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KINETIC STUDIES OF THE REACTIONS OF THE CARBENE COMPLEX $W(CO)_5[C(SCH_3)_2]$ WITH PHOSPHINES TO FORM PHOSPHORANE COMPLEXES $W(CO)_5[(CH_3S)_2C{=}PR_3]$ AND THE SYNTHESIS OF SOME CYCLIC PHOSPHORANE COMPLEXES *

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Summary

The dithiocarbene complex $W(CO)_5[C(SCH_3)_2]$ reacts with tertiary phosphines, PPh_2CH_3, $PPh(CH_3)_2$, $P(C_2H_5)_3$ and $P(OCH_3)_3$ to form the phosphorane complexes $W(CO)_5[(CH_3S)_2C{=}PR_3]$ and with $HPPh_2$ to form the phosphine complex $W(CO)_5\{PPh_2[CH(SCH_3)_2]\}$. Kinetic studies of both types of reactions show that their rates are first order each in $W(CO)_5[C(SCH_3)_2]$ and in the phosphorus ligand. A mechanism involving rate determining phosphorus attack at the carbene carbon followed by rapid rearrangement to the product is consistent with this rate law. Rate constants for the reactions increase with increasing nucleophilicities of the phosphines: $P(OCH_3)_3 < PPh_2H < PPh_2CH_3 \simeq PPh(CH_3)_2 < P(C_2H_5)_3$. The $\Delta H^{\ddagger}$ values decrease ($P(OCH_3)_3 > PPh_2H > PPh_2(CH_3) > PPh(CH_3)_2 > P(C_2H_5)_3$) as the nucleophilicities of the phosphines increase. The $\Delta S^{\ddagger}$ values (~—30 e.u.) remain essentially constant for all the reactions. The cyclic dithiocarbenes $W(CO)_5[\overline{CS(CH_2)_nS}]$, where $n = 3$ or 4, react with $PPh_2(CH_3)$ to form the cyclic phosphorane complexes, $W(CO)_5[\underline{S(CH_2)_nSC}{=}PPh_2(CH_3)]$. The 6- and 7-membered cyclic dithiocarbenes also react with PPh_2H to form the phosphine complexes, $W(CO)_5\{PPh_2[\overline{CS(CH_2)_nS}(H)]\}$.

Introduction

Transition metal carbene complexes are very reactive species [1—3], undergoing reactions at the carbene ligand as well as at the metal center. In spite of

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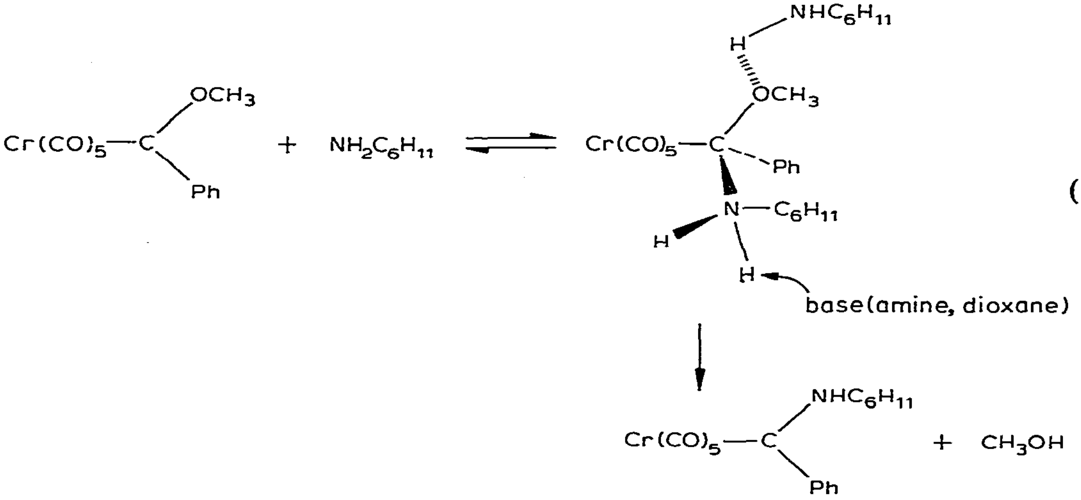
numerous synthetic investigations of carbene complexes only a few kinetic studies of their reactions have been reported [4—12]. It has been found that the reaction of cyclohexylamine with $Cr(CO)_5[C(OCH_3)Ph]$ in decane to form $Cr(CO)_5[C(NHC_6H_{11})Ph]$ and CH_3OH is first order in the complex and third order in amine, whereas in dioxane it is still first order in the complex but only second order in amine [4,5]. The kinetic order difference in the different solvents is thought to occur because of the different abilities of the solvents to participate in hydrogen bonding. The reaction was suggested to proceed by formation of a hydrogen bond between an amine H and the O of the OCH_3 group. An activated amine (HNRH···B) then attacks the carbene carbon forming an adduct which undergoes loss of CH_3OH (eq. 1):



(1)

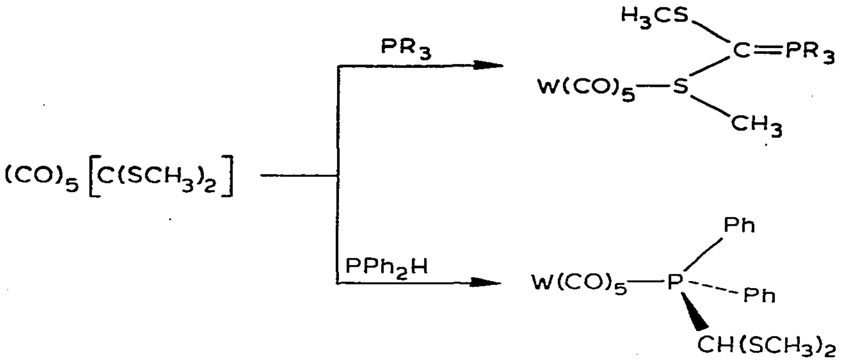
In a related study, $Cr(CO)_5[C(OCH_3)R]$ ($R = CH_3$ or Ph) was observed to react with phosphines ($P(C_6H_{11})_3$, $P(p\text{-}CH_3C_6H_4)_3$, PPh_3, $PPh_2(C_2H_5)$, $PPh(C_2H_5)_2$, $P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$) [6—9] to form $Cr(CO)_4L[C(OCH_3)R]$ and $Cr(CO)_{6-n}L_n$ ($n = 1$ or 2) by a two term rate law (eq. 2):

$$-d[\mathrm{Cr(carbene)}]/dt = k_1[\mathrm{Cr(carbene)}] + k_2[\mathrm{Cr(carbene)}][\mathrm{L}] \tag{2}$$

The second order term was assumed to indicate an associative pathway, and is important only for the nucleophilic trialkylphosphines ($P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$). It is unclear whether nucleophilic attack of the phosphine is on the metal center or on the carbene carbon. However, Fischer et al. [13,14] have isolated $Cr(CO)_5[C(OCH_3)(CH_3)P(n\text{-}C_4H_9)_3]$, and found it to rearrange to the products observed by Werner [6,8], $Cr(CO)_4L[C(OCH_3)R]$ and $Cr(CO)_{6-n}L_n$ ($n = 1$ or 2). This result, as well as the much smaller equilibrium constants for the formation of the carbene-phosphine adduct for the mixed alkyl-aryl or triaryl phosphines as compared to those for the trialkylphosphines, is strong evidence for nucleophilic attack at the carbene carbon (eq. 3):

$$\begin{gathered} Cr(CO)_5[C(OCH_3)R'] + PR_3 \rightleftharpoons Cr(CO)_5[C(OCH_3)R'(PR_3)] \\ \longrightarrow \left\{ \begin{array}{l} \rightarrow Cr(CO)_5PR_3 + [C(OCH_3)R'] \\ \rightarrow \mathit{cis}\text{—}Cr(CO)_4(PR_3)[C(OCH_3)R'] \end{array} \right. \end{gathered} \tag{3}$$

In a previous paper [15] we reported the unusual reactions of the dithiocarbene complex $W(CO)_5[C(SCH_3)_2]$ with tertiary phosphines to form the phosphorane complexes $W(CO)_5[(CH_3S)_2C{=}PR_3]$ and with the secondary phosphine, PPh_2H, to form the phosphine complex $W(CO)_5\{PPh_2[CH(SCH_3)_2]\}$ (eq. 4):



(4)

Kinetic studies of the reactions of $W(CO)_5[C(SCH_3)_2]$ with $P(C_2H_5)_3$, $PPh(CH_3)_2$, $PPh_2(CH_3)$, PPh_2H and $P(OCH_3)_3$ were carried out in order to elucidate the mechanisms of these reactions and the factors which affect their rates. These kinetic results, as well as the preparations of some cyclic phosphorane-pentacarbonyltungsten complexes, are reported herein.

Experimental

eneral

Kinetic and synthetic reactions were performed under argon and nitrogen, respectively, using Schlenk ware. Cyclohexane was distilled from $CaSO_4$ under N_2 onto 4A molecular sieves. All tertiary phosphines and phosphites were fractionally distilled under N_2. The dithiocarbene complexes $W(CO)_5[C(SCH_3)_2]$ [15] and $W(CO)_5[\overline{CS(CH_2)_nS}]$, [16] where $n = 2$, 3 or 4, were prepared as reported previously. All other chemicals were reagent grade and used without further purification.

etermination of reaction rates

The rates of reaction were determined by following the disappearance of the $W(CO)_5[C(SCH_3)_2]$ absorption at 446 nm ($\epsilon = 1.63 \times 10^4\ M^{-1}\ cm^{-1}$). The products, at the concentration used for the kinetic reactions, did not absorb in this region. A stock solution of $4.00 \times 10^{-5}\ M$ $W(CO)_5[C(SCH_3)_2]$ in cyclohexane was prepared, and UV cuvettes of 1 cm pathlength were used. The $W(CO)_5$-$[C(SCH_3)_2]$ stock solution (2 ml) was syringed into the cuvette through a septum. The cuvette and solution were then flushed with a slow stream of argon. The cuvette was submerged in a constant temperature water bath and allowed to reach thermal equilibrium. The cuvette was transferred to the thermostatted cell compartment of the spectrophotometer and again allowed to reach thermal equilibrium. The thermostatted neat ligand was added, by syringe, through the septum, and the solution was mixed well. The Varian 219 spectrophotometer was programmed to automatically take absorption measurements at specific time intervals. The slopes of plots of $\ln(A - A_\infty)$ versus time where A is the absorbance at time t and A_∞ is the absorbance at the completion of the reaction, gave pseudo first-order rate constants k_{obsd}. The plots were linear for at least the first 80% of reaction.

Product identification

Although the products were never isolated from kinetic reaction mixtures, an infrared spectrophotometric study of the reaction of $W(CO)_5[C(SCH_3)_2]$ with $P(C_2H_5)_3$, under conditions of the kinetic reactions, showed formation of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ as the only product. No replacement of the phosphorane ligand of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ by 100-fold excess $P(C_2H_5)_3$ occurred even after 24 hours at room temperature. Total replacement of the phosphorane ligand by $P(C_2H_5)_3$ was achieved by heating a solution of $W(CO)_5$-$[(CH_3S)_2C{=}P(C_2H_5)_3]$ with a 100-fold excess of $P(C_2H_5)_3$ at approximately 60°C for 32 hours.

$W(CO)_5\{\overline{S(CH_2)_3SC}{=}[P(CH_3)Ph_2]\}$ *(IVa)*

To a solution of $W(CO)_5[\overline{CS(CH_2)_3S}]$ (0.0666 g, 0.151 mmol) in 10 ml of hexane was added $P(CH_3)Ph_2$ (0.060 g, 0.30 mmol). The solution was allowed to stir at room temperature for about 1.5 h. During this time a yellow precipitate had started to form. Yellow crystals of IVa (0.042 g, 43%) were obtained from the supernatant liquid upon cooling it to —20°C. The yellow precipitate was recrystallized from CH_2Cl_2 and hexanes at —20°C yielding 0.022 g (23%) of IVa: m.p. 112—117°C(dec); ^1H NMR($CDCl_3$) τ 2.48(m, phenyl), 7.06(t, SCH_2), 7.15(t, SCH_2), 7.47(bm, CH_2), 7.84(d, $J = 13$ Hz, PCH_3); Anal. found: C, 40.78; H, 2.93. Calcd for $C_{22}H_{19}O_5PS_2W$: C, 41.13; H, 2.99%.

$W(CO)_5\{\overline{S(CH_2)_4SC}{=}[PPh_2(CH_3)]\}$ *(IVb)*

A solution of $W(CO)_5[\overline{CS(CH_2)_4S}]$ (0.0523 g, 0.115 mmol) and $PPh_2(CH_3)$ (0.023 g, 0.11 mmol) in 10 ml of hexane was stirred at room temperature for about 1.5 h. The resulting yellow solution was concentrated to approximately 2 ml. The product was crystallized in 52% yield (0.039 g) from the concentrated solution at —20°C: m.p. 103—109°C(dec); ^1H NMR($CDCl_3$) τ 2.42(m, phenyl), 7.40(m, SCH_2), 7.59(m, SCH_2), 7.80(d, $J = 12$ Hz, PCH_3), 8.14(m, CH_2), 8.34(m, CH_2); Anal. found: C, 42.32; H, 3.28. Calcd for $C_{23}H_{21}O_5PS_2W$: C, 42.08; H, 3.23%.

$W(CO)_5[PPh_2\overline{C(H)S(CH_2)_3S}]$ *(Va)*

The complex Va was prepared by heating a solution of $W(CO)_5[\overline{CS(CH_2)_3S}]$ (0.025 g, 0.056 mmol) and PPh_2H (0.022 g, 0.12 mmol) in 8 ml of cyclohexane to 60°C for approximately 12 h, after which the solution was reduced to dryness and taken up in hexane. Crystallization from hexane at —20°C yields 0.015 g (42%) of Va as a yellow solid: m.p. 94°C (begins to decompose); Anal. found: C, 39.44; H, 2.93. Calcd for $C_{21}H_{17}O_5PS_2W$: C, 40.14; H, 2.73%.

$W(CO)_5[PPh_2\overline{C(H)S(CH_2)_4S}]$ *(Vb)*

The complex, Vb, was prepared by a route similar to the one used for preparing IVb, starting with $W(CO)_5[\overline{CS(CH_2)_4S}]$ (0.054 g, 0.12 mmol) and PPh_2H (0.022 g, 0.12 mmol). The product, Vb, was crystallized from hexanes at

−20°C yielding 0.056 g (73%); m.p. 95—99°C; ^{1}H NMR($CDCl_3$) τ 2.50(m, phenyl), 4.82(d, $J = 3$ Hz, PCH), 7.22(m, SCH_2), 8.10(m, CH_2); Anal. found: C, 41.48; H, 3.06. Calcd for $C_{22}H_{19}O_5PS_2W$: C, 41.13; H, 2.99%.

Spectral data

Proton NMR spectra were recorded at room temperature on a Varian HA-100 spectrometer in $CDCl_3$ with $CHCl_3$ or TMS as the internal reference and TMS as the internal lock. The ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer; $Cr(acac)_3$ (~0.1 *M*) was added to the solutions to reduce data collection time. Infrared spectra were taken on a Perkin-Elmer 281 spectrophotometer.

Results

Determination of the rates of reactions of $W(CO)_5[C(SCH_3)_2]$ with phosphines

The rates of reaction (eq. 4) were determined using pseudo first-order conditions (an excess of at least 40-fold of ligand was used in each case) and were

ATE CONSTANTS FOR THE REACTION (eq. 4) OF $W(CO)_5[C(SCH_3)_2]$ WITH L IN
NE SOLVENT

Temp. (°C)	[L] (*M*)	$10^4 k_{obsd}$ (s^{-1})	$10^4 k$ (M^{-1} s^{-1})
20.1	1.69×10^{-3}	57.3	33900
20.1	3.39×10^{-3}	114	33500
20.1	6.78×10^{-3}	235	34600
29.6	1.69×10^{-3}	86.6	51200
29.6	3.39×10^{-3}	17.7	52200
39.3	1.69×10^{-3}	133	78900
20.1	5.79×10^{-2}	26.9	464
20.1	1.16×10^{-1}	50.6	483
20.1	2.28×10^{-1}	99.6	437
29.6	2.81×10^{-2}	23.1	821
29.6	5.79×10^{-2}	45.4	785
29.6	1.16×10^{-1}	89.3	770
39.3	2.81×10^{-2}	39.6	1300
39.3	5.79×10^{-2}	82.0	1420
39.3	1.16×10^{-1}	160	1380
20.1	4.39×10^{-2}	24.4	555
20.1	8.77×10^{-2}	45.7	521
20.1	1.73×10^{-1}	87.9	509
30.3	1.06×10^{-2}	10.4	981
30.3	2.13×10^{-2}	21.4	1000
30.3	4.39×10^{-2}	42.5	968
40.6	1.06×10^{-2}	18.5	1740
40.6	2.13×10^{-2}	37.8	1780
40.6	4.39×10^{-2}	74.8	1710
20.1	3.91×10^{-1}	5.12	13.1
29.1	3.91×10^{-1}	10.5	26.9
39.6	1.93×10^{-1}	10.6	54.9
39.6	3.91×10^{-1}	21.9	56.0
20.1	6.46×10^{-1}	4.77	7.38
20.1	1.20	8.75	7.29
30.3	6.46×10^{-1}	10.4	16.1
30.3	1.20	19.3	16.1
40.4	6.46×10^{-1}	21.2	32.8
40.4	1.20	41.4	34.5

TABLE 2

AVERAGE RATE CONSTANTS k FOR THE REACTION (eq. 4) OF $W(CO)_5[C(SCH_3)_2]$ WITH L IN CYCLOHEXANE SOLVENT

L	Temp. (°C)	10^4k (M^{-1} s^{-1})
$P(C_2H_5)_3$	20.1	34000
	29.6	51700
	39.3	78900
$PPh(CH_3)_2$	20.1	461
	29.6	792
	39.3	1370
$PPh_2(CH_3)$	20.1	528
	30.3	983
	40.6	1740
PPh_2H	20.1	13.1
	29.1	26.9
	39.6	55.5
$P(OCH_3)_3$	20.1	7.34
	30.3	16.1
	40.4	33.7

TABLE 3

ACTIVATION PARAMETERS [a] FOR THE REACTION (eq. 4) OF $W(CO)_5[C(SCH_3)_2]$ WITH L IN CYCLOHEXANE SOLVENT

	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
$P(C_2H_5)_3$	7.4(1)	−30.9(5)
$PPh(CH_3)_2$	9.7(3)	−31.6(10)
$PPh_2(CH_3)$	10.0(2)	−30.1(7)
PPh_2H	12.8(2)	−28.0(7)
$P(OCH_3)_3$	13.0(2)	−28.4(6)

[a] Standard deviations in parentheses.

found to follow the rate law (eq. 5):

$$-d[W(CO)_5[C(SCH_3)_2]]/dt = k_{obsd}[W(CO)_5[C(SCH_3)_2]] = k[W(CO)_5[C(SCH_3)_2]][L] \qquad (5)$$

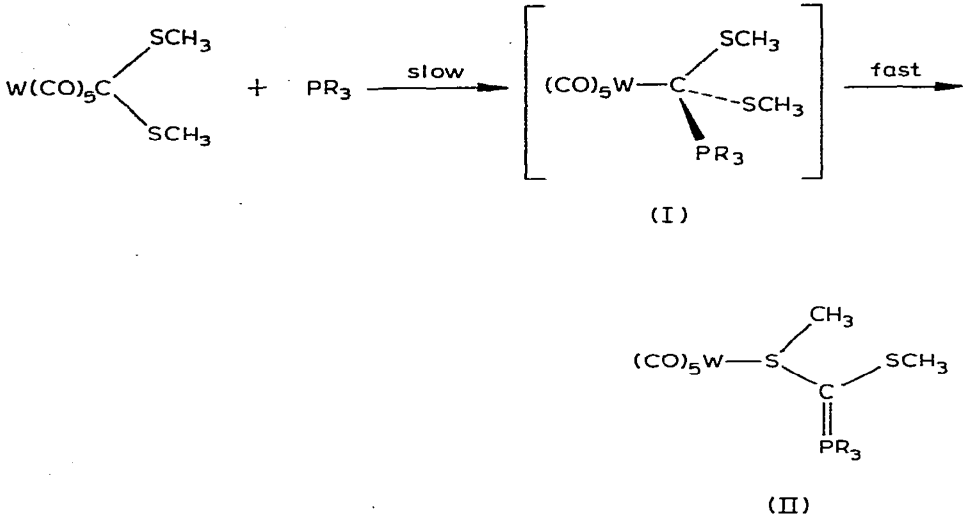
Each of the k_{obsd} values listed in Table 1 is an average of values from 3 to 4 runs; they are dependent on the ligand concentration and follow the expression, $k_{obsd} = k[L]$. Values of k for the same reaction at a specific temperature were constant, to within 10%, over a range of ligand concentrations. Average values of the second order rate constants, k, are given in Table 2. Activation parameters and their associated standard deviations (Table 3) were determined from a least-squares evaluation of the slope and intercept of a plot of $\ln(k/T)$ versus $1/T$.

Discussion

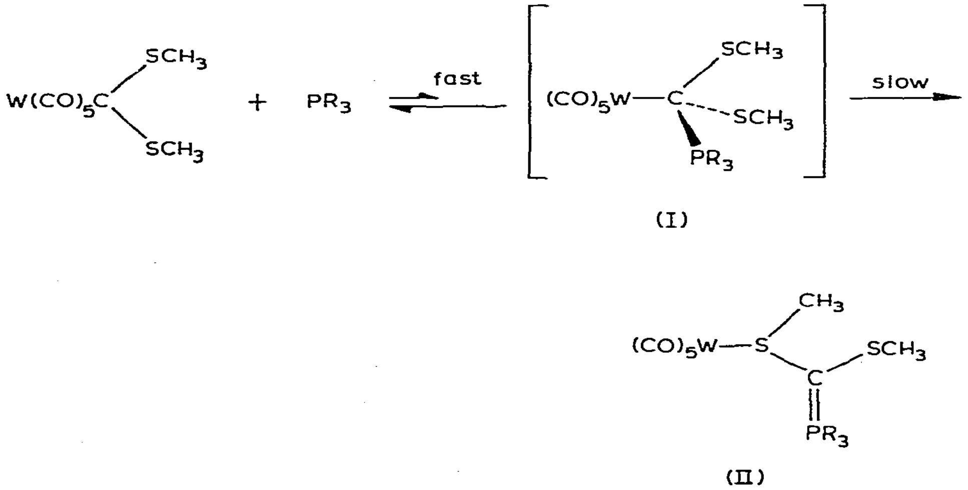
Mechanism of the reaction of $W(CO)_5[C(SCH_3)_2]$ with PR_3 and PPh_2H

The second order rate law which has been observed for the reaction of

$W(CO)_5[C(SCH_3)_2]$ with phosphines is consistent with the following two mechanisms (eqs. 6 and 7):



(6)

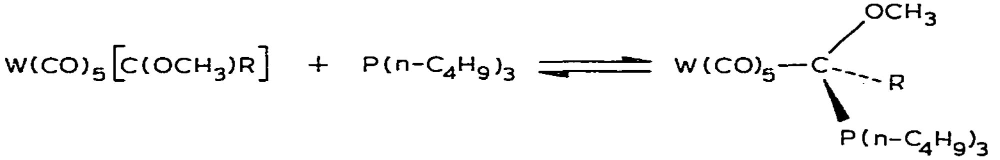


(7)

In mechanism 6, nucleophilic attack of the phosphine is the rate determining step, which is followed by a rapid rearrangement to produce the phosphorane product. In mechanism 7, the first step is a rapid equilibrium which lies far to the left, and the rate determining step is the rearrangement from the carbene-phosphine adduct to the phosphorane. Although mechanism 7 cannot be eliminated unequivocally, we believe the results best fit mechanism 6.

Mechanism 7 would suggest that intermediate I might be observable at high concentrations; however, infrared spectra of the $\nu(CO)$ region show no evidence of any intermediate in the reaction at dithiocarbene concentrations of approximately 50 times greater than those used in the kinetic runs. It should be noted however, that other carbene-phosphine adduct complexes have been well characterized by others [13]. The fact that they are not observed here seems to indicate that once formed they rapidly rearrange to the phosphorane product or they are in such low concentration in the reaction mixture that they cannot be observed, which is consistent with either of the proposed mechanisms.

From equilibrium constants [7,9] of the reaction of oxo-alkyl and oxo-aryl carbene tungsten complexes with $P(n\text{-}C_4H_9)_3$ to form carbene-phosphine adducts (eq. 8) it may be determined that adduct formation with the oxo-



$$W(CO)_5[C(OCH_3)R] + P(n\text{-}C_4H_9)_3 \rightleftharpoons W(CO)_5\text{—}C(OCH_3)(R)[P(n\text{-}C_4H_9)_3] \qquad (8)$$

$R = CH_3$ and $p\text{-}C_6H_4(CF_3)$

carbenes $W(CO)_5[C(OCH_3)R]$ is more favorable than with $W(CO)_5[C(SCH_3)_2]$. At 20°C and concentrations similar to those used in the kinetic experiments about 20% of $W(CO)_5\{C(OCH_3)[p\text{-}C_6H_4(CF_3)]\}$ and 80% of $W(CO)_5[C(OCH_3)(CH_3)]$ would be converted to the carbene-phosphine adducts. The much smaller amount of adduct formation in the dithiocarbene system may be due to the better electron donating ability of the S atoms, as compared to the O and C atoms in the $W(CO)_5[C(OCH_3)R]$ complexes [18,19].

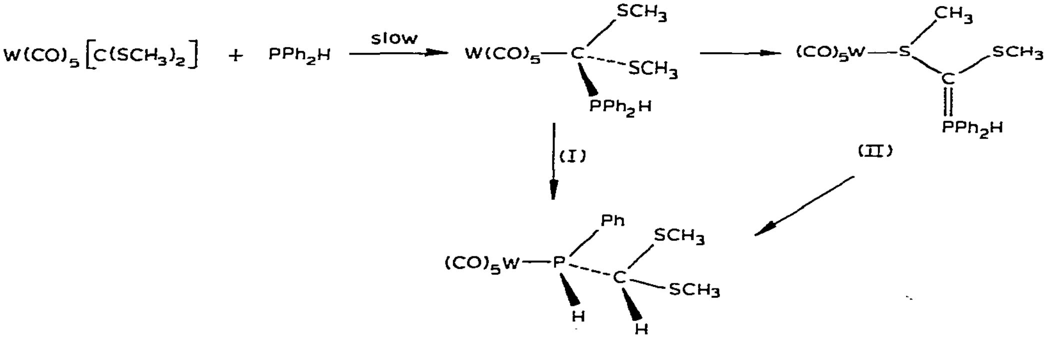
Support for the nucleophilic attack of the phosphines as being the slow step (eq. 6) may be found in the trend of k values. These values (Table 2) decrease with decreasing basicities and nucleophilicities of the phosphine ligands: $P(C_2H_5)_3 > PPh(CH_3)_2 \simeq PPh_2(CH_3) > PPh_2H > P(OCH_3)_3$ [20—23]. (Although the nucleophilicity of PPh_2H is not known exactly, Ellgen and Gerlach [23] found that rates for nucleophilic attack of phosphorus ligands on $Fe_2(CO)_6S_2\text{-}C_6H_3CH_3$ decrease in the following order: $P(n\text{-}C_4H_9)_3 > PPh_2H > P(OCH_3)_3$.) It should be noted that the PPh_2H reaction, which leads to an entirely different product, proceeds at a rate which is consistent with the nucleophilicity of PPh_2H. If rearrangement of the intermediate to the product were rate determining, one might expect the rate of this reaction to be quite different than those which lead to the phosphorane products (eq. 4).

The $\Delta H^{\ddagger}$ values for reaction 4 increase ($P(C_2H_5)_3 < PPh(CH_3)_2 < PPh_2(CH_3) < PPh_2H < P(OCH_3)_3$) with decreasing nucleophilic strength of the phosphines (Table 3).

Neither the nucleophilicities of the phosphines nor the types of product formed has a significant influence on the $\Delta S^{\ddagger}$ values (Table 3). They remain essentially constant for all of the phosphines used in this study. The negative values of $\Delta S^{\ddagger}$ (approximately —30 e.u.) support an associative type of mechanism, but they are somewhat less negative than those of —40 e.u. found for reactions shown in eq. 8. This difference may reflect the greater disorder in the activated complex leading to intermediate I as compared to an isolable carbene-phosphine adduct (eq. 8). Entropies of activation for the reactions of the diarylcarbene complexes, $W(CO)_5[CAr_2]$ with Me_2NCN are also approximately

—30 e.u.; these reactions are suggested to proceed by a mechanism similar to that of eq. 6.

In the reaction of the secondary phosphine PPh_2H with $W(CO)_5[C(SCH_3)_2]$, two routes may be considered for the formation of the phosphine product from the carbene-phosphine adduct (eq. 9):



(9)

Adduct I could rearrange to a phosphorane intermediate (II) (as in the case of the tertiary phosphines) which could then convert to the phosphine product by migration of the H atom from the P to the basic carbon atom followed by migration of the P atom to the W. Alternatively, intermediate I could rearrange directly by H atom migration to the C and P migration to the W. From our kinetic information it is impossible to distinguish between these routes. Even though we have not observed I during the course of these kinetic studies, its formation is supported by the work of Fischer et al. [7]. They have isolated the carbene-phosphine adduct $(CO)_5Cr\{C(OCH_3)(Ph)[P(CH_3)_2H]\}$ and found that upon stirring in acetone for 8 hours at 25°C, it rearranges to the phosphine complex $(CO)_5Cr\{P(CH_3)_2[C(OCH_3)(Ph)H]\}$.

Reactions of phosphines with $W(CO)_5[\overline{CS(CH_2)_nS}]$

As for $W(CO)_5[C(SCH_3)_2]$ (eq. 4) [15], the 6- and 7-membered cyclic dithiocarbene tungsten complexes react with $PPh_2(CH_3)$ to form cyclic phosphorane complexes (eq. 10)

$$\underset{\text{(III)}}{W(CO)_5[\overline{CS(CH_2)_n S}]} + PPh_2CH_3 \rightarrow \underset{\text{(IVa, } n = 3\text{; IVb, } n = 4\text{)}}{(CO)_5W[\overline{S(CH_2)_n SC} = PPh_2(CH_3)]} \tag{10}$$

TABLE 4

INFRARED SPECTRA OF CARBENE AND PHOSPHORANE COMPLEXES

Complex		ν(CO) (cm^{-1})
$W(CO)_5[\overline{CS(CH_2)_2S}]$ [a, b]	(IIIa)	2069w, 1950s
$W(CO)_5[\overline{CS(CH_2)_3S}]$ [a, b]	(IIIb)	2067w, 1944s
$W(CO)_5[\overline{CS(CH_2)_4S}]$ [a, b]	(IIIc)	2067w, 1950(sh), 1944s
$W(CO)_5[\overline{S(CH_2)_3SC}{=}PPh_2(CH_3)]$ [c]	(IVa)	2066w, 1938s, 1915m
$W(CO)_5[\overline{S(CH_2)_3SC}{=}PPh_2(CH_3)]$ [b]	(IVb)	2069w, 1934s, 1917m
$W(CO)_5[PPh_2\overline{C(H)S(CH_2)_3S}]$ [c]	(Va)	2071w, 1942s
$W(CO)_5[PPh_2\overline{C(H)S(CH_2)_4S}]$ [b]	(Vb)	2072w, 1947(sh), 1942s

[a] Ref. 16. [b] In hexanes. [c] In cyclohexane.

TABLE 5

^{13}C NMR SPECTRA OF CARBENE AND PHOSPHORANE COMPLEXES IN $CDCl_3$ [a] (ppm)

Complex	Carbene	*trans* CO	*cis* CO	Others
IIa [b]	282.2	204.6	196.0	47.8 (SCH_2)
IIb [b]	277.5	204.3	196.7	36.3 (SCH_2); 17.4 (CH_2)
IIc [b]	291.1	205.3	197.5	44.3 (SCH_2); 26.7 (CH_2)
IVa [c]		204.1	200.3	133.9, 133.5, 130.9, 130.4, 129.6 (Ph); 39.0, 27.3 (SCH_2); 34.7 (d, PCS_2) [d], 14.9 (d, PCH_3) [e]
IVb		201.7	198.5	131.7, 131.2, 129.0, 128.5, 127.9 (Ph); 50.5, 37.2 (SCH_2); 28.4, 27.9 (CH_2); 20.3 (d, PCS_2) [f]; 13.2 (d, PCH_3) [g]
Vb		198.7(d) [h]	196.6(d) [i]	134.4, 133.0, 132.4, 130.2, 128.0, 127.6(Ph); 52.1 (PCS_2) [j]; 32.6 (d, SCH_2) [k]; 30.9 (CH_2)

[a] All resonances are singlets unless otherwise stated. [b] Ref. 17. [c] Solvent CD_3CN. [d] $J(PC) = 78.2$ Hz. [e] $J(PC) = 65.4$ Hz. [f] $J(PC) = 124.8$ Hz. [g] $J(PC) = 64.6$ Hz. [h] $J(PWC) = 23.5$ Hz. [i] $J(PWC) = 5.9$ Hz. [j] $J(PC) = 11.7$ Hz. [k] $J(PC) = 5.9$ Hz.

The spectral characteristics of IVa and IVb are very similar to those of the phosphorane complexes, $W(CO)_5[(CH_3S)_2C{=}PR_3]$, reported earlier [15]. Their infrared spectra (Table 4) contain three ν(CO) absorptions consistent with the pseudo C_{4v} symmetry of the molecule. The ^{1}H and ^{13}C NMR spectra (Table 5) of IVa and IVb show separate resonances for the two different methylene groups on the sulfur atoms.

The complexes IVa and IVb are yellow crystalline solids. In the solid state, the complexes are stable at −20°C. They are soluble in $CHCl_3$ and CH_2Cl_2, but when exposed to air their solutions show evidence of decomposition within 2 to 4 hours.

The reactivities of the cyclic dithiocarbene tungsten complexes according to eq. 10 increase as the ring size increases. The 7- and 6-membered cyclic dithiocarbenes react in approximately 1.5 hours at room temperature with one and two equivalents of phosphine ligand, respectively. The 5-membered cyclic carbene complex $W(CO)_5[\overline{CS(CH_2)_2S}]$ [16] reacts much more slowly. Reaction occurs upon heating with two equivalents of PPh_2CH_3 in cyclohexane at 60°C for a minimum of 12 hours; however, the product appears to be $W(CO)_5PPh_2CH_3$, rather than the phosphorane. The difference in reactivity may be explained on the basis of steric hindrance. The 5-membered ring is fairly inflexible and allows for little movement to reduce steric hindrance as the $PPh_2(CH_3)$ ligand approaches. Although the 6-membered ring allows for some rearrangement to relieve steric problems, the 7-membered ring has even more flexibility.

Like $W(CO)_5[C(SCH_3)_2]$ (eq. 4) [15], the 6- and 7-membered cyclic dithiocarbenes also react with PPh_2H to form phosphine products (eq. 11):

$$\underset{\text{(III)}}{W(CO)_5[\overline{CS(CH_2)_nS}]} + PPh_2H \rightarrow \underset{\text{(Va, } n = 3\text{; Vb, } n = 4\text{)}}{W(CO)_5\{PPh_2[\overline{CS(CH_2)_nS}(H)]\}} \qquad (11)$$

The PPh_2H reacts slower than $PPh_2(CH_3)$ as would be expected on the basis of their nucleophilicities. Ring size again determines the rate of reaction since the 7-membered ring reacts much more rapidly than the 6-membered ring. The phosphine products are yellow solids which may be stored at −20°C for months. They are soluble in organic solvents ranging in polarity from hexane to CH_2Cl_2. Like $W(CO)_5\{PPh_2[C(H)(SCH_3)_2]\}$ [15], the structural assignment of Vb was based on its ^1H and ^{13}C NMR spectra (Table 5). Consistent with the structure are the equivalence of both SCH_2 groups in both the ^1H and ^{13}C spectra of the complex. The *J*(PWC) values for the *cis* and *trans* CO groups (5.9 and 23.5 Hz, respectively) are very similar to those in related $W(CO)_5PR_3$ complexes [15,25,26]. The small *J*(PH) value (3 Hz) is consistent with the hydrogen atom being bound to the carbon atom rather than remaining on the phosphorus [27].

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