Syntheses and Crystal Structures of Tungsten Complexes with Various Ligands Containing (1,3-Dithioliumyl)diphenylphosphine

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The (dithioalkylcarbonyl)diphenylphosphinotungsten complexes $W(CO)_5[PPh_2(CS_2R)]$ (**2**−**5**) (R = $CH_2C{\equiv}CH$; $CH_2C{\equiv}CD$; $CH_2C{\equiv}N$; $CH(CH_3)C{\equiv}N$) are accessible by the alkylation reactions of the complex $[Et_4N][W(CO)_5PPh_2CS_2]$ (**1**) with unsaturated organic halides. Protonation of **2**−**5** with HBF_4 at room temperature causes intramolecular cyclization to form the cationic complexes $W(CO)_5[PPh_2\overline{CSC(R)C(R')S}][BF_4]$ (**6**−**9**) (R, R′ = H, CH_3; H, CH_2D; H, NH_2; CH_3, NH_2). The complex $W(CO)_5[PPh_2\overline{CSCHC(NHCPh_3)S}][BF_4]$ (**10**) is produced by the reaction of **4** or **8** with Ph_3CBF_4. In complexes **6**−**10**, proton-induced intramolecular cyclization was followed by an unprecedented 1,3-hydrogen shift, forming five-membered cationic 1,3-dithiolium rings. The 1,3-hydrogen shift process did not occur in similar organic compound but in this metal-assisted system. The mechanism was confirmed both by the reactions of **4** with Ph_3CBF_4 and by deuterium-labeling experiments. The protonation reaction of **2** to **6** is not reversible, but deprotonation of **8** by *n*-BuLi or PPh_3 gives **4** quantitatively. Treatment of **8** with *n*-Bu_4NF yielded complex $W(CO)_5PPh_2F$ and **4** in a 1:1 ratio, but in the reaction of **6** and *n*-Bu_4NF only compound $W(CO)_5PPh_2F$ is formed. Complexes **6**, **8**, and **10** are determined by single-crystal X-ray diffraction analyses.

Introduction

Dithioles, mesoionic dithioles, and dithiolium derivatives have widely served as excellent building blocks for construction of many heterocycles.[1] The 1,3-dithiolium[2] is of special interest in the synthetic chemistry of organic materials due to its reactivity, unusual charge distribution, and possible aromatic properties of the five-membered ring. In the literature, there are two unambiguous examples of the metal-carbene dithiole complexes, which are known at least for iron[3] and platinum.[4] However, until now the formation of a metal 1,3-dithiolium complex has been poorly investigated.

We have been interested in the tungsten complexes containing P-coordination of the $Ph_2PCS_2^-$ and $Ph_2PC(S)NPh^-$ ligands, and those compounds bring up some novel chemistry.[5] As an extension of our recent work on the preparation of the various (thiazoliumyl)diphenylphosphine ligands[6] by protonation of the $Ph_2PC(SR)NPh$ ligands, herein we report a simple synthesis of the various (1,3-dithioliumyl)diphenylphosphine ligands by an unprecedented 1,3-hydrogen shift. Three X-ray crystal structure analyses of the (1,3-dithioliumyl)diphenylphosphinotungsten complexes have been carried out to provide accurate structural parameters.

Results and Discussion

Preparation of the Neutral Diphenyl(dithioalkylcarbonyl)phosphinotungsten Complexes. Kunze, Ambrosius, et al.[7] have synthesized the anionic heteroallyl ligands containing phosphorus such as $R_2P(X)C(Y)NR^-$ and $R_2PC(Y)NR^-$ (X = O or S, Y = O

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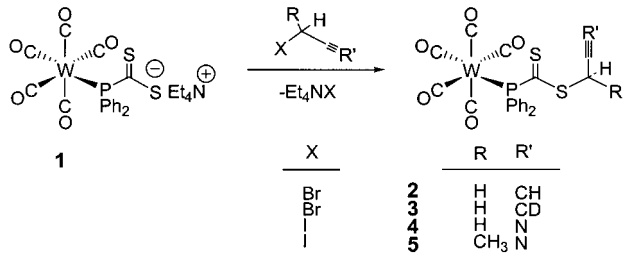
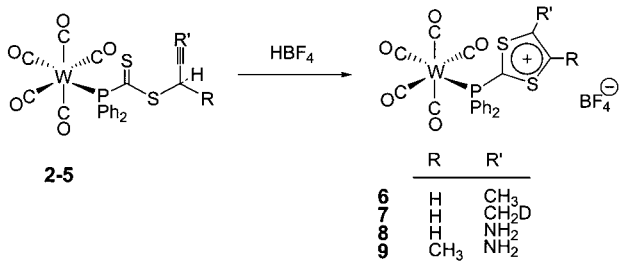
Scheme 1



Scheme 2



or S), and no metal complex includes phosphorus coordination of these ligands. The synthesis of the tungsten complex containing the P-coordination of the $Ph_2PCS_2CH_2C{\equiv}CH$ ligand and the cyclization product has been reported in a previous communication,[5b] and the detailed procedure is given in the Experimental Section together with a full spectroscopic and analytical characterization. Treatment of complex $[Et_4N][W(CO)_5PPh_2CS_2]$ (**1**) with propargyl bromide, $BrCH_2C{\equiv}CH$, in dichloromethane leads to formation of an S−C bond, affording the thiopropargyl complex $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}CH)]$ (**2**) (Scheme 1) in 78% isolated yield. Compound **2** is a red crystalline product and moderately soluble in diethyl ether and *n*-hexane.

The spectroscopic and analytical data of **2** are in agreement with the formulation. The FAB mass spectrum of **2** exhibits a base peak corresponding to the molecular mass. In the IR spectrum of **2**, three terminal carbonyl stretchings appear at 2073(m), 1957(m), and 1919(vs) cm^{-1}, a typical pattern for an $LM(CO)_5$ unit in octahedral geometry. The higher frequencies compared to those of **1** indicate that **2** is a neutral complex. The ^1H NMR spectrum of **2** exhibits a doublet resonance at δ 4.04 and a triplet resonance at δ 2.47 with $^4J_{H-H} = 2.89$ Hz assignable to the S-methylene and terminal methyne proton of the propargyl group, respectively. The corresponding $^{13}C\{^1H\}$ NMR signals appear at δ 26.6 and 72.7, respectively. In the $^{13}C\{^1H\}$ NMR spectrum of **2**, two resonances with an integration ratio of 1:4 at δ 198.7 and 196.8 are attributed to the trans and cis carbonyl groups, respectively. In the $^{31}P\{^1H\}$ NMR spectrum of **2**, a resonance at δ 60.4 with a pair of tungsten satellites ($^1J_{W-P} = 240.0$ Hz) indicates the P-coordination of the $PPh_2C(S)SCH_2C{\equiv}CH$ ligand.

The synthetic method mentioned above is applicable to primary organic halides with various substituents. Thus, the reaction of **1** with $BrCH_2C{\equiv}CD$ (98% deuterium labeling at the terminal alkyne) in CH_2Cl_2 affords $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}CD)]$ (**3**) in 73% yield. The $^{31}P\{^1H\}$ NMR resonance of **3** (δ 59.6 with $^1J_{W-P} = 237.0$ Hz) is similar to that of **2**. The same procedure was used to prepare $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}N)]$ (**4**) and $W(CO)_5[PPh_2CS_2CH(CH_3)C{\equiv}N]$ (**5**), both with high yields. The similar alkylated complex $W(CO)_5[PPh_2(CS_2Me)]$[5e] was structurally confirmed by X-ray diffraction analysis in a previous report.

Syntheses of Various 1,3-Dithiolium Tungsten Complexes. The methodology of the facile synthesis of various thiazolium[6] tungsten complexes can be applied to prepare dithiolium complex. Thus, protonation of **2** by HBF_4 in diethyl ether at 0 °C results in the formation of the 1,3-dithiolium complex $W(CO)_5[PPh_2\overline{CSCHC(CH_3)S}][BF_4]$ (**6**) in 87% yield exclusively (Scheme 2). Compound **6** is an air-stable, brown solid and is readily soluble in polar organic solvents such as dichloromethane and acetonitrile but is insoluble in diethyl ether and *n*-hexane.

The identification of **6** as $W(CO)_5[PPh_2\overline{CSCHC(CH_3)S}][BF_4]$ is according to the spectroscopic data. The FAB mass spectrum of **6** shows a base peak at *m*/*z* 625, which corresponds to a fragment formed by loss of the BF_4^- group from **6**. In the ^1H NMR spectrum, the vinyl proton and methyl protons are observed at δ 8.98 and 2.85, respectively, with coupling constants $^4J_{H-H}$ of 1.0 Hz, and the corresponding resonances in the $^{13}C\{^1H\}$ NMR spectrum appear at δ 145.8 and 16.9, respectively. Notably, the relative downfield $^{13}C\{^1H\}$ resonance of the vinylic carbon reveals the cationic property. The $^{31}P\{^1H\}$ NMR resonance of **6** appears at δ 30.4 with a pair of tungsten satellites ($^1J_{W-P} = 261.8$ Hz), which shifted from δ 60.4 of **2**. This significant upfield shift of the $^{31}P\{^1H\}$ NMR of **6** would suggest a shielding of the phosphorus nucleus caused by the contribution from the resonance structure of the 1,3-dithiolium.

The same procedure was used to prepare other 1,3-dithiolium complexes $W(CO)_5[PPh_2\overline{CSCHC(NH_2)S}][BF_4]$ (**8**) and $W(CO)_5[PPh_2\overline{CSC(CH_3)C(NH_2)S}][BF_4]$ (**9**) with 95% and 90% yields, respectively. In the FAB mass spectra, two base peaks with the typical W isotope distribution are respectively in agreement with the $[M^+ - BF_4^-]$ molecular masses of **8** and **9**. The $^{31}P\{^1H\}$ NMR spectra of **8** (δ 21.8 with $^1J_{W-P} = 259.6$ Hz) and **9** (δ 20.2 with $^1J_{W-P} = 259.7$ Hz) are similar to that of **6**.

To distinguish the mechanism of formation of the dithiolium complex, an intramolecular rearrangement[8] of the S-propargyl group to the S-alleneyl group, or 1,3-hydrogen shift, the following experiments were carried out. The reaction of **2** and CH_3COOD was monitored

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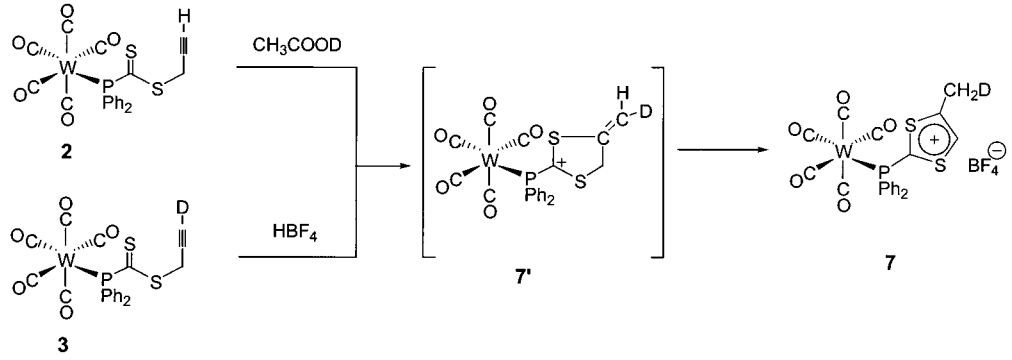
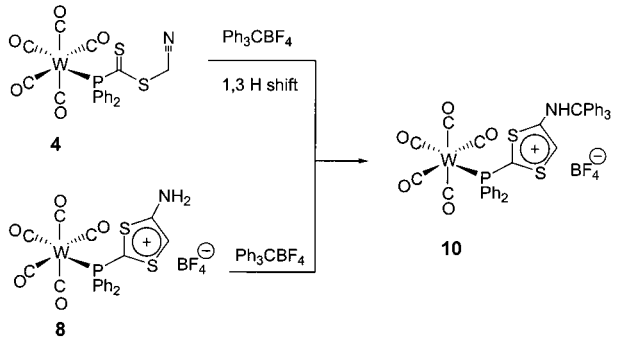
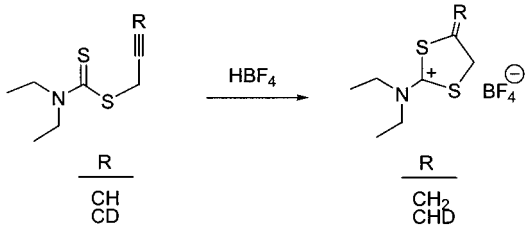
Scheme 3



Scheme 4



Scheme 5



by ^{1}H NMR at −20 °C, giving W(CO)$_5$[PPh$_2$CSCHC(CH$_2$D)S][BF$_4$] (**7**) (Scheme 3) with 87% deuterium labeling at the methyl site. Complex **7** can also be obtained by the reaction of the deuterium-labeled complex W(CO)$_5$[PPh$_2$(CS$_2$CH$_2$C≡CD)] (**3**) and HBF$_4$. During the reactive period, the ^{1}H NMR spectrum reveals two doublet resonances at δ 3.89 and 2.76 with $^2J_{H-H}$ = 12.8 Hz and one singlet at δ 4.92, which confirms the proposed structure of **7′**. The ^{1}H NMR spectrum also shows one triplet resonance at δ 2.85 and one multiplet at δ 8.98 assignable to CH$_2$D protons and the vinyl proton. The increased ratio of **7** corresponds with the decreased ratio of **7′** by the reaction time. No deuterium labeling at the vinylic site of the dithiolium ring of **7** was found.

In the reaction of **4** and triphenyl carbenium tetrafluoroborate, Ph$_3$CBF$_4$, in acetonitrile at room temperature, no abstracted hydride product of **4** could be detected; instead, a 1,3-dithiolium complex, W(CO)$_5$[PPh$_2$CSCHC(NHCPh$_3$)S][BF$_4$] (**10**) (Scheme 4), was isolated with 96% yield. Compound **10** can also be prepared by the reaction of **8** with Ph$_3$CBF$_4$. The ^{1}H NMR spectrum of **10** exhibits a singlet resonance at δ 8.51 assignable to the vinyl proton, and the corresponding ^{13}C{^{1}H} NMR signal appears at δ 168.8. The ^{31}P{^{1}H} NMR resonance of **10** (δ 21.5 with $^1J_{W-P}$ = 259.0 Hz) is similar to that of **8**. Clearly, the result is rather unexpected, as is the formation of **10** through a 1,3-hydrogen shift process.

In an attempt to prepare six- or seven-membered 1,3-dithiolium complexes, we treated W(CO)$_5$[PPh$_2$CS$_2$(CH$_2$)$_n$CN][5e] (n = 2 or 3) with HBF$_4$, yielding no reaction under reaction conditions similar to **8**. However, in the reaction of organic compound Et$_2$NCS$_2$CH$_2$C≡CH and HBF$_4$, instead of cationic 1,3-dithiolium compound [Et$_2$NCSCHC(CH$_3$)S][BF$_4$], the cationic 1,3-dithiolylidene [Et$_2$NCSCH$_2$C(C=CH$_2$)S][BF$_4$] was isolated (Scheme 5). The ^{1}H NMR spectrum shows three multiples at δ 4.61, 5.62, and 5.84 with a 2:1:1 ratio, which are assigned to the SCH$_2$ protons and to two methylene protons.

From the discussion of the spectroscopic data of **6**−**10**, it is clear that there is a cationic 1,3-dithiolium ring. While the dithiolium organic compounds have been extensively studied, very little has been reported about the dithiolium metal complex. Because of the unknown nature of the 1,3-dithiolium complex, we performed X-ray diffraction analyses of three kinds of 1,3-dithiolium complex, i.e., **6**, **8**, and **10**. The ORTEP[9] diagrams with atomic labeling are shown in Figures 1, 2, and 3 for **6**, **8**, and **10**, respectively. Table 2 contains selected bond distances and angles. The coordination geometry around the tungsten metal center in **6**, **8**, and **10** is pseudooctahedral with the (1,3-dithiolium)diphenylphosphine ligand bound to tungsten through the phosphorus atom. The most remarkable features of the three structures are the five-membered cationic 1,3-dithiolium rings. In **6**, **8**, and **10**, the three kinds of 1,3-dithiolium rings are all planar. The deviations from the average plane for five atoms are less than 0.025(11) Å in **6**, 0.021(12) Å in **8**, and 0.022(14) Å in **10**. Notably, the sulfur−carbon bond lengths in the dithiolium ring of **6** (1.650(10)−1.711(11) Å), **8** (1.648(9)−1.713(10) Å), and **10** (1.635(12)−1.699(11) Å) have a range of regular partial double bond character. These parameters are indicative of delocalized bonding in the five-membered ring. Significantly, the C(7)−C(8) bond distances of **6** (1.331(17) Å), **8** (1.371(13) Å), and **10** (1.406(16) Å) have significant differences, but are all in the range of a regular aromatic C−C bond. The C(6)−P and W−P bond distances of 1.852(10) and 2.518(3) Å in **6** are similar to 1.820(9) and 2.498(2) Å in **8** and 1.840(12) and 2.496(3) Å in **10**.

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Table 1. Crystal Data and Refinement Details for Complexes $W(CO)_5[PPh_2CSCHC(CH_3)S][BF_4]$ (6), $W(CO)_5[PPh_2CSCHC(NH_2)S][BF_4]$ (8), and $W(CO)_5[PPh_2CSCHC(NHCPh_3)S][BF_4]$ (10)[a]

	6	8	10
mol formula	$C_{21}H_{14}BF_4O_5PS_2W$	$C_{20}H_{13}BF_4NO_5PS_2W$	$C_{40.5}H_{30.5}BF_4NO_5PS_2W$
fw	712.08	713.07	973.4
cryst syst	triclinic	monoclinic	triclinic
cryst dimens, mm	0.35 × 0.30 × 0.20	0.50 × 0.50 × 0.40	0.35 × 0.35 × 0.30
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	8.745(6)	16.1947(20)	13.270(6)
b, Å	9.662(9)	8.0236(20)	15.250(6)
c, Å	15.421(11)	19.580(4)	19.993(7)
α, deg	87.31(8)		98.42(3)
β, deg	74.07(5)	90.550(12)	94.50(3)
γ, deg	85.36(7)		93.78(4)
V, Å^3	1248.6(16)	2544.1(9)	3978(3)
Z	2	4	4
d_{calcd}, g cm^{-3}	1.894	1.862	1.625
μ(Mo Kα), cm^{-1}	50.067	49.153	31.539
2θ range, deg	0−45	0−45	0−45
T, °C	25	25	25
total no. of rflns	3274	3331	10 406
no. of unique data with $I \geq 2\sigma(I)$	2644	2646	7201
no. of variables	317	353	974
R^b	0.034	0.025	0.043
$R_w{}^c$	0.036	0.028	0.046
S^d	1.44	1.50	1.87

[a] **10** contains two independent molecules in the unit cell and no essential structural difference between them. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observed} - N_{parameters})]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6, 8, and 10

bond lengths		bond angles	
	Compound **6**		
W−P(1)	2.519(3)	S(1)−C(6)−S(2)	114.7(5)
C(6)−P(1)	1.852(9)	C(6)−S(2)−C(8)	97.4(5)
C(6)−S(1)	1.678(9)	S(2)−C(8)−C(7)	114.3(8)
C(7)−S(1)	1.686(11)	C(8)−C(7)−S(1)	116.9(8)
C(6)−S(2)	1.650(10)	C(7)−S(1)−C(6)	96.6(5)
C(8)−S(2)	1.713(10)	C(9)−C(8)−C(7)	125.6(10)
C(7)−C(8)	1.332(16)	C(9)−C(8)−S(2)	120.0(9)
C(8)−C(9)	1.508(17)		
	Compound **8**		
W−P(1)	2.4951(16)	S(1)−C(6)−S(2)	114.3(3)
C(6)−P(1)	1.825(6)	C(6)−S(2)−C(8)	98.7(3)
C(6)−S(1)	1.684(5)	S(2)−C(8)−C(7)	116.5(5)
C(7)−S(1)	1.721(6)	C(8)−C(7)−S(1)	113.4(4)
C(6)−S(2)	1.648(6)	C(7)−S(1)−C(6)	97.0(3)
C(8)−S(2)	1.656(6)	N(1)−C(7)−C(8)	113.4(4)
C(7)−C(8)	1.373(9)	N(1)−C(7)−S(1)	120.3(5)
C(7)−N(1)	1.343(8)		
	Compound **10**		
W(1)−P(1)	2.497(3)	S(1)−C(6)−S(2)	114.6(6)
C(6)−P(1)	1.843(10)	C(6)−S(2)−C(8)	97.3(5)
C(6)−S(1)	1.635(10)	S(2)−C(8)−C(7)	113.8(7)
C(7)−S(1)	1.674(10)	C(8)−C(7)−S(1)	115.2(7)
C(6)−S(2)	1.690(9)	C(7)−S(1)−C(6)	99.1(5)
C(8)−S(2)	1.707(10)	N(9)−C(8)−C(7)	122.9(9)
C(7)−C(8)	1.395(14)	N(9)−C(8)−S(2)	123.2(7)
C(8)−N(9)	1.345(12)		

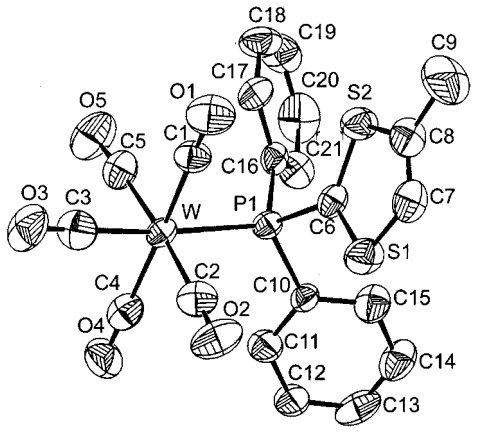


Figure 1. ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the cationic complex $W(CO)_5[PPh_2CSCHC(CH_3)S]^+$ (**6**).

A lot of 1,3-dithiolium organic compounds[2] are known, but their preparations do not involve protonation of a precursor or an unprecedented 1,3-hydrogen shift. In the reaction of **2** with acid, protonation takes place at the terminal carbon of the propargyl moiety of **2** to afford a cationic complex, followed by nucleophilic attack of the sulfur atom of the thiocarbonyl group at the center carbon of the propargyl unit to form the cationic 1,3-dithiolium ring. Similarly, formation of the products **8** and **9** is believed to proceed via protonation at the nitrogen atom of the nitrile group, followed by nucleophilic attack of the sulfur atom of the thiocarbonyl group at the carbon of the nitrile moiety. It is obvious that the dithiolium compounds are induced by a proton and followed by a 1,3-hydrogen shift process. To the best of our knowledge, there is no previous report of formation a 1,3-dithiolium metal complex through the phenomenon of unprecedented 1,3-hydrogen shift.

Remarkably, the protonation reaction of **2**,**3** with HBF_4 in THF at room temperature gave **6**,**7** immediately, and the protonations of **2**,**3** to **6**,**7** are not reversible, but deprotonation of **8** by *n*-BuLi or PPh_3 in THF at room temperature produced **4** quantitatively. To examine the reactivity of the cationic 1,3-dithiolium complex, we carried out the reactions of complex **6** and **8** with several nucleophiles. Treatment of **8** with anhydrous *n*-Bu_4NF in THF at room temperature yielded complex $W(CO)_5PPh_2F$[6] and **4** in a 1:1 ratio (Scheme 6). Interestingly, under similar reactive conditions, treatment of the analogous species **6** with *n*-Bu_4NF gave only $W(CO)_5PPh_2F$ quantitatively. Clearly, the *n*-Bu_4-

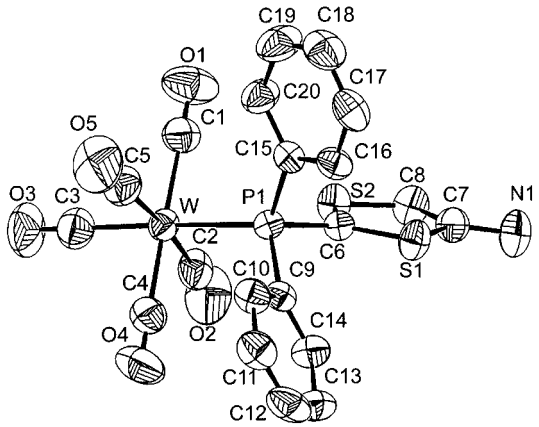


Figure 2. ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the cationic complex $W(CO)_5[PPh_2\overline{CSCHC(NH_2)S}]^+$ (**8**).

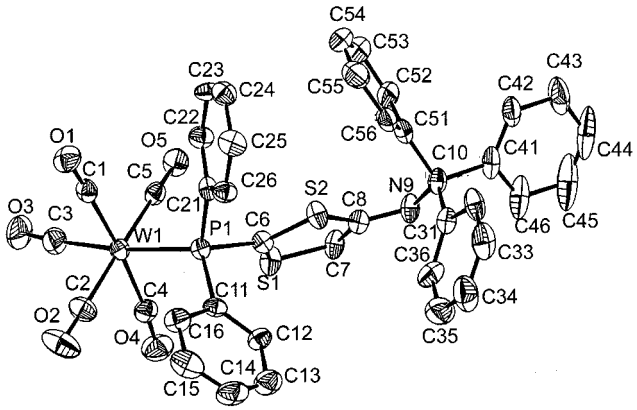


Figure 3. ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the cationic complex $W(CO)_5[PPh_2\overline{CSCHC(NHCPh_3)S}]^+$ (**10**).

NF acts as not only a nucleophile but also a deproton reagent. Attempted reactions of complex **6** or **8** with cyclopentadiene, PhC≡CH, and I_2 in refluxing THF gave no reaction but with other nucleophiles such as Et_2NCS_2Na, Et_2NH, KSCN, and $NaBH_4$ in THF at room temperature gave more than 10 complexes, although these reactions were not pursued further.

In conclusion, through a series of investigation of the cyclization reactions of mesoionic compounds, we have shown that the reactions of this type can be useful for the preparation of five-membered cationic 1,3-dithiolium tungsten complexes.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-200 or on an 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; C_2D_6CO, δ 2.04). IR spectra were measured on a Perkin-Elmer 983 instrument and referenced to polystyrene standard, using cells equipped with calcium fluoride windows. MS 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 used as received. The compounds $[Et_4N][W(CO)_5(PPh_2CS_2)]$ (**1**)[5a] and $W(CO)_5(PPh_2CS_2CH_2CN)$ (**4**)[5e] were prepared according to the literature methods. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University. $W(CO)_6$ and PPh_2H were purchased from Strem Chemical; CS_2, $ICH(CH_3)CN$, ICH_2CN, $BrCH_2C{\equiv}CH$, HBF_4, *n*-BuLi, PPh_3, CH_3COOD, and anhydrous *n*-Bu_4NF were purchased from Merck.

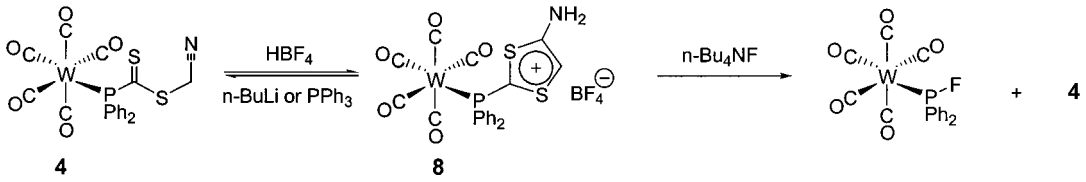
Preparation of 2. Propargyl bromide, $BrCH_2C{\equiv}CH$ (0.08 mL, 1.1 mmol), was added to a solution of **1** (0.715 g, 1.0 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred at room temperature for 2 min. The solvent was removed under vacuum, the residue was extracted with diethyl ether (2 × 10 mL), and the extracts were filtered through Celite. The filtrate was removed under vacuum to give the red product. The crude product was recrystallized from CH_2Cl_2/*n*-hexane (1:10) at −20 °C to give microcrystalline complex $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}CH)]$, **2** (0.49 g, 78%). Spectroscopic data of **2** are as follows. IR (KBr, cm^{-1}): ν(CO) 2073(m), 1957(m), 1919(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 60.4 (J_{W-P} = 240.0 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.47 (t, 1H, CH, $^4J_{H-H}$ = 2.89 Hz), 4.04 (d, 2H, SCH_2, $^4J_{H-H}$ = 2.89 Hz), 7.48 (m, 6H, Ph), 7.69 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 26.6 (s, SCH_2), 72.7 (s, CH), 75.8 (s, CH_2C), 128.6 (d, meta-C of Ph, $^3J_{P-C}$ = 15.4 Hz), 131.2 (s, para-C of Ph), 133.7 (d, ortho-C of Ph, $^2J_{P-C}$ = 11.8 Hz), 134.7 (d, ipso-C of Ph, J_{P-C} = 30.7 Hz), 196.8 (d, cis-CO, $^2J_{P-C}$ = 6.0 Hz), 198.7 (d, trans-CO, $^2J_{P-C}$ = 25.0 Hz). MS (FAB, NBA, *m*/*z*): 625 (M^+), 597 (M^+ − CO), 569 (M^+ − 2CO), 541 (M^+ − 3CO), 513 (M^+ − 4CO), 485 (M^+ − 5CO). Anal. Calcd for $C_{21}H_{13}O_5PS_2W$: C, 40.40; H, 2.10. Found: C, 40.51; H, 2.27.

Preparation of 3. The synthesis and workup were similar to those used in the preparation of complex **2**. The complex $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}CD)]$ (**3**) was isolated in 73% yield as a red microcrystalline solid. Spectroscopic data of **3** are as follows. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2072(m), 1940(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 59.6 (J_{W-P} = 237.0 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 3.96 (s, 2H, SCH_2), 7.45 (m, 6H, Ph), 7.69 (m, 6H, Ph).

Preparation of 5. The synthesis and workup were similar to those used in the preparation of complex **2**. The complex $W(CO)_5[PPh_2CS_2CH(CH_3)CN]$ (**5**) was isolated in 88% yield as a red microcrystalline solid. Spectroscopic data of **5** are as follows. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2074(m), 1936(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 62.1 (J_{W-P} = 254.3 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.70 (dd, 3H, CH_3, $^3J_{H-H}$ = 7.30 Hz, $^5J_{P-H}$ = 1.10 Hz), 4.85 (dd, 1H, SCH, $^3J_{H-H}$ = 7.30 Hz, $^4J_{P-H}$ = 1.20 Hz), 7.48 (m, 6H, Ph), 7.69 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 16.0 (s, CH_3), 33.8 (s, SCH), 117.5 (s, CN), 128.9 (d, meta-C of Ph, $^3J_{P-C}$ = 10.9 Hz), 131.7 (s, para-C of Ph), 132.9 (d, ipso-C of Ph, J_{P-C} = 38.9 Hz), 133.7 (d, ortho-C of Ph, $^2J_{P-C}$ = 11.9 Hz), 196.7 (d, cis-CO, $^2J_{P-C}$ = 6.7 Hz), 198.7 (d, trans-CO, $^2J_{P-C}$ = 25.0 Hz), 235.3 (s, CS_2). MS (FAB, NBA, *m*/*z*): 640 (M^+), 611 (M^+ − CO), 583 (M^+ − 2CO), 555 (M^+ − 3CO), 527 (M^+ − 4CO), 499 (M^+ − 5CO), 443 (M^+ − 5CO − $CHCH_3CN$), 369 (M^+ − 5CO − $CHCH_3CN$ − CS_2). Anal. Calcd for $C_{21}H_{14}NO_5PS_2W$: C, 39.54; H, 2.21; N, 2.19. Found: C, 39.62; H, 2.42; N, 2.25.

Protonation of 2. To a flask containing a diethyl ether solution of $W(CO)_5[PPh_2(CS_2CH_2C{\equiv}CH)]$ (**2**) (0.625 g, 1.0 mmol) was added an aliquot of HBF_4 (0.25 mL of a 54% solution in diethyl ether, 1.23 mmol) at 0 °C. The solution was stirred for 5 min at 0 °C and slowly warmed to room temperature. A brown precipitate formed, which was filtered off (G4) and washed with diethyl ether (2 × 10 mL) to give the crude product. The crude product was further purified by

Scheme 6



recrystallization from CH_2Cl_2/*n*-hexane (1:10) to give complex $W(CO)_5[PPh_2CSCHC(CH_3)S][BF_4]$ (**6**) (0.62 g, 0.87 mmol) as a brown powder in 87% yield. Spectroscopic data of **6** are as follows. IR (KBr, cm^{-1}): ν(CO) 2076(m), 2007(m), 1951(s), 1923(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 30.4 (J_{W-P} = 261.8 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.85 (d, 3H, CH_3, $^4J_{H-H}$ = 1.0 Hz), 7.50 (m, 6H, Ph), 7.66 (m, 4H, Ph), 8.98 (m, 1H, =CH). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 16.9 (s, CH_3), 129.6 (d, meta-C of Ph, $^3J_{P-C}$ = 9.7 Hz), 132.3 (s, para-C of Ph), 134.6 (d, ortho-C of Ph, $^2J_{P-C}$ = 12.2 Hz), 134.9 (d, ipso-C of Ph, J_{P-C} = 36.6 Hz), 145.8 (s, =CH), 166.9 (s, CCH_3), 196.4 (d, cis-CO, $^2J_{P-C}$ = 7.5 Hz), 199.0 (d, trans-CO, $^2J_{P-C}$ = 25.0 Hz). MS (FAB, NBA, *m*/*z*): 625 ($M^+ - BF_4$), 597 ($M^+ - BF_4 - CO$), 569 ($M^+ - BF_4 - 2CO$), 541 ($M^+ - BF_4 - 3CO$), 513 ($M^+ - BF_4 - 4CO$), 485 ($M^+ - BF_4 - 5CO$), 369 ($M^+ - BF_4 - 5CO - CS_2C_3H_4$). Anal. Calcd for $C_{21}H_{14}BF_4O_5PS_2W$: C, 35.42; H, 1.99. Found: C, 35.59; H, 2.12.

Preparation of 7. The synthesis and workup were similar to those used in the preparation of complex **6**. The complex $W(CO)_5[PPh_2CSCHC(CH_2D)S][BF_4]$ (**7**) was isolated in 87% yield as a red-brown microcrystalline solid. Spectroscopic data of **7** are as follows. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2077(m), 1945(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 30.4 (J_{W-P} = 261.8 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 3.06 (t, 2H, CH_2D, $^2J_{H-H}$ = 1.00 Hz), 7.50 (m, 6H, Ph), 7.66 (m, 4H, Ph), 8.98 (m, 1H, =CH).

Complexes $W(CO)_5[PPh_2CSCHC(NH_2)S][BF_4]$ (**8**) and $W(CO)_5[PPh_2CSC(CH_3)C(NH_2)S][BF_4]$ (**9**) were synthesized using the same procedure as that used in the synthesis of **6** by employing **4**, **5**, and HBF_4, respectively. The yields are 95% and 90% for **8** and **9**, respectively.

Spectroscopic data of **8** are as follows. IR (KBr, cm^{-1}): ν(CO) 2075(m), 1991(m), 1948(s), 1922(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 21.8 (J_{W-P} = 259.6 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 7.50 (m, 6H, Ph), 7.66 (m, 4H, Ph), 8.12 (br, 2H, NH_2), 8.20 (d, 1H, CH, $^4J_{H-H}$ = 1.90 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 129.6 (d, meta-C of Ph, $^3J_{P-C}$ = 10.5 Hz), 133.2 (d, ortho-C of Ph, $^2J_{P-C}$ = 13.4 Hz), 133.5 (s, para-C of Ph), 133.7 (d, ipso-C of Ph, J_{P-C} = 43.8 Hz), 172.3 (s, =CH), 175.6 (s, CNH_2), 196.5 (d, cis-CO, $^2J_{P-C}$ = 6.6 Hz), 198.3 (d, trans-CO, $^2J_{P-C}$ = 25.5 Hz). MS (FAB, NBA, *m*/*z*): 626 ($M^+ - BF_4$), 598 ($M^+ - BF_4 - CO$), 570 ($M^+ - BF_4 - 2CO$), 542 ($M^+ - BF_4 - 3CO$), 514 ($M^+ - BF_4 - 4CO$), 486 ($M^+ - BF_4 - 5CO$), 369 ($M^+ - BF_4 - 5CO - CS_2C_2HNH_2$). Anal. Calcd for $C_{20}H_{13}BF_4NO_5PS_2W$: C, 33.68; H, 1.84; N, 1.96. Found: C, 33.31; H, 1.97; N, 1.85.

Spectroscopic data of **9** are as follows. IR (KBr, cm^{-1}): ν(CO) 2076(m), 1964(s), 1915(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 20.2 (J_{W-P} = 259.7 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.67 (s, 3H, CH_3), 7.50 (m, 6H, Ph), 7.66 (m, 4H, Ph), 7.80 (br, 2H, NH_2). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 12.0 (s, CH_3), 129.8 (d, meta-C of Ph, $^3J_{P-C}$ = 10.5 Hz), 132.3 (d, ortho-C of Ph, $^2J_{P-C}$ = 13.3 Hz), 132.7 (s, para-C of Ph), 133.3 (d, ipso-C of Ph, J_{P-C} = 19.0 Hz), 162.2 (s, CH_3C), 171.4 (s, CNH_2), 195.6 (d, cis-CO, $^2J_{P-C}$ = 7.0 Hz), 197.2 (d, trans-CO, $^2J_{P-C}$ = 25.5 Hz). MS (FAB, NBA, *m*/*z*): 640 ($M^+ - BF_4$), 512 ($M^+ - BF_4 - CO$), 584 ($M^+ - BF_4 - 2CO$), 556 ($M^+ - BF_4 - 3CO$), 528 ($M^+ - BF_4 - 4CO$), 500 ($M^+ - BF_4 - 5CO$), 369 ($M^+ - BF_4 - 5CO - CS_2C_2CH_3NH_2$). Anal. Calcd for $C_{21}H_{15}BF_4NO_5PS_2W$: C, 34.68; H, 2.08; N, 1.93. Found: C, 34.82; H, 2.22; N, 1.98.

Preparation of 10. Method A: MeCN (30 mL) was added to a flask (100 mL) containing $W(CO)_5[PPh_2CSCHC(NH_2)S][BF_4]$ (**8**) (0.71 g, 1.0 mmol) and Ph_3CBF_4 (0.33 g, 1.0 mmol). The solution was stirred for 5 min, and an IR spectrum indicated completion of the reaction. After removal of the solvent in vacuo, the residue was redissolved with CH_2Cl_2 (10 mL). *n*-Hexane (15 mL) was added to the solution, and a yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and then dried in vacuo, yielding 0.86 g (90%) of **10**.

Method B: Ph_3CBF_4 (0.33 g, 1.0 mmol) was dissolved in MeCN (10 mL), and the solution was added to a solution of $W(CO)_5(PPh_2CS_2CH_2CN)$ (0.624 g, 1.0 mmol) in MeCN (10 mL). A color change from red to yellow occurred immediately, and an IR spectrum indicated completion of the reaction. Subsequently the solvent was removed under vacuum. The residue was redissolved in 5 mL of CH_2Cl_2. *n*-Hexane (15 mL) was added to the solution, and a yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and then dried in vacuo, yielding 0.92 g (96%) of $W(CO)_5[PPh_2CSCHC(NHCPh_3)S][BF_4]$ (**10**). Spectroscopic data of **10** are as follows. IR (KBr, cm^{-1}): ν(CO) 2076(m), 1944(vs). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 21.5 (J_{W-P} = 259.0 Hz). ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 7.10−7.60 (m, 25H, Ph), 8.51 (d, 1H, CH, $^4J_{H-H}$ = 2.00 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 56.7 (s, $NCPh_3$), 119−146.5 (m, C of Ph), 168.8 (s, =CH), 172.0 (s, *C*$NHCPh_3$), 195.2 (d, cis-CO, $^2J_{P-C}$ = 6.5 Hz), 197.5 (d, trans-CO, $^2J_{P-C}$ = 25.0 Hz). MS (FAB, NBA, *m*/*z*): 868 ($M^+ - BF_4$), 626 ($M^+ - BF_4 - CPh_3$). Anal. Calcd for $C_{39}H_{27}BF_4NO_5PS_2W$: C, 49.02; H, 2.85; N, 1.47. Found: C, 49.62; H, 2.92; N, 1.35.

Single-Crystal X-ray Diffraction Analyses of 6, 8, and 10. Single crystals of **6**, **8**, and **10** suitable from X-ray diffraction analyses were grown by recrystallization from 20:1 *n*-hexane/CH_2Cl_2. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 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.[10]

A suitable single crystal of **6** 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 19.38° to 24.16°. 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 deg min^{-1}. The θ scan angle was determined for each reflection according to the equation 0.80 ± 0.35 tan θ. Three check reflections were measured every 30 min

(10) Gabe, E. J.; Lee, F. L.; Lepage, Y. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; p 167.

throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 3284 unique measured data in which 2644 reflections with $I > 2\sigma(I)$ were considered observed. The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the positions of 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.[11] 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} value of the atom to which they were bonded. The final residuals of this refinement were $R = 0.034$ and $R_w = 0.036$. Selected bond distances and angles are listed in Table 2.

The procedures for **8** and **10** were similar to those for **6**. The final residuals of this refinement were $R = 0.025$ and $R_w = 0.028$ for **8** and $R = 0.043$ and $R_w = 0.046$ for **10**. Selected bond distances and angles are listed in Table 2. Tables of thermal parameters are given in the Supporting Information.

Acknowledgment. We would like to thank the National Science Council of Taiwan, Republic of China, and Hung Kuang Institute of Technology of Humanities and Science Council for support.

Supporting Information Available: For **6**, **8**, and **10** tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM001032Y

(11) *International Tables for X-ray Crystallography*; Reidel: Dordrecht, The Netherlands, 1974; Vol. IV.