Reactions of $(CO)_5WCHC_6H_5$ with Alkenes

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Abstract: Addition of CF_3CO_2H to a CH_2Cl_2 solution of $N(CH_2CH_3)_4^+(CO)_5WCH(OCH_3)C_6H_5^-$ (**5**) at −78 °C produces a red solution of $(CO)_5WCHC_6H_5$ (**4**), which was characterized by low-temperature ^1H NMR and by reaction with $P(n\text{-}Bu_3)$ to give $(CO)_5WCH[P(n\text{-}Bu)_3]C_5H_5$ (**6**). Thermal decomposition of **4** at −56 °C occurs with a half-life of 24 min. The reaction of **4** with alkenes occurs rapidly at −78 °C to give phenylcyclopropanes; no metathesis-like products were observed. The relative reactivity of alkenes toward **4** was in the order $CH_2{=}C(CH_3)_2 > CH_2{=}CHCH_3 \gg CH_2{=}CH_2$, indicating that the reaction involved electrophilic attack of the carbene complex on the alkene. The stereochemistry of cyclopropane formation could not be explained in terms of formation of the most stable intermediate metallacyclobutane. The stereochemistry of cyclopropane formation is explained in terms of transition state **25** which involved formation of a bond from the carbene carbon atom of **4** to the less substituted end of an alkene and interaction of the positively polarized, more substituted end of the alkene with the ipso carbon atom of the phenyl group of **4**.

Introduction

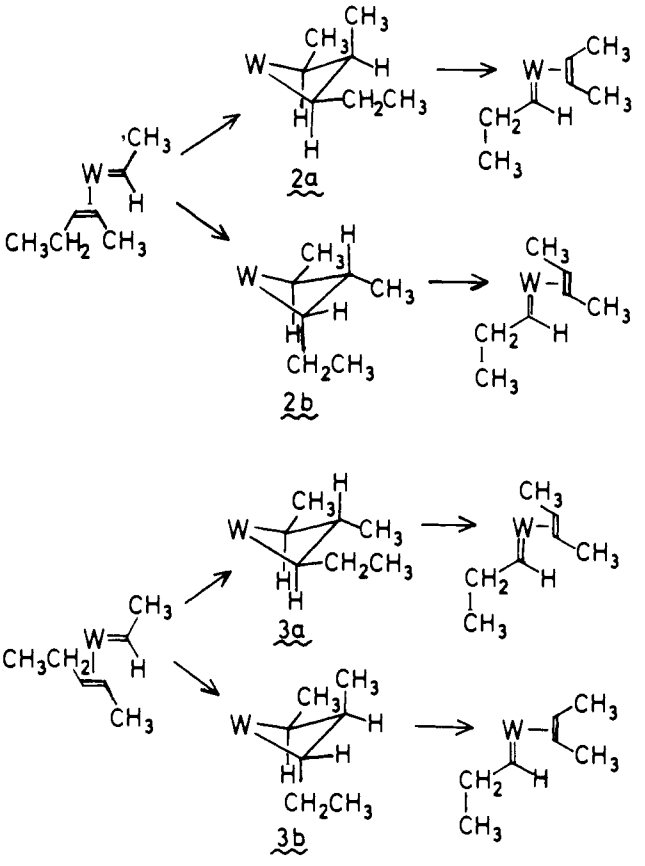
$(CO)_5WC(C_6H_5)_2$ (**1**) reacts with alkenes to give cyclopropanes, olefin scission products, and new carbene complexes.[1] A mechanistic scheme involving the equilibrium between a metallacyclobutane and a metal complex bearing both an alkene and a carbene ligand was proposed to explain these results. Earlier, a similar equilibration had been suggested by Herrisson and Chauvin[2] as a sufficient mechanism for the olefin metathesis reaction.[3] The recent demonstrations that the olefin metathesis reaction proceeds via a nonpairwise exchange of alkylidene groups is consistent with the equilibrium between a metallacyclobutane and a metal complex bearing both carbene and alkene ligands and excludes mechanisms requiring the pairwise exchange of alkylidene groups of a pair of alkenes complexed to a metal.[4]

We have pointed out that the moderate stereospecificity observed in the metathesis of 2-pentenes[5] can be explained in terms of the formation of the more stable puckered metallacyclobutane in which repulsive 1,3-diaxial interactions are minimized.[6,7] The X-ray crystal structure of $(C_3H_6)Pt(C_6H_5N)_2Cl_2$, a metallacyclobutane, indicates that the four-membered ring is puckered: the angle between the plane of the three carbon atoms and the plane of the platinum and two attached carbon atoms is 12.5°.[8] In the related compound $[C_3H_4(C_6H_5)_2]PtCl_2(C_5H_5N)_2$ the ring puckering angle is 28.4°.[9] As a consequence of the ring puckering, the substituents on the ring occupy pseudoaxial and pseudoequatorial positions. Initially, we proposed that the most important steric interaction in the metallacyclobutane would be the 1,3-diaxial interaction between the substituents attached to the carbons bonded to the metal.[10]

A metal complex bearing both a *cis*-2-pentene and an ethylidene ligand can rearrange to form two stereochemically different metallacyclobutane intermediates (Scheme I). Intermediate **2a** is more stable than intermediate **2b**, which has a destabilizing 1,3-diaxial interaction between ethyl and hydrogen. Consequently, cyclization to give **2a** should be preferred and *cis*-2-butene which arises from decomposition of **2a** should be the kinetically favored product. Similarly, the greater stability of **3a** relative to **3b** explains the preferred formation of *trans*-2-butene from *trans*-2-pentene.

A study of the reactions of cis and trans disubstituted alkenes with a metal-carbene complex in which the carbene ligand possesses one sterically large and one sterically small substituent is essential to test the stereochemical implications of a puckered metallacyclobutane intermediate. The puckered

Scheme I



metallacyclobutane hypothesis predicts that the "large-small" carbene complex will react with cis alkenes to give new cis olefins and with trans alkenes to give new trans olefins. In addition, the preferential formation of cis cyclopropanes from the reaction of a "large-small" carbene complex with a 1-alkene would be expected.

Our initial attempts to test the puckered metallacyclobutane hypothesis were frustrated by the rapid decomposition of $(CO)_5WC(C_6H_5)CH_3$ via facile β-hydride elimination from the methyl group.[6] In another attempt to test the puckered metallacyclobutane hypothesis, we set out to prepare $(CO)_5WC(C_6H_5)H$ (**4**), which could not undergo decomposition by β-hydride elimination. Here we report the synthesis

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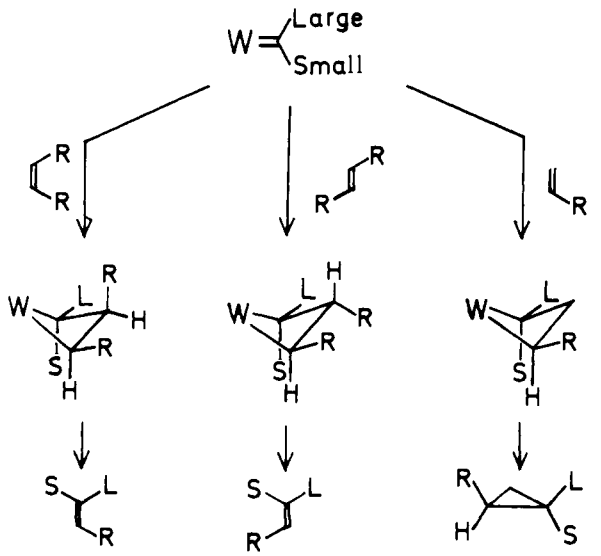


and characterization of **4** and its reactions with alkenes. Since **4** reacts with alkenes to give only cyclopropanes and not metathesis-like products, our attempt to test the puckered metallacyclobutane hypothesis was again frustrated. In a preliminary communication,[11] we suggested that the stereochemistry of the cyclopropanes formed from reaction of **4** with alkenes was controlled by the stability of the proposed puckered metallacyclobutane intermediate. However, the more detailed studies reported here disprove this proposal. The stereochemistry of cyclopropane formation and the relative rate of reaction of **4** with alkenes are explained by the mode of approach of the alkene toward the phenylcarbene complex. There may well be a metallacyclobutane intermediate formed subsequent to this transition state but the stereochemistry and rate of the reaction are determined at an earlier stage.

Results

Generation and Characterization of $(CO)_5WCHC_6H_5$. A two-step synthesis of phenylcarbenepentacarbonyltungsten (**4**) from $(CO)_5WC(OCH_3)C_6H_5$ involving hydride reduction followed by protonation was developed (Scheme II). Metal carbene complexes are readily attacked at the carbene carbon atom by nitrogen, sulfur, and carbon nucleophiles. Analogously, $K^+HB[OCH(CH_3)_2]_3^-$ reacts with $(CO)_5WC(OCH_3)C_6H_5$ to give an 86% yield of $N(CH_2CH_3)_4^+(CO)_5WCH(OCH_3)C_6H_5^-$ (**5**), isolated as a yellow, crystalline solid. The synthesis and X-ray crystal structure of **5** have been reported.[12] By analogy with the syntheses of $(CO)_5WC(C_6H_5)_2$[13] and of $(CO)_5WC(SC_6H_5)$-C_6H_5,[14] treatment of **5** with acid was expected to lead to protonation at the methoxy oxygen, followed by dissociation of methanol to give $(CO)_5WCH(C_6H_5)$ (**4**). Addition of 1.2 equiv of CF_3CO_2H to a 0.01 M solution of **5** in CH_2Cl_2 at −78 °C led to an immediate color change from light yellow to deep red. This color change is similar to that observed in the preparation of $(CO)_5WC(C_6H_5)_2$. The red solutions attributed to **4** did not change color at −78 °C over several hours. However, upon warming to 0 °C, the dark red color faded to light orange.

The 270-MHz ^1H NMR spectrum of the red solution obtained by addition of excess CF_3CO_2H to a 0.014 M solution of **5** in CD_2Cl_2 at −78 °C exhibited absorptions fully consistent with the formation of **4** (Figure 1). The phenyl region of the spectrum consisted of a two-proton doublet at δ 7.87 (J = 7.4 Hz, ortho H), a one-proton triplet at δ 7.79 (J = 7.4 Hz, para H), and a two-proton triplet at δ 7.48 (J = 7.7 Hz, meta H). In addition, the spectrum contained a one-proton singlet at δ 17.2 for the hydrogen attached directly to the electron-deficient

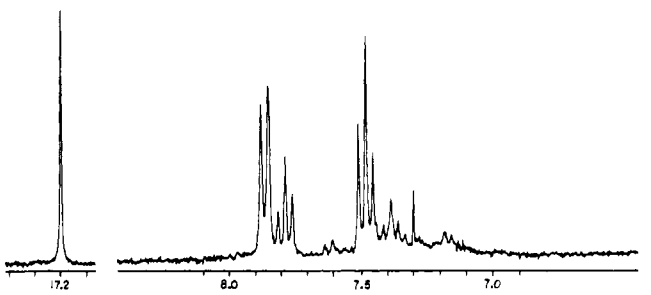
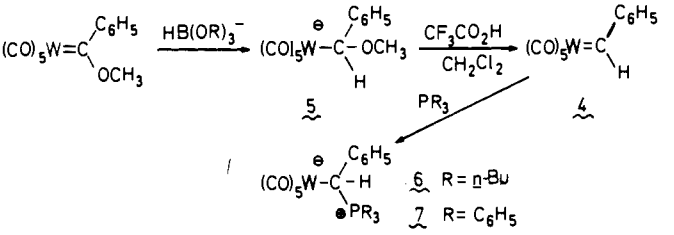


Figure 1. 270-MHz NMR spectrum of $(CO)_5WC(C_6H_5)H$ (**4**) in CD_2Cl_2 at −78 °C.

Scheme II



carbene carbon atom of **4**; similar chemical shifts have recently been reported by Brookhart[15] for cationic phenylcarbene complexes of iron. Upon warming to −56 °C, the absorptions attributed to **4** disappeared within 1.5 h. A plot of the logarithm of the intensity of the δ 17.2 signal vs. time was linear; the half-life for the first-order decomposition of **4** at −56 °C was 24 min.

The addition of nucleophiles to the carbene carbon atom of metal carbene complexes is a characteristic reaction and was used to chemically characterize $(CO)_5W{=}CHC_6H_5$ (**4**). Addition of 3 equiv of CF_3CO_2H to a solution of $N(CH_2CH_3)_4^+(CO)_5WCH(OCH_3)C_6H_5^-$ (**5**) in CH_2Cl_2 at −78 °C gave a deep red solution of **4**. After 5 min at −78 °C, tri-*n*-butylphosphine was added; the dark red color immediately disappeared and an orange solution was obtained. Silica gel chromatography gave a 47% yield of the phosphine adduct, $(CO)_5WCH[P(n\text{-}C_4H_9)_3]C_6H_5$ (**6**), as a pale yellow, crystalline solid. The infrared spectrum of **6** has four CO bands at 2060, 1968, 1915, and 1887 cm^{-1} and is similar to that of **5** and of alkylpentacarbonyltungsten anions.[16] In the 270-MHz ^1H NMR of **6**, the benzylic proton appears at a doublet split by ^{31}P (15.1 Hz) with satellite peaks due to coupling (6.4 Hz) to ^{183}W (natural abundance 14.4%). When CF_3CO_2H was added to a solution of **5** and $P(n\text{-}Bu)_3$ in CH_2Cl_2 at −78 °C, adduct **6** was isolated in 90% yield. When CF_3CO_2H was added to a solution of **5** and $P(C_6H_5)_3$ in CH_2Cl_2 at −78 °C, a 90% yield of the adduct $(CO)_5WCH[P(C_6H_5)_3]C_6H_5$ (**7**) was obtained.

Reaction of $(CO)_5WCHC_6H_5$ with Alkenes. The synthesis of **4** was undertaken in the hope that the reactions of **4** with alkenes might provide a model system which would aid in understanding the retention of stereochemistry observed in the olefin metathesis reaction. However, we have never observed metathesis-like products from the reaction of **4** with alkenes. In all cases, the major products obtained from the reaction of **4** with alkenes were phenylcyclopropanes.

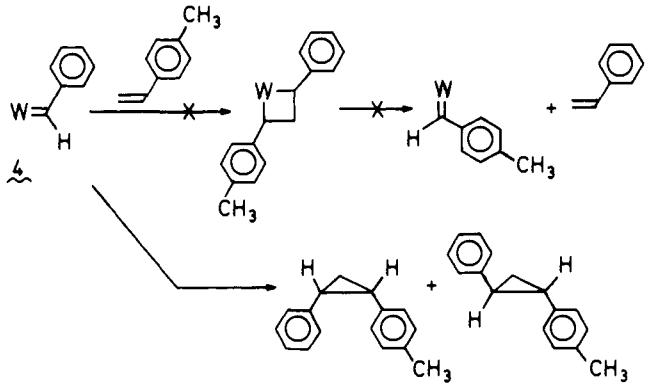
The reaction of **4** with *p*-methylstyrene was studied since it provides a favorable case for formation of metathesis-like products. The expected metallacyclobutane intermediate would be nearly symmetric and might readily give styrene and a *p*-tolylcarbene complex by fragmentation; however, no styrene was observed (<0.2% could have been detected). The major products were *cis*- and *trans*-phenyltolylcyclopropane.

Table I. Phenylcyclopropanes from Reaction of $(CO)_5WCHC_6H_5$ (**4**) with Alkenes[a]

alkene	phenylcyclopropane yield, %	cis:trans ratio
$CH_2{=}CH_2$	<0.1	
$CH_2{=}CHCH_3$	82	1.8
$CH_2{=}CHCH_2CH_3$	73	0.9
$CH_2{=}CHCH(CH_3)_2$	72	0.36
$CH_2{=}CHC(CH_3)_3$	69	0.01
$CH_2{=}CHC_6H_5$	39	9.7
$CH_2{=}C(CH_3)_2$	98	
cis-$CH_3CH{=}CHCH_3$	60	41[b]
trans-$CH_3CH{=}CHCH_3$	82	*c*
$CH_3CH{=}C(CH_3)_2$	81	94
$(CH_3)_2C{=}C(CH_3)_2$	36	
cyclopentene	40	2.6
1-methylcyclopentene	50	8[d]

[a] See Experimental Section for reaction conditions and analysis procedures. [b] A 41:1 ratio of *syn*-1-phenyl-*cis*-2,3-dimethylcyclopropane and *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropane was found. [c] Only 1-phenyl-*trans*-2,3-dimethylcyclopropane was observed. [d] An 8:1 ratio of *endo*-:*exo*-6-phenyl-1-methylbicyclo[3.1.0]hexane was observed.

Similarly the reaction of **4** with 1,1-di-*p*-tolylethylene was investigated as a favorable case for observing metathesis-like



products since cleavage of the metallacyclobutane could give the more stable $(CO)_4WC(C_6H_4CH_3)_2$. Again, none of the expected di-*p*-tolylcarbene complex was observed by TLC analysis of the reaction mixture. The major product from the reaction was 1,1-di-*p*-tolyl-2-phenylcyclopropane, isolated in 37% yield by chromatography.

The reactions of alkenes with **4** were studied in CH_2Cl_2. The addition of 3 equiv of CF_3CO_2H to 0.01 M solutions of **5** in CH_2Cl_2 containing excess alkene resulted in the formation of the deep red color attributed to **4**. The reaction mixtures were stirred at −78 °C for 0.5–8.0 h depending upon the alkene, warmed to room temperature, and analyzed by gas chromatography (Table I). The identity of the phenylcyclopropane products was established by comparison of their gas chromatographic retention times with those of authentic samples and by comparison of the 270-MHz ^1H NMR spectra of the phenylcyclopropane products isolated by preparative gas chromatography with the spectra of authentic samples.

The stereochemistry of the cyclopropanes formed was of particular interest since the puckered metallacyclobutane hypothesis predicts the preferential formation of cis cyclopropanes. Fortunately, the assignment of relative stereochemistries for epimeric phenylcyclopropanes has been rigorously established by Closs and Moss.[17] Their NMR studies revealed that (1) alkyl groups cis to the phenyl groups are shielded, and therefore absorb at ~0.4 ppm higher field than trans alkyl groups, which in fact experience a small net deshielding; (2) for epimeric phenylcyclopropanes, the benzylic proton in the cis epimer absorbs at 0.3–0.5 ppm lower field than in the trans epimer;[18] (3) the coupling of cis vicinal cyclopropyl hydrogens (8–8.5 Hz) is larger than the coupling of trans vicinal cyclopropyl hydrogens (5–5.5 Hz). Any ambiguities resulting from the overlap of important absorptions in the 60-MHz NMR spectra of Closs and Moss have essentially been eliminated in our studies by obtaining spectra at 270 MHz (see Table IV, Experimental Section). Closs and Moss's NMR assignments are further supported by the equilibration of *syn*- and *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropane,[17] of *cis*- and *trans*-1-*p*-tolyl-2-*tert*-butylcyclopropane,[18] and of *cis*- and *trans*-1-*p*-tolyl-2-isopropylcyclopropane[18] using potassium *tert*-butoxide in dimethyl sulfoxide and by the stereospecific conversion of *trans*-1-phenyl-1-butene to *trans*-1-phenyl-2-ethylcyclopropane using the Simmons–Smith reaction.[17]

Several aspects of the reactions of **4** with alkenes merit special comment. First, ethylene was the only alkene that failed to react with **4**; mono-, di-, tri-, and tetrasubstituted alkenes all reacted with **4** to give cyclopropanes. Second, the reactions of **4** with *cis*- and with *trans*-2-butene led to formation of cyclopropanes with complete retention of the stereochemistry of the alkene precursor. In the case of *cis*-2-butene, the syn,cis isomer was formed preferentially. Third, for monosubstituted alkenes $CH_2{=}CHR$ there was a progressive change of the cyclopropane cis:trans ratio to lower values as R became sterically larger in the series R = methyl, ethyl, isopropyl, *tert*-butyl.

Relative Reactivity of Alkenes toward $(CO)_5WCH(C_6H_5)$. The relative reactivity of alkenes toward $(CO)_5WCHC_6H_5$ (**4**) was determined using competition techniques (Table II). **4** was generated in the presence of a large excess of a mixture of two different alkenes and the ratio of cyclopropanes formed was determined by gas chromatography. Good reproducibility was obtained in the competition studies; for example, the relative reactivity of propene:*cis*-2-butene was found to be 1.36 and 1.44 in two separate determinations. Direct competition between *cis*-2-butene and *trans*-2-butene gave a relative reactivity of 2.21 in close agreement with a relative reactivity of 2.06 calculated from competition of propene vs. *cis*-2-butene (1.40) and propene vs. *trans*-2-butene (2.89).

The results in Table II indicate that the reactivity of the alkenes is determined by the number of alkyl groups attached to the *more substituted* end of the carbon–carbon double bond. Thus, 2-methylpropene is 318 times more reactive than propene and ethylene gave no observable reaction.

The high reactivity of *gem*-dialkyl substituted alkenes led to experimental difficulties as illustrated by the reaction of **4** with commercial 1-butene containing less than 1% isobutylene, which gave 59% 1,1-dimethyl-2-phenylcyclopropane and 20% of 1-ethyl-2-phenylcyclopropane. When the same reaction was carried out using 1-butene which had been purified by preparative gas chromatography, none of the adduct of isobutylene was detected. Similar problems from contaminants in commercial 3,3-dimethyl-1-butene were also encountered. Four cyclopropane products were isolated from the reaction, none of which corresponded to the expected 1-phenyl-2-*tert*-butylcyclopropanes. When the reaction was run using 3,3-dimethyl-1-butene synthesized by a Wittig reaction of pivalaldehyde and methylenetriphenylphosphorane, *trans*-1-phenyl-2-*tert*-butylcyclopropane was formed in 69% yield.

The relative reactivity of monosubstituted alkenes $CH_2{=}CHR$ decreased as the bulk of the R group increased: R = $-CH_3$ (11); $-CH_2CH_3$ (5.6); $-CH(CH_3)_2$ (2.4); $-C(CH_3)_3$ (1).

NMR of Reactions of Alkenes with $(CO)_5WC(C_6H_5)H$. In an attempt to determine whether observable intermediates are formed in the reactions of **4** with alkenes at −78 °C, the re-

Table II. Relative Reactivities of Alkenes toward $(CO)_5WCHC_6H_5$[a]

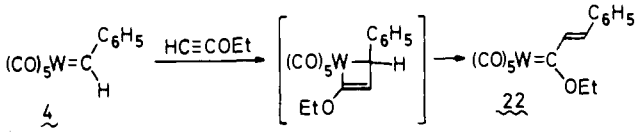
alkene	rel reactivity	cyclopropane cis:trans ratio	rel rate of formation of cyclopropanes	
			cis	trans
$CH_2{=}CH_2$	0			
$CH_2{=}CHC(CH_3)_3$	1.0	0.01	0	1.0
$CH_2{=}CHCH(CH_3)_2$	2.4	0.36	0.64	1.7
$CH_2{=}CHCH_2CH_3$	5.6	0.9	2.7	2.9
$CH_2{=}CHCH_3$	11	1.8	7.0	3.9
trans-$CH_3CH{=}CHCH_3$	3.5			
cis-$CH_3CH{=}CHCH_3$	7.6	41[b]	7.4[b]	0.2[b]
$CH_2{=}C(CH_3)_2$	3500			
$CH_3CH{=}C(CH_3)_2$	820	94	811	9
$(CH_3)_2C{=}C(CH_3)_2$	3.5			
cyclopentene	6.0	2.6	4.3	1.7
$CH_2{=}CHC_6H_5$	410	9.7	371	38

[a] See Experimental Section for details. [b] Ratio of *syn*-:*anti*-1-phenyl-*cis*-2,3-dimethylcyclopropanes. Ratio of *endo*-:*exo*-6-phenylbicyclo[3.1.0]hexane.

actions with *cis*-2-butene and with isobutylene were monitored by low-temperature NMR spectroscopy. The addition of excess CF_3CO_2H to a 0.035 M solution of **5** in CD_2Cl_2 at −78 °C which contained an excess of isobutylene gave a red color attributed to **4**. After 5 min at −78 °C the red color had completely faded. An NMR spectrum at −78 °C of the resulting light yellow solution exhibited two singlets of equal intensity at δ 0.68 and 1.22. Warming the solution had no appreciable effect on these peaks other than a slight shift of the high-field absorption to δ 0.72. The NMR spectrum of authentic 2,2-dimethyl-1-phenylcyclopropane (**13**) exhibits methyl singlets at δ 0.74 and 1.22 in $CDCl_3$ at ambient probe temperature.

The reaction of **4** with *cis*-2-butene gave similar results. However, the reaction was slow at −78 °C. After 2 h the absorptions due to **4** had diminished only slightly in intensity. Upon raising the temperature of the sample to −56 °C the absorptions of **4** disappeared within 40 min. Simultaneous with the disappearance of **4**, two pseudodoublets at δ 0.83 and 2.08 were observed. Raising the temperature further resulted in a slight shift of the high-field doublet to δ 0.92 and an increase in the intensity of the δ 2.08 absorption. Based on a decoupling experiment, the δ 2.08 doublet was assigned to $(CO)_5W$(*cis*-2-butene). The δ 0.92 absorption was assigned to the methyl groups of *syn*-1-phenyl-*cis*-2,3-dimethylcyclopropane (**15s**). The NMR spectrum of authentic cyclopropane shows an identical chemical shift and coupling pattern for the syn methyl group.

Reaction of $(CO)_5WCHC_6H_5$ with Ethoxyacetylene. The reaction of $N(CH_2CH_3)_4^+(CO)_5WCH(OCH_3)C_6H_5^-$ (**5**) with CF_3CO_2H in the presence of excess ethoxyacetylene gave a 21% yield of the styrylethoxycarbene complex, **22**, which is



the product of insertion of ethoxyacetylene into the carbene metal bond. The reaction can be envisioned as proceeding via a metallacyclobutene intermediate. Ethoxyacetylene also reacts with $(CO)_5WC(C_6H_5)_2$, $(CO)_5WC(OCH_3)C_6H_5$, and $(CO)_5WC(OCH_3)CH_2CH_2CH_2CH_3$ to give similar products in which ethoxyacetylene has been inserted into the carbene-metal bond.

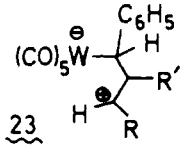
Discussion

Electrophilic Character of Carbene Carbon of 4. The reaction of $(CO)_5WCH(OCH_3)C_6H_5^-$ with acid at low temperature generates a reactive, highly electrophilic phenylcarbene complex. The electrophilic nature of the carbene carbon of $(CO)_5WCHC_6H_5$ (**4**) is reflected in the ^1H NMR of the complex—the proton attached to the carbene carbon atom appears at δ 17.2. The extreme downfield shift of this proton is probably due both to its attachment to a very electron-deficient carbene carbon atom and to the magnetic anisotropy of the neighboring W=C double bond. The electrophilic nature of the carbene carbon atom is also demonstrated by the reaction of phosphines with **4** to give stable adducts.

The relative reactivity of alkenes toward $(CO)_5WCHC_6H_5$ (**4**) can be understood in terms of an initial interaction between the electrophilic carbene carbon atom and one terminus of the alkene. Thus, $(CH_3)_2C{=}CH_2$ is much more reactive than $CH_3CH{=}CH_2$ toward **4** and ethylene is the only alkene which does not react with **4** to give cyclopropanes. The similar reactivities of propene and the 2-butenes and of $(CH_3)_2C{=}CH_2$ and $(CH_3)_2C{=}CH(CH_3)$ demonstrate that the number of substituents attached to the more substituted end of the alkene controls the relative reactivity of alkenes. This reactivity pattern suggests that reaction of an alkene with **4** proceeds via a transition state in which positive charge develops at only one carbon atom of the alkene.

The reactivity pattern of **4** toward alkenes is the opposite of that observed in the reactions of $(CO)_5WC(C_6H_5)_2$ (**1**) with alkenes. For **1**, the least substituted alkene was the most reactive; the relative reactivities of 1-pentene:isobutylene:*cis*-2-butene were 49:10.4:1.[19] The reactivity pattern for **1** is similar to the relative stability of Ag^+ and Ni complexes of alkenes.[20] The exchange of ^{13}CO with **1** has a half-life of 21 h at 30 °C[21] and is fast relative to the reaction of **1** with alkenes. Thus, we have proposed that the reactions of $(CO)_5WC(C_6H_5)_2$ (**1**) with alkenes proceed by prior CO dissociation and formation of an intermediate $(CO)_4W$(alkene)(carbene) complex. The contrasting electrophilic reactivity pattern of **4** leads us to believe that the reaction of **4** with alkenes proceeds without prior formation of an alkene-metal complex. In addition, it seems unlikely that **4** would dissociate CO rapidly enough at −78 °C for a $(CO)_4WCHC_6H_5$ intermediate to be important in the reactions of **4**.

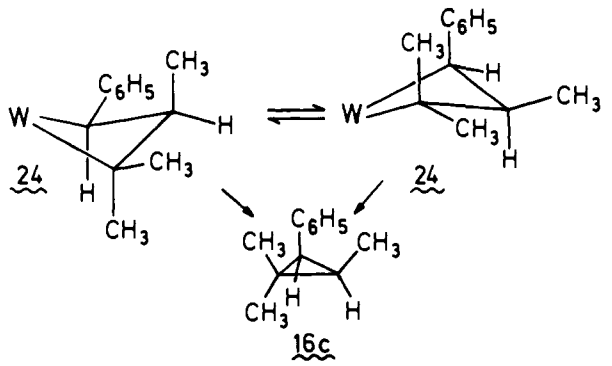
While some positive charge is built up on one carbon of an alkene at the transition state for reaction with **4**, three lines of evidence demonstrate that a carbonium ion intermediate such as **23** is not involved. First, while added alkyl groups on an al-



kene substantially increased the reactivity toward **4**, the reactivity increase is much less than the 10^6-10^8 expected from

the relative stability of secondary and tertiary carbonium ions.[21] Second, if the reaction proceeded through **23**, rotation about the carbon–carbon bond of the alkene would have been expected to occur and to lead to nonstereospecific cyclopropane formation; in contrast, both *cis*- and *trans*-2-butene react stereospecifically with **4** to give cyclopropanes. Third, if reaction of **4** with $CH_2{=}CHC(CH_3)_3$ occurred via an intermediate such as **23**, then methyl migration to the positive center would have been expected to lead to rearrangement products;[22] the reaction of **4** with $CH_2{=}CHC(CH_3)_3$ led to no rearrangement products.

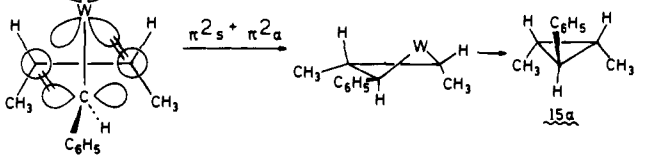
Rejection of Metallacyclobutane Explanation of Cyclopropane Stereochemistry. In our preliminary communication, the preferred cis stereochemistry of the cyclopropanes obtained on reaction of **4** with propene was explained in terms of formation of the most stable metallacyclobutane intermediate with equatorial phenyl and methyl groups. This explanation fails to explain why *cis*-2-butene should react to give a higher (41:1) cis:trans ratio than is obtained from propene (1.8:1). The introduction of an axial methyl group on the β carbon of the metallacyclobutane would have been expected to destabilize the intermediate and give rise to a decreased cis:trans ratio of cyclopropanes. The puckered metallacyclobutane hypothesis totally fails to explain the smooth decrease in cis:trans ratio of cyclopropane formed from monosubstituted alkenes as the substituent becomes sterically larger. Finally, the puckered metallacyclobutane hypothesis totally fails to explain the highly selective formation of cis cyclopropane **16c** (cis:trans



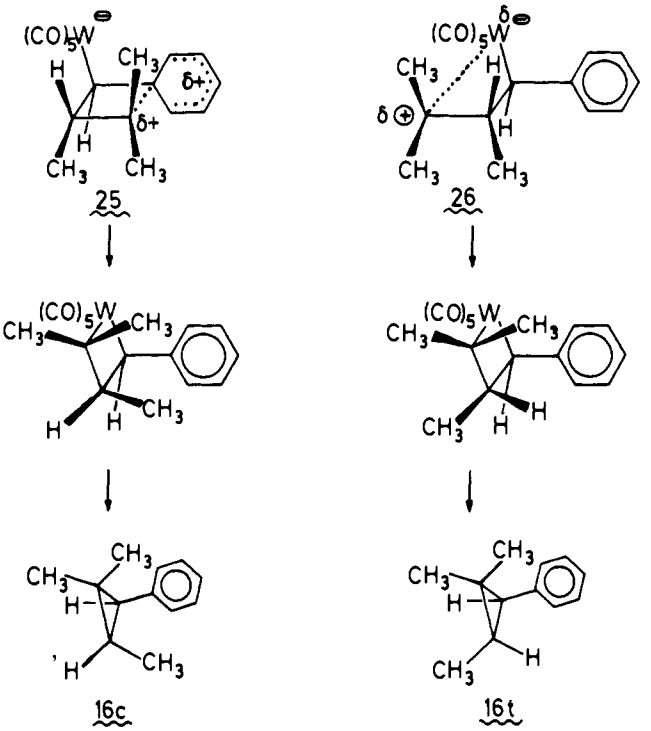
= 94:1) from the reaction of **4** with 2-methyl-2-butene. If the cyclopropane arises from a metallacyclobutane, then the cis stereochemistry requires intermediate **24** in which there is either a preference for an axial α-phenyl group or an axial β-methyl group. Examination of models indicates that the all-equatorial isomer which would give trans cyclopropane is less crowded than either conformation of **24.**

Clearly, the stereochemistry of cyclopropane formation is not being controlled by the stability of a related metallacyclobutane precursor. The transition state that controls the rate and stereochemistry of cyclopropane formation must be very different from a metallacyclobutane. The metallacyclobutane can be an intermediate in the formation of cyclopropanes only if it occurs after a transition state which determines the rate and the stereochemistry of cyclopropane formation.

The possibility that the reaction of **4** with alkenes proceeds by a $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition of the W=C double bond to the alkene to give a metallacyclobutane followed by reductive elimination of cyclopropane was briefly considered. Such a



Scheme III



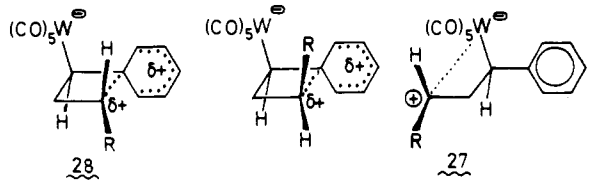
mechanism was rejected since it predicts preferred formation of anti cyclopropane from *cis*-2-butene.

π-Electron Donation from Phenyl to Developing Positive Center. The best explanation for the observed stereochemistry of cyclopropane formation that we have been able to concoct involves a competition between two processes—one normally dominant process leading selectively to cis cyclopropanes and a second process leading selectively to trans cyclopropanes (Scheme III). This mechanistic explanation can account for (1) the formation of cis cyclopropane from 2-methyl-2-butene, (2) the systematic change from a cis cyclopropane to a trans cyclopropane preference in the reaction of **4** with monosubstituted alkenes as the steric bulk of the substituent increases, and (3) the greater selectivity of cis cyclopropane formation from *cis*-2-butene than from propene.

A consideration of the reaction of **4** with 2-methyl-2-butene will illustrate the two processes. Transition state **25** suggested for the major pathway leading to cis cyclopropanes has extensive bond formation between the carbene carbon atom of **4** and the least substituted end of the alkene. Some positive charge is built up on the more substituted end of the alkene. Stabilization of this positive charge can be achieved if the positive carbon is held over the ipso carbon of the phenyl; this allows some π-electron donation from the phenyl ring to the partially positively charged more substituted carbon of the alkene. In this transition state, interaction between the bulky $W(CO)_5$ unit and cis alkyl group on the least substituted alkene carbon atom is substantial and causes 2-methyl-2-butene to approach so that the $W(CO)_5$ and methyl groups are separated as shown for **25.** The stereochemistry of the approach of the alkene to **4** is then largely controlled by interaction between the $W(CO)_5$ and methyl group. This interaction is responsible for the >94:1 preference for formation of the cis cyclopropane from 2-methyl-2-butene. It should be noted that the reactivity of **4** toward 2,3-dimethyl-2-butene is 230 times less than toward 2-methyl-2-butene and that the transition state for reaction with 2,3-dimethyl-2-butene necessarily involves a nearly eclipsing interaction between $W(CO)_5$ and a methyl group.

Rotation of the alkene carbon held over the phenyl ring in

Scheme IV. Relative Rates of Cyclopropene Formation Proceeding via Various Proposed Transition States



$-C(CH_3)_3$	0.0	0.0	1.0
$-CH(CH_3)_2$	0.6	0.7	1.0
$-CH_2CH_3$	2.7	1.9	1.0
$-CH_3$	7.0	2.9	1.0

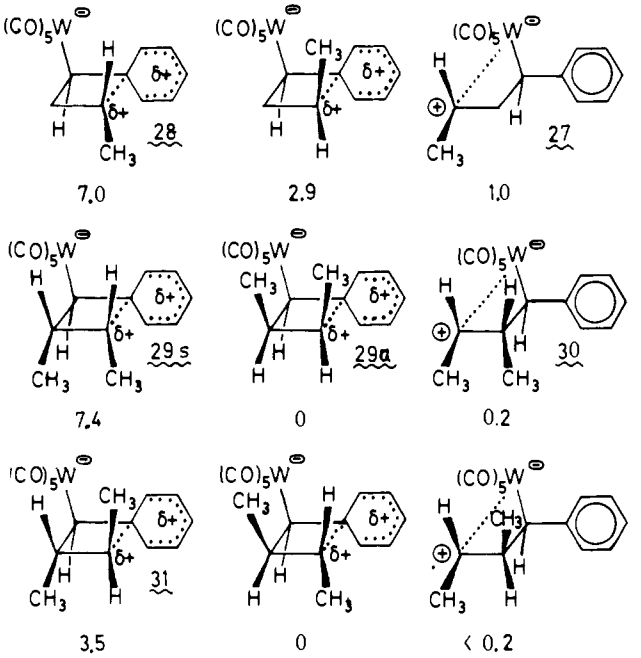
transition state **25** toward the $W(CO)_5$ unit leads to the geometry needed for cyclopropane formation. In the course of this rotation, a geometry similar to that of a metallacyclobutane is achieved. However, since the rate and stereochemistry of cyclopropane formation are determined by transition state **25**, we have no way of discerning whether a metallacyclobutane intermediate is involved at any stage in the reaction.

The stereochemistry of cyclopropanes formed from reaction of **4** with monosubstituted alkenes requires consideration of a second transition state **27** for reaction with alkenes bearing very bulky substituents (Scheme IV). We will begin by considering the reaction of **4** with *tert*-butylethylene, which gives a 99:1 ratio of trans:cis cyclopropanes. A transition state **28** involving phenyl participation similar to that which explains the selective formation of cis cyclopropane from 2-methyl-2-butene would be destabilized by a steric interaction between the phenyl group and the *tert*-butyl group of *tert*-butylethylene. Little reaction appears to go via this closed transition state. For *tert*-butylethylene, reaction involving the open transition state **27** would lead to trans cyclopropane. In transition state **27** (R = *t*-Bu), *tert*-butylethylene approaches the carbene carbon atom with the bulky *tert*-butyl group away from the $W(CO)_5$ fragment. The closed transition state **28** (R = *t*-Bu) is sufficiently destabilized that the majority of the cyclopropane is formed via the open transition state **27**. It should be pointed out that *tert*-butylethylene was the least reactive alkene toward **4** and reacted more than ten times slower than propene.

In proceeding down the series of isopropylethylene, 1-butene, and propene, the size of the alkyl group decreases continuously and the rate of reaction of the alkenes with **4** increases steadily. Reactions proceeding via the open transition state **27** which leads to trans cyclopropane should occur at approximately the same rate as for *tert*-butylethylene. The increased reaction rate as the size of the alkyl substituent decreases can be attributed to increased rates of reaction proceeding via the closed transition state **28**. In the closed transition state, the alkyl group has a minor preference for a trans orientation relative to the $W(CO)_5$ group three carbons removed and this orientation leads to selective formation of cis cyclopropanes.[23] Thus, as the bulk of the substituent on the more substituted alkenes is decreased, there is a shift from preferred reaction via an open transition state **27** which favors trans cyclopropanes to a closed transition state **28** that favors cis cyclopropanes.

This mechanistic scheme also provides a rationale for the higher syn:anti cyclopropane ratio observed for *cis*-2-butene as compared with propene (Scheme V). For *cis*-2-butene, two closed transition states could lead to cyclopropane formation. Transition state **29s** with both alkyl groups away from the bulky $W(CO)_5$ unit should lead to reaction at about the same

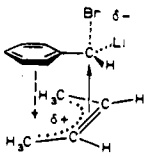
Scheme V. Relative Rates of Cyclopropane Formation from *cis*- and *trans*-2-Butene via Various Proposed Transition States



relative rate as formation of cis cyclopropane from propene.[23] The observed rates of formation of syn cyclopropane from *cis*-2-butene and of cis cyclopropane from propene were 7.4 and 7.0 relative to reaction of *tert*-butylethylene. On the other hand, closed transition state **29a** which would lead to anti cyclopropane from *cis*-2-butene is greatly destabilized by a 1,2-methyl-$W(CO)_5$ interaction and to a lesser extent by a 1,3 methyl-$W(CO)_5$ interaction. The decreased rate of anti cyclopropane formation is largely responsible for the higher syn:anti ratio for *cis*-2-butene.

Reaction of *trans*-2-butene with **4** would be expected to proceed via transition state **31**, which is very similar to the closed transition state for formation of trans cyclopropane from propene in that both transition states have cis 1,3 methyl-$W(CO)_5$ interactions. It is remarkable that the relative rates of reaction of **4** with *trans*-2-butene and with propene to give trans cyclopropane are 3.5 and 3.9 (2.9 + 1.0) relative to the rate of reaction with *tert*-butylethylene.[23]

Previously, Closs and Moss observed that aryl carbenoids generated by the reaction of alkyllithium reagents with benzal bromides reacted with alkenes to give cyclopropanes predominantly of cis configuration.[17] The preference for formation of cis cyclopropanes was explained in terms of transition state **32** in which the positive charge which builds up in the alkene moiety during the reaction is electrostatically stabilized by interaction with the negatively polarized phenyl ring. It was also suggested that charge transfer from the phenyl ring to the alkene added to the overall stabilization of **32**. Electron



32

donation from a phenyl ring is common both to Closs and Moss's transition state **32** and to transition states **25** proposed here for the reactions of $(CO)_5WCHC_6H_5$ (**4**). However, the specific interaction between the more substituted carbon atom of the alkene and the ipso carbon of the phenyl ring of **4** which

Table III. Reaction of Alkenes with **4**

alkene (mmol)	**5**, mmol	CH_2Cl_2, mL	CF_3CO_2H, mmol	products (yield, %)	GC anal.[a] (column, *T*, retention time)
$CH_2{=}CH_2$ (11)	0.115	10	0.344	**8** (<0.1)	B, 160 °C, 17 min
$CH_3CH{=}CH_2$ (8.4)	0.089	10	0.267	**9c** (53)	A, 90 °C, 21 min
				9t (26)	A, 90 °C, 26 min
$CH_2{=}CHCH_2CH_3$[b] (19)	0.093	10	0.280	**10c** (34)	B, 145 °C, 30 min
				10t (39)	B, 145 °C, 33 min
$CH_2{=}CH(CH_3)_2$[g] (18)	0.080	10	0.396	**11c** (19)	B, 150 °C, 24 min
				11t (53)	B, 150 °C, 27 min
$CH_2{=}CHC(CH_3)_3$[c] (31)	0.185	20	0.553	**12c** (<0.6)	A, 139 °C, 12 min
				12t (67)	A, 139 °C, 14 min
$(CH_3)_2C{=}CH_2$ (60)	0.093	10	0.281	**13** (98)	A, 106 °C, 19 min
trans-$CH_3CH{=}CHCH_3$ (67)	0.096	10	0.290	**14** (82)	C, 85 °C, 25 min
cis-$CH_3CH{=}CHCH_3$ (38)	0.094	10	0.281	**15a** (1.4)	C, 95 °C, 28 min
				15s (58)	C, 95 °C, 24 min
$CH_3CH{=}C(CH_3)_2$ (19)	0.088	10	0.265	**16c** (81)	B, 156 °C, 19 min
				16t (<0.7)	B, 156 °C, 13 min
$(CH_3)_2C{=}C(CH_3)_2$ (17)	0.092	10	0.278	**17** (37)	B, 165 °C, 13 min
$CH_2{=}CHC_6H_5$ (17)	0.091	10	0.272	**18c** (36)	A, 196 °C, 9 min
				19t (3.4)	A, 196 °C, 15 min
$CH_2{=}C(C_6H_4\text{-}p\text{-}CH_3)_2$[d] (0.29)	0.271	30	0.811	**19** (37)	isolated by TLC
$\overline{CH_2CH{=}CHCH_2CH_2}$ (23)	0.096	10	0.288	**20-endo** (29)	E, 108 °C, 11 min
				20-exo (11)	E, 108 °C, 19 min
$\overline{CH_2CH{=}C(CH_3)CH_2CH_2}$[e]	0.105	10	0.316	**21-endo** (44)	E, 108 °C, 10 min
				21-exo (6.2)	E, 108 °C, 14 min
$CH_2{=}CH(C_6H_4\text{-}p\text{-}CH_3)$[f] (7.5)	0.103	10	0.308	styrene (<0.2)	B, 157 °C, 12 min

[a] See General section of Experimental Section. [b] $CH_2{=}CHCH_2CH_3$ was purified by preparative gas chromatography at 24 °C on a $AgNO_3$-ethylene glycol column to remove the ~0.77% 2-methylpropene present in CP grade 1-butene. [c] This alkene was synthesized from pivaldehyde and $CH_2{=}PPh_3$ in Me_2SO since commercial samples of $CH_2{=}CHC(CH_3)_3$ (99%) contained small amounts of reactive alkene impurities that selectively reacted with **4**. [d] No $(CO)_5WC(C_6H_5)_2$ was detectable by analytical TLC (silica gel-hexane). [e] In addition, some 1-phenylspiro[2.4]heptane was found in the reaction mixture (retention time 17 min); this product probably arises from small amounts of methylenecyclopentane present in 1-methylcyclopentene. [f] In this experiment, no analysis for *cis*- or *trans*-1-*p*-tolyl-2-phenylcyclopropane was performed. [g] CF_3CO_2H was added to the reaction mixture as a ~1.6 M solution in CH_2Cl_2.

is proposed for transition state **25** is quite different from the electrostatic stabilization proposed by Closs and Moss.

At this point we do not know whether or not a metallacyclobutane is involved at all in the reactions of **4** with alkenes. The only evidence for such an intermediate comes from the reaction of **4** with ethoxyacetylene, which gives a styryl-ethoxycarbene complex. The reaction probably proceeds via initial formation of a metallacyclobutene which subsequently ring opens. Previously similar reactions of aminoacetylenes with metal carbene complexes have been reported.[24]

Contrasting Behavior of $(CO)_5WCHC_6H_5$ and $(CO)_5WC(C_6H_5)_2$. The reactions of the phenylcarbene complex **4** with alkenes differ in four major respects from the corresponding reactions of the diphenylcarbene complex **1**. First, phenylcarbene complex **4** is much more reactive toward alkenes than the diphenylcarbene complex **1**. Whereas **4** reacts with alkenes rapidly at −78 °C, **1** must be heated to 40 °C to achieve reaction with alkenes. Second, the ^{13}CO exchange with diphenylcarbene complex is more rapid than reaction with alkenes; it seems unlikely that loss of CO from **4** at −78 °C could be more rapid than reaction with alkenes. Third, the diphenylcarbene complex **1** is most reactive toward the least substituted alkene while phenylcarbene complex **4** shows the opposite reactivity pattern characteristic of electrophilic attack on alkenes. Fourth, diphenylcarbene complex **1** reacts with alkenes to give both cyclopropanes and metathesis-like products while phenylcarbene complex **4** reacts with alkenes to give only cyclopropanes.

The phenylcarbene complex **4** is a very electrophilic reagent and apparently does not require a vacant coordination site to react with an alkene. The carbene carbon atom of **4** is a much more electrophilically reactive center than that of diphenylcarbene complex **1** since stabilizing electron donation occurs from only a single phenyl group and since the carbene carbon atom is sterically shielded by only a single phenyl group. The diphenylcarbene complex is much less reactive toward electrophilic attack on an alkene and reacts only via CO dissociation and formation of a metal-carbene-alkene complex.

The reactions of diphenylcarbene complex **1** can proceed via formation of a six-coordinate metallacyclobutane. The six-coordinate metallacyclobutane can react to give either cyclopropane and $W(CO)_4$ or to give metathesis-like products via a new metal-carbene-alkene complex. The ability of a metallacyclobutane to give metathesis-like products may be strongly related to its ability to give an alkene which, at least initially, is coordinated to the metal atom. Such a process would be greatly favored by the metal-alkene complex bond energy.

The failure of phenylcarbene complex **4** to give even a trace of metathesis-like products may be due to the fact that its reactions with alkenes do not involve a metallacyclobutane intermediate. As pointed out above, we have no way of knowing whether a metallacyclobutane intermediate occurs after transition state **25** for reaction of **4** with alkenes. However, even if the reactions of **4** with alkenes proceed through a seven-coordinate metallacyclobutane intermediate, metathesis products may not result. Conversion of the seven-coordinate metallacyclobutane intermediate to a 20-electron seven-coordinate metal-carbene-alkene complex would be a very high energy process. Conversion to a new 18-electron six-coordinate metal carbene complex and a free alkene might be possible but the process would not be aided by metal-alkene bond formation. Thus, while the six-coordinate metallacyclobutane intermediate formed from diphenylcarbene complex,

1, can give either cyclopropanes or metathesis-like products, a seven-coordinate metallacyclobutane (even if formed in the reactions of phenylcarbene complex **4**) would be more likely to give only cyclopropanes.

Experimental Section

General. All reactions involving organometallic reagents were carried out in flame-dried glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) used as solvent was distilled from sodium and benzophenone under a nitrogen atmosphere. Other solvents were either purged with nitrogen or degassed on a vacuum line ($<10^{-3}$ mm Hg) prior to use. Solutions were transferred by syringe or cannula (hypodermic wire) under positive nitrogen pressure. ^1H NMR spectra were recorded on a Jeolco MH-100, Varian XL-100, or Bruker WH-270 spectrometer. ^{13}C NMR spectra were recorded on a Jeolco FX-60, Varian XL-100, or Bruker WH-270 spectrometer. IR spectra were recorded on a Perkin-Elmer 267 spectrophotometer in the solvent specified and are reported in cm^{-1}. Mass spectra were recorded on an AEI-903 mass spectrometer at 70 eV. Analytical vapor phase chromatography was carried out on either a Hewlett-Packard 5750 or 5700A gas chromatograph with flame ionization detector and either disk integrator or Hewlett-Packard 3380A integrator-recorder. Preparative vapor phase chromatography was carried out on a Varian Aerograph 90P gas chromatograph with a thermal conductivity detector.

Cyclopentene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 3,3-dimethyl-1-butene were purchased from Phillips Co. and used directly. Styrene was bulb-to-bulb transferred under high vacuum immediately before use. Gaseous alkenes (1-butene, *cis*- and *trans*-2-butene, 2-methylpropene, and propene) were purchased from Matheson Gas Corp. and were used directly from the cylinder unless specified otherwise.

Phenylcyclopropanes were analyzed by gas chromatography on one or more of the following columns: (A) 12 ft × 1/8 in. 25% QF-1 on Chromosorb P (60/80), (B) 12 ft × 1/8 in. 20% DEGS on Chromosorb P (60/80), (C) 12 ft × 1/8 in. 10% DEGS on Chromosorb W A/W DMCS (80/100), (D) 6 ft × 1/8 in. 25% SF-96 on Chromosorb P (60/80), (E) 6 ft × 1/8 in. 10% OV-225 on Chromosorb W A/W DMCS (80/100).

Reaction of 5 with CF_3CO_2H in the Presence of $P(C_6H_5)_3$. The infrared spectrum of a yellow solution of **5** (0.518 g, 0.901 mmol) and $P(C_6H_5)_3$ (0.284 g, 1.082 mmol) in 50 mL of CH_2Cl_2 indicated no interaction between **5** and $P(C_6H_5)_3$. When CF_3CO_2H (0.20 mL, 0.31 g, 2.7 mmol) was added to the solution at −78 °C, a light red color formed and faded to give a yellow solution. After 0.5 h at −78 °C, the solution was warmed to room temperature. Silica gel (2.0 g) was added, solvent was evaporated, and the resulting solid was purified by column chromatography (silica gel, 1:1 $CHCl_3$–hexane). A single pale yellow band was eluted and concentrated on a rotary evaporator to about 15 mL to initiate crystallization. Cooling to −20 °C gave $(CO)_5\overline{W}CH(C_6H_5)P^+(C_6H_5)_3$ (**7**, 0.550 g, 90%) as a yellow, crystalline solid: IR (THF) ν_{CO} 2052 (w), 1962 (w), 1911 (s), 1881 cm^{-1} (m); NMR ($CDCl_3$) δ 3.82 (1 H, doublet, J = 15.6 Hz, with additional coupling due to ^{183}W, J = 6.4 Hz), 6.97 (5 H, m), 7.57 (15 H, m).

Anal. Calcd for $C_{30}H_{21}O_5PW$: C, 53.28; H, 3.13; W, 27.18. Found: C, 53.28; H, 3.20; W, 26.55.

Reaction of 5 with CF_3CO_2H in the Presence of $P(Bu_3)$. CF_3CO_2H (43 μL, 0.067 g, 0.584 mmol) was added to a solution of **5** (0.112 g, 0.195 mmol) and $P(n\text{-}Bu)_3$ (84 μL, 0.39 mmol) in 10 mL of CH_2Cl_2 at −78 °C. A transient red color appeared at −78 °C and faded to yellow. Column chromatography (silica gel, 1:1 $CHCl_3$–hexane) gave $(CO)_5\overline{W}CH(C_6H_5)[P^+(n\text{-}Bu)_3]$ (**6**, 0.108 g, 90%) as a pale yellow, crystalline solid: IR (THF) ν_{CO} 2060 (w), 1968 (m), 1915 (s), 1887 cm^{-1} (m); NMR ($CDCl_3$) δ 0.92 (9 H, t, J = 7.0 Hz), 1.42 (12 H, m), 2.02 (6 H, m), 2.71 (1 H, doublet with additional coupling due to ^{183}W, J = 6.4 Hz), 7.18–6.88 (5 H, m). MS: calcd for $C_{24}H_{33}O_5P^{184}W$, 616.1592; found, 616.1576.

Trapping of 4 with $P(n\text{-}Bu)_3$. CF_3CO_2H (94 μL, 0.145 g, 1.275 mmol) was added to a solution of **5** (0.245 g, 0.425 mmol) in 50 mL of CH_2Cl_2 at −78 °C. After the resulting dark red solution was stirred at −78 °C for 5 min, $P(n\text{-}Bu)_3$ (200 μL, 1.0 mmol) was added. The dark red color immediately disappeared to give an orange solution. Column chromatography gave **6** (0.124 g, 47%).

General Procedure for Reaction of 4 with Alkenes. The details for reaction of **5** with CF_3CO_2H in the presence of propene are given as an example of the general procedure used for the reactions listed in Table III.

On a vacuum line, degassed CH_2Cl_2 (10.0 mL) was distilled into a 25-mL round-bottom flask containing **5** (51.2 mg, 0.0890 mmol) and a magnetic stirring bar. The stopcock to the flask was then closed and the contents allowed to warm to dissolve **5**. Propene (8.43 mmol) was condensed into a second flask cooled to liquid nitrogen temperature, further degassed by two freeze-pump-thaw cycles, and then vacuum transferred into the flask containing **5**. The amount of propene was estimated by measuring the pressure drop (178 mmHg) in the vacuum line for which the volume had been determined (1144 mL) and assuming ideal gas behavior. The flask was removed from the line under a slight positive nitrogen pressure and capped with a rubber septum. CF_3CO_2H (20 μL, 30 mg, 0.2670 mmol) was added rapidly via syringe to give a dark red solution. After stirring for 4 h at −78 °C, the solution was removed from the cooling bath and allowed to warm to room temperature. Solid Na_2CO_3 (0.5 g) and internal standards (*n*-undecane and triphenylmethane) were added to the resulting light orange solution and the solvent was removed at aspirator vacuum on a rotary evaporator at or below room temperature. Extraction of the residue with hexane (1 mL) and subsequent gas chromatographic analysis [column (A), 90 °C, *n*-undecane and triphenylmethane internal standards] showed two peaks corresponding to *cis*- and *trans*-1-phenyl-2-methylcyclopropane (**9c** and **9t**, 80%; **9c**, 21.5 min; **9t**, 26.0 min; undecane, 13.5 min; **9c**/**9t** = 2.0). The average cis/trans ratio for the cyclopropanes was 1.8 (range 1.7–2.0) for three reactions.

In a separate reaction the cyclopropanes were isolated by preparative GC (10 ft × 1/4 in. 25% QF-1, 100 °C). NMR spectra (270 MHz) of the isolated products corresponded accurately with spectra of authentic samples. Table IV lists the NMR spectra of the cyclopropane products.

In some cases noted in Table III, an ~1.6 M solution of CF_3CO_2H in CH_2Cl_2 was added instead of pure CF_3CO_2H, which has a tendency to freeze upon addition to CH_2Cl_2 at −78 °C. Alkenes which are liquids at room temperature were weighed and then vacuum transferred into solutions of **5** in CH_2Cl_2 at −78 °C.

Reaction of 5 with CF_3CO_2H in the Presence of Two Alkenes. Competition Reactions. The procedure used for competition reactions is given below for propene and *cis*-2-butene. The quantities of gaseous alkenes were determined according to the procedure used for the reaction of **5** with propene.

On a vacuum line, degassed CH_2Cl_2 (10.0 mL) was distilled into a 25-mL round-bottom flask containing a sample of **5** (0.0561 g, 0.0975 mmol) and a magnetic stirring bar. The stopcock to the flask was closed and the contents allowed to warm to dissolve **5**. The solution was cooled to −78 °C, first propene (12.5 mmol) and then *cis*-2-butene (12.5 mmol) were condensed into the solution, and the solution was removed from the line under a slight positive pressure of nitrogen. CF_3CO_2H (22 μL, 33 mg, 0.29 mmol) was added rapidly via syringe and the resulting dark red solution stirred at −78 °C for 3 h. After the solution had warmed to room temperature, solid Na_2CO_3 (0.5 g) was added and the solvent removed at aspirator pressure on a rotary evaporator. Hexane was added to the residue and the mixture analyzed by GC [column (D), 103 °C]. GC analysis indicated that the weight ratio for the cyclopropanes (propene adducts/butene adducts) was 1.23/1. The relative reactivity (R) of propene (a)/*cis*-2-butene (b) was calculated using the formula

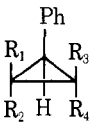
$$R\left(\frac{a}{b}\right) = \frac{M_a}{M_b}\frac{C_b}{C_a}$$

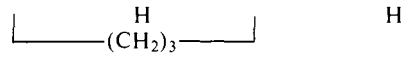
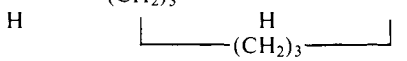
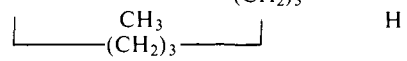
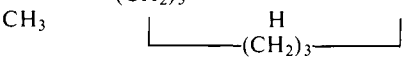
where M_a/M_b is the molar ratio of the phenylcyclopropanes and C_b/C_a is the molar ratio of the alkene reactants. The accurate determination of relative reactivities by this method requires that each alkene be present in a large excess so that their concentrations remain essentially constant throughout the reaction.

Using the equation above, a relative reactivity for propene vs. *cis*-2-butene of 1.36 was determined. Table V shows the results of the other competition reactions. Results are summarized in Table II.

Preparation of Phenylcyclopropanes. Two routes were used to obtain authentic samples of phenylcyclopropanes. The reaction of hydrazine with an α,β-unsaturated ketone, the Kishner reaction,[25] provided a preparation of an isomeric mixture of 1,2-disubstituted cyclopropanes (method A). The α,β-unsaturated ketones were obtained by the routine base-catalyzed condensations of ketones with

Table IV. 270-MHz NMR Data for Phenylcyclopropanes[a]



compd	R_1	R_2	R_3	R_4	chemical shifts and coupling constants
8	H	H	H	H	0.69 (2 H, m), 0.94 (2 H, m), 1.88 (1 H, t of t, J = 8.5, 5.0 Hz), 7.22 (5 H, m)
9c	CH_3	H	H	H	0.57 (1 H, d of d, J = 5.0, 5.8 Hz), 0.79 (3 H, d, J = 6.1 Hz), 0.97 (1 H, d of t, J = 5.0, 8.5 Hz), 1.13 (1 H, m), 2.07 (1 H, d of t, J = 5.8, 8.7 Hz), 7.22 (5 H, m)
9t	H	CH_3	H	H	0.72 (1 H, d of t, J = 8.8, 5.0 Hz), 0.87 (1 H, d of t, J = 8.8, 5.0 Hz), 1.05 (1 H, m), 1.17 (3 H, d, J = 5.9 Hz), 1.56 (1 H, d of t, J = 8.8, 5.0 Hz), 7.12 (5 H, m)
10c	Et	H	H	H	0.63 (1 H, d of t, J = 5.0, 6.1 Hz), 0.83 (3 H, t, J = 6.4 Hz), 0.90-1.17 (4 H, m), 2.12 (1 H, d of t, J = 6.4, 8.5 Hz), 7.22 (5 H, m)
10t	H	Et	H	H	0.75 (1 H, m), 0.86 (1 H, d of t, J = 8.2, 4.6 Hz), 1.01 (4 H, CH_3 triplet, J = 7.3 Hz), 1.40 (2 H, quintet, J = 7.3 Hz), 1.60 (1 H, d of t, J = 8.2, 4.8 Hz), 7.13 (5 H, m)
11c	*i*-Pr	H	H	H	0.61 (3 H, d, J = 6.1 Hz), 0.75 (4 H, m), 0.89 (3 H, d, J = 6.1 Hz), 2.07 (1 H, d of t, J = 6.9, 8.7 Hz), 7.18 (5 H, m)
11t	H	*i*-Pr	H	H	0.83 (3 H, m), 1.02 (7 H, m), 1.65 (1 H, d of t, J = 8.2, 5.1 Hz), 7.18 (5 H, m)
12c	*t*-Bu	H	H	H	0.70 (9 H, s), 0.78-1.06 (3 H, m), 2.14 (1 H, broad pseudoquartet), 7.13 (5 H, m)
12t	H	*t*-Bu	H	H	0.74 (1 H, d of t, J = 9.1, 5.0 Hz), 0.83-1.04 (11 H, *t*-Bu singlet at 0.90), 1.75 (1 H, d of t, J = 8.6, 5.0 Hz), 7.15 (5 H, m)
13	CH_3	CH_3	H	H	0.82-0.73 (5 H, CH_3 singlet 0.79), 1.22 (3 H, s), 1.88 (1 H, d of d, J = 5.9, 8.1 Hz), 7.25 (5 H, m)
14	CH_3	H	H	CH_3	0.79-0.99 (5 H, broad singlet at 0.81), 1.17 (3 H, d, J = 5.7 Hz), 1.73 (1 H, d of d, J = 5.1, 8.3 Hz), 7.18 (5 H, m)
15a	H	CH_3	H	CH_3	1.16 (9 H, broad singlet), 7.26 (5 H, m)
15s	CH_3	H	CH_3	H	0.92 (1 H, doublet with small complex coupling, J_d = 6.2 Hz), 1.18 (2 H, m), 2.00 (1 H, t, J = 8.8 Hz), 7.23 (5 H, m)
16c	CH_3	CH_3	CH_3	H	0.90 (3 H, s), 0.94 (4 H, m), 1.22 (3 H, s), 1.77 (1 H, broad doublet), 7.20 (5 H, m)
16t	CH_3	CH_3	H	CH_3	0.78 (3 H, s), 1.06 (1 H, d of q, J = 7.3, 5.3 Hz), 1.18 (6 H, m), 1.46 (1 H, d, J = 5.5 Hz), 7.19 (5 H, m)
17	CH_3	CH_3	CH_3	CH_3	0.93 (6 H, s), 1.25 (6 H, s), 1.53 (1 H, s), 7.19 (5 H, m)
18c	Ph	H	H	H	1.33-1.50 (2 H, m), 2.48 (2 H, d of d, J = 6.2, 8.6 Hz), 7.02 (10 H, m)
18t	H	Ph	H	H	1.44 (2 H), 2.15 (2 H), AA'BB'; 6.98 (10 H, m)
19	*p*-tol	*p*-tol	H	H	1.74 (1 H, d of d, J = 5.2, 9.0 Hz), 1.89 (1 H, d of d, J = 5.2, 6.5 Hz), 2.18 (3 H, s), 2.27 (3 H, s), 2.77 (1 H, d of d, J = 6.5, 9.0 Hz), 6.98 (13 H, m)
20-*endo*					−0.07 (1 H, 16-line multiplet), 1.23 (1 H, m), 1.59-1.87 (6 H, m), 1.95 (1 H, t, J = 8.3 Hz), 7.23 (5 H, m)
20-*exo*					1.28 (1 H, 16-line multiplet), 1.54-1.95 (8 H, m), 7.13 (5 H, m)
21-*endo*					0.02 (1 H, 16-line multiplet), 1.92-1.19 (10 H, CH_3 singlet at 1.38, benzylic proton doublets at 1.85, J = 8.5 Hz), 7.23 (5 H, m)
21-*exo*					0.97 (3 H, s), 1.36-1.93 (8 H, m), 7.18 (5 H, m)

[a] All NMR spectra were obtained in $CDCl_3$.

benzaldehyde. The second route (method B) consisted of the stereospecific reaction of benzal bromide with methyllithium in the presence of an alkene.[17] An example of each procedure is given below.

Method A. Hydrazine hydrate (20 mL, 85%) was added to a solution of 5 g of 2,2-dimethyl-5-phenyl-4-penten-3-one in 10 mL of 95% ethanol. NaOH (5 or 6 pellets) was added and the solution refluxed for 2 h. Ethanol and excess hydrazine were removed by slow distillation and the temperature was then raised to 200 °C for 1 h. The flask was cooled and hexane was added. The organic layer was washed with water (3 × 25 mL), dried (Na_2SO_4), concentrated, and distilled to give *cis*- and *trans*-1-phenyl-2-*tert*-butylcyclopropane (**12c** and **12t**,[18] 3.4 g, 73%) as a clear liquid, bp 110-113 °C (15 mmHg). Pure samples of each isomer (cis/trans = 0.3) were obtained by preparative GC (10 ft × 1/8 in. 25% QF-1, 130 °C). Other cyclopropanes prepared by this method were **8**,[26] **9c** and **9t**,[18] **10c** and **10t**,[17] **11c** and **11t**,[18] and **18c** and **18t**.[27]

Method B. Methyllithium (33 mL, 1.0 M in ether, 33 mmol) was added over a 1-h period to a solution of benzal bromide (6.25 g, 25 mmol) in 15 mL of 2,3-dimethyl-2-butene cooled to −5 °C. The reaction mixture was washed with water (3 × 25 mL) and dried (Na_2SO_4), and the excess alkene removed on a rotary evaporator. The resulting liquid was distilled (aspirator vacuum, bp 90-120 °C). The distillate was dissolved in absolute ethanol (20 mL) and $AgNO_3$ (~6 g) was added to remove alkenes as an insoluble metal complex which precipitated from solution. Ethanol was removed on a rotary evaporator, the residue extracted with hexane, and the resulting solution filtered through a short column of alumina. A pure sample of 2,2,3,3-tetramethyl-1-phenylcyclopropane (**17**)[28] was obtained from the filtrate by preparative GC (10 ft × 1/4 in. 20% DEGS, 150 °C). Other cyclopropanes prepared by this method were **13**,[17] **14**,[17] **15a** and **15s**,[17] **16c** and **16t**,[17] **20**-*endo* and **20**-*exo*,[29] and **21**-*endo* and **21**-*exo*. For **21**-*exo*: exact mass calcd for $C_{13}H_{16}$, 172.1255; found, 172.1252.

Low-Temperature NMR of $(CO)_5WCHC_6H_5$ (5). The apparatus shown schematically in Figure 2 was used to prepare a solution of **4**. Solid **5** (3.2 mg, 5.6 μmol) and a magnetic stirring bar were placed

Table V. Results of Competition Reactions

A_1	A_2	molar ratio of alkenes (C_2/C_1)	molar ratio of cyclopropanes (M_1/M_2)	rel reactivity $R(A_1/A_2)$	GC column (temp, °C)
$CH_3CH{=}CH_2$	*cis*-$CH_3CH{=}CHCH_3$	1.00	1.36	1.36	C (95)
$CH_3CH{=}CH_2$	*cis*-$CH_3CH{=}CHCH_3$	1.21	1.19	1.44	C (95)
$CH_3CH{=}CH_2$	*trans*-$CH_3CH{=}CHCH_3$	1.22	2.37	2.89	D (103)
cis-$CH_3CH{=}CHCH_3$	*trans*-$CH_3CH{=}CHCH_3$	1.00	2.21	2.21	C (93)
trans-$CH_3CH{=}CHCH_3$	$(CH_3)_3CCH{=}CH_2$	0.60	5.70	3.42	B (165)
$CH_3CH{=}CH_2$	$CH_3CH_2CH{=}CH_2$	1.00	1.88	1.88	D (110)
cyclopentene	*trans*-$CH_3CH{=}CHCH_3$	1.34	1.27	1.70	E (125)
$(CH_3)_2C{=}CHCH_3$	$CH_3CH{=}CH_2$	10.6	7.30	77.4	D (115)
$(CH_3)_2C{=}CHCH_3$	$C_6H_5CH{=}CH_2$	3.68	0.54	1.99	*a*
$(CH_3)_2C{=}CH_2$	$(CH_3)_2C{=}CHCH_3$	3.88	1.10	4.27	B (161)
$(CH_3)_3C{=}CH_2$	$CH_3CH{=}CH_2$	27.5	13.0	358	C (96)
trans-$CH_3CH{=}CHCH_3$	$(CH_3)_2C{=}C(CH_3)_2$	0.85	1.19	1.01	B (160)
$CH_3CH{=}CH_2$	$(CH_3)_2CHCH{=}CH_2$	0.98	4.24	4.16	D (112)

[a] Two columns were used for the analysis: for adduct 1, column (B), 164 °C, *n*-heptadecane internal standard; for adduct 2, column (E), 200 °C, triphenylmethane internal standard.

in the flask. The apparatus was attached to a vacuum line and CD_2Cl_2 (0.4 mL) was distilled from alumina into the flask. The flask was warmed to dissolve **5** and cooled to −78 °C, and CF_3CO_2H (3.0 μL, 40.5 μmol) was added through a rubber septum on the side arm. The resulting red solution was stirred for 1 min at −78 °C; the apparatus was then rotated so that the solution flowed into the attached NMR tube which was also cooled to −78 °C. At this point the special cooling device was removed and quickly replaced with a conventional Dewar flask containing a −78 °C bath. A slight vacuum was applied to the flask and the tube sealed. A 270-MHz NMR spectrum of the sample at −78 °C is shown in Figure 1. The signal at δ 17.2 assigned to the proton on the carbene carbon atom showed no appreciable loss of intensity over a period of 1 h at −78 °C. Upon raising the temperature to −56 °C, the absorptions assigned to **4** disappeared within 1.5 h.

NMR Observation of Reactions of 4 with Alkenes. Using the apparatus described in Figure 2, CF_3CO_2H (1.0 μL, 14.1 μmol) was added to a solution of **5** (2.7 mg, 4.7 μmol) in ~0.4 mL of CD_2Cl_2 which contained excess isobutylene (300 μmol). After stirring for 5 min at −78 °C, the initial red color had completely faded. The resulting yellow solution was poured into the NMR tube at −78 °C and sealed under vacuum. A 270-MHz NMR spectrum of the sample (taken at −78 °C 15 min after addition of acid) showed two singlets at δ 0.68 and 1.22 of equal intensity (1,1-dimethyl-2-phenylcyclopropane exhibits methyl resonances at δ 0.74 and 1.22 at ambient probe temperature). The relative intensities of the two absorptions did not change upon warming to 23 °C.

In a similar experiment, CF_3CO_2H (3.5 μL, 47 μmol) was added to a solution of **5** (3.7 mg, 6.4 μmol) in 0.4 mL of CD_2Cl_2 at −78 °C containing an excess of *cis*-2-butene (~0.3 mmol). The resulting dark red solution was stirred for 15 min, then poured into the attached NMR tube. The tube was sealed and a 270-MHz NMR obtained at −78 °C exhibited the δ 17.2 singlet and phenyl absorptions assignable to **4**. After 113 min at −78 °C doublets at δ 0.83 (J = 6.62 Hz) had grown in while the intensity of the δ 17.2 singlet had diminished slightly. When the sample was warmed to −56 °C, the absorptions due to **4** disappeared in about 40 min as the doublets at δ 0.83 and 2.08 increased in intensity. After complete disappearance of **4** further increases in temperature (−56 to −10 °C) moved the doublet absorption at δ 0.83 to slightly lower field. At 23 °C the spectrum exhibited the high-field doublet at δ 0.92, exactly matching a spectrum of authentic *syn*-1-phenyl-*cis*-2,3-dimethylcyclopropane (**15s**).

Reaction of 5 with CF_3CO_2H and Ethoxyacetylene. CF_3CO_2H (79 μL, 0.121 g, 1.06 mmol) was added to a solution of **5** (0.204 g, 0.354 mmol) and ethoxyacetylene (1.0 mL of 50% solution in hexane, ~6 mmol) in 50 mL of CH_2Cl_2 at −78 °C. The resulting dark red solution was warmed to room temperature. Solid Na_2CO_3 (0.5 g) was added, solvent was evaporated, and the residues were purified by preparative thin layer chromatography (silica gel, hexane) to give a dark red solid. Recrystallization from hexane at −20 °C gave $(CO)_5WC(OCH_2CH_3)CH{=}CHC_6H_5$ (**22**, 0.352 g, 21%): mp 103–104 °C; IR (hexane) ν_{CO} 2064 (m), 1984 (w), 1958 (sh), 1947 cm^{-1} (s); 270-MHz NMR (acetone-d_6) δ 1.70 (3 H, t, J = 6.99 Hz), 5.05 (2 H, q, J = 6.99 Hz), 7.43 (4 H, m), 7.80 (2 H, m), 8.07 (1 H, d, J = 15.44 Hz). MS: calcd for $C_{16}H_{12}O_6{}^{184}W$, 484.0143; found, 484.0144.

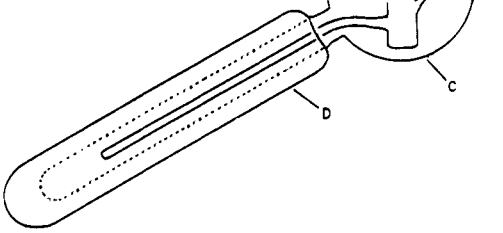


Figure 2. Apparatus for the preparation of low-temperature NMR samples: A, 14/20 ☤ outer joint; B, rubber septum; C, 250-mL flask (halved); D, insulator (30 mm o.d. × 250 mm), evacuated.

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Optically Active Trivalent Phosphorus Compounds. 2. Reactivity of Alkylthio- and Alkylselenophosphonium Salts. The First Stereospecific Synthesis of a Chiral Phosphinite

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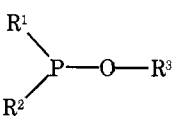
Abstract: It was shown that alkylthio- and alkylselenophosphonium salts react with alkylmercaptide anions to give trivalent phosphorus compounds and disulfides. Reaction of (−)-(*S*)-methylthiomethyl-*n*-propylphenylphosphonium triflate (**6**) with ethylmercaptide anion gave completely racemic methyl-*n*-propylphenylphosphine (**7**). However, when *tert*-butylmercaptide anion was used, optically active phosphine **7** was formed with 59% of initial optical activity and with retention of configuration. Reaction between (−)-(*S*)-methylthioethyl-*tert*-butylphenylphosphonium triflate (**8**) and sodium ethylmercaptide was found to occur with full stereospecificity to give (+)-(*R*)-ethyl-*tert*-butylphenylphosphine (**10**). (−)-(*S*)-*O*-Methyl-*Se*-methyl-*tert*-butylphenylphosphonium triflate (**11**) obtained from (−)-(*S*)-*tert*-butylphenylphosphinoselenoic acid (**12**) was converted stereospecifically to (+)-(*R*)-*O*-methyl *tert*-butylphenylphosphinite (**2**). The latter reaction represents the first stereospecific synthesis of a chiral trivalent phosphorus acid ester.

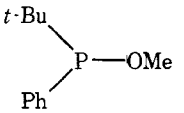
Chiral tertiary phosphines, first prepared by Horner in 1961,[1,2] occupy a central position in the study of dynamic phosphorus stereochemistry.[3] Recently, chiral phosphines have found very important application as ligands for catalysts employed in asymmetric hydrogenation in soluble systems.[4] The efficiency of this process was found to be strongly dependent on the structure of chiral phosphorus ligands. In this connection the synthesis of other classes of chiral trivalent phosphorus compounds is of great interest.

Especially interesting are optically active trivalent phosphorus acids esters (**1**) because the great majority of organophosphorus reactions is based on their conversion into P^{IV}, P^{V}, and P^{VI} compounds. Till now, however, the synthetic approaches to chiral trivalent phosphorus acids esters (**1**) with phosphorus as a sole chirality center are few in number and for the most part of limited applicability.[5,6] Thus, the trimethylsilyl ester **1a** obtained by Benschop et al.[5] by silylation of *O*-isopropyl methylphosphonate was found to be very sensitive to moisture. On the other hand, asymmetric reaction of racemic chlorophosphines with alcohols in the presence of chiral tertiary amines,[6] though very simple and general, leads to chiral esters **1b–d** with low optical purities.



1a, R^1 = Me; R^2 = O-Pr-*i*; R^3 = $SiMe_3$
b, R^1 = Ph; R^2 = Me; R^3 = Me or Pr-*n*
c, R^1 = Ph; R^2 = Et; R^3 = Me or Pr-*n*
d, R^1 = Et; R^2 = SEt; R^3 = Et

We report here the first stereospecific synthesis of chiral *O*-methyl *tert*-butylphenylphosphinite (**2**) as well as the results of a relevant study on the reactivity of alkylthio- and alkylselenophosphonium salts which, as it was found, are useful precursors of chiral trivalent phosphorus compounds.



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Results and Discussion

Generally, phosphonium salts bearing the alkylthio group may react with a nucleophile in three different ways shown schematically below. Nucleophilic attack at phosphorus and carbon [directions (a) and (b)] is well known.[7,8] On the contrary, the attack at sulfur [direction (c)] leading to P^{III} com-

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