[4] G. S. Wilson, H. L. Anderson, *Chem. Commun.* **1999**, 1539–1540; R. Schlözer, J.-H. Fuhrhop, *Angew. Chem.* **1975**, *87*, 388; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 363; L. R. Nudy, H. G. Hutchinson, C. Schieber, F. R. Longo, *Tetrahedron* **1984**, *40*, 2359–2363.

[5] M. Uno, K. Seto, M. Masuda, W. Ueda, S. Takahashi, *Tetrahedron Lett.* **1985**, *26*, 1553–1556.

[6] J. Diekmann, W. R. Hertler, R. E. Benson, *J. Org. Chem.* **1963**, *28*, 2719–2724.

[7] R. Wagner, S. Berger, *Magn. Reson. Chem.* **1997**, *35*, 199–202; J. Kawabata, E. Fukushi, J. Mizutani, *J. Am. Chem. Soc.* **1992**, *114*, 1115–1117.

[8] NOESY and HSQC-NOESY experiments were carried out with a 300 ms mixing time at 294 K on a Bruker DRX500 instrument. All NOEs were negative.

[9] Crystals were grown by slow diffusion of *n*-pentane into a solution of $\mathbf{3}\cdot 2\,C_5H_5N$ in $CHCl_3$, over two weeks. Crystal data for $\mathbf{3}\cdot 2\,C_5H_5N\cdot 0.5\,C_5H_{12}\cdot 3\,H_2O$: $M_r = 1901.05$, monoclinic, space group $P21/c$, $a = 15.440(4)$, $b = 33.765(5)$, $c = 20.485(2)$ Å, $\beta = 94.64(2)°$, $V = 10644.5(33)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\rho_{calcd} = 1.186$ g cm^{-3}, $\mu = 0.508$ mm^{-1}, blue/green prisms $0.30 \times 0.20 \times 0.15$ mm^3, Enraf-Nonius DIP2000 image plate diffractometer, radiation $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), ω scans, range $1.45 < \theta < 20$; measured reflections: 4436; independent reflections: 4436 ($R_{int} = 0.0000$), R values ($I < 2\sigma I$): $R1 = 0.1159$, $wR2 = 0.3212$, all data: $R1 = 0.1628$, $wR2 = 0.3711$. Structure refinement: full-matrix-block least-squares on F^2. max/min residual electron density $1.255/-0.393$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139644. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] A search of the Cambridge Structural Database showed that the average C=C bond lengths in cumulenes are 1.34 and 1.25 Å for the sp^2-sp^1 and sp^1-sp^1 bonds, respectively; D. A. Fletcher, R. F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749; F. H. Allen, O. Kennard, *Chem. Design Autom. News* **1993**, *8*, 31–37.

[11] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, pp. 544–550; G. Märkl, M. Hafner, P. Kreitmeier, C. Stadler, J. Daub, H. Nöth, M. Schmidt, G. Gescheidt, *Helv. Chim. Acta* **1997**, *80*, 2456–2476; J.-H. Fuhrhop, E. Baumgartner, H. Bauer, *J. Am. Chem. Soc.* **1981**, *103*, 5854–5861.

[12] S. Yamaguchi, T. Hanafusa, T. Tanaka, M. Sawada, K. Kondo, M. Irie, H. Tatemitsu, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1986**, *27*, 2411–2414.

[13] N. Yoshida, H. Shimidzu, A. Osuka, *Chem. Lett.* **1998**, 55–56; A. Nakano, H. Shimidzu, A. Osuka, *Tetrahedron Lett.* **1998**, *39*, 9489–9492.

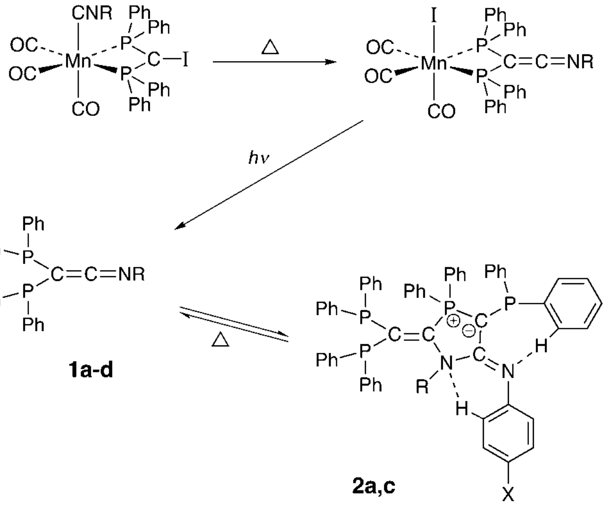
[14] No ^{12}C-H$_D$ to ^{13}C-H$_D$ NOE was observed in **6**, which is explained by the larger H$_D$–H$_D$ distance in **6** (calculated: 2.9 Å for D_2 isomer; 2.6 Å for C_{2h} isomer) compared to that in **3** (crystallographic: 2.47 and 2.41 Å; calculated: 1.9 Å). The ^{1}H and ^{13}C NMR spectra of **6** were assigned by assuming that the most shielded β-pyrrolic proton is H$_D$.

[15] Molecular mechanics calculations were carried out using the CAChe 4.1 software from Oxford Molecular Ltd. with augmented MM2 parameters; MM3 gave similar results.

Fully Reversible Cyclic Dimerization of Diphosphanylketenimines Promoted by Intramolecular C–H···N Hydrogen Bonds[**]

Javier Ruiz,[*] Fernando Marquínez, Víctor Riera, Marilín Vivanco, Santiago García-Granda, and M. Rosario Díaz

Ketenimines are important functional groups that show enhanced reactivity in nucleophilic addition and cycloaddition reactions. Furthermore, compounds containing this moiety are useful starting materials which have been applied in heterocycle chemistry.[1] We recently reported the synthesis of the diphosphanylketenimines $(PPh_2)_2C{=}C{=}NR$ (**1a**: R = Ph, **1b**: R = *t*Bu) by metal-assisted coupling of a transient diphosphanylcarbene with isocyanides (Scheme 1).[2] As these molecules combine the properties of diphosphanes with those of ketenimines, it was anticipated that new reactivity patterns could arise from them. Here we report a unique cyclic dimerization of *N*-aryldiphosphanylketenimines involving a new type of [2+3] cycloaddition reaction to give an azaphospha five-membered heterocycle featuring a phosphorus-ylide functionality. This dimerization is reversible under mild conditions and appears to be promoted by nonconventional CH···N hydrogen bonds.



Scheme 1. Metal-assisted synthesis of diphosphanylketenimines **1**. In the case of R = Ph or *p*-tolyl, reversible dimerization takes place to form **2**. **1a**: R = Ph; **1b**: R = *t*Bu; **1c**: R = *p*-tolyl; **1d**: R = xylyl; **2a**: R = Ph, X = H; **2c**: R = *p*-tolyl, X = Me.

---

[*] Dr. J. Ruiz, F. Marquínez, Prof. Dr. V. Riera, Dr. M. Vivanco
Departamento de Química Orgánica e Inorgánica
Facultad de Química, Universidad de Oviedo
33071 Oviedo (Spain)
Fax: (+34) 985-103-446
E-mail: jruiz@sauron.quimica.uniovi.es

Dr. S. García-Granda, Dr. M. R. Díaz
Departamento de Química Física y Analítica
Facultad de Química, Universidad de Oviedo
33071 Oviedo (Spain)

[**] This work was supported by the Spanish Ministerio de Educación y Ciencia (project nos. DGE-96-PB-0317 and PB96-0556)

The *N*-phenylketenimine **1a** forms colorless solutions in different organic solvents which are stable for weeks. However, when a solution of **1a** in hexane is very slowly concentrated to dryness under vacuum, and the process of adding and removing hexane is repeated at least three times, an orange solid corresponding to the unsymmetrical dimer **2a** is formed (Scheme 1). This dimerization is fully reversible, and refluxing a solution of **2a** in toluene for 10 min leads to the quantitative formation of monomer **1a**. By contrast, the *N-tert*-butylketenimine **1b** did not dimerize at all, showing the strong influence of the substituent at nitrogen in this process. It has been described that ketenimines tend to dimerize, but only upon prolonged thermolysis at high temperatures, and usually by [2+2] cycloaddition reactions to give azetidines;[3] related processes such as base-induced dimerization[4] and anodic oxidation[5] of ketenimines to give heterocyclic dimers and trimers are also known. Therefore the present reaction is a rare example of ketenimine dimerization occurring during crystallization.

The ^{31}P NMR spectrum of **2a** revealed the presence of four strongly coupled signals corresponding to the four inequivalent phosphorus atoms of the molecule (see the Experimental Section). The structure of **2a** was definitively established by X-ray crystallography[6] (Figure 1). The five-membered heterocycle C(1)-P(1)-C(3)-C(2)-N(1) is essentially planar. The short C(2)–C(3) (1.40(2) Å) and C(3)–P(1) bonds (1.70(2) Å) suggest that the negative charge at the ylide carbon atom C(3) is strongly shared with the neighboring atoms. An important feature of the structure of **2a** is the presence of two intramolecular CH···N hydrogen bonds. Thus, a phenyl ring at phosphorus atom P(2) acts as a hydrogen-bond donor through an *ortho* proton toward the exocyclic nitrogen atom N(2), with a rather short H(2)···N(2) contact of 2.44(2) Å (C–H···N 141(1)°). A much longer contact exists between an *ortho* proton of the phenyl group at N(2) and the endocyclic nitrogen atom N(1) (H(1)···N(1) 2.94(2) Å) with a very closed C–H···N angle of 90(1)°. These two parameters appear to indicate that this last interaction cannot be considered as a real hydrogen bond, when taking into account the cut-off of 2.7 Å based on van der Waals criteria and the preference for a linear geometry.[7] However, it has been shown that the electrostatic component of the hydrogen bond also operates beyond the van der Waals separation, and that directionality is blurred if other factors such as steric restrictions comes into play.[8] Additionally, a structural feature in favor of a hydrogen-bonding interaction is that the H(1)–N(1) vector is approximately directed toward the sp^3 lone pair of N(1).[9, 8a] Moreover, some cooperativity[8a] could exist, as the two hydrogen bonds are interconnected (the N(2)Ph group acts simultaneously as hydrogen-bond donor and acceptor), resulting in an enhancement of the total bond energy.

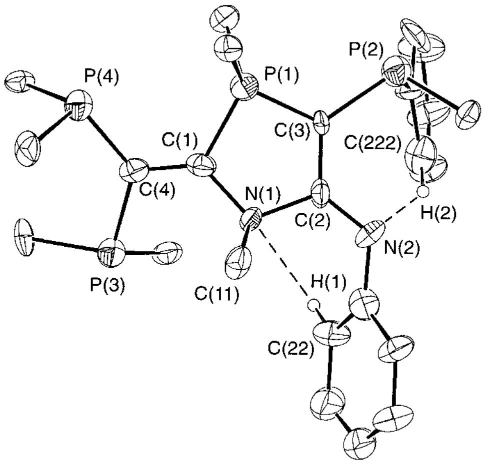
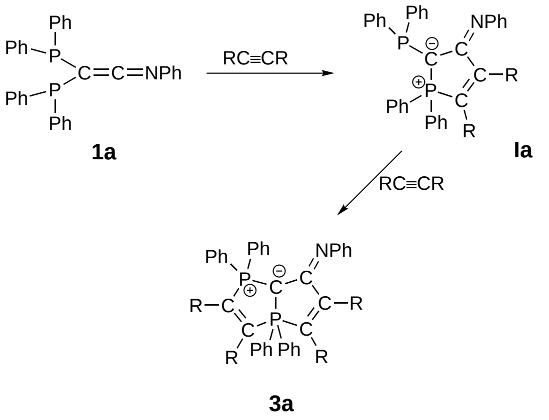


Figure 1. Molecular structure of **2a**. Hydrogen atoms and phenyl groups, except those involved in hydrogen bonds, are omitted for clarity (ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: N(1)-C(1) 1.45(2), N(1)-C(2) 1.45(2), P(1)-C(1) 1.80(2), P(1)-C(3) 1.70(2), C(2)-C(3) 1.40(2), N(1)-C(11) 1.45(2), C(1)-C(4) 1.38(2), C(2)-N(2) 1.27(2), C(3)-P(2) 1.83(2), C(4)-P(3) 1.88(2), C(4)-P(4) 1.77(2), N(1)···H(1) 2.94(2), N(2)···H(2) 2.44(2), C(22)···N(1) 3.09(3), C(222)···N(2) 3.22(3); C(22)-H(1)···N(1) 90(1), C(222)-H(2)···N(2) 141(1), C(1)-P(1)-C(3) 91(1), C(1)-N(1)-C(2) 111.(1), C(4)-C(1)-N(1) 126(2), C(4)-C(1)-P(1) 125(2), N(1)-C(1)-P(1) 108(4), N(1)-C(2)-N(2) 120(2), N(2)-C(2)-C(3) 129(2), N(1)-C(2)-C(3) 112(2), C(2)-C(3)-P(1) 114(1), C(2)-C(3)-P(2) 124(4), P(1)-C(3)-P(2) 122(1), C(1)-C(4)-P(4) 114(1), C(1)-C(4)-P(3) 115(1), P(3)-C(4)-P(4) 129(1).

To assess the influence of the substituent at nitrogen in this dimerization process, the new *N*-aryldiphosphanylketenimines **1c** (R = 4-methylphenyl = *p*-tolyl) and **1d** (R = 2,6-dimethylphenyl = xylyl) were prepared following the same procedure used for the synthesis of **1a** (Scheme 1). The *N-p*-tolylketenimine **1c** tends to dimerize under the same conditions as **1a** to give **2c**, whereas the *N*-xylylketenimine **1d**, which lacks *ortho* hydrogen atoms for the substituent at N, does not dimerize at all. This result suggests that not only the H(2)···N(2) hydrogen bond but also the very weak interaction H(1)···N(1) could have some influence in the dimerization of **1a** and **1c**, although other factors such as steric hindrance of the R substituent at nitrogen and packing forces in the crystal must also be considered.

The dimerization of diphosphanylketenimines described here is noteworthy because: 1) it takes place under mild conditions (room temperature), 2) it is reversible, 3) it involves a new type of [2+3] cycloaddition, and 4) it appears to be promoted by intramolecular nonconventional CH···N hydrogen bonds. Furthermore, the involvement of the phosphanyl substituent in the annelation process suggests an enhancement of the synthetic potential of **1a–d** with respect to normal ketenimines. This is clearly shown in the reaction of **1a** with two equivalents of dimethyl acetylenedicarboxylate, which takes place instantaneously at room temperature to give **3a** (Scheme 2, see the Experimental Section).[10] This unique bicyclic compound contains two fused five-membered phosphaheterocycles resulting from two successive [2+3] cycloaddition reactions involving both phosphorus atoms of the original ketenimine **1a**.[11] Very likely this reaction proceeds through the formation of the intermediate species **Ia**, although it was not detected in the reaction mixture (even at low temperature), suggesting an enhancement of the reactivity after the first [2+3] cycloaddition process. Other preliminary studies show that **1a–d** react at room temperature not only with electron-poor alkynes but also with heterocumulenes such as isocyanates and isothiocyanates.

0044-8249/00/11210-1892 $ 17.50+.50/0



Scheme 2. Two [2+3] cycloaddition reactions of **1a** with dimethyl acetylenedicarboxylate provide **3a**. R = CO_2Me.

Experimental Section

2a: A solution of **1a** (0.1 g, 0.2 mmol) in hexane (10 mL) was very slowly evaporated to dryness under vacuum. Hexane (10 mL) was added to the residue, giving an orange precipitate corresponding to the dimer **2a**; the monomer **1a** remained in solution. The solution was filtered off and then retreated with hexane to afford a new fraction of **2a**. The process was repeated three times; yield 70% (0.07 g). The yield can be improved by repeating the process as many times as possible. Crystals suitable for X-ray diffraction were grown from a solution in CH_2Cl_2/hexane. Elemental analysis calcd for $C_{64}H_{50}N_2P_4$: C 79.16, H 5.19, N 2.88; found: C 78.84, H 5.27, N 2.78; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.90$ (4H, dd, $^3J_{P,H} = 13$, $^3J_{H,H} = 7$ Hz), 6.4–7.4 (44H, m), 5.85 (2H, d, $^3J_{H,H} = 7$ Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 28.5$ (ddd, $^2J_{P,P} = 52$, $^3J_{P,P} = 24$, $^3J_{P,P} = 6$ Hz), 14.3 (dd, $^3J_{P,P} = 24$, $^3J_{P,P} = 4$ Hz), 6.8 (dd, $^3J_{P,P} = 4$, $^3J_{P,P} = 6$ Hz), -22.8 (d, $^2J_{P,P} = 52$ Hz).

2b: Compound **2b** was prepared analogous to **2a**. Elemental analysis calcd for $C_{66}H_{54}N_2P_4$: C 79.35, H 5.45, N 2.80; found: C 79.26, H 5.32, N 2.75; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.85$ (4H, dd, $^3J_{P,H} = 13$, $^3J_{H,H} = 7$ Hz), 6.4–7.4 (42H, m), 5.84 (2H, d, $^3J_{H,H} = 7$ Hz), 2.35 (3H, s), 2.12 (3H, s); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 28.6$ (m), 13.7 (m), 6.5 (s, br), -23.8 (m).

3a: To a solution of **1a** (0.05 g, 0.1 mmol) in CH_2Cl_2 (10 mL) was added dimethyl acetylenedicarboxylate (0.025 mL, 0.2 mmol). The color changed to red instantly. After 5 min of stirring at room temperature the solvent was evaporated to dryness, and the brown residue recrystallized from CH_2Cl_2/hexane to afford red crystals; yield 85% (0.065 g). Elemental analysis calcd for $C_{44}H_{37}NO_8P_2$: C 68.65, H 4.84, N 1.81; found: C 68.43, H 4.80, N 1.83; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.99$ (4H, dd, $^3J_{P,H} = 14$, $^3J_{H,H} = 7$ Hz), 6.8–7.8 (19H, m), 6.52 (2H, d, $^3J_{H,H} = 7$ Hz), 3.50 (3H, s), 3.35 (3H, s), 3.27 (3H, s), 2.89 (3H, s); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 8.97$ (d, $^2J_{P,P} = 71$ Hz), -81.40 (d, $^2J_{P,P} = 71$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 199.43$ (dd, $J_{P,C} = 32$, 22 Hz), 170.30 (dd, $J_{P,C} = 25$, 4 Hz), 170.05 (dd, $J_{P,C} = 14$, 10 Hz), 169.15 (dd, $J_{P,C} = 3$, 1 Hz), 166.51 (dd, $J_{P,C} = 6$, 2 Hz), 162.41 (dd, $J_{P,C} = 16$, 2 Hz), 159.52 (dd, $J_{P,C} = 23$, 13 Hz), 151.86 (d, $J_{P,C} = 5$ Hz), 131.28 (dd, $J_{P,C} = 12$, 7 Hz), 117.2 (dd, $J_{P,C} = 93$, 6 Hz), 52.60 (s, 1 × CH_3), 51.57 (s, 3 × CH_3); signals for phenyl groups not given.

Received: November 26, 1999 [Z14322]

---

[1] "The Chemistry of Ketenes, Allenes and Related Compounds": M. W. Barker, W. E. McHenry in *The Chemistry of Functional Groups, Part* 2 (Ed.: S. Patai), Interscience, New York, **1980**, chap. 17, pp. 701–720; G. Tennant in *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds, Vol. 2* (Eds.: D. Barton, W. D. Ollis, I. O. Sutherland), Pergamon, Oxford, **1979**, pp. 521–527.

[2] J. Ruiz, V. Riera, M. Vivanco, M. Lanfranchi, A. Tiripicchio, *Organometallics* **1998**, *17*, 3835–3837.

[3] M. W. Barker, J. D. Rosamond, *J. Heterocycl. Chem.* **1972**, *9*, 1147–1148; M. W. Barker, J. D. Rosamond, *J. Heterocycl. Chem.* **1972**, *9*, 1419–1421.

[4] R. Gertzmann, R. Fröhlich, M. Grehl, E. Würthwein, *Tetrahedron* **1995**, *51*, 9031–9044.

[5] J. Y. Becker, E. Shakkour, J. A. R. P. Sarma, *J. Chem. Soc. Chem. Commun.* **1990**, 1016–1017; J. Y. Becker, E. Shakkour, J. A. R. P. Sarma, *J. Org. Chem.* **1992**, *57*, 3716–3720.

[6] Crystal data for **2a** ($C_{64}H_{50}N_2P_4$): $M_r = 970.94$, orthorhombic, space group $P2_12_12_1$, $a = 10.609(7)$, $b = 13.36(1)$, $c = 36.06(2)$ Å, $V = 5111(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.262$ g cm^{-3}, $F(000) = 2032$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.191$ mm^{-1}; crystal dimensions 0.20 × 0.20 × 0.13. Diffraction data were collected on a Enraf-Nonius at 293 K. The structure was solved with direct methods and refined using full-matrix least squares on F^2 with all non-hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions, isotropically refined with common thermal parameters, and allowed to ride on their parent carbon atoms. For 5590 unique reflections and 632 parameters, $R = 0.063$ and $wR2 = 0.109$. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136772. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] a) R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070; b) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.

[8] a) T. Steiner, *Chem. Commun.* **1997**, 727–734; b) T. Steiner, B. Lutz, J. van der Maas, A. M. M. Schreurs, J. Kroon, M. Tamm, *Chem. Commun.* **1998**, 171–172.

[9] The H(1) atom, together with C(1), C(2), and C(11), completes a virtual distorted tetrahedron around N(1): C(1)-N(1)-H(1) 132°, C(2)-N(1)-H(1) 107°, C(11)-N(1)-H(1) 77°, C(1)-N(1)-C(2) 111°, C(1)-N(1)-C(11) 111°, C(2)-N(1)-C(11) 115°.

[10] A preliminary X-ray diffraction study of **3a** confirms the proposed bicyclic structure. Furthermore, **3a** has been fully spectroscopically characterized (see the Experimental Section).

[11] For other cycloaddition reactions involving phosphorus atoms, see for instance G. Veneziani, R. Réau, F. Dahan, G. Bertrand, *J. Org. Chem.* **1994**, *59*, 5927–5929; J. Grobe, D. L. Van, B. Broschk, M. Hegemann, B. Lüth, G. Becker, M. Böhringer, E. U. Würthwein, *J. Organomet. Chem.* **1997**, *529*, 177–187, and references therein.

Dianionic Homoleptic Biphosphinine Complexes of Group 4 Metals[**]

Patrick Rosa, Nicolas Mézailles, Louis Ricard,
François Mathey,[*] and Pascal Le Floch[*]

The stabilization of anionic transition metal centers is generally associated with the use of ancillary ligands possessing strong π-acceptor properties. For the most part, it was achieved with molecules such as CO,[1] isocyanides,[2] ethylene,[3] and arenes[4] which display a suitable synergistic effect between σ-donor and π-acceptor capabilities, and in rare cases, by using tailored tertiary phosphanes.[5] However, only little is known about the stabilizing effects provided by

---

[*] Prof. F. Mathey, Dr. P. Le Floch, P. Rosa, Dr. N. Mézailles,
Dr. L. Ricard
Laboratoire "Hétéroéléments et Coordination", Ecole Polytechnique
91128 Palaiseau Cedex (France)
Fax: (+33) 1-69-33-39-90
E-mail: francois.mathey@polytechnique.fr, lefloch@mars.polytechnique.fr

[**] This work was supported by the CNRS and the Ecole Polytechnique.