Trisodium heptaphosphide in reactions with cyclopropenyl complexes of nickel

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Reactions of trisodium heptaphosphide with half-sandwich cyclopropenyl complexes of nickel gave sodium 1,2-diphosphacyclopentadienide. The influence of the ligand environment of the nickel atom on the formation of sodium 1,2-diphosphacyclopentadienide was studied.

Key words: trisodium heptaphosphide, cyclopropenyl complexes of nickel, sodium 1,2-diphosphacyclopentadienide.

Alkali metal polyphosphides,[1] which are intermediates in the transformation of the white phosphorus molecule P_4,[2] are promising ligands for construction of complex polymetallic systems and clusters. The presence of several P atoms in different electronic states in one molecule allows various types of coordination to transition metals.

The heptaphosphide trianion P_7^{3-} (**1**), which has the nortricyclane structure[3] and exists in solution as a mixture of valence tautomers due to the Cope rearrangement,[4,5] is one of the most accessible polyphosphides. However, the reactivity of trianion **1** toward transition metal compounds has been poorly studied. It is known[6] that reactions of tripotassium heptaphosphide with carbonyls of Group VIB metals (Cr, Mo, and W) give the corresponding complexes with transformation of nortricyclane configuration of the phosphorus framework into the norbornadiene one. Oligomeric polyphosphides (P_{16}^{2-}, P_{21}^{3-}, and P_{14}^{2-}) have been detected in reactions of trianion **1** with chromium[7] and nickel derivatives.[8] At the same time, the nortricyclane structure of trianion **1** remains intact in reactions with some transition metal derivatives, which has been clearly illustrated with reactions of trianion **1** with platinum(II) compounds[9] and half-sandwich iron complexes.[10]

One can assume that a structural change in the phosphorus framework of trianion **1** during reactions with transition metal derivatives largely depends on both the metal and its ligand environment. When cationic 18-electron complexes of transition metals are used in the reaction, the nortricyclane structure of heptaphosphide **1** usually remains intact. In connection with this, it was interesting to involve trianion **1** in reactions with some cyclopropenyl complexes of nickel to study possible transformation pathways for the polyphosphorus framework.

Results and Discussion

We found that reactions of trisodium heptaphosphide with nickel complexes **2** in diglyme follow a fundamentally new pathway leading to sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**3**) as the major product (Scheme 1). A similar transformation of the cyclopropenyl ligand in nickel complexes has been observed earlier[11] in reactions with NaP_5. Compound **3** was isolated in high yields and characterized by ^1H, ^{13}C, and ^{31}P NMR spectra.

Replacement of half-sandwich nickel complexes **2** by dimeric complex **4** (see Ref. 12) in combination with Na_3P_7 did not change the reaction pathway, giving compound **3** in a close yield.

Complex **3** was also obtained in a reaction of trisodium heptaphosphide with uncharged sandwich nickel complex **5** [13] (Scheme 2).

Based on the results obtained, one can conclude that the formation of sodium 1,2-diphosphacyclopentadienide occurs *via* a nucleophilic attack of the polyphosphide anion on the C atom of the cyclopropenyl ring in complexes **2**, **4**, or **5** with a subsequent rearrangement (Scheme 3).

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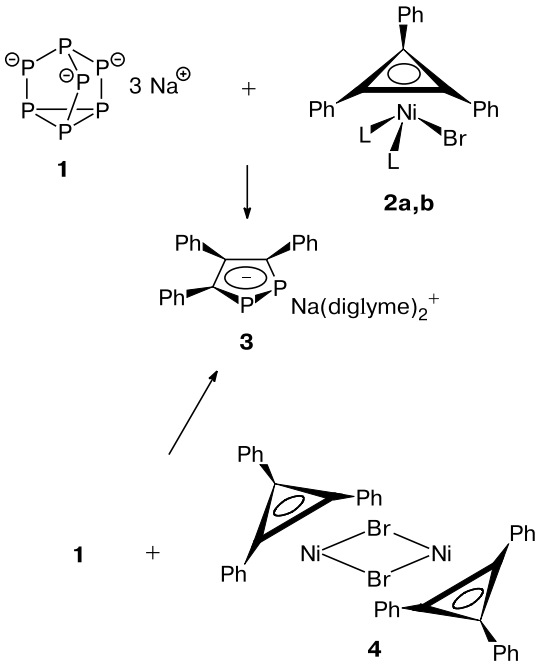
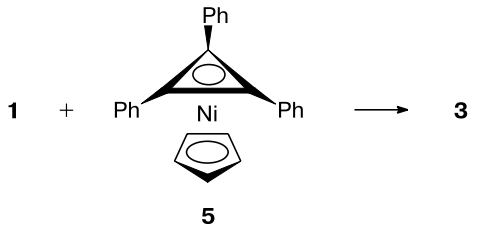
Scheme 1

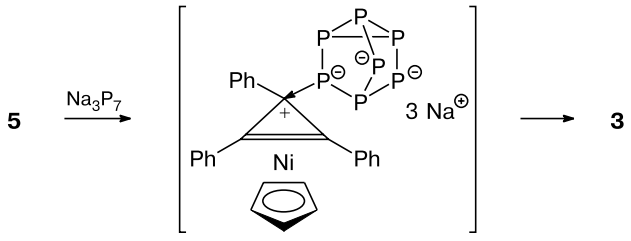


L = $PhPMe_2$ (**a**), Ph_3P (**b**)

Scheme 2



Scheme 3



This hypothesis is corroborated by the aromaticity of the cyclopropenyl ligand[14] satisfying the Hückel rule with two π-electrons and a positive charge, which is undoubtedly favorable for a nucleophilic attack of the polyphosphide anion on the C atom of the cyclopropenyl ring.

Thus, we discovered a novel transformation of the phosphorus framework of the heptaphosphide trianion in the presence of nickel cyclopropenyl complexes, which gives rise to sodium 1,2-diphosphacyclopentadienide.

Experimental

All manipulations for the preparation of the starting reagents, the synthesis and isolation of products were carried out in an inert atmosphere in standard Schlenk flasks. Solvents were used freshly distilled over Na/benzophenone. NMR spectra were recorded on a Bruker MSL-400 instrument (400 (^{1}H), 121.7 (^{31}P), and 100.6 MHz (^{13}C)) with Me_4Si as the internal standard for ^{1}H and ^{13}C and 85% H_3PO_4 as the external standard for ^{31}P. The starting reagents Ph_3C_3Br,[15] $Ni(cod)_2$ (cod is cycloocta-1,5-diene),[16] $[Na(diglyme)_2]_3P_7$,[17] $Ph_3C_3Ni(PhPMe_2)_2Br$ (**2a**),[11] and $Ph_3C_3NiC_5H_5$ (**5**)[13] were prepared according to known procedures.

(Triphenylcyclopropenyl)bis(triphenylphosphine)nickel bromide (2b). A solution of Ph_3P (1.05 g, 4 mmol) in THF (10 mL) was added at −78 °C to a suspension of $Ni(cod)_2$ (0.55 g, 1.98 mmol) in THF (50 mL). The mixture was stirred at this temperature for 1 h and then triphenylcyclopropenyl bromide (0.71 g, 2.00 mmol) was added. The reaction mixture was stirred at ~20 °C for 12 h, filtered, and concentrated. The residue was dissolved in toluene (10 mL) and precipitated with hexane (50 mL). The resulting precipitate was filtered off, washed with cold hexane, and dried *in vacuo*. The yield of bromide **2b** was 1.32 g (72%), a red-brown powder, m.p. 127 °C. Found (%): C, 71.34; H, 4.65; Br, 8.24; P, 6.11. $C_{57}H_{45}BrNiP_2$. Calculated (%): C, 73.57; H, 4.87; Br, 8.59; P, 6.66. ^{1}H NMR (C_6D_6), δ: 6.8—7.2 (m, Ph). ^{31}P NMR (C_6D_6), δ: 17.2 (s). ^{13}C NMR (THF-d_8), δ: 125.7, 126.80 (both s, *m*-C_{Ph}); 127.44, 127.85 (both s, *p*-C_{Ph}); 127.97 (d, *i*-C_{P-Ph}, $^1J_{P,C}$ = 11.6 Hz); 128.56 (s, *i*-C_{Ph}); 129.34, 130.34 (both s, *o*-C_{Ph}); 134.34 (s, C_3-ring).

Dimer of triphenylcyclopropenylnickel bromide (4). Triphenylcyclopropenyl bromide (0.71 g, 2.00 mmol) was added at −78 °C to a suspension of $Ni(cod)_2$ (0.54 g, 1.96 mmol) in THF (50 mL). The reaction mixture was stirred at ~20 °C for 12 h, filtered, and evaporated to dryness. The residue was washed three times with cold hexane and dried *in vacuo*. The yield of complex **4** was 0.72 g (92%), a red-brown powder, m.p. 177 °C. Found (%): C, 61.04; H, 3.65; Br, 19.52. $C_{42}H_{30}Br_2Ni_2$. Calculated (%): C, 62.13; H, 3.72; Br, 19.68. ^{1}H NMR (THF-d_8), δ: 6.7—7.2 (m, Ph). ^{13}C NMR (THF-d_8), δ: 123.8 (s, *m*-C_{Ph}); 126.44 (s, *p*-C_{Ph}); 128.13 (s, *i*-C_{Ph}); 130.23 (s, *o*-C_{Ph}); 133.67 (s, C_3-ring).

Sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (3). ***A.*** Complex **2a** (1.36 g, 1.99 mmol) was added to a suspension of a Na_3P_7—diglyme complex[17] (4.36 g, 4.2 mmol) in diglyme (30 mL). The reaction mixture was stirred at 60 °C for 3 h. The black precipitate that formed was filtered off, the solvent was removed *in vacuo*, and the product was extracted from the residue with toluene—THF (5 : 1). The extract was concentrated and washed with hexane to give adduct **3**·(diglyme)$_2$ (0.88 g, 72%), a light brown powder, m.p. 125 °C (decomp.). Found (%): C, 64.20; H, 7.04; P, 9.57. $C_{33}H_{43}NaO_6P_2$. Calculated (%): C, 63.86; H, 6.98; P, 9.98. ^{1}H NMR (THF-d_8), δ: 3.15 (s, 18 H, MeO); 3.30, 3.38 (both t, 6 H each, OCH_2, $^3J_{H,H}$ = 5.1 Hz); 6.63 (t, 2 H, *p*-H_{Ph}, $^3J_{H,H}$ = 7.3 Hz); 6.75 (br.s, 9 H, Ph, H arom.); 6.93 (br.d, 4 H, *o*-H_{Ph}, $^3J_{H,H}$ = 7.3 Hz). ^{31}P NMR (THF-d_8), δ: 190.0 (s). ^{13}C NMR (THF-d_8), δ: 58.07 (s, MeO);

69.69, 71.39 (both s, OCH_2); 121.77, 122.96 (both s, *m*-C_{Ph}); 125.91, 126.20 (both s, *p*-C_{Ph}); 129.73 (t, *i*-C_{Ph}, $^1J_{P,C}$ = 4.9 Hz); 131.93 (s, *i*-C_{Ph}); 143.88, 144.27 (both s, *o*-C_{Ph}); 147.02 (t, C—Ph, $^2J_{P,C}$ = 8.9 Hz); 161.61 (t, C—Ph, $^1J_{P,C}$ = 28.5 Hz).

B. Compound **3** was obtained analogously from a Na_3P_7—diglyme complex[17] (3.45 g, 3.31 mmol) and complex **2b** (1.54 g, 1.65 mmol). The yield of adduct **3**·(diglyme)$_2$ was 0.77 g (75%).

C. Compound **3** was also obtained from a Na_3P_7—diglyme complex[17] (4.67 g, 4.5 mmol) and (cyclopentadienyl)(triphenylcyclopropenyl)nickel (**5**) (0.87 g, 2.2 mmol). The yield of adduct **3**·(diglyme)$_2$ was 0.98 g (73%).

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