Structural Characterization of a Crystalline Monomeric Trialkoxytungsten Alkyne: Tri-*tert*-butoxybenzylidynetungsten, $(Me_3CO)_3WCPh$

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Summary: In our continuing study of the reactions of diphenylacetylene and other acetylenes with ditungsten hexa-*tert*-butoxide we have obtained the title compound in crystalline form and determined its structure accurately, using data collected at 166 K. It forms molecular crystals with no association between essentially tetrahedral mononuclear molecules. The principal molecular dimensions are $W\equiv C$ = 1.758 (5) Å, W–O(mean) = 1.865 [4] Å, $O—W\equiv C$ = 107.8 [11]°, W—O—C = 141 [1]°, and $W\equiv C—C$ = 175.8 (4)°.

Reactions between ditungsten hexa-*tert*-butoxide and acetylenes have led to a variety of products. Under mild reaction conditions and with aliphatic acetylenes, Schrock, Listemann, and Sturgeoff obtained W(VI) alkylidyne complexes.[1] While their procedure fails in the case of diphenylacetylene (tolane), we have been able to isolate two dinuclear products by reaction of substoichiometric amounts of tolane with $W_2(OCMe_3)_6$ at elevated temperatures.[2] Interestingly, aliphatic acetylenes, under our conditions, also give rise to polynuclear complexes.[3] Phenylmethyacetylene, which, at least in a formal sense, is a hybrid between tolane and aliphatic acetylenes, yields under Schrock's conditions a mixture of alkylidynes that can be converted, by virtue of thermodynamic control, into the benzylidyne complex and 2-butyne. Under our conditions $W_2(\mu\text{-}CC_6H_5)(OCCMe_3)_4$, viz., the main product of the tolane reaction, is the only isolated product. As part of our attempts to gain insight into the reaction mechanisms, an accurate structure determination of tri-*tert*-butoxytungsten benzylidyne was performed. This compound does not readily form good crystals, but suitable ones were obtained by a process of very slow sublimation in high vacuum.

The crystals[4] consist of an ordered array of mononuclear molecules with no intermolecular interactions other than van der Waals forces. An ORTEP diagram of the molecule is shown in Figure 1. The coordination geometry of the tungsten atom is almost ideally tetrahedral with all L–W–L bond angles in the range 107–111°. The average W–O distance is 1.865 [4] Å, and W–O–C bond angles range from 139 to 143°. The $W\equiv C$ bond length is 1.758 (5) Å, and the $W\equiv C—C$ bond angle is 175.8 (4)°.

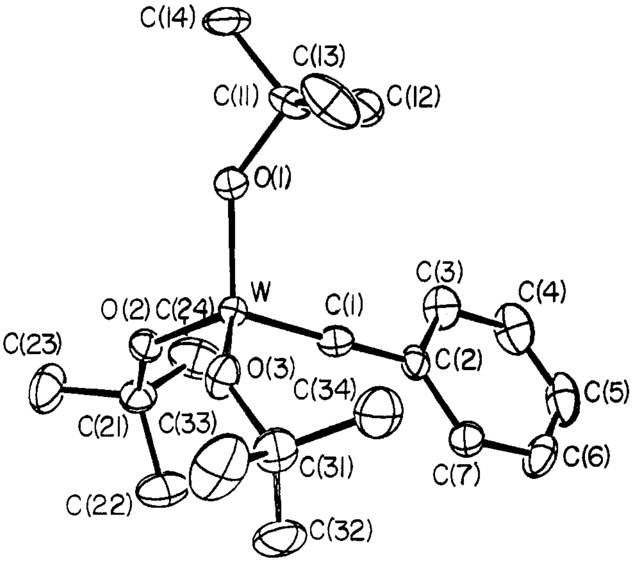

Figure 1. The $(Me_3CO)_3WCC_6H_5$ molecule. Each atom is represented by its ellipsoid of thermal vibration at the 40% level. Hydrogen atoms, which were included in the model refined, are omitted for clarity.

Table I. Structures of Some Tungsten Alkylidyne Compounds

compound	$W\equiv C$, Å	$W\equiv C—C$, deg	ref
trans-$I(CO)_4WCC_6H_5$	1.90	162 (4)	5
trans-$Cl(CO)_4WCCH_3$	2.02 (4)	173	5
$\eta\text{-}C_5H_5(CO)_2WCC_6H_4pCH_3$	1.82 (2)	177 (2)	5
trans-$Br(CO)_2(py)_2WCC_6H_5$	1.84 (2)	173.8 (6)	6
$W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$	1.808 (6)	174.0 (4)	7
$[(t\text{-}BuO)_3W(CMe)]_2$	1.759 (6)	179.8 (6)	8
$(t\text{-}BuO)_3W(CC_6H_5)$	1.758 (5)	175.8 (4)	this work

Table I summarizes $W\equiv C$ bond lengths and $W\equiv C—C$ bond angles from other carbyne complexes. The $W\equiv C$ bond lengths are significantly shorter in the W(VI) alkynes (1.75–1.80 Å) than in the W(IV) carbynes (1.82–2.02 Å). This is to be expected if the differences are due to differences in ionic radii.

This structure provides a point of departure to discuss the possible additivity of bond lengths and bond energies in multiply bonded metal-containing compounds. If the conventional triple-bond radius for carbon is subtracted from the $W\equiv C$ bond length and the remainder doubled, we have 2.32 Å as the $W\equiv W$ triple bond length; this is in good accord with the values found in a variety of $X_3W\equiv WX_3$ type molecules.[9] Unfortunately, for $W_2(OCMe_3)_6$ itself, which is the only known molecule of this sort in which X = OR, all efforts to obtain its structure have been frustrated by what appears to be intimate twinning.[10] The fact that bond length additivity seems to apply in going from an $(RO)_3W\equiv CR'$ molecule in which tungsten is clearly six-valent to X_3WWX_3 species supports the position that tungsten should be regarded as six-valent in the latter. On that basis, it could be contended that in assessing the

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[3] Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1340.

[4] Crystal data: space group $P2_1/n$, a = 10.011 (3) Å, b = 21.041 (7) Å, c = 10.064 (2) Å, β = 94.66 (2), Z = 4, V = 2113 (1) Å^3, d_{calcd} = 1.55 g/cm^3. A hemisphere of 3699 reflections was measured at −107 °C on a CAD-4 diffractometer located at The Molecular Structure Corp., College Station, TX. Of these, 2917 unique reflections with $I > 3\sigma(I)$ were used for solution of the structure by Patterson methods and least-squares refinement. The final residuals were R_F = 0.023 and R_w = 0.030 for the fit of 337 variables to 2917 data. All hydrogen atoms were included in the refinement.

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[8] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

[9] See: Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; pp 198–235.

[10] Unpublished studies in this laboratory.

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W≡W bond energy, within the range of values consistent with thermochemical data[11] (ca. 80–230 kcal/mol), a choice toward the high end of the range might be justified.

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Registry No. $(Me_3CO)_3WCC_6H_5$, 82228-87-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters, crystallographic data, bond lengths, bond angles, and structure factors (24 pages). Ordering information is given on any current masthead page.

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[11] See ref 9, p 353.

Access to Novel [2-(Diphenylphosphino)alkenethiolato]iron Complexes via Reactions of the η^2-Alkoxythiocarbonyl Ligand

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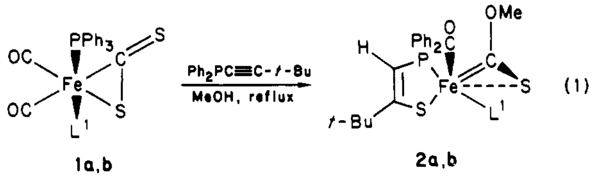
Summary: Complexes of type Fe(η^2-CSOMe)(CO)(PR_3)-($\widehat{P\ S}$)[**2**, $\widehat{P\ S}$ = $Ph_2PCH{=}C(t\text{-}Bu)S$] on treatment with basic phosphines L give Fe(η^1-CSOMe)(CO)$(L)_2$($\widehat{P\ S}$) (**3**, **4**). **3** reacts with CH_3I/PF_6^- (aqueous) to lead to [Fe($\widehat{P\ S}$)$(CO)_2(PMe_2Ph)_2$]PF_6 **5**. On reaction with concentrated HCl **2** affords $FeCl(CO)_2(PPh_3)$($\widehat{P\ S}$) (**6**), which is a precursor to Fe($\widehat{P\ S}$) complexes, such as Fe($\widehat{P\ S}$)(CO)(η^5-C_5H_5) (**7**) obtained by reaction of **6** with NaC_5H_5.

Although chelating ligands of type ($R_2PCH{=}CHS$) are potentially useful as ancillary ligands owing to both their rigidity and electron-donor capability, as suggested by the chemistry of analogous [$RPCH{=}C(R)Y$] metal complexes (Y = O[1,2] and NH[3]), their use has been limited by the lack of good methods for the preparation of their complexes. Recently, the intramolecular coupling of phosphinoalkyne and η^2-carbon disulfide ligands, in the presence of an alcohol, has offered a ready route (in only two steps from $Fe(CO)_5$ and via complexes 1) to the (2-phosphinoalkenethiolato)iron derivatives 2[4] that contain an η^2-alkoxythiocarbonyl ligand (eq 1). We now report that whereas



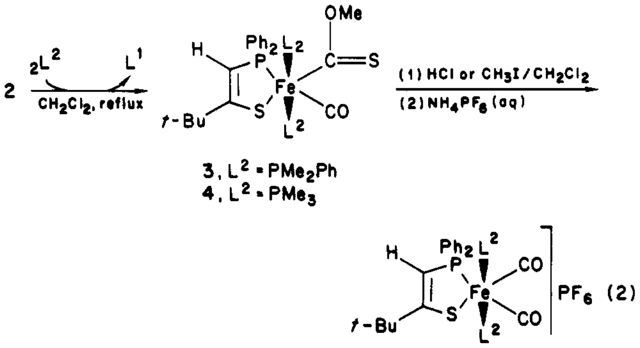
(1)

1a,b **2a,b**

a, L^1 = PPh_3; b, L^1 = PMe_2Ph

the $Ph_2PCH{=}C(R)S$ ligand is inert and strongly bonded to the iron atom, the three-electron η^2-CSOR group is the reactive site in complexes **2**. It can be easily transformed, thus opening a route to a variety of [$Ph_2PCH{=}C(R)S$] Fe complexes.

Although the Fe–S bond length of the Fe(η^2-CSOMe) moiety in complexes **2** is very long [2.512 (2) Å in **2c** (L^1 = $P(OMe)_3$)],[4] its sulfur atom is strongly coordinated in iron. The sulfur atom was displaced at the same time as the ligand L^1 only when complexes **2** were heated with an excess of a very basic phosphine. Thus the yellow Fe(η^1-CSOMe) complexes **3** (66%) and **4** (60%) were obtained from **2a** with PMe_2Ph and from **2b** with PMe_3, respectively[5,6] (eq 2). No reaction was observed on treatment of **2a** with the less basic phosphorus compounds PPh_3 and $P(OMe)_3$. The trans position of the equivalent ligands L^2 was indicated by the ^1H NMR spectra of **3** and **4**[6] and the ^{31}P NMR spectrum of **3** [^{31}P NMR (32.38 MHz, $CDCl_3$) δ (referenced to H_3PO_4) 54.06 (t, PPh_2), 13.76 (d, PMe_2Ph), $^2J_{PP}$ = 32.3 Hz].

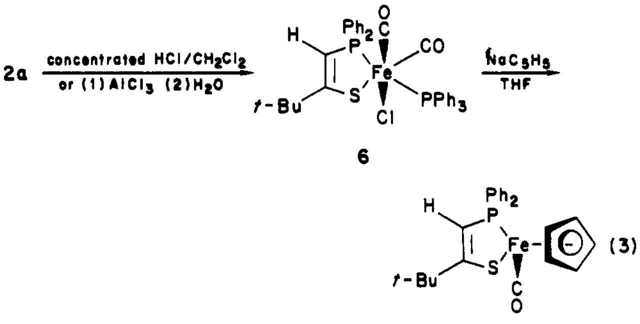


(2)

3, L^2 = PMe_2Ph
4, L^2 = PMe_3

5, L^2 = PMe_2Ph

The protonation of complexes **2** was investigated on the assumption that protonation of the sulfur atom of the Fe(η^2-CSOMe) moiety would facilitate its displacement by a small ligand such as carbon monoxide. The protonation of **2a** in dichloromethane, by HPF_6 in ether, is reversible; no coordination of CO takes place and complex **2a** is recovered after addition of water to the solution. In contrast, concentrated HCl reacts with **2a** in dichloromethane to afford, even in the absence of a carbon monoxide atmosphere and at room temperature, a yellow product that was isolated in 90% yield and identified as complex **6**[7] (eq 3)



(3)

6

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[6] **3**: mp 133–136 °C; IR (Nujol) 1935 cm^{-1} (C≡O), 1585 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.20 (m, C_6H_5), 6.19 (d, PCH=, $^2J_{PH}$ = 4.0 Hz), 3.31 (s, OMe), 1.57 (s, *t*-Bu), 1.23 (dt, PMe_2, $|^2J_{PH} + {}^4J_{PH}| = 9.0$ Hz). Anal. Calcd for $C_{37}H_{45}O_2P_3S_2Fe$: C, 60.49; H, 6.13; P, 12.67. Found: C, 60.16; H, 6.08; P, 12.44. **4**: mp 118–121 °C; IR (Nujol) 1925 (C≡O), 1585 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.36 (m, C_6H_5), 6.30 (d, PCH=, $^2J_{PH}$ = 5.0 Hz), 4.14 (s, OMe), 1.50 (s, *t*-Bu) 1.00 (t, PMe_3, $|^2J_{PH} + {}^4J_{PH}| = 8.0$ Hz). Anal. Calcd for $C_{27}H_{41}O_2P_3S_2Fe$: C, 53.12; H, 6.77; P, 15.22. Found: C, 52.82; H, 6.43; P, 14.98.

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