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Conjugative effects in $W(CO)_5$ complexed phosphirane rings illustrated by substituent effects on ^{31}P NMR chemical shifts

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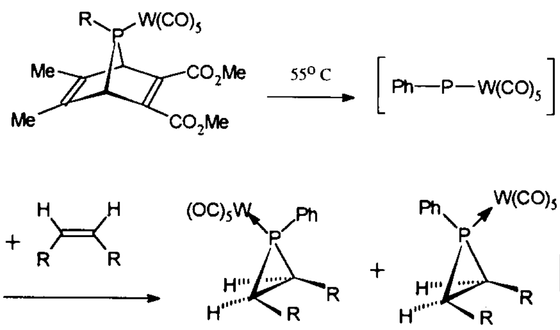
Abstract

Correlations between ^{31}P NMR chemical shifts and Hammett σ substituent constants are reported for a total of 22 *anti*- and *syn*-phosphiranes, obtained from the reactions of the carbene-like phosphinidenes $Ph–P–W(CO)_5$ and $H_3C–P–W(CO)_5$ with various *para*-substituted styrenes. The origins of these four sets of correlations with respect to electronic and electrostatic interactions are discussed. Arguments are presented that strongly suggest significant conjugation between the remote *p*-X-phenyl and *trans*-P-phenyl groups in the *syn*-1 substituted phosphiranes. Electrostatic forces do not play an important role in these $P–W(CO)_5$ complexed phosphiranes and neither do steric interactions.

Keywords: Tungsten; Phosphinidene; Nuclear magnetic resonance; Hammett constants

The synthesis of transition metal complexed phosphiranes from olefins and phosphinidenes leads to mixtures of *syn* and *anti* isomers (Eq. (1)), which differ in their ^{31}P NMR chemical shifts [1]. Structural assignments are preferably based on X-ray structure determinations, however, because those based on phosphorus chemical shifts remain speculative. The latter requires an understanding of the substituent effect on phosphorus, which is not available for the rapidly growing class of phosphiranes. In our search to unravel the reactivities and properties of the carbene-like phosphinidenes and their products, we now report on remarkable systematic substituent effects in $W(CO)_5$ complexed phosphiranes and the importance of conjugation.

Four groups of phosphirane isomers were available from our earlier work on the determination of the Hammett reaction constants for the styrene additions of the phosphinidenes $Ph–P–W(CO)_5$ ($\rho^+ = -0.76$) [2] and $H_3C–P–W(CO)_5$ ($\rho^+ = -0.60$) [3]. These are the *syn*- and *anti*-isomers of both the P-methyl and P-phenyl substituted phosphiranes **1** and **2**, respectively. The *syn*-isomers are defined as having a *cis* orientation between the $P–W(CO)_5$ group and the *p*-X-phenyl substituent of the phosphirane ring and conversely these groups have a *trans*-orientation in the *anti*-isomers. Closer scrutiny of their ^{31}P NMR chemical shifts (δ) reveals remarkably linear relationships with Hammett constants (σ) of the *para*-phenyl substituents (OCH_3, CH_3, H, F, Cl, and Br) for each class of compounds. These are summarized in Table 1 and illustrated in Figs. 1 and 2 [4]. The nature of the correlations will be discussed.



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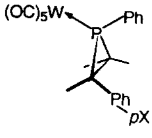
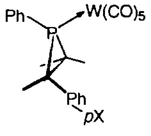


anti-**1**



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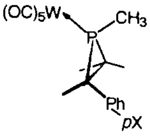

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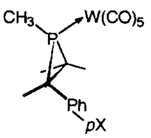

syn-**2**

$X = OCH_3, CH_3, H, F, Cl, Br$

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Table 1
Correlation of ^{31}P NMR chemical shifts of phosphiranes **1–2** with Hammett σ_{para} substituent constants

p-X	σ_{para}	*anti*-**1**	*syn*-**1**	*anti*-**2**	*syn*-**2**
OCH_3	−0.268	−156.9	−150.8	−177.8	−164.9
CH_3	−0.17	−155.6	−150.2	−176.7	−164.1
H	0.000	−154.7	−149.6	−175.7	−163.4
F	0.062	−154.7	−149.2		
Cl	0.227	−152.7	−148.4	−174.0	−161.8
Br	0.232	−152.6	−148.3	−173.9	−161.7
Slope		8.00	4.82	7.45	6.18
Intercept		−154.6	−149.5	−175.7	−163.2
Correlation coefficient		0.981	0.997	0.997	0.996

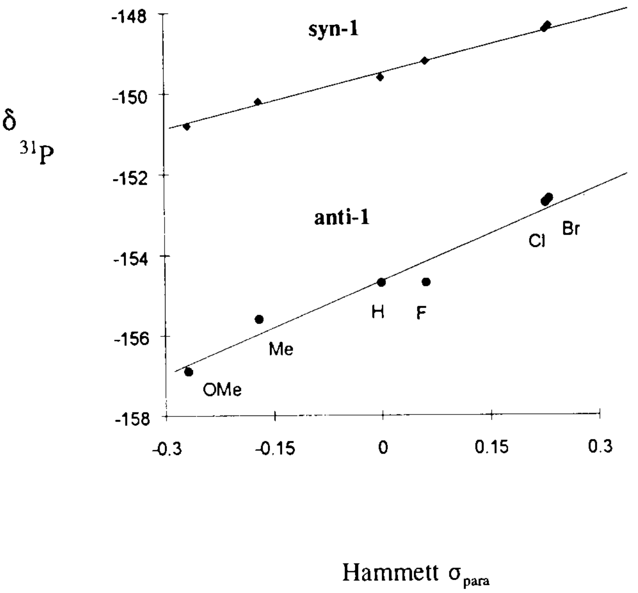


Fig. 1. Correlation of ^{31}P NMR chemical shifts of *anti*-**1** and *syn*-**1** with Hammett substituent constants.

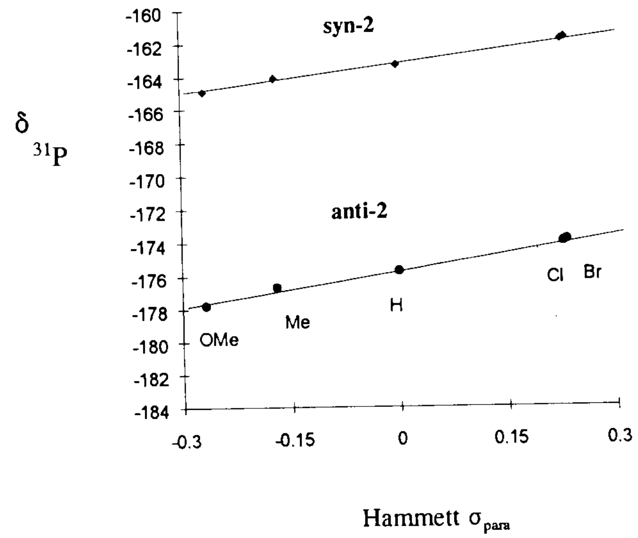


Fig. 2. Correlation of ^{31}P NMR chemical shifts of *anti*-**2** and *syn*-**2** with Hammett substituent constants.

Generally, a variety of effects influence the NMR chemical shifts. Of the many empirical relationships, a particularly successful one [5] is

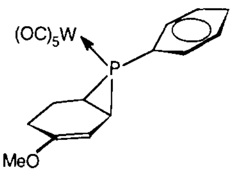
$$\Delta_P = -C\Delta X + k\Delta n_\pi + A\Delta\theta \qquad (1)$$

where ΔX is the difference in electronegativity between the phosphorus atom and its substituent X, Δn_x is the change in π-electron overlap, $\Delta\theta$ is the change in bond (or cone) angle, and C, k, and A are constants. It has further been shown for phosphines (e.g. $(X\text{–}Ph)_3P$ [6] and (X–Ph)PRR′) [7,8] phosphine oxides (e.g. $R_2P(O)(OPh\text{–}X)$ [9–11] $R_2P(O)(Ph\text{–}X)$ [11–14] and $R_2P(O)X)$ [15] and metal complexes $((OC)_5MoP(Ph)_2(OPh\text{–}X))$ [16] that Hammett (Taft) substituent constants σ_x correlate linearly with ^{31}P NMR chemical shifts. In such cases it has generally been assumed that Δn_π and $\Delta\theta$ are constant within the same class of compounds. Therefore, $\Delta\delta$ varies only with ΔX and linear ^{31}P NMR chemical shift correlations are observed with both Hammett (Taft) σ constants and electronegativity values. As expected, the correlations are poorest when the P-substituents are changed (i.e. R instead of X). This is a result of electronic and steric factors that influence the hybridization and bond angles which cause non-zero contributions in Δn_π and $\Delta\theta$. Whereas the magnitude of the slope of the δ–σ relationship depends largely on the substituent effect (σ_x), its sign is often determined by the other substituents [5]. For example, the sign of the δ–σ relationship for the B-substituent effect in compounds of the $A_nP\text{–}B$ type is determined by the electronegativity of the A-group(s) [15]. Thus, if the electron density at phosphorus is larger than that at group B (i.e. $P^-\text{–}B^+$), electron withdrawing substituents on group B increase ΔX and cause upfield shifts which results in a negative δ–σ slope. Conversely, a positive slope is obtained when the electron density at phosphorus is less than that at group B, i.e. $P^+\text{–}B^-$. The size of the slope then illustrates the sensitivity of the B-substituent to the charge separation. We apply this methodology, for the first time, to transition metal stabilized phosphiranes in an attempt to unravel some of their electronic features.

Only positive slopes ρ of 8.00 ($r = 0.981$) and 4.82 ($r = 0.997$) are obtained for the δ–σ correlation of the *anti*- and *syn*-isomers, respectively, of the P-phenyl substituted phosphiranes **1**. Similarly, positive slopes of 7.45 ($r = 0.997$) and 6.18 ($r = 0.996$) are found for the corresponding *anti*- and *syn*-isomers of the P-methyl substituted phosphirane **2**; all correlations are at the 95% confidence levels. This leads to the conclusion that the phosphorus atom in these $W(CO)_5$ complexed phosphiranes **1** and **2** is electropositive.

The slopes of the correlations vary but are in all cases sizable, which illustrates that the p-X-phenyl substituent has a remarkably large electronic effect on the far removed phosphorus of the three-membered PCC ring. The extent of this effect can be determined, at least on a relative basis, by evaluation of the magnitude of the δ–σ slopes. The larger slopes and therefore the more pronounced substituent effects are found for the *anti*-isomers of both **1** ($\rho = 8.00$) and **2** ($\rho = 7.45$). The difference in magnitude of the δ–σ slopes of the *anti*- and *syn*-isomers of the P–Ph substituted phosphiranes **1** amounts to 3.18. A smaller difference of 1.27 is found for the corresponding *anti*- and *syn*-isomers of the P–CH_3 derivatives **2**. Because of the similarity in ρ values for the *anti* isomers of **1** and **2**, these *anti-syn* differences in δ–σ slopes (i.e. 3.18 for **1** and 1.27 for **2**) suggest a reduced substituent effect that is specific to the *syn*-isomers and which is the most pronounced for *syn*-**1** ($\rho = 4.82$). We speculate that the smaller slopes for the *syn*-isomers result from a modest through-bond conjugative interaction between the *p*-X-phenyl substituent of the phosphirane ring and its *trans*-P-phenyl (methyl) group (i.e. W-conformation). Such a conjugative effect diminishes the electronic effect of the *p*-X-phenyl substituent on the phosphorus atom and therefore gives smaller differences in the ^{31}P NMR chemical shifts.

The sensitivity of the P–Ph and P–CH_3 substituents on the δ–σ correlations can also be expressed by cross-correlating the ^{31}P NMR chemical shifts of the *syn*-isomers with those of the *anti* isomers. For the P-methyl substituted phosphiranes *syn*-**2** and *anti*-**2** this results in a correlation with a slope of 0.83 ($r = 0.998$). The origin of this modest deviation from unity may lie in (a) a small conjugative effect between the P-methyl and *p*-X-phenyl groups in the *syn*-isomer and/or (b) a small electrostatic/steric repulsion between the same groups in the *anti*-isomer. Although the latter is less viable for a methyl group in *anti*-**2** ($\rho = 7.45$), electrostatic, electronic, and/or particularly steric interactions are feasible between the *cis* P-phenyl and *p*-X-phenyl groups in *anti*-**1** and might be responsible for its slightly larger δ–σ slope of 8.00. The effect is very small, however, as illustrated by the cross-correlation with a near unity slope ($\rho = 0.91$, $r = 0.999$) of the ^{31}P NMR shifts of the sets of *anti* conformers of **1** and **2**, which then suggest a negligible steric effect. In sharp contrast to the correlation of the isomers of **2** ($\rho = 0.83$), a much smaller slope of 0.59 ($r = 0.986$) is obtained on cross-correlating the ^{31}P NMR chemical shifts of the *syn*- and *anti*-isomers of the P-phenyl substituted phosphirane **1**. These arguments then imply the presence of a sizable conjugative interaction between the two *trans* phenyl groups in *syn*-**1**. Coplanarity between these groups would maximize this conjugative effect. Whereas no structural information is available for **1** nor for **2**, the X-ray structures of both **3** and **4** do indeed display coplanarity of the P–Ph group and the *trans* olefinic rings [17].



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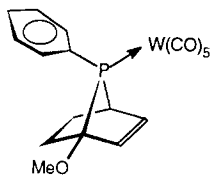

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Conclusions

Remarkably good linear correlations between ^{31}P NMR chemical shifts and Hammett σ_X constants (X = OCH_3, CH_3, H, F, Cl, and Br) of the remote *p*-X-phenyl substituents are obtained for four sets of $W(CO)_5$ complexed phosphiranes. The significant positive slopes of these correlations suggest a surprisingly strong electronic effect of the remote *p*-X group on the electropositive phosphorus atom. Arguments are presented that strongly suggest conjugation between the *p*-X-phenyl and *trans*-P–Ph groups in the transition metal complexed *syn*-phosphiranes. Electrostatic forces are argued neither to play an important role between the *cis* P–Ph/P–CH_3 and *p*-X-phenyl groups of the *anti*-phosphiranes nor between the *cis* $W(CO)_5$ and *p*-X-phenyl groups of the *syn*-phosphiranes.

Acknowledgments

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