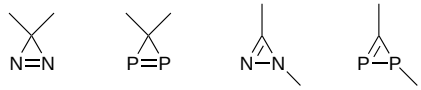
New routes to free and coordinated 1*H*-diphosphirenes

Didier Bourissou, Yves Canac, Maria Isabel Collado, Antoine Baceiredo and Guy Bertrand*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cédex 04, France

Diphosphirenium salt 1 reacts with $LiAlH_4$ leading to *P*-hydrophosphaalkene 2, which on treatment with a catalytic amount of $BF_3{\cdot}OEt_2$ affords 1*H*-diphosphirene 3, while with a stoichiometric amount of $W(CO)_5$(thf), complex 4 is obtained.

Among the smallest dinitrogen- and diphosphorus-containing unsaturated heterocycles **A**–**D**, only the chemistry of 3*H*-diazirines **A** has been extensively explored.[1] So far, no 3*H*-diphosphirenes **B** have been observed,[2] and only one 1*H*-diazirine **C**[3] has been spectroscopically characterized. The only known free 1*H*-diphosphirene **D** was isolated as long ago as 1989 by Niecke *et al.*,[4a] although two complexes featuring heterocycle **D** as an η^1-ligand have been prepared more recently.[4b,c] The lack of simple synthetic methods for the preparation of heterocycles **D** has undoubtedly hampered the development of their chemistry. Indeed, all the known examples have been obtained by addition of free[4a] or coordinated phosphinidenes[4b,c] to phosphaalkynes. Here we report new synthetic routes to free and coordinated heterocycles **D** which are reminiscent of the Neber synthesis of 2*H*-azirines[5] and the Graham synthesis of 3-halogeno-3*H*-diazirines.[6]

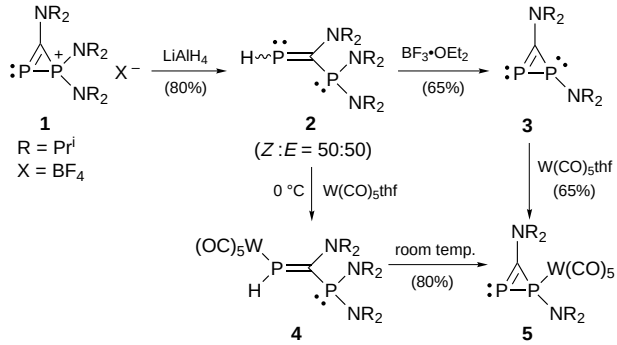


A **B** **C** **D**

We have already shown that ring opening reactions occur when the readily available diphosphirenium salt **1**[7a,b] is treated with nucleophiles.[7c,d] In a similar way, addition of one equivalent of lithium aluminium hydride to a thf solution of **1** afforded the corresponding *P*-hydrophosphaalkene **2** as a 50 : 50 mixture (according to NMR spectroscopy) of *Z* and *E* isomers in 80% total yield.†

The similarity between compound **2** and the Neber and especially the Graham amidine precursors is obvious. However, instead of using a base to induce the 1,3-elimination reaction, a thf solution of **2** was treated with a catalytic amount (5%) of $BF_3{\cdot}OEt_2$ at room temperature. After work up, the 1*H*-diphosphirene **3** was obtained as a light yellow oil in 65% yield. The spectroscopic data† for **3** compared well with those reported for the other known 1*H*-diphosphirene.[4a]

The corresponding coordinated 1*H*-diphosphirene **5** can be obtained by treatment of **3** with $W(CO)_5$(thf);[8] from **2**, the two step process gave access to complex **5** in 42% yield. Interestingly, addition of one equivalent of $W(CO)_5$(thf) to phosphaalkene **2** directly afforded **5** which was isolated after workup in 80% yield. Monitoring the reaction by ^{31}P NMR spectroscopy at 0 °C showed the primary formation of complex **4** as a single isomer in an *E* configuration,[9] where the metal is η^1-bonded to the σ^2-phosphorus atom [^{31}P NMR: −71.0 (s, $^1J_{PH}$ 267.4, $^1J_{PW}$ 129.4 Hz, P–H), +66.5 (s, P–NR_2)]. The transformation of **4** into **5** involved both the elimination of diisopropylamine and the migration of the metal fragment. The former process is probably induced by a catalytic amount of $W(CO)_5$(thf) which acts as a Lewis acid. The metal shift is governed by the higher thermodynamic stability of **5** compared to the isomeric complex featuring the metal fragment at the σ^2-phosphorus atom.



Scheme 1

These new synthetic routes can be used on multi-gram scales readily allowing for the development of the chemistry of 1*H*-diphosphirenes, as shown by the recent preparation of a diphosphirenylium salt complex[8] and a diphosphirenyl radical dimer.[10]

Footnotes and References

* E-mail: gbertran@lcctoul.lcc-toulose.fr

† Satisfactory elemental analyses for compounds **2** and **3** have been obtained.

Selected spectroscopic data for **2**, **3**, **4** and **5**: **2**, δ_P($CDCl_3$, 32.438 MHz, *J*/Hz) +23.8 (d, $^2J_{PP}$ 39.8, $^1J_{PH}$ 137.6, σ^2-P–H), +53.7 (d, $^2J_{PP}$ 39.8, σ^3-P) and +34.3 (s, $^1J_{PH}$ 173.6, σ^2-P–H), +55.9 (s, σ^3-P); δ_C($CDCl_3$, 62.896 MHz, *J*/Hz) 205.1 (dd, $^1J_{PC}$ 97.6 and 40.1, PCP) and 212.8 (dd, $^1J_{PC}$ 65.4 and 58.8, PCP); δ_C($CDCl_3$, 200.132 MHz) 4.66 (dd, $^1J_{PH}$ 173.6, $^3J_{PH}$ 1.0, H–P) and 4.96 (dd, $^1J_{PH}$ 137.6, $^3J_{PH}$ 7.4, H–P). **3**, δ_P($CDCl_3$, 32.438 MHz, *J*/Hz) −121.7 (d, $^1J_{PP}$ 121.3 P–NPr^i_2), −23.7 (d, $^1J_{PP}$ 121.3, σ^2-P); δ_C($CDCl_3$, 100.614 MHz, *J*/Hz) 191.2 (dd, J_{PC} 82.2 and 77.9, PCP), 58.4 (t, J_{PC} 4.2, CNCH), 51.3 (s, CNCH), 43.4 (d, $^2J_{PC}$ 5.6, PNCH), 24.5 (d, J_{PC} 5.2, CH_3), 24.2 (d, J_{PC} 12.2, CH_3), 21.8 (s, CH_3), 21.6 (d, J_{PC} 2.1, CH_3), 20.1 (d, J_{PC} 2.7, CH_3), 19.1 (d, J_{PC} 4.9, CH_3); δ_H($CDCl_3$, 200.132 MHz, *J*/Hz) 4.19 (2 H, septet d, $^3J_{HH}$ 6.6, $^3J_{PH}$ 1.8, PNCH), 3.60 (2 H, septet, $^3J_{HH}$ 6.7, CNCH), 1.32 (6 H, d, $^3J_{HH}$ 6.7, CH_3), 1.15 (6 H, d, $^3J_{HH}$ 6.6, CH_3), 1.13 (6 H, d, $^3J_{HH}$ 6.7, CH_3), 0.95 (6 H, d, $^3J_{HH}$ 6.6, CH_3); CIMS (NH_3) *m/z* 275 (M + 1). **4**, δ_P(C_7D_8, 161.98 MHz, *J*/Hz) −71.0 (s, $^1J_{PH}$ 267.4, $^1J_{PW}$ 129.4, P–H), 66.5 (s, P–NPr^i_2); δ_C(C_7D_8, 100.614 MHz, *J*/Hz) 233.6 (dd, $^1J_{PC}$ 72.3 and 50.3, PCP), 203.3 (d, $^2J_{PC}$ 7.7, CO); δ_H(C_7D_8, 400.14 MHz, *J*/Hz δ 4.95 (d, $^1J_{PH}$ 267.4, H–P). **5**, δ_P(C_6D_6, 32.438 MHz, *J*/Hz) −123.0 (d, $^1J_{PP}$ 164.3, $^1J_{PW}$ 295.1, P–NPr^i_2), 15.0 (d, $^1J_{PP}$ 164.3, σ^2-P).

1 M. T. H. Liu, *Chem. Soc. Rev.*, 1982, **11**, 127; H. W. Heine, in *The Chemistry of Heterocyclic Compounds Small Ring Heterocycles, Part 2*, Wiley, New York, 1983, vol. 42, p. 588; *Chemistry of Diazirines*; ed. M. T. H. Liu, CRC Press, Boca Raton, FL, 1987, vols. I and II.

2 The transient formation of a 3*H*-diphosphirene has been postulated: E. Niecke, R. Streubel and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 90.

3 N. Dubau-Assibat, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1996, **118**, 5216.

4 (*a*) E. Niecke, R. Streubel, M. Nieger and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1673; (*b*) F. Mercier, L. Ricard, F. Mathey and M. Regitz, *J. Chem. Soc., Chem. Commun.*, 1991, 1305; (*c*) R. Streubel, L. Ernst, J. Jeske and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1995, 2113.

5 V. Nair, *J. Org. Chem.*, 1968, **33**, 2121; H. G. Corkins, L. Storace and E. Osgood, *J. Org. Chem.*, 1980, **45**, 3146.
6 W. H. Graham, *J. Am. Chem. Soc.*, 1965, **87**, 4396; R. A. Moss, J. Wlostowska, W. Guo, M. Fedorynski, J. P. Springer and J. M. Hirshfield, *J. Org. Chem.*, 1981, **46**, 5048; X. Creary, *Acc. Chem. Res.*, 1992, **25**, 31.
7 (*a*) F. Castan, A. Baceiredo, J. Fischer, A. de Cian, G. Commenges and G. Bertrand, *J. Am. Chem. Soc.*, 1991, **113**, 8160; (*b*) M. Soleilhavoup, Y. Canac, A. M. Polozov, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1994, **116**, 6149; (*c*) M. Soleilhavoup, A. Baceiredo, F. Dahan and G. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1994, 337; (*d*) Y. Canac, M. Soleilhavoup, L. Ricard, A. Baceiredo and G. Bertrand, *Organometallics*, 1995, **14**, 3614.
8 D. Bourissou, Y. Canac, M. I. Collado, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1997, **119**, 9923.
9 All the *P*-substituted-*C*-amino-*C*-phosphinophosphaalkenes we have obtained so far present the *E* configuration.
10 Y. Canac, A. Baceiredo, H. Gornitzka, W. W. Schoeller and Guy Bertrand, unpublished work.

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