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## Preliminary Communication

# Transfer of the (dithiomethyoxycarbonyl)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 $Pd(PPh_3)_4$ and $W(CO)_5[PPh_2(CS_2Me)]$, **1**, forms $\{Pd(PPh_3)[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]\}_2$, **3**, as the final product. The reaction proceeds via a $\eta^2$-coordination of the C=S fragment to Pd, giving $\{Pd(PPh_3)\text{-}[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]W(CO)_5\}$, **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 $R_3P^+CS_2^-$ 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 $Ph_2PCS_2R$ [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 coordination of C=S to the Pd. X-ray crystal structure determination of the two Pd complexes clarifies the transfer mechanism.

Treatment of $W(CO)_5[PPh_2(CS_2Me)]$, **1** [6*], with $Pd(PPh_3)_4$ in ether affords a yellow crystalline product, identified as $\{Pd(PPh_3)_2[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]\text{-}W(CO)_5\}$, **2**, in 55% yield and a small amount of trans-$W(CO)_4(PPh_3)_2$. 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 $M(CO)_5L$ unit in octahedral geometry. The $^1H$ NMR spectrum of **2** exhibits a singlet at $\delta$ 2.09 assignable to the thiomethoxy protons and the corresponding $^{13}C$ NMR signal is at $\delta$ 18.7. The $^{31}P$ NMR spectrum of **2** exhibits a resonance at $\delta$ 51.6 with a tungsten satellite ($^1J_{P-W} = 257$ Hz) assignable to the $PPh_2(CS_2Me)$ ligand on W and two more resonances at $\delta$ 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 $PPh_2(CS_2Me)$ ligand onto the Pd metal. This unusual bonding mode for the $PPh_2$-$(CS_2Me)$ 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 $PPh_2(CS_2Me)$ ligand with no metal–metal contact. The ligand is $\pi$-bonded through the C=S coordination to Pd and $\sigma$-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 $\{Pd(PPh_3)[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]\}_2$, **3**, in 31% isolated yield, and $W(CO)_5PPh_3$, 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 $\delta$ 2.18 assignable to the thiomethoxy protons and the corresponding $^{13}C$ NMR signal is at $\delta$ 19.7. The $^{31}P$ NMR spectrum of **3** exhibit resonances at $\delta$ 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.

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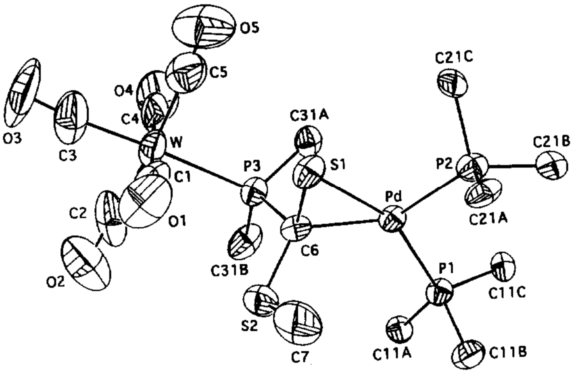

Fig. 1. X-ray structure with atom numbering scheme for complex $\{(Ph_3P)_2Pd[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]W(CO)_5\}$, **2**, the phenyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: $Pd-P_1$, 2.321(3); $Pd-P_2$, 2.360(3); $Pd-C_6$, 2.134(9); $Pd-S_1$, 2.273(3); $C_6-S_1$, 1.720(9); $C_6-S_2$, 1.793(9); $C_7-S_2$, 1.74(1); $P_2-Pd-P_1$, 105.8(1); $S_1-Pd-C_6$, 45.8(2); $C_6-Pd-P_1$, 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 $Pd(PPh_3)$ fragments are held together by the two $PPh_2(CS_2Me)$ ligands. The $PPh_2(CS_2Me)$ ligand is $\pi$-bonded to the Pd atom through the C=S and $\sigma$-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)°] and the requirement of the six-membered ring [11]. A least-squares plane calculation reveals the planarity of the $P_2P_1C_1S_1$ core (largest deviation 0.07(1) Å). The $Pd-PPh_3$ distance, 2.349(2) Å, is significantly longer than the corresponding value of 2.267(2) Å found in $PdCl(CH_2SMe)(PPh_3)_2$, [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 $\pi$-coordination to Pd. Chemical reactivities of the (dithiomethoxycarbonyl)-phosphine metal complexes are currently under investigation.

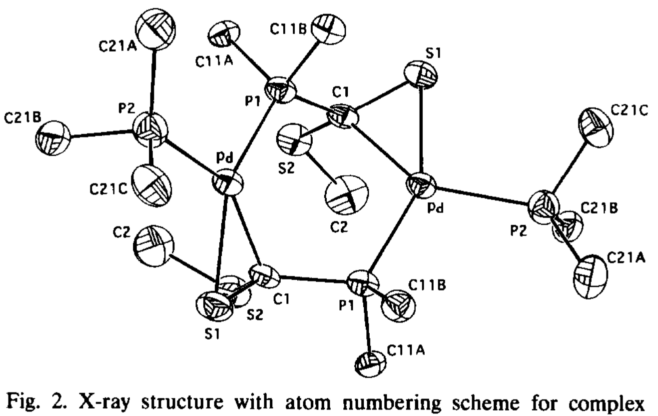

Fig. 2. X-ray structure with atom numbering scheme for complex $\{(Ph_3P)Pd[\mu,\eta^1,\eta^2\text{-}(MeS_2C)PPh_2]\}_2$, **3**, the phenyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: $Pd-P_1$, 2.311(1); $Pd-P_2$, 2.349(2); $Pd-C_1$, 2.113(5); $Pd-S_1$, 2.296(1); $C_1-S_1$, 1.739(5); $C_1-S_2$, 1.793(5); $C_2-S_2$, 1.788(6); $P_2-Pd-P_1$, 108.16(5); $P_2-Pd-S_1$, 100.67(5); $S_1-Pd-C_1$, 46.2(1); $C_1-Pd-P_1$, 116.1(2); $Pd-C_1-S_1$, 72.5(2); $Pd-S_1-C_1$, 61.3(2); $Pd-P_1-C_1$, 116.9(2).

## Acknowledgment

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

= 247.95 Hz). $^1$H NMR (200 MHz, $\delta$): 2.71 (s, 3H, $CH_3$); 7.50 (m, 6H, Ph); 7.66 (m, 4H, Ph). $^{13}$C NMR (50 MHz, $\delta$): 21.86 ($CH_3$); 129.62 (d, meta-C of Ph, $^3J_{P-C} = 9.72$ Hz); 132.28 (s, para-C of Ph); 134.63 (d, ortho-C of Ph, $^2J_{P-C} = 12.2$ Hz); 134.88 (d, ipso-C of Ph, $^1J_{P-C} = 36.6$ Hz); 198.04 (d, $^2J_{P-C} = 7.5$ Hz, CO), 200.01 (d, $^2J_{P-C} = 25.0$ Hz, $CS_2$), 240.28 (d, $^2J_{P-C} = 7.4$ Hz, *C*O). MS: 600.7 [$M^+$]; 571 [$M^+$-CO]; 543.6 [$M^+$-2CO]; 515.6 [$M^+$-3CO]; 487 [$M^+$-4CO]; 459.7 [$M^+$-5CO]; 444.7 [$M^+$-5CO-$CH_3$]; 368.9 [$M^+$-5CO-$CH_3$-$CS_2$].

7 Spectroscopic data for **2:** IR (KBr, $\nu_{CO}$): 2060(m), 1914(vs), 1887(s) $cm^{-1}$. $^{31}$P NMR (81 MHz, $CDCl_3$): 51.6 ($^1J_{W-P} = 257.6$ Hz), 22.2, 22.4 ($PPh_3$). $^1$H NMR (200 MHz, $\delta$, $CDCl_3$): 2.09 (s, 3H, $SCH_3$), 7.0–7.4 (m, 40H, Ph). $^{13}$C NMR (50 MHz, $\delta$, $CDCl_3$): 18.7 ($SCH_3$), 127–134 (Ph), 198.75 (d, $PCS_2Me$, $^1J_{P-C} = 6.75$ Hz), 208, 214 (s, *C*O). MS: 1231, [$M^+$]; 1217, [$M^+$-$CH_3$].

8 Crystal data for **2:** $C_{55}H_{43}O_5P_3S_2PdW$, space group $P\bar{1}$; $a = 10.920(3)$, $b = 14.707(5)$, $c = 16.654(5)$ Å; $V = 2586.3(14)$ Å$^3$, $Z = 2$; $\alpha = 99.98(3)$, $\beta = 93.75(3)$, $\gamma = 99.44(3)°$; $D_c = 1.581$ g $cm^{-3}$; $\mu = 28.268$ $cm^{-1}$; 4772 observed reflections; $2\theta_{max} = 45°$; $R = 0.043$, $R_w = 0.034$; Mo K$\alpha$ radiation; $\lambda = 0.7093$ Å; $T = 298$ K.

9 Spectroscopic data for **3:** $^{31}$P NMR (81 MHz, $\delta$, $CDCl_3$): 22.2 ($PPh_3$), 53.7 ($Ph_2PCS_2Me$). $^1$H NMR (200 MHz, $CDCl_3$): 2.18 (s, 6H, $SCH_3$), 7.0–7.4 (m, 50H, Ph). $^{13}$C NMR (50 MHz, $\delta$, $CDCl_3$): 19.69 (s, $SCH_3$), 198.1 (d, $PCS_2Me$, $^1J_{P-C} = 6.50$ Hz), 127–134 (Ph). MS: 1243, [$M^+$-$SCH_3$]; 980, [$M^+$-$SCH_3$-$PPh_3$].

10 Crystal data for **3:** $C_{32}H_{28}P_2S_2Pd$, space group $P2/c$; $a = 15.106(3)$, $b = 9.848(3)$, $c = 20.528(4)$ Å; $V = 2951.6(11)$ Å$^3$, $Z = 4$; $\beta = 104.854(16)°$; $D_c = 1.452$ $gcm^{-3}$; $\mu = 49.539$ $cm^{-1}$; 2930 observed reflections; $2\theta_{max} = 45°$; $R = 0.033$; $R_w = 0.026$; Mo K$\alpha$ radiation; $\lambda = 0.70930$ Å; $T = 298$ K.

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