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Olefin Reactivities toward the Ph−P−W(CO)$_5$ Phosphinidene

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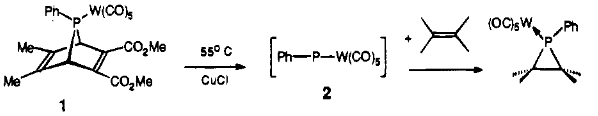
Abstract: Phosphinidene complex Ph−P−W(CO)$_5$ (**2**), generated from the appropriate phosphanorbornadiene complex **1**, reacts with olefins to give the expected phosphiranes. The relative olefin reactivity toward **2** in toluene at 55 °C is tetramethylethylene (0.2), trimethylethylene (0.8), isobutylene (2−4), *cis*-2-butene (1.0), *trans*-2-butene (0.3), and 1-butene (0.2). The modest stereoselectivity of the phosphinidene addition reactions is reflected in the *syn-/anti*-phosphirane product ratios of several olefins and results form opposing steric and electronic influences. For *cis*-2-butene the *syn*/*anti* ratio is 0.25 and the X-ray structure of the *anti*-isomer was determined. The surprising lack of olefin selectivity is compared with the olefin reactivities of various carbenes and particularly that of isopropylidene. The phosphinidene−olefin additions behave analogously to the carbene cyclopropanations and suggest the importance of entropic factors in the thermodynamically controlled reactions.

The now decade old discovery of a convenient route to *in situ* generated terminal phosphinidene complexes RPW(CO)$_5$ has already contributed significantly to the syntheses of small-ring phosphorus compounds (eq 1).[1] Although evidence for their singlet carbene-like properties has been mounting steadily, mechanistic detail is still rudimentary as compared to the carbenes, silylenes, nitrenes, and singlet oxygen.



[1]

Limited, but insightful mechanistic information on phosphinidenes has been reported. For example, Mathey found that reaction of PhPW(CO)$_5$ with *cis*- and *trans*-stilbenes forms phosphiranes with retention of the olefin configuration, which does imply singlet character of the phosphinidene.[2] In an elegant kinetic study, Mathey also showed that the (uncatalyzed) thermal decomposition of its 7-phosphanorbornadiene precursor is a first-order process that is independent of the trapping reagent.[3] From competitive (CuCl catalyzed) reactions we determined Hammett reaction constants for the styrene addition of PhPW(CO)$_5$ ($\varrho^+ = -0.76$),[4] MePW(CO)$_5$ ($\varrho^+ = -0.60$),[5] and PhPW(CO)$_5$ ($\varrho^+ = -0.55$).[6] These reactivities not only quantify the slightly electrophilic, carbene-like behavior of the phosphinidenes—the ϱ values of halocarbenes and alkylidene carbenes are similar in sign and magnitude—but also indicate that the olefin addition reaction follows second-order kinetics. This seeming disparity supports the formation of an intermediate phosphinidene and calls for a closer comparison with the thoroughly studied carbenes.

For example, from a detailed study on singlet arylhalocarbene additions to olefins, using time-resolved laser flash spectroscopy to determine absolute rate constants and thermodynamic parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$), Turro, Moss, and co-workers[6] suggested the intermediacy of a loose charge-transfer complex or contact cage prior to product formation. The authors found that the cyclopropanations are entropy controlled (with $\Delta\Delta S^\ddagger$ values similar in magnitude for all) but that the differences in their (negative) enthalpy requirements govern the small positive values of $\Delta\Delta G^\ddagger$ and hence the rate constants. Their work quantified earlier studies that concentrated on the entropy factor and negative activation energies for carbene−olefin additions.[7] For example, from a computational investigation Houk and co-workers[8] concluded that the activation energies for the ethylene additions of CCl_2 and CBr_2 are solely due to entropy effects.

Similar to the CH_2−ethylene reaction, Gonbeau and Pfister-Guillouzo[9] concluded from a theoretical study that the uncomplexed singlet phosphinidene (^{1}PH) addition to ethylene occurs also without π-complex formation. Fully analogous to the theoretical studies on the parent carbene, silylene, and nitrene insertion reactions most of the ^{1}PH insertions into the X−H bonds (X = O, N, F, S, P, Cl) of solvent molecules take place with small or negative activation energies via intermediate complexes.[10] With respect to PhPW(CO)$_5$, it is reasonable to assume that the transition metal group significantly stabilizes the phosphinidene with a concomitant reduction in reactivity. In fact, it is this stabilizing effect of the transition metal ligand that led Mathey in 1984 to the development of the seemingly well-controlled phosphinidene chemistry, which had hitherto been virtually inaccessible.[1,2,11] It is therefore with some surprise that we recently found the relative reactivities for addition of RPW(CO)$_5$ (R = Me, Ph) to the exocyclic olefins $(CH_2)_nC{=}CH_2$ ($n = 2-5$) (a) to vary only within one order of

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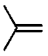
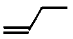
Table 1. Relative Olefin Reactivities toward Carbenes and Ph−P−W(CO)₅

olefin	CFCl[a]	CCl_2[a,b]	$HCCO_2Et$[c]	C=CMe_2[d]	Ph−P−W$(CO)_5$	*syn*/*anti*
	221.4	28.3	0.7	0.1	0.2	
	46.4	12.2	1	0.3	0.8	40:60
	7.1	4.4	1	0.1	2−4[e]	
	1.0	1.0	1.0	1.0	1.0	20:80
	0.7	0.7	0.8	0.2	0.3	
				0.2	0.2	25:75
$\varrho(\sigma^+)$		−0.69[f]		−0.75	−0.76	

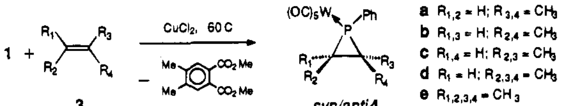
[a] Reference 17. [b] Reference 18. [c] Reference 19. [d] Reference 20. [e] Reference 21. [f] Reference 22.

magnitude and (b) to correlate only with NMR parameters of the phosphaspiro[2.*n*]alkane products.[12] These observations point to a much higher phosphinidene reactivity than assumed until now and might imply that RPW(CO)₅ like carbenes can add to olefins with negative activation energies. It is of interest to note that PhPW(CO)₅ reacts with gaseous ethylene which does suggest a rather high phosphinidene reactivity.[12] This high reactivity is also evident from the failed attempts by Cowley[13] and Gladysz[14] to synthesize and isolate sterically hindered phosphinidene complexes, which instead gave intramolecular C−H insertions.

The similarities between carbenes and W(CO)₅ complexed phosphinidenes appear to be more than incidental. Of course a further quantification of the carbene-like properties of the phosphinidenes is ideally accomplished by determination of absolute reaction constants and thermodynamic properties, but the elusiveness of PhPW(CO)₅ and the limited temperature domain of the CuCl catalyzed reaction make this approach impractical if not impossible. However, meaningful qualitative information can be obtained, which is the purpose of this paper, by a direct comparison of the phosphinidene and carbene additions to a set of simple olefins which are commonly used to quantify carbene philicities.

Results and Discussion

Competitive relative reactivities for the addition to *cis*- and *trans*-2-butene, isobutylene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 1-butene have been determined for the phosphinidene complex **1** (eq 2). The relative reactivities, which are listed in Table 1, are based on product distributions as determined from integrated ^{31}P NMR resonances. In cases where *syn*- and *anti*-phosphiranes are formed, their combined yield is used to determine the relative olefin reactivity. The *syn*/*anti* ratios are also listed in the table. To ascertain this assignment we determined the X-ray structure of the major *anti*-phosphirane resulting from *cis*-2-butene—in the *anti*-isomer the P−W(CO)₅ and the methyl groups of the phosphirane ring are in a *trans* orientation. Table 1 also lists reported relative reactivities for the related carbene additions of CClF,[15] CCl_2,[16] $HCCO_2Et$,[17] and C=CMe_2.[18] Phosphinidene additions to 4,7-dihydroindan, and 1,2-dihydro- and 1,4,5,7-tetrahydronaphthalene are also reported. All reaction products are new W(CO)₅-complexed phosphiranes, and these have been characterized spectroscopically.



[2]

Reactivities. The relative olefin reactivity for PhPW(CO)₅ addition is isobutylene > *cis*-2-butene > 2-methyl-2-butene > *trans*-2-butene > 2,3-dimethyl-2−butene ≃ 1-butene. The range in these reactivities is surprisingly small and spans only one order of magnitude. Equally unexpected is that the olefin reactivity order does not reveal any apparent pattern in steric and/or electronic substituent effects. For example, the mono-, di-, and tetra-substituted olefins *trans*-2-butene, 2,3-dimethyl-2-butene, and 1-butene all have similar affinities to the phosphinidene complex, while isobutylene is clearly the most reactive olefin. How do these observations relate to those reported for carbene additions? In the following sections we highlight in a comparative fashion the eminent features that characterize the PhPW(CO)₅ addition to olefins.

Comparisons with Carbenes. The olefin reactivity order for the phosphinidene addition differs significantly from those of the halocarbenes CClF and CCl_2 ($\varrho^+ = -0.69$), both of which show a progressive preference for higher substituted olefins. In fact, all electrophilic carbenes (*e.g.*, MeCCl)[20] show a higher reactivity toward olefins with higher alkyl substitution patterns and only for nucleophilic carbenes (*e.g.*, $(MeO)_2C$)[21] are reversed trends observed—ambiphilic carbenes (*e.g.*, PhOCCl),[22] which react both with electron-rich and electron-poor olefins, tend to show little discrimination between the various methylated

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olefins. The numerous studies in this area led Moss[23] to the development of the carbene selectivity index m_{CXY}, which is defined as the slope of log $(k_i/k_0)_{CXY}$ vs log $(k_i/k_0)_{CCl_2}$ where k_i/k_0 (at 25 °C) represents the relative olefin reactivity with isobutylene as standard and $m_{CCl_2} = 1.0$. For example, CClF with an m_{CClF} index of 1.28 is less reactive and more selective than CCl_2. The difference with the still more electrophilic CBr_2 ($m_{CBr_2} = 0.65$) is even more pronounced. Nucleophilic carbenes have larger m_{CXY} values, *e.g.*, $m = 2.2$ for $C(OMe)_2$, while those of ambiphilic carbenes like MeOCCl ($m = 1.59$) are intermediate.[23] Even the very electrophilic $BrCCO_2Et$ ($m = 0.29$) still shows a small systematic differentiation in its addition to methylated olefins, but with the parent carboethoxycarbene $HCCO_2Et$ ($m = 0.059$) there is no longer discrimination in olefin reactivity.[17] Inexplicably, the reactivity pattern of the $PhPW(CO)_5$ additions best resembles those of ambiphilic carbenes as well as the very electrophilic, indiscriminate carboethoxycarbene. However, neither comparison seems well suited as judged by Hammett reaction constants, although *a priori* the magnitudes of the ϱ^+ values for phosphinidene and carbene additions do not have to mirror each other.

Comparisons with $C{=}CMe_2$. The olefin–phosphinidene reactivity order compares much better with the alkylidene carbene $C{=}CMe_2$[24] addition to olefins, but also here there are disconcerting observations. For example, while CCl_2, $C{=}CMe_2$, and $PhPW(CO)_5$ all have similar Hammett reactivity constants for the addition to styrenes, the ϱ value of -0.75 for $C{=}CMe_2$ is based on σ substituent constants instead of the Brown σ^+ values.[25] In their combined experimental and theoretical (*ab initio* STO-3G and MNDO) study Apeloig, Stang, and coworkers[26] explained quantitatively the contrasting behavior of saturated carbenes and the propylidene carbene $C{=}C(CH_3)_2$ to result from a combination of electronic (enhanced reactivity with additional methyl substituents) and steric effects (steric hindrance for isobutylene and 2,3-dimethyl-2-butene). Support for this argument is found in the olefin additions of the extended unsaturated carbenes $C{=}C{=}C(CH_3)_2$ ($\varrho(\sigma^+) = -0.95$)[27] and $C{=}C{=}C{=}C(CH_3)_2$ which both show "normal" selectivities for electrophilic carbenes of $m = 0.70$[28] and 0.77,[29] respectively, with the higher reactivities for the tetrasubstituted olefin. It follows that if steric arguments are important in the $C{=}CMe_2$ addition to isobutylene (which is the least reactive olefin), the same may be expected to apply for the isolobal and sterically much more congested $PhPW(CO)_5$. However, this is in contrast with our observations which show that isobutylene reacts the fastest. On the other hand, because of the longer C–P bonds and possibly different trajectory for $PhPW(CO)_5$, the phosphinidene addition could be less prone to steric hindrance than the isopropylidene carbene. This steric argument is not very convincing, however, in light of the behavior of the related methylenecycloalkanes (see Table 2).[12] For example, neither steric nor electronic effects can explain satisfactorily why $PhPW(CO)_5$ reacts 5.6 times faster with methylenecyclopentane than with methylenecyclopropane. In fact, we demonstrated that the relative reactivity pattern for phosphinidene addition of these methylenecycloalkanes only correlates with NMR data of the phosphirane products, which minimally suggests thermodynamic control of the reaction![12] Further, the relative methylenecyclohexane/cyclohexene reactivity ratio of 4 is very similar to that of the structurally related acyclic isobutylene/*cis*-2-butene pair.

Table 2. Relative Reactivities for the Addition of Ph–P–$W(CO)_5$ to Methylenecycloalkanes

olefins	rel reactivity
methylenecyclopropane	0.38
methylenecyclobutane	1.22
methylenecyclopentane	2.14
methylenecyclohexane	1.00
cyclohexene	0.26

Steric Considerations. That steric factors can play an important role is illustrated by the internal competition between the *cis*-di- and tetrasubstituted double bonds in 1,2-dimethyl-1,4-cyclohexadiene (**5**),[30] 4,7-dihydroindan (**6**), and isotetralin (**7**). In all three cases $PhPW(CO)_5$ adds exclusively to the disubstituted double bond. This behavior is again similar to that of the $C{=}CMe_2$, which shows the same preference for the side double bonds of isotetralin,[31] but sharply contrasts that of CCl_2, NH, and ^1O all of which add instead mainly to the central C=C bond, the products of which are precursors to [10]-annulenes.[32] The steric aspect of the phosphinidene addition is further highlighted by the inability of $PhPW(CO)_5$ to add to the double bond of 4,5,6,7-tetrahydroindan. However, as eloquently illustrated in the computational analysis by Apeloig and Stang for the olefin addition of $C{=}CMe_2$,[26] this could mainly be a reflection of the steric interactions on the trajectory for addition, hampering a proper initial (orbital) orientation of the phosphinidene with the C=C bond, because sterically congested phosphiranes can be synthesized with ease as illustrated by the exo-adduct of norbornadiene **9**.[33]

Stereoselectivities. Steric and electronic contributors to a reaction are often revealed in the stereoselectivity of product formation. Because of its two different P-substitutents the phosphinidene–olefin addition reaction should be no exception provided rigorous assignment of the isomeric phosphirane products is available. Therefore, the stereoselectivity for the $PhPW(CO)_5$ addition to *cis*-2-butene was ascertained by a single crystal X-ray structure determination of the major *anti*-phosphirane (Figure 1) which has the P–$W(CO)_5$ group *anti* to the methyl substitutents. Representative bond lengths and angles are given in Table 3. The phosphirane P–C and C–C bond lengths are similar to those of the unsubstituted $PhP(C_2H_4)W(CO)_5$ system.[12] Noteworthy is that the P-phenyl ring is nearly periplanar with the methyl groups and that the phosphirane P–C bonds are in an eclipsed orientation with two of the W carbonyls.

It is not unreasonable to assume that this less crowded *anti*-isomer is formed in favor over the *syn*-isomer (the *syn*/*anti* ratio is 0.25), due to a lower degree of steric interaction between the $W(CO)_5$ group and the two methyls. This steric repulsion can only be illustrated by interchanging the P-phenyl and $W(CO)_5$ groups. Both projecting the $W(CO)_5$ along the P-phenyl vector of the X-ray structure and molecular mechanics modeling give nonbonded distances between the methyl hydrogen and a staggered W carbonyl as short as 2.4 Å. It follows that the

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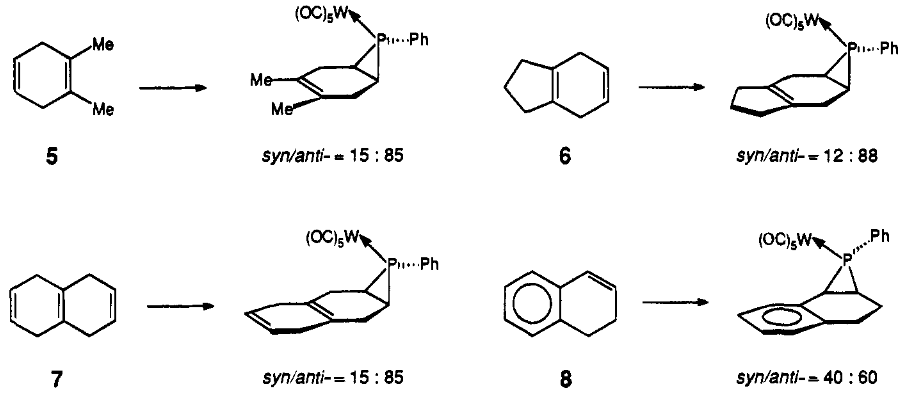
Scheme 1



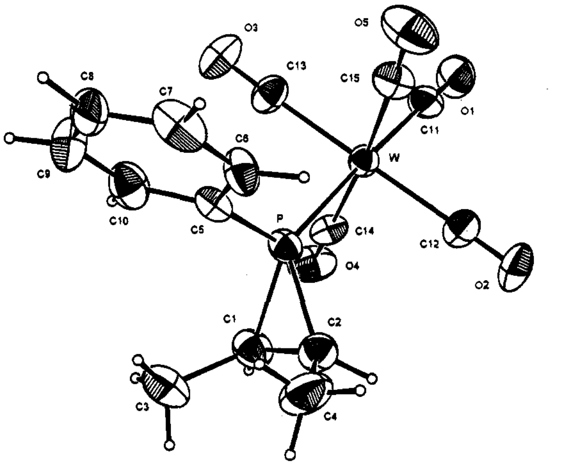


Figure 1. ORTEP drawing with the atom-labeling scheme of the molecular structure of *anti*-**4b**.

Table 3. Selected Bond Distances, Bond Angles, and Dihedral Angles for 4b

atoms	distance	atoms	angle
W–P	2.483(3)	W–P–C(5)	122.4(4)
W–C(12)	2.06(1)	W–C(12)–O(2)	178(1)
W–C(14)	2.01(1)	W–C(14)–O(14)	178(1)
P–C(1)	1.83(1)	P–W–C(12)	87.2(4)
P–C(2)	1.85(2)	P–W–C(14)	86.9(4)
P–C(5)	1.79(1)	P–C(1)–C(3)	124(1)
O(2)–C(12)	1.13(2)	P–C(2)–C(4)	125(1)
O(4)–C(14)	1.12(2)	C(1)–P–C(2)	27.0(8)
C(1)–C(2)	1.47(2)	C(1)–C(2)–C(4)	122(1)
C(1)–C(3)	1.55(2)	C(2)–C(1)–C(3)	121(1)
C(2)–C(4)	1.45(2)	C(1)–P–C(5)	109.3(6)
C(5)–C(6)	1.35(2)	C(2)–P–C(5)	107.4(6)
C(5)–C(10)	1.40(2)		

syn-isomer is sterically more congested. Apparent confirmation of this hypothesis is obtained from a comparison with the stereoselectivities of other phosphinidene–olefin additions For example, the selectivity reduces to a *syn*/*anti* ratio of 0.67 upon introduction of an additional methyl substituent, *i.e.* 2-methyl-2-butene, which deminishes the steric discrimination. A similar reduction in selectivity is seen for the cyclic olefins cyclohexene and 1,4-cyclohexadiene which both have *syn*/*anti* ratios of 0.54[30] and 1,2-dihydronaphthalene (**8**) which has a ratio of 0.67. The larger selectivity found for 1,2-dimethyl-1,4-cyclohexene (**5**) (*syn*/*anti* = 0.18)[30] is similar to that of *cis*-2-butene and likewise due to the methyl "interlocking" of a staggared W carbonyl.

Electronic factors can influence the stereoselectivity, however, and they tend to favor formation of *syn*-isomers as is the case with conjugated dienes.[30] For example, a *syn*-phosphirane is formed nearly exclusively (~95%) from 1-methoxy-1,3-cyclohexadiene.[34] In the absence of the activating methoxy group a lower *syn*/*anti* ratio of 1.5 is obtained for 1,3-cyclohexadiene.[30] These conjugated *syn*-phosphiranes undergo thermally allowed 1,3-sigmatropic shifts to phospholenes, while their *trans*-isomers decompose under the reaction conditions. Additions of $PhPW(CO)_5$ to cyclopenta-, hepta-, and octadienes also render *syn*- and *anti*-phosphiranes of which the *syn*-isomers rearrange into the thermodynamically more stable *anti*-isomers.[35]

Conclusions. The important observation that emerges from this competitive reactivity study is that the reactivity of the *in situ* formed $PhPW(CO)_5$ shows little selectivity in its addition to methyl-substituted olefins. Its olefin selectivity is similar to that of the isolobal isopropylidene carbene $C{=}C(CH_3)_2$ but much lower than those reported for halocarbenes. This lack of olefin selectivity suggests a much higher reactivity than would be anticipated for a phosphinidene which is stabilized by a transition metal ligand.

The high stereospecificity of addition to both *cis*- and *trans*-2-butene is further confirmation of the singlet carbene-like character of $PhPW(CO)_5$, which was earlier inferred from the addition to stilbenes and the Hammett ρ^+ value of −0.76 for the addition to styrenes.

The modest stereoselectivity of the olefin addition reaction, as reflected in the *syn*-/*anti*-phosphirane product ratios, suggests the presence of opposing steric and electronic influences—the thermodynamically more stable products prefer the $P\text{-}W(CO)_5$ group in the *anti* position.

The observed lack of intermolecular selectivity does suggest a high reactivity for $PhP(WO)_5$ and a resemblance in behavior with carbenes. Also indicative of this high reactivity is the decomposition of the $PhPW(CO)_5$ precursor which has been reported to be a first-order process independent of trapping reagents.[3] The observed lack of olefin selectivity work is further

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(39) An alternative interpretation was offered by one of the referees, who argued that Cu complexation of $PhPW(CO)_5$ would reduce the phosphinidene electrophilicity, leading to lower polarization in the transition state and lower selectivity between the alkenes. This interpretation is not likely in light of the contrasting, well behaved CuCl catalyzed phosphinidene addition to styrenes that enabled the determination of three Hammett reaction constants for $RPW(CO)_5$ (R = Ph, CH_3, and CH_3O), which show significant electrophilicity in the expected order, Ph > CH_3 > CH_3O.[4-6] Whereas the exact role of the CuCl catalyst is not known,[1d] it enables a reduction of the reaction temperature from ca. 110 to 55–60 °C for the dissociation of the $PhPW(CO)_5$ precursor, thereby limiting side reactions, without an apparent influence on olefin selectivities.

in line with an earlier study[12] in which we found the reactivity of exocyclic olefins to correlate with properties of their spirophosphirane products. Therefore, these observations may be indicative of the importance of entropy factors for the thermodynamically driven addition of the PhPW(CO)$_5$ phosphinidene to olefins in a manner analogous to the well-studied carbene cyclopropanation.

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore spectrometer. Chemical shifts are referenced in ppm to internal Me$_4$Si for the ^{1}H and ^{13}C NMR spectra and to external 85% H$_3$PO$_4$ for the ^{31}P NMR spectra. Downfield shifts are reported as positive. IR spectra were recorded on a Nicolet IR44 spectrometer. Mass spectra were recorded on a HP 5985 at 70 eV. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of dry, high-purity nitrogen. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium–benzophenone prior to use, and toluene, which was dried over molecular sieves. The olefins were purchased from Aldrich and Fluka Chemical Co. and were used without further purification. Chromatographic separations were performed on silica gel columns (230–400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**1**) is described in ref 2b.

General Procedure for the Competition Reactions. One milliliter each of two alkenes were transferred at −40 to −60 °C to a precooled autoclave filled with 5 mL of dry toluene and a magnetic stirrer. To this was added 200 mg (0.3 mmol) of complex **1** and 10 mg (0.1 mmol) of CuCl, after which the reaction mixture was placed under a nitrogen atmosphere. The sealed autoclave was heated for 1−1.5 h at 60 °C. After cooling and removal of CuCl by filtration, aliquots of the reaction mixtures were subjected to ^{31}P NMR analysis. Relative phosphirane product ratios were determined from integration of the ^{31}P resonances.

Isobutylene (3a). The reaction was executed as described for *cis*-2-butene. A 450 mg (60.3%) yield of a colorless solid was obtained starting from 1.00 g of complex **1**. Mp (hexane) 48.5–50.5 °C; ^{31}P NMR (C$_6$D$_6$) −144.0 ($^1J_{PW}$ = 256.7 Hz); ^{13}C NMR (C$_6$D$_6$) 23.3 (s, $^2J_{CP}$ = 0 Hz, $^1J_{CH}$ = 129.1 Hz, *trans*-CH$_3$), 23.7 (d, $^1J_{CP}$ = 13.0 Hz, $^1J_{CH}$ = 159.5 Hz, CH$_2$P), 26.1 (s, $^2J_{CP}$ = 0 Hz, $^1J_{CH}$ = 128.2 Hz, *cis*-CH$_3$), 26.4 (s, C$_2$CP), 128.7 (d, $^3J_{PC}$ = 8.5 Hz, *m*-Ph), 130.0 (s, *p*-Ph), 132.2 (d, $^2J_{PC}$ = 8.2 Hz, *o*-Ph), 196.3 (d, $^2J_{PC}$ = 8.8 Hz, *cis*-CO), 198.3 (d, $^2J_{PC}$ = 27.2 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.69 (d, $^3J_{PH}$ = 12.0 Hz, 3H, *trans*-CH$_3$), 0.94 (d, $^2J_{PH}$ = 8.1 Hz, 1H, *trans*-CH$_2$P), 1.13 (s, 1H, *cis*-CH$_2$P), 1.13 (d, $^3J_{PH}$ = 18.6 Hz, 3H, *cis*-CH$_3$), 6.89–7.02 (m, 5H, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 488 (M, 11.7), 432 (PhPW(CO)$_5$, 15.5), 404 (PhPW(CO)$_4$, 32.1), 348 (PhPW(CO)$_2$, 100.0), 320 (PhPWCO, 44.3), 292 (PhPW, 85.2). Anal. Calcd for C$_{15}$H$_{13}$PWO$_5$: C, 36.92; H, 2.68. Found: C, 37.02; H, 2.69.

***cis*-2-Butene (3b).** *cis*-2-Butene (1.0 mL) was condensed and transferred to an autoclave containing a solution of complex **1** (0.70 g, 1.07 mmol) and CuCl (23 mg, 0.23 mmol) in 30 mL of toluene and heated at 58 °C for 2 h. The reaction mixture was filtrated, evaporated to dryness, and chromatographed over silica gel with hexane/benzene (4:1) as eluents to give 260 mg (48.4%) of a 4:1 mixture of a colorless solid. Major product (hexane): mp 77–78 °C; ^{31}P NMR (C$_6$D$_6$) −164.8 ($^1J_{PW}$ = 251.0 Hz); ^{13}C NMR (C$_6$D$_6$) 10.3 (s, CH$_3$), 22.8 (d, $^1J_{CP}$ = 14.9 Hz, CHP), 129.0 (s, *p*-Ph), 129.1 (d, $^3J_{PC}$ = 9.4 Hz, *m*-Ph), 133.5 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Ph), 196.4 (d, $^2J_{PC}$ = 8.0 Hz, *cis*-CO), 198.9 (d, $^2J_{PC}$ = 24.8 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.69 (ddd, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, CH$_3$), 1.26–1.32 (m, $^2J_{PH}$ 0 Hz, 2H, CHP), 6.89–7.02 (m, 5H, Ph). Anal. (major isomer). Calcd for C$_{15}$H$_{13}$PWO$_5$: C, 36.92; H, 2.68. Found: C, 36.82; H, 2.66. Minor product (analyzed from a mixture): ^{31}P NMR (C$_6$D$_6$) −149.9 ($^1J_{PW}$ = 256.5 Hz); ^{13}C NMR (C$_6$D$_6$) 11.2 (s, CH$_3$), 23.3 (d, $^1J_{CP}$ = 13.3 Hz, CHP), 129.3 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Ph), 129.8 (s, *p*-Ph), 131.5 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Ph), 196.1 (d, $^2J_{PC}$ = 9.7 Hz, *cis*-CO), 198.6 (d, $^2J_{PC}$ = 25.1 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.97 (ddd, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.8 Hz, 6H, CH$_3$), 1.33–1.39 (m, $^2J_{PH}$ 6.8 Hz, 2H, CHP), 6.90–7.10 (m, 5H, Ph); mass spectrum of the mixture (^{184}W) *m/e* (relative intensity) 488 (M, 12.0), 432 (PhPW(CO)$_5$, 15.7), 404 (PhPW(CO)$_4$, 31.6), 348 (PhPW(CO)$_2$, 100.0), 320 (PhPWCO, 47.0), 292 (PhPW, 86.9).

***trans*-2-Butene (3c).** The reaction was executed as described for *cis*-2-butene. A 460 mg (61.6%) yield of a colorless liquid was obtained starting from 1.00 g of complex **1**. ^{31}P NMR (C$_6$D$_6$) −146.1 ($^1J_{PW}$ = 252.6 Hz); ^{13}C NMR (C$_6$D$_6$) 15.4 (s, $^2J_{CP}$ = 0 Hz, $^1J_{CH}$ = 128.3 Hz, *trans*-CH$_3$), 17.3 (s, $^2J_{CP}$ = 0 Hz, $^1J_{CH}$ = 134.4 Hz, *cis*-CH$_3$), 25.0 (d, $^1J_{CP}$ = 11.5 Hz, $^1J_{CH}$ = 159.0 Hz, CHP), and 27.9 (d, $^1J_{CP}$ = 15.2 Hz, $^1J_{CH}$ = 164.7 Hz, CHP), 128.8 (d, $^3J_{PC}$ = 9.2 Hz, *m*-Ph),130.0 (s, *p*-Ph), 132.8 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Ph), 196.2 (d, $^2J_{PC}$ = 7.2 Hz, *cis*-CO), 198.2 (d, $^2J_{PC}$ = 29.4 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.64 (dd, $^3J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 6.4 Hz, 3H, *trans*-CH$_3$), 0.80–0.97 (m, 1H, *trans*-CHP), 1.11 (d, $^3J_{PH}$ = 15.3 Hz, 3H, *cis*-CH$_3$), 1.23 (s, br, 1H, *cis*-CHP), 6.89–7.11 (m, 5H, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 488 (M, 14.0), 432 (PhPW(CO)$_5$, 14.1), 404 (PhPW(CO)$_4$, 33.1), 348 (PhPW(CO)$_2$, 100.0), 320 (PhPWCO, 46.6), 292 (PhPW, 78.4). Anal. Calcd for C$_{15}$H$_{13}$PWO$_5$: C, 36.92; H, 2.68. Found: C, 36.99; H, 2.70.

2-Methyl-2-butene (3d). The reaction was executed as described for *cis*-2-butene. A 210 mg (54.7%) yield of a 3:2 product mixture was obtained as a colorless solid from 500 mg of complex **1**. Major product (hexane): mp 70–72 °C; ^{31}P NMR (C$_6$D$_6$) −141.9 ($^1J_{PW}$ = 250.2 Hz); ^{13}C NMR (C$_6$D$_6$) 11.5 (d, $^1J_{CP}$ = 4.0 Hz, $^1J_{CH}$ = 128.8 Hz, *trans*-*C*H$_3$CH), 18.4 (s, $^1J_{CH}$ = 127.0 Hz, *trans*-*C*H$_3$C), 28.4 (d, $^1J_{CP}$ = 5.8 Hz, $^1J_{CH}$ = 126.8 Hz, *cis*-CH$_3$), 28.5 (d, $^1J_{CP}$ = 12.5 Hz, C$_2$CP), 30.9 (d, $^1J_{CP}$ = 13.7 Hz, $^1J_{CH}$ = 165.5 Hz, CHP), 129.0 (d, $^3J_{PC}$ = 9.2 Hz, *m*-Ph), 129.9 (s, *p*-Ph), 133.3 (d, $^2J_{PC}$ = 9.2 Hz, *o*-Ph), 196.6 (d, $^2J_{PC}$ = 7.8 Hz, *cis*-CO), 198.6 (d, $^2J_{PC}$ = 29.3 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.75 (d, $^3J_{PH}$ = 11.1 Hz, 3H, *trans*-CH$_3$C), 0.76 (dd, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 4.1 Hz, 3H, *trans*-CH$_3$CH), 1.16 (d, $^3J_{PH}$ = 18.8 Hz, 3H, *cis*-CH$_3$), 1.17 (m, 1H, CH), 6.90–7.07 (m, 5H, Ph). Anal. Calcd for C$_{16}$H$_{15}$PWO$_5$: C, 38.27; H, 3.02. Found: C, 38.38; H, 2.98. Minor product (analyzed from a mixture): ^{31}P NMR (C$_6$D$_6$) −130.0 ($^1J_{PW}$ = 252.6 Hz); ^{13}C NMR (C$_6$D$_6$) 12.3 (s, $^1J_{CH}$ = 126.8 Hz, *cis*-CH$_3$), 20.2 (d, $^1J_{CP}$ = 7.9 Hz, $^1J_{CH}$ = 128.6 Hz, *cis*-*C*H$_3$C), 25.5 (s, $^1J_{CH}$ = 128.0 Hz, *trans*-CH$_3$), 29.8 (d, $^1J_{CP}$ = 13.8 Hz, CP), 29.9 (d, $^1J_{CP}$ = 14.7 Hz, CHP), 129.7 (d, $^3J_{PC}$ = 9.2 Hz, *m*-Ph), 129.8 (s, *p*-Ph), 132.3 (d, $^2J_{PC}$ = 10.0 Hz, *o*-Ph), 196.2 (d, $^2J_{PC}$ = 8.5 Hz, *cis*-CO), 198.0 (d, $^2J_{PC}$ = 26.9 Hz, *trans*-CO); ^{1}H NMR (C$_6$D$_6$) 0.72 (d, $^3J_{PH}$ = 12.3 Hz, 3H, *trans*-CH$_3$), 1.08 (dd, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 4.1 Hz, 3H, *cis*-CH$_3$), 1.08 (m, 1H, CH), 1.18 (d, $^3J_{PH}$ = 18.8 Hz, 3H, *cis*-CH$_3$C), 6.90–7.07 (m, 5H, Ph); mass spectrum of the mixture (^{184}W) *m/e* (relative intensity) 502 (M, 7.3), 432 (PhPW(CO)$_5$, 14.7), 404 (PhPW(CO)$_4$, 35.2), 348 (PhPW(CO)$_2$, 100.0), 320 (PhPWCO, 53.6), 292 (PhPW, 98.0).

2,3-Dimethyl-2-butene (3e). The reaction was executed as described for *cis*-2-butene. A 110 mg (27.9%) yield of colorless solid was obtained starting from 500 mg of complex **1**. Mp (hexane) 132−134°C; ^{31}P NMR (C_6D_6) −125.4 ($^1J_{PW} = 249.7$ Hz); ^{13}C NMR (C_6D_6) 21.2 (s, *trans*-CH_3), 23.0 (d, $^2J_{CP} = 5.6$ Hz, *cis*-CH_3), 32.7 (d, $^1J_{CP} = 14.3$ Hz, CP), 128.9 (d, $^3J_{PC} = 8.2$ Hz, *m*-Ph), 129.6 (s, *p*-Ph), 132.3 (d, $^2J_{PC} = 9.1$ Hz, *o*-Ph), 196.6 (d, $^2J_{PC} = 7.7$ Hz, *cis*-CO), 198.2 (d, $^2J_{PC} = 29.6$ Hz, *trans*-CO); ^{1}H NMR (C_6D_6) 0.81 (d, $^3J_{PH} = 11.1$ Hz, 6H, *trans*-CH_3), 1.17 (d, $^3J_{PH} = 17.7$ Hz, 6H, *cis*-CH_3), 6.89−7.02 (m, 5H, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 516 (M, 8.4), 432 ($PhPW(CO)_5$, 16.0), 404 ($PhPW(CO)_4$, 32.5), 348 ($PhPW(CO)_2$, 83.2), 320 (PhPWCO, 49.9), 292 (PhPW, 100.0). Anal. Calcd for $C_{17}H_{17}PWO_5$: C, 39.56; H, 3.33. Found: C, 39.67; H, 3.28.

1-Butene (3f). The reaction was executed as described for *cis*-2-butene to give a product mixture of two phosphiranes in a ratio of 75:25 as identified by integration of their respective ^{31}P NMR resonances. Major product: ^{31}P NMR (C_6D_6) −166.9 ($^1J_{PW} = 253.2$ Hz); ^{13}C NMR ($CDCl_3$) 15.2 (d, $^3J_{PC} = 5.9$ Hz, CH_3), 15.9 (d, $^2J_{PC} = 5.9$ Hz, CH_2), 25.2 (d, $^1J_{CP} = 4.2$ Hz, CH_2P), 29.3 (d, $^1J_{CP} = 14.7$ Hz, CHP), 129.9 (d, $^3J_{PC} = 9.9$ Hz, *m*-Ph), 131.5 (s, *p*-Ph), 133.9 (d, $^2J_{PC} = 12.0$ Hz, *o*-Ph), 197.0 (*cis*-CO), 197.1 (*trans*-CO); ^{1}H NMR ($CDCl_3$) 0.69 (d, $^2J_{HH} = 6.9$ Hz, 3H, *trans*-CH_3), 0.76−1.1 (m, 4H, *trans*-CHP, *cis*-CH_2P; *cis*-CH_2), 1.55 (s, 1H, *cis*-CH_2P), 6.88−7.12 (m, 5H, Ph). Minor product: ^{31}P NMR (C_6D_6) −166.7 ($^1J_{PW} = 257.1$ Hz)

Bicyclo[4.3.0]nona-3,6(1)-diene (6). The reaction with dihydroindan was executed as described for tetrahydronaphthalene to give a 55% isolated yield of a 88:12 mixture of phosphiranes. Major product (hexane): mp 135 °C; ^{31}P NMR (C_6D_6) −178.6 ($^1J_{PW} = 249.7$ Hz); ^{13}C NMR (C_6D_6) 20.7 (s, CH_2), 22.9 (d, $^2J_{CP} = 4.3$ Hz, CH_2), 23.6 (d, $^1J_{CP} = 14.0$ Hz, CHP), 35.3 (s, CH_2), 196.5 (d, $^2J_{CP} = 8.2$ Hz, *cis*-CO), 198.9 (d, $^2J_{CP} = 29.4$ Hz, *trans*-CO); ^{1}H NMR (C_6D_6) 0.9−1.3 (m, 4H), 1.6−2.2 (m, 8H, CH_2), 6.7−6.9 (m, 5H, Ph). Anal. (major isomer). Calcd for $C_{20}H_{19}PWO_5$: C, 43.47; H, 3.07. Found: C, 43.25; H, 3.08. Minor product (analyzed from a mixture): ^{31}P NMR (C_6D_6) −153.6; mass spectrum of the mixture (^{184}W) *m/e* (relative intensity) 552 (M, 6.9), 432 ($PhPW(CO)_5$, 15.3), 404 ($PhPW(CO)_4$, 55), 376 ($PhPW(CO)_3$, 19.8), 348 ($PhPW(CO)_2$, 85.2), 320 (PhPWCO, 49.2), 292 (PhPW, 81.0).

1,4,5,8-Tetrahydronaphthalene (7). Complex **1** (70 mg, 0.1 mmol) and isotetralin (40 mg, 0.3 mmol) in toluene with a catalytic amount of CuCl were heated at 55 °C for 2 h to give in 39% isolated yield a product mixture of two phosphiranes in a ratio of 85:15 as identified by integration of their respective ^{31}P NMR resonances. Major product (hexane): mp 154 °C; ^{31}P NMR (C_6D_6) −176.6 ($^1J_{PW} = 249.5$ Hz); ^{13}C NMR (C_6D_6) 23.7 (d, $^1J_{CP} = 14.3$ Hz, CHP), 26.1 (d, $^2J_{CP} = 4.6$ Hz, CH_2), 30.64 (s, CH_2), 123.6 (s, HC=), 196.5 (d, $^2J_{CP} = 8.3$ Hz, *cis*-CO), 198.8 (d, $^2J_{CP} = 29.3$ Hz, *trans*-CO); ^{1}H NMR (C_6D_6) 1.5−1.7 (m, 2H, CHP), 2.1−2.7 (m, 8H, CH_2), 5.31 (s, 2H, HC=), 6.7−6.9 (m, 5H, Ph). Anal. (major isomer). Calcd for $C_{21}H_{17}PWO_5$: C, 44.68; H, 3.01. Found: C, 44.55; H, 3.07. Minor product (analyzed from a mixture): ^{31}P NMR (C_6D_6) −154.6; mass spectrum of the mixture (^{184}W) *m/e* (relative intensity) 564 (M, 8.1), 432 ($PhPW(CO)_5$, 22.9), 404 ($PhPW(CO)_4$, 53.1), 376 ($PhPW(CO)_3$, 24.4), 348 ($PhPW(CO)_2$, 100.0), 320 (PhPWCO, 61.1), 292 (PhPW, 95.5).

1,2-Dihydronaphthalene (8). The reaction was executed as described for tetrahydronaphthalene to give a 35% isolated yield of a 60:40 mixture of phosphiranes. Major product (hexane): mp 111 °C; ^{31}P NMR (C_6D_6) −146.9 ($^1J_{PW} = 251.6$ Hz); ^{13}C NMR (C_6D_6) 20.1 (d, $^2J_{CP} = 3.9$ Hz, CH_2), 26.1 (s, CH_2), 26.8 (d, $^1J_{CP} = 16.0$ Hz, CHP), 28.7 (d, $^1J_{CP} = 15.8$ Hz, CHP), 196.3 (d, $^2J_{CP} = 8.8$ Hz, *cis*-CO), 198.7 (d, $^2J_{CP} = 29.2$ Hz, *trans*-CO); ^{1}H NMR (C_6D_6) 1.12 (m, 1H), 1.75 (m, 2H), 1.84 (m, 2H), 2.73 (d, $^2J_{HP} = 9.9$ Hz, HCP), 6.4−7.2 (m, 5H, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 562 (M, 7.5), 432 ($PhPW(CO)_5$, 23.0), 404 ($PhPW(CO)_4$, 55.9), 376 ($PhPW(CO)_3$, 17.1), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 52.6), 292 (PhPW, 76.9). Anal. Calcd for $C_{21}H_{15}PWO_5$: C, 44.83; H, 2.66. Found: C, 44.92; H, 2.68. Minor product (analyzed from a mixture): mp 92−3 °C; ^{31}P NMR (C_6D_6) −129.5 ($^1J_{PW} = 265.6$ Hz); ^{13}C NMR (C_6D_6) 23.1 (d, $^1J_{CP} = 13.0$ Hz, CHP), 23.8 (s, CH_2), 27.4 (d, $^1J_{CP} = 16.6$ Hz, CHP), 28.2 (d, $^2J_{CP} = 5.4$ Hz, CH_2), 195.2 (d, $^2J_{CP} = 7.3$ Hz, *cis*-CO), 197.6 (d, $^2J_{CP} = 27.9$ Hz, *trans*-CO); mass spectrum (^{184}W) *m/e* (relative intensity) 562 (M, 8.2), 432 ($PhPW(CO)_5$, 27.3), 404 ($PhPW(CO)_4$, 65.2), 376 ($PhPW(CO)_3$, 17.3), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 56.6), 292 (PhPW, 91.0). Anal. Calcd for $C_{21}H_{15}PWO_5$: C, 44.83; H, 2.66. Found: C, 44.98; H, 2.71.

X-ray Structure Determination of *anti*-4b. Structure Solution and Refinement. A well-formed single crystal, attached to glass fibers with epoxy cement, was mounted on an Enraf-Nonius CAD4 diffractometer. Least-squares refinement of 25 well-centered reflections ($25 \le \theta \le 35$) yielded precision lattice constants for the crystal. Intensity data were collected at room temperature using Ni-filtered monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å) with an $\omega/2\theta$ scan mode (scan width 2.04°, background/scan ratio = 0.5)) up to $2\theta = 148°$. Three reflections were measured periodically during data collection to monitor crystal decay. The data were processed using the Enraf-Nonius MolEN software on a VAX/VMS. Intensities were corrected for Lorentz and polarization effects; a linear decay correction and an analytical absorption correction were also applied. Variances were assigned based on standard counting statistics, with the addition of an instrumental uncertainty term $0.02F_o^2$. The structure was solved by standard Patterson and difference Fourier techniques and refined by weighted full-matrix least squares. A secondary extinction correction (Zachariasen) was applied and the coefficient was refined (1.4529×10^{-7}). The final model contains anisotropic thermal parameters for all non-hydrogen atoms, and isotropic hydrogens atoms in calculated positions riding on their attached carbon atoms. The final difference Fourier map contained maximum $\Delta\varrho$ values near the W atom, with no peaks interpretable as extra atoms. The atomic scattering factors were taken from the *International Tables for Crystallography*.

Crystal and Intensity Data. $C_{15}H_{13}O_5PW$ (*anti*-**4b**), MW = 488.09, orthorhombic unit cell, $a = 6.710(1)$ Å, $b = 15.276(2)$ Å, $c = 16.692(3)$ Å, $V = 1711.0$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.895$ g/cm^3, crystal dimensions 0.25 × 0.11 × 0.09 mm, abs. coeff. 137.422 cm^{-1}, reflections measured with index ranges of $0 \le h \le 8$, $0 \le k \le 19$, $0 \le l \le 20$, 2015 unique reflections from which 1706 were observed having $I > 3\sigma(I)$, 200 parameters, $R = 4.26\%$, $R_w = 5.37\%$, GOF = 1.122, $A_{max} = 39.03\%$, $A_{min} = 17.61\%$, $\Delta\varrho_{max} = 1.175$ e Å^{-3}, $\Delta\varrho_{min} = -0.322$ e Å^{-3}, $\Delta/\sigma_{max} = 0.00$.

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Supplementary Material Available: Listings of bond distances and angles, positional parameters, least-square planes, and anisotropic thermal parameters for *anti*-**4b** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.