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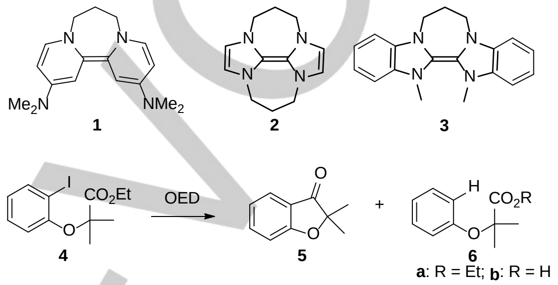
Iminophosphorano-substituted Bispyridinylidenes: Redox Potentials and Substituent Constants from Tolman Electronic Parameters

Nicholas A. Richard, Chun Keat Khor, Sydney M. Hetherington, Scott L. Mills, Andreas Decken and C. Adam Dyker*[a]

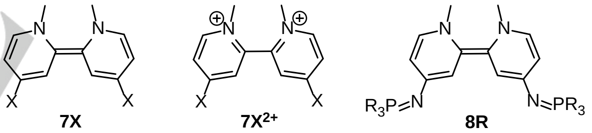
Abstract: Bispyridinylidenes (BPYs) have emerged as an important class of neutral organic electron donors, with redox potentials that vary widely with choice of substituent. Methods to predict the effect of substitution on the redox potential are therefore highly desirable. Here we show that the redox potential of BPYs featuring iminophosphorano substituents (R_3P=N-), which represent the most reducing class of BPYs, can be predicted based on the well-known Tolman electronic parameter (TEP) for the respective phosphine fragment (R_3P). Moreover, building on earlier work relating redox potentials to Hammett-type substituent constants, it is now possible to quantitatively predict σ_p^+ values for iminophosphorano substituents from TEP values. These results provide a path for precisely tailoring redox potentials of iminophosphorano-substituted BPYs, but also give quantitative descriptors for how these highly versatile iminophosphorano substituents can impact the properties of any molecular scaffold.

Organic electron donors (OEDs) are homogeneous reagents that offer complementarity to more traditional metal-based reductants.[1,2] Such species can serve as stoichiometric or catalytic,[3,4] single or double electron transfer agents and can effect a variety of transformations including cyclizations, polymerizations, cascade processes and reductions of various functional groups.[5–10] In these processes, the reaction outcome can be tied to subtle changes in the redox potential of the OED. For example, electron donors **1** [$E_{1/2}$ = -1.24 V vs SCE (DMF, $2e^-$)], **2** [$E_{1/2}$ = -1.20 V vs SCE (DMF, $2e^-$)], and **3** [$E^1_{1/2}$ = -0.82 V; $E^2_{1/2}$ = -0.75 V vs SCE (DMF)], convert iodoester **4** into cyclized ketone **5** or arene **6** in varying ratios according to the donors ability to promote an aryl anion or aryl radical intermediate in the process (Scheme 1).[7,11,12]



	5	6
3	-	83% (**6a**)
2	51%	21% (**6a**)
1	83%	8% (**6b**)

Scheme 1. Reductions of iodoester **4** to products **5** or **6** in varying isolated yields depending on the strength of the OED used (**1**, **2**, or **3**).



7X **7X^{2+}** **8R**

For organic systems, not only are a variety of scaffolds available with varying redox potentials,[6,7,9,13–17] but it is possible to tune the redox potential of a given scaffold by substitution. For example, the disubstituted bispyridinylidene scaffold **7X** (X = substituent), which generally undergoes a reversible two-electron oxidation to **7X^{2+}**, has derivatives with redox potentials spanning over 1 V from -0.26 V vs SCE (CH_3CN) for **7CO$_2$Me**,[18] to -1.35 V vs SCE (CH_3CN) [or -1.27 V vs SCE (DMF)[19,20]] for **7NMe$_2$**. Clennan observed a good correlation (R^2 = 0.9845) between the Hammett σ_p constant of the substituent X, and the redox potential of **7X** in CH_3CN.[18,21] We and others, have found that some of these OEDs undergo more electrochemically reversible processes and have greater stability in DMF than in CH_3CN,[22] and we subsequently established a correlation between σ_p^+ (substituent constants designed for cases where X involves a donor atom in direct conjugation with a positively charged reaction center)[23,24] and the related **7X**/**7X^{2+}** (X = $N(CH_2)_4$, NMe_2, $N(CH_2)_4O$, OMe, SMe) redox potentials in this solvent (R^2 = 0.9920):[25]

$$E_{1/2}\text{ (V vs SCE, DMF)} = 0.4078(\sigma_p^+) - 0.5988 \tag{1}$$

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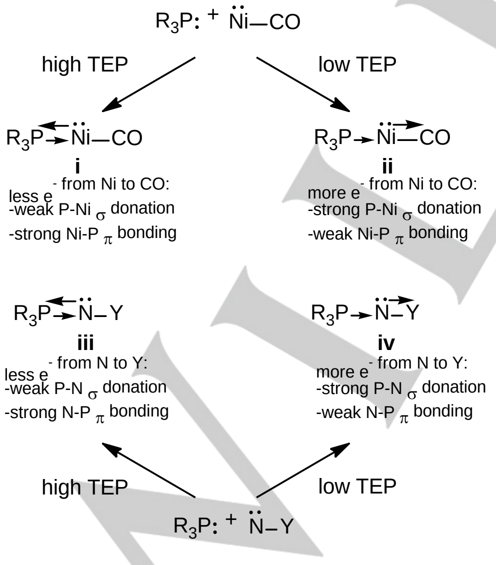
Such correlations provide a means of quantitatively guiding the design of OEDs with specific redox potentials, with the limit that substituent constants must be known.[24] For eq. 1, and considering only uncharged substituents to maintain neutrality of **7X**, this covers the range (vs SCE) from -0.30 V (for X = $-COCF_3$, $\sigma_p^+ = 0.85$) to -1.43 V (for X = $-NEt_2$, $\sigma_p^+ = -2.07$)

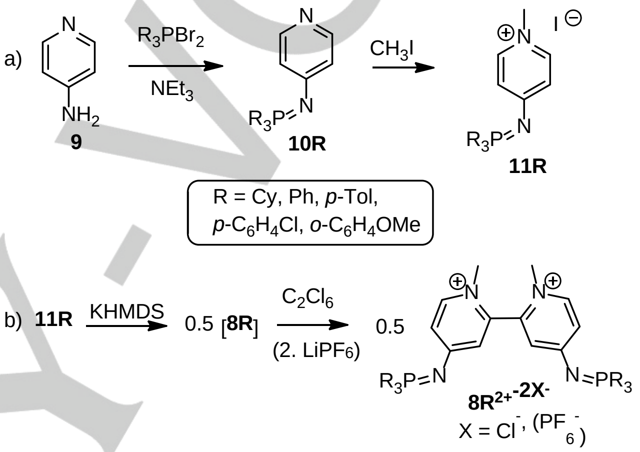
In 2015 we reported the first iminophosphorano substituted bispyridinylidenes **8Ph** and **8Cy**. The redox potentials for these compounds (-1.34, -1.51 V vs SCE (DMF), respectively) showed them to be more reducing than even **7NMe₂**. This demonstrated that iminophosphorano substituents can be more donating than amino groups, and that the donating ability of the $R_3P{=}N$- substituents is highly tunable by changing R. Therefore, a variety of redox potentials should be available from iminophosphorano-substituted BPYs **8R**; however, since substituent constants are unknown for these groups, predictable changes in redox potential are not yet achievable.

Like σ_p^+, which measures net electron donating/withdrawing effects of the substituent towards a parent structure, the Tolman electronic parameter (TEP)[26] quantifies the net σ donating and π-accepting properties of phosphines (or other ligands)[27] towards a $Ni(CO)_3$ fragment. Inspired by the dative bonding model for the P-C and P-N interactions in carbodiphosphoranes ($R_3P{\to}C{\leftarrow}PR_3$) and related N(I) species ($[R_3P{\to}N{\leftarrow}PR_3]^+$),[28] we rationalized that the nature of the P-N bond in iminophosphoranes could be viewed as analogous to the P-Ni bond (Scheme 2). In turn, the ability of the N atom to behave as an electron donor to an attached conjugated scaffold (Y) should correspond to the ability of the Ni atom to π-backbond to the CO ligands. In such a way, it should be possible to correlate well-known TEPs of R_3P with σ_p^+ of the iminophosphorano group $R_3P{=}N$-, as well as the $E_{1/2}$ of the of the corresponding BPY **8R**. Herein we validate this proposal for a variety of **8R**/**8R²⁺** couples.



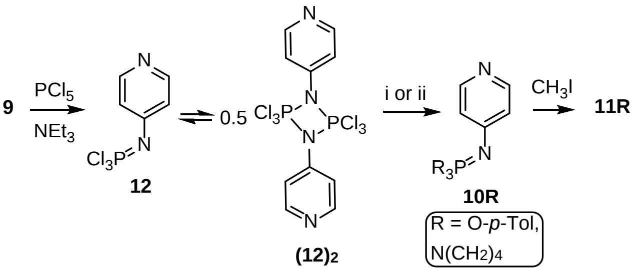
Scheme 2. Qualitative comparison of the bonding in Ni-carbonyls (top) with iminophosphorano substituents (bottom), for phosphines with high (left, i and iii) or low (right, ii and iv) TEP.

Pyridinium salts **11R** are the direct precursors to the respective BPYs **8R** and their oxidized forms **8R²⁺** (Scheme 3b).[12,25] These compounds were prepared by one of two routes. The primary route (Scheme 3a), is based on our published preparation of **8Ph** and **8Cy**,[25] and was used for aryl substituted derivatives (**11R**, R = *p*-Tol, *p*-C_6H_4Cl, *o*-C_6H_4OMe). The route starts from the commercially available phosphines, which are subsequently oxidized and condensed with 4-aminopyridine in the presence of triethylamine to afford the iminophosphorano substituted pyridines **10R**. The pyridines could be alkylated directly without isolation to give the N-methyl pyridinium salts **11R** in moderately good yields (53 – 79%).



Scheme 3. Synthetic route to pyridinium iodides **11R** from phosphines (a) and their conversion to bipyridinium ions **8R²⁺** (b).

For preparing derivatives of **11R** with heteroatoms bonded to phosphorus (R = $N(CH_2)_4$, O-*p*-Tol) a secondary route (Scheme 4) was devised. The key compound in this route, **12**, which has labile chlorine atoms on the phosphorus, was prepared in an 80% yield via the condensation of 4-aminopyridine with phosphorus pentachloride in the presence of triethylamine. Interestingly, **12** was found to exist in a concentration dependent equilibrium between monomeric (**12**) and dimeric (**(12)₂**) species, with characteristic ^{31}P NMR chemical shifts at -35.1 and -83.4 ppm for the monomer and dimer, respectively. These are in line with the shifts reported for monomeric (-48.6 ppm) and dimeric (-77.0 ppm) $Cl_3P{=}NPh$.[29] In the solid state, **12** occurs exclusively as the dimeric form, as confirmed by X-ray crystallography (Figure 1). Immediate NMR spectroscopic analysis of the dissolved solid in $CDCl_3$ shows signals for the dimer, which converts to predominantly (>95%) monomer over 15 hours in solution (see Supplementary Information). The preparation of iminophosphorano substituted pyridines featuring 4-methylphenoxy (**10O-*p*-Tol**) and pyrrolidinyl (**10N(CH₂)₄**) substituents on phosphorus was accomplished in 90, and 59% yields, respectively, by the introduction of an excess of nucleophilic substituent (sodium 4-methylphenoxide, or pyrrolidine, respectively) to a suspension of **(12)₂** in diethyl ether (Scheme 4). The pyridines **10O-*p*-Tol** and **10N(CH₂)₄** were subsequently alkylated with iodomethane to afford the corresponding N-methyl pyridinium salts **11R** in 80 and 91% yields, respectively.



Scheme 4. Alternate synthetic route to pyridinium iodides **11R** featuring heteroatoms on phosphorus, from **12**. Conditions i: excess sodium 4-methylphenoxide; ii: excess pyrrolidine

The solid state structure of **(12)₂** (Figure 1) is similar to that of the N-methyl-trichloroiminophosphorane dimer.[30] The unit cell contains three unique molecules, two of which contain a planar central four-membered ring, while the third P_2N_2 ring deviates only slightly from perfectly planar. In each molecule, the phosphorus atoms are approximately trigonal bipyramidal, with a nitrogen occupying an axial and an equatorial position for each. The central cores are composed of alternating elongated $P\text{-}N_{axial}$ (1.796(2) – 1.804(2) Å; see P1-N1/P2-N2 in Figure 1) and short $P\text{-}N_{equitorial}$ (1.630(2) – 1.649(3) Å; see P1-N2/P2-N1, Figure 1) bonds. Similarly, the axial P-Cl bonds are found to be longer (2.1113(10) – 2.1274(10) Å; see P1-Cl3/P2-Cl6) than the equatorial ones (2.0192(10) – 2.0380(10) Å).

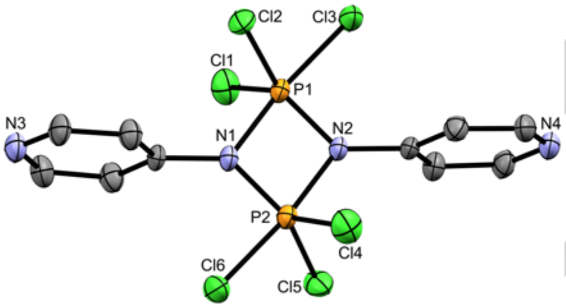


Figure 1. Solid state structure of **(12)₂**, showing one of three independent molecules in the unit cell. Ellipsoids are plotted at the 50% probability level and hydrogen atoms are omitted for clarity. Carbon atoms are unlabelled.

Because of their stability towards air and moisture, the bipyridinium salts (**8R**$^{2+}$) were targeted for electrochemical characterization rather than their air-sensitive reduced forms **8R** (Scheme 3b). To this end, the bispyridinylidenes **8R** were generated by deprotonation at the C2 position of the corresponding pyridinium salts **11R**. The reactions were carried out in C_6D_6 and within 90 minutes ^{31}P and ^{1}H NMR spectroscopic analysis of the reaction mixtures showed two distinct species, corresponding to the *E* and *Z* bispyridinylidene isomers, in varying ratios (see Table 1 and Supporting Information). *In situ* nuclear Overhauser effect spectroscopy (NOESY) on the reaction mixtures containing **8R** (R = O-*p*-Tol, *p*-C_6H_4Cl, *p*-Tol, $N(CH_2)_4$, *o*-C_6H_4OMe) confirmed the *Z* isomer to be the major constituent in all cases (see Supporting Information), as had been already observed for **8Ph** and **8Cy**.[25] The reaction mixtures were filtered to remove potassium iodide and any residual **11R**, and hexachloroethane was added to generate the respective dichloride salts **8R**$^{2+}$·**2Cl**$^{-}$. In some cases (R = O-*p*-Tol, *o*-C_6H_4OMe), purification of the hygroscopic dichlorides was forgone in favor of anion metathesis with lithium hexafluorophosphate to generate the respective bis(hexafluorophsphate) salts. In the case of **8O-*p*-Tol** $^{2+}$·**2PF**$_6^-$**,** the salt could not be separated from four minor impurities and was further characterized in the mixture, while the other bipyridinium ions could be isolated in 28 – 72% yields.

Cyclic voltammograms for each bipyridinium salt were obtained in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dimethylformamide (DMF). In each case a single, quasi-reversible redox event was observed for the **8R/8R**$^{2+}$ couple (see Supporting Information). The redox potentials span the range from -1.14 V vs SCE for R = O-*p*-Tol, to -1.51 V for R = Cy (Table 2, entries 1 – 7). Considering the two-electron process, this 370 mV span represents over 12 orders of magnitude in terms of the ratio of equilibrium constants for a given redox reaction involving these electron donors. Moreover, it demonstrates a remarkable sensitivity of the donor properties of the iminophosphorano group itself to changes in R. Indeed, from the experimental redox potentials and eq 1, σ_p^+ values for the respective $R_3P{=}N\text{-}$ groups can be determined (Table 2). These substituent constants span the range of -1.33 for R = O-*p*-Tol, which is comparable to the amino group ($-NH_2$, σ_p^+ = -1.30)[24] to -2.28 for R = *o*-C_6H_4OMe, which signifies superior electron donating ability than even the most donating amino functionalities (*cf.* σ_p^+ = -1.80 for $-N(CH_2)_4$ to as low as σ_p^+ = -2.11 when the amino group is annulated with the reaction center)[31].

Table 1. ^{31}P NMR data for **8R** and the oxidized form **8R**$^{2+}$.

R	^{31}P **8R** (δ, ppm) [a]	*Z*:*E* for **8R** (δ, ppm) [b]	^{31}P **8R**$^{2+}$ (δ, ppm)
O-*p*-Tol	-29.8, -29.4	8.1:1	-14.2
p-C_6H_4Cl	-6.1, -4.2	3.5:1	14.2
Ph[25]	-4.3, -1.5	2.2:1	16.5
p-Tol	0.3, -1.2	2.4:1	17.1
$N(CH_2)_4$	6.2, 7.6	6.4:1	17.6
Cy[25]	15.8,18.7	3.9:1	37.7
o-C_6H_4OMe	-7.8, -6.7	2.6:1	13.4

[a] For the *Z*, and *E* isomers, respectively. [b] *E* isomer unambiguously assigned based on *in situ* ^{1}H NOESY (see Supporting Information).

Qualitatively, it was immediately apparent that the more reducing bispyridinylidenes involved iminophosphorano substituents derived from more electron donating phosphine ligands (R_3P), the latter being characterized by a lower Tolman electronic parameter (TEP) (Table 2, entries 1 – 7).[26] Indeed, a plot of $E_{1/2}$ for the iminophosphorano-substituted bispyridinylidenes vs the TEP for the phosphine shows a strong linear correlation (Figure 2, $R^2 = 0.9886$), relating to equation 2 (see Supporting Information for the equivalent equation vs Fc^+/Fc):

$$E_{1/2}\text{ (V vs SCE, DMF)} = 0.014244(\text{TEP}) - 30.822 \qquad (2)$$

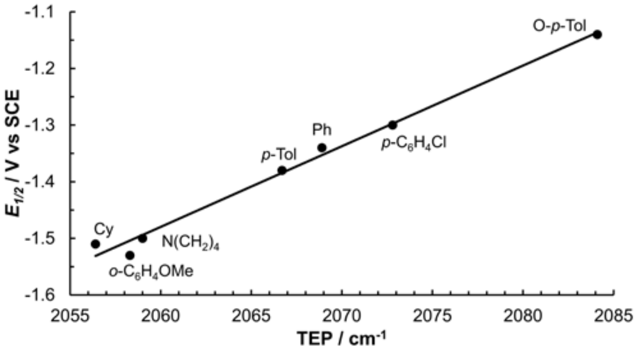


Figure 2. Plot of redox potential for the two-electron couple (**8R**/**8R**$^{2+}$) in $R_3P{=}N$- substituted bispyridinylidenes against the TEP for the corresponding R_3P fragment. Labels represent the R groups.

Considering the large number of TEPs available for phosphines, the predictive value of this relationship is substantial (Table 2, entries 8 – 12). In terms of weaker reductants, this equation yields $E_{1/2}$ values for **8R** of -0.76 V for R = F (TEP = 2110.8 cm^{-1}), or -1.01 V for more synthetically accessible R = O-*p*-C_6H_4CN (TEP = 2092.8 cm^{-1}). On the other hand, the recent reports[32–38] of a variety of phosphines that are more donating than the classical benchmark P*t*Bu$_3$ (TEP = 2056.1 cm^{-1}) provide new possibilities for highly reducing derivatives of **8R** with predicted redox potentials as low as -2.12 V vs SCE. (see Table 2). Remarkably, entries 11 and 12 represent BPYs that are even more reducing than the reported BPY featuring four $Ph_3P{=}N$- substituents (-1.70 V vs SCE (DMF)).[39]

Moreover, since both σ_p^+ and TEP are each strongly correlated to $E_{1/2}$, the two equations (eq 1 and 2) can be used to derive an expression for σ_p^+ of new iminophosphorano substituents as a function of experimental TEPs (eq. 3, see Supplementary Information):

$$\sigma_p^+\ (R_3P{=}N\text{-}) = 0.034927(\text{TEP}) - 74.110 \qquad (3)$$

This equation allows for predicting generally applicable σ_p^+ constants for $R_3P{=}N$- substituents from the broad range of known TEPs for phosphines. It needs to be stressed that this relationship is only as good ($R^2 = 0.9886$) as that between TEP and $E_{1/2}$, and its legitimacy depends on both eq 1 and eq 2 being valid; therefore caution must be exercised in relying on values outside the demonstrated range of valid σ_p^+ and TEP values. Nevertheless, since substituent constants for $R_3P{=}N$- groups are virtually unknown, it is the only means of quantitatively predicting the electron releasing power of these substituents. This information should be of great assistance in guiding the development of new molecules and materials, particularly where electron releasing substituents are desirable. Some exemplary values are in Table 2 (entries 8 – 12), and indicate that such iminophosphorano substituents can span a range of donating ability from $\sigma_p^+ = -0.39$ (R = F, entry 8), which is less donating than -SMe ($\sigma_p^+ = -0.60$), up to $\sigma_p^+ = -3.75$ (R = dmaP$_2$, entry 12), which is only surpassed by some negatively charged substituents such as -O$^-$ and -NH$^-$.[24,40]

Table 2. Experimental and predicted (in parenthesis) data related to correlations described by equations 1-3.

Entry	R[a]	$E_{1/2}$ **8R^{2+}/8R** (V vs SCE) [b]	TEP for R_3P (cm^{-1})[26]	σ_p^+ for $R_3P{=}N$- [d, e]
1	O-*p*-Tol	-1.14	2084.1	-1.33
2	*p*-C_6H_4Cl	-1.30	2072.8	-1.72
3	Ph	-1.34	2068.9	-1.82
4	*p*-Tol	-1.38	2066.7	-1.92
5	N(CH$_2$)$_4$	-1.50	2059[c]	-2.21
6	Cy	-1.51	2056.4	-2.23
7	*o*-C_6H_4OMe	-1.53	2058.3	-2.28
8	F	(-0.76)	2110.8	(-0.39)
9	O-*p*-C_6H_4CN	(-1.02)	2092.8	(-1.01)
10	Ad	(-1.59)	2052.1[32]	(-2.44)
11	NI*i*Pr	(-1.91)	2029.7[37]	(-3.22)
12	dmaP$_2$	(-2.12)	2014.5[38]	(-3.75)

[a] Ad = adamantly, NI*i*Pr = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenamino, dmaP$_2$ = [$(Me_2N)_3P{=}N$]$(Me_2N)_2P{=}N$- (see Supporting Information for structures). [b] Values in parentheses are predicted from TEP using equation 2. [c] Based on IR data from $L_2RhCOCl$ complex[41,42] using Roodt's conversion.[43] [d] Determined from $E_{1/2}$ using equation 1. [e] Values in parenthesis are predicted from TEP using equation 3.

In summary, we have prepared and characterized a variety of new **8R**/**8R^{2+}** couples (R = O-*p*-Tol, *p*-C_6H_4Cl, *p*-Tol, N(CH$_2$)$_4$, *o*-C_6H_4OMe) and, along with data for known derivatives (R = Ph, Cy), demonstrated that their redox potentials are strongly correlated with experimental TEPs for the respective phosphine (R_3P) fragment ($R^2 = 0.9886$). This relationship allows for TEPs to be used for the prediction of redox potentials for new iminophosphorano-substituted BPYs. This covers a predicted range of redox potentials of 1.36 V, including derivatives with record low redox potentials for neutral organic molecules (**8R**, R = dmaP2, $E_{1/2}$ = -2.12 V vs SCE), up to -0.76 V vs SCE (for R = F).

This work was extended more generally by use of the existing relationship between $E_{1/2}$ for BPYs and σ_p^+ of the substituent, to allow for predicting substituent constants for iminophosphorano groups. These values suggest an impressive range of donating ability for these functional groups from σ_p^+ = -0.39 (R = F) to σ_p^+ = -3.75 (R = dmaP2)! Iminophosphorano substituents are easily introduced via an amino (-NH$_2$) group or an azide (via a Staudinger reaction), and also offer the advantage of a ^{31}P NMR handle for monitoring reactions, therefore such quantitative data should be immensely valuable to promoting the widespread adoption of these versatile and powerful substituents in the design of new molecules with properties that cannot be unlocked by traditional functional groups.

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Keywords: Tolman electronic parameter • substituent constant • organic electron donor • bispyridinylidene • redox potential

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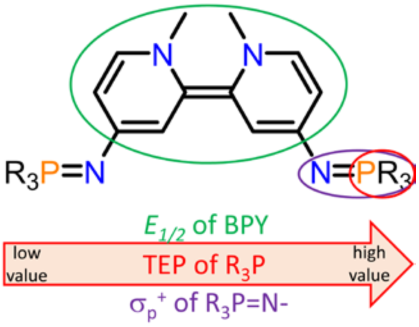

TEP shows the way: The Tolman electronic parameter (TEP) of the phosphine unit is found to be directly related to the redox potential of the corresponding iminophosphorano-substituted bispyridinylidene (BPY). With the earlier established relationship between the $E_{1/2}$ of BPYs and the related substituent constants (σ_p^+), TEP can now be used to design BPYs with specific redox potentials and to predict generally applicable σ_p^+ for R_3PN- substituents.