe$_3$ bond is such that two types of aryl oxide ligand is expected. The fact that only one set of OAr′ signals is observed in the ^{1}H NMR spectrum of I implies that rapid rotation is occurring about this bond.

On thermolysis (toluene/120 °C) solutions of I liberate Me$_4$Si and cleanly convert to a bis-cyclometalated compound II, in which each of the aryl oxide ligands has undergone attack on one of the CH bonds of a *tert*-butyl group. Compound II is related to previously reported bis-cyclometalated compounds Ta(OC$_6$H$_3$-*t*-BuCMe$_2$CH$_2$)$_2$R (R = Me, Ph),[9] and its ^{1}H NMR spectrum is consistent with this formulation.[10] When solutions of I in toluene-d_8 are thermolyzed and the reaction is monitored by ^{1}H NMR, the smooth formation of II and Me$_4$Si from I is seen to take place with no detectable intermediates. Clearly at one stage of the reaction an aliphatic CH bond has been added across the alkylidene function. However, a number of possible pathways exist for the overall reaction (Scheme I). This observation raises the possibility that activation of the CH bonds in these d^0 metal systems is dependent on the presence of an unsaturated function at the metal center to which the CH bond can be added and that a direct loss of alkane by interaction of a CH bond with a Ta–R group is not taking place. This would rule out steps b and c, leaving pathway B, in which the second alkylidene function is formed by an α-hydrogen abstraction (step e). Paths A and C involve two types of hydrocarbon activation, one being addition to the alkylidene function (step a or d) and the other presumably involving a four-center transition state leading to alkane loss and formation of a new Ta–C bond (steps b and c). If the latter mechanism is not operative, then it implies that the cyclometalation reactions involving the methyl and phenyl compounds[4] proceed via intermediate methylene and benzyne complexes, respectively. However, studies on the labeled compound Ta(OAr′)$_2$(CD$_3$)$_3$ show that in this case the four-center mechanism is operative, the final product of thermolysis being Ta(OC$_6$H$_3$-*t*-BuCMe$_2$CH$_2$)$_2$(CD$_3$) with no detectable incorporation of H in the tantalum-methyl group.[11]

Two possible mechanisms are hence available for CH bond activation at this d^0 metal center. One involves the direct interaction of a CH bond with a tantalum-alkyl group[12] while the

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(10) ^{1}H NMR (benzene-d_6, 30 °C) of II δ 6.9–7.5 (m, C$_6$H$_3$), 1.22 (s, C$_6$H$_3$C*Me*$_2$CH$_2$), 1.40 (s, C$_6$H$_3$CMe$_2$C*H*$_2$), an AB pattern between 1.55 and 1.80 obscured by *t*-Bu group, δ(Ta-*CH*$_2$SiMe$_3$) obscured by *t*-Bu and C*Me*$_2$, 0.12 (s, Ta-CH$_2$Si*Me*$_3$). Anal. Calcd for TaSiO$_2$C$_{32}$H$_{51}$: C, 56.78; H, 7.60. Found: C, 56.85; H, 7.89.

(11) Ta(OAr′)$_2$(CD$_3$)$_3$ was prepared from Ta(OAr′)$_2$Cl$_3$ and LiCD$_3$ (synthesized from CD$_3$I; 99.5 atom % D purchased from Merck and Co.) as outlined previously.[7] Mass spectral analysis showed the compound to be 95% d_9 with 5% d_8. Thermolysis of the compound in toluene/120 °C yielded Ta(OC$_6$H$_3$-*t*-BuCMe$_2$CH$_2$)$_2$(CD$_3$). No proton incorporation into the Ta–Me function could be detected by ^{1}H NMR, and mass spectral analysis showed the compound to be 98% d_3 with only 2% d_2.

(12) A four-center mechanism for hydrogenolysis of d^0 metal alkyls has been outlined: Gell, K. I.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

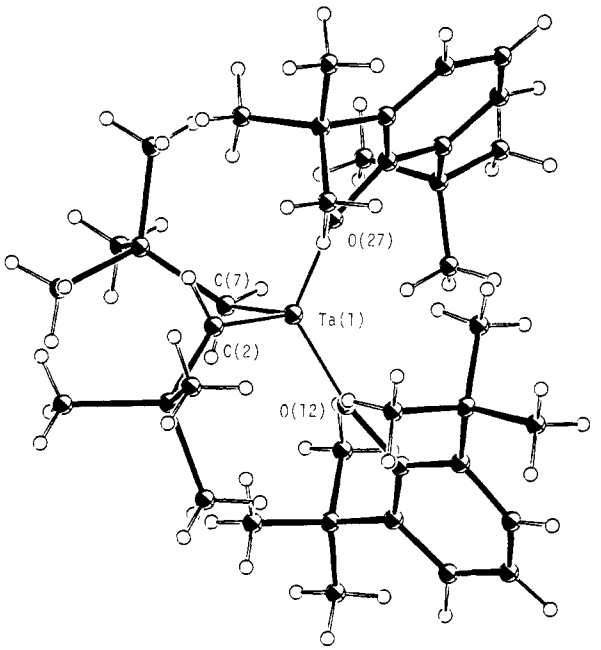

Figure 1. View of the $Ta(OC_{14}H_{21})_2(CH_2SiMe_3)(=CHSiMe_3)$ molecule. Some pertinent bond distances (Å) and angles (deg) are Ta(1)-O(12) = 1.854 (15), Ta(1)-O(27) = 1.845 (16), Ta(1)-C(2) = 1.888 (29), Ta(1)-C(7) = 2.165 (24), O(12)-Ta(1)-O(27) = 126.97 (7), O(12)-Ta(1)-C(2) = 107.4 (10), O(12)-Ta(1)-C(7) = 108.0 (8), O(27)-Ta(1)-C(2) = 108.3 (10), O(27)-Ta(1)-C(7) = 103.0 (8), c(2)-Ta(1)-C(7) = 100.1 (11).

other involves addition of the CH bond to a tantalum-carbon double bond.

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Unambiguous Assignments of the Imino Proton Resonances of a G·U Wobble Base Pair

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Guanine-uracil hydrogen-bonded base pairs, which were initially proposed by Crick in his wobble hypothesis for codon-anticodon interactions,[1] are assumed to be commonly involved in double helical structures of RNA.[2,3] Direct evidence for the presence of the G·U pair has been provided by X-ray analysis of yeast $tRNA^{phe}$ crystals.[4] ^1H NMR studies of a tRNA[5] and an rRNA fragment[3] in H_2O solution suggested that the imino proton resonances appearing in the 10-12 ppm region can be assigned to those of a G·U base pair. These assignments of G·U pair resonances of tRNA's were confirmed by nuclear Overhauser effects between the two imino protons.[6-8] However some ambiguity remains in these assignments since these tRNA's and the rRNA fragment contain many base pairs with different environments, and they can form non-Watson-Crick-type base pairs in tertiary structures. In order to define the location of the G·U pair resonances and unambiguously assign the individual signals to N^1H of G (G-N^1H) and N^3H of U (U-N^3H), we synthesized a ribotetranucleotide, G-G-C-Up, and its ^{15}N-labeled compound, G*-G-C-Up, and measured their ^1H and ^{15}N NMR spectra. When the tetramer forms a duplex, it contains two identical G·C base pairs and two identical G·U base pairs. Our results revealed that G-G-G-Up does form a duplex at low temperature, and G-N^1H of the G·C pair and U-N^3H and G-N^1H of the G·U pair give proton signals at 13.6, 12.0, and 10.6 ppm downfield from DSS reference, respectively, at 3 °C.

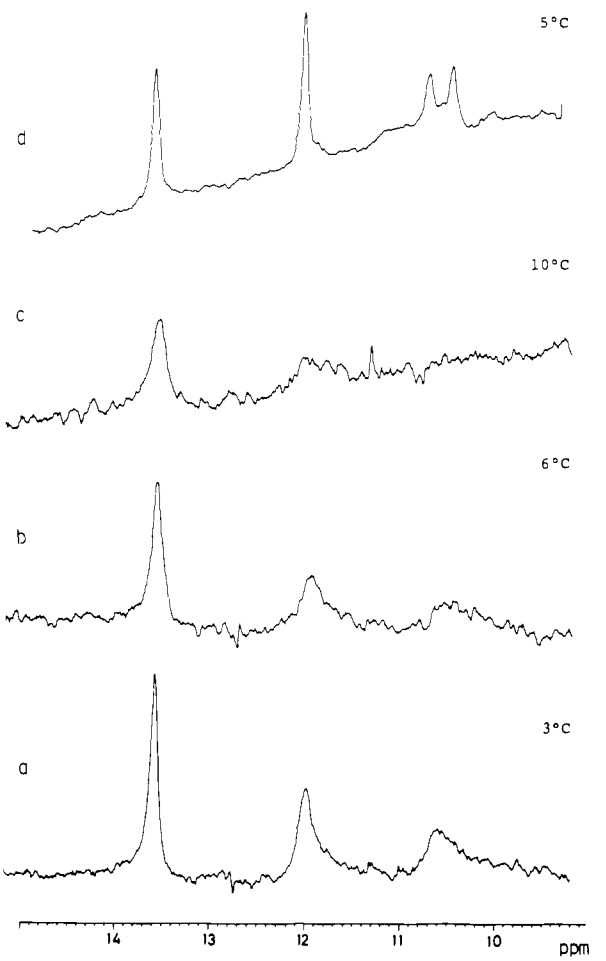

Figure 1. Imino proton region of the 360-MHz ^1H NMR spectrum in aqueous solution: G-G-C-Up (44 mM in 0.1 M NaCl), taken by Redfield pulse sequences at (a) 3 °C, (b), 6 °C and (c) 10 °C (accumulated 100 times); (d) 95% ^{15}N-enriched G*-G-C-Up (73 mM in 0.1 M NaCl), taken by normal single-pulse method with 16 bits AD converter (accumulated 100 times).

G-G-C-Up was synthesized by the modified triester method.[9] G*-G-C-Up, which contains a uniformly ^{15}N-labeled guanosine residue (95% enrichment) at the 5′-terminal, was synthesized by essentially the same procedure except that a 2′-*O*-tetrahydrofuranyl group was used for protection of the 5′-terminal unit. The low-field

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