ELSEVIER

Journal of Organometallic Chemistry 643–644 (2002) 516–521

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Electronic effects on the acidity of phosphorus(III) triflates[☆]

Sylvie L. Renard, Terence P. Kee *

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Received 10 August 2001; accepted 14 November 2001

Abstract

A range of chiral phosphorus(III) triflates has been prepared and their donor–acceptor behaviour towards the representative donor 4-phenylpyridine investigated. Correlations between ^{31}P-NMR shifts, relative binding strengths (K_r) and the electronic nature of the phosphorus complex are observed. A scale of relative Lewis acidity (A_r) is proposed for this class of phosphorus compound towards donor molecules using 4-phenylpyridine as a reference. © 2002 Published by Elsevier Science B.V.

Keywords: Phosphorus(III) triflates; Electronic effects; Chiral

---

1. Introduction

There has been considerable interest over the last 20 years in phosphenium compounds [1] which are formally examples of $\sigma^2\lambda^3$ phosphorus and recently, efforts have intensified due to the range of applications envisaged in organometallic and co-ordination chemistry championed, among others, by Nakazawa and Baker, respectively, [2]. We [3] and others [4] have examined chiral phosphorus(III) halides and triflates, the latter of which have been shown to possess significant phosphenium character both in the solid state and solution, especially when in the presence of donor molecules such as amines and phosphines [3]. Our studies were inspired by earlier work of Bertrand et al. on the heterolysis of the phosphorus–halogen bond in the presence of a strong nucleophile such as 1,8-diazabicyclo[5.4.0]undec-7-ene [5]. More recently, some beautiful work by Gudat and colleagues [6] has revealed that, on the basis of structural, computational and donor–acceptor interactions with Lewis bases, 1,3,2-diazaphospholene triflates are comparable in electronic nature to their carbon cousins the Arduengo class of carbenes.

In this contribution, we wish to extend our earlier work in the definition of a relative basicity scale (B_r) for various donor molecules towards a reference phosphorus(III) triflate [3b] towards defining the degree to which phosphorus Lewis acidity may be influenced by distal, non-steric substitution of the organic framework. The method we have chosen is based on isothermal measurements of relative binding strengths of phosphorus(III) triflates against 4-phenylpyridine at fixed concentrations. We recognise that this approach is less rigorous than full NMR titration analysis but has been used effectively nonetheless in a relative capacity.

2. Results and discussion

Full synthetic details of all halide compounds **4** and triflate derivatives **5** are available as Section 3 but are summarised in Scheme 1; representative general methods for the synthesis of one such derivative, **2a**–**5a** have been reported previously [3b]. Each X-substituent is in a position to cause minimal steric differentiation at the phosphorus centre, a feature we have explored in some detail on the ligand frameworks alone [7]. Indeed, the substituents are some seven bonds distant from the phosphorus centre and thus, might be expected to have a somewhat attenuated through-bond electronic influence, especially since any extended conjugation should

---

[☆] C'est un très grand plaisir pour nous de présenter cette petite offrande en l'honneur du Professeur François Mathey; un chimiste et une personne d'excellence.

* Corresponding author. Tel.: +44-113-233-6421; fax: +44-113-233-6565.

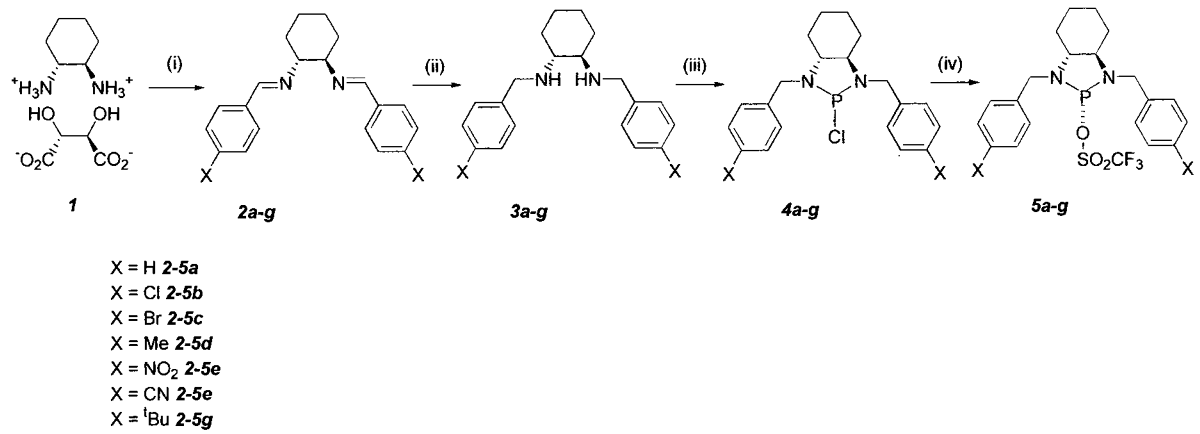
E-mail address: p.kee@chem.leeds.ac.uk (T.P. Kee).

0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(01)01460-7

be partially compromised by the presence of the methylene function. Nevertheless, in related electronic investigations, we have found that similar aromatic substitution formally eight bonds distant from the active site can influence reactivity at that site [8]. We present here preliminary investigations into how such distal electronic substitution may influence the electronic character at the phosphorus centre and degree of interaction between that phosphorus centre in **5** and a representative base, 4-phenylpyridine. This, we argue, allows us to quantify phosphorus Lewis acidity in this particular class of phosphorus triflates through definition of a relative acidity parameter (A_r, vide infra).

The $^{31}P\{^1H\}$ chemical shifts of compounds **4a**–**g** and **5a**–**g** at a concentration of 0.25 M (298 K; NMR probe temperature) in $CDCl_3$ and CD_2Cl_2 solvent respectively are reproduced in Table 1. There is the suggestion, from these data, especially when presented in graphical format in Fig. 1 and Fig. 2 respectively, that there exists a correlation between ^{31}P chemical shifts in both **4** and **5** series and the electronic Hammett parameter of the X-substituent. In both cases the trend is in the same direction where higher resonance frequencies are favoured by the more electron-donating substituents. Whilst, a detailed explanation of this trend must be treated with some caution due to the small changes involved and rather lower than desirable R^2 values, it is worth commenting that there is an 13% variation in triflate ^{31}P-NMR resonances such that the nature of the X-function, even when seven bonds distant from the phosphorus centre has an influence over the ^{31}P-NMR chemical shift and hence the electromagnetic environment of the system. Given the considerable through-bond distances involved our feeling is that field and dipolar effects in solution may play a role.

In the presence of one equivalent (0.25M) of the base 4-phenylpyridine ($B_r = 1.1$ [3b]), triflates **5a**–**g** return far lower ^{31}P-NMR chemical shifts due to rapid reversible interaction with the base (Scheme 2). Indeed, a graphical representation of the change in ^{31}P-NMR shift ($\Delta\delta P$) upon interaction with 4-phenylpyridine against Hammett σ_p (Fig. 3) reveals a similar trend to



Scheme 1. Syntheses of compounds **4** and **5**. (i) K_2CO_3, $CHOC_6H_4X$; (ii) $LiAlH_4$; (iii) PCl_3, *N*-methylmorpholine; (iv) $Me_3SiOSO_2CF_3$ (TMSOTf). See Section 3 for more details.

Table 1
Selected NMR and computed equilibrium data for compounds **4** and **5**

System	δ_P (ppm) [a]	System	δ_P (ppm) [b]	σ_p	System	δ_P (ppm) [c]	$\Delta\delta_P$ (ppm)	δ_C (ppm) [d]	F_I	K_r (mol^{-1} l)	A_r [e]
4a	181.9	**5a**	260.7	0.0	**5a**+base	163.6	97.1	121.34	0.88	253	7
4b	180.0	**5b**	264.9	0.24	**5b**+base	169.8	95.1	121.30	0.82	103	10
4c	179.9	**5c**	262.7	0.26	**5c**+base	177.2	85.5	121.09	0.67	25	27
4d	182.4	**5d**	256.7	−0.14	**5d**+base	165.8	90.9	121.47	1.04	2100	–
4e	177.4	**5e**	223.7	0.81	**5e**+base	158.0	65.7	121.19	0.84	125	19
4f	178.0	**5f**	238.3	0.70	**5f**+base	158.4	79.9	121.26	0.76	54	13
4g	183.0	**5g**	272.1	−0.15	**5g**+base	165.1	107.0	121.39	0.94	1077	3

[a] In $CDCl_3$; 0.25 M.

[b] In CD_2Cl_2; 0.25 M.

[c] Base = 4-phenylpyridine; CD_2Cl_2; 0.25 M.

[d] CF_3 signal, 0.25 M, CD_2Cl_2; $\delta_I = 121.42$ ($^nBu_4NOTf$) and δ_C = shift for base-free, precursor triflate **5a**–**g** at same concentration and in same solvent.

[e] A_r (relative acidity) = $[\delta_I - \delta_S]/\delta_I$; $\times 10^4$ [9].

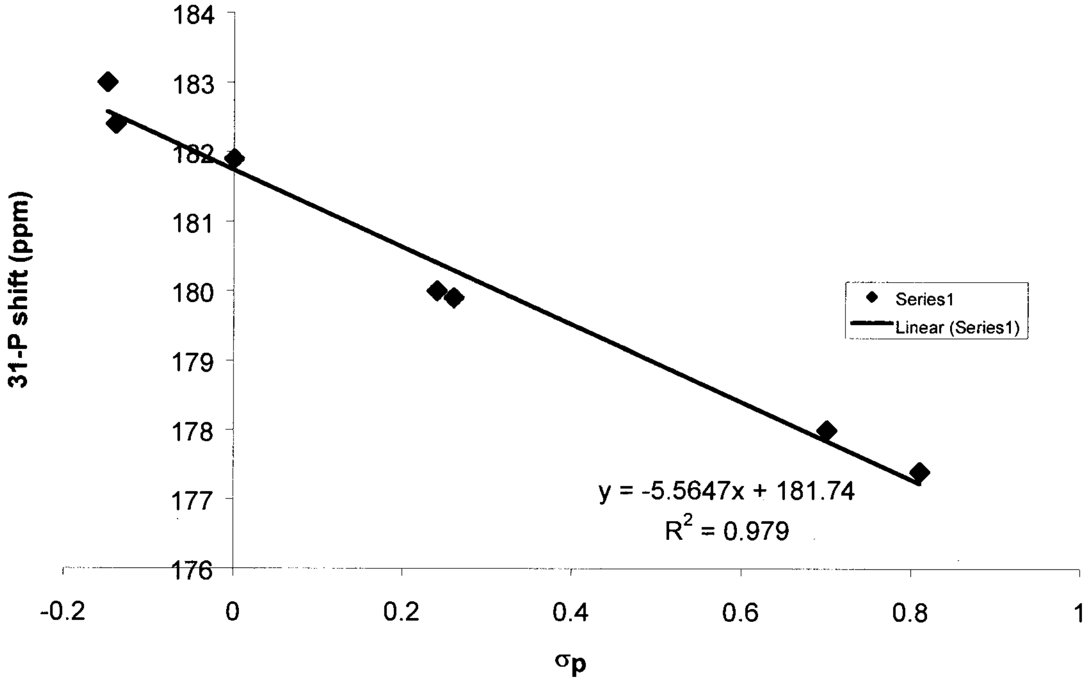


Fig. 1. Correlation between $^{31}P\{^1H\}$-NMR shifts for **4a**–**g** vs. Hammett σ_p parameter of X (Scheme 1).

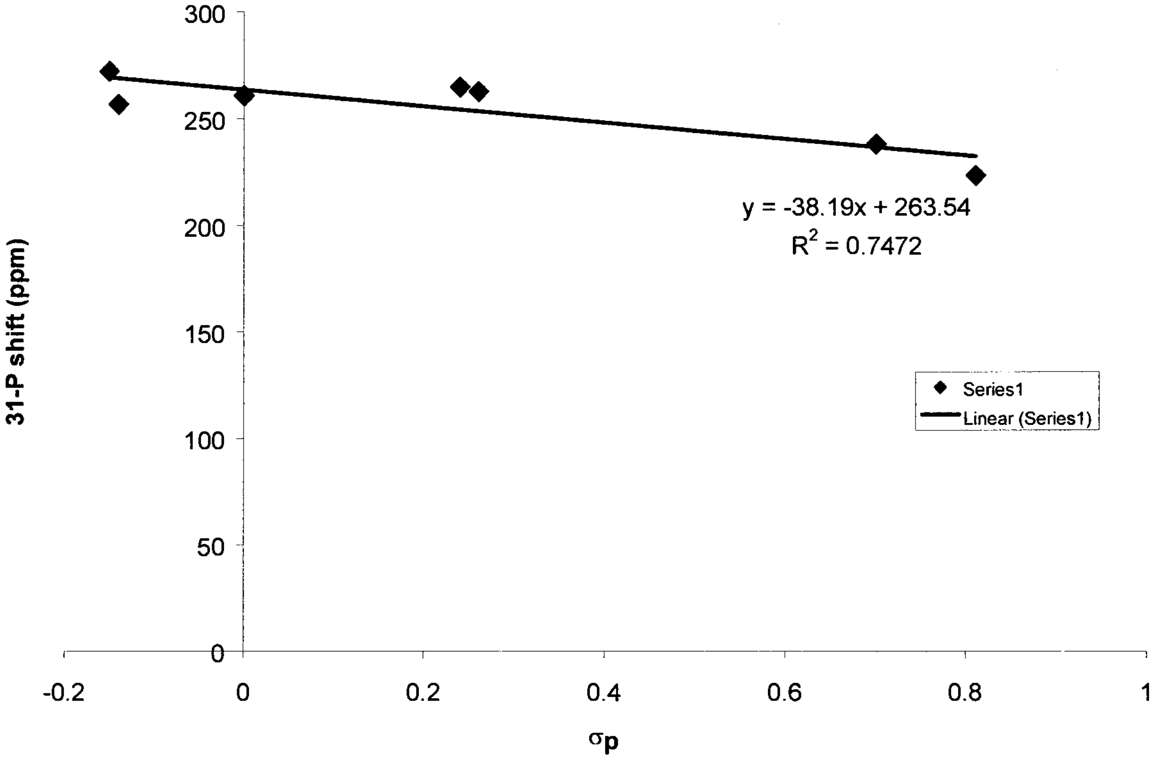
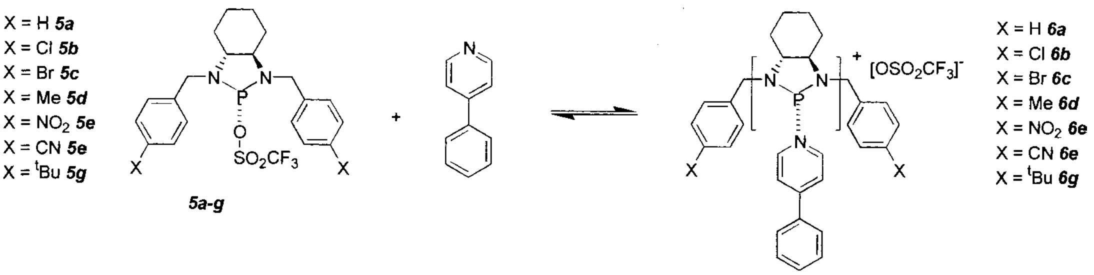


Fig. 2. Correlation between $^{31}P\{^1H\}$-NMR shifts for **5a**–**g** vs. Hammett σ_p parameter of X (Scheme 1).

those in Figs. 1 and 2. Using the same approach as proposed earlier for quantifying the interactions between this class of phosphorus(III) triflates and donor molecules [3b], it is possible to derive internally consistent relative binding strengths for the interactions between **5a**–**g** and 4-phenylpyridine. Thus, if we define the equilibrium between Lewis acid and Lewis base as in Scheme 2, the relative binding strength K_r may be represented by the equation $K_r = F_I/\{[A_o].\ (1-F_I)^2\}$ where F_I is the mole fraction of ionic form **6a**–**g** and

[A_o] is the total concentration of phosphorus compound in the system [3b]. We arrange that [A_o] = 0.25 M and we calculate F_I from the equation $F_I = [\delta_S - \delta_C]/[\delta_I - \delta_C]$ where δ_S represents the NMR chemical shift of the system under investigation (chosen to be the $^{13}C\{^1H\}$ resonance of the triflate CF_3 group) and δ_C and δ_I are the corresponding chemical shifts of base-free, precursor triflate **5a–g** and ionic ($^nBu_4NOTf$; δ_I 121.42) triflates, respectively, in the same solvent and at same concentrations as the subject samples. Representative $^{13}C\{^1H\}$-NMR data and computed F_I and K_r values are given in Table 1 and relationship between K_r and σ_p illustrated in Fig. 4. The latter reveals a trend although, a distinctly non-linear one such that the strongest degree of interactions between phosphorus centre and 4-phenylpyridine results from compounds **5** with the more electron-donating X substituents (e.g. ^{t}Bu and Me), perhaps counter-intuitive to that expected should through-bond inductive effects play a large part. We envisage a full explanation to involve components of dipole moment and field effects.

In the same way as we proposed a scale of relative basicity (B_r) for donor molecules interacting with this class of phosphorus(III) triflates, we can suggest a complementary scale of relative acidity $A_r = [\delta_I - \delta_S]/\delta_I$, whereby, the smaller the A_r value, the greater the relative acidity against 4-phenylpyridine ($B_r = 1.1$). However, it is clear from Table 1 and graphical correlation in Fig. 5, that the correlation between A_r and K_r is far from regular, although, a trend is apparent. We believe that this is due to the definition $A_r = [\delta_I - \delta_S]/\delta_I$, neglecting the vitally important feature that each compound analysed has a different δ_C value which is not accounted for explicitly in the aforementioned equation. Consequently, we advocate caution in



Scheme 2.

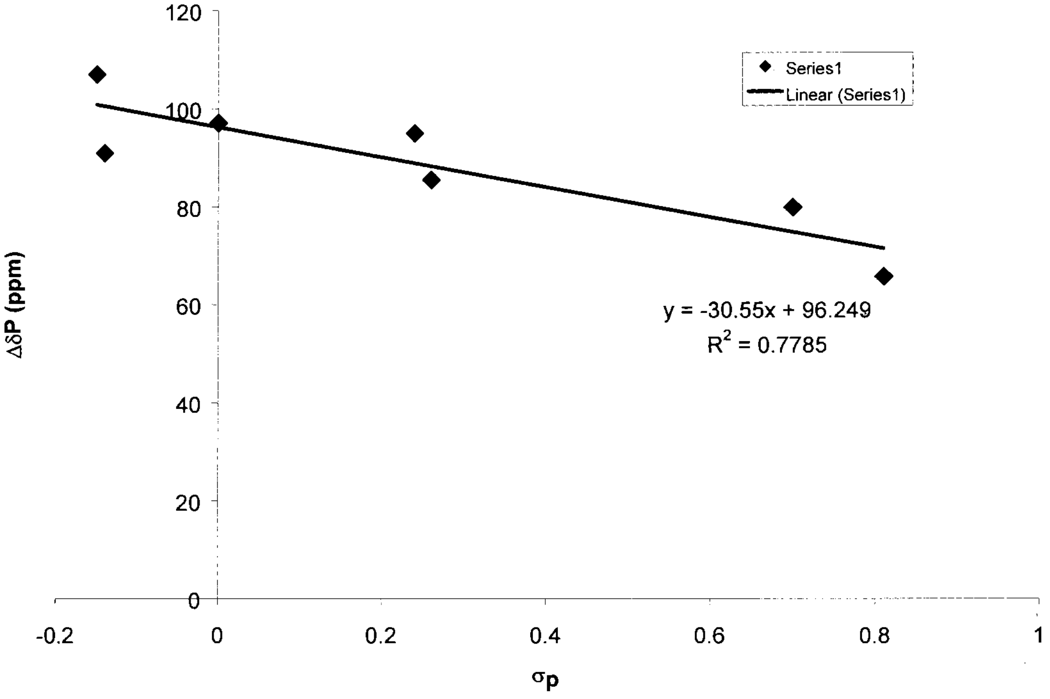


Fig. 3. Correlation between $^{31}P\{^1H\}$-NMR shift differences for **5a–g** in the presence and absence (ΔP) of 4-phenylpyridine (0.25 M) vs. Hammett σ_p parameter of X (Scheme 1).

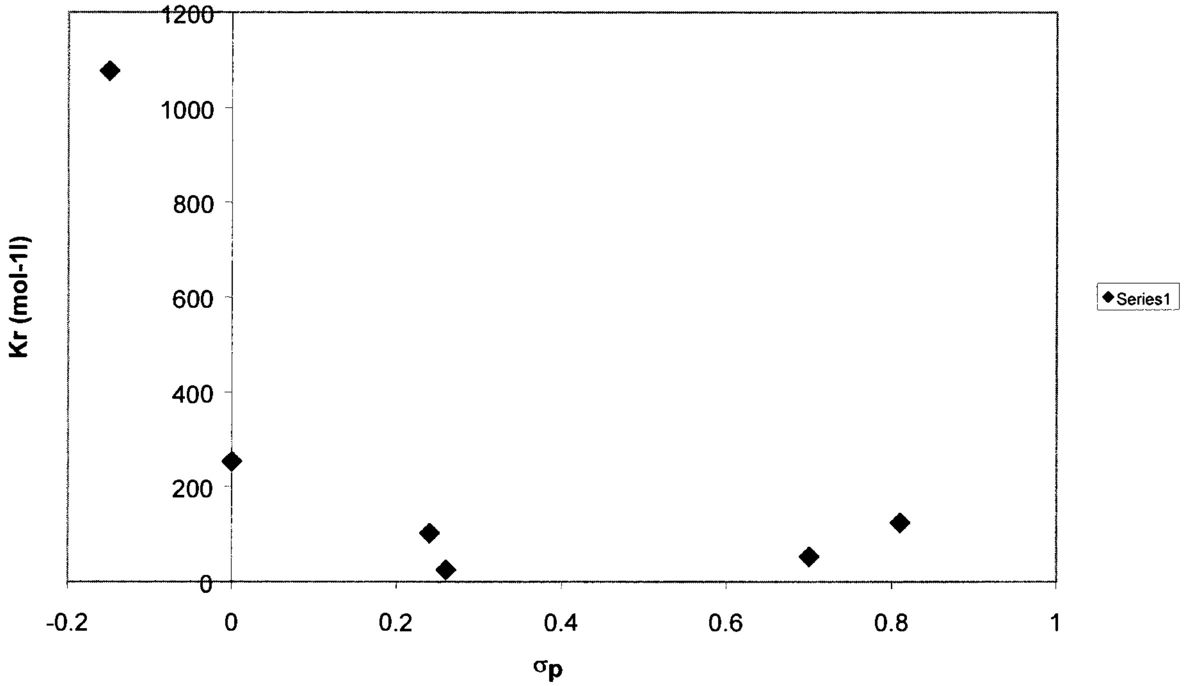


Fig. 4. Correlation between relative binding strength K_r for **5a**–**g** in the presence of 4-phenylpyridine (K; 298 K; 0.25 M; CD_2Cl_2) vs. Hammett σ_p parameter of X (Scheme 1).

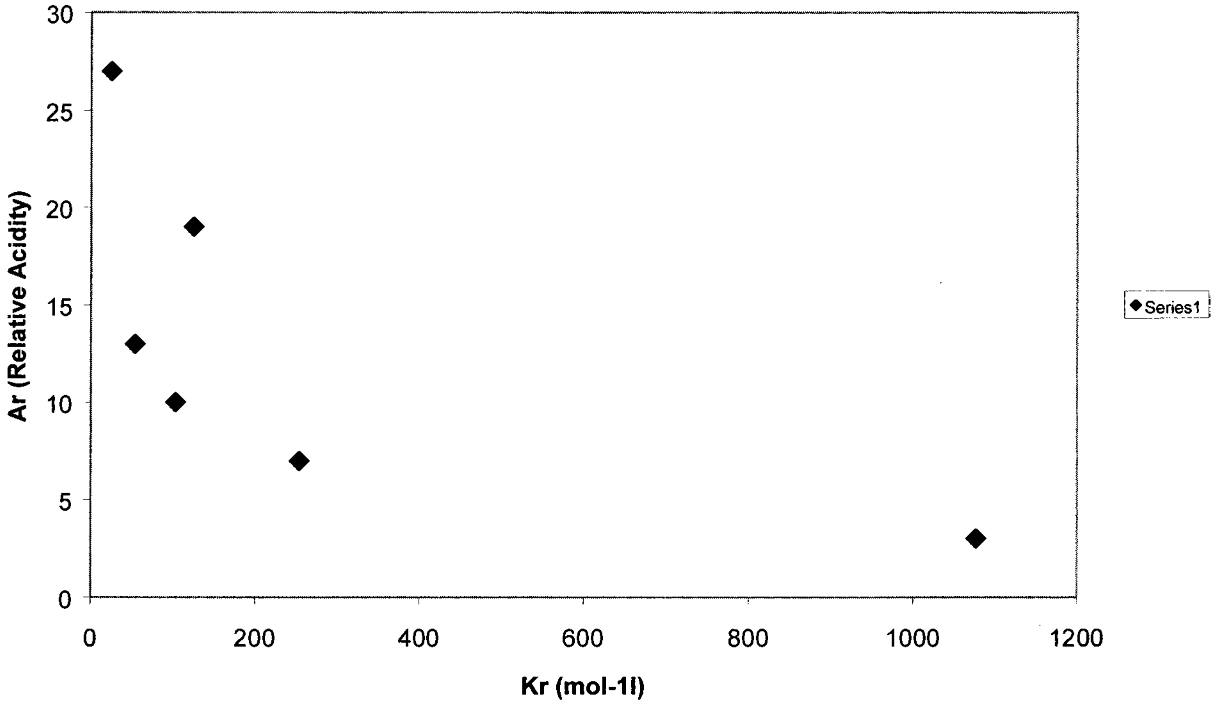


Fig. 5. Correlation between relative binding strength K_r for **5a**–**g** in the presence of 4-phenylpyridine (K; 298 K; 0.25 M; CD_2Cl_2) vs. relative acidity parameter A_r (Scheme 1).

the assignment of such values and suspect, as in the case of relative basicity parameters B_r defined earlier [3b] most effective correlations will result where the number of system variables is limited.

3. Supplementary material

Full synthetic, characterising and NMR experimental data for all compounds reported here are available as

Table 2

Triflate	6/Otf	6*p*-Br/OTf	6*p*-^{t}Bu/OTf	6*p*-Cl/OTf	6*p*-CN/OTf
m (g)	0.059	0.079	0.073	0.068	0.066
	^{n}Bu$_4$NCl	6*o*$_2$F$_2$/OTf	6*p*-Me/OTf	6*o*-NO$_2$/OTf	6*p*-NO$_2$/OTf
m (g)	0.049	0.068	0.063	0.070	0.070

Mass of triflate used.

Supplementary Information in the form of an electronic Word document available by e-mail free of charge from t.p.kee@chem.leeds.ac.uk.

Acknowledgements

The authors extend their grateful thanks to the EPSRC and to Dr Julie Fisher and Simon Barratt for their invaluable help with NMR experiments. We thank one of the referees for several valuable suggestions.

References

[1] See for example (a) Phosphorus: The Carbon Copy, K.B. Dillon, F. Mathey J.F. Nixon (Eds.), Wiley, Chichester, (1998);
(b) N. Nakazawa, J. Organomet. Chem., 611 (2000) 349;
(c) A.H. Cowley, R.A. Kemp, Chem. Rev., 85 (1985) 367;
(d) M. Sanchez, M.R. Mazières, L. Lamandé R. Wolf in Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry, Eds. M. Regitz O. Scherer, Thieme, Stuttgart, (1990) 129;
(e) A. Schmidpeter, in Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry, Eds. M. Regitz, O. Scherer, Thieme, Stuttgart, (1990) 149;
(f) D. Gudat, Coord. Chem. Rev., 173 (1997) 71;
(g) M.G. Thomas, C.W. Schultz, R.W. Parry, Inorg. Chem., 16 (1977) 994;
(h) A.H. Cowley, M.C. Cushner, M. Lattman, M.L. McKee, J.S. Szobota, J.C. Wilburn, Pure and Appl. Chem., 52 (1980) 789;
(i) N. Burford, P. Losier, S.V. Sereda, T.S. Cameron, G. Wu, J. Am. Chem. Soc., 116 (1994) 6474;
(j) M.K. Denk, S. Gupta, R. Ramachandran, Tetrahedron Lett., 37 (1996) 9025;
(k) C.J. Carmalt, V. Lomeli, B.G. McBurnett, A.H. Cowley, Chem. Commun., (1997) 2095;
(l) D. Gudat, Eur. J. Inorg. Chem., (1998) 1087;
(m) N. Burford, P. Losier, P.K. Bakshi, T.S. Cameron, J. Chem. Soc., Dalton Trans., (1993) 201;
(n) R.W. Kopp, A.C. Bond, R.W. Parry, Inorg. Chem., 15 (1976) 3042;
(o) C.W. Schultz, R.W. Parry, Inorg. Chem., 15 (1976) 3046;
(p) B.E. Maryanoff, R.O. Hutchins, J. Org. Chem., 37 (1972) 3475;
(q) S. Fleming, M.K. Lupton, K. Jekot, Inorg. Chem., 11 (1972) 2534;
(r) G. David, E. Niecke, M. Nieger, V. van der Goenna, W.W. Schoeller, Chem. Ber., 126 (1993) 1513;
(s) M. Sanchez, V. Romanenko, M.R. Mazieres, A. Gudima, L. Markovskii, Tetrahedron Lett., 32 (1991) 2775;
(t) A. Schmidpeter G. Jochem, Tetrahedron Lett., 33 (1992) 471.

[2] Some of the most recent contributions include (a) H. Nakazawa, M. Kishishita, T. Ishiyama, T. Mizuta K. Miyoshi, J. Organomet. Chem., 617 (2001) 453;
(b) D. Gudat, A. Haghverdi M. Nieger, J. Organomet. Chem., 617 (2001) 383;
(c) M.B. Abrams, B.L. Scott T.R. Baker, Organometallics, 19 (2000) 4944;
(d) H. Nakazawa, M. Kishishita, N. Tadahiro, T. Ishiyama K. Miyoshi, Chem. Lett., (2000) 230;
(e) W. Malisch, K. Grun, Oliver Fey, C. Abd El Baky, J. Organomet. Chem., 595 (2000) 285;
(f) S. Loss, C. Widauer H. Grutzmacher, Angew. Chem. Int. Ed. Engl., 38 (1999) 3329.

[3] (a) S.L. Renard, J. Fisher T.P. Kee, manuscript in preparation;
(b) V.A. Jones, S. Sriprang, M. Thornton-Pett, T.P. Kee, J. Organomet. Chem. 567 (1998) 199;
(c) V.A. Jones, M. Thornton-Pett T.P. Kee, J. Chem. Soc., Chem. Commun. (1997) 1317.

[4] J.-M. Brunel, R. Villard, G. Buono, Tetrahedron Lett. 40 (1999) 4669.

[5] R. Reed, R. Réau, F. Dahan, G. Bertrand, Angew. Chem. Int. Ed. Engl. 32 (1993) 399.

[6] (a) D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, Chem. Eur. J. 6 (2000) 3414;
(b) See also C. Payastre, Y. madaule, J.G. Wolf, T.C. Kim, M-R. Mazières, R. Wolf, M. Sanchez, Heteroatom. Chem. 3 (1992) 157.

[7] S.L. Renard, N. Dixon, M. Thronton-Pett, C.A. Kilner, M. Hardie T.P. Kee, manuscript in preparation.

[8] E.A. Bugnet, A.R. Brough, R. Greatrex T.P. Kee, Tetrahedron, in the press.

[9] The 4-phenylpyridine was stirred and heated under vacuum, so that any traces of water were trapped. For each NMR tube the total volume was 0.5 ml and the concentration of phosphorus(III) triflate was 0.25 mol l^{-1}, the corresponding masses are given in Table 2. A solution of dried 4-phenylpyridine was made and the amount per tube was 0.019 g, 0.125 mmol and 0.25 mol l^{-1}.