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Assembly of η^2-Alkynethiol and η^2-Thioketenyl Ligands from Alkylidyne Ligands and Carbon Disulfide[†]

Tsung-Yi Lee and Andreas Mayr*

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

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Recently, we reported the formation of alkynyl trithiocarbonato tungsten complexes of the type $[WX(PhCCSC(S)S)(CO)(PMe_3)_2]$ from $[W(CPh)X(CO)(PMe_3)_3]$ (X = halide, SR) and CS_2 and postulated that the alkyne thiolate (PhCCS) moiety results from an alkynyl-thiocarbonyl coupling step.[1] We furthermore suggested that carbon disulfide might assist the coupling step as an electrophile by interaction with the thiocarbonyl ligand.[2] To establish closer analogies with the better studied alkylidyne–carbonyl[3] and alkylidyne–isocyanide[4] coupling reactions,[2] we investigated the reaction of the alkylidene complex $[W(CHPh)I_2(CO)(PMe_3)_2]$, **1**,[5,6] with CS_2 in the presence of PPh_3. Triphenylphosphine was expected to play a dual role, namely, as a base to dehydrohalogenate **1** and as an agent for the abstraction of sulfur from coordinated carbon disulfide.[7] If these two steps lead to the formation of the alkylidyne thiocarbonyl complex $[W(CPh)I(CO)(CS)(PMe_3)_2]$, then the protonated phosphine, $[HPPh_3]I$, could serve as a proton source in a proton-assisted alkylidyne–thiocarbonyl coupling step. As reported here, the investigation of this system led to the characterization of tungsten complexes containing η^2-alkyne thiol and η^2-thioketenyl ligands, two paradigmatic alkylidyne–thiocarbonyl coupling products, and η^2-alkynyl thiolethers via further transformations. This work establishes a close chemical and structural relationship between alkylidyne–carbonyl and alkylidyne–thiocarbonyl coupling products.

The reaction between **1**, CS_2, and PPh_3 in THF proceeds slowly at room temperature to give the phenylalkynyl complex $[WI_2(PhCCSH)(CO)(PMe_3)_2]$, **2** (eq 1).[8] Reaction of complex **2** with *n*-BuLi and isocyanides affords the η^2-thioketenyl complexes $[W(PhCCS)I(CNR)(CO)(PMe_3)_2]$, **3** (**a**: R = CMe_3; **b** = 2,6-$C_6H_3Me_2$) (eq 2).[9]

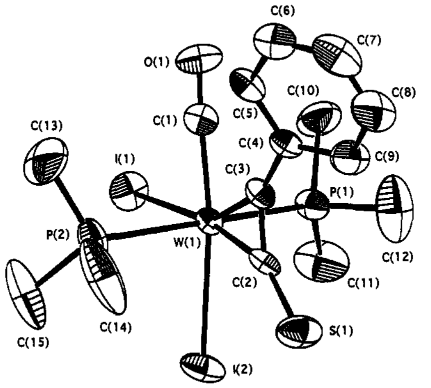
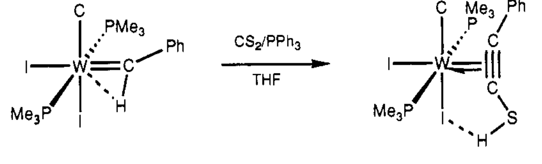
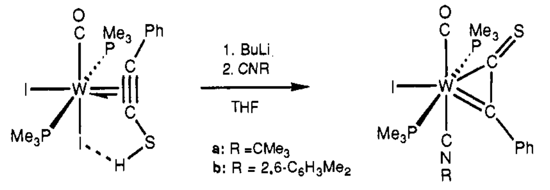


Figure 1. Molecular structure of complex **2**. Selected bond distances (Å) and bond angles (deg): W(1)–C(1), 1.95(1); W(1)–C(2), 1.98(1); W(1)–C(3), 2.00(1); W(1)–I(1), 2.8374(9); W(1)–I(2), 2.892(1); W(1)–P(1), 2.513(3); W(1)–P(2), 2.521(3); C(2)–C(3), 1.32(1); C(3)–C(4), 1.48(1); S(1)–C(2), 1.71(1); W(1)–C(2)–S(1), 152.6(7); W(1)–C(3)–C(4), 155.1(9); C(1)–W(1)–C(3), 75.9(5); I(1)–W(1)–C(1), 77.1(3); I(1)–W(1)–I(2), 86.63(3); I(2)–W(1)–C(2), 81.7(3); P(1)–W(1)–P(2), 168.2(1).



(1)

1 **2**



(2)

2 **3**

The solid state structures of complexes **2** and **3b** were determined by X-ray crystallography and are shown in Figures 1 and 2, respectively.[10] The structural parameters of the alkyne thiol and thioketenyl ligands are remarkably similar in both compounds. This is evident from the superimposition of the relevant parts of both molecules shown in Figure 3. Deprotonation of the alkyne thiol ligand thus does not significantly alter the bonding of the PhCCS unit. A similar relationship has previously been found for η^2-alkoxyalkyne and η^2-ketenyl metal complexes.[11] The alkyne thiol and thioketenyl ligands are aligned parallel to the metal–carbonyl axis as found in other four-electron-donor

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[†] Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

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(5) **1** is obtained by stirring a solution of $[W(CHPh)Cl_2(CO)(PMe_3)_2]^6$ (97 mg, 0.185 mmol) and NaI (235 mg, 1.568 mmol) in 20 mL of THF at room temperature for 18 h. Then the solvent is removed under vacuum, and the product is recrystallized from ether to give red-brown crystals (99 mg, 76%): IR (THF, cm^{-1}) 1934 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 7.45–7.25 (m, 5 H. Ph), 1.88 (t, J_{PH} = 4.0 Hz, 18 H, PMe_3), –2.20 (t, J_{PH} = 2.5 Hz, J_{WH} = 20.6 Hz, 1 H, C(*H*)(Ph)); ^{13}C NMR ($CDCl_3$, 298 K) δ 222.4 (t, J_{PC} = 6.3 Hz, CO), 222.0 (t, J_{PC} = 11.8 Hz, *C*HPh). Anal. Calcd for $C_{14}H_{24}I_2OP_2W$ (M_r 707.95): C, 23.75; H, 3.42; I, 35.85. Found: C. 23.93; H, 3.47; I, 35.66.

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(8) **2**: A solution of **1** (399 mg, 0.564 mmol), PPh_3 (148 mg, 0.564 mmol), and CS_2 (100 μL, 1.663 mmol) in 30 mL of THF is stirred at room temperature for 140 h. All volatile components are removed under vacuum, and the product is recrystallized from ether to give green crystals (241 mg, 57%): IR (THF, cm^{-1}) 1946 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 7.72–7.54 (m, 5 H, Ph), 7.44 (s, 1 H. SH), 1.53 (t, J_{PH} = 4.2 Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 225.2 (t, J_{PC} = 5.5 Hz, J_{WC} = 128.3 Hz, CO), 210.2 (t, J_{PC} = 5.3 Hz, Ph*C*CSH), 208.8 (t, J_{PC} = 5.3 Hz, PhC*C*SH; enhanced, if $^{13}CS_2$ is used as reagent).

(9) **3a**: A solution of **2** (52 mg, 0.0691 mmol) in 30 mL of THF is cooled to –78 °C, and *n*-BuLi (1.6 M, 100 μL, 0.16 mmol) and Me_3CNC (150 μL, 1.326 mmol) are added sequentially. After warming to room temperature and stirring for 17.5 h, 1 mL of MeOH is added, and all volatile components are removed under vacuum. The product is recrystallized from ether to give brown crystals (25 mg, 51%): IR (THF, cm^{-1}) 2154 (m, $CNCMe_3$), 1960 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 8.19–7.44 (m, 5 H, Ph), 1.68 (s, 9 H, CMe_3), 1.41 (t, J_{PH} = 4.0 Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 230.1 (PHC*C*S; enhanced, if $^{13}CS_2$ is used as reagent), 219.1 (Ph*C*CS), 215.6 (t, J_{PC} = 6.1 Hz, CO), 149.4 (*C*$NCMe_3$). Anal. Calcd for $C_{20}H_{32}NIOP_2SW$ (M_r 707.24): C, 33.97; H, 4.56. Found: C, 33.76; H, 4.41. Complex **3b** is obtained in an analogous fashion in 73% yield: IR (THF, cm^{-1}) 2120 (m, CNC_8H_9), 1964 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 8.02–7.12 (m, 8 H, C*Ph*, 2,6-Me_2*C_6H_3*NC), 2.32 (s, 6 H, 2,6–*Me_2*C_6H_3NC), 1.48 (t, J_{PH} = 3.8 Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 229.6 (PhC*C*S), 220.2 (Ph*C*CS), 213.7 (t, J_{PC} = 6.1 Hz, CO), 165.6 (t, J_{PC} = 12.2 Hz, 2,6-$Me_2C_6H_3N$*C*).

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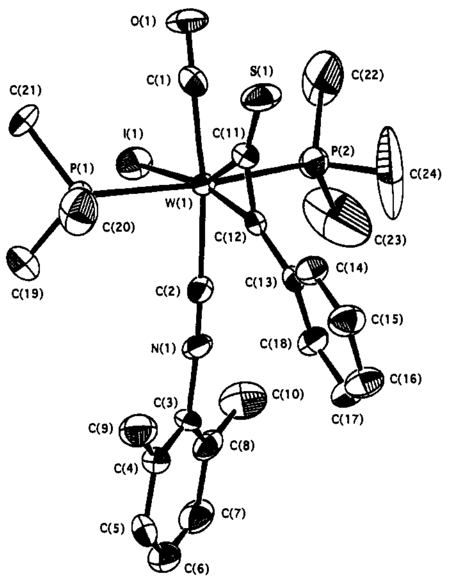


Figure 2. Molecular structure of complex **3b**. Selected bond distances (Å) and bond angles (deg): W(1)–C(1), 1.99(1); W(1)–C(2), 2.15(1); W(1)–C(11), 2.09(1); W(1)–C(12), 1.991(9); W(1)–I(1), 2.8523(9); W(1)–P(1), 2.519(3); W(1)–P(2), 2.503(3); C(11)–C(12), 1.35(1); C(12)–C(13), 1.48(1); S(1)–C(11), 1.65(1); W(1)–C(11)–S(1), 152.3(6); W(1)–C(12)–C(13), 152.5(7); C(1)–W(1)–C(11), 71.2(4); C(2)–W(1)–C(12), 84.6(4); I(1)–W(1)–C(1), 84.7(3); I(1)–W(1)–C(2), 81.(3); P(1)–W(1)–P(2), 168.2(1).

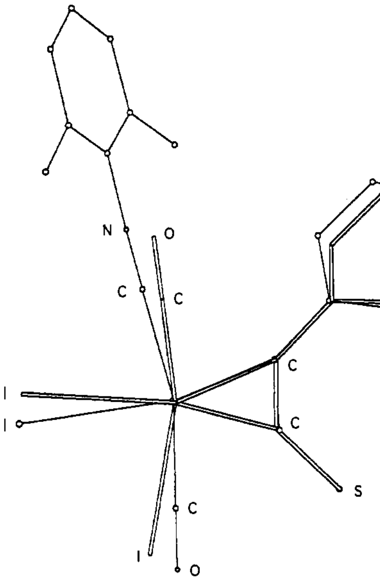
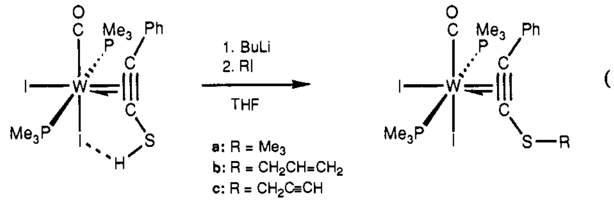


Figure 3. Superimposition of complexes **2** (highlighted) and **3b**. The trimethylphosphine ligands are omitted for clarity.

alkyne metal complexes of the same type.[12] However, the alkyne thiol and thioketenyl ligands are oriented in opposite directions. The orientation of the thioketenyl ligand in **3b**, in which the sulfur-substituted carbon atom is proximal to the carbonyl ligand, is as predicted by molecular orbital models for ketenyl ligands.[13] In **2**, the sulfur-substituted carbon atom of the alkyne thiol ligand is distal to the carbonyl group. This orientation is probably electronically less favorable and appears to be stabilized by the presence of an S–H···I hydrogen bond. On the basis of the location of the IR stretching frequency of the SH group at 2391 cm^{-1}, this hydrogen bond is of significant strength.[14] A similar situation was previously found for the hydroxyalkyne complex [$WCl_2(PhCCOH)(CO)(PMe_3)_2$].[3b]

The coordination of phenylalkyne thiolate as an η^1-C-bonded (MCPh=C=S) and η^1-S-bonded (MSC≡CPh) ligand was demonstrated by Weigand.[15] A thioketenyl tungsten intermediate was postulated by Weiss as an intermediate in the formation of thioalkyne ligands in the reaction of [$W(CCMe_3)Cl_3(DME)$] and isothiocyanates.[16]

Sequential treatment of complex **2** with *n*-BuLi and electrophiles provides access to a variety of alkynyl thioether complexes of the type [$WI_2(PhCCSR)(CO)(PMe_3)_2$], **4** (**a**, R = Me; **b**, R = $CH_2CH{=}CH_2$; **c**, R = $CH_2C{\equiv}CH$) (eq 3).[17]



(3)

2 **4**

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Supplementary Material Available: Tables of positional parameters, bond lengths, and bond angles for **2** and **3b** (15 pages); tables of observed and calculated structure factors for **2** and **3b** (37 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Crystal data for **2** and **3b**. **2**: $C_{15}H_{24}I_2P_2OSW$, FW = 752.02, orthorhombic, *Pbca*, $a = 11.7217(9)$ Å, $b = 13.994(1)$ Å, $c = 27.939(2)$ Å, $V = 4582.7(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.180$ g cm^{-3}, μ(Mo Kα) = 80.423 cm^{-1}, 2635 unique reflections, $0° < 2\theta < 50°$, $R = 0.039$, $R_w = 0.038$. **3b**: $C_{24}H_{32}INOP_2S$, FW = 755.29, orthorhombic, *Pbca*, $a = 18.403(1)$ Å, $b = 21.487(3)$ Å, $c = 14.260(1)$ Å, $V = 5638.5(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.779$ g cm^{-3}, μ(Mo Kα) = 54.672 cm^{-1}, 2895 unique reflections, $0° < 2\theta < 50°$, $R = 0.037$, $R_w = 0.039$. All intensity measurements were made at room temperature, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), and a variable-rate, ω–2θ scan technique. Empirical absorption corrections were applied. The structures were solved by conventional heavy-atom methods and refined by full-matrix least squares. All calculations were performed using the TEXRAY programs.

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(17) **4a**: A solution of **2** (68 mg, 0.0904 mmol) in 30 mL of THF is cooled to –78 °C, and *n*-BuLi (1.6 M, 100 μL, 0.16 mmol) and CH_3I (100 μL, 1.606 mmol) are added sequentially. After warming to room temperature and stirring for 10 min, 1 mL of MeOH is added, and all volatile components are removed under vacuum. The product is recrystallized from THF/hexane to give green crystals (22 mg, 32%): IR (THF, cm^{-1}) 1945 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 7.52–7.19 (m, 5 H, Ph), 2.59 (s, 3 H, SCH_3), 1.62 (t, $J_{PH} = 4.3$ Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 223.5 (CO), 215.5 (Ph*C*CSCH$_3$), 213.9 (PhC*C*SCH$_3$). Anal. Calcd for $C_{16}H_{26}I_2OP_2SW$ (M_r 766.05): C, 25.09; H, 3.42. Found: C, 25.36; H, 3.61. Complexes **4b** and **4c** are obtained in analogous fashion in 53% and 35% yields, respectively. **4b**: IR (THF, cm^{-1}) 1945 (s, CO); ^1H NMR ($CDCl_3$, 298 k) δ 7.53–7.14 (m, 5 H, Ph), 5.70–5.54 (m. 1H, SCH$_2$C*H*CH$_2$), 4.88, 4.66 (d,d, 2 H, $J_{trans} = 10.3$ Hz, $J_{cis} = 17.5$ Hz, SCH$_2$CHC*H*$_2$), 3.79–3.76 (m, 2 H, SC*H*$_2$CHCH$_2$), 1.63 (t, $J_{PH} = 4.3$ Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 223.2 (t, $J_{PC} = 5.6$ Hz, CO), 215.0 (Ph*C*CS), 212.6 (PhC*C*S). Anal. Calcd for $C_{18}H_{28}I_2OP_2SW$ (M_r 792.09): C, 27.29; H, 3.56. Found: C, 27.50; H, 3.59. **4c**: IR (THF, cm^{-1}) 1947 (s, CO); ^1H NMR ($CDCl_3$, 298 K) δ 7.52–7.20 (m, 5 H, Ph), 3.87 (2 H, SC*H*$_2$CCH), 2.06 (t, $J = 2.6$ Hz, 1 H, SCH$_2$CC*H*), 1.64 (t, $J_{PH} = 4.3$ Hz, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 298 K) δ 223.0 (t, $J_{PC} = 6.1$ Hz, CO), 215.2 (Ph*C*CS), 210.5 (PhC*C*S). Anal. Calcd for $C_{18}H_{26}I_2OP_2SW$ (M_r 790.07): C, 27.36; H, 3.32. Found: C, 27.46; H, 3.35.