

Preliminary Communication

Transfer of the (dithiomethoxycarbonyl)-diphenylphosphine ligand from tungsten to palladium: syntheses and crystal structures of two palladium (dithiomethoxycarbonyl)phosphine complexes

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Abstract

The (dithiomethoxycarbonyl)phosphine transfer reaction between $\text{Pd}(\text{PPh}_3)_4$ and $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CS}_2\text{Me})]$, **1**, forms $\{\text{Pd}(\text{PPh}_3)[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\}_2$, **3**, as the final product. The reaction proceeds via a η^2 -coordination of the C=S fragment to Pd, giving $\{\text{Pd}(\text{PPh}_3)-[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\text{W}(\text{CO})_5\}$, **2** as an intermediate. Complexes **2** and **3** are characterized by X-ray diffraction analysis.

Key words: Palladium; Tungsten; Phosphine; X-ray diffraction

Transition metal CS_2 complexes have attracted considerable attention in recent years. The first preparation of such a complex was reported in 1967 [1]. CS_2 possesses versatile coordinating capabilities; i.e. it can be a monodentate [2] or a multidentate ligand [3]. Such coordinating ability can be employed in the study of chemical reactivities of the ligands containing CS_2 . The zwitterionic $\text{R}_3\text{P}^+\text{CS}_2^-$ ligand is a typical example. Metal complexes containing such a ligand have been extensively studied in recent years [4]. To date, however, little effort has been directed toward investigating the reactivity of the (dithioformato)phosphine ligand, R_2PCS_2^- . An efficient method of synthesis of metal complexes with the (dithioalkoxycarbonyl)phosphine ligand $\text{Ph}_2\text{PCS}_2\text{R}$ [5], recently developed by us, allows more extensive exploration of the chemistry of these complexes. This communication describes an intermolecular transfer of the (dithiomethoxycarbonyl)phosphine ligand from W to Pd via a prior coordina-

tion of C=S to the Pd. X-ray crystal structure determination of the two Pd complexes clarifies the transfer mechanism.

Treatment of $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CS}_2\text{Me})]$, **1** [6*], with $\text{Pd}(\text{PPh}_3)_4$ in ether affords a yellow crystalline product, identified as $\{\text{Pd}(\text{PPh}_3)_2[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\text{W}(\text{CO})_5\}$, **2**, in 55% yield and a small amount of $\text{trans-W}(\text{CO})_4(\text{PPh}_3)_2$. The spectroscopic [7*] and analytical data of **2** correlate with the formulation. The FAB mass spectrum of **2** shows a parent peak at $m/e = 1231$. The IR spectrum of **2** shows three terminal carbonyl stretches at 2060, 1914 and 1887 cm^{-1} ; a typical pattern of a $\text{M}(\text{CO})_5\text{L}$ unit in octahedral geometry. The ^1H NMR spectrum of **2** exhibits a singlet at δ 2.09 assignable to the thiomethoxy protons and the corresponding ^{13}C NMR signal is at δ 18.7. The ^{31}P NMR spectrum of **2** exhibits a resonance at δ 51.6 with a tungsten satellite ($^1J_{\text{P-W}} = 257$ Hz) assignable to the $\text{PPh}_2(\text{CS}_2\text{Me})$ ligand on W and two more resonances at δ 22.2 and 22.4 assignable to the two inequivalent PPh_3 ligands. Results indicate an asymmetrical coordination of the C=S moiety of the $\text{PPh}_2(\text{CS}_2\text{Me})$ ligand onto the Pd metal. This unusual bonding mode for the $\text{PPh}_2(\text{CS}_2\text{Me})$ ligand is confirmed by an X-ray diffraction study [8*]. The structure of **2** is shown in Fig. 1. It is clear that the palladium and tungsten metal centers are bridged by the $\text{PPh}_2(\text{CS}_2\text{Me})$ ligand with no metal-metal contact. The ligand is π -bonded through the C=S coordination to Pd and σ -bonded to W through the phosphorus atom.

At room temperature complex **2** is unstable and slowly undergoes disproportionation in CHCl_3 to form a complex $\{\text{Pd}(\text{PPh}_3)[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\}_2$, **3**, in 31% isolated yield, and $\text{W}(\text{CO})_5\text{PPh}_3$, in 40% yield, which are identified by spectroscopic methods including mass spectroscopy [9*]. The FAB mass spectrum of **3** shows a peak at $m/e = 1242.8$ which corresponds to a fragment formed from cleavage of the SMe group from **3**. The ^1H NMR spectrum of **3** exhibits a singlet at δ 2.18 assignable to the thiomethoxy protons and the corresponding ^{13}C NMR signal is at δ 19.7. The ^{31}P NMR spectrum of **3** exhibit resonances at δ 22.4 and 53.7. Complex **3** is also identified on the basis of its

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* Reference number with asterisk indicates a note in the list of references.

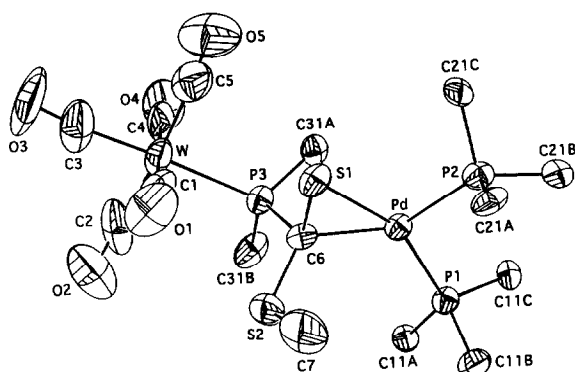


Fig. 1. X-ray structure with atom numbering scheme for complex $\{(\text{Ph}_3\text{P})_2\text{Pd}[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\text{W}(\text{CO})_5\}_2$, **2**, the phenyl groups are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) are as follows: Pd–P₁, 2.321(3); Pd–P₂, 2.360(3); Pd–C₆, 2.134(9); Pd–S₁, 2.273(3); C₆–S₁, 1.720(9); C₆–S₂, 1.793(9); C₇–S₂, 1.74(1); P₂–Pd–P₁, 105.8(1); S₁–Pd–C₆, 45.8(2); C₆–Pd–P₁, 110.1(2).

single crystal X-ray diffraction analysis [10*]. The ORTEP drawing of **3** is shown in Fig. 2. It is clear that the two Pd(PPh₃) fragments are held together by the two PPh₂(CS₂Me) ligands. The PPh₂(CS₂Me) ligand is π -bonded to the Pd atom through the C=S and σ -bonded to the other Pd atom through the phosphorus atom; this gives a six-membered ring. The coordination around each Pd atom is distorted squared planar, mainly because of the short bite of angle the C=S linkage [C–Pd–S, 46.2(1) $^\circ$] and the requirement of the six-membered ring [11]. A least-squares plane calculation reveals the planarity of the P₂P₁C₁S₁ core (largest deviation 0.07(1) Å). The Pd–PPh₃ distance, 2.349(2) Å, is significantly longer than the corresponding value

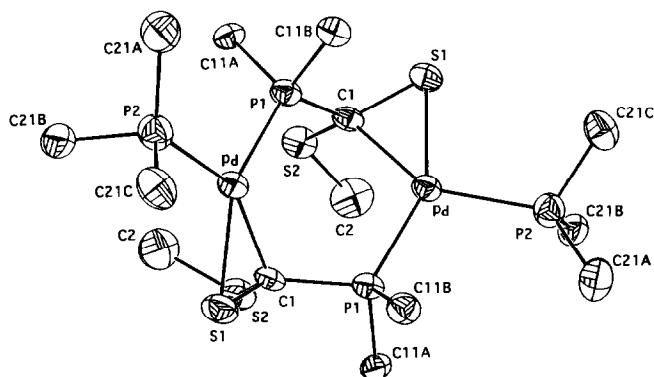


Fig. 2. X-ray structure with atom numbering scheme for complex $\{(\text{Ph}_3\text{P})\text{Pd}[\mu, \eta^1, \eta^2-(\text{MeS}_2\text{C})\text{PPh}_2]\}_2$, **3**, the phenyl groups are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) are as follows: Pd–P₁, 2.311(1); Pd–P₂, 2.349(2); Pd–C₁, 2.113(5); Pd–S₁, 2.296(1); C₁–S₁, 1.739(5); C₁–S₂, 1.793(5); C₂–S₂, 1.788(6); P₂–Pd–P₁, 108.16(5); P₂–Pd–S₁, 100.67(5); S₁–Pd–C₁, 46.2(1); C₁–Pd–P₁, 116.1(2); Pd–C₁–S₁, 72.5(2); Pd–S₁–C₁, 61.3(2); Pd–P₁–C₁, 116.9(2).

of 2.267(2) Å found in PdCl(CH₂SMe)(PPh₃)₂, [2(h)] possibly because of the influence of the C=S coordination. The dissociation of the phosphine ligand from W may be caused by labilization of the P–W bond caused by the C=S π -coordination to Pd. Chemical reactivities of the (dithiomethoxycarbonyl)–phosphine metal complexes are currently under investigation.

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- Spectroscopic data for **1**: IR (KBr, ν_{CO}): 2071(m), 1988(s), 1957(sh), 1911(vs) cm^{-1} . ^{31}P NMR (81 MHz, δ): 64.26 (t, $^1J_{\text{W-P}}$

- = 247.95 Hz). ^1H NMR (200 MHz, δ): 2.71 (s, 3H, CH_3); 7.50 (m, 6H, Ph); 7.66 (m, 4H, Ph). ^{13}C NMR (50 MHz, δ): 21.86 (CH_3); 129.62 (d, meta-C of Ph, $^3J_{\text{P-C}} = 9.72$ Hz); 132.28 (s, para-C of Ph); 134.63 (d, ortho-C of Ph, $^2J_{\text{P-C}} = 12.2$ Hz); 134.88 (d, ipso-C of Ph, $^1J_{\text{P-C}} = 36.6$ Hz); 198.04 (d, $^2J_{\text{P-C}} = 7.5$ Hz, CO), 200.01 (d, $^2J_{\text{P-C}} = 25.0$ Hz, CS_2), 240.28 (d, $^2J_{\text{P-C}} = 7.4$ Hz, CO). MS: 600.7 [M^+]; 571 [$\text{M}^+ - \text{CO}$]; 543.6 [$\text{M}^+ - 2\text{CO}$]; 515.6 [$\text{M}^+ - 3\text{CO}$]; 487 [$\text{M}^+ - 4\text{CO}$]; 459.7 [$\text{M}^+ - 5\text{CO}$]; 444.7 [$\text{M}^+ - 5\text{CO} - \text{CH}_3$]; 368.9 [$\text{M}^+ - 5\text{CO} - \text{CH}_3 - \text{CS}_2$].
- 7 Spectroscopic data for **2**: IR (KBr, ν_{CO}): 2060(m), 1914(vs), 1887(s) cm^{-1} . ^{31}P NMR (81 MHz, CDCl_3): 51.6 ($^1J_{\text{W-P}} = 257.6$ Hz), 22.2, 22.4 (PPh₃). ^1H NMR (200 MHz, δ , CDCl_3): 2.09 (s, 3H, SCH_3), 7.0–7.4 (m, 40H, Ph). ^{13}C NMR (50 MHz, δ , CDCl_3): 18.7 (SCH_3), 127–134 (Ph), 198.75 (d, PCS_2Me , $^1J_{\text{P-C}} = 6.75$ Hz), 208, 214 (s, CO). MS: 1231, [M^+]; 1217, [$\text{M}^+ - \text{CH}_3$].
- 8 Crystal data for **2**: $\text{C}_{55}\text{H}_{43}\text{O}_5\text{P}_3\text{S}_2\text{PdW}$, space group $P\bar{1}$; $a = 10.920(3)$, $b = 14.707(5)$, $c = 16.654(5)$ Å; $V = 2586.3(14)$ Å³, $Z = 2$; $\alpha = 99.98(3)$, $\beta = 93.75(3)$, $\gamma = 99.44(3)^\circ$; $D_c = 1.581$ g cm^{-3} ; $\mu = 28.268$ cm^{-1} ; 4772 observed reflections; $2\theta_{\text{max}} = 45^\circ$; $R = 0.043$, $R_w = 0.034$; Mo $\text{K}\alpha$ radiation; $\lambda = 0.7093$ Å; $T = 298$ K.
- 9 Spectroscopic data for **3**: ^{31}P NMR (81 MHz, δ , CDCl_3): 22.2 (PPh₃), 53.7 ($\text{Ph}_2\text{PCS}_2\text{Me}$). ^1H NMR (200 MHz, CDCl_3): 2.18 (s, 6H, SCH_3), 7.0–7.4 (m, 50H, Ph). ^{13}C NMR (50 MHz, δ , CDCl_3): 19.69 (s, SCH_3), 198.1 (d, PCS_2Me , $^1J_{\text{P-C}} = 6.50$ Hz), 127–134 (Ph). MS: 1243, [$\text{M}^+ - \text{SCH}_3$]; 980, [$\text{M}^+ - \text{SCH}_3 - \text{PPh}_3$].
- 10 Crystal data for **3**: $\text{C}_{32}\text{H}_{28}\text{P}_2\text{S}_2\text{Pd}$, space group $P2_1/c$; $a = 15.106(3)$, $b = 9.848(3)$, $c = 20.528(4)$ Å; $V = 2951.6(11)$ Å³, $Z = 4$; $\beta = 104.854(16)^\circ$; $D_c = 1.452$ g cm^{-3} ; $\mu = 49.539$ cm^{-1} ; 2930 observed reflections; $2\theta_{\text{max}} = 45^\circ$; $R = 0.033$; $R_w = 0.026$; Mo $\text{K}\alpha$ radiation; $\lambda = 0.70930$ Å; $T = 298$ K.
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