Synthesis of the sodium diphenylbis(cyanamido)phosphonium diylide by a new variation of the Staudinger reaction

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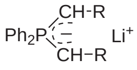
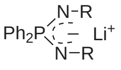
Received (in Liverpool, UK) 3rd November 1998, Accepted 4th February 1999

The first example of a stabilized diaminophonium diazaylide, sodium diphenylbis(cyanamido)phosphonium diylide, has been synthesized by a new variation of the Staudinger reaction; the corresponding copper complex can be described as a discrete dimeric unit with $[Ph_2P(NCN)_2]^-$ in both uni- and bi-dentate modes (X-ray structure).

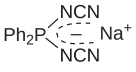
Lithium phosphonium diylides **1** were first discovered by Wittig in 1949.[1] As part of the study of the reactivity of these reagents,



1 R = H, alkyl, C(O)R' *etc.*



2 R = alkyl
3 R = aryl
4 R = electron withdrawing group



4a

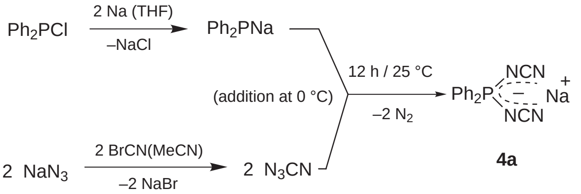
we have developed a general synthetic route to their direct precursors, the dialkyldiphenylphosphonium salts.[2] Our method thus allowed a convenient access to all types of diylides, regardless of their having non-stabilized, semi-stabilized or stabilized characters.

Thanks to their strong nucleophilic character, the phosphonium diylides **1**, until recently mainly used in coordination chemistry,[3] are excellent and versatile tools in organic synthesis.[2] Therefore, we have also developed a synthesis of their nitrogen analogs, the lithium diaminophosphonium diazaylides, in order to test their potential in synthesis.[4]

Until now our method, involving the direct dilithiation of the corresponding diaminophosphonium salts, was limited, in spite of many attempts, to the formation of non- and semi-stabilized diaminophosphonium diylides **2** and **3**.[4] We report here the synthesis of the first example of a stabilized diaminophosphonium diazaylide of type **4**, the sodium diphenylbis(cyanamido)-phosphonium diylide $Na[Ph_2P(NCN)_2]$ **4a**.

The diazaylide **4a**, which has a stronger nucleophilic character than the corresponding monoazaylide (Ph_3PNCN), has been obtained through a new variation of the Staudinger reaction, namely the reaction of Ph_2PNa with N_3CN (Scheme 1).

Under nitrogen, a solution of Ph_2PNa (30 mmol) in dry THF (80 ml) was added dropwise at 0 °C to a solution of N_3CN (65 mmol) in MeCN (80 ml). After the end of the addition, the reaction, performed under mild conditions, affords the sodium diphenylbis(cyanamido)phosphonium diylide $Na[Ph_2P(NCN)_2]$ **4a** in 80%.†



Scheme 1

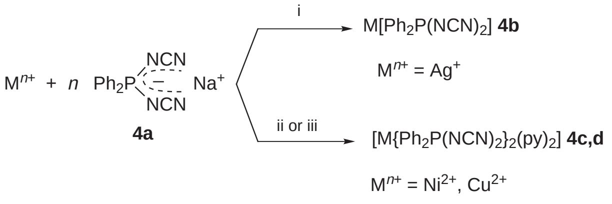
The Staudinger reaction is usually described as a two-step reaction corresponding to a nucleophilic addition of a tricoordinated phosphorus center (R_3P) on an azide followed by N_2 elimination.[5] To the best of our knowledge, our reaction constitutes the first example of a Staudinger reaction involving a phosphide.

The diazaylide **4a**, whose reactivity we are currently testing in organic synthesis, may also attract interest in the field of coordination chemistry. Indeed, the corresponding non-stabilized diaminophosphonium diazaylides of type **2** are well-known bidentate ligands. The majority of the known complexes exhibit four membered MN_2P rings involving diazaylides substituted on the nitrogens by trimethylsilyl groups.[6] They are mainly represented by two categories with pentavalent phosphorus, the 1,3,2λ⁵,4-diazaphosphametalletidines and the 1,3,5,7,2λ⁵,6λ⁵,4-tetraazadiphosphametallaspiro[3.3]bicycloheptanes.

The stabilized diazaylide $Na[Ph_2P(NCN)_2]$ **4a**, in aqueous solution with or without pyridine, forms quantitatively with metal ions (Ag^+, Ni^{2+}, Cu^{2+}) the complexes **4b–d** (Scheme 2).

The molecular structure of the copper complex **4d**,§ illustrated in Fig. 1, shows different structural features in comparison to corresponding complexes with non-stabilized diazaylides. Indeed, **4d** contains $[Ph_2P(NCN)_2]^-$ in two coordination modes. It can be described as a discrete dimeric unit with $[Ph_2P(NCN)_2]^-$ in both uni- and bi-dentate modes. The two copper atoms are doubly bridged by $[Ph_2P(NCN)_2]^-$ ligands, forming a 16-membered puckered cycle, which exhibits crystallographic $\bar{1}$ symmetry. The maximum deviation from the least-squares plane defined by all ring atoms amounts to −0.409(2) and +0.432(2) Å for P2 and P2′. The coordination of the copper atoms is trigonal bipyramidal. The phosphorus atoms are nearly tetrahedrally coordinated. Bonding distances and angles agree well with standard values and previous experience.[7] Lastly, it is noteworthy that, in comparison to diaminophosphonium diazaylides **2**, the $[Ph_2P(NCN)_2]^-$ anion shows different coordination properties, the preferential donor atoms being the terminal nitrogens.

The ligand properties of the $[Ph_2P(NCN)_2]^-$ anion are under investigation, as well as the synthetic potential of the corre-



Scheme 2 Synthesis of the coordination complexes **4b** (M = Ag), **4c** (M = Ni) and **4d** (M = Cu). *Reagents and conditions*: i, **4a** (2.5 mmol), H_2O (15 ml), then $AgNO_3$ (2.7 mmol), 1 min, 25 °C,→**4b** (80%); ii, **4a** (2.5 mmol), H_2O (15 ml), then $NiCl_2\cdot6H_2O$ (1.25 mmol), py (5 mmol), 1 min, 25 °C,→**4c** (90%); iii, **4a** (2.5 mmol), H_2O (15 ml), then $CuCl_2\cdot2H_2O$ (1.25 mmol), py (5 mmol), 1 min, 25 °C,→**4d** (90%).‡

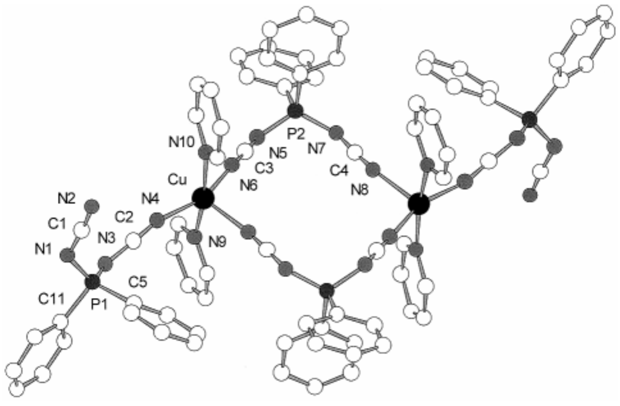


Fig. 1 Molecular structure of **4d** (dimer) in the crystal. Selected bond lengths (Å) and angles (°): Cu–N4 1.987(3), Cu–N6 1.974(3), Cu–N9 2.032(3), Cu–N10 2.042(3), Cu–N8′ 2.178(3), C1–N2 1.170(5), C1–N1 1.287(5), C2–N4 1.136(4), C2–N3 1.288(4), C3–N6 1.148(4), C3–N5 1.282(4), C4–N8 1.148(4), C4–N7 1.293(4), N1–P1 1.604(4), N3–P1 1.601(3), N5–P2 1.597(3), N7–P2 1.595(3), N2–C1–N1 174.6(5), N4–C2–N3 173.2(4), N6–C3–N5 174.9(4), N8–C4–N7 175.3(4), C1–N1–P1 124.9(3), C2–N3–P1 130.4(3), C3–N5–P2 128.4(3), C4–N7–P2 124.7(2), C2–N4–Cu 164.1(3), C3–N6–Cu 165.0(3), C4–N8–Cu′ 164.7(3). Symmetry transformations used to generate equivalent atoms A′: $-x + 1, -y + 1, -z + 2$.

sponding stabilized diazaylides **4a–d**. The reactivity of these reagents will be tested towards various electrophiles, particularly in aza-Wittig type reactions.

Notes and references

† Compound **4a** is a colourless solid obtained in a yield of 80%. *Selected data* for **4a**: mp 182 °C; ν_{max}(KBr)/cm^{-1} 2190vs (NCN), 2140vs (NCN) δ_P (80 MHz, [$^2H_6$]DMSO, 25 °C, H_3PO_4 80%) 19.23; δ_C (50.3 MHz, [$^2H_6$]DMSO, 25 °C, TMS) 133.1 (d, $^1J_{C,P}$ 129.3, *i*-C, C_6H_5), 131 (d, $^2J_{C,P}$ 9.6, *o*-C, C_6H_5), 128.4 (d, $^3J_{C,P}$ 12.6, *m*-C, C_6H_5), 131.5 (d, $^4J_{C,P}$ 2.3, *p*-C, C_6H_5), 119.3 (s, NCN). A correct elemental analysis for $C_{14}H_{10}N_4NaP$ was obtained.

‡ Single crystals of **4d** were obtained from a concentrated solution of the complex in 2 ml of pyridine which was overlayed with about 6 ml of n-hexane: mp 192 °C (decomp.) ν_{max}(KBr)/cm^{-1} 2230vs (NCN), 2190vs (NCN), 2180vs (NCN). A correct elemental analysis for $C_{38}H_{30}N_{10}CuP_2$ was obtained.

§ *Crystal data* for **4d**: STOE IPDS, graphite monochromated Mo-Kα radiation, λ = 0.71069 Å, T = 293 K. The structure was solved by direct methods (program system SHELXS-86) [ref. 8(*a*)]. Structure refinement on F^2 was performed using full-matrix least-squares techniques with SHELXL-93 [ref. 8(*b*)] with anisotropic displacement parameters for the non-H atoms. $C_{38}H_{30}CuN_{10}P_2$, M = 752.20, triclinic, $P\bar{1}$, a = 8.432(1), b = 13.542(1), c = 16.555(2) Å, α = 107.588(8), β = 91.82(1), γ = 98.65(1)°, V = 1775.7(4) Å^3, Z = 2, μ(Mo-Kα) = 0.749 mm^{-1}, $2\theta_{max}$ = 52.0°, reflections collected = 10554, independent reflections = 6478 [R_{int} = 0.0513], parameters = 580, $R1$ = 0.0479, $wR2$ = 0.1186 [$I > 2\sigma(I)$], $R1$ = 0.0739, $wR2$ = 0.1320 (all data), $\Delta\rho$ (max./min.) = 0.378/−0.739 e Å^{-3}. CCDC 182/1169. Crystal data are available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/565/

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Communication 8/08641I

Typeset and printed by Black Bear Press Limited, Cambridge, England