

Malonodinitrile $\text{CH}_2(\text{CN})_2$ as Synthon for the Preparation of Unprecedented *N*-Metalla- and *N*-Phosphino- β -diimine Ligands

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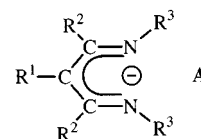
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Summary: Unprecedented *N*-phosphino- β -diimine ligands **4** and **5** have been prepared from a facile one-pot synthesis using malonodinitrile, $\text{CH}_2(\text{CN})_2$, the Schwartz reagent $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ (**1**), and the corresponding chlorophosphines R_2PCl **2** and **3**. An alkyl aluminum complex and the corresponding bidentate lithium salt ligand have been isolated. We showed that the reactivity of the *N*-phosphino- β -diimine compound **4** and that of the corresponding *N*-thiophosphino- β -diimine derivative **6** with HCl are completely different. The chemistry reported suggests unique and interesting chelating behavior which may differ from that of existing β -diimine ligands.

Bidentate, monoanionic, nitrogen-based $\text{L}-\text{X}^-$ ligands are the subject of intense studies.¹ Among this class of compounds, β -diiminates of the type **A** which form six-membered chelate rings are of particular interest.^{2–5} Even though the list of successful applications of β -diimine ligands **A** is steadily growing,⁶ by comparison with the analogous β -diketonates (“acac” complexes), their chemistry is largely undeveloped, although they offer the potential advantages of modulating steric and electronic properties by varying the nature of the substituents bonded to the nitrogen atoms. In all the systems that have been active in catalytic processes, sterically demanding substituents on the nitrogen atoms

of the β -diiminates were needed.⁷ Electronic properties are another important feature to consider in ligand design, but the routes described for the preparation of β -diimine ligands do not allow a large variety of groups on the nitrogen atoms. Main group elements linked on the imino nitrogen atoms, as differently coordinated phosphorus moieties, could be a way to tune the coordination ability of the β -diimine system **A**. Part of our studies in the interactions of main group elements with zirconocene complexes have been devoted to the synthesis of new heterosubstituted imino ligands.⁸ Herein we report, starting with malonitrile and following a hydrosilylation/transmetalation reaction process, the synthesis of unprecedented *N*-phosphino- β -diketiminate ligands. Malonodinitrile, $\text{CH}_2(\text{CN})_2$, has been used widely in organic synthesis as a stabilized nucleophile in some of the most important carbon–carbon bond forming reactions, the Michael addition,⁹ and Knoevenagel condensation.¹⁰ To the best of our knowledge, malonodinitrile has not yet been used as a synthon for the preparation of stable imine–enamine compounds.



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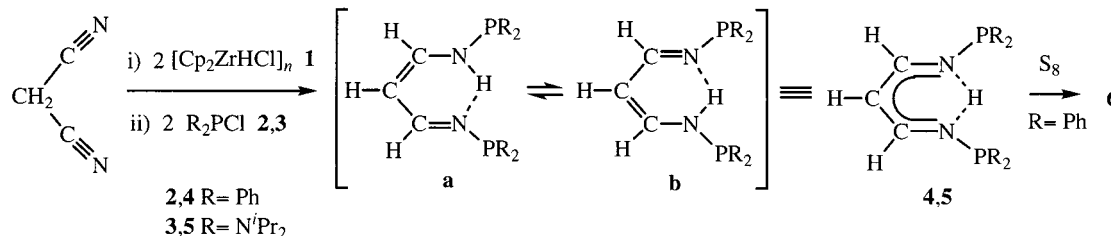
In a first experiment, malonodinitrile, $\text{CH}_2(\text{CN})_2$, was successively treated with 2 equiv of the Schwartz's reagent $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ **1**, and 2 equiv of Ph_2PCl , **2**, to form the *N*-phosphino- β -diketimine **4** in 77% isolated yield (Scheme 1).¹¹ The parent ion detected $[\text{M} + 1]^+$ in mass spectrometry was in agreement with the general formula $[\text{CH}_4(\text{CN})_2(\text{PR}_2)_2]$ for **4**. The ^{31}P NMR spectrum of **4** displayed a singlet at 51.2 ppm. ^1H and ^{13}C NMR spectra exhibited (besides the chemical shifts corresponding to the protons and carbons of the aromatic

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Scheme 1. Synthesis of *N*-Phosphorus- β -diimine Ligands 4–6

rings) the signals in the region expected for a CH=N–aldimine group [δ ¹H 7.60 and δ ¹³C 160.8 ppm] and a CH–alkene enamine fragment [δ ¹H 4.90 and δ ¹³C 99.9 ppm]. In ¹H NMR the large low-field shift of the N–H proton [δ ¹H 11.79 ppm] established the structure as a hydrogen-bonded chelate form.^{2b} The chemical shift equivalence of the two Ph₂P–NCH fragments in **4** is accommodated by a rapid tautomeric conversion. One characteristic band in IR appeared at 1625 cm^{−1}, which can be assigned to the imine–enamine stretching mode of **4**.¹³ Under the same experimental conditions, **5** was formed after treatment of malonodinitrile with 2 equiv of **1** followed by addition of 2 equiv of (*i*-Pr₂N)₂PCL, **3**, to the resulting reaction mixture. The β -diimine compound **5** displays the same spectroscopic features as those observed for **4**.¹¹ To confirm the spectroscopic assignments and to have a better insight into the molecular structure of the latter β -diimine species prepared, an X-ray diffraction study was carried out on the phosphinesulfide product **6** obtained after addition of elemental sulfur on **4** (Figure 1).¹⁴ The molecule has a C₂ symmetry; consequently the hydrogen atom H(N) on the N atom is statistically distributed on two sites related by the 2-fold axis. All the atoms in **6** except those of the aryl groups lie in the same plane. As expected, the C(2)–N (1.317 Å) and C(1)–C(2) (1.381 Å) bonds in the N–C–C–N skeleton are halfway from a single and double bond and are equivalent to those found in six-

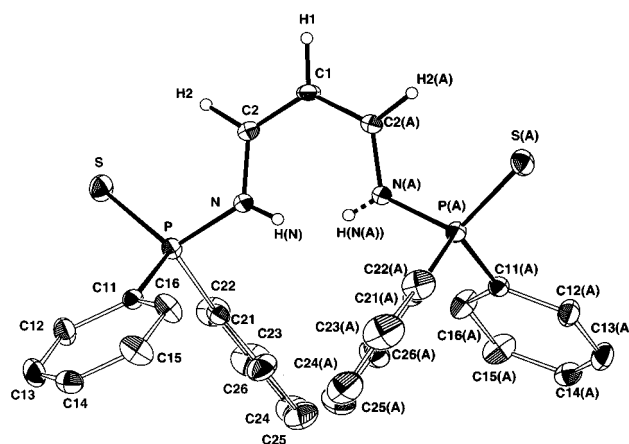
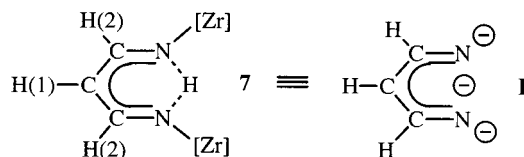


Figure 1. Molecular structure of **6**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.381(4), C(2)–N 1.317(4), N–P 1.685(3), P–S 1.9349(12); C(1)–C(2)–N 124.0(3), C(2)–C(1)–C(2A) 124.4(4), C(2)–N–P 123.1(3), C(2)–N–H(N) 111(3), N–P–S 114.70(11).

membered aromatic rings.¹⁷ Therefore, the simplest picture to consider for compounds **4**–**6** is the superposition of the two tautomers **a** and **b** (Scheme 1).

The first attempts to identify the metalated compound resulting from the addition of malonitrile to **1** were not satisfactory, as they gave by ¹H NMR several sets of resonances impossible to assign. However, when a catalytic amount of MeI (10%) was added to the malonodinitrile/**1** reaction mixture, the ¹H NMR spectrum became considerably simplified to show the formation of **7** as the unique product of the reaction. At 293 K in



both proton and carbon NMR spectra, only one signal was observed for the two CH–N groups of the β -diket-imine skeleton (δ ¹H 7.48 ppm, δ ¹³C 157.6 ppm), indicative of a process that rapidly interconverts on the NMR time scale the two imine–enamine isomers. The CH–N protons appear as a doublet of doublets ($^3J_{\text{H(2)}-\text{H(1)}} = 5.8$ Hz, $^3J_{\text{H(2)}-\text{H(N)}} = 12.6$ Hz). An excitation-sculpted singly selective 1D TOCSY NMR experiment allowed the assignment of the H(N) proton.¹⁸ TOCSY transfers were detected to the two aldimine H(2) protons and to the H(N) proton which appears as a very broad peak (δ 6.94 ppm, half-height line width $\Delta\nu \approx 500$ Hz). It was

(11) **4**: 77% yield, ³¹P{¹H} NMR (C₆D₆) δ 51.2 (s); ¹H NMR (C₆D₆) δ 4.90 (tt, $^3J_{\text{HH}} = 6.1$ Hz, $^4J_{\text{HP}} = 0.9$ Hz, 1H, CH), 7.39–7.57 (m, 20H, Ph), 7.60 (ddd, $^3J_{\text{HH}} = ^3J_{\text{HH}} = 6.1$ Hz, $^3J_{\text{HP}} = 18.0$ Hz, 2H, CHN), 11.79 (tt, $^3J_{\text{HH}} = 6.1$ Hz, $^2J_{\text{HP}} = 6.1$ Hz, 1H, NH); ¹³C{¹H} NMR (C₆D₆) δ 99.9 (t, $^3J_{\text{CP}} = 13.0$ Hz, CH), 130.5 (s, *p*-Ph), 130.9 (d, $^3J_{\text{CP}} = 7.8$ Hz, *m*-Ph), 133.7 (d, $^2J_{\text{CP}} = 20.5$ Hz, *o*-Ph), 141.5 (d, $^1J_{\text{CP}} = 11.8$ Hz, *i*-Ph), 160.8 (d, $^2J_{\text{CP}} = 28.0$ Hz, CHN); C₂₇H₂₄N₂P₂ (438.45), calcd C 73.96, H 5.52, N 6.39, found C 73.43, H 5.41, N 6.27; FT-IR (KBr) 1625 cm^{−1} ν (C=N); MS (DCI/NH₃) m/z 439 [M + H]⁺. **5**: ³¹P{¹H} NMR (C₆D₆) δ 89.6 (s); ¹H NMR (C₆D₆) δ 1.02 (d, $^3J_{\text{HH}} = 6.6$ Hz, 24H, CH₃), 1.17 (d, $^3J_{\text{HH}} = 6.6$ Hz, 24H, CH₃), 3.68 (m, 8H, CHCH₃), 4.74 (t, $^3J_{\text{HH}} = 8.0$ Hz, 1H, CH), 6.71 (ddd, $^3J_{\text{HH}} = ^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HP}} = 15.1$ Hz, 2H, CHN), 11.82 (m br, 1H, NH); C₂₇H₆₀N₆P₂ (530.76), calcd C 61.10, H 11.39, N 15.83, found C 60.88, H 11.25, N 15.78; FT-IR (KBr) 1632 cm^{−1} ν (C=N); MS (DCI/CH₄) m/z 531 [M + H]⁺.

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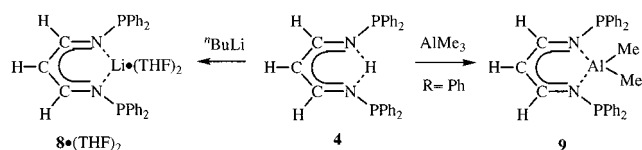
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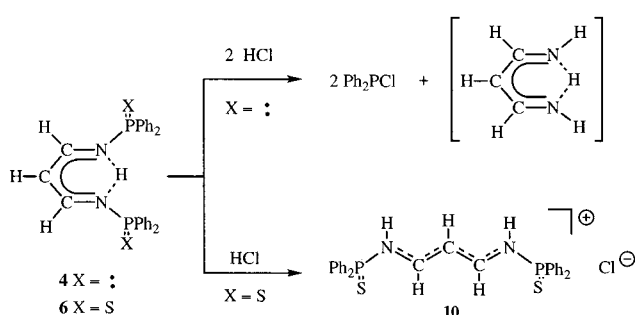
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Scheme 2. Reactivity of the *N*-Phosphino- β -diimine Ligand **4**


clear from this experiment that the H(N) proton was involved in an exchange that is in the intermediate range on the NMR time scale.¹⁹ Interestingly, before the addition of MeI, **7** was detected among the other zirconated species formed in the reaction mixture obtained from malonitrile and **1**. This clearly demonstrated that MeI induced the rearrangement of the different zirconocene intermediates to the thermodynamic product of the reaction **7**. However, alkylation on nitrogen did not occur.^{20,21} In the reaction resulting in the quantitative formation of the *N*-phosphino- β -dialdimine compounds **4** and **5**, the chlorophosphine derivatives R₂PCl **2** and **3** may have played the same role as MeI to induce the unique formation of **7** in the reaction mixture. In that case the transmetalation reaction took place at the nitrogen center to give the corresponding imino-*N*-phosphine products. It is important to note that chlorophosphines R₂PCl were reported to induce the migration of the metal fragment ZrCp₂Cl along a saturated carbon chain, followed then by the electrophilic substitution reaction to give the corresponding phosphorus product.²²

Addition at $-78\text{ }^{\circ}\text{C}$ in THF of 1 equiv of *n*BuLi on **4** led quantitatively to the formation of the corresponding β -diiminate lithium salt **8** as a (THF)₂ adduct (Scheme 2). In ¹H NMR complete disappearance of the NH signal [δ ¹H 11.79 ppm] was observed. The chemical shifts in both ¹H [δ 7.94 and 5.05 ppm] and ¹³C [δ 165.4 and 98.3 ppm] NMR spectra are consistent with the CH=N aldimine and the central methine CH fragments, respectively, in the anionic bidentate ligand **8**. The β -diimine **4** reacted with AlMe₃ to eliminate methane, affording quantitatively the diiminate complex **9** (δ ¹³P 55.1 ppm) (Scheme 2). All the NMR data (¹³P, ¹H, and ¹³C) indicated symmetric ligand environments. Besides the signals corresponding to the backbone of the β -di-

Scheme 3. Reactivity of *N*-Phosphino- β -diimine Ligands **4 and **6** with HCl**


iminate ligand, ¹H and ¹³C NMR of **9** showed the presence of the methyl groups on the aluminum metal fragment at δ ¹H -0.45 and δ ¹³C -6.4 ppm.

Interestingly addition of HCl (2 equiv) on **4** resulted in the cleavage of the P–N bond to give a diphenylchlorophosphine compound as the sole phosphorus product of the reaction along with an organic product which has not yet been fully identified but which may be attributed to the corresponding parent compound C₂H₆N₂. Starting from the thiophosphino β -diiminate derivative **6**, addition of HCl (1 equiv) led to the quantitative formation of the corresponding vinamidinium compound **10**, which has been fully characterized by NMR spectroscopy and an X-ray crystal structure analysis.²³

In summary, we have described a highly efficient method for the preparation of unprecedented *N*-phosphino- β -diketiminato ligands **4–6** via a mild one-pot synthesis starting from commercially available reagents (for the preparation of **4**: malonitrile, MeI, Schwartz's reagent, **1**, and chlorodiphenylphosphine, **2**). The general applicability of this method for the synthesis of new *N*-(hetero)substituted β -diketiminato ligands and the activity of the corresponding aluminum complexes (i.e., **9**) in olefin polymerization are in development. Vinamidinium salts as product **10** easily obtained from the corresponding neutral *N*-phosphino- β -diketiminato compounds belongs to the family of polymethine dyes, which are a fundamental group of organic dyes widely used for practical purposes. This class of derivatives are also of special preparative value due to their reactivity toward electrophiles (at C $_{\beta}$) and nucleophiles (C $_{\alpha}$).²⁴ We have preliminary demonstrated that the isolated and stable metalated compound **7** is the appropriate synthon for the preparation of a large variety of compounds; it can be viewed as the formal "unmasked" trianionic trimethine–cyanine parent compound **B**.

Acknowledgment. Financial support of this work by the CNRS, France, is gratefully acknowledged.

Supporting Information Available: Experimental details for the preparation of **5**, **8**, **9**, and **10**; spectroscopic and X-ray crystal analysis data for **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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