the presence of (DL)-α-(monofluoromethyl)dopa (50 μM), a potent enzyme-activated irreversible inhibitor of AADC,[14] formation of **1a** from **2a** was completely blocked. In addition, incubation of an MAO preparation with aliquots from the solution containing AADC and **2a** resulted in an inhibition of MAO activity that increased with the amount of conversion of **2a** into **1a**. No MAO inhibition occurred when AADC was omitted from the incubation medium nor when both AADC and (DL)-α-(monofluoro-methyl)dopa were added together, indicating that **2a** is not an inhibitor of MAO per se but must be decarboxylated to **1a** before inhibition takes place. A comparison of the V_{max} values for **2a** and L-Dopa, a natural substrate of AADC, showed that the rate of decarboxylation of **2a** by AADC was approximately 65% of that of L-Dopa.

In conclusion, **2a** is the first example of an enzyme-activated irreversible inhibitor of MAO requiring activation by AADC.[16] This approach to enzyme inhibition, relying on a biosynthetic enzyme of a given metabolic pathway to generate in situ an enzyme-activated inhibitor of a catabolic enzyme in the same pathway, undoubtedly adds a new dimension of site selectivity to target enzyme specificity.[17]

Supplementary Material Available: X-ray experimental section and tables of positional and thermal parameters, temperature factors, and crystal structure data (10 pages). Ordering information is given on any current masthead page.

(14) (a) Jung, M. J.; Palfreyman, M. G.; Wagner, J.; Bey, P.; Ribereau-Gayon, G.; Zraika, M.; Koch-Weser, J. *Life Sci.* **1979**, *24*, 1037–1042. (b) Maycock, A. L.; Aster, S. D.; Patchett, A. A. *Biochemistry* **1980**, *19*, 709–718.

(15) Christmas, A. J.; Coulson, C. J.; Maxwell, D. R.; Riddel, D. *Br. J. Pharmacol.* **1972**, *45*, 490–503.

(16) In rats, **2a** (0.5 mg/kg given orally) inhibits brain MAO A and B by 63% and 34%, respectively. The amine **1a** at 0.25 mg/kg does not affect brain MAO activity.

(17) A similar dual enzyme-activated approach leading to site-selective inhibition of AADC has recently been reported by: Jung, M.; Hornsperger, J. M.; Gerhart, F.; Wagner, J. *Biochem. Pharmacol.* **1984**, *33*, 327–330.

Transformation of a Tungstenacyclobutadiene Complex into a Nonfluxional η³-Cyclopropenyl Complex by Addition of a Donor Ligand. The X-ray Structure of W(η⁵-C₅H₅)[C₃(CMe₃)₂Me](PMe₃)Cl₂

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We have reported recently that tungstenacyclobutadiene complexes are formed when internal acetylenes react with tungsten alkylidyne complexes. In trigonal-bipyramidal W[C(CMe₃)C-(Me)C(Me)]Cl₃[1] (and two other trigonal-bipyramidal complexes[2]) the symmetric WC₃ ring is found in the equatorial plane. In W(η⁵-C₅H₅)[C(Ph)C(CMe₃)C(Ph)]Cl₂,[3] however, the tungstenacyclobutadiene ring is bent and the bonds alternate (double-single–double–single) around the WC₃ ring. The bent WC₃ ring could be regarded as being halfway between a planar WC₃ ring

(1) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

(2) The X-ray structures of W(C₃Et₃)[O-2,6-C₆H₃(i-Pr)₂]₃ and W-(C₃Et₃)[OCH(CF₃)₂]₃ are similar to that of W[C(CMe₃)C(Me)C(Me)]Cl₃.[1] Full details in press.

(3) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Oganometallics* **1983**, *2*, 1046.
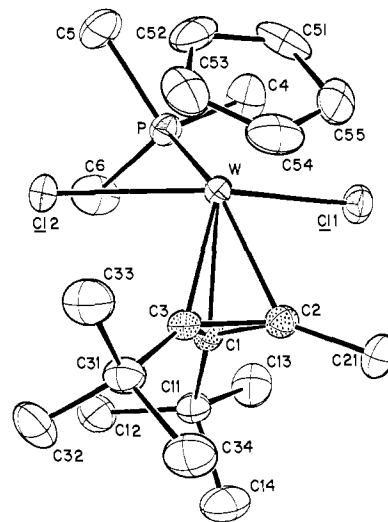
Figure 1. ORTEP II drawing of the structure of W(η⁵-C₅H₅)[C₃(CMe₃)-Me](PMe₃)Cl₂ (30% ellipsoids).

and a WC₃ tetrahedron. Here we show that a molecule containing the WC₃ tetrahedron forms when trimethylphosphine is added to what is probably a bent WC₃ ring in a complex analogous to W(η⁵-C₅H₅)[C(Ph)C(CMe₃)C(Ph)]Cl₂. This finding has important implications for the mechanism of acetylene metathesis and of forming cyclopentadienyl complexes from tungstena-cyclobutadiene complexes and acetylenes,[1,3] and also raises some fundamental questions concerning the nature of MC₃R₃ complexes containing a tetrahedral MC₃ core.

When Me₃CC≡CMe is added to an ether solution of purple W(η⁵-C₅H₅)(CCMe₃)Cl₂, a green complex with the formula W(η⁵-C₅H₅)(CCMe₃)(Me₃CC≡CMe)Cl₂ is formed.[4] This molecule appears to be a bent tungstenacyclobutadiene complex analogous to W(η⁵-C₅H₅)[C(Ph)C(CMe₃)C(Ph)]Cl₂[3] on the basis of observing only one type of *tert*-butyl group by ¹H and ¹³C NMR and a broad peak at ~202 ppm for the ring carbon atoms. We have proposed that such "bent" tungstenacycles are rearranging on the NMR time scale.[3] When PMe₃ is added to W(η⁵-C₅H₅)[C₂(CMe₃)₂CMe]Cl₂ a red crystalline "monoadduct" is formed in which the two *tert*-butyl groups are inequivalent, and all three "ring" carbon atoms are inequivalent (88.59, 64.30, and 56.65 ppm) and coupled to phosphorus by 9.8, ~2, and ~0 Hz, respectively. Large red cubes grown slowly from pentane at ~−30 °C over a period of ~2 weeks were used for an X-ray study.[5]

The molecular geometry of the complex is illustrated in Figure 1. It is approximately a "four-legged piano stool" with the C₃ ring taking up the position trans to the PMe₃ ligand. The two tungsten–chloride distances (W–Cl(1) = 2.538 (2) and W–Cl(2) = 2.504 (2) Å) and the tungsten–phosphorus distance (W–P = 2.600 (2) Å) are normal. Individual W–C distances to the C₅ ring range from 2.334 (8) to 2.373 (9) Å, C–C distances within the C₅ ring range from 1.359 (12) to 1.408 (11) Å, and the W–C₅ ring centroid distance is 2.046 Å; all are unexceptional. The three carbon atoms of the C₃ ring are nearly equidistant from the metal [W–C(1) = 2.139 (5), W–C(2) = 2.150 (6), W–C(3) = 2.200 (6) Å]. Since the C(2)–C(3) bond roughly parallels the Cl-

(4) Anal. Calcd for WC₁₇H₂₆Cl₂: C, 42.09; H, 5.40. Found: C, 41.75; H, 5.46.

(5) The complex crystallizes in the centrosymmetric monoclinic space group P2₁/c with a = 10.302 (3) Å, b = 15.314 (3) Å, c = 14.130 (2) Å, β = 98.036 (16)°, V = 2207.4 (8) Å³, and D(calcd) = 1.69 g cm⁻³ for Z = 4 and M_r = 561.28. There is no crystallographic symmetry imposed upon the molecule. Diffraction data were collected on a Syntex P2₁ automated four-circle diffractometer via a coupled θ(crystal)–2θ(counter) scan technique[6] and were corrected for the effects of absorption (μ = 58.5 cm⁻¹). The structure was solved by a combination of Patterson, difference-Fourier, and least-squares refinement techniques; resulting discrepancy indices are R_F = 4.7% and R_{wF} = 3.4% for all 3913 unique data in the range 2θ = 4.5–50.0° (Mo Kα radiation) and R_F = 3.4% and R_{wF} = 3.2% for those 3290 data with |F_o| > 3σ|F_o|.

(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

Table I. Metal–Ring Distances in η^3-C_3R_3 Complexes

complex	M–C_3 centroid	M–C distances
Ni(C_3Ph_3)Cl_2(py)·(py)[7b]	1.941 (5)	1.896 (8), 1.958 (8), 1.968 (8)
Ni(C_3Ph_3)(η^5-C_5H_5)[7c]	1.961 (4)	1.953 (6), 1.961 (6), 1.968 (6)
Co(C_3Ph_3)(CO)$_3$[7d]	2.01 (1)	2.008 (3), 1.995 (3), 2.024 (3)
Mo(C_3Ph_3)(CO)$_2$(bpy)Br[7e]	2.06	2.193 (18), 2.204 (26), 2.262 (22)
W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2	1.991	2.139 (5), 2.150 (6), 2.200 (6)

(2)–W–Cl(1) axis, the longer W–C(3) bond might be ascribed to steric interaction between Cl(2) and the *tert*-butyl group containing C(31). The tungsten atom lies 1.991 Å from the C_3 ring. The three ring substituents are displaced by –0.908 (C(11)), –0.632 (C(21)), and –0.752 Å (C(31)) from the C_3 ring, which translates into a bending back of C(11) by 36.7°, C(21) by 25.2°, and C(31) by 29.5° from the C_3 plane. The ring to substituent distances are C(1)–C(11) = 1.520 (8), C(2)–C(21) = 1.483 (9), and C(3)–C(31) = 1.525 (8) Å. Within the C_3 ring the distances are C(1)–C(2) = 1.466 (7), C(2)–C(3) = 1.416 (8), and C-(3)–C(1) = 1.473 (8) Å; the shorter C(2)–C(3) bond is statistically just barely significant.

Several structures of molecules containing the C_3Ph_3 ring have been reported.[7] The metal–carbon distances in the C_3Ph_3 complexes in which the ring is symmetrically bound to the metal[7b–e] are listed in Table I. There appears to be a trend toward relatively short W–C distances in W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2. This trend is supported by the fact that in Ni(η^3-C_3Ph_3)(η^5-C_5H_5) the C_3 ring is *further* from the Ni than the C_5 ring by ∼0.05 Å (1.779 vs. 1.726 Å) while in the W complex the C_3 ring is *closer* to the metal than the C_5 ring by ∼0.05 Å (1.991 vs. 2.046 Å). Second, the phenyl rings in each η^3-C_3Ph_3 complex are bent out of the C_3 plane by ∼20° while in the W complex the angles vary from ∼25° (for the methyl substituent) to between ∼30° and 37° (for the *tert*-butyl substituents). The structural evidence suggests that the tungsten complex contains a more tightly bound, less cyclopropenium-like, η^3-C_3 ring. The difference between the average C–C distance in the WC$_3$ system (1.45 Å) vs. in the C_3Ph_3 systems (1.42–1.43 Å), although barely significant, is consistent with this view.[8]

Of more impact than structural arguments is the fact that while the C_3 ring rotates readily in η^3-C_3R_3 complexes where ring rotation (or lack thereof) can be established,[8–10] in W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2 the C_3 ring does not rotate readily.[11] It would not seem prohibitively difficult for solely steric reasons for the C_3 ring to rotate counterclockwise by 60° to produce an intermediate complex containing a plane of symmetry that passes through the PMe$_3$ ligand and C(2) and bisects the

η^5-C_5H_5 ligand and the C(1)–C(3) bond. Therefore, we must conclude that the C_3 ring in W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$]-(PMe$_3$)Cl_2 is significantly different from those in lower oxidation state η^3-C_3R_3 complexes. Although the data might support the argument that the complex contains W(VI) and a $C_3R_3^{3-}$ ligand, we prefer the less extreme point of view that it contains W(IV) and a $C_3R_3^-$ (i.e., η^3-cyclopropenyl) ligand.

Stable Simple Enols. 6. A Shift in the Threshold Mechanism of Correlated Rotation in 2,2-Dimesitylethenols from a One- to a Two-Ring Flip[1]

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Diaryl- and triarylvinyl systems Ar'ArC=C(Y)R and Ar'ArC=C(Y)Ar″ exist in a propeller conformation[2,3] and are the vinyl analogues of the molecular propellers Ar'ArXYR and Ar″Ar'ArXY.[3] Correlated rotation in molecular propellers is commonly analyzed in terms of flip mechanisms,[4,5] involving helicity reversal. For the Ar″Ar'ArX and Ar″Ar'ArXY systems the rotational mode of lowest activation energy (threshold mechanism) is the two-ring flip[4c,6] while for highly hindered Ar$_2$C=C(Y)Ar' systems it is the three-ring flip.[3]

Only four[7] and three-ring[3] flips were so far reported for vinyl propellers. The threshold mechanism in these species should depend on the nature and the bulk of the double-bond substituents.[3b] Calculations[8] predict a propeller conformation for

(7) (a) The list comprises Ni(C_3Ph_3)Cl(py)$_2$·(py),[7b] Ni(C_3Ph_3)(η^5-C_5H_5),[7c] Co(C_3Ph_3)(CO)$_3$,[7d] Mo(C_3Ph_3)(CO)$_2$(bpy)Br,[7e] and [M(C_3Ph_3)(PPh$_3$)$_2$]$^+$ (M = Ni,[7f] Pd,[7f] Pt[7g]). In the latter cationic complexes the C_3Ph_3 ring is usually not symmetrically bound to the metal. (b) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1971**, *10*, 2599; (c) *Ibid.* **1971**, *10*, 1504. (d) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Ibid.* **1979**, *18*, 1687. (e) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310. (f) Mealli, C.; Midollini, S.; Moneti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95. (g) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1974**, *54*, C59.

(8) R. P. Hughes and A. L. Rheingold have informed us of two unpublished structures of the generic type Mo(η^5-C_5H_5)(CO)$_2$(C_3R_3) in which the C_3 ring substitutents (R = Ph or *t*-Bu) are bent back from the metal by 37–44° but in which the C_3 ring is still further from the metal by ∼0.05 Å. NMR evidence suggests that the phenyl substituents in Mo(η^5-C_5H_5)-(CO)$_2$[C_3(*t*-Bu)Ph$_2$] are equivalent on the NMR time scale, although they are not equivalent in the solid-state structure.

(9) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Organometallics* **1982**, *1*, 1403.

(10) The estimated barrier to ring rotation in hypothetical Fe(η^3-C_3H_3)(CO)$_3$ is 6–7 kcal mol^{-1}: Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(11) When a sample of W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2 is heated to 70 °C, a broad spectrum is obtained (reversibly) that is characteristic of a rapidly equilibrating mixture of W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2, W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$]Cl_2, and free PMe$_3$. We note that W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$](PMe$_3$)Cl_2 reacts slowly at 25 °C with C_2Cl_6 to give W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$]Cl_2 in high yield and that PEt$_3$ does not react with W(η^5-C_5H_5)[$C_3(CMe_3)_2Me$]Cl_2, presumably for steric reasons.

(1) Part 5: Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.*, in press.

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(5) A "flip" is a passage through a plane perpendicular to the reference plane with no edge interchange. The nonflipping rings pass through the reference plane with edge interchange.

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