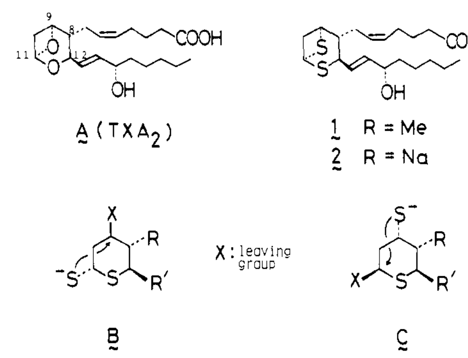
Chart I



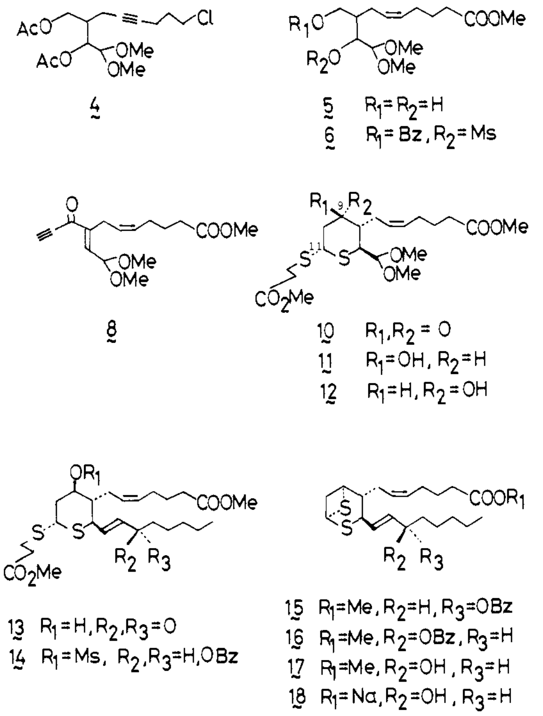
A (TXA$_2$)

1 R = Me
2 R = Na

B

C

Chart II



4

5 R$_1$=R$_2$=H
6 R$_1$=Bz, R$_2$=Ms

8

10 R$_1$,R$_2$ = O
11 R$_1$=OH, R$_2$=H
12 R$_1$=H, R$_2$=OH

13 R$_1$=H, R$_2$,R$_3$=O
14 R$_1$=Ms, R$_2$,R$_3$=H,OBz

15 R$_1$=Me, R$_2$=H, R$_3$=OBz
16 R$_1$=Me, R$_2$=OBz, R$_3$=H
17 R$_1$=Me, R$_2$=OH, R$_3$=H
18 R$_1$=Na, R$_2$=OH, R$_3$=H

to the methyl ester 1[10] (4 equiv of NaOMe, MeOH, 0-20 °C, 90%). Compound 1 was hydrolyzed with 0.2 N aqueous NaOH (1 equiv) (THF, 20 °C) to afford cleanly the sodium salt 2 (>90%).[22] Similary, the C$_{15}$-isomer 17 and its sodium salt 18 were obtained from 16.

Biological Activities: These compounds were very effective in contracting rat aorta strip (contracting dose, CD$_{50}$: **1**, 5×10^{-9} M; **2**, 7×10^{-10} M; **17**, 3×10^{-8} M; **18**, 2×10^{-8} M). Compound **2** caused marked, rapid, and irreversible aggregation of human platelets (effective dose, ED$_{50}$: 4.3×10^{-6} M); however, other compounds showed no aggregation effect.

The TXA$_2$ analogues thus obtained possessed very potent biological activities. In particular, compound 2 showed properties very similar to natural TXA$_2$. We believe that these analogues will be of great value in biological studies.

Acknowledgment. We thank Mr. Hideo Naoki, Suntory Institute for Bioorganic Research, for measurement of ^{1}H NMR (360 MHz) spectra.

Supplementary Material Available: A listing of spectral data (6 pages). Ordering information is given on any current masthead page.

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(21) The value of the coupling constant ($J_{8,12}$) was 7.2 Hz.

(22) The free acids of **2** and **18** were not very stable. The sodium salts were, without further purification, used to study biological activities.

A Tungsten T-Shaped Methylene Complex and Related Methylidyne Hydride Complexes[1]

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A neopentylidene ligand in certain types of Nb and Ta complexes has a large M–C$_\alpha$–C$_\beta$ angle due to what is postulated to be an attraction of the metal for H$_\alpha$ or the C–H$_\alpha$ electron pair.[2] When the metal is formally reduced by two electrons, H$_\alpha$ can either remain in a "bridging" position between C$_\alpha$ and the metal [e.g., as in Ta(CHCMe$_3$)(PMe$_3$)$_4$Cl], or it can actually transfer to the metal to give a neopentylidyne hydride complex.[3] A structural study of a benzylidene complex[4] suggests that the benzylidene ligand, too, can distort significantly from the expected M–C$_\alpha$–C$_\beta$ angle. Since distortion of both the neopentylidene and the benzylidene ligands would be encouraged by steric interaction of the *tert*-butyl or phenyl substituent with the metal, a major question is whether a methylene ligand in certain situations will also distort toward, and in some cases give, a methylidyne hydride complex. We present evidence here that both can happen in tungsten complexes which are isoelectronic with Ta(CHCMe$_3$)(PMe$_3$)$_4$Cl. In all cases, the two inequivalent protons interconvert at room temperature at a rate which is rapid on the M–C$_\alpha$–C$_\beta$ time scale at 25 °C.

W(CH)(PMe$_3$)$_4$Cl[5] reacts with CF$_3$SO$_3$H (or Me$_3$PH$^+$CF$_3$SO$_3^-$, to give red crystals of [W(CH$_2$)(PMe$_3$)$_4$Cl]$^+$CF$_3$SO$_3^-$ (**1**).[6] The chemical shift for the methylene α carbon atom (220 ppm) and J_{CH} (120 Hz) are appropriate for a methylene complex. The ^{1}H NMR spectrum at 298 K in CD$_2$Cl$_2$ shows a signal for the equivalent methylene protons at –0.16 ppm (J_{HW} = 51 Hz), and the ^{31}P{^{1}H} NMR spectrum shows a single peak at –31 ppm (J_{PW} = 248 Hz). The couplings to ^{183}W suggest that neither the methylene protons nor the phosphine ligands dissociate at a rate which is rapid on the NMR time scale at 298 K.

NMR spectra of [W(CH$_2$)L$_4$Cl]$^+$ (L = PMe$_3$) are temperature dependent. When an ^{1}H NMR sample of [W(CH$_2$)L$_4$Cl]$^+$ in CFHCl$_2$/CD$_2$Cl$_2$ is cooled, the -0.16-ppm peak broadens and shifts upfield to ~–0.30 ppm at ~215 K and then disappears into the base line. At 165 K a new, broad peak appears at -7.97 ppm with an estimated area of one proton. Another peak (presumably also of area one) can be located at ~7.05 ppm as part of the shoulder on the CFHCl$_2$ peak. This was confirmed by irradiating at 7.05 ppm and observing that the -7.97-ppm peak nearly disappeared due to transfer of the magnetization from one proton site (7.05 ppm) to the other (-7.97 ppm).[7] The average of the positions of these two peaks (–0.46 ppm) is slightly further upfield of the observed position for the average peak (–0.30 ppm) before it disappeared into the base line. The ^{31}P NMR spectrum at 165 K shows two identical singlets (-22 and -33 ppm) with ^{183}W satellites (J_{PW} = 248 Hz).

A plausible explanation of these findings is that this molecule contains a grossly distorted, approximately "T-shaped" methylene ligand in which one H$_\alpha$ is oriented over one face of the octahedron (A, eq 1). Since grossly distorted neopentylidene and benzylidene ligands are alkylidyne-like,[2a,4,8] we expect H$_A$ to be a methyli-

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(1) Multiple Metal–Carbon Bonds. 22. For part 21, see: Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

(2) (a) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169–176; (b) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 7667–7676.

(3) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6609–6611.

(4) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744–6752.

(5) Sharp, P.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965–966.

(6) Anal. Calcd for WC$_{14}$H$_{38}$ClP$_4$F$_3$SO$_3$: C, 24.48; H, 5.54. Found: C, 24.65; H, 5.72.

(7) Forsé, S.; Hoffman, R. A. *J. Chem. Phys.* **1964**, *39*, 2892–2901.

(8) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–175; (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930–1935.

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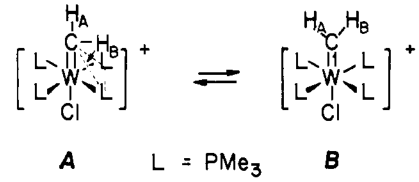
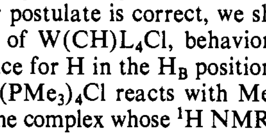


(1)

dyne-like proton with a chemical shift of ~7 ppm.[5] Therefore the high-field signal must be due to H_B. This is entirely consistent with the chemical shift of H_α in grossly distorted neopentylidene complexes [e.g., −7.4 ppm in $Ta(CHCMe_3)(PMe_3)_4Cl$[3]]. As the temperature is raised H_B begins to exchange with H_A, possibly via a symmetric methylene intermediate, B. We cannot exclude the possibility that the H_A/H_B exchange consists *only* of a "rocking" motion, but on the basis of other results in our laboratory on neopentylidene complexes,[9] we believe H_B may actually migrate around the four octahedral faces in the upper half of A before exchanging with H_A.

If our postulate is correct, we should be able to see, by deuteration of $W(CH)L_4Cl$, behavior which is consistent with a preference for H in the H_B position and D in the H_A position.[10] $W(CH)(PMe_3)_4Cl$ reacts with $Me_3PD^+CF_3SO_3^-$ to give a red crystalline complex whose ^1H NMR spectrum shows a methylene peak for $[W(CH_2)L_4Cl]^+$ at −0.16 and a broader peak at −1.40 ppm with approximately the same area. Each shows ^{183}W satellites and the total area is one proton. After this sample was recrystallized in the presence of 20 equiv of CH_3OD, the −1.40-peak was the more intense. We propose that the initial product is a mixture of $[W(CH_2)L_4Cl]^+$, $[W(CHD)L_4Cl]^+$, and $[W(CD_2)L_4Cl]^+$ in approximately a 1:2:1 ratio and that the −1.40-ppm peak in the ^1H NMR spectrum is that due to the methylene proton in $[W(CHD)L_4Cl]^+$. The position of this resonance allows us to determine what the H occupancy of the H_B position is at room temperature in $[W(CHD)L_4Cl]^+$. Let us assume that the position of the resonance for H_A would also be 7.05 ppm at 298 K. Since the average at 298 K for $[W(CH_2)L_4Cl]^+$ is at −0.16 ppm, the resonance for H_B at 298 K would be at −7.37 ppm.[11] In $[W(CHD)L_4Cl]^+$ the average peak at 298 K is at −1.40 ppm. Therefore the proton occupancy of the H_B site is $(7.05 + 1.40)/(7.05 + 7.37) = 0.59$, the equilibrium constant between the $[W(CHD)L_4Cl]^+$ complex in which H_B = H and that in which H_A = H is 0.70, and the former is ~0.20 kcal lower in energy (eq 2). These numbers are inaccurate because of the assumptions

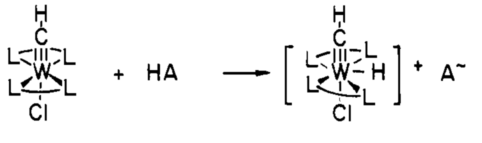


$K_{eq} = 0.70$

$\Delta G = 0.20$ kcal (2)

we made and the uncertainty of the location of the resonance for H_A, but they at least provide some idea of their magnitudes.[12]

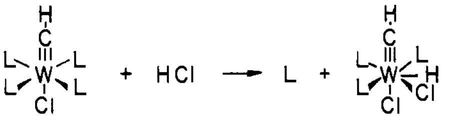
We felt that one reason why $[W(CH_2)(PMe_3)_4Cl]^+CF_3SO_3^-$ is not actually a methylidyne hydride complex might be that a pentagonal bipyramidal molecule in which four PMe_3 ligands and a hydride ligand lie in the pentagonal plane is sterically untenable. Since we know that two dmpe ligands in a related tantalum complex can accomodate a hydride in the pentagonal plane,[13] we prepared $W(CH)(dmpe)_2Cl$,[14] and protonated it with CF_3SO_3H *or* HCl, hoping to find a methylidyne hydride complex instead of a distorted methylene complex. This is the case [eq 3; ν_{WH} 1830 cm^{-1}(w)]. The ^1H NMR spectrum in CD_2Cl_2 at 200 K shows a signal for the methylidyne proton at 5.16 ppm (J_{HW} = 80 Hz), but the signal for the hydride is obscured by the signals for the four dmpe methyl groups. At 325 K in CD_3CN the signal for the methylidyne proton and that for the hydride average to give a quintet (J_{HP} = 18 Hz) at 3.60 ppm. In the ^{13}C NMR spectrum at 243 K the signal due to the methylidyne α carbon is found at 263 ppm, a broad doublet with J_{CH} = 125 Hz. At 295 K it is a *triplet* of quintets (J_{CP} = 12 Hz) with J_{CH} = *69* Hz and J_{CW} = 189 Hz. All these data are consistent with the molecule being a methylidyne hydride complex in which the methylidyne and hydride protons exchange. Note that this equilibration process, as one would expect, appears to have a higher activation energy than that in the distorted methylene complex.



(3)

L—L = $Me_2PCH_2CH_2PMe_2$, $A^- = CF_3SO_3^-$, Cl^-

We knew for some time that $W(CH)(PMe_3)_4Cl$ reacted differently with HCl than with CF_3SO_3H. We now know the product with HCl is actually neutral $W(CH)(H)(PMe_3)_3Cl_2$, with, we believe, a pentagonal-bipyramidal structure related to that postulated for $[W(CH)(H)(dmpe)_2Cl]^+$ (eq 4).[15] A PMe_3 ligand in $[W(CH_2)L_4Cl]^+Cl^-$ (but not a dmpe ligand in $[W(CH_2)(dmpe)_2Cl]^+$) must be labile on the chemical time scale, and Cl^- (but not $CF_3SO_3^-$) can compete with it for the coordination site.



(4)

These results confirm that a methylene ligand is subject to the distortion and reversible α-elimination reaction that neopentylidene or benzylidene ligands are subject to in similar circumstances. We believe the driving force is "oxidation" of the metal from "W^{4+} (d^2)" to "W^{6+} (d^0)". This process must be related to the elimination of an α hydrogen in $[WCp_2(CH_3)]^+$ to give $[WCp_2(CH_2)(H)]^+$ (both postulated intermediates).[16] A plausible extension of these findings is that α-elimination equilibria (either alkyl → alkylidene hydride or alkylidene → alkylidyne hydride) lie to the right only in reduced metal complexes. In d^0 species the alkyl or alkylidene ligand is at most only distorted so as to place H_α in a position from which it can be abstracted by a leaving group on the metal or an external base.[17]

Acknowledgment. R.R.S. thanks the National Science Foundation for support (Grant CHE 79 05307).

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(9) In complexes such as $Ta(CHCMe_3)(PMe_3)_4Cl$ or $Ta(CHCMe_3)(dmpe)_2Cl$, all phosphorus nuclei are equivalent by ^{31}P NMR down to ~140 K. Since the neopentylidene ligands are highly distorted toward neopentylidyne ligands ($J_{CH} \approx 60$ Hz), we believe the process by which this occurs is an "apparent rotation" of the alkylidene ligand, one which simply consists of migration of H_α about the four octahedral faces in the upper half of the molecule. (Turner, H. W., unpublished results.)

(10) (a) Kreevoy, M. M.; Liang, T. M. *J. Am. Chem. Soc.* **1980**, *1028*, 3315–3222 and references therein. (b) Kirchen, R. P.; Okazawa, N.; Ranganayahulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 587–604. (c) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726–7727.

(11) For various reasons which we cannot go into here, we believe the resonance for H_B would shift more than that for H_A as the methylene ligand distorts, and the amount of distortion would increase on lowering the temperature. This would explain why the signal for H_B shifts from −7.37 ppm (estimated) at 298 K to −7.97 ppm at 165 K and therefore why the average resonance shifts upfield.

(12) In an osmium cluster in which H or D in $OsCH_2D$ can interact with a neighboring Os atom, the energy difference between the two forms is 130 ± 10 cal.[10c]

(13) Churchill, M. R.; Wasserman, H. W.; Turner, H. J.; Schrock, R. R., to be published.

(14) This molecule was prepared by heating $W(CH)(PMe_3)_4Cl$ in neat, excess dmpe at 110 °C for 48 h.

(15) Anal. Calcd for $WC_{10}H_{29}Cl_2P_3$: C, 24.15; H, 5.84. Found: C, 24.55; H, 5.95. At 200 K the CH resonance is found at 6.46 ppm (broad singlet, J_{HW} = 78 Hz) and the WH resonance is found at 4.53 ppm (~dt, $J_{HP'}$ = 18 Hz, J_{HP_2} = 95 Hz) in the ^1H NMR spectrum. The W≡C resonance is found at 246 ppm (d, J_{CH} = 150 Hz). ν_{WH} is found at 2050 cm^{-1} (w, br). At 293 K the CH and WH resonances average in the ^1H NMR spectrum to give a single peak at +4.6 ppm, a broad quartet with J_{HP} = 24 Hz. One explanation of why the average resonance at room temperature is not near the average of the two peak positions in the low temperature spectrum is that at room temperature a *nonnegligible* fraction of the molecule at room temperature is actually a distorted methylene complex or a cationic species.

(16) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

(17) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.