Organometallics 1992, 11, 4365–4366

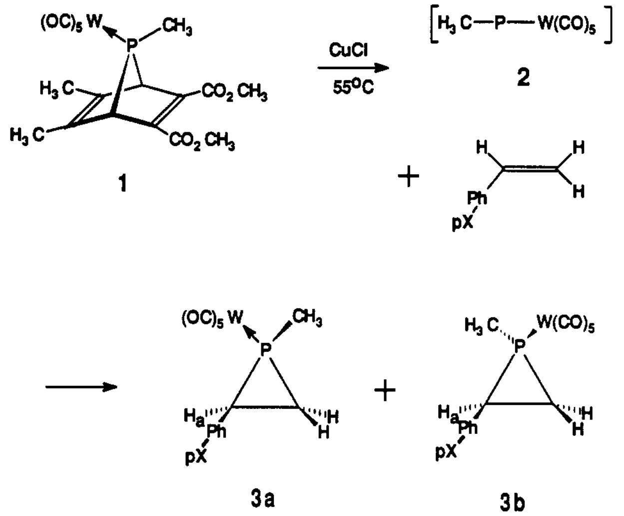
Hammett Reaction Constant for a Terminal Methylphosphinidene Complex

Jui-Te Hung and Koop Lammertsma*

Department of Chemistry, University of Alabama at Birmingham, UAB Station 227 PSB, Birmingham, Alabama 35294

Received April 28, 1992

Summary: A Hammett reaction constant ρ^+ of −0.60 has been determined for the styrene addition of H_3C–P–W(CO)$_5$, as generated from the appropriate 7-phosphanorbornadiene complex. The *anti-/syn*-phosphirane product ratio is ca. 4.



Less than a decade ago Mathey[1] found that terminal transition metal complexed phosphinidenes are conveniently generated in situ from the thermal decomposition of 7-phosphanorbornadiene precursors. This discovery made available the hitherto inaccessible class of phosphinidenes and led to the rapid development of its carbene-like chemistry.[2] However, whereas the synthetic potential of the phosphinidenes has been amply demonstrated, the reactivity–selectivity properties for this class of compounds have received little attention. In a recent study[3] we reported a Hammett reaction constant ρ^+ of −0.76 for the addition of Ph–P–W(CO)$_5$ to styrenes, thereby confirming its electrophilic, carbene-like nature. To establish that this similarity in ρ value with those of carbenes[4] is not coincidental, and to broaden the quantitative characterization for the carbene-like behavior of the transition metal complexed phosphinidenes, we now report on the reaction of the methylphosphinidene complex H_3C–P–W(CO)$_5$ (2) with styrenes.

Relative phosphinidene 2 reactivities were determined from relative (total) phosphirane product ratios (3) that resulted from competitive reactions of the W(CO)$_5$-complexed 7-phosphanorbornadiene precursor (1)[5] with a 10-fold excess of equimolar mixtures of *p*-phenyl-substituted styrenes, executed at 50–55 °C in the presence of 10% CuCl catalyst for 0.5–1 h; the *p*-phenyl substituents were OCH_3, CH_3, Ph, H, Cl, and Br. The phosphirane product ratios in reaction aliquots were determined by ^{31}P NMR integration of the phosphirane resonances; the anti and syn isomer of each styrene were combined in the analyses. The resulting relative product ratios are summarized in Table I. Correlating these product ratios as log k_X/k_H with the Brown substituent constants σ^+ results in a linear relationship (Figure 1) and gives a Hammett reaction constant ρ of −0.60 (r = 0.997, 95% confidence). The ρ value is based on the OCH_3-, CH_3-, Ph-, and H-substituted styrenes, since the slower reacting Cl and Br derivatives yield noticeably more decomposition products.[6]

The Hammett reaction constant ρ^+ of −0.60 for the H_3C–P–W(CO)$_5$ addition to styrene is slightly smaller than of −0.76 for the addition of Ph–P–W(CO)$_5$ and compares very well with the ρ values of −0.62 (σ^+)[7] and −0.57 (σ^+)[8] for the styrene additions of the CCl_2 and CF_2 carbenes, respectively. This similarity in small negative ρ values for the W(CO)$_5$ complexes of both the H_3C–P and Ph–P phosphinidenes supports[2,3,5] quantitatively that they behave as unencumbered carbene-like species with a slightly polar (electrophilic) transition for concerted addition to olefins.

Addition of H_3C–P–W(CO)$_5$ to styrenes yields a mixture of *anti*- and *syn*-phosphirane isomers 3a and 3b, respectively. Based on the relative shielding of the ^1H NMR chemical shifts of the P–methyl and the styrene H_a hydrogens, the major product is assigned to anti isomer **3a** (i.e. the P–W(CO)$_5$ and *p*-X-Ph groups are in a anti orientation) which is also reasonable on steric grounds.[9] The *anti-/syn*-phosphirane product ratios, as determined by ^{31}P NMR and listed in Table I, range from 3.3 to 4.1 with the higher selectivities for the less reactive styrenes. The average ratio of ca. 4 is significantly smaller than the ratio of ca. 9 that was found for the Ph–P–W(CO)$_5$ addition. If the reactivity–selectivity principle applies to the phosphinidene addition reactions, then the lower selectivity of the methyl- vs phenyl-substituted phosphinidene complex is to be expected from the smaller reaction constant value of −0.60 vs −0.76, respectively. Whereas it cannot be excluded that electrostatic factors, e.g. secondary orbital interactions between the styrene and *P*-phenyl group, enhance the anti/syn product selectivity for Ph–P–W(CO)$_5$, the data suggest that steric factors do not play a dominant role in the reactivities of the CH_3- and phenyl-substituted phosphinidenes toward styrenes.

---

[1] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Chem. Soc., Chem. Commun.* 1982, 667; *J. Am. Chem. Soc.* 1982, *104*, 4484. Marinetti, A.; Mathey, F. *Organometallics* 1982, *1*, 1488.

[2] For recent reviews, see: Mathey, F. *Chem. Rev.* 1990, *90*, 997; *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 275; *Pure Appl. Chem.* 1987, *59*, 993.

[3] Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-T. *Organometallics* 1988, *7*, 1875.

[4] For reviews, see: Jones, M., Jr.; Moss, R. A. *Reactive Intermediates*; Wiley: New York, 1985; Vol. 3. Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984.

[5] Mathey's procedure was followed: Marinetta, A.; Mathey, F. *Organometallics* 1984, *3*, 456.

[6] Including the k_X/k_H values for *p*-Cl- and *p*-Br-styrene gives a ρ^+ value of −0.75 with a correlation constant of 0.976.

[7] Seyferth, D.; Mui, J. Y. P.; Damrauer, R. *J. Am. Chem. Soc.* 1968, *90*, 6182.

[8] Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* 1975, *97*, 344.

[9] In the anti (syn) isomers the ^1H NMR chemical shifts are for the PCH_3 group 0.39 (0.70) ppm and for the phosphirane ring HC(Ph) 2.42 (2.07) ppm. This assignment is consistent with recent literature data: Marinetta, A.; Mathey, F. *Tetrahedron* 1989, *45*, 3061. Likewise the $^2J_{PH}$ coupling constants are ~0 Hz for the anti-phosphiranes. In related to be published studies we have found $^2J_{PH}$ coupling constants of ~0 (~8) Hz for the anti(syn)-phosphiranes resulting from reaction of Ph–P–W(CO)$_5$ with cyclic olefins.

0276-7333/92/2311-4365$03.00/0

Table I. Relative Reactivities (k_X/k_H) and Anti/Syn Addition Ratios of *p*-X-styrenes toward H_3C-P-$W(CO)_5$

substituent	k_X/k_H	anti/syn
OCH_3	3.00	3.25 ± 0.14
phenyl[a]	1.20	
CH_3	1.67	3.65 ± 0.08
H	1.00	3.89 ± 0.05
Cl	0.65	3.83 ± 0.25
Br	0.57	4.14 ± 0.50
ρ value	−0.60	

[a] Unable to determine the anti/syn ratio.

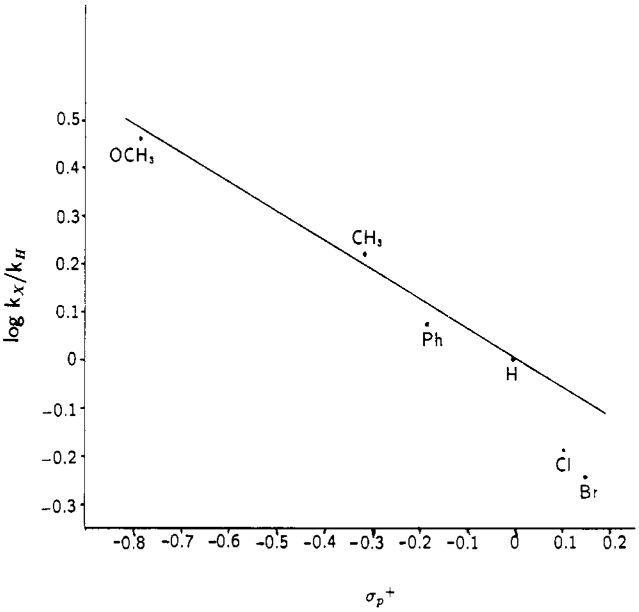


Figure 1. Hammett σ^+–ρ plot of CH_3—P—$W(CO)_5$ addition to *p*-$XPhCH{=}CH_2$.

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore FT-NMR spectrometer. Chemical shifts are referenced in ppm to internal $(CH_3)_4Si$ for the ^1H 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-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten, 1, is described in ref 1a.

Competition Reactions. Reactions of complex 1 with styrenes (10 equiv) were executed in toluene at 50–55 °C in the presence of ca. 10% CuCl catalyst for 0.5–1 h until all of complex 1 was converted as determined by ^{31}P NMR. Competition reactions were executed with mixtures of OCH_3-, CH_3-, Ph-, H-, Cl-, and Br-substituted styrenes (10 equiv each of two styrenes). A total of 20 competitive experiments were conducted to determine relative product ratios, which were determined from integration of the following ^{31}P NMR chemical shifts (in ppm, toluene) for the phosphiranes resulting from the reaction of *p*-X-styrene with 1: *p*-CH_3O δ −177.8 (major) and −164.9 (minor); *p*-Ph δ −175.8 (major); *p*-CH_3 δ −176.7 (major) and −164.1 (minor); *p*-H δ −175.7 (major) and −163.4 (minor); *p*-Cl −174.0 (major) and −161.8 (minor); *p*-Br −173.9 (major) and −161.7 (minor).

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, chromatography (hexane–benzene, 4:1), and fractional crystallization from pentane.

(1-Methyl-2-(methoxyphenyl)phosphirane)pentacarbonyltungsten resulted from the reaction of p-methoxystyrene with complex 1 in 20% isolated yield (anti and syn): mp 64–66 °C; ^{31}P NMR (C_6H_6, reference H_3PO_4) δ −177.8 ($^1J(^{31}P–^{183}W)$ = 261.4 Hz); ^{13}C NMR (C_6D_6) δ 54.8 (*p*-CH_3OPh), 27.2 (d, ^1J(C–P) = 13.0 Hz, CHP), 13.2 (d, ^1J(C–P) = 8.0 Hz, PCH_3), 10.5 (d, ^1J(C–P) = 17.0 Hz, CH_2P), 196.1 (cis CO); ^1H NMR (C_6D_6) δ 6.73 and 6.64 (dd, J = 8.2 and 8.6 Hz, Ph), 3.27 (s, *p*-CH_3O), 2.42 (t, J = 9.6 Hz, HCP), 0.88–1.02 (m, H_2CP), 0.40 (d, J = 6.9 Hz, H_3CP); mass spectrum (^{184}W), *m/e* (relative intensity) 504 (M^+, 30), 420 (M^+ − 3CO, 20), 342 ($CH_3PW(CO)_4$, 100), 314 ($CH_3PW(CO)_3$, 57), 286 ($CH_3PW(CO)_2$, 55), 258 ($CH_3PW(CO)$, 65).

(1-Methyl-2-tolylphosphirane)pentacarbonyltungsten resulted from the reaction of *p*-methylstyrene with complex 1 in a 16% (combined) isolated yield: mp 51–52 °C; ^{31}P NMR (C_6H_6, reference H_3PO_4) δ −176.7 ($^1J(^{31}P–^{183}W)$ = 243.5 Hz); ^{13}C NMR (C_6D_6) δ 21.1 (*p*-CH_3Ph), 27.4 (d, ^1J(C–P) = 14.4 Hz, CHP), 13.0 (d, ^1J(C–P) = 8.8 Hz, PCH_3), 10.7 (d, ^1J(C–P) = 14.0 Hz, CH_2P), 194.7 (trans CO), 196.0 (d, ^2J(C–P) = 9.5 Hz, cis CO), ^1H NMR (C_6D_6) δ 6.85 and 6.75 (dd, J = 8.0 and 7.7 Hz, Ph), 2.07 (s, *p*-CH_3O), 2.45 (t, J = 9.5 Hz, HCP), 0.91–0.99 (m, H_2CP), 0.39 (d, J = 6.9 Hz, H_3CP); mass spectrum (^{184}W), *m/e* (relative intensity) 488 (M^+, 20), 404 (M^+ − 3CO, 10), 342 ($CH_3PW(CO)_4$, 100), 314 ($CH_3PW(CO)_3$, 52), 286 ($CH_3PW(CO)_2$, 48), 258 ($CH_3PW(CO)$, 45).

(1-Methyl-2-phenylphosphirane)pentacarbonyltungsten resulted from the reaction of styrene with complex 1 in a 12% (combined) isolated yield: mp 58 °C; ^{31}P NMR (C_6H_6, reference H_3PO_4) δ −175.3 ($^1J(^{31}P–^{183}W)$ = 211.5 Hz); ^{13}C NMR (C_6D_6) δ 27.7 (d, ^1J(C–P) = 14.4 Hz, CHP), 13.0 (d, ^1J(C–P) = 8.0 Hz, PCH_3), 11.1 (d, ^1J(C–P) = 14.3 Hz, CH_2P), 196.0 (cis CO); ^1H NMR (C_6D_6) δ 7.02, 7.00, and 6.78 (m, J = 6.8 and 6.7 Hz, Ph), 2.42 (t, J = 9.5 Hz, HCP), 0.93–0.97 (m, H_2CP), 0.34 (d, J = 6.9 Hz, H_3CP); mass spectrum (^{184}W), *m/e* (relative intensity) 474 (M^+, 30), 390 (M^+ − 3CO, 13) 342 ($CH_3PW(CO)_4$, 100), 314 ($CH_3PW(CO)_3$, 70), 286 ($CH_3PW(CO)_2$, 72), 258 ($CH_3PW(CO)$, 70). Anal. Calcd for $C_{14}H_{11}O_5PW$: C, 35.45; H, 2.32. Found: C, 35.55; H, 2.34.

(1-Methyl-2-(chlorophenyl)phosphirane)pentacarbonyltungsten resulted from the reaction of *p*-chlorostyrene with complex 1: ^{31}P NMR (C_6H_6, reference H_3PO_4) δ −173.7 ($^1J(^{31}P–^{183}W)$ = 257.7 Hz); ^{13}C NMR (C_6D_6) δ 27.0 (d, ^1J(C–P) = 14.1 Hz, CHP), 13.1 (d, ^1J(C–P) = 7.2 Hz, PCH_3), 10.9 (d, ^1J(C–P) = 13.4 Hz, CH_2P), 195.9 (cis CO); ^1H NMR (C_6D_6) δ 7.18 and 6.81 (dd, J = 7.5 Hz, Ph), 2.25 (t, J = 9.3 Hz, HCP), 0.10–0.82 (m, H_2CP), 0.34 (d, J = 6.9 Hz, H_3CP).

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

OM920234U