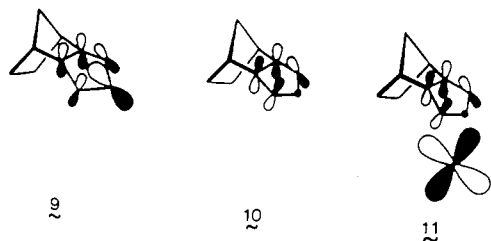


control in these reactions.¹³ The model, which is depicted in 9, visualizes the disrotatory tilting deformations that INDO calculations¹⁴ indicate arise within ψ_1 from σ/π mixing with the neighboring norbornyl framework. To the extent that ψ_1 exerts the more important overlap control, metal ions might well prefer above-plane approach because their d_{z^2} , s , and p_z orbitals (all symmetry related to ψ_1) would be directed to the center of the more electron-rich cyclopentadienide core.



The impact of ψ_1 is not anticipated to be controlling, however, because of its sub-frontier status and the customary greater significance of $d\pi-\psi_2$ interactions relative to those of the $d_0-\psi_1$ type. Therefore, to the extent that the $p\pi$ orbitals within ψ_2 remain tilted as in 10 (or at least in this manner in the transition state), a large metal atom with diffuse $d\pi$ orbitals could engage in more effective overlap on the endo face as shown in 11.

Verification of this working hypothesis clearly must await the results of future work. On the other hand, the stereoselectivity crossover as described herein has clearly been defined experimentally. These fascinating findings are presently viewed as an overriding of electronic control (endo directive) by steric considerations when the incoming ligand is sterically bulky. The exclusive formation of 3 conforms to this interpretation, as does the response of a camphor-derived fused cyclopentadiene ligand where the presence of a syn-oriented apical methyl group is adequate to deter the capacity for above-plane complexation.¹⁵

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The Reactivity of a Terminal Phosphinidene Complex toward Styrenes

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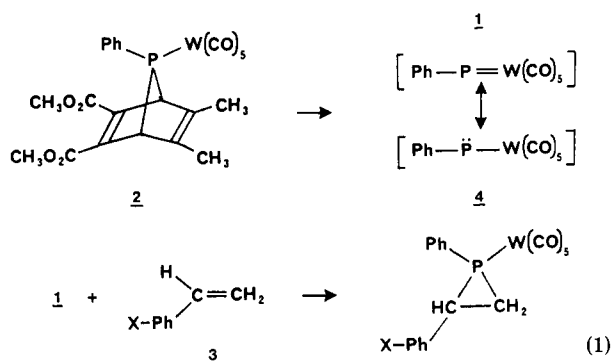
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Summary: The Hammett reaction constant for the reaction of the terminal phosphinidene complex $[\text{Ph}-\text{P}=\text{W}(\text{CO})_5]$, as generated from the appropriate 7-phosphanorbornadiene complex, toward styrenes is reported and compared to those of "free" carbenes. The mild electrophilicity supports the unencumbered carbene-like nature of the phosphinidene complex and suggests a concerted addition to olefins with a slightly polar transition state.

Mathey's discovery¹ of in situ generation of terminal phosphinidene complexes has resulted in an avalanche of studies that rapidly develop this carbene-like chemistry.² Most attention has focussed on the synthetic versatility of the phosphinidene complex.² Additional interest centers on the bonding nature between the phosphorus atom and its complexed transition metal.³ However, in contrast to the broad understanding of carbenic reactivity and selectivity,⁴ such characteristics for phosphinidenes are virtually unexplored. Here we report the Hammett reaction constant for the reaction of the terminal phosphinidene complex $\text{Ph}-\text{P}=\text{W}(\text{CO})_5$ (1) with olefins to form phosphiranes.

The phosphinidene complex 1 was generated in situ following Mathey's procedure,⁵ from the 7-phosphanorbornadiene precursor 2 in toluene at 55 °C with CuCl as catalyst (eq 1), and reacted with an excess of a series of



substituted styrenes 3 to form the corresponding phosphiranes; the *p*-phenyl substituents in 3 were OCH_3 , CH_3 , Ph , F , Cl , and Br .⁶ Relative reaction rates were determined from relative (total) phosphirane product ratios resulting from competitive reactions of 2 with equimolar ratios of substituted and unsubstituted styrenes; two cross checks verified the accuracies of the determined reactivities. The product ratios were determined from integration of the ³¹P NMR spectra.⁷ The obtained selectivities of 1 toward the substituted styrenes are listed in Table I. A plot of the logarithms of the relative reaction rates (selectivities), $\log k_X/k_H$, versus the Brown substituent constant σ^+ results in a linear relationship (Figure 1) and gives a Hammett reaction constant of $\rho = -0.76$ ($r = 0.99$). A similar correlation with σ values is unsatisfactory.

The Hammett reaction constant of -0.76 supports the singlet electrophilic nature previously assumed^{2a,5} for the phosphinidene complex $\text{Ph}-\text{P}=\text{W}(\text{CO})_5$. The mild electrophilicity of 1 suggests a concerted addition to olefins with a slightly polar transition state. The relatively small value of -0.76 also is indicative for the unencumbered carbene-like nature⁸ of the phosphinidene complex 1, thermally generated from the 7-phosphanorbornadiene precursor 2.

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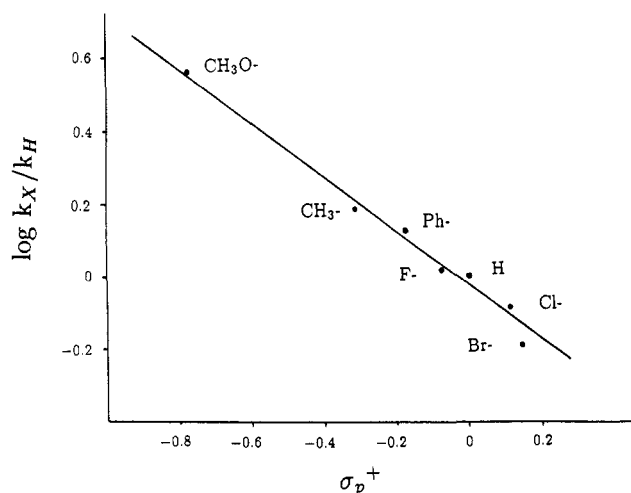


Figure 1. Hammett σ^+ - ρ plot of Ph-P=W(CO)₃ addition to p-XPhCH=CH₂.

Comparison of the Hammett reaction constant of 1 with those of "free" carbenes is instructive. Representative ρ 's for the latter are H₂C: -1.6 (σ),⁹ cyclopentadienyldiene -0.76 (σ),¹⁰ (CH₃)₂C=C: -0.75 (σ),¹¹ Cl₂C: -0.62 (σ^+),¹² and F₂C: -0.57 (σ^+).¹³ The reactivities of Ph-P=W(CO)₅ and the uncomplexed (CH₃)₂C=C: appear remarkably similar.¹⁴ The reduced reactivity of the vinylidene carbene versus H₂C: has been explained in terms of hyperconjugative stabilization.¹⁵ The mild electrophilicity of the W(CO)₅ complexed terminal phenylphosphinidene can be

(6) For quantitative analysis of selected phosphiranes the procedure of Mathey was followed.⁵ Complex 2 (654 mg, 1 mmol) was reacted with p-X-styrene (4 mmol) and CuCl (60 mg, 0.6 mmol) at 55 °C in toluene (30 mL) for 2–5 h. Following evaporation and chromatography mixtures were crystallized from pentane. The product resulting from styrene, (1,2-diphenylphosphirane)pentacarbonyltungsten, has been reported previously by Mathey.⁵ The major phosphirane isomers were characterized for the p-methyl- and p-chlorostyrene in 67 and 70% isolated yields, respectively. (1-Phenyl-2-tolylphosphirane)pentacarbonyltungsten: mp 95–97 °C; ³¹P NMR (C₆D₆, reference H₃PO₄) δ -155.4 (¹J(³¹P-¹⁸³W) = 249 Hz); ¹³C NMR (C₆D₆) δ 30.8 (d, ¹J(C-P) = 17.9 Hz, CHP), 20.8 (s, CH₃Ph), 13.8 (d, ¹J(C-P) = 12.1 Hz, CH₂P), 196.1 (d, ²J(C-P) = 7.5 Hz, cis CO), 198.4 (d, ²J(C-P) = 29.5 Hz, trans CO). Anal. Calcd for C₂₀H₁₅O₅PW: C, 43.63; H, 2.72. Found: C, 43.71; H, 2.74. (1-Phenyl-2-(p-chlorophenyl)phosphirane)pentacarbonyltungsten: mp 118–119 °C; ³¹P NMR (C₆D₆) δ -152.7 (¹J(³¹P-¹⁸³W) = 259 Hz); ¹³C NMR (C₆D₆) δ 30.2 (d, ¹J(C-P) = 18.1 Hz, CHP), 14.1 (d, ¹J(C-P) = 11.2 Hz, CH₂P), 196.0 (d, ²J(C-P) = 9.8 Hz, cis CO), 198.1 (d, ²J(C-P) = 31.7 Hz, trans CO). Anal. Calcd for C₁₉H₁₂ClO₅PW: C, 39.96; H, 2.10. Found: C, 40.06; H, 2.11. (1-Phenyl-2-(p-methoxyphenyl)phosphirane)pentacarbonyltungsten: 78% isolated yield for the mixture. Anal. Calcd for C₂₀H₁₅O₆PW: C, 42.40; H, 2.65. Found for the mixture: C, 42.20; H, 2.72. Major isomer: ³¹P NMR (C₆D₆) δ -156.8 (¹J(³¹P-¹⁸³W) = 252 Hz); ¹³C NMR (C₆D₆) δ 54.6 (s, CH₃O), 30.6 (d, ¹J(C-P) = 18.2 Hz, CHP), 13.9 (d, ¹J(C-P) = 11.7 Hz, CH₂P), 196.2 (d, ²J(C-P) = 7.5 Hz, cis CO), 198.4 (d, ²J(C-P) = 29.6 Hz, trans CO). Minor isomer: ³¹P NMR (C₆D₆) δ -150.7 (¹J(³¹P-¹⁸³W) = 265 Hz); ¹³C NMR (C₆D₆) δ 54.9 (s, CH₃O), 30.0 (d, ¹J(C-P) = 17.0 Hz, CHP), 15.1 (d, ¹J(C-P) = 13.4 Hz, CH₂P), 195.6 (d, ²J(C-P) = 6.7 Hz, cis CO), 197.2 (d, ²J(C-P) = 29.0 Hz, trans CO).

(7) In a typical competitive experiment complex 2 (65 mg, 0.1 mmol) was heated at 55 °C with two styrenes (each 0.4 mmol) and CuCl (6 mg, 0.06 mmol) in toluene (3–4 mL) until all of complex 2 was converted. Relative phosphirane product ratios resulting from the different styrenes were determined from integration of the ³¹P NMR spectra. For each substituted styrene both phosphirane stereoisomers were included in the analysis; their ratio is 9:1, except for p-methoxystyrene which yields a ratio of 3:1. The ³¹P NMR chemical shifts (in ppm, toluene) for the phosphiranes resulting from p-X-styrene are as follows: p-CH₃O, δ -156.9 (ma) and -150.8; p-CH₃, δ -155.6 (ma) and -150.2; p-Ph, δ -153.6 and -148.6; p-F, δ -154.7 (ma) and -149.2; p-H, δ -154.7 (ma) and -149.6; p-Cl, δ -152.7 (ma) and -148.4; p-Br, δ -152.6 and -148.3, where ma = major isomer. The competition reaction (duplicates) were performed between styrene and p-methoxy-, p-methyl-, p-phenyl-, p-chloro-, and p-bromostyrene, between p-methoxystyrene and p-chlorostyrene, and between p-fluorostyrene and p-bromostyrene.

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Table I. Selectivity of Ph-P=W(CO)₅ toward Styrenes (p-XC₆H₄CH=CH₂)

substrate	k_X/k_H (substrate/ styrene)	substrate	k_X/k_H (substrate/ styrene)
p-CH ₃ O	3.65	H	1.00
p-CH ₃	1.57	p-Cl	0.82
p-phenyl	1.35	p-Br	0.65
p-F	1.05		

explained similarly by p-d overlap. Recent EH and ab initio theoretical studies on the HP=Cr(CO)₅ complex indeed suggest such a ligand-metal transfer.¹⁶ Although these computational studies disagree significantly on the P-Cr bond lengths,^{16c} they show both the HOMO and LUMO to be considerably localized on the phosphorus atom and in fact demonstrate the frontier orbitals of HP=Cr(CO)₅ and the singlet phosphinidene HP to be of the same type. Consequently, the phosphinidene complex R-P=W(CO)₅ and the vinylidene carbene R₂C=C: may be considered isolobal. In light of these analogies and the value of the Hammett reaction constant, the phosphinidene complex 1 may better be represented by structure 4, which is in agreement with arguments presented by Cowley and Barron³ in a recent review.

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Registry No. 1, 82888-50-4; 2, 82265-64-3; 3 (X = p-CH₃O), 637-69-4; 3 (X = p-CH₃), 622-97-9; 3 (X = p-Ph), 2350-89-2; 3 (X = p-F), 405-99-2; 3 (X = H), 100-42-5; 3 (X = p-Cl), 1073-67-2; 3 (X = p-Br), 2039-82-9; (*trans*-1-phenyl-2-tolylphosphirane)-pentacarbonyltungsten, 115290-40-9; (*cis*-1-phenyl-2-tolylphosphirane)pentacarbonyltungsten, 115362-06-6; (*trans*-1-phenyl-2-(p-chlorophenyl)phosphirane)pentacarbonyltungsten, 115290-41-0; (*cis*-1-phenyl-2-(p-chlorophenyl)phosphirane)pentacarbonyltungsten, 115362-09-9; (*trans*-1-phenyl-2-(p-methoxyphenyl)phosphirane)pentacarbonyltungsten, 115290-42-1; (*cis*-1-phenyl-2-(p-methoxyphenyl)phosphirane)pentacarbonyltungsten, 115362-05-5; (*trans*-1-phenyl-2-(p-phenylphenyl)phosphirane)pentacarbonyltungsten, 115290-43-2; (*cis*-1-phenyl-2-(p-phenylphenyl)phosphirane)pentacarbonyltungsten, 115362-07-7; (*trans*-1-phenyl-2-(p-fluorophenyl)phosphirane)pentacarbonyltungsten, 115290-44-3; (*cis*-1-phenyl-2-(p-fluorophenyl)phosphirane)pentacarbonyltungsten, 115362-08-8; (*trans*-1,2-diphenylphosphirane)pentacarbonyltungsten, 88000-32-2; (*cis*-1,2-diphenylphosphirane)pentacarbonyltungsten, 88080-15-3; (*trans*-1-phenyl-2-(p-bromophenyl)phosphirane)pentacarbonyltungsten, 115290-45-4; (*cis*-1-phenyl-2-(p-bromophenyl)phosphirane)pentacarbonyltungsten, 115362-10-2.

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