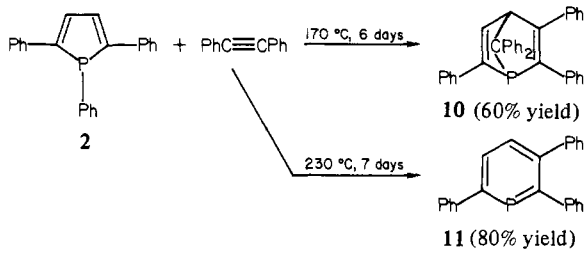
(C) Methylenephosphines are known to give [2 + 4] Diels–Alder cycloadducts with conjugated dienes.[10] We thus reacted **1** with 2,3-dimethyl-1,3-butadiene at 170 °C. We obtained the expected adduct **9** together with a minor byproduct which was not fully characterized.[11]

Then we wanted to check if the formation of **6** by thermolysis of **1** was a general phenomenon. Indeed 2,5 disubstitution could prevent the 1,5 migration of the 1-phenyl substituent. We thus reacted **2** with tolane. In fact we noted that the reaction was more sluggish and gave a lower yield but, nevertheless, produced the expected 1-phosphanorbornadiene **10**.[12]



10 (60% yield)

11 (80% yield)

In the mass spectrum of **10** we noted strong peaks corresponding to the loss of the CPh_2 bridge. We thus suspected that the thermolysis of **10** could produce the phosphorin **11**. Indeed when **2** was reacted with tolane at 230 °C, 2,3,6-triphenylphosphorin[13] was directly obtained in high yield. The diphenylcarbene was mainly recovered as diphenylmethane[14] which is known to be one of the main products resulting from the evolution of this carbene at high temperature.[15] This very simple one-step synthesis of phosphorins from phospholes offers numerous possibilities and supplements nicely the earlier procedures.[16] Since the structure of **3** was a key point of our demonstration, we decided to perform a full X-ray crystal structure analysis of this product. Suitable single crystals of **3** were selected from the recrystallization vessel. They belong to the monoclinic system, space group $P2_1/n$ (C_{2h}^5) with a = 10.588 (1), b = 10.694 (1), c = 17.676 (2) Å; β = 92.83 (2)°; V = 1999 Å^3; z = 4; ρ_{calcd} = 1.218 g/cm^{-3}; F_{000} = 776 e.

Diffraction data were collected in the $\theta/2\theta$ scan mode by using a CAD4 Enraf–Nonius automatic diffractometer and Ni-filtered Cu Kα radiation. The structure was solved by direct methods[17] using the Enraf–Nonius SDP/V17[18] package on a PDP11/60 computer. Full matrix refinement using 1770 reflections having $I > 3\sigma(I)$ converged to conventional agreement factors R_1 and R_2 of 0.048 and 0.066. Hydrogen atoms were introduced by their computed coordinates but not refined.

The structure (Figure 1)[19] consists of discrete molecules only linked by van der Waals contacts and hydrogen bonds. Selected geometric details are given in the caption of Figure 1.

The most interesting observation is related to the strain around phosphorus. This strain appears to be higher in **3** than in 1-phosphanorbornanes[20] as monitored by the mean CPC angle values (89° in **3** vs. 96.2° in 1-phosphanorbornane 1-oxide[20]). This explains the loss of the CPh_2 bridge of **10** upon heating.

The broad new chemistry of 2*H*-phospholes will be described in due course.

Supplementary Material Available: Table I gives the atomic coordinates and β_{ij} for all nonhydrogen atoms and Table II lists the observed and calculated structure factors times 10 for all observed reflections (9 pages). Ordering information is given on any current masthead page.

(9) Phospholene oxide (**8**) is purified by chromatography on silica gel (AcOEt–MeOH = 90:10) and kugelrohr distillation (bp ca. 170 °C (0.1 torr)]. ^{1}H NMR ($CDCl_3$) δ 1.25 (d, $^3J_{H-H}$ = 7.1 Hz, *Me*CH), 1.34 (d, $^3J_{H-H}$ = 6.8 Hz, *Me*CH), 1.49 (d, $^2J_{H-P}$ = 12.9 Hz, MeP), 1.53 (d, $^2J_{H-P}$ = 12.7 Hz, MeP), 1.86 (d, $^4J_{H-P}$ = 2.4 Hz, MeC=), 1.87 (d, $^4J_{H-P}$ = 2.4 Hz, MeC=), 7.34–7.39 (m, Ph); ^{31}P NMR ($CDCl_3$) δ +58.2, +59.7; IR (Nujol) $\nu_{C=C}$ 1620 cm^{-1}; $\nu_{P=O}$ 1150 and 1190 cm^{-1}; mass spectrum (70 eV, 90 °C), *m/e* 220 (M, 100%).

(10) The reaction of methylenephosphines with conjugated dienes has been described in a preliminary communication: Klebach, Th. C.; Lourens, R.; Wisse, J.; Bickelhaupt, F. International Conference on Phosphorus Chemistry, Halle, Sept 1979 (ICPC 79). Conjugated dienes also cycloadd onto the P=C bond of 1,2,3-diazaphospholes: Carrié, R., personal communication. Arbuzov, B. A.; Dianova, E. N., ICPC 79.

(11) Chromatography on silica gel (hexane–toluene = 80:20) affords first the incompletely characterized minor byproduct (^{31}P NMR –9.37 δ), which seems to be an isomer of **9** according to its mass spectrum, and then **9** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.34 (m, 3 H, Me), 1.70 (m, 3 H, Me), 1.75 (pseudo s, 6 H, Me), 1.99–2.56 (complex m, 6 H, CH_2), 7.21 (narrow m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 12.0 (s, Me), 17.2 (s, Me), 20.4 (s, Me), 21.5 (s, Me), 31.0 (d, J_{C-P} = 20.5 Hz, CH_2), 36.2 (d, J_{C-P} = 14.6 Hz, CH_2), 37.9 (s, CH_2), 62.3 (d, $^1J_{C-P}$ = 12.7 Hz, PhCP), 125–148.7 (sp^2 carbons); ^{31}P NMR ($CDCl_3$) δ –5.60, mass spectrum (70 eV, 100 °C) *m/e* 270 (M, 73%), 188 (M – C_6H_{10}, 100%).

(12) The reaction is performed with a great excess of tolane: molar ratio **2**:tolane = 1:2.8. Compound **10** is purified by chromatography on silica gel (hexane–toluene = 80:20). Yellow crystals; mp 148 °C (methanol); ^{1}H NMR ($CDCl_3$) δ 5.26 (A*M*X, 1 H, $^3J_{AM}$ = 3.9 Hz, $^3J_{M-P}$ = 3.05 Hz, saturated proton), 6.9–7.55 (m, 25 H, Ph), 7.65 (*A*MX, 1 H, $^3J_{A-P}$ = 6.60 Hz, ethylenic proton); ^{31}P NMR ($CDCl_3$) δ + 19.9; ^{13}C NMR ($CDCl_3$) δ 70.6 (d, $^2J_{C-P}$ = 4.9 Hz, saturated CH); 88.6 (pseudo s, $^1J_{C-P} \sim 0$ Hz, CPh_2), 125.6–157.7 (sp^2 carbons); mass spectrum (70 eV, 140 °C) *m/e* 490 (M, 100%), 166 (CPh_2, 22%), 165 (48%).

(13) Except for the temperature, the overall procedure is identical for the preparations of **10** and **11**. The phosphorin **11** is obtained as pale yellow crystals; mp 150 °C (hexane). ^{1}H NMR ($CDCl_3$) δ 7.61 (A*B*X, $^4J_{B-P}$ = 3.9 Hz, H_γ), 8.02 (*A*BX, $^3J_{A-P}$ = 5.5 Hz, $^3J_{A-B}$ = 8.66 Hz, H_β); ^{13}C NMR ($CDCl_3$) δ 169.7 (d, $^1J_{C-P}$ = 53.7 Hz, C_α), 170.4 (d, $^1J_{C-P}$ = 53.7 Hz, C_α); ^{31}P NMR ($CDCl_3$) δ +198; mass spectrum (70 eV, 150 °C), *m/e* 324 (M, 100%).

(14) Diphenylmethane was identified in the crude phosphorin by its ^{1}H and ^{13}C NMR spectra: ^{1}H NMR ($CDCl_3$) δ 3.94 (s, CH_2Ph_2); ^{13}C NMR ($CDCl_3$) δ 41.9 (s, CH_2Ph_2). See for comparison: Stibor, I.; Srogl, J.; Janda, M.; Salajka, Z.; Trška, P. *Collect. Czech. Chem. Commun.* **1977**, *42*, 987.

(15) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *J. Am. Chem. Soc.* **1979**, *101*, 6009 and references cited herein.

(16) Märkl, G. *Phosphorus Sulfur* **1977**, *3*, 77. Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. Mathey, F. *Tetrahedron Lett.* **1979**, *20*, 1753.

(17) Germain, G.; Main, P.; Woolfson, M. H. *Acta Crystallogr., Sect. B* **1970**, *26*, 274. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.

(18) Frenz, B. A. "The Enraf-Nonius CAD4-SDP. Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., Van Koenigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

(19) Drawing performed by using program ORTEP II: Johnson, C. K. Report ORNL 3794, Oak Ridge, TN, 1965.

(20) Milbrath, D. S.; Verkade, J. G.; Kenyon, G. L.; Eargle, D. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 3167.

Synthesis of Thromboxane A_2 Analogues: DL-9,11:11,12-Dideoxa-9,11:11,12-diepithiothromboxane A_2

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Received April 23, 1981

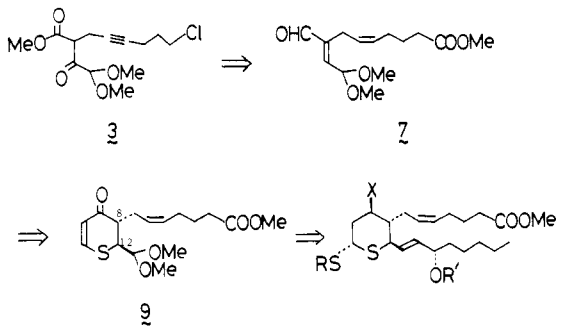
The metabolic pathway of arachidonic acid involves the formation of cyclic endoperoxides which are rapidly converted into thromboxane A_2 (TXA_2), prostaglandin I_2(PGI_2), and other prostaglandins. TXA_2 is an unstable substance with potent thrombotic and vasoconstricting properties generated by platelets.[1] Samuelsson and his associates proposed formula A (Chart I) as a possible structure for TXA_2 on the basis of its origin and stable degradation products and deduced a physiological half-life ($t_{1/2}$ = 32 s in aqueous pH 7.4 solution at 37 °C).[2] TXA_2 with these biological activities has been identified in many tissues, including platelets, leucocytes, spleen, inflammatory glanuloma, brain, and kidney. It is of considerable pathophysiological interest in thrombotic diseases and anaphylatic reactions and plays a

(1) For review, see: Samuelsson, B.; Goldyne, M.; Granström, E.; Hamberg, M.; Hammarström, S.; Malmsten, C. *Annu. Rev. Biochem.* **1978**, *47*, 997.

(2) Hamberg, M.; Svensson, J.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2994.

0002-7863/81/1503-4597$01.25/0

Scheme I



physiological role in hemostasis.

Stable relatives of this chemically unusual and intriguing structure with agonistic or antagonistic actions would facilitate research in this area and may prove to be therapeutically useful. Recently a few interesting papers on the synthesis of stable TXA_2 analogues have been reported.[3,4] In this communication we wish to report the synthesis and properties of TXA_2 analogues **1** and **2** in which two oxygen atoms in the bicyclic framework of TXA_2 are replaced by two sulfur atoms[4] and which are the first compounds in this class.

The most difficult problem in our synthesis was construction of the 2,6-dithiabicyclo[3.1.1]heptane skeleton.[5] Two possible intermediates B and C are the obvious precursors of the desired framework. After some model experiments,[6] it was found to be easy to control stereochemistry of the substituents on the six-membered ring starting from the intermediate B. Our synthetic strategy is outlined in Scheme I which was designed such that the two sulfur atoms were introduced into the system by different conjugate addition reactions with full stereoselectivity.

The synthesis of the key intermediate **7** started from β-keto ester **3**[7] which was easily obtained by reaction of methyl 4,4-dimethoxyacetoacetate[8] with 6-chloro-1-iodo-2-hexyne[9] (NaOMe, MeOH, 25 °C–reflux, 77%). Compound **3** was converted to the diacetate **4** in 61% overall yield by a three-step sequence: (1) reduction of ketone ($NaBH_4$, MeOH, −55 °C), (2) reduction of ester (3.2 equiv of diisobutylaluminum hydride, toluene, −78 °C), and (3) acetylation of the resulting two alcohols (AcCl, pyridine, CH_2Cl_2, 25 °C). After replacement of the chloro group of **4** by a cyano functionality (NaCN, HMPA, 25 °C), hydrolysis of the resulting cyanodiacetate (10% aqueous NaOH, reflux), followed by esterification with diazomethane and then hydrogenation of the triple bond by Lindlar catalyst afforded the diol-ester **5** in 66% yield from **4**. Compound **5**, after protection of the primary alcohol as its benzoate (1.1 equiv of benzoyl chloride, pyridine, CH_2Cl_2, 0 °C), was transformed into the mesylate **6** (1.2 equiv of methanesulfonyl chloride (MsCl), 1.2 equiv of Et_3N, −20 °C, 84% in two steps). Conversion of **6** into the aldehyde **7**[10] was achieved in 69% overall yield by the following sequence: removal of the benzoyl group (1.2 equiv of NaOMe, MeOH, 0–25 °C), Collins oxidation of the resulting alcohol to the corresponding aldehyde at 0 °C, and treatment with 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) (1.3 equiv) in benzene at 25 °C.

Compound **7** was condensed with lithium acetylide[11] (2 equiv) in a THF solution containing 1.5 equiv of HMPA and 1.5 equiv of tetramethylethylenediamine (TMEDA)[12] at −78 °C to form the acetylenic alcohol which was immediately oxidized to the acetylenic ketone **8** (Collins reagent, −20 °C, 57% from **5**). Exposure of **8** to H_2S[13] (2 equiv of NaOAc, EtOH, reflux) predominantly gave the trans-isomer **9**[10] (78%) accompanied by the cis isomer (5%).[14] Conjugate addition of methyl 3-mercaptopropionate to **9** was realized with stereoselectivity by using diisopropylethylamine (0.2 equiv) in DMF at 25 °C to yield the ketone **10**[10,15] (73%) which was reduced ($NaBH_4$, EtOH, 0 °C) to the equatorial alcohol **11**.[16] Transformation of **11** into the enone **13**[10] was effected by removal of dimethylacetal (0.1 equiv of *p*-toluenesulfonic acid, acetone, 0 °C) followed by condensation of the resulting aldehyde with 1-(tributylphosphoranylidene)-2-heptanone (excess) in ether at 25 °C (77% in two steps).

The synthesis was completed by constructing the 2,6-dithiabicyclo[3.1.1]heptane skeleton.[17] This crucial reaction was performed on the precursor **14**, which was easily obtained from **13** in three steps: mesylation with MsCl, reduction of the enone to the corresponding allylic alcohol with $NaBH_4$,[18] and protection of the resulting alcohol as the benzoate group. After a number of attempts to effect base-catalyzed ring closure of **14**, it was found that potassium *tert*-butoxide (1.5 equiv) in HMPA (25 °C) led to the desired bicyclic compounds (21%), which were a mixture of C_{15} isomers and were separated by column chromatography on silica gel (**15**:**16** = 1:2.4).[19-21] Compound **15** was converted

(3) (a) Ohuchida, S.; Hamanaka, N.; Hayashi, M. *Tetrahedron Lett.* **1979**, 3661. (b) Ansell, M. F.; Caton, M. P. L.; Palfreyman, M. N.; Stuttle, K. A. *Ibid.* **1979**, 4497. (c) Nicolaou, K. C.; Magolda, R. L.; Smith, J. B.; Aharony, D.; Smith, E. F.; Lefer, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2556. (d) Lefer, A. M.; Smith, E. F.; Araki, H.; Smith, J. B.; Aharony, D.; Claremon, D. A.; Magolda, R. L.; Nicolaou, K. C. *Ibid.* **1980**, *77*, 1706. (e) Corey, E. J.; Ponder, J. W.; Ulrich, P. *Tetrahedron Lett.* **1980**, *21*, 137. (f) Maxey, K. M.; Bundy, G. L. *Ibid.* **1980**, *21*, 445.

(4) For some other sulfur analogues, see: (a) Kosuge, S.; Hamanaka, N.; Hayashi, M. *Tetrahedron Lett.* **1981**, *22*, 1345. (b) Ohuchida, S.; Hamanaka, N.; Hayashi, M. *Ibid.* **1981**, *22*, 1349.

(5) To the best of our knowledge, the synthesis of this skeleton has not been repororted yet.

(6) This result will be reported in detail elsewhere.

(7) Each compound described herein was fully characterized by IR, ^1H NMR, and mass spectroscopy.

(8) Royals, E. E.; Robinson, A. G., III. *J. Am. Chem. Soc.* **1956**, *78*, 4161.

(9) Rachlin, A. I; Wasyliw, N.; Goldberg, M. W. *J. Org. Chem.* **1961**, *26*, 2688.

(10) Partial spectral data. **7**: NMR δ 9.46 (s, 1 H), 6.36 (d, J = 6 Hz, 1 H), 5.57–5.12 (m, 2 H), 5.27 (d, J = 6 Hz, 1 H), 3.68 (s, 3 H), 3.37 (s, 6 H), 3.09 (d, J = 5 Hz, 2 H); IR (cm^{-1}) 1730, 1680; mass spectrum, m/e 270 (M^+). **9**: NMR δ 7.33 (d, J = 10 Hz, 1 H), 6.07 (d, J = 10 Hz, 1 H), 5.43 (m, 2 H), 4.67 (d, J = 8 Hz, 1 H), 3.85 (dd, J = 8 and 3.5 Hz, 1 H), 3.67 (s, 3 H), 3.38 (s, 3 H), 3.37 (s, 3 H); IR (cm^{-1}) 1725, 1655; mass spectrum, m/e 328 (M^+). **10**: NMR δ 5.43 (m, 1 H), 5.32 (m, 1 H), 4.64 (dd, J = 8.7 and 4.7 Hz, 1 H), 4.43 (d, J = 4.1 Hz, 1 H), 3.70 (s, 3 H), 3.67 (s, 3 H), 3.52 (dd, J = 4.3 and 4.1 Hz, 1 H), 3.42 (s, 3 H), 3.37 (s, 3 H); IR (cm^{-1}) 1725, 1705; mass spectrum, m/e 448 (M^+). **13**: NMR δ 6.85 (dd, J = 16 and 8 Hz, 1 H), 6.25 (dd, 16 and 1 Hz, 1 H), 5.42 (m, 2 H), 4.16 (dd, J = 9 and 4 Hz, 1 H), 3. 70 (s, 3 H), 3.67 (s, 3 H), 0.90 (t, J = 6 Hz, 3 H); IR (cm^{-1}) 3500, 1730, 1690, 1660, 1610, 970; mass spectrum, m/e 500 (M^+). **1**: NMR δ 6.24 (dd, J = 14.4 and 10.0 Hz, 1 H), 5.55 (dd, J = 14.4 and 6.5 Hz, 1 H), 5.42 (m, 1 H), 5.28 (m, 1 H), 4.28 (dd, J = 5.7 and 3.8 Hz, 1 H), 4.23 (dd, J = 10.0 and 7.2 Hz, 1 H), 4.15 (dt, J = 6.5 and 6.5 Hz, 1 H), 3.88 (ddd, J = 10.1, 6.0, and 5.7 Hz, 1 H), 3.68 (s, 3 H), 3.46 (ddd, J = 6.0, 3.8, and ca. 3.5 Hz, 1 H), 2.57 (d, J = 10.1 Hz, 1 H), 2.31 (t, J = 7.3 Hz, 2H), 0.88 (t, J = 6.6 Hz, 3 H); IR (cm^{-1}) 3450, 1730, 970; mass spectrum 398 (M^+).

(11) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.

(12) This reaction did not proceed smoothly in the absence of TMEDA.

(13) Chen, C. H.; Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1977**, *42*, 2777.

(14) Although these isomers showed very similar values of the coupling constant ($J_{8,12}$), the major product (J = 3.5 Hz) was assigned as the trans-isomer **9** and the other (J = 2.6 Hz) as the cis isomer on the basis of ^1H NMR spectral data. That was verified by further conversion of **9** to the final compound.[21]

(15) The C_{11} epimer was isolated in 18% yield.

(16) The ratio **11**/C_9-epimer **12** was 1:2 (total yield 92%). The epimer **12** was oxidized with pyridinium dichromate (PDC) (excess) to the starting ketone **8** (91%), which was used again. The compound **11** was obtained in 44% yield from **10** by repeating oxidation-reduction twice.

(17) We have recently reported the synthesis of 6-thiabicyclo[3.1.1]heptane skeleton.[4b]

(18) The reduction provided a diastereomeric mixture of allylic alcohols which showed as one spot on a silica gel plate under many solvent systems; so we were unsuccessful in separating these diastereomers in this step.

(19) This ratio is inexplicable. We think that $NaBH_4$ reduction in **13** → **14** produced about an equal amount of diastereomers.

(20) TLC R_f values of these diastereomers were 0.35 and 0.40 (cyclohexane–AcOEt 9:1 developed twice). According to previous experience, the more polar isomer was assigned to **15** ($C_{15}\alpha$) and the less polar to **16** ($C_{15}\beta$).[3a]

Chart I

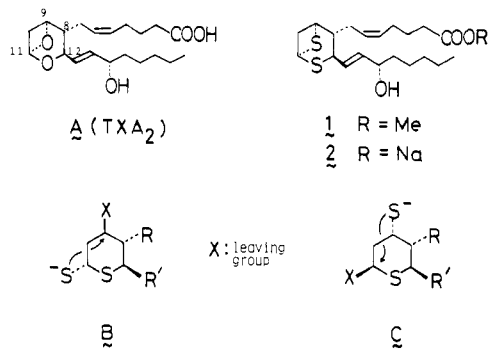
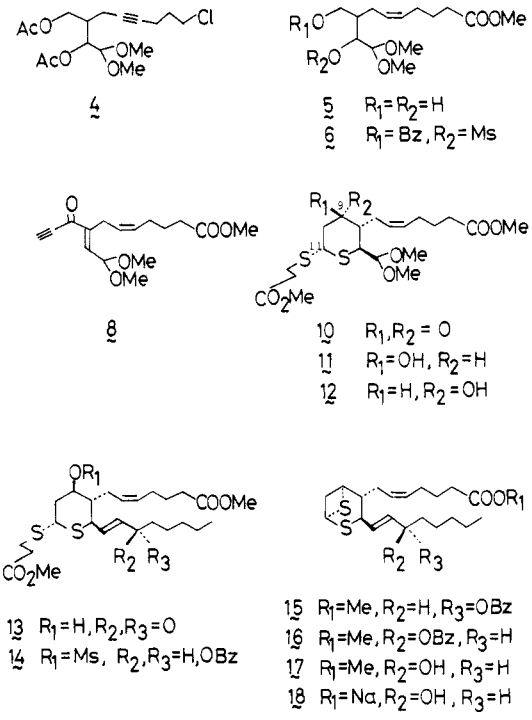


Chart II



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 ^1H NMR (360 MHz) spectra.

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

(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_α or the $C-H_\alpha$ electron pair.[2] When the metal is formally reduced by two electrons, H_α can either remain in a "bridging" position between C_α and the metal [e.g., as in $Ta(CHCMe_3)(PMe_3)_4Cl$], 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 $Ta(CHCMe_3)(PMe_3)_4Cl$. 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.

$W(CH)(PMe_3)_4Cl$[5] reacts with CF_3SO_3H (or $Me_3PH^+CF_3SO_3^-$, to give red crystals of $[W(CH_2)(PMe_3)_4Cl]^+CF_3SO_3^-$ (**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 ^1H NMR spectrum at 298 K in CD_2Cl_2 shows a signal for the equivalent methylene protons at −0.16 ppm (J_{HW} = 51 Hz), and the $^{31}P\{^1H\}$ 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 $[W(CH_2)L_4Cl]^+$ ($L = PMe_3$) are temperature dependent. When an ^1H NMR sample of $[W(CH_2)L_4Cl]^+$ in $CFHCl_2/CD_2Cl_2$ 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_α 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-

(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.
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