Synthesis, Structure, and Dynamic Behavior of Dichloro(alkylidene)(alkyne)bis(trimethylphosphine)-tungsten Complexes

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The mechanism of alkyne polymerization by molybdenum- and tungsten-based catalysts has been proposed to propagate via metal alkylidene intermediates (Scheme I).[1] For mononuclear systems each mechanistic cycle involves coordination of an alkyne to the transition-metal center, formation of a metallacyclobutene, and regeneration of the metal carbene by ring opening. Fischer-type carbyne complexes are among the best catalyst precursors and transformation of the carbyne ligand into a carbene ligand for catalytic activity has been postulated.[2] We have developed simple methods for the synthesis of group 6 transition-metal carbyne complexes[3] and we have begun to investigate the reactions of these compounds with unsaturated hydrocarbons. Reactions of pyridine-substituted tungsten carbyne complexes $[(W{\equiv}CR)Cl(CO)_2(py)_2]$ with activated olefins leading to stable tungsten alkene carbyne complexes have already been described.[4] Analogous reactions of $[(W{\equiv}CR)Cl(CO)_2(py)_2]$ with alkynes did not afford isolable tungsten alkyne carbyne complexes; rather, polymerization of alkynes was observed. More recently, we have developed routes to trimethylphosphine-stabilized metal carbyne complexes and we have shown that deprotonation of the tungsten alkylidene complex $[(W{=}CHPh)(Cl)_2(CO)(PMe_3)_2]$ (**1**) provides an anionic tungsten carbyne complex, $[(W{\equiv}CPh)(Cl)_2(CO)(PMe_3)_2]^-$, containing a labile chloride ligand.[5] Dehydrochlorination of **1** in the presence of ligands L thus provides good access to substituted tungsten carbyne complexes $[(W{\equiv}CPh)Cl(CO)L(PMe_3)_2]$, and we hoped this method might allow the synthesis of stable tungsten carbyne complexes containing alkyne ligands. Here we report about reactions of **1** with acetylenes in the presence of base which afford stable transition-metal alkyne alkylidene complexes,[6] possibly via labile tungsten alkyne carbyne complexes. The products exhibit the elements of the first intermediate in Masuda's mechanism for acetylene polymerization and they serve as precursors for moderately active alkyne polymerization catalysts.

An equimolar mixture of **1**, diphenylacetylene, and 1,8-bis(dimethylamino)naphthalene is allowed to react for 30 min at 0 °C in methylene chloride. At this point, a new compound has formed with a characteristic infrared absorption, ν_{CO} = 1928 cm. This new compound is postulated to be the expected tungsten alkyne carbyne complex $[(W{\equiv}CPh)Cl(CO)(PhC{\equiv}CPh)(PMe_3)_2]$ (**2**). However, extraction of the reaction residue with ether and recrystallization from ether/pentane gave a 28% yield of a brown product which was identified as the tungsten (diphenylacetylene)benzylidene complex $[(W{=}CHPh)(Cl)_2(PhC_2Ph)(PMe_3)_2]$ (**3**) (Figure 1).[9] Apparently, upon concentration of the reaction solution the intermediate **2** takes up HCl from the hydrochloride salt of the added base and looses the carbon monoxide ligand.[8]

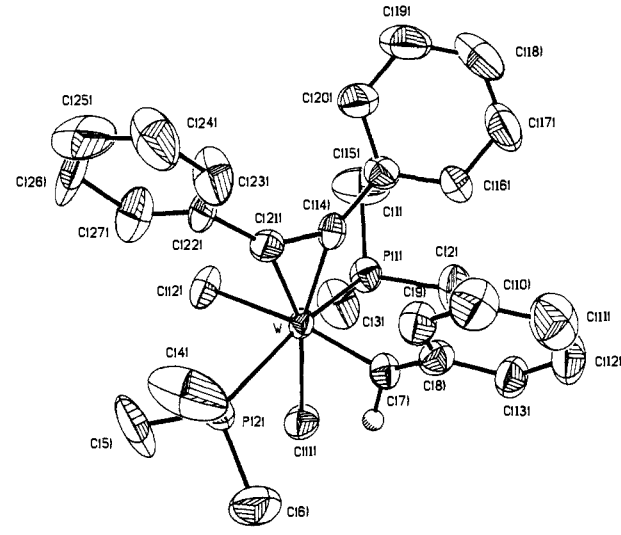
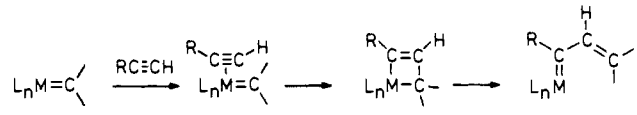


Figure 1. Molecular structure of $[(W{=}CHPh)(Cl)_2(PhC_2Ph)(PMe_3)_2]$ (**3**). W-C(7), 1.97 (2); W-C(14), 2.061 (7); W-C(21), 2.04 (2); W-Cl(1), 2.508 (3); W-Cl(2), 2.548 (5); W-P(1), 2.552 (5); W-P(2), 2.544 (5); C(14)-C(21), 1.33 (3) Å. Cl(2)-W-C(7), 167.5 (3)°; centroid [C(14)-C(21)]-W-Cl(1), 176.3 (6)°; P(1)-W-P(2), 157.2 (1)°; W-C(7)-C(8), 137 (1)°; W-C(7)-H(7), 92.1°. Dihedral angle, plane [C(14)-W-C(21)]-plane [Cl(1)-W-C(7)], 59.4°.

Scheme I



Several spectroscopic and structural features show that **3** is best described as an 18-electron complex with the alkyne as a four-electron-donor ligand. The ^{13}C NMR resonance for the acetylene carbon atoms at 223.0 ppm and the average carbon–tungsten bonding distance of 2.05 Å are typical for four-electron-donor alkyne ligands.[11,12] Moreover, electronic saturation of the tungsten center is indicated by the rather nondistorted nature of the benzylidene ligand. In the related electron-deficient tungsten alkylidene complex $[(W{=}CHPh)(Cl)_2(CO)(PMe_3)_2]$ (**1**) the W=C

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(4) Mayr, A.; Dorries, A. M.; McDermott, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 7775–7776.

(5) Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; Van Engen, D., manuscript in preparation.

(6) Previous to this work, two types of tungsten alkyne alkoxycarbene complexes, [W[C(OMe)Ph](alkyne)$(CO)_4$][7a] and [W(η-C_5H_5)[C(OEt)R](alkyne)(CO)][BF_4],[7b] have been prepared.

(7) (a) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073. (b) Alt, H. G. *J. Organomet. Chem.* **1983**, *256*, C12–C14.

(8) Support for the proposed reaction pathway comes from the independent synthesis of **3** by reaction of $[W(CPh)Cl(CO)(PMe_3)_2(py)]$ with diphenylacetylene, which provides the same intermediate **2** (by IR), and *subsequent* addition of $HNEt_3Cl$.

(9) **3**: ^1H NMR (ppm, $CDCl_3$) 11.8 (t, 1, $^3J_{PH}$ = 4.7 Hz) (C*H*Ph); ^{13}C NMR (ppm, $CDCl_3$) 283.6 ($^1J_{CH}$ = 125.8, $^1J_{CW}$ = 118.2 Hz) (*C*HPh), 223.0 (Ph*C*$_2$Ph); ^{31}P NMR (ppm, $CDCl_3$) −8.27 (PMe_3).

(10) $C_{27}H_{34}Cl_2P_2W$: monoclinic, $C2/c$, a = 38.902 (14) Å, b = 9.188 (2) Å, c = 32.929 (9) Å, β = 147.38 (1)°, V = 6346 (3) Å^3, Z = 8, μ(Mo Kα) = 41.3 cm^{-1}, ρ(calcd) = 1.41 g cm^{-3}. Of the 4158 unique reflections measured, 3610 were considered observed [$|F_o| \geq 3\sigma(F_o)$] after Lorentz, polarization, and empirical absorption corrections (min trans. 0.75, max trans. 1.00). The structure was solved by standard heavy-atom techniques and refined by blocked-cascade least-squares refinement. All hydrogens except those of C(4) methyl were located on different Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, H(7) was held fixed, and all other hydrogens were idealized. R = 0.057, R_w = 0.063, GOF = 1.08. Highest peak in final difference Fourier map = 2.0 e$^-$ Å^{-3} near W. Five additional peaks (0.61–1.99 e$^-$ Å^{-3}) were attributed to disordered solvent.

(11) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290.

(12) (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318–1320. (b) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956–6963.

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distance is 1.860 Å, the W=C—C angle is widened up to 164.6°, and the W=C—H angle is only 74.6°.[5] The less activated nature of the alkylidene C-H bond in **3** compared to **1** is also reflected in the larger C-H coupling constant (**3**, $^1J_{CH}$ = 125.8 Hz, vs. **1**, $^1J_{CH}$ = 82.3 Hz) and in the shift of the NMR signal for the alkylidene hydrogen atom from −1.2 ppm for **1** to the low-field value of 11.8 ppm found for **3**. Thus, donation of the second π-bond ($\pi\perp$) of the alkyne to the metal center exerts a marked influence on the geometry of the benzylidene ligand; it also determines the orientation of the alkylidene ligand such that the tungsten-alkylidene π-bond is orthogonal to the tungsten alkyne π-bonds; i.e., the plane of the benzylidene ligand is perpendicular to the P(1)-W-P(2) axis.

Due to interaction of the alkyne ligand with two perpendicular metal d_π orbitals, no high electronic barrier for alkyne rotation is expected.[11,13] In the structure of **3**, the preferred orientation of the alkyne is apparently along the P(1)-W-P(2) axis, but significant rotation from this orientation is observed, which is attributed to steric interaction between the acetylene phenyl groups and the trimethylphosphine ligands. In order to be able to probe the dynamic behavior of the alkyne ligand by NMR we prepared a sample of the complex $[(W{=}CHPh)(Cl)_2(PhC_2H)(PMe_3)_2]$ (**4**),[14] containing an unsymmetrically substituted alkyne. The calculated activation barrier for site exchange is $\Delta G^\ddagger$ = 50.61 ± 2.9 kJ mol^{-1} at 273 K.[15] This value is comparable to those obtained for formally related tungsten complexes containing four-electron-donor alkyne ligands.[11,17]

When the acetylene complex **3** is dissolved in phenylacetylene at 40 °C, slow polymerization of the alkyne is induced.[18] In the early phase (24 h) of the reaction compound **4** can be identified by NMR as the major organometallic component. Since the structural and dynamic studies reported here clearly show that the alkyne and alkylidene ligands in **3** and **4** do not interact with each other, we propose that dissociation of a trimethylphosphine ligand in **4** and coordination of a second phenylacetylene may lead to the active acetylene polymerization catalyst. In this situation the metal would not be able to provide d-electrons for independent π-bonding to the second alkyne ligand which then may interact with the alkylidene ligand according to Scheme I.[19]

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles for **2** (5 pages); table of observed and calculated structure factors for **2** (22 pages). Ordering information is given on any current masthead page.

(13) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am Chem. Soc.* **1979**, *101*, 585-591.

(14) **4** was prepared by the same method as **3**. However, pure samples of **4** are difficult to obtain. **4**: ^{1}H NMR (ppm, CD_2Cl_2, 298 K) 12.85 (t, 1, $^3J_{PH}$ = 6.9 Hz) (PhC_2H), 11.20 (t, 1, $^3J_{PH}$ = 4.5 Hz) ($CHPh$); ^{13}C NMR (ppm, CD_2Cl_2, 253 K) 289.6 ($^1J_{CH}$ = 125.7 Hz), 217.9 ($PhCCH$), 211.0 ($^1J_{CH}$ = 201.1 Hz), $PhCCH$); ^{31}P NMR (ppm, CD_2Cl_2, 193 K) −8.5, −5.1 ($^2J_{PP}$ = 141.0 Hz) (PMe_3), coalescence temperature 283 K.

(15) Free energies of activation were calculated from the Eyring equation by least-squares fit of rate constants obtained from line-shape analysis (^{31}P NMR) using the program DNMR3.[16]

(16) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(17) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532-1538. (b) Templeton, J. L.; Ward, B. C.; Chen, G.-G. J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248-1253. (c) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745-750.

(18) Polyphenylacetylene was isolated by precipitation from CH_2Cl_2 solution with CH_3OH and characterized by ^{1}H NMR.[2]

(19) Insertion of alkynes into metal-carbene bonds in high-valent[20] and in low-valent transition-metal carbene complexes[21] has been observed or implicated in a variety of systems. There are also a few examples for the formation of metallacyclobutenes via coupling of coordinated alkynes and carbene ligands.[22]

(20) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210-3222.

(21) (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309-314. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282-7292. (c) Dötz, K. H. *Angew Chem.* **1984**, *96*, 573-594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587-608 and references therein. (d) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363-5364. (e) Wulff, W. D.; Gilbertson. S. R., Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520-522 and references therein. (f) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8-C12.

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Terminal Epoxidation of Farnesate Attached to Helical Peptides

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In the last stage of cholesterol biosynthesis, squalene is regio- and enantioselectively transformed to squalene 2,3-epoxide in the presence of an enzyme squalene monooxygenase.[1] A remarkably regioselective nonenzymatic oxidation of the terminal double bond of squalene was accomplished by van Tamelen and co-workers.[2] They showed that the regioselectivity was dependent on the solvent and the oxidizing agent. van Tamelen suggested that the solvent effect related to the conformation of the substrate in solution; in polar medium the terpene exists in a coiled conformation in which the internal double bond might be sterically shielded and hence less reactive than the terminal double bond. Accepting that squalene and related terpenes exist as coiled structures in polar solvents,[3] we envisioned an intriguing possibility to make this process asymmetric.[4] Upon coupling a terpene such as farnesic acid with a chiral helical molecule, the terpene moiety might be induced to coil only in one direction, for example in a screw form. Once such a preferential chiral helix formation is obtained in the terpene moiety, one face of the terminal double bond will preferentially be exposed to the oxidizing reagent. In this paper, we would like to describe experiments aimed at testing this concept.

Among several classes of compounds known to form helices,[5,6] we have chosen polypeptides, since they are easy to prepare on a large scale and their secondary structures (helices) are stable in many solvents.[7] The only potential drawback of polypeptides is their poor solubility in organic solvents. We first studied the chemical behavior of the substrate **1**, prepared from hexa-L-phenylalanine methyl ester;[8] however, to our great disappointment, neither NBS or MCPBA oxidation of **1** gave promising results. A possible explanation for this unsuccessful experiment was, we felt, that the low solubility of the hexapeptide **1** might result from aggregation of the β-sheet structure through intermolecular hy-

(1) For a review on this subject, see, for example: Harrison, D. M. *Nat. Prod. Rep.* **1985**, *2*, 525.

(2) For reviews on this subject, see: van Tamelen, E. E. *Acc. Chem. Res.* **1968**, *1*, 111. Also see: van Tamelen, E. E.; Storni, A.; Hessler, E. J.; Schwartz, M. A. *Bioorg. Chem.* **1982**, *11*, 133.

(3) The ^{13}C NMR spectrum of squalene in media of different polarity does not necessarily support this proposal (van Dommelen, M. E.; Wilson, A. R. N.; de Haan, J. W.; Buck, H. M. *Bull. R. Neth. Chem. Soc.* **1975**, *94*, 206), but we used it as a working hypothesis to design an experimental system.

(4) Asymmetric epoxidation of squalene was studied by Otsuka and his co-workers: Tani, K.; Hanafusa, M.; Otsuka, S. *Tetrahedron Lett.* **1979**, 3017.

(5) For example, see: Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1.

(6) A possibility of utilizing optically active hexahelicene-2-carboxylic acid as a chiral inducer was studied by Dr. Yamasaki (1978-1979) and Dr. McWhorter, Jr., (1980) in our laboratories. However, asymmetric induction was not significant for this system.

(7) There are excellent books and reviews on the conformation of peptides. For example, see: *The Peptides*; Gross, E., Meienhofer, J., Eds.; Academic Press: New York, 1981; Vol. 4.

(8) Hexa-L-alanine methyl ester was also synthesized. However, as its solubility in organic solvents was extremely poor, we were unable to study its chemistry.

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