10486 *J. Am. Chem. Soc.* **1994,** *116,* 10486–10488

Hammett Reaction Constant for a Terminal Methoxyphosphinidene Complex. Absence of Ambiphilicity

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Received June 6, 1994⊗

Abstract: The Hammett reaction constant ϱ^+ has been determined for the styrene addition of MeO–P–W(CO)$_5$, as generated from the appropriate 7–phosphanorbornadiene complex. The phosphinidene reactivity is evaluated and compared with that of the ambiphilic MeO–C–Cl carbene.

Terminal transition metal complexed phosphinidenes R–P–W(CO)$_5$ are intriguing intermediates of remarkable and undetermined reactivity.[1] These phosphinidenes are generated from the thermal decomposition of 7-phosphanorbornadiene precursors but elude direct observation. *In situ* they add to olefins to give phosphiranes.[2] The high stereospecificity is indicative of a singlet cycloaddition. To reveal the characteristics of these reactive intermediates, we recently reported Hammett reaction constants (ϱ^+) of -0.76[3] and -0.60[4] for the cycloaddition of Ph–P–W(CO)$_5$ and Me–P–W(CO)$_5$ to styrenes, respectively. These reaction constants are very similar to those of halocarbenes (*e.g.*, $\varrho^+(CCl_2) = -0.60$[5] and $\varrho^+(CBr_2) = -0.57$)[6] and isopropylidene ($\varrho = -0.75$)[7] and thereby lend quantitative support for the electrophilic "carbene-like" reactivity of the phosphinidenes. However, this similarity in phosphinidene and carbene reaction constants is limited in scope and may be coincidental. A better understanding of this relationship can be expected from the study of substituent effects, because these are known to influence the character of carbenes dramatically.[8] For example, olefin selectivity studies identify MeO–C–Cl[9] and PhO–C–Cl[10] as ambiphilic carbenes, while MeO–C–OMe is even nucleophilic.[11] Therefore, we now report on the addition reaction of the methoxyphosphinidene complex MeO–P–W(CO)$_5$ to styrenes. The results are used to evaluate the phosphinidene reactivities.

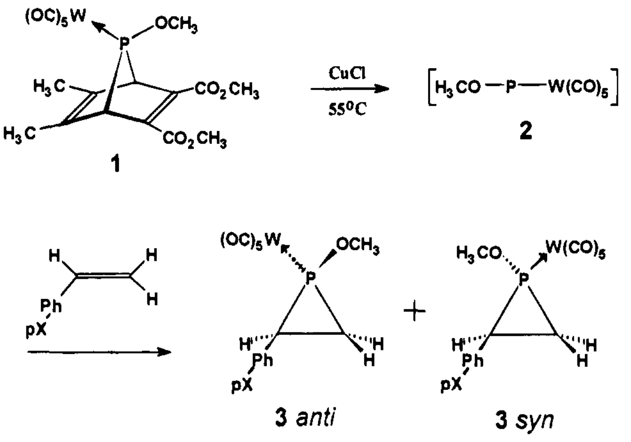
Table 1. Relative Reactivities (k_X/k_H) and *anti*/*syn* Addition Ratios of *p*-X-styrenes toward MeO–P–W(CO)$_5$ and ^{13}C NMR Chemical Shifts of the Phosphirane Products

substituent	k_X/k_H	*anti*/*syn*	δ_C(*anti*)	δ_C(*syn*)
OCH$_3$	2.57	3.6	−26.7	−44.4
phenyl	1.05	3.2	−25.0	−42.9
CH$_3$	1.71	4.0	−26.0	−44.0
H	1.00	4.3	−24.8	−43.1
Cl	0.57	4.5	−24.3	−42.1
Br	0.41	4.3	−23.7	−42.1
CE$_3$[a]	0.21		−22.5	

[a] Unable to determine the *syn*-isomer.

Results and Discussion

Relative phosphinidene **2** reactivities were determined from relative (total) phosphirane product **3** ratios that resulted from competitive reactions of the W(CO)$_5$-complexed 7-phosphanorbornadiene precursor **1**[12] with a 4-fold excess of equimolar mixtures of *p*-phenyl substituted styrenes.[13,14] The reactions were executed at 50–55 °C in the presence of 10% CuCl catalyst for 1–2 h; the *p*-phenyl substituents were OMe, Me, Ph, H, Cl, Br, and CF$_3$. The phosphirane product ratios were determined from reaction aliquots by ^{31}P NMR integration of the phosphirane resonances. The resulting relative product ratios and ^{31}P NMR chemical shifts are summarized in Table 1. Figure



[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

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(14) In this approach it is assumed (a) that the decomposition of **1** is independent of the nature and concentration of the trapping substrate (see ref 21 and the text) and (b) that the product ratios depend on the relative concentrations of the trapping substrates.

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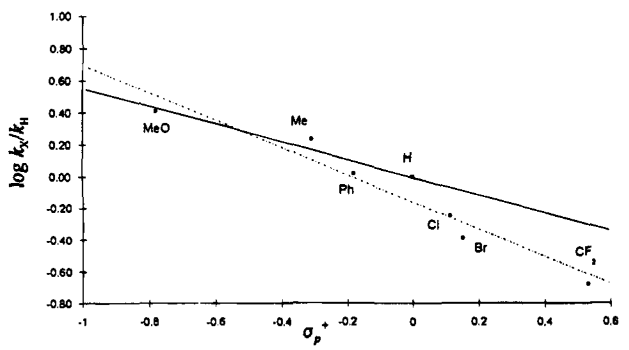


Figure 1. Hammett $\sigma^+-\varrho$ plot for the MeO—P—W(CO)$_5$ addition to p-XPhCH=CH$_2$.

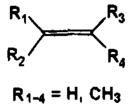
1 displays the linear correlation of these product ratios as log (k_X/k_H) with the Brown substituent constants σ^+. A Hammett reaction constant ϱ^+ of -0.55 ($r = 0.9529$, 95% confidence level) is obtained from the correlation of only the OMe-, CH$_3$-, Ph-, H-substituted styrenes. Limiting the data set to these styrenes leads to a more reliable ϱ^+ value because noticeable decomposition products are obtained with the slower reacting Cl, Br, and CF$_3$ derivatives.[15] To include all styrenes leads consequently to a larger ϱ^+ value of -0.87 ($r = 0.9596$, 95% confidence level).

Quite contrary to the carbenes, the observed negative sign of the Hammett constant for MeO—P—W(CO)$_5$ shows that the methoxy substituent does not influence the electrophilic nature of the phosphinidene complex regardless of whether the value of -0.55 or the less accurate -0.87 is used. The decrease in magnitude of the ϱ^+ values from -0.76 for Ph—P—W(CO)$_5$ to -0.60 for Me—P—W(CO)$_5$, to -0.55 for MeO—P—W(CO)$_5$ does suggest, however, a small P-substituent effect reflecting a corresponding increase in reactivity in the order MeO > Me > Ph. The similarity in small negative ϱ^+ values for these three W(CO)$_5$-complexed phosphinidenes supports quantitatively (a) their unencumbered singlet carbene-like character and (b) a slightly polar (electrophilic) transition for their concerted addition to olefins.

The stereoselectivity for the MeO—P—W(CO)$_5$—olefin addition resembles that of the Me and Ph derivatives which further underscores the close similarity between the differently substituted phosphinidenes. Thus, addition of MeO—P—W(CO)$_5$ to the styrenes yields *anti/syn*-phosphirane product ratios ranging from 3.2 to 4.5 with the higher selectivities for the less reactive styrenes. Very similar *anti/syn* product ratios and reactivity—selectivity trends were recently reported for the Me—P—W(CO)$_5$—styrene cycloadditions.[4]

Why is the methoxy-substituted phosphinidene MeO—P—W(CO)$_5$ electrophilic and the methoxy-substituted carbene MeO—C—Cl ambiphilic? The ambiphilic nature of MeO—C—Cl and the consequential lack of a Hammett reaction constant[16] are apparent from its enhanced relative reactivities toward olefins with both increased and decreased π-electron availability.[9] This is reflected in the carbene selectivity index m_{CXY},[17] developed by Moss,[8] which is set at unity for the electrophilic CCl$_2$, and which amounts to 1.59 for MeO—C—Cl and has a value of 2.2 for the nucleophilic C(OMe)$_2$. In contrast, as the negative ϱ^+ value for MeO—P—W(CO)$_5$ reveals, the electrophilicity of the phosphinidene is maintained despite the strong electron donating methoxy substituent. The electrophilic character of the phosphorus is also maintained in its cycloaddition products. This is evident from the correlation of the phosphirane ^{31}P NMR chemical shifts with the Brown σ^+ constants of its 2-p-phenyl substituents which leads to positive $\delta-\sigma$ slopes of 4.98 ($r = 0.985$, 95% confidence) for the *anti*-isomers and 4.49 ($r = 0.995$, 95% confidence) for the *syn*-isomers.[18] Positive $\delta-\sigma$ slopes of similar magnitude were recently obtained for the P—Me and P—Ph-substituted phosphiranes.[18b] For these systems the intercepts of the slopes range from -149.5 to -175.7 ppm versus the -25.1 and -43.1 ppm for the *anti*- and *syn*-P—OMe-substituted phosphiranes, respectively. Hence, while the electron donating methoxy group does influence the ^{31}P NMR chemical shifts, it is quite clear that the philicity of the more electropositive phosphorus atom (χ(phosphorus) = 2.19 versus χ(carbon) = 2.55)[19] is not significantly influenced.[20]

Can the empirical Hammett ϱ^+ values shed more light on the reaction profile of the complexed phosphinidenes? This question can only be addressed in concert with other recent mechanistic studies of which we highlight the most revealing. First, kinetic studies[21] have shown that the decomposition of the Ph—P—W(CO)$_5$ precursor is a first-order process that is independent of the trapping substrate, which identifies the phosphinidene formation as the rate-determining step. Second, this phosphinidene does not show intermolecular selectivity with the set of methylated olefins **4** that is used to identify the philicity (m_{CXY}) of carbenes.[22] Third, the relative reactivities for the addition of Ph—P—W(CO)$_5$ with exocyclic olefins **5** correlates with properties of the phosphirane products instead of those of the olefins, which suggests a thermodynamic relationship.[23] These three observations identify the cycloaddition step as fast and rather unselective. The limited or lack of substrate selectivity points to a small activation energy for the addition and possibly even to an absence thereof.[24-26] How then do Hammett reaction constants, which are determined from competitive reactions, fit into the picture? The distinction in substrate selectivities must be associated with the identity/profile of the second step, which points to a delicate balance between



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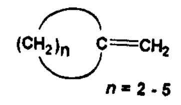

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[15] The R—P—W(CO)$_5$ complexes interact with the halogen substituents.

[16] The reported relative reactivities of MeO—C—Cl toward X-styrenes are 1.50 (p-OMe), 1.07 (p-Me), 1.0 (H), 1.04 (m-Cl), and 1.27 (m-NO$_2$). See: Moss, R. A.; Guo, W.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1982**, *23*, 15.

[17] m_{CXY} 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 $m_{CCl_2} = 1.0$.

[18] The sign of the $\delta-\sigma$ relationship for the B-substituent effect in compounds of the A$_n$P—B type is determined by the electronegativity of the A-group(s) (*i.e.*, MeO in the present case). Thus, if the electron density at phosphorus is less than that at group B (*i.e.*, P$^+$—B$^-$), electron withdrawing substituents on group B decrease the difference in electronegativity between P and B and cause downfield shifts which results in a positive $\delta-\sigma$ slope. Conversely, a negative slope is obtained when the electronegativity at phosphorus is more than that at group B, *i.e.*, P$^-$—B$^+$. The size of the slope then illustrates the sensitivity of the B-substituent to the charge separation. See: (a) Rezvukhin, A. I.; Dolenko, G. N.; Krupodeer, S. A. *Magn. Res. Chem.* **1985**, *23*, 221 and references cited therein. (b) Hung, J.-T; Lammertsma, K. *J. Organomet. Chem.*, submitted for publication.

[19] The electropositive character has also been emphasized in an ab initio theoretical study on HPCr(CO)$_5$ for which a net Mulliken charge of +0.41 was calculated for the phosphorus atom. See: Gonbeau, D.; Pfister-Gouillouzo, G.; Marinetti, A. Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133.

[20] The Pauling electronegativity scale is used: Pauling, L. *J. Am. Chem. Soc.* **1934**, *54*, 3570; Alfred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215. See also Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

[21] Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

[22] The relative reactivities toward Ph—P—W(CO)$_5$ are 0.2 for tetramethylethylene, 0.8 for trimethylethylene, 2—4 for isobutylene, 1.0 for *cis*-2-butene, 0.3 for *trans*-2-butene, and 0.2 for 1-butene. Hung, J.-T.; Lammertsma, K. Submitted for publication.

[23] Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786.

the enthalpy and entropy terms. For example, for the styrenes, the remote *p*-phenyl substituents influence the olefin π-electron availability and thereby the enthalpy of cycloaddition much more than the entropy. Accordingly, changes in the activation barrier for the competitive reactions with styrenes must be enthalpy controlled, thereby enabling the determination of relative reactivities and hence Hammett constants. In fact, such a reaction profile is similar to the arylhalocarbene addition of styrenes for it has been shown that the enthalpy requirements govern the relative energies (and thus the Hammett reaction constants), even though the reactions are essentially entropy controlled.[24] In the phosphinidene addition to methylated olefins on the other hand, the varying number of methyl substituents influences the enthalpy and entropy terms for reactions in opposite directions, which diminishes the olefin substrate selectivity. Finally, for the relative reactivities of the R$-$P$-$W(CO)$_5$ (R = Me, Ph) cycloaddition to exocyclic olefins of different ring sizes, however, the activation energy must be entropy controlled because there are no correlations between the reactivities and any of the olefin's electronic properties.

In conclusion, the Hammett reactivity constants support a high reactivity of the complexed phosphinidenes that is remarkably similar to that of the extensively documented carbenes.[8] The only difference between them is that all complexed phosphinidenes, including the methoxy derivative, display electrophilic character. Their high reactivity is indeed most surprising and contrary to what is expected for a second-row species stabilized by metal complexation. This underscores the importance of the W(CO)$_5$ complexation, which enables the syntheses of phosphinidene precursor molecules and stable phosphirane products without diminishing the carbene-like reactivity of the singlet, electrophilic phosphinidenes.

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore FT-NMR spectrometer. Chemical shifts are referenced in parts per million to internal $(CH_3)_4Si$ for the ^{1}H and ^{13}C NMR spectra and to external 85% H_3PO_4 for the ^{31}P NMR spectra. Downfield shifts are reported as positive. NOE ^{31}P NMR experiments were performed to obtain pulse delays that ensure quantitative relative integrations. Mass spectra were recorded on a HP 5985 at 70 eV. 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. Chromatographic separations were performed on silica gel columns (230$-$400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-methoxy-7$-$phosphanorbornadiene]pentacarbonyltungsten, **1**, is described in ref 12.

Competition Reactions. Reactions of complex **1** with styrenes (4 equiv) were executed in toluene at 50$-$55 °C in the presence of ca. 10% CuCl catalyst for 1$-$2 h until all of complex **1** was converted as determined by ^{31}P NMR. Competition reactions were executed with mixtures of OMe-, Me-, Ph-, H-, Cl-, and Br-substituted styrenes (4 equiv each of two styrenes). A total of 34 competitive experiments were conducted to determine relative product ratios, which were determined from integration of the *anti*- (major) and *syn*-phosphirane ^{31}P NMR chemical shifts. These are listed in Table 1. The major products are assigned to the *anti*-phosphiranes (which are defined as having the *p*-X-phenyl and P$-$W(CO)$_5$ substituents in a *trans* orientation) and are based on comparisons with the P$-$Me- and P$-$Ph-substituted phosphiranes.

Isolated Products. The major phosphirane isomers resulting from the described reactions with a single styrene were characterized for styrene, and its *p*-methoxy, *p*-methyl, and *p*-chloro *derivatives*, after evaporation of the reaction mixture and chromatography (hexane: benzene = 4:1) as viscous liquids.

(1-Methoxy-2-(*p*-methoxyphenyl)phosphirane)pentacarbonyltungsten resulted from the reaction of *p*-methoxystyrene with complex **1** in 25% isolated yield: ^{31}P NMR (C_6H_6, reference H_3PO_4) δ -26.7 ($^1J(^{31}P-^{183}W) = 298.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 54.8 (s, *p*-CH_3OPh), 50.7 (d, $^1J(C-P) = 15.1$ Hz, CHP), 61.0 (s, $POCH_3$), 34.7 (d, $^1J(C-P) = 13.6$ Hz, CH_2P), 128.4$-$130.6 (Ph), 193.9 (*trans*-CO), 198.7 (*cis*-CO); ^{1}H NMR (C_6D_6) δ 7.45 and 7.02 (d, $J = 4.2$ Hz, Ph), 4.16 (d, $^3J(H-P) = 4.5$ Hz, $POCH_3$), 3.90 (s, *p*-CH_3OPh), 1.38$-$1.55 (m, CH_2P), 1.00 (m, CHP); mass spectrum (^{184}W), *m/e* (relative intensity) 520 (M^+, 25), 358 ($CH_3OPW(CO)_4$, 100), 330 ($CH_3OPW(CO)_3$, 40), 302 ($CH_3OPW(CO)_2$, 60), 274 ($CH_3PW(CO)$, 60).

(1-Methoxy-2-*p*-tolylphosphirane)pentacarbonyltungsten resulted from the reaction of *p*-methylstyrene with complex **1** in a 23% isolated yield: ^{31}P NMR (C_6D_6, reference H_3PO_4) δ -26.0 ($^1J(^{31}P-^{183}W) = 297.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.8 (s, *p*-CH_3Ph), 50.5 (d, $^1J(C-P) = 23.8$ Hz, CHP), 61.0 (s, $POCH_3$), 34.5 (d, $^1J(C-P) = 26.6$ Hz, CH_2P), 127.0$-$129.0 (Ph), 198.7 (*cis*-CO), 194.0 (*trans*-CO); ^{1}H NMR (C_6D_6) δ 7.35 and 7.25 (t, $J = 7.8$ Hz, Ph), 4.12 (m, $POCH_3$), 2.41 (s, *p*-CH_3-Ph), 1.62$-$1.20 (m, CH_2P), 0.96 (m, CHP); mass spectrum (^{184}W), *m/e* (relative intensity) 504 (M^+, 30), 420 ($M^+ - 3CO$, 5), 358 ($CH_3PW(CO)_4$, 100), 330 ($CH_3PW(CO)_3$, 30), 302 ($CH_3PW(CO)_2$, 20), 274 ($CH_3PW(CO)$, 40). Anal. Calcd for $C_{15}H_{13}O_6PW$: C, 35.71; H, 2.58. Found: C, 36.59; H, 2.57.

(1-Methoxy-2-phenylphosphirane)pentacarbonyltungsten resulted from the reaction of styrene with complex **1** in a 20% isolated yield: ^{31}P NMR (C_6H_6, reference H_3PO_4) δ -24.8 ($^1J(^{31}P-^{183}W) = 298.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 50.5 (d, $^1J(C-P) = 11.4$ Hz, CHP), 61.2 (s, $POCH_3$), 34.7 (d, $^1J(C-P) = 12.4$ Hz, CH_2P), 127.1$-$129.9 (Ph), 193.8 (*cis*-CO), 191.2 (*trans*-CO) ^{1}H NMR (C_6D_6) δ 7.52 (m, Ph), 4.18 (m, $POCH_3$), 1.56$-$1.40 (m, CH_2P), 1.03 (m, CHP); mass spectrum (^{184}W), *m/e* (relative intensity) 490 (M^+, 30), 358 ($CH_3OPW(CO)_4$, 100), 330 ($CH_3OPW(CO)_3$, 40), 302 ($CH_3OPW(CO)_2$, 60), 274 ($CH_3OPW(CO)$, 60).

(1-Methoxy-2-(*p*-chlorophenyl)phosphirane)pentacarbonyltungsten resulted from the reaction of *p*-chlorostyrene with complex **1** in a 12% isolated yield: ^{31}P NMR (C_6H_6, reference H_3PO_4) δ -24.3 ($^1J(^{31}P-^{183}W) = 301.2$ Hz); ^{13}C NMR (C_6D_6) δ 48.3 (d, $^1J(C-P) = 14.2$ Hz, CHP), 60.3 (s, $POCH_3$), 34.3 (d, $^1J(C-P) = 11.2$ Hz, CH_2P), 127.5$-$129.3 (Ph), 193.8 (*cis*-CO), 191.2 (*trans*-CO); ^{1}H NMR ($CDCl_3$) δ 7.20 (m, Ph), 3.90 (m, $POCH_3$), 1.31 (s, CH_2P), 1.19 (s, CHP); mass spectrum (^{184}W), *m/e* (relative intensity) 524 (M^+, 16), 358 ($CH_3OPW(CO)_4$, 100), 330 ($CH_3OPW(CO)_3$, 50), 302 ($CH_3OPW(CO)_2$, 60), 274 ($CH_3OPW(CO)$, 80).

(1-Methoxy-2-(*p*-bromophenyl)phosphirane)pentacarbonyltungsten resulted from the reaction of *p*-bromostyrene with complex **1** in a 13% isolated yield: ^{31}P NMR (C_6H_6, reference H_3PO_4) δ -23.7 ($^1J(^{31}P-^{183}W) = 300.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 49.0 (d, $^1J(C-P) = 13.4$ Hz, CHP), 61.0 (s, $POCH_3$), 34.1 (d, $^1J(C-P) = 14.7$ Hz, CH_2P), 128.1$-$132.1 (Ph), 198.6 (*cis*-CO), 193.2 (*trans*-CO); ^{1}H NMR (C_6D_6) δ 7.29 and 7.08 (dd, $J = 8.4$ Hz, Ph), 3.80 (m, $POCH_3$), 1.19 (m, CH_2P), 0.73 (m, CHP).

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[24] Turro, Moss, and co-workers advocated the existence of transient carbene/alkene intermediates from time-resolved flash spectroscopic measurements of the addition of singlet arylhalocarbenes to styrenes. They demonstrated the subtle balance for enthalpy- and entropy-controlled reactions. See: Gould, J. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron Lett.* **1985**, *41*, 1587.

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