Syntheses and Crystal Structures of Tungsten Complexes Containing Various (Thiazoliumyl)diphenylphosphine Ligands

Kuang-Hway Yih, Sung-Chih Yeh, Ying-Chih Lin,* Gene-Hsiang Lee, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Alkylation reactions at the S atom of the anionic $PPh_2C(=NPh)S^-$ ligand coordinated to a tungsten pentacarbonyl group afford the neutral complexes $W(CO)_5PPh_2C(=NPh)SR$ (**4**, R = $CH_2C{\equiv}CH$; **5**, R = $CH_2C{\equiv}N$; **6**, R = CH_2CONH_2; **7**, R = $CH_2CH{=}CH_2$; **8**, R = CH_2CO_2-Me). Protonation of **4** with HBF_4 at room temperature causes cyclization to the cationic complex $W(CO)_5PPh_2[CSCH_2C(CH_2)NPh]BF_4$ (**10**), which contains a (thiazoliumyl)diphenylphosphine ligand. Similarly, protonation reactions of **5** and **6** with HBF_4 give the cationic complex $[W(CO)_5PPh_2CSCHC(NH_2)NPh]BF_4$ (**11**) and the neutral complex $W(CO)_5PPh_2CSCHC(OBF_3)NPh$ (**12**), respectively, both of which contain (thiazoliumyl)diphenylphosphine ligands. The structures of **10** and **12** are determined by X-ray diffraction analyses.

Introduction

Thiazoles, mesoionic thiazoles, and thiazolium derivatives have attracted considerable attention because of their unusual charge distribution and possible aromatic properties of the five-membered rings. Some methods for the synthesis of thiazolium derivatives[1] as well as bivalent metal thiazolium salts[2] have been reported. Furthermore, much work has been carried out on the nucleophilic reactivity,[3] cycloaddition reactions,[4] and infrared, visible absorption, and resonance Raman[5] studies of organic thiazolium compounds. However, only a few metal thiazolium derivatives have been reported.[6] Our previous report dealt with alkylation reactions of the complex $[Et_4N][W(CO)_5PPh_2(CS_2)]$ by unsaturated organic halides and their subsequent reactions.[7] In this paper, we wish to report a new method for the synthesis of tungsten complexes containing (thiazoliumyl)diphenylphosphine ligands.

Results and Discussion

Coordinated $PPh_2C(=NPh)S^-$ Ligand and Its Alkylation Reactions. Facile deprotonation of $W(CO)_5PPh_2H$ by *n*-BuLi followed by exchange of the cation with Et_4NBr gives $Et_4N[W(CO)_5PPh_2]$ (**1**). The IR spectrum of **1** has two relatively high frequency CO stretching bands at 2070 and 1910 cm^{-1}, indicating that the anionic charge is localized at the phosphide ligand. Thus, treatment of **1** with PhN=C=S leads to the formation of a P−C bond to give $[Et_4N][W(CO)_5PPh_2C(=NPh)S]$ (**2a**).[8] Complex **2a** can also be obtained directly from $W(CO)_5PPh_2H$, without going through the isolation of **1**, in ca. 85% yield. Complex **2a** is an air-stable yellow solid. The IR spectrum in the ν_{CO} region shows a pattern characteristic for an octahedral $M(CO)_5L$ group, and the ^{31}P NMR spectrum shows a resonance at δ 34.3 with J_{W-P} = 238.9 Hz. These data indicate a monodentate P-coordination mode of the phosphine ligand in **2a**. This bonding mode contrasts with the chelation through P and S atoms by a similar ligand in complexes reported by Kunze and co-workers.[9] Interestingly, there is no reaction between **1** and the aliphatic isothiocyanate $PhCH_2N{=}C{=}S$. A reaction between PhN=C=O and **1** was found to occur, but no product could be isolated and identified.

Photolysis of **2a** by UV radiation leads to loss of CO and formation of $[Et_4N]W(CO)_4[\eta^2\text{-}PPh_2C(=NPh)S]$ (**3a**), in which the phosphine ligand binds to the metal in a

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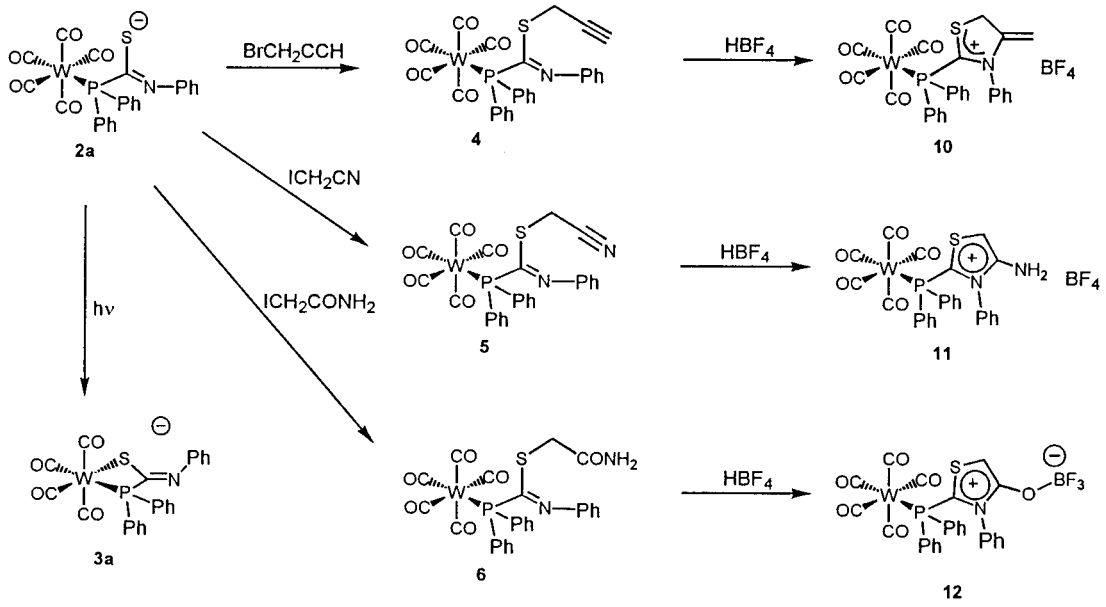
Scheme 1



bidentate fashion through the P and S atoms. The IR spectrum of **3a** in the ν_{CO} region displays four bands characteristic of a *cis*-$M(CO)_4L_2$ group. The ^{31}P NMR resonance of **3a** appears at δ 14.89 with $^1J_{W-P} = 189.6$ Hz, shifted from δ 34.3 for **2a**. The different chemical shifts reflect the dissimilar bonding modes of the phosphine ligand. The bonding of the chelating phosphine ligand in **3a** is analogous to that reported by Kunze and co-workers[9] and is responsible for the inactive nature of **3a**. In comparison, the monodentate P-coordinated bonding mode of the $PPh_2C(=NPh)S^-$ ligand in **2a** results in this complex being much more reactive.

Surprisingly, the reaction of **1** with EtOC(O)N=C=S yields directly the decarbonylation product $[Et_4N]W(CO)_4[\eta^2\text{-}PPh_2C(=NCO_2Et)S]$ (**3b**), possibly due to higher photosensitivity or thermal reactivity of its precursor **2b**. The ^{31}P NMR spectrum of the phosphine ligand in **3b** has a resonance at δ 16.36 ($^1J_{W-P} = 193.8$ Hz).

The alkylation reaction of **2a** with alkyl halides leads to formation of a S−C bond. Thus, the reaction of **2a** with $BrCH_2C{\equiv}CH$ affords the neutral complex $W(CO)_5PPh_2C(=NPh)SCH_2C{\equiv}CH$ (**4**) in 84% yield. In the FAB mass spectrum of **4**, the parent peaks as well as the peaks due to fragmentation are in agreement with the molecular formula. The IR spectrum of **4** shows two terminal carbonyl stretchings at 2073 and 1934 cm^{-1}. The higher frequencies compared to those of **2a** indicate that **4** is a neutral complex. The ^{31}P NMR spectrum of **4** has a resonance at δ 38.03 with a pair of tungsten satellites ($^1J_{W-P} = 246.8$ Hz), similar to that of **2a**, indicating monodentate phosphorus coordination. In the ^1H NMR spectrum of **4**, a doublet resonance at δ 2.88 and a triplet resonance at δ 2.04 with $^4J_{H-H} = 1.80$ Hz are assigned to the *S*-methylene and terminal methyne protons of the propargyl group, respectively. In the ^{13}C NMR spectrum the corresponding ^{13}C resonances appear at δ 21.6 and 72.8, respectively.

The synthetic methodology described above is applicable to primary organic halides with various substituents. Thus, the reaction of **2a** with $ICH_2C{\equiv}N$ in CH_2Cl_2 affords $W(CO)_5PPh_2C(=NPh)SCH_2C{\equiv}N$ (**5**) in 88% yield. The ^{31}P NMR spectrum of **5** (δ 38.72 with $^1J_{W-P} = 247.4$ Hz) is similar to that of **4**. The reaction of **2a** with ICH_2CONH_2 affords the analogous complex $W(CO)_5PPh_2C(=NPh)SCH_2CONH_2$ (**6**) in high yield. The same procedure was used to prepare $W(CO)_5PPh_2C(=NPh)SCH_2CH{=}CH_2$ (**7**) and $W(CO)_5PPh_2C(=NPh)SCH_2CO_2Me$ (**8**), both in high yield. In the reactions of **2a** with various acyl halides, both S-acylation and N-acylation are observed.[10]

Proton-Induced Cyclization. We previously reported spontaneous intermolecular cycloaddition[7] of $W(CO)_5PPh_2C(=S)SCH_2C{\equiv}CH$ (**9**) leading to dimerization. In the presence of Et_3N or $PhCH_2NH_2$, a different type of dimerization of **9** yields a dinuclear complex of 6a-thiathiophthene.[8] However, unlike **9**, complex **4**, by itself or in the presence of an amine, is stable. Protonation of **4** by HBF_4 in *n*-hexane at room temperature results in formation of $W(CO)_5PPh_2[\overline{CSCH_2C(CH_2)NPh}]BF_4$ (**10**) (see Scheme 1). The ^1H NMR spectrum of **10** has a resonance at δ 5.11 assignable to the S-bonded methylene and a pair of resonances at δ 4.68 and 5.65 assignable to the terminal methylene protons. The ^{13}C NMR signal of the S-bonded methylene is at δ 74.06, while that of the terminal methylene carbon is masked by the aromatic carbon atoms.

Similarly, protonation of **5** by HBF_4 results in the formation of the cationic cyclic complex $[W(CO)_5PPh_2\overline{CSCHC(NH_2)NPh}]BF_4$ (**11**), which contains a (thiazoliumyl)diphenylphosphine ligand. In this reaction the proton-induced cyclization is also accompanied by a 1,3-hydrogen shift. In the ^1H NMR spectrum of **11** the methyne proton appears at δ 6.22. Protonation of **6** induces a similar cyclization with loss of a NH_2 group to yield $W(CO)_5PPh_2\overline{CSCHC(OBF_3)NPh}$ (**12**). In **12**, the BF_3 group acts as a Lewis acid and bonds to the oxygen atom of the enol group. Under similar reaction conditions complexes **7** and **8** are inert and no cyclization was observed.

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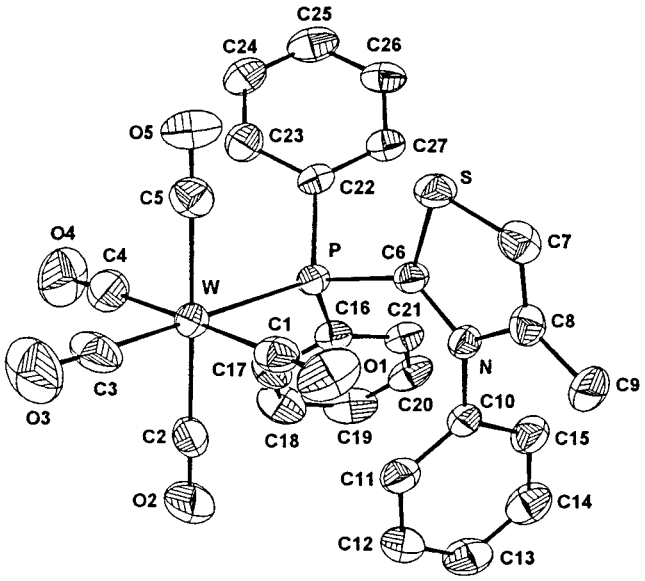

Figure 1. ORTEP drawing for the cation of $W(CO)_5[PPh_2CSCH_2C(CH_2)NPh][BF_4]$ (**10**).

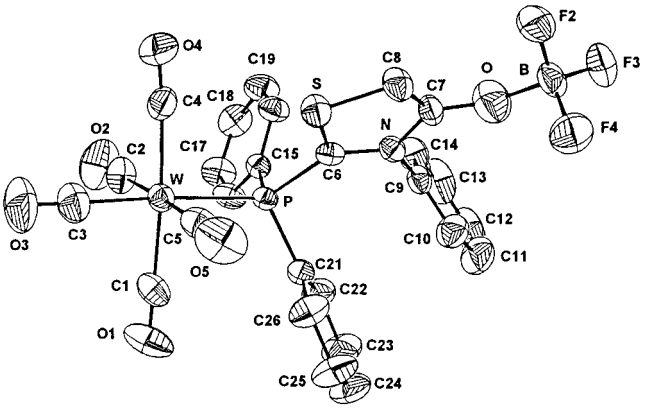

Figure 2. ORTEP drawing for $W(CO)_5[PPh_2CSCHC(OBF_3)NPh]$ (**12**).

Since the spectroscopic data of the thiazoliumylphosphine complexes are not sufficient for establishment of their structure, single crystals of **10** and **12** were grown and the structures determined by X-ray diffraction analysis. ORTEP drawings are shown in Figures 1 and 2 for **10** and **12**, respectively. The coordination geometry around the tungsten metal center in **10** is pseudooctahedral. The phosphine ligand with a thioazolium group is coordinated to the tungsten metal center through the phosphorus atom. In the five-membered ring of **10**, delocalization occurs only between the S−C−N atoms, as indicated by the bond distances C(6)−S (1.700(9) Å) and C(6)−N (1.312(11) Å), which show partial double-bond character, and the C(7)−C(8) bond distance (1.50(1) Å), which is close to a normal C−C single bond. It is thus not unexpected that the five atoms of the thiazolium ring are not planar. Deviations from the average plane are in the range of 0.12(1) to −0.11(1) Å. The dihedral angle between the planes S−C(6)−N and S−C(7)−C(8) is 12.6(9)°. The bond length C(8)−C(9) (1.307(15) Å) is normal for a C−C double bond.

In **12** the five-membered thiazolium ring is planar. The deviations from the average plane for all atoms are less than 0.006(5) Å. The C(7)−C(8) (1.353(5) Å) distance is in the range of a regular aromatic C−C bond, confirming the presence of an enol unit (which is stabilized by a BF_3 group attached to the oxygen atom). The BF_3 unit attached to an enol group has been observed in several diiron complexes.[11] The bond distances C(6)−S (1.669(3) Å) and C(6)−N (1.353(4) Å) in **12** are comparable to the corresponding bond distances of **10**, but the other C(8)−S (1.691(4) Å) distance is much shorter than the corresponding C(7)−S (1.808(11) Å) in **10**. The thioazolium ring in **12** differs from the thiazole in **10** by protonation at C(7) in the latter.

A few thiazolium complexes are known,[12] but their preparations do not involve protonation of a precursor. Formation of the intramolecular cyclization product **10** is believed to proceed via protonation at the terminal carbon of **4** to afford a cationic complex, followed by nucleophilic attack of the nitrogen atom of the PhNCS group at the center carbon of the propargyl unit to form the cationic thiazolium ring. In the reaction of **5** with acid, protonation very likely takes place at the nitrogen atom of the nitrile group, and the cyclization is followed by a 1,3-hydrogen shift, giving complex **11**. In the process of forming **12**, the cyclization is accompanied by loss of the amine group and is further assisted by addition of a BF_3 group to the oxygen atom.

Treatment of **11** with *n*-Bu_4NF at room temperature affords $W(CO)_5PPh_2F$. The ^{31}P NMR spectrum of this product shows a doublet resonance at δ 171.37 with J_{W-P} = 148.4 and J_{F-P} = 862.2 Hz, indicating P-coordination of the PPh_2F ligand. Interestingly, treatment of analogous species **10** and **12** with *n*-Bu_4NF gave no reaction under the same reaction conditions.

In conclusion, the facile synthesis of the $PPh_2C(=NPh)SR$ ligand coordinated to a tungsten pentacarbonyl group is reported. For R = propargyl, CH_2CN, and CH_2CONH_2, the organic part attached to the diphenylphosphine unit is converted to the thiazolium group by strong acid.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on the Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation located at the National Taiwan University. $W(CO)_6$ and PPh_2H were purchased from Strem Chemical, PhNCS, ICH_2CN, $BrCH_2CH{=}CH_2$, ICH_2CONH_2, and $BrCH_2CO_2Me$ were purchased from Merck, and propargyl bromide, purchased also from Merck, was distilled before use. $W(CO)_5(PPh_2H)$ (**1a**) was prepared according to a literature method.[8a]

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Preparation of 2a. A solution of **1a** (0.61 g, 1.20 mmol) in diethyl ether (20 mL) was treated with *n*-BuLi (1.6 M, 0.80 mL, 1.28 mmol) at 0 °C, and the mixture was stirred for 5 min and slowly warmed to room temperature. To the mixture was added 0.15 mL of PhNCS (1.30 mmol), and the solution was stirred for 10 min. Addition of a solution of tetraethylammonium bromide (0.32 g, 1.52 mmol in 10 mL of methanol) to the mixture caused formation of a yellow precipitate, which was filtered, with 2 × 10 mL of hexane, and then dried under vacuum to give $[Et_4N][W(CO)_5PPh_2C(=NPh)S]$ (**2a**; 0.79 g, 85% yield). Spectroscopic data for **2a** are as follows. IR (THF): 2062 (m), 1963 (w), 1919 (vs). ^{31}P NMR ($CDCl_3$): δ 34.3 (J_{W-P} = 238.9 Hz). ^1H NMR ($CDCl_3$): δ 1.15 (tt, 12H, CH_3, $^3J_{N-H}$ = 1.7, J_{H-H} = 7.4 Hz), 3.08 (q, 8H, CH_2, J_{H-H} = 7.4 Hz), 6.85−7.77 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 7.3 (CH_3), 52.2 (CH_2), 121.3 (s), 122.3 (s), 127.4 (d, $^3J_{P-C}$ = 8.7 Hz), 128.8 (s), 129.8 (s), 134.0 (d, $^2J_{P-C}$ = 9.8 Hz), 134.9 (s), 139.0 (d, J_{P-C} = 35.7 Hz), 190.3 (d, CS, J_{P-C} = 29.3 Hz), 198.8 (dd, cis-CO, $^2J_{P-C}$ = 6.8, J_{W-C} = 123.8 Hz), 201.9 (d, trans-CO, $^2J_{P-C}$ = 22.5 Hz). MS: *m*/*z* 774 ($M^+ + Et_4N$), 611 ($M^+ + Et_4N - CO - PhNCS$). Anal. Calcd for $C_{32}H_{35}O_5N_2PSW$: C, 49.62; N, 3.62; H, 4.56. Found: C, 49.54; N, 3.54; H, 4.23.

Photodecarbonylation of 2a. Complex **2a** (0.14 g, 0.18 mmol) was dissolved in 10 mL of benzene, and the solution was photolyzed by UV radiation for 5 min at room temperature. The solvent was removed under vacuum, and the product was redissolved in 10 mL of CH_2Cl_2/hexane (1/2). The mixture was stored at −20 °C for 12 h to give the yellow crystalline product $[Et_4N]W(CO)_4[\eta^2\text{-}PPh_2C(=NPh)S]$ (**3a**; 0.09 g, 68% yield). Spectroscopic data for **3a** are as follows. IR (THF): 1987 (m), 1919 (m), 1871 (vs), 1819 (s) cm^{-1}. ^{31}P NMR (CD_3CN): δ 14.89 (J_{W-P} = 189.61 Hz). ^1H NMR (CD_3CN): δ 1.18 (tt, 12H, CH_3, $^3J_{N-H}$ = 1.93 Hz, $^3J_{H-H}$ = 7.23 Hz), 3.12 (q, 8H, CH_2, $^3J_{H-H}$ = 7.25), 7.01−7.88 (m, 15H, Ph). ^{13}C NMR (CD_3CN): δ 7.7 (s, CH_3), 53.0 (s, CH_2), 122.5 (s), 124.4 (s), 129.2 (d, $^3J_{P-C}$ = 9.1 Hz), 129.5 (s), 131.0 (s), 135.8 (d, J_{P-C} = 26.0 Hz), 133.9 (d, $^2J_{P-C}$ = 12.3 Hz), 150.4 (d, $^3J_{P-C}$ = 16.9 Hz), 189.2 (d, CS, J_{P-C} = 42.8 Hz), 205.7 (d, 2C, cis-CO, $^2J_{P-C}$ = 7.3 Hz), 213.5 (d, 1C, cis-CO, $^2J_{P-C}$ = 7.3 Hz), 215.8 (d, trans-CO, $^2J_{P-C}$ = 29.1 Hz). MS: *m*/*z* 876 ($M^+ + Et_4N$), 848 ($M^+ + Et_4N - CO$). Anal. Calcd for $C_{31}H_{35}O_4N_2PSW$: C, 49.88; N, 3.75; H, 4.73. Found: C, 49.77; N, 3.71; H, 5.01.

Preparation of 3b. A solution of $W(CO)_5(PPh_2H)$ (**1a**; 0.61 g, 1.20 mmol) in diethyl ether (20 mL) was treated with *n*-BuLi (1.6 M, 0.80 mL, 1.28 mmol) at 0 °C, and the mixture was stirred for 5 min and slowly warmed to room temperature. To the mixture was added 0.17 mL of EtOC(O)NCS (1.45 mmol), and the solution was stirred for 10 min. Addition of a solution of tetraethylammonium bromide (0.32 g, 1.52 mmol in 10 mL of methanol) to the mixture caused formation of a yellow precipitate, which was filtered and washed with 2 × 10 mL of hexane to give $[Et_4N]W(CO)_4[\eta^2\text{-}PPh_2C(=NCO_2Et)S]$ (**3b**) (0.42 g, 47% yield). Single crystals of **3b** can be obtained by recrystallization from a mixture of 1/1 CH_2Cl_2/hexane. Spectroscopic data for **3b** are as follows. IR (CH_2Cl_2): 2003 (m), 1993 (m), 1877 (vs), 1817 (s) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 16.4 (J_{W-P} = 193.8 Hz). ^1H NMR ($CDCl_3$): δ 1.22 (tt, 12H, CH_3, $^3J_{N-H}$ = 1.8, $^3J_{H-H}$ = 7.3 Hz), 1.29 (t, 3H, CH_3, $^3J_{H-H}$ = 7.3 Hz), 3.18 (q, 8H, CH_2, $^3J_{H-H}$ = 7.3 Hz), 4.16 (q, 2H, CH_2, $^3J_{H-H}$ = 7.3 Hz), 7.35−7.78 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 7.6 (s, NCH_2CH_3), 14.6 (s, OCH_2CH_3), 52.6 (t, NCH_2, J_{N-C} = 2.8 Hz), 62.1 (s, OCH_2), 128.3 (d, $^3J_{P-C}$ = 9.1 Hz), 130.1 (s), 133.5 (d, J_{P-C} = 26.8 Hz), 133.2 (d, $^2J_{P-C}$ = 13.2 Hz), 197.6 (d, CS, J_{P-C} = 32.9 Hz), 204.5 (d, 2C, *cis*-CO, $^2J_{P-C}$ = 7.3 Hz), 212.3 (d, 1C, *cis*-CO, $^2J_{P-C}$ = 7.8 Hz), 214.9 (d, *trans*-CO, $^2J_{P-C}$ = 29.6 Hz). MS: *m*/*z* 872 ($M^+ + 2Et_4N$), 844 ($M^+ + 2Et_4N - CO$), 816 ($M^+ + 2Et_4N - 2CO$). Anal. Calcd for $C_{28}H_{35}O_6N_2PSW$: C, 45.29; N, 3.77; H, 4.75. Found: C, 46.79; N, 4.01; H, 4.51.

Preparation of 6. To a solution of **2a** (0.79 g, 1.02 mmol) in CH_3CN (40 mL) was added ICH_2CONH_2 (0.20 g, 1.10 mmol) at room temperature, the solution was stirred for 10 min, and then the solvent was removed under vacuum. The residue was extracted with 2 × 20 mL of diethyl ether. After filtration, the volume of the solution was reduced to about 8 mL and the solution was stored at −20 °C to yield a crystalline solid, which was filtered and dried under vacuum to give $W(CO)_5PPh_2C(=NPh)SCH_2CONH_2$ (**6**; 0.57 g, 80% yield). Spectroscopic data for **6** are as follows. IR (KBr): 2070 (s), 1934 (vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 38.0 (J_{W-P} = 244.6 Hz). ^1H NMR ($CDCl_3$): δ 2.98 (s, 2H, SCH_2), 5.33 (br, 1H, NH_2), 5.52 (br, 1H, NH_2), 6.97−7.74 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 36.0 (d, SCH_2, $^3J_{P-C}$ = 1.9 Hz), 119.0 (s), 125.4 (s), 128.7 (d, $^3J_{P-C}$ = 9.8 Hz), 129.5 (s), 131.0 (s), 132.9 (d, J_{P-C} = 40.6 Hz), 133.6 (d, $^2J_{P-C}$ = 11.7 Hz), 147.3 (d, $^3J_{P-C}$ = 15.5 Hz), 163.1 (d, CS, J_{P-C} = 45.0 Hz), 168.5 (s, CO), 196.6 (d, cis-CO, $^2J_{P-C}$ = 6.6 Hz), 198.7 (d, trans-CO, $^2J_{P-C}$ = 24.0 Hz). MS: *m*/*z* 702 (M^+), 674 ($M^+ - CO$), 646 ($M^+ - 2CO$), 618 ($M^+ - 3CO$), 590 ($M^+ - 4CO$), 562 ($M^+ - 5CO$), 504 ($M^+ - 5CO - CH_2CONH_2$). Anal. Calcd for $C_{26}H_{19}N_2O_6PSW$: C, 44.46; N, 3.99; H, 2.73. Found: C, 45.21; N, 4.16; H, 3.02. $W(CO)_5PPh_2C(=NPh)SCH_2C{\equiv}CH$ (**4**), $W(CO)_5PPh_2C(=NPh)SCH_2C{\equiv}N$ (**5**), $W(CO)_5PPh_2C(=NPh)SCH_2CH{=}CH_2$ (**7**), and $W(CO)_5PPh_2C(=NPh)SCH_2CO_2Me$ (**8**) were synthesized using the same procedure as that used in the synthesis of **6** by employing **2a** and the corresponding halides $BrCH_2C{\equiv}CH$, $ICH_2C{\equiv}N$, $BrCH_2CH{=}CH_2$, and $BrCH_2CO_2Me$, respectively. The yields are 84%, 88%, 86%, and 75% for **4**, **5**, **7**, and **8**, respectively.

Spectroscopic data for **4** are as follows. IR (CH_2Cl_2): 2073 (m), 1934 (vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 38.03 (J_{W-P} = 246.8 Hz). ^1H NMR ($CDCl_3$): δ 2.04 (t, 1H, CH, $^4J_{H-H}$ = 1.80 Hz), 2.88 (d, 2H, $S-CH_2$, $^4J_{H-H}$ = 1.80 Hz), 7.04−7.74 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 1.64 ($S-CH_2$), 72.82 ($\equiv CH$), 77.82 ($C{\equiv}CH$), 118.92 (s), 125.1 (s), 128.52 (d, $^3J_{P-C}$ = 7.5 Hz), 129.21 (s), 132.8 (s), 133.66 (d, $^2J_{P-C}$ = 11.3 Hz), 132.84 (s), 147.73 (d, J_{P-C} = 18.0 Hz), 162.92 (d, CS, J_{P-C} = 51.2 Hz), 196.70 (dd, cis-CO, $^2J_{P-C}$ = 7.5, J_{W-C} = 127.5 Hz), 199.12 (d, trans-CO, $^2J_{P-C}$ = 24.0 Hz). MS: *m*/*z* 683 (M^+), 655 ($M^+ - CO$). Anal. Calcd for $C_{27}H_{18}NO_5PSW$: C, 47.46; N, 2.05; H, 2.66. Found: C, 48.22; N, 2.31; H, 2.94.

Spectroscopic data for **5** are as follows. IR (CH_2Cl_2): 2073 (m), 1936 (vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 38.72 (J_{W-P} = 247.4 Hz). ^1H NMR ($CDCl_3$): δ 2.97 (s, 2H, CH_2), 7.04−7.74 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.81 (CH_2), 114.6 (CN), 118.86 (s), 125.76 (s), 128.77 (d, $^3J_{P-C}$ = 9.8 Hz), 129.59 (s), 131.19 (s), 133.59 (d, $^2J_{P-C}$ = 8.3 Hz), 134.92 (s), 146.72 (d, J_{P-C} = 15.0 Hz), 160.92 (d, CS, J_{P-C} = 48.5 Hz), 196.43 (d, cis-CO, $^2J_{P-C}$ = 6.8 Hz), 198.50 (d, trans-CO, $^2J_{P-C}$ = 24.8 Hz). MS: *m*/*z* 684 (M^+), 656 ($M^+ - CO$), 544 ($M^+ - 5CO$). Anal. Calcd for $C_{26}H_{17}N_2O_5PSW$: C, 45.63; N, 4.09; H, 2.50. Found: C, 45.92; N, 4.11; H, 2.97.

Spectroscopic data for **7** are as follows. IR (CH_3CN): 2072 (m), 1931 (vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 39.13 (J_{W-P} = 244.4 Hz). ^1H NMR ($CDCl_3$): δ 2.87 (d, 2H, SCH_2, J_{H-H} = 6.8 Hz), 4.76 (dd, 1H, =CH, J_{H-H} = 16.9, 1.2 Hz), 4.83 (d, 1H, =CH, J_{H-H} = 9.5 Hz), 5.22 (m, 1H, =CH), 7.07−7.76 (m, 15H, Ph). MS: *m*/*z* 685 (M^+), 657 ($M^+ - CO$), 601 ($M^+ - 3CO$), 573 ($M^+ - 4CO$), 545 ($M^+ - 5CO$), 504 ($M^+ - 5CO - C_3H_5$). Anal. Calcd for $C_{27}H_{20}O_5NPSW$: C, 47.32; N, 2.04; H, 2.94. Found: C, 48.01; N, 2.25; H, 3.11.

Spectroscopic data for **8** are as follows. IR (CH_3CN): 2073 (m), 1935 (vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 38.17 (J_{W-P} = 248.8 Hz). ^1H NMR ($CDCl_3$): δ 3.07 (s, 2H, SCH_2), 3.48 (s, 3H, CH_3), 6.97−7.75 (m, 15H, Ph). MS: *m*/*z* 717 (M^+), 689 ($M^+ - CO$), 633 ($M^+ - 3CO$), 605 ($M^+ - 4CO$), 532 ($M^+ - 4CO - CH_2CO_2CH_3$). Anal. Calcd for $C_{27}H_{20}O_7NPSW$: C, 45.21; N, 1.95; H, 2.81. Found: C, 45.79; N, 2.15; H, 2.99.

Protonation of 4. To a solution of complex **4** (0.79 g, 1.16 mmol) in 10 mL of hexane was slowly added HBF_4 (0.25 mL of a 54% solution in ether, 1.23 mmol) at 0 °C. The mixture was stirred for 5 min at 0 °C and slowly warmed to room temperature. A precipitate formed, which was filtered and

Table 1. Crystal and Intensity Collection Data for $W(CO)_5[PPh_2CSCH_2C(CH_2)NPh]BF_4$ (10) and $W(CO)_5[PPh_2CSCHC(OBF_3)NPh]$ (12)

mol formula	$C_{27}H_{19}O_5NSPWBF_4$ (**10**)	$C_{27}H_{18}O_6NSCl_2PWBF_3$ (**12**)[a]
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.905(5)	9.3967(10)
b, Å	10.437(4)	10.6208(13)
c, Å	17.044(4)	16.7676(12)
α, deg	85.84(3)	76.979(8)
β, deg	83.32(4)	86.792(7)
γ, deg	83.78(4)	72.73(9)
V, Å^3	1419.2(11)	1556.8(3)
Z	2	2
cryst dimens, mm	0.10 × 0.40 × 0.45	0.30 × 0.30 × 0.40
radiation	Mo Kα, $\lambda = 0.7107$ Å	
2θ range, deg	2−50	
scan type	$\theta/2\theta$	
total no. of rflns	4999	5458
no. of unique rflns, $I > 2\sigma(I)$	4162	4839
R, R_w ($I > 2\sigma(I)$)	0.053, 0.055	0.023, 0.018
R, R_w (all data)	0.068, 0.056	0.029, 0.018

[a] The lattice of single crystals of **12** contains solvated CH_2Cl_2 molecules.

washed with 2 × 20 mL of hexane to give the crude product, which was further purified by recrystallization from CH_2Cl_2/hexane (2/1) to give $W(CO)_5PPh_2[CSCH_2C(CH_2)NPh]BF_4$ (**10**; 0.58 g, 65%). Spectroscopic data for **10** are as follows. IR (CH_2Cl_2): 2077 (m), 1941 (s) cm^{-1}. ^{31}P NMR (C_2D_6CO): δ 41.42 ($J_{W-P} = 254.2$ Hz). ^{1}H NMR (C_2D_6CO): δ 4.68 (m, 1H, =CH_2), 5.11 (m, 2H, CH_2), 5.65 (m, 1H, =CH_2), 6.93−7.53 (m, 15H, Ph). ^{13}C NMR (C_2D_6CO): δ 74.06 (CH_2), 118−135 (m, Ph), 163.45 (d, CS, $J_{P-C} = 25.2$ Hz), 196.02 (br, cis-CO), 196.81 (d, trans-CO, $^2J_{P-C} = 7.5$ Hz). MS: *m*/*z* 684 ($M^+ - BF_4$), 628 ($M^+ - BF_4 - 2CO$). Anal. Calcd for $C_{27}H_{19}BF_4NO_5PSW$: C, 42.05; N, 3.63; H, 2.48. Found: C, 41.77; N, 3.53; H, 3.10.

Protonation of **5** (0.92 g, 1.34 mmol) was similarly carried out in hexane to give $[W(CO)_5PPh_2CSCHC(NH_2)NPh]BF_4$ (**11**; 0.67 g) in 65% yield. Spectroscopic data for **11** are as follows. IR (CH_2Cl_2): 2079 (m), 1941 (vs) cm^{-1}. ^{31}P NMR (C_2D_6CO): δ 18.89 ($J_{W-P} = 256.5$ Hz). ^{1}H NMR (C_2D_6CO): δ 6.02 (br, NH_2), 6.22 (br, 1H, CH), 6.85−7.60 (m, 15H, Ph). ^{13}C NMR (C_2D_6CO): δ 102.67 (d, =C, $^3J_{P-C} = 5.5$ Hz), 127−133 (m, Ph), 158.76 (s, CNH_2), 160.88 (br, CS), 196.91 (br, cis-CO), 198.56 (d, trans-CO, $^2J_{P-C} = 32.0$ Hz). MS: *m*/*z* 685 ($M^+ - BF_4$), 601 ($M^+ - BF_4 - 3CO$), 573 ($M^+ - BF_4 - 4CO$), 545 ($M^+ - BF_4 - 5CO$). Anal. Calcd for $C_{26}H_{18}BF_4N_2O_5PSW$: C, 40.44; H, 2.35. Found: C, 40.71; H, 2.83.

Protonation of 6. An aliquot of HBF_4 (0.22 mL, 1.10 mmol) was added at room temperature to complex **6** (0.70 g, 1.0 mmol) dissolved in 40 mL of diethyl ether. The solution was stirred for 10 min, and then the solvent was removed under vacuum. The residue was washed with 2 × 10 mL of hexane, and the product was purified by recrystallization from CH_2Cl_2/hexane (2/1) to give $W(CO)_5PPh_2CSCHC(OBF_3)NPh$ (**12**; 0.54 g, 72% yield). Spectroscopic data for **12** are as follows. IR (KBr): 2076 (s), 1920 (vs), (CN) 1579 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 23.47 ($J_{W-P} = 261.7$ Hz). ^{1}H NMR ($CDCl_3$): δ 7.26 (1H), 6.4−7.6 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 101.1 (s, CH), 127.1 (s, *m*-C of Ph), 129.47 (s, *p*-C of Ph), 129.5 (d, *m*-C of Ph, $^3J_{P-C} = 10.6$ Hz), 130.9 (s, *p*-C of Ph), 132.0 (s, *o*-C of Ph), 130.4 (d, ipso C of Ph, $J_{P-C} = 44.4$ Hz), 131.7 (d, *o*-C of Ph, $^2J_{P-C} = 12.9$ Hz), 133.7 (s, ipso C of Ph), 159.1 (s, COB), 162.7 (s, PCN), 195.5 (d, cis-CO, $^2J_{P-C} = 6.3$ Hz), 196.7 (d, trans-CO, $^2J_{P-C} = 25.9$ Hz). ^{19}F NMR ($CDCl_3$): −154.70 (s), −154.76 (s). MS: *m*/*z* 773 ($M^+ + HF$), 689 ($M^+ + HF - 3CO$), 661 ($M^+ + HF - 4CO$). Anal. Calcd for $C_{26}H_{16}BNF_3O_6PSW$: C, 41.46; N, 1.86; H, 2.14. Found: C, 40.96; N, 1.88; H, 2.40.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) of the $W(CO)_5[PPh_2CSCH_2C(CH_2)NPh]$ Cation and $W(CO)_5[PPh_2CSCHC(OBF_3)NPh]$ (12)[a]

cation of **10**		**12**	
W−P	2.532(3)	W−P	2.5185(10)
W−C(1)	1.999(11)	W−C(1)	2.047(4)
W−C(2)	1.998(10)	W−C(2)	2.077(5)
W−C(3)	1.995(11)	W−C(3)	1.982(4)
W−C(4)	2.034(12)	W−C(4)	2.040(4)
W−C(5)	2.000(10)	W−C(5)	2.024(4)
P−C(6)	1.860(10)	P−C(6)	1.842(3)
P−C(16)	1.830(9)	P−C(15)	1.825(3)
P−C(22)	1.829(9)	P−C(21)	1.827(4)
S−C(6)	1.700(9)	S−C(6)	1.669(3)
S−C(7)	1.808(11)	S−C(8)	1.691(4)
C(1)−O(1)	1.163(14)	N−C(6)	1.353(4)
C(2)−O(2)	1.165(13)	N−C(7)	1.399(4)
C(3)−O(3)	1.129(13)	N−C(9)	1.456(4)
C(4)−O(4)	1.131(15)	C(1)−O(1)	1.131(5)
C(5)−O(5)	1.155(12)	C(2)−O(2)	1.120(6)
C(6)−N	1.312(11)	C(3)−O(3)	1.154(5)
C(7)−C(8)	1.497(14)	C(4)−O(4)	1.137(5)
C(8)−C(9)	1.307(15)	C(5)−O(5)	1.144(5)
C(8)−N	1.448(12)	C(7)−C(8)	1.353(5)
C(10)−N	1.455(11)	C(7)−O	1.304(4)
		B−O	1.500(5)
		B−F(2)	1.377(5)
		B−F(3)	1.369(5)
		B−F(4)	1.367(5)
P−W−C(1)	89.6(3)	P−W−C(1)	88.02(11)
P−W−C(2)	93.1(3)	P−W−C(2)	90.44(12)
P−W−C(3)	175.8(4)	P−W−C(3)	175.89(13)
P−W−C(4)	94.0(3)	P−W−C(4)	96.00(11)
P−W−C(5)	89.1(3)	P−W−C(5)	92.93(12)
W−P−C(6)	105.3(3)	W−P−C(6)	114.43(11)
W−P−C(16)	120.3(3)	W−P−C(15)	112.31(11)
W−P−C(22)	118.0(3)	W−P−C(21)	115.10(12)
C(6)−P−C(16)	108.5(4)	C(6)−P−C(15)	104.36(15)
C(6)−P−C(22)	100.6(4)	C(6)−P−C(21)	101.64(15)
C(16)−P−C(22)	102.2(4)	C(15)−P−C(21)	107.94(16)
C(6)−S−C(7)	92.4(5)	C(6)−S−C(8)	93.67(17)
P−C(6)−S	115.7(5)	C(6)−N−C(7)	113.6(3)
P−C(6)−N	128.9(7)	C(6)−N−C(9)	125.9(3)
S−C(6)−N	114.7(7)	C(7)−N−C(9)	120.4(3)
S−C(7)−C(8)	105.9(7)	P−C(6)−S	118.40(20)
C(7)−C(8)−C(9)	126.7(10)	P−C(6)−N	131.27(24)
C(7)−C(8)−N	109.8(8)	S−C(6)−N	110.20(23)
C(9)−C(8)−N	123.4(9)	N−C(7)−C(8)	112.1(3)
C(6)−N−C(8)	114.9(7)	N−C(7)−O	115.9(3)
C(6)−N−C(10)	127.0(8)	C(8)−C(7)−O	131.9(3)
C(8)−N−C(10)	118.0(7)	S−C(8)−C(7)	110.4(3)
		O−B−F(2)	110.8(3)
		O−B−F(3)	104.9(3)
		O−B−F(4)	108.6(3)
		F(2)−B−F(3)	111.6(3)
		F(2)−B−F(4)	109.2(4)
		F(3)−B−F(4)	111.6(4)
		C(7)−O−B	122.4(3)

[a] Bond distances and angles of the three phenyl groups for both complexes are listed in the Supporting Information.

X-ray Analysis of 10 and 12. Single crystals of **10** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.10 × 0.40 × 0.45 mm^3 was glued to a glass fiber and mounted on an Enraf-Nonius CAD4 diffactometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections with $10.0° < 2\theta < 25°$. Cell constants and other pertinent data are collected in the Supporting Information. Data were collected using the $\theta/2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The scan angle was determined for each reflection according to the equation $0.8 + 0.35 \tan\theta$.

The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, Lorentz, and polarization effects. An empirical correction for absorption, based on the azimuthal scan, was appplied to the data set. Crystallgraphic computations were carried out on a Microvax III computer using the NRCC structure determination package.[13] Merging of equivalent and duplicate reflections gave a total of 4999 unique measured data, from which 4162 were considered observed ($I > 2.0\sigma(I)$). The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the position of the metal, and then refined via standard least-squares and difference Fourier techniques. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$. The analytical forms of the scattering factor tables for the neutral atoms were used.[14] All other non-hydrogen atoms were refined by using anisotropic thermal parameters. 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. Final refinement using full-matrix least squares converged smoothly to values of $R = 0.053$ and $R_w = 0.055$. Crystal and intensity collection data are given in Table 1, while bond distances and angles are given in Table 2. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

The procedures for **12** were similar. The final residuals of the refinement were $R = 0.023$ and $R_w = 0.018$. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

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Supporting Information Available: Details of the structural determination for complexes **10** and **12**, including tables of crystal data and structure refinement, fractional coordinates, anisotropic thermal parameters, and all bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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