Synthesis and Reactivity of a 1-Aza-2,3-Diphosphaallyl Anion

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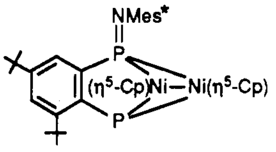
Summary: The 1-aza-2,3-diphosphaallyl system [Mes*PPNMes*]Li (**2**; Mes* = 2,4,6-t-$Bu_3C_6H_2$) was obtained from the corresponding aminodiphosphene **1** by abstraction of the amine proton by n-BuLi. Reaction of **2** with nickelocene affords the metalloiminophosphane complex **3**, the structure of which was determined by X-ray crystallography.



The use of allylic carbanion systems as η^3 ligands in transition-metal complexes is well established, and a vast number of such species are known.[1] Heteroallylic systems involving 2-fold-coordinated phosphorus centers (I–IV) were reported recently[2] (Chart I), but their utility as η^3 ligands in transition-metal complexes has not been proven in every case.[3]

Here, we report the synthesis of the first azadiphosphaallyl system (V) and its reactivity toward nickelocene. [Mes*PPNMes*]Li (**2**) was prepared from the *trans*-aminodiphosphene Mes*P=PN(H)Mes* (**1**)[4] as follows: Treatment of 2.83 g (5.0 mmol) of **1**, dissolved in 12 mL of THF and 8 mL of toluene, with an equimolar quantity of n-butyllithium (1.6 M in hexane) produced a dark red solution. The product precipitated upon addition of n-pentane and was isolated as an orange solid that was extremely sensitive toward hydrolysis. While stable in the solid state, it slowly decomposes in THF solution at ambient temperatures to give polymeric products.[7] The ^{31}P NMR spectrum shows four lines of an AX pattern (δ 244, 494 ppm; $^1J_{PP}$ = 544 Hz). The observed changes in the chemical shifts as compared to the shifts for **1** (δ 313, 454 ppm; J_{PP} = 536 Hz) point to an additional polarization of the P=P double bond in **2**. In the ^{7}Li NMR spectrum at room temperature one observes a broad line at δ −3.67 ppm (vs external LiBr). Higher temperatures (+60 °C) as well as lower ones (−80 °C) cause a sharpening of this resonance signal, but splitting with one of the phosphorus nuclei is not observed. All NMR data are consistent with the formation of a lithio-1-aza-2,3-diphosphaallyl system (**2**).

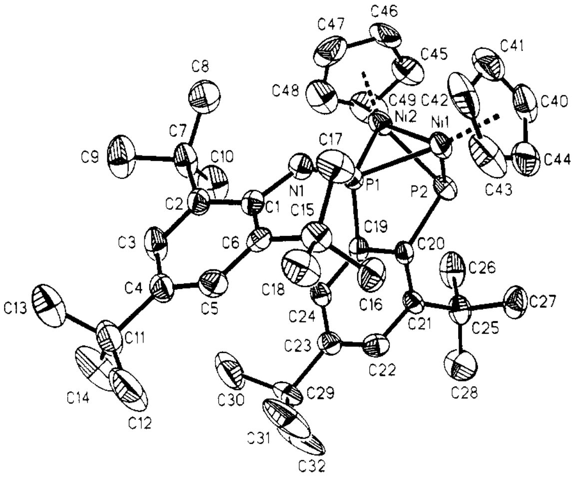
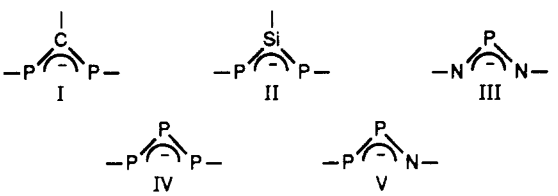
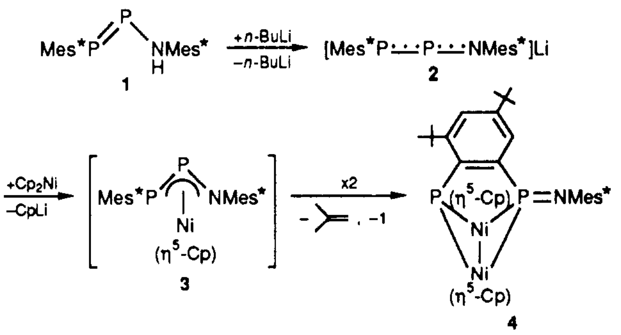


Figure 1. View of **3** with important bond lengths (pm) and angles (deg): Ni(1)–Ni(2) = 235.3 (1), Ni(1)–P(1) = 218.1 (2), Ni(1)–P(2) = 220.2 (2), Ni(2)–P(1) = 218.3 (2), Ni(2)–P(2) = 219.9 (2), P(1)–N(1) = 154.8 (5), P(1)–C(19) = 180.2 (6), N(1)–C(1) = 143.0 (6), P(2)–C(20) = 185.6 (6); Ni(2)–Ni(1)–P(1) = 57.4 (1), Ni(2)–Ni(1)–P(2) = 57.6 (1), P(1)–Ni(1)–P(2) = 81.7 (1), Ni(1)–Ni(2)–P(1) = 57.3 (1), Ni(1)–Ni(2)–P(2) = 57.8 (1), P(1)–Ni(2)–P(2) = 81.7 (1), Ni(1)–P(1)–Ni(2) = 65.3 (1), Ni(1)–P(1)–N(1) = 125.8 (2), Ni(2)–P(1)–N(1) = 127.7 (2), Ni(1)–P(1)–C(19) = 105.7 (2), Ni(2)–P(1)–C(19) = 103.1 (2), N(1)–P(1)–C(19) = 117.5, Ni(1)–P(2)–Ni(2) = 64.6 (1), Ni(1)–P(2)–C(20) = 102.6 (2), Ni(2)–P(2)–C(20) = 100.5 (2), P(1)–N(1)–C(1) = 134.6 (4); C(19)–P(1)–N(1)–C(1) = 0.0 (7).

Chart I



Scheme I



Mes* = 2,4,6-t-$Bu_3C_6H_2$; Cp = C_5H_5

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[2] NPN (III): Lappert, M. F.; Hitchcock, P. B.; Rai, A. K.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1633. Niecke, E.; Detsch, R.; Nieger, M. *Chem. Ber.* **1990**, *123*, 797. PCP (I): Karsch, H. H. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 419. Schuhn, W. Thesis, Universität Bonn, 1988. Appel, R.; Schuhn, W. Unpublished results. PPP (VI): Jutzi, P.; Meyer, U. *Phosphorus Sulfur Relat. Elem.* **1988**, *40*, 275. PSiP (II): Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751.

[3] (a) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1634. (b) Appel, R.: Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 420; *J. Organomet. Chem.* **1987**, *313*, 345. Appel, R., Schuhn, W. *Ibid.* **1987**, *329*, 179. Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416.

[4] **1** was prepared in a one-step synthesis by starting with Mes*N=PCl.[5] Mes*PHTms[6] (0.1 mol) was added to a solution of 1 equiv of Mes*N=PCl[5] in 100 mL of hexane at 0 °C and the reaction mixture stirred for 2 days at room temperature, affording the aminodiphosphene **1**. The product was purified by filtration, and the yellow, thermally stable residue was washed with 20 mL of warm hexane. **1** was identified by its analytical and spectroscopic data (MS, EI, 70 eV, m/e (relative intensity); ^{1}H NMR, δ, C_6D_6; ^{31}P NMR δ, $CDCl_3$): MS 567 (1, M^+), 510 (32, $M^+ - C_4H_9$), 245 (53, Mes^{*+}); ^{1}H NMR 1.30 (s, 9 H, p-CCH-Ar(2)), 1.35 (s, 9 H, p-CCH-Ar(1)), 1.54 (s, 18 H, o-CCH-Ar(2)), 1.81 (s, 18 H, o-CCH-Ar(1)), 6.64 (b, 1 H, >NH), 7.58 (s, 2 H, arom H, Ar(2)), 7.73 (s, 2 H, arom H, Ar(1)); ^{31}P NMR +316.2, +450.0, $^1J_{PP}$ = 532 Hz, $^2J_{PH}$ = 8.4 Hz; yield 70.4%; mp 130–133 °C. Compound **1** gives a satisfactory analysis.

[5] Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.

[6] Paulen, W. Thesis, Universität Bonn, 1984.

[7] A more stable lithium salt of **2** is the crown ether complex **2**·2(18-crown-6): Niecke, E.; Kramer, B. Unpublished results.

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Reaction of **2** with nickelocene was found to proceed in a 1:2 molar ratio. In a typical preparation, 5.0 mmol of $(C_5H_5)_2Ni$, dissolved in 16 mL of toluene, was added to 5.0 mmol of **2** at −78 °C, and the resulting mixture was stirred for 12 h. $^{31}P\{^1H\}$ NMR spectroscopy revealed the resonances of **1** together with another AX pattern (δ 151.8, 479.1 ppm; J_{PP} = 54.6 Hz) as the only detectable signals. After removal of the solvents and volatiles, the residue was extracted with 15 mL of hexane. The mixture was filtered, and the extracts were evaporated. The solid residue was recrystallized from hexane at −30 °C, yielding **4** as thermally stable and moderately air-sensitive crystals (mp 128–129 °C; yield 38%). The constitution of **4**, which was initially inferred from NMR and mass spectroscopic data,[8] was corroborated by an X-ray structure analysis[9] (Figure 1).

The central tricyclic Ni(1)–Ni(2)–P(1)–P(2)–C(20)–C(19) system of **4** corresponds to a benzvalene analogue, with the double bond between the two carbon atoms. The two phosphorus atoms, P(1) and P(2), which are components of the benzvalene ring, exhibit a μ coordination toward the Ni_2Cp_2 unit. The bonding situation of P(2) corresponds to that found in $\mu(P)$-coordinated phosphinidene complexes,[10] while that of P(1) is equivalent to the situtation in $\mu(P)$-coordinated iminophopshanes.[11] The P–N bond length (155 pm) lies in the range for organo-substituted *trans*-iminophosphanes[12] and corresponds to the value found in the trinuclear cluster obtained by reaction of a tris(iminophosphane)platinum complex with carbon monoxide.[11]

On the basis of the results of metalation reactions of heteroallylic systems containing 2-fold-coordinated phosphorus centers,[3b,7] we proposed an allylic type complex (**3**) as an intermediate. Dimerization upon insertion of the transition metal in the double bond, recycling of **1**, and abstraction of isobutene from the aromatic unit then forms the final product (**4**). Further studies of the reactivity of the allylic anion (**2**) toward reactions with transition-metal complexes are in progress.

Registry No. **1**, 127581-79-7; **2**, 130353-54-7; **4**, 130353-55-8; $(C_5H_5)_2Ni$, 1271-28-9; Mes*PNTms, 86487-13-0; Mes*N=PCl, 124775-15-1.

Supplementary Material Available: Listings of atomic coordinates for non-hydrogen atoms, bond distances and angles, thermal parameters, and hydrogen atom coordinates (7 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(8) Spectroscopic and analytical data for compound **4** (MS, EI, 70 eV, *m/e* (relative intensity); ^1H NMR, δ, C_7D_8; $^{31}P\{^1H\}$ NMR δ, C_7D_8): MS 755 (31, M), 633 (11, M − NiCp), 290 (17.5, Mes*NP); ^1H NMR 1.15 (s, 9 H, *p*-CC*H*-Ar(2)), 1.64 (s, 9 H, *p*-CC*H*-Ar(1)), 1.72 (s, 9 H, *o*-CC*H*-Ar(2)), 1.85 (s, 18 H), *o*-CCH-Ar(1)), 5.79 (s, 10 H, Cp), 7.48 (s, 1 H, arom H, Ar(2)), 7.57 (s, 1 H, arom H, Ar(2)), 7.70 (s, 2 H, arom H, Ar(1)); $^{31}P\{^1H\}$ NMR +151.8, +479.1, $^1J_{PP}$ = 54.6 Hz; yield 35%; mp 128–129 °C. Compound **4** gives a satisfactory analysis.

(9) Some crystal data for **4** are as follows: $C_{42}H_{59}NP_2Ni_2{\cdot}C_7H_8$, M_r = 849.0, monoclinic, space group $P2_1/c$ (No. 14), brownish crystals from toluene, dimensions 0.15 × 0.30 × 0.60 mm^3, a = 1747.7 (9) pm, b = 1200.5 (9) pm, c = 2257.3 (13) pm, β = 104.77 (4)°, V = 4.580 nm^3, Z = 4, D_c = 1.23 g cm^{-3}, μ(Mo Kα) = 0.93 mm^{-1}, 5976 symmetry-independent reflections ($2\theta_{max}$ = 45°), 3868 reflections with $|F| > 4\sigma(F)$ used for the structure solution (direct methods) and refinement (487 parameters), non-hydrogen atoms refined anisotropically, H atoms localized by difference electron density determination and refined with a "riding" model, R = 0.057 (R_w = 0.053, $w^{-1} = \sigma^2(F) + 0.0005F^2$).

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A New Approach to *N*-Aryl- and *N*-(2-Heteroaryl)imidates from Chromium Carbenes and Sulfilimines

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Summary: Irradiation of pentacarbonyl(alkoxymethylcarbene)chromium(0) complexes in the presence of a number of *N*-aryl- or *N*-heteroaryl-substituted sulfilimines gives *N*-aryl- or *N*-heteroarylimidates in fair to excellent yields.

Irradiation of chromium carbene (Fischer) complexes is believed to produce ketene–chromium-bonded intermediates in a reversible fashion.[1] Taking advantage of this fact, Hegedus has developed elegant syntheses of β-lactams,[2] α-amino esters,[3] and cyclobutanones.[4] On the other hand, the reactions between these complexes and ylides have been scarcely investigated. Isolation of vinyl ethers in the reaction of pentacarbonyl(methoxyphenylcarbene)tungsten(0) and simple phosphorus ylides has been reported by Casey.[5] 1,1-Diphenylethylene has also been prepared by reacting pentacarbonyl(diphenylcarbene)tungsten(0) and methylenetriphenylphosphorane.[6] Furthermore, sulfoxides react with Fischer carbenes, replacing the metal–carbene bond with a carbon–oxygen double bond.[6,7] No reports referring to the photochemical behavior of chromium carbene complexes toward ylides have appeared to date.

Sulfilimines, having an ylide nature, are known to react with free ketenes, yielding different ketene-derived products.[8] Therefore, either ketene derivatives or imidates

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(2) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109 and references therein.

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