

Reactions of the Dithiocarbene Complex $W(CO)_5[C(SCH_3)_2]$ with Phosphines. Crystal Structure of a Phosphorane Product $W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$

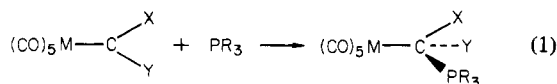
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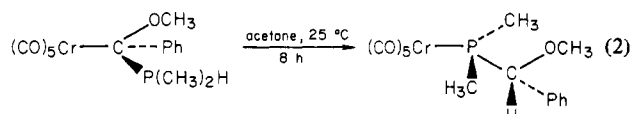
Abstract: The dithiocarbene complex, $W(CO)_5[C(SCH_3)_2]$, is prepared in good yield by reaction of $W(CO)_5CS$ with $NaSCH_3$ followed by methylation of the resulting dithioester anion, $W(CO)_5C(=S)SCH_3^-$, with CH_3I . Novel phosphorane complexes, $W(CO)_5[(CH_3S)_2C=PR_3]$, are formed when $W(CO)_5[C(SCH_3)_2]$ reacts with tertiary phosphines, PPh_3 , PPh_2CH_3 , $PPh(CH_3)_2$, PPh_3 , $P(C_2H_5)_3$, and $P(OCH_3)_3$. An X-ray diffraction study of $W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$ shows that the phosphorane ligand is bound to the tungsten via one sulfur atom. Thus, the net effect of the reaction of $W(CO)_5[C(SCH_3)_2]$ with tertiary phosphines is to transfer the carbene group, $C(SCH_3)_2$, from the tungsten to the phosphorus atom. In contrast, the secondary phosphine PPh_2H reacts with $W(CO)_5[C(SCH_3)_2]$ to give a phosphine complex $W(CO)_5[PPh_2[CH(SCH_3)_2]]$, containing a W-P bond. These tertiary and secondary phosphine reactions presumably proceed by initial phosphine attack at the carbene carbon atom followed by rearrangement to the phosphorane or phosphine product.

Introduction

Although the first group 6 transition-metal carbene was reported by Fischer and Maasböl in 1964,² it is only recently that dithiocarbene complexes $M(CO)_5[C(SPh)_2]$ ^{3,4} and $M(CO)_5[C(SC_2H_5)_2]$,⁵ where $M = Cr$ or W , were prepared. Their yields, however, were low, ranging from 2⁴ to 15%.³ While little is known about the reactivity of dithiocarbene complexes, group 6 transition-metal carbenes of other types are known to react with nucleophiles to form a variety of products.⁶⁻¹⁵ Of special relevance to this report are the reactions of secondary and tertiary phosphines⁹⁻¹⁴ with group 6 metal carbenes according to eq 1. With secondary phosphines a rearrangement product is also formed¹¹ (eq 2).



$M = Cr$ or W , $R =$ alkyl or H , $X = OCH_3$, SCH_3 , or Ph , and $Y = CH_3$ or aryl



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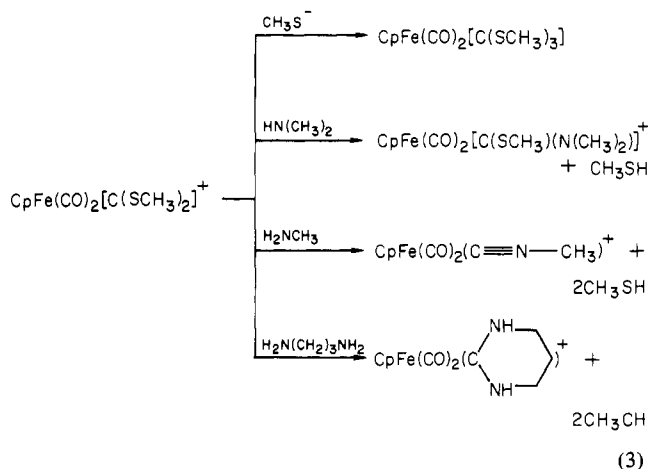
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The only reported systematic study of the reactivity of dithiocarbene complexes was that carried out on the cyclopentadienyl(dithiocarbene)iron cationic complexes $CpFe(CO)_2-[C(SR)_2]^+$.¹⁶⁻¹⁹ McCormick and Angelici¹⁶⁻¹⁹ found that the dithiocarbene ligand in these complexes was highly reactive toward amines and CH_3S^- (eq 3). Under the mild conditions of these



reactions there was no reaction with secondary or tertiary phosphines. In the present paper we report some surprising reactions of phosphines with the new dithiocarbene complex $W(CO)_5[C(SCH_3)_2]$, whose high yield synthesis is also described.

Experimental Section

General Remarks. All reactions were performed under prepurified N_2 by using standard inert atmosphere techniques. The thiocarbonyl complex, $W(CO)_5CS$,²⁰ was prepared according to the published procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone under N_2 immediately before use. Tertiary phosphines and phosphites were fractionally distilled under N_2 or, when appropriate, recrystallized from hexanes. All other chemicals were reagent grade and used without further purification.

$W(CO)_5[C(SCH_3)_2]$ (II). A solution of $NaSCH_3$ was prepared by bubbling $HSCH_3$ through a THF (80 mL) suspension of NaH (0.0636 g of a 57% oil dispersion, 1.51 mmol) for 30 min. The bubbling was

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discontinued, and the solution was allowed to stir for an additional 30 min. A mixture²⁰ of 74.8% $W(CO)_5CS$ (0.669 g, 1.36 mmol) in $W(CO)_6$ was dissolved in 20 mL of THF. This solution was added to the $NaSCH_3$ solution resulting in a color change from yellow to orange. The orange solution was allowed to stir for 5 min followed by addition of CH_3I (0.22 g, 1.5 mmol). After the solution was stirred for approximately 20 min, it was evaporated to dryness under a stream of N_2 . The resulting residue was extracted with hexanes, and the hexane extracts were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CS_2 and placed on a 2 × 36 cm Florisil column. Slow elution with CS_2 led to the separation of two bands. The first eluted band was yellow and was identified as a mixture of $W(CO)_5CS$ and $W(CO)_6$. The second band was orange-red and contained $W(CO)_5[C(SCH_3)_2]$ (0.49 g, 84%). An analytically pure red sample was obtained by recrystallization from pentane at $-20^\circ C$: mp 63–65 $^\circ C$; IR (hexanes) $\nu(CO)$ 2067 (m), 1984 (vw), 1950 (s), 1941 (s) cm^{-1} ; 1H NMR ($CDCl_3$) τ 7.04 (s, CH_3); ^{13}C NMR ($CDCl_3$) 300.0 (carbene C), 204.4 (trans CO), 197.4 (cis CO), 29.5 (CH_3) ppm; mass spectrum, m/e 430.02 (M^+), 402.04, 374.06, 346.02, 318.04, 290.02 ($M^+ - (CO)_n$, $n = 1-5$). Anal. Calcd for $C_8H_6O_5S_2W$: C, 22.34; H, 1.41; S, 14.91. Found: C, 22.64; H, 1.48; S, 14.75.

$W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$ (IVa). To a solution of $W(CO)_5[C(SCH_3)_2]$ (0.101 g, 0.234 mmol) in 15 mL of THF was added PPh_2CH_3 (0.050 g, 0.25 mmol). After the solution was stirred 6 h, it was evaporated to an oil under a stream of N_2 . The oil was recrystallized from pentane at $-20^\circ C$ to give 0.12 g (82%) of yellow product crystals, which decompose upon standing at room temperature for a few days: mp 95–105 $^\circ C$; IR (hexanes) $\nu(CO)$ 2073 (w), 1937 (s), 1922 (m) cm^{-1} ; 1H NMR ($CDCl_3$) τ 2.38 (m, phenyl), 7.48 (s, SCH_3), 7.75 (d, $J = 12$ Hz, PCH_3), 7.91 (s, SCH_3); ^{13}C NMR ($CDCl_3$) 202.1 (trans CO), 198.6 (cis CO), 132.0, 131.6, 129.2, 128.6, 127.8 (phenyl), 37.1 (SCH_3), 28.4 ($J = 132.8$ Hz, PCS_2), 26.1 (SCH_3), 14.0 ($J = 68.4$ Hz, PCH_3) ppm. Anal. Calcd for $C_{21}H_{19}O_5PS_2W$: C, 40.01; H, 3.04. Found: C, 40.31; H, 3.07.

$W(CO)_5[(CH_3S)_2C=P(CH_3)_2Ph]$ (IVb). This complex was prepared by the same method as IVa, starting with $W(CO)_5[C(SCH_3)_2]$ (0.102 g, 0.237 mmol) and $P(CH_3)_2Ph$ (0.033 g, 0.24 mmol). The solution was evaporated to dryness after 10 min. A yield of 81% of yellow needles recrystallized from pentane was obtained: mp 45–49 $^\circ C$; IR (hexanes) $\nu(CO)$ 2069 (w), 1931 (s), 1916 (m) cm^{-1} ; 1H NMR ($CDCl_3$) τ 2.34 (m, phenyl), 7.39 (s, SCH_3), 7.83 (s, SCH_3), 8.02 (d, $J = 13$ Hz, PCH_3).

$W(CO)_5[(CH_3S)_2C=P(C_2H_5)_3]$ (IVc). The method used to prepare IVa was also used for this complex, starting with $W(CO)_5[C(SCH_3)_2]$ (0.102 g, 0.237 mmol) and $P(C_2H_5)_3$ (0.028 g, 0.24 mmol). Yellow crystals of $W(CO)_5[(CH_3S)_2C=P(C_2H_5)_3]$ (0.12 g, 89%) were obtained after recrystallization from pentane: mp 81–85 $^\circ C$; IR (hexanes) $\nu(CO)$ 2069 (w), 1931 (s), 1917 (m); 1H NMR ($CDCl_3$) τ 7.35 (s, SCH_3), 7.80 (s, SCH_3), 8.06 (m, PCH_2), 8.81 (d of t, $J = 13$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) 201.9 (trans CO), 198.2 (cis CO), 38.6 (SCH_3), 26.8 (PCS_2), 21.2 (SCH_3), 15.7 (d, $J = 56.6$ Hz, PCH_2), 5.7 (d, $J = 3.9$ Hz, CH_3) ppm. Anal. Calcd for $C_{14}H_{21}O_5PS_2W$: C, 30.67; H, 3.87. Found: C, 30.68; H, 3.99.

$W(CO)_5[(CH_3S)_2C=P(OCH_3)_3]$ (IVd). This complex was prepared by a route analogous to that used for IVa, starting with $W(CO)_5[C(SCH_3)_2]$ (0.101 g, 0.234 mmol) and $P(OCH_3)_3$ (0.145 g, 1.17 mmol) in 15 mL of cyclohexane. This solution was evaporated to an oil after being stirred for approximately 27 h. This product was always contaminated with some $W(CO)_5P(OCH_3)_3$: mp 49–54 $^\circ C$; IR (hexane) $\nu(CO)$ 2074 (w), 1937 (s), 1924 (m) cm^{-1} ; 1H NMR ($CDCl_3$) τ 6.18 (d, $J = 13$ Hz, OCH_3), 7.34 (s, SCH_3), 7.79 (s, SCH_3).

$W(CO)_5[(CH_3S)_2C=PPh_3]$ (IVe). This complex was prepared by the method used for IVa, starting with $W(CO)_5[C(SCH_3)_2]$ (0.100 g, 0.232 mmol) and PPh_3 (0.305 g, 1.16 mmol) in 15 mL of cyclohexane. The solution was evaporated to dryness after being stirred for 3 days. The product was never obtained pure: IR (hexanes) $\nu(CO)$ 2070 (w), 1938 (s), 1930 (sh), 1917 (m).

$W(CO)_5[PPh_2CH(SCH_3)_2]$ (V). This compound was prepared in the same manner as IVa, from the reaction of $W(CO)_5[C(SCH_3)_2]$ (0.0953 g, 0.222 mmol) and $PPh_2CH(SCH_3)_2$ (0.0413 g, 0.222 mmol) in 5 mL of hexanes. The solution was allowed to stir for 8 h at approximately 35 $^\circ C$. After crystallization from pentane, 0.094 g of $W(CO)_5[PPh_2CH(SCH_3)_2]$ (69%) was obtained: mp 104–107 $^\circ C$; IR (hexanes) $\nu(CO)$ 2072 (w), 1949 (s), 1945 (s), 1939 (sh); 1H NMR ($CDCl_3$) τ 2.39 (m, phenyl), 5.56 (d, $J = 8$ Hz, CH), 8.02 (s, SCH_3); ^{13}C NMR (CH_3CN) 200.9 (d, $J = 22$ Hz, trans CO), 198.7 (d, $J = 5$ Hz, cis CO), 137.0, 135.1, 134.6, 132.4, 130.3, 129.9 (phenyl), 57.2 (d, $J = 14$ Hz, PCS_2), 17.1 (d, $J = 2$ Hz, SCH_3) ppm. Anal. Calcd for $C_{21}H_{12}O_5PS_2W$: C, 38.97; H, 2.79. Found: C, 38.84; H, 2.82.

Spectral Data. Proton NMR spectra were recorded at room temperature on a Varian HA 100 spectrometer in $CDCl_3$ with $CHCl_3$ as the internal reference and Me_4Si as the internal lock; temperature-dependent

^{13}C NMR were recorded on a JEOL FX-90Q spectrometer. The ^{13}C NMR spectra were also recorded on the JEOL FX-90Q spectrometer; $Cr(acac)_3$ (~ 0.1 M) was added to the solutions to reduce data collection time. Infrared spectra were determined on a Perkin-Elmer 281 spectrometer. Mass spectra were recorded on a Finnigan 4000.

Crystal Data. $W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$: mol wt 630.34, monoclinic $P2_1/n$, $a = 13.681$ (3) Å, $b = 11.064$ (1) Å, $c = 15.913$ (2) Å, $\beta = 94.42$ (2)°, $V = 2401.53$ Å³, $\rho(\text{calcd}) = 1.743$ g/cm³, $Z = 4$, $\mu = 53.49$ cm⁻¹ for Mo $K\alpha$.

A single crystal of pentacarbonyl(bis(thiomethyl)methylenediphenylmethylphosphorane)tungsten, $W(CO)_5[(CH_3S)_2C=PPh_2CH_3]$, of approximate dimensions $0.6 \times 0.4 \times 0.3$ mm was mounted on a glass fiber. The fiber was subsequently positioned on a standard goniometer head. Four preliminary ω oscillation photographs at various χ and φ settings were taken on an automated four-circle X-ray diffractometer, and the coordinates of 12 independent reflections were input to the automatic indexing program ALICE.²¹ The resulting cell and reduced-cell scalars indicated $P2_1/n$ (monoclinic) symmetry. Inspection of the axial ω -oscillation photographs confirmed this symmetry. The lattice constants were obtained by using least-squares refinement based on precise $\pm 2\theta$ measurements of 15 independent reflections on a previously aligned diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.70954$ Å) at 25 $^\circ C$.

Collection and Reduction of X-ray Intensity Data. The data were collected at 25 $^\circ C$ with graphite-monochromated Mo $K\alpha$ radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory and previously described by Rohrbaugh and Jacobson.²² All data (4575 reflections) within a 2θ sphere of 50° in the hkl and $\bar{h}\bar{k}l$ octants were measured by using an ω step-scan technique (step size 0.01°, 0.5-s counting time/step).

As a general check on electronic and crystal stability, the intensities of the 3 standard reflections were remeasured every 75 reflections. These standards did not vary significantly throughout the entire data collection period. Examination of the data revealed systematic absences for $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, thus uniquely defining the space group as $P2_1/n$.

The measured intensities were corrected for Lorentz and polarization effects, and an absorption correction was also applied. The estimated error in each intensity was calculated by $\sigma_I^2 = C_T + K_C C_B + (0.03 C_T)^2 + (0.03 C_B)^2$ where C_T , K_C , and C_B represent the total count, a counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method.²³ Equivalent data were averaged and yielded 3726 reflections with $I_0 > 3\sigma(I)$ which were retained for structural solution and refinement.

Solution and Refinement of the Structure. The position of the tungsten atom was obtained by analysis of a sharpened three-dimensional Patterson function. All the remaining atoms (except the H atoms on C8) were found by successive structure factor²⁴ and electron density map calculations.²⁵ The atomic positional parameters for the nonhydrogen atoms were refined by using anisotropic parameters by a block-matrix least-squares procedure,²⁶ with final refinement using a full-matrix least-squares procedure²⁴ and minimizing the functions $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma(F)^2)$ to a conventional residual index of $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.043$ and the associated weighted index $R_2 = 0.062$. The hydrogen positions were included but not refined during the least-squares refinement cycles. The scattering factors were those of Hanson et al.,²⁷ modified for the real and imaginary parts of anomalous dispersion.²⁸

Results and Discussion

Preparation and Characterization of $W(CO)_5[C(SCH_3)_2]$. When a solution of $W(CO)_5CS$ in THF is added to a THF solution of $NaSCH_3$ at room temperature, an immediate color change from

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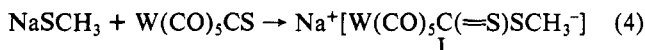
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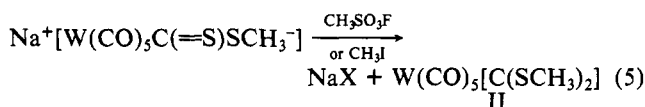
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yellow to orange-red is observed. The red coloration is presumably due to the formation of the tungsten methyl dithioester anion (eq 4). Fortunately, $W(CO)_6$ does not react with $NaSCH_3$ under



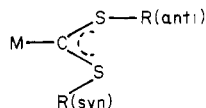
these conditions. Thus, the $W(CO)_5CS$ can be used as it is obtained directly from its preparation²⁰ without separating it from $W(CO)_6$. No attempts have been made to isolate the anionic methyl dithioester. However, it is methylated in situ with either methyl fluorosulfonate or methyl iodide (eq 5) to give $W(C-$



$O)_5[C(SCH_3)_2]$ in a yield of about 84%. The carbene complex shows no noticeable decomposition upon exposure to air for a period of several months in the solid state. It is soluble in nonpolar solvents such as hexanes and $(C_2H_5)_2O$ as well as in more polar solvents such as $CHCl_3$, THF, CH_2Cl_2 , acetone, and C_2H_5OH , but it is insoluble in H_2O . Solutions of II exposed to air at room temperature are stable for a period of 3 or 4 days.

The IR spectrum of II is composed of four $\nu(CO)$ absorptions at 2067 (m), 1984 (vw), 1950 (s), and 1941 (s) cm^{-1} , which yield approximate C–O stretching force constants²⁹ of $k_1 = 15.6$ (trans) and $k_2 = 15.9$ (cis) $mdyn/\text{\AA}$. While the constants are lower than those of the corresponding carbonyl $W(CO)_6$, $k = 17.7$ $mdyn/\text{\AA}$ ³⁰ indicating that the carbene ligand has a lower π acceptor/ σ donor ratio than CO,¹⁶ they are very similar to those of $W(CO)_5(PPh_3)$ ($k_1 = 15.5$, $k_2 = 15.9$ $mdyn/\text{\AA}$).³¹ This result indicates that the π acceptor/ σ donor ratio of the $C(SCH_3)_2$ carbene ligand is comparable to that of PPh_3 ; a similar conclusion was reached previously for the analogous $CpFe(CO)_2L^+$ complexes.¹⁷

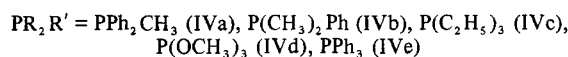
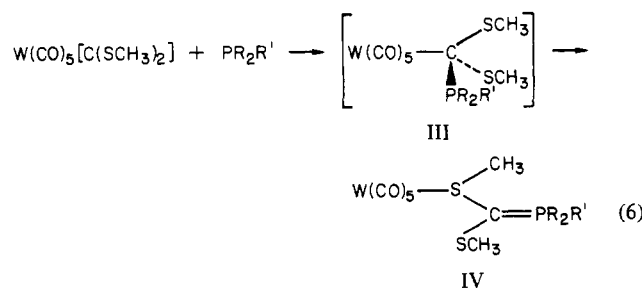
The 1H NMR spectrum of II in acetone- d_6 shows a singlet at τ 6.95 for the two methyl groups. Equivalent alkyl groups in the carbene ligands were also observed in the NMR spectra of other tungsten and chromium dithiocarbenes $M(CO)_5[C(SPh)_2]$ ⁴ and $M(CO)_5[C(SC_2H_5)_2]$,⁵ where $M = W$ or Cr and iron dithiocarbenes^{16,17} $CpFe(CO)L[C(SCH_3)_2]^+$, where $L = CO$, CH_3CN , PPh_3 , $AsPh_3$, $P(OCH_3)_3$, $SbPh_3$, C_5H_5N . In the cases of $\{PtCl[C(SCH_3)_2](PPh_3)_2\}BF_4$,³² $\{PtI[C(SCH_3)_2](PPh_3)_2\}I$,³³ and $\{PtI[SC_2H_5)_2](PPh_3)_2\}I$ ³³ the carbene alkyl groups were inequivalent in their room-temperature 1H NMR spectra. This inequivalence presumably results from restricted rotation about the C(carbene)–S bond giving rise to syn and anti alkyl groups.^{32,33}



Such restricted rotation is presumably favored by the positive Pt which promotes $\pi\pi$ -electron donation from the S to the p_z orbital of the C(carbene) atom.¹⁶ Restricted rotation is also observed in $W(CO)_5[C(SCH_3)_2]$. Although the CH_3 groups occur as a singlet in the room-temperature spectrum, two sharp singlets at τ 6.75 and 7.15 are observed upon cooling an acetone- d_6 solution to $-22^\circ C$. These singlets broaden and coalesce at $-4^\circ C$ as the solution is warmed. Similar behavior has previously been observed for $\{CpFe(CO)L[C(SCH_3)_2]\}PF_6$ ^{16,17} ($L = CO$, CH_3CN , PPh_3 , $AsPh_3$, $P(OCH_3)_3$, $P(OPh)_3$, $SbPh_3$, C_5H_5N).

McCormick and Angelici¹⁶ rationalized the difference in the rate of rotation in the platinum and iron carbenes by suggesting that the $Cl(PPh_3)_2Pt^+$ moiety is probably more electron withdrawing than the $CpFe(CO)_2^+$. This suggestion is supported by the higher $\nu(CO)$ force constant of $[Cl(PPh_3)_2Pt(CO)]^+BF_4^-$ (18.2 $mdyn/\text{\AA}$)³⁴ as compared to that of $[CpFe(CO)_3]^+PF_6^-$ (17.6 $mdyn/\text{\AA}$).³⁵ Since the force constant (17.7 $mdyn/\text{\AA}$)³⁰ for $W(CO)_6$ is very similar to that of $CpFe(CO)_3^+$, both $W(CO)_5[C(SCH_3)_2]$ and $CpFe(CO)_2[C(SCH_3)_2]^+$ should have similar rotational barriers. Qualitatively, this is observed to be true since their coalescence temperatures (-4 and $-2.5^\circ C$,¹⁶ respectively) are nearly identical.

Reactions of $W(CO)_5[C(SCH_3)_2]$ with Tertiary Phosphines. The reaction (eq 6) of II with tertiary phosphines and phosphites



provides a general, high-yield synthesis of a new class of compounds, IV. The reaction at room temperature proceeds almost instantaneously with $P(C_2H_5)_3$ but requires about 3 days with PPh_3 . It presumably proceeds by initial attack of the phosphine or phosphite on the empty p_z orbital of the carbene C followed by rapid rearrangement to the final product IV. The net effect is to transfer the $C(SCH_3)_2$ carbene unit from the tungsten to the phosphorus. The complexes IV decompose upon standing at room temperature when exposed to air over a period of 1 or 2 days. However, they may be stored in air at $-20^\circ C$ for a period of months without noticeable decomposition. They are soluble in most common organic solvents ranging in polarity from hexane to acetone.

Because there is no precedent in the literature for a complex having structure IV or for the rearrangement leading to it, an X-ray diffraction study of IVa was undertaken. The unit cell contains four molecules and has $P2_1/n$ symmetry. A stereoview of the unit cell is shown in Figure 1. Figure 2 shows IVa as discrete molecules having a slightly distorted octahedral symmetry around the tungsten atom in which the bis(thiomethyl)methylenediphenylmethylphosphorane ligand is bound to the tungsten atom via S1. Final positional parameters, bond distances, and bond angles are given in Tables I, II and III, respectively.

The bond lengths and angles ($W-C$, 2.043 (9)–1.972 (9) \AA ; $C-O$, 1.139 (11)–1.133 (10) \AA ; cis $C-W-C$, 86.8 (3)–93.1 (3) $^\circ$; trans $C-W-C$, 175.9 (3)–178.5 (3) $^\circ$; $W-C-O$, 175.4 (7)–178.4 (8) $^\circ$) for the $W(CO)_5$ portion of the molecule are very similar to values observed in other molecules.^{36,37}

The bond between W and C5 (C5 is trans to S1) is shorter than the other $W-C$ bonds by at least 0.05 \AA , indicating that the π acceptor/ σ donor ratio is lower for the phosphorane ligand than for CO. The tungsten–sulfur bond length of 2.555 (2) \AA compares favorably with those in $(CO)_5WSCH_2CH_2NHC(=O)CCH_2$ (2.551 (14) \AA)³⁷ and $(CO)_4W-[S(t-Bu)CH_2CH_2S(t-Bu)]$ (2.565 (4) and 2.559 (5) \AA).³⁶

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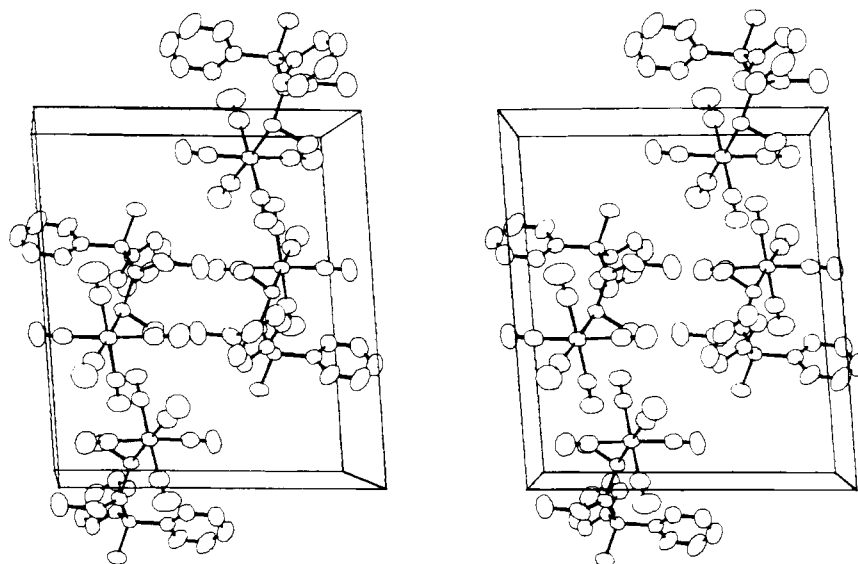


Figure 1. Stereoscopic view of the unit cell with the *a* axis horizontal and the *c* axis vertical.

Table I. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)^a for $W(CO)_5[(CH_3)_2C=PPh_2(CH_3)]$

	<i>x</i>	<i>y</i>	<i>z</i>
W	0.816 63 (2)	0.150 98 (2)	0.605 37 (1)
S1	0.758 43 (13)	0.344 31 (13)	0.529 20 (10)
S2	0.626 25 (17)	0.204 12 (21)	0.401 02 (12)
P	0.742 80 (11)	0.419 13 (15)	0.353 71 (9)
O1	0.852 97 (65)	0.021 15 (58)	0.434 10 (42)
O2	0.602 13 (51)	0.039 11 (70)	0.598 97 (43)
O3	0.791 81 (51)	0.270 30 (76)	0.783 47 (35)
O4	1.035 54 (43)	0.240 77 (66)	0.597 13 (44)
O5	0.903 47 (57)	0.928 67 (67)	0.704 72 (46)
C1	0.835 81 (62)	0.068 78 (71)	0.494 31 (49)
C2	0.677 55 (64)	0.082 85 (75)	0.600 52 (45)
C3	0.798 95 (58)	0.229 72 (84)	0.718 71 (47)
C4	0.956 54 (61)	0.212 88 (70)	0.602 16 (41)
C5	0.871 11 (62)	0.009 08 (81)	0.667 52 (50)
C6	0.709 84 (47)	0.316 90 (60)	0.426 42 (36)
C7	0.660 62 (65)	0.410 11 (81)	0.584 67 (48)
C8	0.506 14 (74)	0.272 44 (150)	0.410 36 (73)
C9	0.691 32 (62)	0.375 70 (73)	0.250 73 (42)
C10	0.873 65 (47)	0.428 17 (59)	0.345 48 (37)
C11	0.936 18 (59)	0.343 56 (66)	0.384 30 (51)
C12	1.036 56 (69)	0.347 16 (82)	0.373 35 (65)
C13	1.071 66 (64)	0.436 34 (106)	0.323 91 (66)
C14	1.009 00 (75)	0.518 28 (87)	0.284 22 (66)
C15	0.910 79 (60)	0.516 27 (67)	0.295 68 (50)
C16	0.704 50 (46)	0.573 44 (59)	0.372 97 (39)
C17	0.752 73 (60)	0.639 23 (59)	0.438 04 (51)
C18	0.720 38 (64)	0.752 54 (70)	0.457 74 (56)
C19	0.639 35 (75)	0.800 56 (85)	0.413 63 (64)
C20	0.591 41 (62)	0.736 56 (85)	0.349 28 (60)
C21	0.622 63 (56)	0.622 86 (77)	0.328 38 (52)
H1	0.606 25	0.356 25	0.571 88
H2	0.637 56	0.475 00	0.556 25
H3	0.675 00	0.453 12	0.631 25
H4	0.728 12	0.296 87	0.242 19
H5	0.614 06	0.384 37	0.248 43
H6	0.706 25	0.443 75	0.210 94
H7	0.918 75	0.268 75	0.412 50
H8	1.078 12	0.265 62	0.414 06
H9	1.143 75	0.423 44	0.307 03
H10	1.028 12	0.581 25	0.242 19
H11	0.865 63	0.590 62	0.267 19
H12	0.834 75	0.603 12	0.460 94
H13	0.771 87	0.800 00	0.512 50
H14	0.606 25	0.890 62	0.421 87
H15	0.531 25	0.775 00	0.321 87
H16	0.590 62	0.579 69	0.271 87

^a The positional parameters are presented in fractional unit cell coordinates.

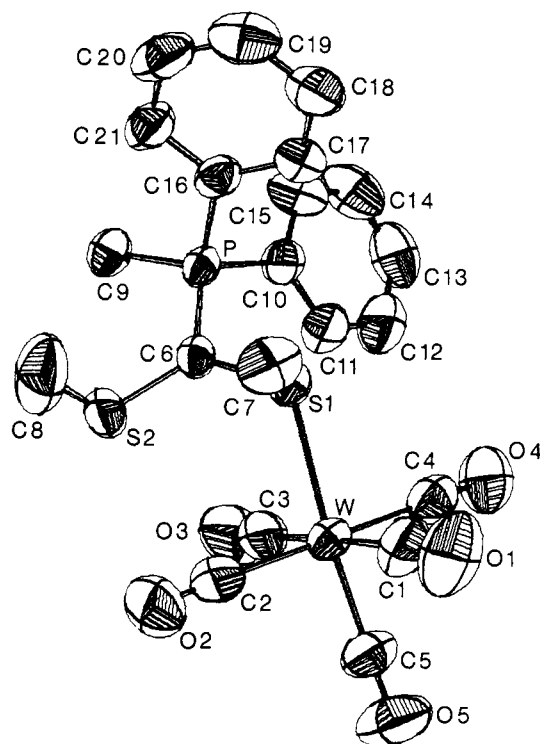


Figure 2. Structure of $W(CO)_5[(CH_3)_2C=PPh_2(CH_3)]$.

Table II. Selected Interatomic Distances (Å) and Their Estimated Standard Deviations (in Parentheses) for $W(CO)_5[(CH_3)_2C=PPh_2(CH_3)]$

W-S1	2.555 (2)	O3-C3	1.135 (10)
W-C1	2.022 (8)	O4-C4	1.133 (10)
W-C2	2.043 (9)	O5-C5	1.138 (11)
W-C3	2.034 (8)	C10-C11	1.382 (10)
W-C4	2.037 (8)	C10-C15	1.377 (10)
W-C5	1.972 (9)	C11-C12	1.398 (12)
S1-C6	1.744 (6)	C12-C13	1.373 (15)
S1-C7	1.812 (9)	C13-C14	1.368 (15)
S2-C6	1.719 (7)	C14-C15	1.370 (13)
S2-C8	1.825 (12)	C16-C17	1.390 (10)
P-C6	1.704 (6)	C16-C21	1.391 (10)
P-C9	1.799 (7)	C17-C18	1.373 (10)
P-C10	1.808 (7)	C18-C19	1.373 (13)
P-C16	1.819 (7)	C19-C20	1.371 (14)
O1-C1	1.134 (10)	C20-C21	1.391 (12)
O2-C2	1.139 (11)		

Table III. Selected Bond Angles (Deg) and Their Estimated Standard Deviations (in Parentheses) for $W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$

S1-W-C1	91.1 (2)	W-C3-O3	177.1 (8)
S1-W-C2	92.0 (2)	W-C4-O4	175.4 (7)
S1-W-C3	90.5 (3)	W-C5-O5	178.4 (8)
S1-W-C4	88.1 (2)	C6-S1-C7	106.5 (3)
C1-W-C5	175.4 (3)	C6-S2-C8	105.5 (5)
C1-W-C2	89.1 (3)	C6-P-C9	109.6 (3)
C1-W-C3	178.5 (3)	C6-P-C10	113.7 (3)
C1-W-C4	86.8 (3)	C6-P-C16	114.5 (3)
C1-W-C5	90.6 (3)	C9-P-C10	105.6 (3)
C2-W-C3	91.0 (3)	C9-P-C16	107.9 (3)
C2-W-C4	175.9 (3)	C10-P-C16	105.1 (3)
C2-W-C5	92.3 (3)	S1-C6-P	114.8 (4)
C3-W-C4	93.1 (3)	S1-C6-S2	123.1 (4)
C3-W-C5	87.9 (3)	S2-C6-P	121.9 (4)
C4-W-C5	87.8 (3)	P-C10-C11	120.8 (5)
W-S1-C6	112.4 (2)	P-C10-C15	119.5 (5)
W-S1-C7	108.7 (3)	P-C16-C17	119.4 (5)
W-C1-O1	175.4 (8)	P-C16-C21	121.0 (5)
W-C2-O2	176.4 (8)		

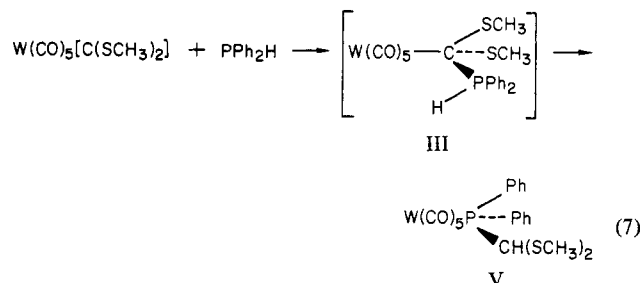
The methylene carbon C6 and the atoms bound to it (S1, S2, and P) are coplanar with bond angles ranging from 114.8 (4) to 123.1 (4)°, indicating the sp^2 -hybridized character of the carbon atom. The P-C6 bond length of 1.704 (6) Å is similar to that (1.709 (19) Å)³⁸ found in $Ph_3P=CH[SO_2(C_6H_4CH_3-p)]$ and that (1.71 (5) Å)³⁹ found in $Ph_3P=C(I)(C=OPh)$. The S1-C6 and the S2-C6 distances, 1.744 (6) and 1.718 (7) Å, respectively, are within the range of normal C(sp^2)-S bonds.⁴⁰⁻⁴² The S1-C6 bond distance of the coordinated S atom is slightly longer than the S2-C6 distance of the uncoordinated S.

The spectral characteristics of IVa-c are, in general, very similar and are expected on the basis of the above structural assignment. Their IR spectra are consistent with the pseudo C_{4v} symmetry, found for IVa, containing three $\nu(CO)$ absorptions in a weak-strong-medium pattern. Their 1H NMR spectra show a singlet for each of the two different methyl groups on the sulfur atoms, and the ^{13}C NMR spectra of IVa,c also show separate peaks for these different methyl groups. Although spectra of the related complex $M(CO)_5[(PhS)_2C=PPh_3]$, where M = Cr or W, were not given in the conference report³ describing their synthesis from $M(CO)_6$ and $(PhS)_2C=PPh_3$, a structure was proposed in which the phosphorane carbon, rather than S, was coordinated to the metal. It is possible that this complex has a structure analogous to IV.

Since amines cannot form phosphorane analogues, $(CH_3)_2C=NR_3$, it seemed that they may give stable carbene adducts, III, in eq 6. There is, however, no evidence of reaction between $W(CO)_5[C(SCH_3)_2]$ and $N(C_2H_5)_3$ or 1,4-diazabicyclo[2.2.2]octane. Thus it appears that the carbene adduct is

unstable relative to the reactants. This result also suggests that it is the formation of the phosphorane product which provides the overall driving force for reaction 6. It is interesting that $W(CO)_5[C(SCH_3)_2CH_3]$ reacts¹¹ with $P(CH_3)_3$ to give only the carbene adduct $W(CO)_5[C(SCH_3)(CH_3)[P(CH_3)_3]]$ of structure III. This adduct does not rearrange to the phosphorane structure, IV, even though the sulfur atom of the $(CH_3)_3P=C(SCH_3)(CH_3)$ ligand is available for coordination to the tungsten.

With a Secondary Phosphine. Reaction of the secondary phosphine PPh_2H with II does not give a phosphorane complex (eq 6) as found with the tertiary phosphines but instead yields the phosphine derivative (eq 7). Product V is pale yellow in the



solid state, is soluble in most common solvents, and is stable at -20 °C for a period of months. The structure assigned to complex V is based on its 1H and ^{13}C NMR spectra. Consistent with this structure is the equivalence of both SCH_3 groups in both the 1H and ^{13}C spectra of the complex. The J_{PCH} coupling constant (8 Hz) is consistent⁴³ with the hydrogen atom being bound to the carbon rather than remaining on the phosphorus in which case the J_{PH} would be expected to be in the range of 200-700 Hz.⁴³ The J_{PWC} values for the cis and trans CO groups (5 and 22 Hz, respectively) are very similar to those in related PR_3 complexes.^{31,44}

The reaction presumably proceeds by initial attack of the phosphine on the p_z orbital of the carbene C to give intermediate III. This intermediate could rearrange directly to the product by H atom migration to the C and P migration to the W as was suggested¹¹ for reaction 2, or it could rearrange first to the corresponding phosphorane complex IV which could then convert to V by migration of the H from P to the basic C atom followed by migration of P to the W.

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Supplementary Material Available: Tables of the final thermal parameters and observed and calculated structure factors for $W(CO)_5[(CH_3S)_2C=PPh_2CH_3]$ and also complete tables of interatomic distances and angles and least-squares planes (18 pages). Ordering information is given on any current masthead page.

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