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Aminomethylphosphines in Template Synthesis on Pt(II), Pd(II), and Hg(II).

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ABSTRACT

Reactions of 5-p-toluidinomethyl-1,3-ditolyl-1,3,5-diazaphosphorinane **1** *with Pt(II), Pd(II), Hg(II) salts are reported. Complex formation was followed by template synthesis of novel bicyclic ligand and chelate complexes. Compounds* **2**, **3**, **4** *have been formed. The mercury complex* **4** *was also obtained in high yield by electrochemical oxidation of compound* **1** *at the Hg-anode. Conformational features of new ligands are discussed on the basis of NMR data.*

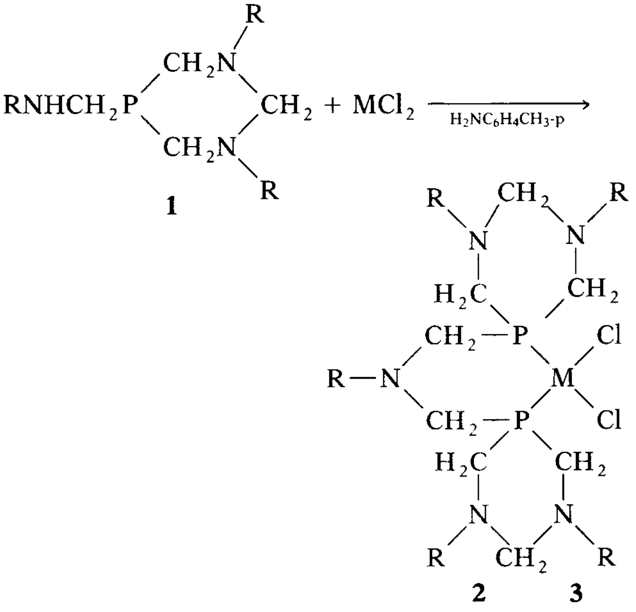
INTRODUCTION

Aminomethylphosphines and their derivatives with labile hydrogen give novel types of P, N-containing compounds in the course of nucleophilic substitution at the α-carbon atom [1–3]. Coordination of several molecules of aminomethylphosphine with a transition metal ion leads to the approach of their nucleophilic and electrophilic centers. G. Märkl [4–6] and B. A. Arbuzov [7, 8] have previously examined complex formation by aminomethylphosphines. Stable complexes of 1,3,5-diazaphosphorinanes with transition metals have previously been described [8], but no template processes were discovered in this work.

RESULTS AND DISCUSSION

5-p-Toluidinomethyl-1,3-ditolyl-1,3,5-diazaphosphorinane **1** is an easily prepared [9], air stable solid. Compound **1** contains a diazaphosphorinane ring, and an aminomethyl group with a labile hydrogen. It therefore represents an interesting material for the study of template reactions. It has been shown in our work [9] that **1** is stable in solutions and forms complexes with Cu(I) and Ag(I) [10]. We have now studied the reactions of **1** with bivalent metals salts.

Compound **1** reacts with Pt(II) and Pd(II) chlorides at room temperature in CH_3CN and $CHCl_3$, respectively. In both cases coordination of two ligands with the metal atom was followed by nucleophilic substitution at the exocyclic carbon atom. Complexes **2** and **3** of a novel bicyclic chelate ligand with Pt(II) and Pd(II) have been formed in the course of the template processes.



R = p-Me—C_6H_4, M = Pt(II), Pd(II)

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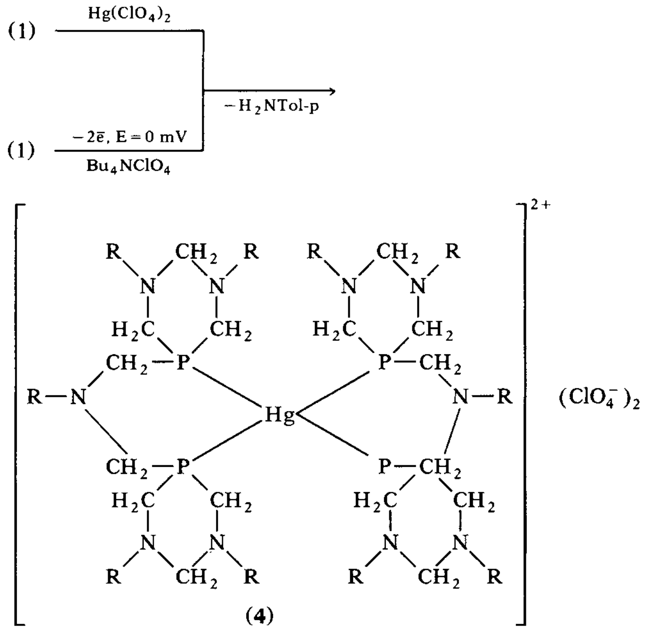
Compounds **2** and **3** are grey and yellow crystals, respectively. Their IR spectra do not contain peaks in the interval 2900-3700 cm^{-1}, while compound **1** has a strong adsorption at 3340 cm^{-1}, which was assigned to ν (N—H) [9]. Two intensive absorptions at 309, and 292 $cm^{-1}\nu$ (Pt—Cl) for **2** and a wide band at 290 cm^{-1} for **3** prove that complexes exist in the *cis*-configuration [11]. The value of the ^{31}P—^{195}Pt coupling constant (3210 Hz) observed in the ^{31}P NMR spectrum of compound **2** confirms the *cis*-position of the phosphorus atoms [11]. There are observed narrow singlets with $\delta = -23.2$ and -3.4 in the ^{31}P NMR spectra of **2** and **3**, respectively. A coordination shift ($\Delta\delta$ 40) relative to **1** ($\delta^{31}P = -48$) is consistent with the formation of the P—M bond [12]. ^1H NMR spectra of **2** and **3** will be discussed below. Low molar electroconductivities of compounds **2** and **3** exclude other plausible ionic structures.

If the metal ion has four coordination sites, the linkage of four molecules of **1** can occur. Reaction of four molecules of **1** with mercury(II) perchlorate in CH_3CN produced complex **4** in poor yield. It has been shown that electrochemical oxidation of some phosphines at a mercury anode leads to the complexes of Hg(II) with the phosphines used [13]. Complex **4** has been synthesized in high yield during the electrochemical oxidation of ligand **1** under these conditions.



(4)

Compound **4** is obtained as a white solid after recrystallization from CH_3CN. The absorption of the N—H bond has not been observed in its IR spectrum. There is only one signal in the ^{31}P NMR spectrum with $\delta = -0.5$ and a ^{199}Hg—^{31}P coupling constant of 1543 Hz. The ^{31}P NMR data are in accord with a tetrahedral configuration of the mercury ion coordinated with four equivalent phosphorus atoms [14]. The high molar electroconductivity of **4** [160 Ω cm^2mol^{-1}] corresponds well to the fact of complex **4** dissociating into three ions.

Discussion of the ^1H NMR Spectra

The ^1H NMR spectra provide additional information about the structures of the novel ligands. The ^1H NMR spectra of complexes **2**, **3**, and **4** in $CDCl_3$ are similar. The four equivalent tolyl-groups and the separate tolyl-group of the chelate fragment can be seen in the spectra. The methylene hydrogens (H^E) of the chelate fragment are equivalent and are recorded as a sharp singlet. This is the evidence of the ring's symmetry and the easy inversion of the metal-containing ring.

We have shown earlier [10] that the 1,3,5-diazaphosphorinane ring exists in solution as a conformational equilibrium of three forms. The NMR spectra represent an average picture of these forms. For **2** and **3** the resolved ^1H NMR spectra where obtained at room temperature. Signals of **4** were broad at room temperature but became resolved at 55°C.

A spectrum of the ring methylene hydrogens represent $(AB)_2X(PCH_2N)$ and CDX (NCH_2N) spin systems, which are typical for the diazaphosphorinanes in predominant chair conformations. The methylene protons of $N—CH_2—N$ (H^C and H^D) resonate at lower field than the hydrogens of the $P—CH_2—N$ fragment. Chemical shifts and ^1H—^1H couplings (13 Hz) of H^C and H^D are similar to those of **1**. Small $^4J(P—H)$ coupling (0-4 Hz) for the equatorial proton H^D was observed according to the W rule [15]. Downfield shifts of H^A and H^B resonances for compounds **2**, **3**, **4** relative to **1** confirm the formation of M—P bonds. It is established that the values of $^2J(P—H)$ constants are determined by the angles between the X—P—C and P—C—H planes [15, 16]. The small magnitude of the ^{31}P—^1H coupling constants (0-4 Hz) for H^A and H^B of the complexes under discussion shows that the angles between the planes (M—P—C and P—C—H^A) and (M—P—C and P—C—H^B) are similar, and the dominant conformation of the heterocycles is a chair with an equatorial P—M bond position. The ligand **1** exists mainly in the chair conformation with an axial P-lone pair position [10].

EXPERIMENTAL

Reactions and manipulations were carried out under an atmosphere of dry argon. Solvents were dried using standard procedures. ^1H and ^{31}P NMR spectra of **1**, **2** and **3** were recorded on a WM-250

Bruker spectrometer, and for **4** on a MSL-400 Bruker spectrometer. Chemical shifts are reported in ppm (δ) with positive values down field of the reference (^1H: Me_4Si, ^{31}P: ext. 85% H_3PO_4). IR spectra were obtained on a Specord M-80 spectrometer. Reported melting points are uncorrected. Elemental analyses are within 0.50% of theoretical. The starting materials **1** were synthesized as described previously [9]. The apparatus and cells for preparative electrolysis have been described earlier [17].

cis-Dichloro-[p-Tolyl-bis(1,3-di-p-tolyl-1,3,5-diazaphosphorinane-5-yl-methyl)amine]-platinum(II) **2**.

A solution of **1** (1.5 g, 37 mmol) in 30 mL of CH_3CN was treated with solid $PtCl_2$ (0.49 g, 18 mmol). The resulting mixture was allowed to stand for 24 hours under mixing. A resulting grey precipitate was isolated by filtration and recrystallized from CH_3CN. Compound **2** was an air stable solid: 1.6 g (80%), m.p. > 300°. NMR spectra: ^1H ($CDCl_3$) δ 7.08 (d, 8H, $^2J_{HH} = 8.5$ Hz, Ar—H), 6.96 (d, 8H, $^2J_{HH} = 8.5$ Hz, Ar—H), 6.52 (d, 2H, $^2J_{HH} =$ 7.4 Hz, Ar—H*), 6.35 (d, 2H, $^2J_{HH} = 7.4$ Hz, Ar—H*), 4.87 (d, 2H, $^2J_{HH} = 12.9$ Hz, N—CH^D—N), 4.26 (d, 2H, $^2J_{HH} = 12.9$ Hz, $^4J_{PH} = 4$ Hz, N—CH^C—N), 3.77 (s, 4H, P—CH_2^E—N), 4.64 (d, 4H, $^2J_{HH} = 14.8$ Hz, $^2J_{PH} = 0$ Hz, P—CH^A—N), 4.05 (d, 4H, $^2J_{HH} = 14.8$ Hz, $2J_{PH} = 4.5$ Hz, P—CH^B—N) 2.25 (s, 12H, Ar—CH_3), 2.06 (s, 3H, Ar—CH_3^*), $^{31}P\{^1H\}$ (DMA) δ -23.2, $^1J_{Pt-P} = 3210$ Hz; IR (polyethylene) 309, 292 (Pt—Cl) cm^{-1}. Anal. ($C_{43}H_{51}N_5P_2PtCl_2$): C, H, N, P, Cl.

cis-Dichloro-[p-Tolyl-bis(1,3-di-p-tolyl-1,3,5-diazaphosphorinane-5-yl-methyl)amine]-palladium(II) **3**.

In a procedure similar to that described above for **2**, **1** (1.25 g, 3.1 mmol) was mixed with $PdCl_2$ (0.22 g, 3.1 mmol) in 20 mL of $CHCl_3$. After 1 day the reaction mixture was filtered and the filtrate concentrated to about 1 mL. A yellow solid that had formed was collected by filtration and washed with ether. Compound **3** was an air stable solid: 1.14 g (78%), m.p. 228°C. NMR spectra: ^1H ($CDCl_3$) δ 7.09 (d, 8H $^2J_{HH} = 8.5$ Hz, Ar-H) 6.97 d, 8H, $^2J_{HH} = 8.5$ Hz, Ar-H), 6.44 (d, 2H, $^2J_{HH} = 8.6$ Hz, Ar-H*) 6.35 (d, 2H, $^2J_{HH} = 8.6$ Hz, Ar-H*), 4.88 (d, 2H, $^2J_{HH} =$ 13.5 Hz, N-CH^D-N) 4.54 (d, 2H, $^2J_{HH} = 13.5$ Hz, $^4J_{PH} = 0$ Hz, N-CH^C-N) 3.77 (s, 4H, P-CH_2^E-N) 4.81 (d, 4H, $^2J_{HH} = 15.0$ Hz, $^2J_{PH} = 0$ Hz, P-CH_A-N) 4.16 (d, 4H, $^2J_{HH} = 15.0$ Hz, $^2J_{PH} = 0$ Hz, P-CH^B-N) 2.26 (s, 12H, Ar-CH_3) 2.09 (s, 3H, Ar-CH_3^*); $^{31}P\{^1H\}$ (DMA) δ -3.4. IR spectrum (polyethylene) 301, 286 (Pd-Cl). Anal. ($C_{43}H_{51}N_5P_2PdCl_2$): C, H, N, P, Cl.

Bis-[p-Tolyl-bis(1,3-di-p-tolyl-1,3,5-diazaphosphorinane-5-yl-methyl)amine]-mercury(II) di-perchlorate **4**.

A. In a procedure similar to that described above for **2**, **1** (1.3 g, 3.2 mmol) and $Hg(ClO_4)_2$ were mixed in 20 mL of CH_3CN. After 2 days 0.4 g (28%) of a resulting grey precipitate of **4** was separated: m.p. 158–160°. NMR spectrum: $^{31}P\{^1H\}$ (MeCN) δ -0.5, $^1J_{HgP} = 1543$ Hz.

B. Into the anode compartment of the divided cell with an Hg-anode and a Pt-cathode filled with a 0.1 M solution of Et_4NClO_4, acetonitrile (100 mL) **1** (0.7 g, 1.7 mmol) was added. The potential was maintained at a fixed value (E = 0 mV) with an initial current of 58 mA. Electrolysis was finished when the current dropped to 6 mA, which took 1 hour. A grey solid precipitate was isolated by filtration and recrystallized from acetonitrile to give **4** as a white stable solid: 0.73 g (95%), m.p. 162°C. NMR spectra: ^1H ($CDCl_3$) δ 7.10 (d, 8H, $^2J_{HH} = 8.5$ Hz, Ar—H) 7.06 (d, 8H, $^2J_{HH} = 8.5$ Hz, Ar—H), 6.64 (d, 2H, $^2J_{HH} = 8.6$ Hz, Ar—H*) 6.50 (d, 2H, $^2J_{HH} =$ 8.6 Hz, Ar—H*), 4.81 (d, 2H, $^2J_{HH} = 13.1$ Hz, N—CH^D—N) 4.81 (d, 2H, $^2J_{HH} = 13.1$ Hz, $^4J_{PH} = 0$ Hz, N—CH^C—N) 4.40 (s, 4H, P—CH_2^E—N) 4.38 (d, 4H, $^2J_{HH} = 14.9$ Hz, $^2J_{PH} = 0$ Hz, P—CH^A—N) 4.07 (d, 4H, $^2J_{HH} = 14.9$ Hz, $^2J_{PH} = 0$ Hz, P—CH^B—N) 2.28 (s, 12H, Ar—CH_3) 2.06 (s, 3H, Ar—CH_3^*) $^{31}P\{^1H\}$ (MeCN) δ -0.5, $^1J_{Hg-P} = 1543$ Hz, $\Lambda = 160$ Ω cm^2mol^{-1}. Anal. $C_{86}H_{102}N_{10}P_4HgClO_4$: C, H, N, P, Cl.

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* Groups of chelate fragment.

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