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Synthesis and Structural Characterization of Configurational Isomers of Tungsten−Palladium Complexes with Bridging Diphenyl(dithioalkoxycarbonyl)phosphine as a Ligand and Phosphine Transfer from Tungsten to Palladium

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Treatment of the complex $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**) with $[Pd(PPh_3)_4]$ (**1**) affords binuclear complexes such as *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**), *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**4**), and *trans*-$[W(CO)_4(PPh_3)_2]$ (**5**). In **3** and **4**, respectively, the W and Pd atoms are in anti and syn configurations with respect to the $P{-}CS_2$ bond of the diphenyl(dithiomethoxycarbonyl)phosphine ligand, $PPh_2(CS_2Me)$. Complex **3** undergoes extensive rearrangement in $CHCl_3$ at room temperature by transfer of a PPh_3 ligand from Pd to W, eliminating $[W(CO)_5(PPh_3)]$ (**7**), while the PPh_2CS_2Me ligand transfers from W to Pd to give $[[(Ph_3P)Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]]_2]$ (**6**). In complex **6**, the $[Pd(PPh_3)]$ fragments are held together by two bridging $PPh_2(CS_2Me)$ ligands. Each $PPh_2(CS_2Me)$ ligand is π-bonded to one Pd atom through the C═S linkage and σ-bonded to the other Pd through the phosphorus atom, resulting in a six-membered ring. Treatment of $Pd(PPh_3)_4$ with $[W(CO)_5[PPh_2[CS_2(CH_2)_nCN]]]$ ($n = 1$, **8a**; $n = 2$, **8b**) in CH_2Cl_2 affords *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}[CS_2(CH_2)_nCN]PPh_2]W(CO)_5]$ ($n = 1$, **9a**; $n = 2$, **9b**). Similar configurational products *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2R)PPh_2]W(CO)_5]$ (R $= C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN$, **11a−d**) are synthesized by the reaction of $Pd(PPh_3)_4$ with $[W(CO)_5[PPh_2(CS_2R)]]$ (R $= C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN$, **10a−d**). Although complexes **11a−d** have the same configuration as **9a**,**b**, the SR group is oriented away from Pd in the former and near Pd in the latter. In these complexes, the diphenyl(dithioalkoxycarbonyl)phosphine ligand is bound to the two metals through the C═S π-bonding and to phosphorus through the σ-bonding. All of the complexes are identified by spectroscopic methods, and the structures of complexes **3**, **6**, **9a**, and **11d** are determined by single-crystal X-ray diffraction. Complexes **3**, **9**, and **11d** crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$, whereas **6** belongs to the monoclinic space group $P2/c$ with $Z = 4$. The cell dimensions are as follows: for **3**, $a = 10.920(3)$ Å, $b = 14.707(5)$ Å, $c = 16.654(5)$ Å, $\alpha = 99.98(3)°$, $\beta = 93.75(3)°$, $\gamma = 99.44(3)°$; for **6**, $a = 15.106(3)$ Å, $b = 9.848(3)$ Å, $c = 20.528(4)$ Å, $\beta = 104.85(2)°$; for **9a**, $a = 11.125(3)$ Å, $b = 14.089(4)$ Å, $c = 17.947(7)$ Å, $\alpha = 80.13(3)°$, $\beta = 80.39(3)°$, $\gamma = 89.76(2)°$; for **11d**, $a = 11.692(3)$ Å, $b = 13.602(9)$ Å, $c = 18.471(10)$ Å, $\alpha = 81.29(5)°$, $\beta = 80.88(3)°$, $\gamma = 88.82(1)°$.

Introduction

Since the first CS_2 metal complex $[Ni_2(CS_2)_2(PPh_3)_2]$ was prepared by Baird and Wilkinson[1] in 1967, transition metal−CS_2 complexes have attracted considerable attention. Carbon disulfide, CS_2, has proved to be a versatile ligand, being capable of coordinating to one[2−11] or more[12−14] metals and it showing a variety of insertion[15,16] and disproportionation[17] reactions. Moreover, CS_2-containing metal complexes can be used as models for CO_2 complexes, which are much more difficult to investigate.[18,19] Consequently, three CS_2 derivatives, $R_3P^+CS_2^-$, $R_2PCS_2^-$, and $R_2NCS_2^-$, were synthesized to understand variable coordination chemistry.

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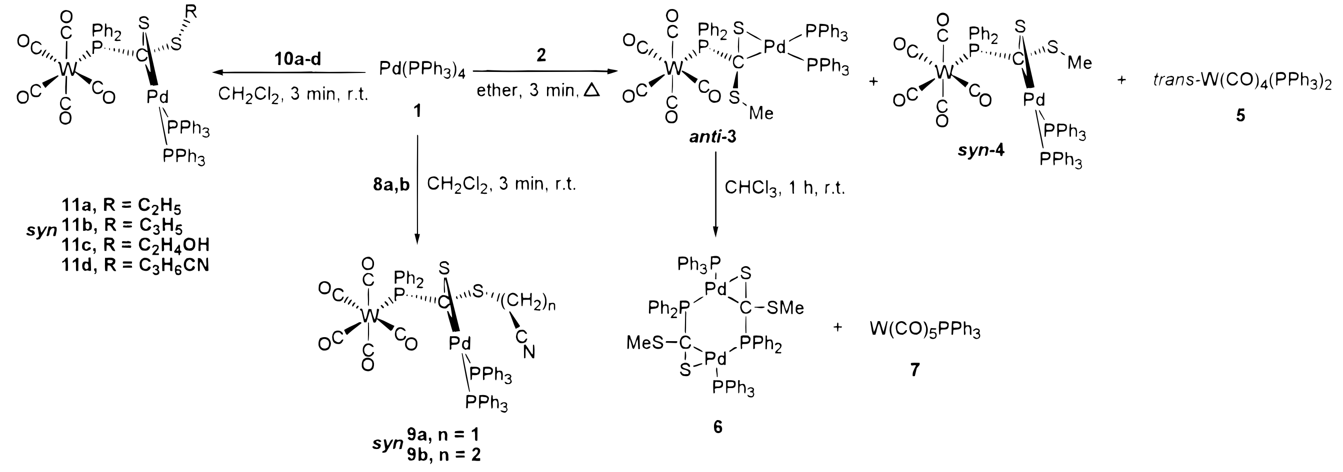
Scheme 1



2: $W(CO)_5(PPh_2CS_2Me)$

8: $W(CO)_5[PPh_2CS_2(CH_2)_nCN]$ (**a**, n = 1; **b**, n = 2)

10: $W(CO)_5(PPh_2CS_2R)$ (**a**, $R = C_2H_5$; **b**, $R = C_3H_5$; **c**, $R = C_2H_4OH$; **d**, $R = C_3H_6CN$)

A typical example, the zwitterionic $R_3P^+CS_2^-$ [20−25] ligand, has various bonding modes, which include monodentate coordination through one S atom,[20] chelation[21] or bridging[22] through two S atoms, and dinuclear pesudoallylic bridging forms, i.e., an η^3,σ mode with donation of six electrons[22−24] and an η^2,η^3 mode with donation of eight electrons.[25] The anionic ligands $R_2PCS_2^-$ and $R_2NCS_2^-$ [26,27] normally show monodentate coordination through P or S and bidentate coordination through P and S and through N and S, respectively. Little effort has been directed toward investigating the reactivity of the ligand $R_2PCS_2^-$ and its derivative R_2PCS_2R. To date, the neutral alkyl (diorganothiophosphinoyl)dithioformate compound, $R_2P(S)C(S)R$, is the only analogous example that has been used to react with $[Pt(PPh_3)_2C_2H_4]$, forming the C═S π-coordination complex.[28] Notably, in metal complexes containing the abovementioned ligands, no phosphine transfer reactions or configurational isomers have been observed.

Recently, we developed an efficient method to synthesize metal complexes with the diphenyl(dithioalkoxycarbonyl)phosphine ligand, $Ph_2P(CS_2R)$,[29] which allows more extensive exploration of the chemistry of these complexes. In a previous communication,[30] we reported the $Ph_2P(CS_2Me)$ ligand transfer reaction between $[Pd(PPh_3)_4]$ (**1**) and $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**), forming *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**) as an intermediate.

On the basis of these experimental results, we investigated the existence of configurational isomers in complexes between [diphenyl(dithioalkoxycarbonyl)phosphine]tungsten(0) compounds and $Pd(PPh_3)_4$. We report our results in this article, along with four X-ray crystal structure analyses that were carried out to provide accurate structural parameters.

Results and Discussion

Reaction of $[Pd(PPh_3)_4]$ (1) with $[W(CO)_5[PPh_2(CS_2Me)]]$ (2). The reaction of $[Pd(PPh_3)_4]$ (**1**) and $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**) in refluxing diethyl ether affords a yellow crystalline product, identified as *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**) (Scheme 1), in 55% yield. Compound **3** is moderately soluble in dichloromethane and acetonitrile, slightly soluble in diethyl ether and tetrahydrofuran, and insoluble in *n*-hexane.

The spectroscopic and analytical data of **3** are in agreement with the formulation. The FAB mass spectrum of **3** exhibits a base peak corresponding to its molecular mass. In the IR spectrum of **3**, three terminal carbonyl stretching bands at 2060 (m), 1914 (vs), and 1887 (s) cm^{-1} are observed, which is a typical pattern for an $LM(CO)_5$ unit in octahedral geometry. The ^1H NMR spectrum of **3** exhibits a resonance at δ 2.09 assignable to the methyl protons of the $PPh_2(CS_2Me)$ ligand, and the corresponding $^{13}C\{^1H\}$ NMR signal appears at δ 18.7. In the $^{13}C\{^1H\}$ NMR spectrum of **3**, three resonances appear in the carbonyl region. The two resonances at δ 214.9 and 198.8 with a ratio of 1/4 are attributed to the trans and cis carbonyl groups, respectively. The resonance at δ 208.2 is assigned to the carbon atom of CS_2 in the $PPh_2(CS_2Me)$ ligand. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, a resonance at δ 51.6 with a tungsten satellite ($^1J_{W-P} = 257.6$ Hz) and two broad resonances at δ 22.2 and 22.4 indicate P-coordination of the $PPh_2(CS_2Me)$ ligand to W and of the two triphenylphosphine ligands to Pd in the cis geometry.

To confirm the bonding mode of the $PPh_2(CS_2Me)$ ligand, complex **3** was characterized by an X-ray diffraction analysis. Its ORTEP diagram with atom labeling is shown in Figure 1. Table 2 contains selected bond distances and angles. The most remarkable features of the whole structure are the π-bonding of the C═S moiety in the $PPh_2(CS_2Me)$ ligand to the Pd atom

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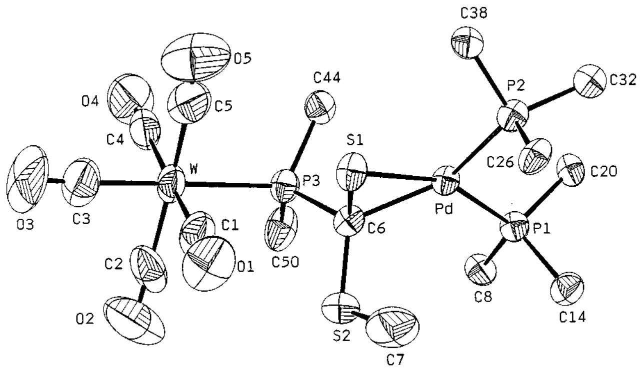

Figure 1. ORTEP plot of the molecular structure of compound **3**. The phenyl groups are omitted for clarity.

and the σ-bonding to the W atom through the phosphorus atom. Notably, the two metal atoms are on two different sides with respect to the P−CS$_2$ bond of the PPh$_2$(CS$_2$Me) ligand. The Pd atom and its neighboring atoms, P(1), P(2), S(1), and C(6), lie in a distorted square plane, the distortion being mainly due to the short bite of the C=S linkage [C−Pd−S = 46.09(21)°]. The W−Pd bond distance in **3**, 5.620(2) Å, indicates that there is no bonding interaction between the two metal atoms. The sulfur−carbon bond lengths in the PPh$_2$(CS$_2$Me) ligand range from 1.736(8) to 1.794(8) Å. Compared with the typical S−C single- and double-bond lengths of 1.81 and 1.71 Å, these parameters are indicative of delocalized bonding for the four atoms S(1), C(6), S(2), and C(7). Moreover, the C(6)−S(1) bond distance of 1.736(8) Å is longer than the corresponding carbon−sulfur bond distances observed in η^2-CS$_2$ (sp^2) transition metal complexes [1.65(3) Å in [(PPh$_3$)$_2$Pd(η^2-CS$_2$)],[2] 1.66 Å in [(PPh$_3$)$_2$Ru(η^2-CS$_2$Me)(CO)$_2$][ClO$_4$],[3] 1.68(1) Å in [CpCo(PMe$_3$)(η^2-CS$_2$)],[4] 1.676(7) Å in [Fe(PPh$_3$)(PMe$_3$)(CO)$_2$(η^2-CS$_2$)],[5] 1.667(4) Å in [(Cp)$_2$V(η^2-CS$_2$)],[6] 1.68(1) Å in [(triphos)Co(η^2-CS$_2$)],[12] 1.658(6) Å in [(PhMe$_2$P)$_2$(CO)$_2$FeCS$_2$Mn(CO)$_2$Cp],[13] 1.63(1) Å in [(PPh$_3$)Ni(μ-CS$_2$)$_2$Ni(PPh$_3$)],[31] and 1.674(6) Å in [(PPh$_3$)Pt(μ-CS$_2$)$_2$Pt(PPh$_3$)][32]]. The C−S bond lengths are longer than those in free CS$_2$ (1.554 Å), indicating coordination of CS$_2$ in an η^2 fashion, which reduces the bond order of the C=S bonds. A comment must be made about the carbon atom of the CS$_2$ group. An examination of its bond distances and angles shows a geometrical environment characteristic of an sp^3 hybridization. The Pd−C(6)−S(1) angle, 71.0(3)°, is significantly different from the others, which are in the range 107.0(5)−124.1(4)°.

For the PPh$_3$ ligands, the average values of ∠C−P−C′S and ∠Pd−P−C′S are 103 and 115°, respectively, and the geometry around the P atom is distorted tetrahedral. The Pd−P(1) distance in **3**, 2.317(2) Å, is considerably shorter than the sum of covalent radii (2.42 Å). This value is similar to those in [(C$_4$H$_7$)PdPPh$_3$] (2.31 Å) and [(PPh$_3$)$_2$Pd(η^2-CS$_2$)] (2.316(8) Å). The Pd−S(1) distance, 2.278(2) Å, is within the normal Pd−S length range (2.23−2.31 Å).[5] The Pd−C(6) bond length, 2.145(8) Å, is also within the usual range for Pd−C(sp^3) σ bonds. No bonding interaction between the palladium and the phenyl carbon atoms is apparent.

The singularity of the diphenyl(dithiomethoxycarbonyl)phosphine complex **3** does not allow a direct comparison with any other compounds reported in the literature. However, **3** shows some structural analogies with the complex [Ph$_2$PCH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$Ni(CS$_2$Me)][BPh$_4$].[9] In this compound, the nickel atom is coordinated in an η^2 fashion by the C=S moiety and the carbon in the thiocarbonyl shows an sp^3 hybridization character, albeit the nickel complex is mononuclear, unlike the binuclear complex **3**, in which the two metals are bridged by PPh$_2$CS$_2$Me ligand.

The reaction of **1** and **2** yields not only complex **3** but also small amounts of complexes *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$Me)PPh$_2$]W(CO)$_5$] (**4**) (10%) and *trans*-[W(CO)$_4$(PPh$_3$)$_2$] (**5**) (20%) (Scheme 1). Although complex **4** is too unstable for its ^{13}C{^{1}H} NMR spectrum to be obtained, its mass spectrum is the same as that of complex **3**. Interestingly, complex **4** exhibits an ^{31}P{^{1}H} NMR pattern significantly different from that of complex **3**. The ^{31}P{^{1}H} NMR spectrum of **4** displays a resonance at δ 28.8 with a tungsten satellite ($^1J_{W-P}$ = 204.5 Hz, $^3J_{P-P}$ = 7.0 Hz) which is coupled with a resonance of one of the PPh$_3$ ligands on Pd. Two other peaks resonating at δ 21.7 (d, $^2J_{P-P}$ = 39.1 Hz) and δ 25.2 (dd, $^3J_{P-P}$ = 7.0 Hz, $^2J_{P-P}$ = 39.1 Hz) with low coupling constants are in favor of a cis geometry for the phosphines on Pd. In complex **3**, the PPh$_2$(CS$_2$Me) ligand on W does not couple with a PPh$_3$ on Pd, but in complex **4**, such coupling does occur. Clearly, complexes **3** and **4** possess the same molecular weight but differ in their configurations. This is possibly due to different coordinations of the thiocarbonyl group of [W(CO)$_5$[PPh$_2$(CS$_2$Me)]] (**2**) with [Pd(PPh$_3$)$_4$]. The thiocarbonyl group may coordinate with the Pd fragment in two ways: one is to form the anti configurational complex by occupying the two metal atoms on opposite sides of the P−CS$_2$R bond and the other is to form the syn configurational complex by occupying the Pd and W atoms on the same side of the P−CS$_2$R bond.

In the reaction of **1** and **2**, the complex *trans*-[W(CO)$_4$(PPh$_3$)$_2$] (**5**) is also isolated. Hieber[33] and co-workers synthesized it 40 years ago. An improved preparation of tertiary phosphines and related substitution products of group VI metal carbonyls in high yields through sodium borohydride catalysis in boiling ethanol was developed by Chatt[34] in 1971.

Disproportionation Reaction of Complex 3. At room-temperature, complex **3** is unstable in CHCl$_3$ and slowly forms the complex [Pd(PPh$_3$)[PPh$_2$(CS$_2$Me)]]$_2$ (**6**) in 31% isolated yield and the complex [W(CO)$_5$(PPh$_3$)] (**7**) in 40% yield (Scheme 1). Compound **6** is an air-stable, yellow solid that is readily soluble in polar organic solvents such as dichloromethane, toluene, and acetonitrile but insoluble in saturated hydrocarbons.

The identification of **6** as [Pd(PPh$_3$)[PPh$_2$(CS$_2$Me)]]$_2$ was based on the spectroscopic data. The FAB mass spectrum of **6** shows a peak at *m/z* 1243 which corresponds to a fragment formed by the cleavage of the SMe group from **6**. The ^{1}H NMR spectrum of **6** exhibits a singlet at δ 2.18 assignable to the thiomethoxy protons, and the corresponding ^{13}C{^{1}H} NMR signal is at δ 19.7. A downfield singlet at δ 53.7 without a tungsten satellite in the ^{31}P{^{1}H} NMR spectrum is assigned to the PPh$_2$(CS$_2$Me) ligand whereas a signal at higher field (δ 22.2) is due to the PPh$_3$ group on Pd. The ^{13}C{^{1}H} NMR spectrum of **6** displays one set of resonances for the PPh$_2$(CS$_2$Me) ligand. In addition, no carbonyl absorption in the IR spectrum and tungsten isotope distribution in the mass spectrum have been observed. It can be summarized that the diphenyl(dithiomethoxycarbonyl)phosphine ligand is transferred from tungsten to palladium to form a dipalladium complex.

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Table 1. Crystal Data and Refinement Details for Complexes **3**, **6**, **9a**, and **11d**·$CHCl_3$

	3	**6**	**9a**	**11d**·$CHCl_3$
empirical formula	$C_{55}H_{43}O_5P_3S_2PdW$	$C_{64}H_{56}P_4S_4Pd_2$	$C_{56}H_{42}NO_5P_3S_2PdW$	$C_{59}H_{47}Cl_3NO_5P_3S_2PdW$
fw	1231.22	1290.07	1256.23	1403.66
space group	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.920(3)	15.106(3)	11.125(3)	11.692(3)
b, Å	14.707(5)	9.848(3)	14.089(4)	13.602(9)
c, Å	16.654(5)	20.528(4)	17.947(7)	18.471(10)
α, deg	99.98(3)		80.13(3)	81.29(5)
β, deg	93.75(3)	104.85(2)	80.39(3)	80.88(3)
γ, deg	99.44(3)		89.76(2)	88.82(1)
V, Å^3	2586.3(14)	2934.2(12)	2731.7(15)	2867(3)
Z	2	2	2	2
ρ_{calcd}, g cm^{-3}	1.581	1.46	1.527	1.626
μ(Mo Kα), cm^{-1}	28.268	8.843	26.785	25.538
λ, Å	0.70930	0.71073	0.71073	0.71073
T, °C	25	25	25	25
R^a	0.040	0.034	0.047	0.038
$R_w{}^b$	0.042	0.037	0.044	0.041

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **3**, **6**, **9a**, and **11d**

bond lengths		bond angles	
Compound **3**			
W−P(3)	2.542(2)	Pd−S(1)−C(6)	62.9(3)
Pd−P(1)	2.317(2)	Pd−C(6)−S(1)	71.0(3)
Pd−P(2)	2.364(2)	S(1)−Pd−C(6)	46.09(21)
Pd−S(1)	2.278(2)	S(2)−C(6)−Pd	117.6(4)
Pd−C(6)	2.145(8)	W−P(3)−C(6)	114.1(3)
C(6)−S(1)	1.736(8)	P(1)−Pd−P(2)	105.73(8)
C(6)−S(2)	1.794(8)	P(3)−C(6)−Pd	124.1(4)
C(6)−P(3)	1.871(8)	P(3)−C(6)−S(2)	110.4(4)
Compound **6**			
Pd−P(1)	2.310(1)	Pd−S(1)−C(1)	61.14(16)
Pd−P(2)	2.340(2)	Pd−C(1)−S(1)	72.73(18)
Pd−S(1)	2.296(1)	S(1)−Pd−C(1)	46.13(13)
Pd−C(1)	2.106(5)	S(2)−C(1)−Pd	118.50(25)
C(1)−S(1)	1.734(5)	C(1)−P(1)−Pd	116.81(16)
C(1)−S(2)	1.793(5)	P(1)−Pd−P(2)	108.02(5)
C(1)−P(1)	1.836(5)	P(1)−C(1)−Pd	112.97(23)
Compound **9a**			
W−P(1)	2.565(3)	Pd−S(1)−C(1)	66.2(3)
Pd−P(3)	2.333(3)	Pd−C(1)−S(1)	68.1(3)
Pd−P(2)	2.323(3)	S(1)−Pd−C(1)	45.7(3)
Pd−S(1)	2.249(3)	S(2)−C(1)−Pd	111.1(5)
Pd−C(1)	2.217(10)	W−P(1)−C(1)	119.6(3)
C(1)−S(1)	1.734(10)	P(2)−Pd−P(3)	103.68(11)
C(1)−S(2)	1.836(10)	P(1)−C(1)−Pd	127.7(5)
C(1)−P(1)	1.811(11)	P(1)−C(1)−S(2)	113.9(5)
Compound **11d**			
W−P(1)	2.558(3)	Pd−S(1)−C(1)	66.6(3)
Pd−P(3)	2.341(2)	Pd−C(1)−S(1)	68.2(3)
Pd−P(2)	2.344(3)	S(1)−Pd−C(1)	45.18(20)
Pd−S(1)	2.261(2)	S(2)−C(1)−Pd	114.6(4)
Pd−C(1)	2.235(8)	W−P(1)−C(1)	120.6(3)
C(1)−S(1)	1.727(8)	P(2)−Pd−P(3)	104.00(9)
C(1)−S(2)	1.813(8)	P(1)−C(1)−Pd	124.3(4)
C(1)−P(1)	1.846(8)	P(1)−C(1)−S(2)	111.3(4)

We also performed an X-ray diffraction study of **6**. It ORTEP drawing with atom labeling is shown in Figure 2. Table 2 contains selected bond distances and angles. The two $Pd(PPh_3)$ fragments, which are related by a crystallographic inversion center, are held together by two doubly bridging PPh_2CS_2Me moieties. Each $PPh_2(CS_2Me)$ ligand is π-bonded to one Pd atom through the C═S linkage and σ-bonded to the other Pd through the phosphorus atom, resulting in a six-membered ring. The coordination around each Pd atom is a distorted square plane, the distortion being mainly due to the short bite of the C═S linkage [C−Pd−S = 46.13(13)°] and the requirements of the six-membered ring. A least-squares plane calculation reveals the planarity of the P(2)P(1)C(1)S(1) core (largest deviation 0.07(1) Å). The $Pd-PPh_3$ distance, 2.325(2) Å, is significantly longer than the corresponding value of 2.267(2) Å found in $[PdCl(CH_2SMe)(PPh_3)_2]$,[5] possibly because of the influence of the C═S coordination.

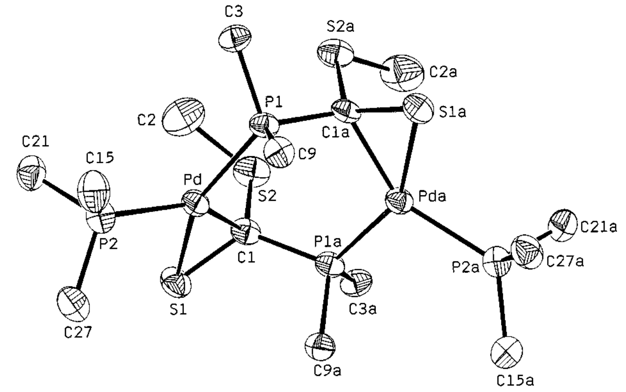

Figure 2. ORTEP plot of the molecular structure of compound **6**. The phenyl groups are omitted for clarity.

In the literature, two six-membered-ring doubly CS_2-bridged binuclear complexes, $[(PPh_3)Ni(\mu\text{-}CS_2)_2Ni(PPh_3)]$[31] and $[(PPh_3)Pt(\mu\text{-}CS_2)_2Pt(PPh_3)]$,[32] were reported by Bianchini and Farrar. The differences between the doubly CS_2-bridged and doubly $PPh_2(CS_2Me)$-bridged complexes are due to the hybridization of the carbon atom of the C═S moiety. Because of the sp^3 hybridization of the C atom, the six-membered ring of complex **6** adopts a distorted chair conformation. However, sp^2 hybridization of the C atom results in planarity of the $Ni(\mu\text{-}CS_2)_2Ni$ entity (largest deviation from the mean plane 0.034 Å), creating the possibility of an overall electronic delocalization.

Thus, the (dithiomethoxycarbonyl)phosphine transfer reaction between $[Pd(PPh_3)_4]$ and $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**) forms $[[(Ph_3P)Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]]_2]$ (**6**) as the ultimate product. The reaction proceeds via an η^2-coordination of the C═S fragment to Pd, giving *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**) as an intermediate. To the best of our knowledge, there is no previous report of diphenyl(dithiomethoxycarbonyl)phosphine acting as a doubly bridging ligand and of the phenomenon of a phosphine transfer reaction.

The $R_2P(S)C(S)SR$ ligand has successfully been used in reactions with $[Pt(PPh_3)_2C_2H_4]$ to form η^2-CS complexes.[28] In an attempt to find another preparation method for complex **6**,

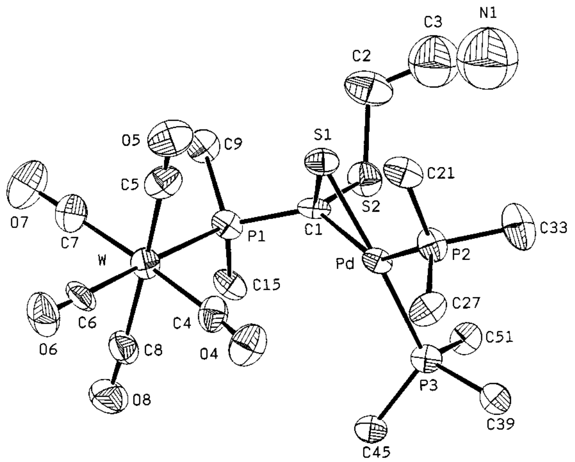

Figure 3. ORTEP plot of the molecular structure of compound **9a**. The phenyl groups are omitted for clarity.

we treated $PPh_2(CS_2Me)$ with $Pd(PPh_3)_4$ in CH_2Cl_2 at ambient temperature. Although the C═S π-coordination complex was observed, more than six other complexes were also found and the reaction was not pursued further. $Et_2N(CS_2Me)$ and Et_2N-[C(S)NHPh] were also treated with $[Pd(PPh_3)_4]$, but no reaction occurred even under extreme experimental conditions.

Synthesis of *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}[CS_2(CH_2)_nCN]PPh_2]W(CO)_5]$ (*n* = 1, 9a; *n* = 2, 9b). The proposed differently configured complexes, **3** and **4**, were identified only by their $^{31}P\{^1H\}$ NMR spectra. Unfortunately, we could not obtain a good-quality sample of the syn product **4** for X-ray diffraction analysis. Steric hindrance of the chemical reactions controls the reactive direction, which influences the stereoselectivity of the product. To explore the syn configurational complex, we carried out the reactions of the two hindered thionitrile complexes **8a**,**b** with $[Pd(PPh_3)_4]$ (Scheme 1).

The reactions of $[W(CO)_5[PPh_2[CS_2(CH_2)_nCN]]]$ ($n = 1$, **8a**; $n = 2$, **8b**) with $[Pd(PPh_3)_4]$ in CH_2Cl_2 at room temperature were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Only one kind of product was detected which was identified as *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}CS_2(CH_2)_nCNPPh_2]W(CO)_5]$ ($n = 1$, **9a**; $n = 2$, **9b**) (Scheme 1). Complexes **9a** and **9b** were isolated in 85 and 90% yields, respectively. They are yellow, moderately air-stable, and readily soluble in chlorinated solvents but insoluble in nonpolar solvents. The FAB mass spectra show two base peaks at *m/z* 1216 corresponding to $(Ph_3P)_2Pd[(S_2C)PPh_2]W(CO)_5^+$, formed by the loss of CH_2CN and C_2H_4CN groups from **9a** and **9b**, respectively. In the ^1H NMR spectra of **9a** and **9b**, AB resonances (δ 2.81, 3.19) and two triplet resonances (δ 2.90, 3.44) are respectively assignable to the thiomethylene and thioethylene protons. The corresponding $^{13}C\{^1H\}$ NMR signals appear at δ 20.1 and at δ 15.2, 21.7, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **9a** exhibits a resonance at δ 54.2 with a tungsten satellite ($^1J_{W-P} = 255.0$ Hz, $^3J_{P-P} = 10.0$ Hz) and a small coupling with PPh_3 on Pd. Two other signals exhibit AB resonances at δ 22.5 (dd, $^2J_{P-P} = 37.1$ Hz, $^3J_{P-P} = 10.0$ Hz) and δ 24.7 ($^2J_{P-P} = 37.1$ Hz). The three $^{31}P\{^1H\}$ NMR resonances of **9b** appear at δ 55.7 ($^1J_{W-P} = 258.4$ Hz), δ 23.4 (dd, $^2J_{P-P} = 33.5$ Hz, $^3J_{P-P} = 7.9$ Hz), and δ 24.2 (d, $^2J_{P-P} = 33.5$ Hz), respectively. The most interesting point is that the $^{31}P\{^1H\}$ NMR patterns of **9a**,**b** are similar to that of **4**. We thus believe that complexes **9a**,**b** and **4** have similar configurations.

To verify this hypothesis, the structure of complex **9a** was determined identified by a single-crystal X-ray diffraction analysis. Figure 3 shows its ORTEP drawing with atom labeling of **9a**. Selected bond distances and angles are listed in Table 2. It is clear that the palladium and tungsten metal centers are in a syn configuration with respect to the $P-CS_2$ bond of the $PPh_2(CS_2CH_2CN)$ ligand. The Pd−S(1) and Pd−C(1) bond distances of **9a** are 2.249(3) and 2.217(10) Å, respectively, which are considered to be normal for Pd−S bonds (2.23−2.31 Å) and Pd−C(sp^3) σ bonds.[5] The C(1)−Pd, W−P(1), and C(1)−S(2)R bond distances of 2.217(10), 2.565(3), and 1.836(10) Å in **9a** are longer than those of 2.145(8), 2.542(2), and 1.794(3) Å, respectively, in **3**, but the C(1)−P(1) (1.811(11) Å) and S(1)−Pd (2.249(3) Å) bond distances in **9a** are shorter than those in **3** [1.871(8) and 2.278(2) Å, respectively]. This is due to the large steric hindrance of the syn configuration and can be confirmed by the W−Pd bond distances, 5.620(2) Å in **3** and 4.610(2) Å in **9a**.

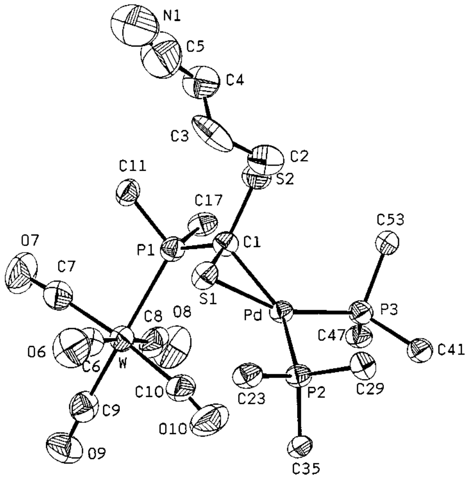

Figure 4. ORTEP plot of the molecular structure of compound **11d**. The phenyl groups are omitted for clarity.

Reaction of $[W(CO)_5[PPh_2(CS_2R)]]$ (R = C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN, 10a−d) with $[Pd(PPh_3)_4]$. To investigate the factors that influence the stability of η^2-CS_2 bonds to palladium and the configurations of the binuclear complexes, we extended the range of diphenyl(dithioalkoxycarbonyl)phosphine ligands in $[W(CO)_5[PPh_2(CS_2R)]]$ (R = C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN, **10a**−**d**). Complexes of the type *syn*-$[[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2R)PPh_2]W(CO)_5]]$ (R = C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN, **11a**−**d**) were achieved by the reactions of $[W(CO)_5[PPh_2(CS_2R)]]$ (R = C_2H_5, C_3H_5, C_2H_4OH, C_3H_6CN, **10a**−**d**) with $[Pd(PPh_3)_4]$ in CH_2Cl_2. Compounds **11a**−**d** are air-stable, yellow solids and are readily soluble in polar organic solvents such as dichloromethane and acetonitrile, slightly soluble in tetrahydrofuran, and insoluble in saturated hydrocarbons. All of the spectroscopic and analytical data of **11a**−**d** are in agreement with their formulations. The most interesting observation is the $^{31}P\{^1H\}$ NMR pattern of these complexes. The $^{31}P\{^1H\}$ NMR spectrum of **11a** shows a resonance at δ 52.6 with a tungsten satellite ($^1J_{W-P} = 249.0$ Hz) and a singlet resonance at δ 22.7 with a ratio of 1/2, indicating that one $PPh_2(CS_2C_2H_5)$ ligand is P-coordinated to W and two triphenylphosphines are coordinated to Pd in a cis geometry. Complex **11a** is very stable in the solid state and does not decompose in air over a period of 1 week. The structures of **11a**−**d** were proposed to have syn configurations, which were proved by an X-ray structural analysis of **11d**. Figure 4 shows its ORTEP diagram with atom labeling. Selected bond distances and angles are presented in Table 2. It is apparent that the palladium and tungsten metal centers are in a syn configuration with respect to the $P-CS_2$ bond of the $PPh_2(CS_2C_3H_6CN)$ ligand and the thioalkoxy portion points away from the Pd metal. The C═S, C−Pd, S−Pd, P−CS, and W−P bond distances of **11d** are similar to those of compound **9a** within experimental error. The W−Pd bond distance in **11d**, 4.575(3) Å, is shorter than that (5.620(2) Å) in **3**, indicating no bonding interaction between the two metal atoms. The conspicuously short C−SR bond distance of **11d** (1.813(8) Å) is attributed to the smaller hindrance between the SC_3H_6CN moiety and the Pd atom. To the best of our knowledge, the anti and syn dimetallic complexes **3**, **9a**,**b**, and **11a**−**d** are the first examples prepared with different $PPh_2(CS_2R)$ ligands. Complexes **3**, **9a**,**b**, and **11a**−**d** show three kinds of $^{31}P\{^1H\}$ NMR patterns owing to the different thioalkoxy groups in $[W(CO)_5[PPh_2(CS_2R)]]$. The effects of the geometric positions of the two phosphorus atoms, the metal, and the remaining ligands and the types of substituents bound to phosphorus on the $^{31}P\{^1H\}$ NMR patterns and coupling constants of the $[Pd(X)_2(PR_3)_2]$ system have already been reported in the literature.[35] We attempted to produce dipalladium complexes like **6** from the disproportionation reactions of the two syn configurational complexes **9a** and **11a**, but neither reaction occurred nor was there any exchange of the syn and anti configurations, even by refluxing in $CHCl_3$ for 1 h.

Conclusion

We have compared the reactions of a range of diphenyl(dithioalkoxycarbonyl)phosphine complexes $[W(CO)_5[PPh_2(CS_2R)]]$ with $[Pd(PPh_3)_4]$. $PPh_2(CS_2R)$, which acts as a bridging ligand through phosphorus σ-bonding and C═S π-bonding forms syn and anti configurational dimetallic complexes. The diphenyl(dithiomethoxycarbonyl)phosphine transfer reaction between $[Pd(PPh_3)_4]$ and $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**) forms $[[(Ph_3P)Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]]_2]$ (**6**) as the ultimate product. The reaction proceeds via a η^2-coordination of the C═S fragment to Pd, giving *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**) as an intermediate. Increased hindrance of the thioalkoxy groups exerts stereospecific control leading to the formation of syn configurational complexes. Useful $^{31}P\{^1H\}$ NMR patterns are able to differentiate configurational compounds. In the syn form, one of the triphenylphosphines couples with $PPh_2(CS_2R)$ to give a doublet of doublet resonance or only one singlet resonance when the thioalkoxy group is oriented away from the Pd metal. In the anti form, the two singlet resonances of the triphenylphosphines on Pd do not couple with the response of the $PPh_2(CS_2R)$ ligand on W.

Experimental Section

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-200 or a Bruker AM-300 WB FT-NMR spectrometer and are reported in units of parts per million with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_6D_6, δ 7.15; CD_3COCD_3, δ 2.04). IR spectra were measured on a Perkin-Elmer 983 instrument and referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF, and benzene were distilled from sodium−benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol was distilled from magnesium. All other solvents and reagents were of reagent grade and were used as received. The compounds $[W(CO)_5[PPh_2(CS_2R)]]$[29] (R = CH_3, C_2H_5, C_3H_5, C_2H_4OH, CH_2CN, CH_2CH_2CN, $CH_2CH_2CH_2CN$) and $[Pd(PPh_3)_4]$[36] were prepared according to the literature methods. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation located at the National Taiwan University.

***anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (3), *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (4), and *trans*-$[W(CO)_4(PPh_3)_2]$ (5).** Diethyl ether (30 mL) was added to a flask (100 mL) containing $[Pd(PPh_3)_4]$ (**1**) (1.155 g, 1.0 mmol) and $[W(CO)_5[PPh_2(CS_2Me)]]$ (**2**) (0.600 g, 1.0 mmol). The solution was refluxed for 3 min, and the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction was complete. The solvent was removed under reduced pressure, and the residue was purified by chromatography on activated silica gel (length of column 20 cm). PPh_3 was eluted with diethyl ether. Three fractions were separated with 1/5 CH_2Cl_2/diethyl ether. The yellow product from band 1 was concentrated and cooled to −18 °C for 12 h to give a crystalline solid. This product was recrystallized from 2/1 *n*-hexane/CH_2Cl_2 to give the yellow complex *anti*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**3**). Yield: 0.68 g, 55%. IR (KBr, cm^{-1}): ν(CO) 2060 (m), 1914 (vs), 1887 (s). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 22.2, 22.4 (br, PPh_3), 51.6 ($^1J_{W-P}$ = 257.6 Hz, PPh_2CS_2Me). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.09 (s, 3H, SCH_3), 7.0−7.4 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 18.7 (s, SCH_3), 127−134 (m, C of Ph), 198.8 (d, $^2J_{P-C}$ = 6.7 Hz, cis CO), 208.2 (s, CS_2), 214.9 (s, trans CO). MS (FAB, NBA, *m/z*): 1231 [M^+], 1216 [$M^+ - CH_3$]. Anal. Calcd for $C_{55}H_{43}O_5P_3PdS_2W$: C, 53.65; H, 3.52. Found: C, 53.41; H, 3.65. The yellow-orange product from band 2 was recrystallized from 5/1 *n*-hexane/CH_2Cl_2 to give the complex *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]W(CO)_5]$ (**4**). Yield: 0.12 g, 10%. IR (KBr, cm^{-1}): ν(CO) 2059 (m), 1914 (sh), 1875 (s). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 21.7 (d, $^2J_{P-P}$ = 39.1 Hz, PPh_3), 25.2 (dd, $^3J_{P-P}$ = 7.0 Hz, $^2J_{P-P}$ = 39.1 Hz, PPh_3), 28.8 (d, $^1J_{W-P}$ = 204.5 Hz, $^3J_{P-P}$ = 7.0 Hz, PPh_2CS_2Me). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.22 (s, 3H, SCH_3), 7.0−7.4 (m, 40H, Ph). MS (FAB, NBA, *m/z*): 1231 [M^+]. The orange-red complex from band 3 is *trans*-$[W(CO)_4(PPh_3)_2]$ (**5**). Yield: 0.16 g, 20%. IR (KBr, cm^{-1}): ν(CO) 1873 (s). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 27.7 ($^1J_{W-P}$ = 281.3 Hz, PPh_3). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 7.4−7.6 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 127−134 (m, C of Ph). MS (FAB, NBA, *m/z*): 819 [M^+]. Anal. Calcd for $C_{40}H_{30}O_4P_2W$: C, 58.55; H, 3.69. Found: C, 58.85; H, 3.53.

$[[(Ph_3P)Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]]_2]$ (6) and $[W(CO)_5(PPh_3)]$ (7). A $CHCl_3$ (10 mL) solution of **3** (0.123 g, 0.1 mmol) was stirred at room temperature for 1 h, and the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction was complete. The solvent was removed, and recrystallization from 2/1 *n*-hexane/CH_2Cl_2 gave the yellow crystalline product $[[(Ph_3P)Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2Me)PPh_2]]_2]$ (**6**). Yield: 0.04 g, 31%. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 22.2 (s, PPh_3), 53.7 (s, PPh_2CS_2Me). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.18 (s, 6H, SCH_3), 7.0−7.4 (m, 50H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 19.7 (s, SCH_3), 127−134 (m, C of Ph), 198.1 (d, $^1J_{P-C}$ = 26.5 Hz, PCS_2). MS (FAB, NBA, *m/z*): 1243 [$M^+ - SCH_3$], 981 [$M^+ - SCH_3 - PPh_3$]. Anal. Calcd for $C_{64}H_{56}P_4Pd_2S_4$: C, 59.58; H, 4.38. Found: C, 59.24; H, 4.60. Another yellow complex, $[W(CO)_5(PPh_3)]$ (**7**), was isolated from the reaction in 40% yield. IR (KBr, cm^{-1}): ν(CO) 2060 (m), 1914 (vs), 1887 (s). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −10.2 ($^1J_{W-P}$ = 257.2 Hz, PPh_3). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 7.0−7.4 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 127−134 (m, C of Ph), 213.6, 214.9 (s, CO). MS (FAB, NBA, *m/z*): 586 [M^+], 558 [$M^+ - CO$].

***syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2CH_2CN)PPh_2]W(CO)_5]$ (9a).** A CH_2Cl_2 (10 mL) solution of **8a** (0.313 g, 0.5 mmol) was added to a suspension of $[Pd(PPh_3)_4]$ (0.576 g, 0.5 mmol) in 10 mL of *n*-hexane. After the mixture was stirred for 3 min, the orange-yellow solution was evaporated to dryness. The residue was washed five times with *n*-hexane (each 10 mL) to give a yellow precipitate, which was collected by filtration (G4) and dried in vacuo. Crystals of **9a** were obtained from CH_2Cl_2/*n*-hexane by slow diffusion. The complex *syn*-$[(Ph_3P)_2Pd[\mu\text{-}\eta^1,\eta^2\text{-}(CS_2CH_2CN)PPh_2]W(CO)_5]$ (**9a**) as a yellow microcrystalline solid was isolated in 85% yield. IR (KBr, cm^{-1}): ν(CO) 2064 (s), 1973 (m), 1910 (vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 22.5 (dd, $^3J_{P-P}$ = 10.0 Hz, $^2J_{P-P}$ = 37.1 Hz, PPh_3), 24.7 (d, $^2J_{P-P}$ = 37.1 Hz, PPh_3), 54.2 (d, $^1J_{W-P}$ = 255.0 Hz, $^3J_{P-P}$ = 10.0 Hz, PPh_2CS_2). ^1H

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NMR (200 MHz, CDCl$_3$, 298 K): δ 2.81 (d, $^2J_{\mathrm{H-H}} = 16.4$ Hz, 1H, SCH$_2$), 3.19 (d, $^2J_{\mathrm{H-H}} = 16.4$ Hz, 1H, SCH$_2$), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 20.1 (s, SCH$_2$), 117.7 (s, CN), 127−137 (m, C of Ph), 198.6 (d, $^2J_{\mathrm{P-C}} = 6.7$ Hz, *cis*-CO), 200.6 (s, CS$_2$). MS (FAB, NBA, *m/z*): 1216 [M$^+$ − CH$_2$CN], 1160 [M$^+$ − CH$_2$CN − 2CO], 1076 [M$^+$ − CH$_2$CN − 5CO], 630 [M$^+$ − CH$_2$CN − 5CO − WPPh$_2$CS$_2$]. Anal. Calcd for C$_{56}$H$_{42}$NO$_5$P$_3$PdS$_2$W: C, 53.54; H, 3.37; N, 1.12. Found: C, 53.32; H, 3.62; N, 1.54.

***syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$CH$_2$CH$_2$CN)PPh$_2$]W(CO)$_5$] (9b).** The procedures for synthesis and workup were similar to those for **9a**. The yellow, microcrystalline complex *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$CH$_2$CH$_2$CN)PPh$_2$]W(CO)$_5$] (**9b**) was isolated in 90% yield. IR (THF, cm^{-1}): ν(CO) 2072 (m), 1972 (vs). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 298 K): δ 23.4 (dd, $^3J_{\mathrm{P-P}} = 7.9$ Hz, $^2J_{\mathrm{P-P}} = 33.5$ Hz, PPh$_3$), 24.2 (d, $^2J_{\mathrm{P-P}} = 33.5$ Hz, PPh$_3$), 55.7 (br, $^1J_{\mathrm{W-P}} = 258.4$ Hz, PPh$_2$CS$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 2.90 (t, $J_{\mathrm{H-H}} = 6.7$ Hz, 2H, SCH$_2$), 3.44 (t, $J_{\mathrm{H-H}} = 6.7$ Hz, 2H, CH$_2$CN), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 15.2 (s, SCH$_2$), 21.7 (s, *C*H$_2$CN), 117.1 (s, CH$_2$*C*N), 127−137 (m, C of Ph), 198.6 (d, $^2J_{\mathrm{P-C}} = 6.9$ Hz, cis CO), 200.6 (s, CS$_2$), 210.2 (s, trans CO). MS (FAB, NBA, *m/z*): 1216 [M$^+$ − C$_2$H$_4$CN], 1076 [M$^+$ − C$_2$H$_4$CN − 5CO], 630 [M$^+$ − C$_2$H$_4$CN − 5CO − WPPh$_2$CS$_2$]. Anal. Calcd for C$_{57}$H$_{44}$NO$_5$P$_3$PdS$_2$W: C, 53.89; H, 3.49; N, 1.10. Found: C, 53.95; H, 3.60; N, 1.01.

***syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_2$H$_5$)PPh$_2$]W(CO)$_5$] (11a).** CH$_2$Cl$_2$ (10 mL) was added to a flask (50 mL) containing **10a** (0.307 g, 0.5 mmol) and [Pd(PPh$_3$)$_4$] (0.577 g, 0.5 mmol). The color of the solution turned from red to yellow in 3 min. The solution was then evaporated to dryness. The yellow residue was stirred with 30 mL of *n*-hexane/diethyl ether (2/1) to yield a yellow precipitate, which was crystallized from CH$_2$Cl$_2$/*n*-hexane by slow diffusion. The yellow crystals were collected and dried in vacuo to give the complex *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_2$H$_5$)PPh$_2$]W(CO)$_5$] (**11a**) in 82% yield. IR (THF, cm^{-1}): ν(CO) 2072 (m), 1933 (vs). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 298 K): δ 22.7 (s, PPh$_3$), 52.6 ($^1J_{\mathrm{W-P}} = 249.0$ Hz, PPh$_2$CS$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 1.29 (t, $J_{\mathrm{H-H}} = 7.4$ Hz, 3H, CH$_3$), 3.30 (q, $J_{\mathrm{H-H}} = 7.4$ Hz, 2H, SCH$_2$), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 12.7 (s, CH$_3$), 30.6 (s, SCH$_2$), 127−137 (m, C of Ph), 197.0 (d, $^2J_{\mathrm{P-C}} = 8.3$ Hz, cis CO). MS (FAB, NBA, *m/z*): 1245 [M$^+$], 1217 [M$^+$ − CO], 630 [M$^+$ − W(CO)$_5$PPh$_2$CS$_2$C$_2$H$_5$]. Anal. Calcd for C$_{56}$H$_{45}$O$_5$P$_3$PdS$_2$W: C, 54.01; H, 3.64. Found: C, 54.31; H, 3.80.

***syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_3$H$_5$)PPh$_2$]W(CO)$_5$] (11b).** The procedures for synthesis and workup were similar to those for complex **11a**. The yellow, microcrystalline complex *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_3$H$_5$)PPh$_2$]W(CO)$_5$] (**11b**) was isolated in 88% yield. IR (THF, cm^{-1}): ν(CO) 2068 (m), 1928 (vs). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 298 K): δ 22.7 (s, PPh$_3$), 53.1 ($^1J_{\mathrm{W-P}} = 252.6$ Hz, PPh$_2$CS$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 3.42 (d, $^3J_{\mathrm{H-H}} = 6.6$ Hz, 2H, SCH$_2$), 4.93 (m, 2H, CHC*H$_2$*), 5.66 (m, 1H, C*H*CH$_2$), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 40.1 (s, SCH$_2$), 117.1 (s, HC=), 117.6 (s, =CH$_2$), 127−137 (m, C of Ph), 198.8 (d, $^2J_{\mathrm{P-C}} = 6.9$ Hz, cis CO). MS (FAB, NBA, *m/z*): 1257 [M$^+$], 1216 [M$^+$ − C$_3$H$_5$], 630 [M$^+$ − C$_3$H$_5$ − W(CO)$_5$PPh$_2$CS$_2$]. Anal. Calcd for C$_{57}$H$_{45}$O$_5$P$_3$PdS$_2$W: C, 54.45; H, 3.61. Found: C, 54.60; H, 3.82.

***syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_2$H$_4$OH)PPh$_2$]W(CO)$_5$] (11c).** The procedures for synthesis and workup were similar to those for complex **11a**. The yellow, microcrystalline complex *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_2$H$_4$OH)PPh$_2$]W(CO)$_5$] (**11c**) was isolated in 80% yield. IR (THF, cm^{-1}): ν(CO) 2071 (m), 1932 (vs). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 298 K): δ 23.6 (s, PPh$_3$), 55.3 ($^1J_{\mathrm{W-P}} = 255.8$ Hz, PPh$_2$CS$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 3.52 (m, 2H, SCH$_2$), 3.78 (m, 2H, CH$_2$O), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 39.4 (s, SCH$_2$), 60.8 (s, CH$_2$OH), 127−137 (m, C of Ph), 197.1 (d, $^2J_{\mathrm{P-C}} = 8.3$ Hz, cis CO). MS (FAB, NBA, *m/z*): 1261 [M$^+$], 1216 [M$^+$ − CH$_2$CH$_2$OH], 630 [M$^+$ − C$_2$H$_5$OH − W(CO)$_5$PPh$_2$CS$_2$]. Anal. Calcd for C$_{56}$H$_{45}$O$_6$P$_3$PdS$_2$W: C, 53.32; H, 3.60. Found: C, 53.75; H, 3.87.

***syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$C$_3$H$_6$CN)PPh$_2$]W(CO)$_5$] (11d).** The procedures for synthesis and workup were similar to those for complex **11a**. The yellow, microcrystalline complex *syn*-[(Ph$_3$P)$_2$Pd[μ-η^1,η^2-(CS$_2$CH$_2$CH$_2$CH$_2$CN)PPh$_2$]W(CO)$_5$] (**11d**) was isolated in 92% yield. IR (THF, cm^{-1}): ν(CO) 2065 (m), 1926 (vs). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 298 K): δ 23.3 (s, PPh$_3$), 54.5 (br, $^1J_{\mathrm{W-P}} = 252.9$ Hz, PPh$_2$CS$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 1.80 (m, 2H, C*H$_2$*CH$_2$CN), 2.16 (t, $^3J_{\mathrm{H-H}} = 8.1$ Hz, 2H, CH$_2$CN), 2.83 (t, $^3J_{\mathrm{H-H}} = 8.1$ Hz, 2H, SCH$_2$), 7.0−7.4 (m, 40H, Ph). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 298 K): δ 16.0 (s, *C*H$_2$CH$_2$CN), 24.7 (s, *C*H$_2$CN), 34.7 (s, SCH$_2$), 119.3 (s, CN), 127−137 (m, C of Ph), 198.6 (d, $^2J_{\mathrm{P-C}} = 6.9$ Hz, cis CO), 212.5 (s, CS$_2$), 220.4 (s, trans CO). MS (FAB, NBA, *m/z*): 1284 [M$^+$], 1216 [M$^+$ − CH$_2$CN − CO], 630 [M$^+$ − CH$_2$CN − W(CO)$_5$PPh$_2$CS$_2$CH$_2$CH$_2$]. Anal. Calcd for C$_{58}$H$_{46}$NO$_5$P$_3$PdS$_2$W: C, 54.24; H, 3.61; N, 1.09. Found: C, 54.62; H, 3.20; N, 0.98.

Single-Crystal X-ray Diffraction Analyses of 3, 6, 9a, and 11d. Single crystals of **3**, **6**, **9a**, and **11d** suitable for X-ray diffraction analyses were grown by recrystallization from 20/1 *n*-hexane/CH$_2$Cl$_2$. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[37]

A suitable single crystal of **3** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with 2θ values in the range from 18.86 to 30.22°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the θ/2θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2.06 to 8.24° min^{-1}. The θ scan angle was determined for each reflection according to the expression 0.85 ± 0.35 tan θ. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 6742 unique measured data, of which 4777 reflections with $I > 2\sigma(I)$ were considered observed. The first step of the structure solution used the heavy-atom method (Patterson synthesis), which revealed the positions of the metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.[38,39] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1−2 Å^2 larger than the equivalent B_{iso} values of the atoms to which they were bonded. The final residuals of this refinement were $R = 0.040$ and $R_w = 0.042$.

The procedures for **6**, **9a**, and **11d** were similar to those for **3**. The final residuals of the refinements were $R = 0.034$ and $R_w = 0.037$ for **6**, $R = 0.047$ and $R_w = 0.044$ for **9a**, and $R = 0.038$ and $R_w = 0.041$ for **11d**.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of complexes **3**, **6**, **9a**, and **11d**·CHCl$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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