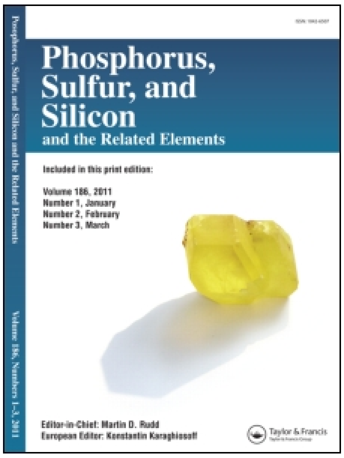

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Preparation, Properties, and Reactions of Metal-Containing Heterocycles, 102[1] a Three-Dimensional Triplatinacyclophane with an Eleven-Membered Bridge

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Synthesis of 1,3,5-tris(4′-bromobutyl)benzene has been achieved by means of two step reaction. This compound reacts with ethyl diphenylphosphonic ester to form phosphoryl oxide which transformed to tertiary phosphine ligand. Employing the high dilution method from the ligand and $Cl_2Pt(NCPh)_2$ a cage compound is formed.

Keywords: Metallacyclophanes; Phosphorus ligand; Cage compound; Supramolecular Chemistry; Platinum

INTRODUCTION

Cyclophanes[2] have played a central role in the development of host-guest chemistry. The incorporation of transition metal centers into such structures can confer new properties[3]. In addition transition metal complexes containing suitably oriented ligands provide a means of forming macrocyles in a single reaction step. As a part of our research[4], we sought to create a flexible ligand system with an aromatic nucleus containing three alkyl (arm) groups as spacers provided with functional tertiary phosphines at its end. It is anticipated that two molecules of this ligand assemble via three platinum atoms to establish an elastic three-dimensional molecular

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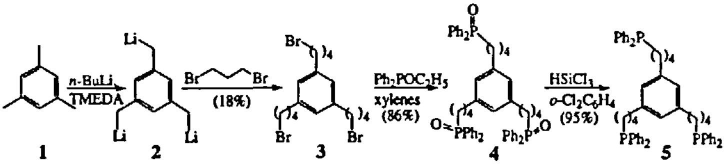
cage suitable for host-guest complexation-decomplexation. We would like to report here the synthesis of the ligand.

RESULTS AND DISCUSSION

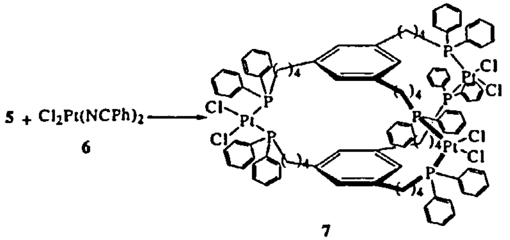
The starting material for the ligand is **3** which is prepared from mesitylene (**1**), (see Scheme 1). Lithiation of **1** with *n*-BuLi give **2**. Reaction of **2** with 1,3-dibromopropane leads directly to **3**. To our knowledge this is the first report of this compound and its synthesis. Several enlargements of the number of methylene groups are possible with longer dibromoalkanes.

The ligand is synthesized by reaction of **3** with ethyldiphenylphosphonic ester. The subsequent reduction of the product **4** afforded the corresponding ligand (see Scheme 1).



SCHEME 1.

The nanoscaled triplatinacyclophane **7** is formed by the reaction of **5** and **6** (see Scheme 2) under dilution principle. Thus in



SCHEME 2.

a single reaction, the five separate components have undergone self assembly to form this metallacyclophane in good yield. Progress is made now to obtain single crystal to study its X-ray crystal structure. Physical properties of the cage molecule will be reported separately with the X-ray crystal structure.

EXPERIMENTAL

All reactions were carried out under dry argon. Solvents were dried with appropriate reagents and stored under dry argon. Mass spectra: EI-MS Finnigan TSQ 70 (200 °C). ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR: Bruker DRX250 spectrometer operating at 250.13, 62.90, and 101.26 MHz, respectively. Mesitylene, 1,3-dibrompropane, and trichlorosilane were of commercial grade and were used without further purifications; 1,3,5-tris(lithiomethyl)benzene[5], ethyldiphenylphosphonic ester[6], and $Cl_2Pt(NCPh)_2$[7] were synthesized according to literature methods.

1,3,5-Tris(4-bromobutyl)benzene (3): Pyrophoric 1,3,5-tris(lithiomethyl)-benzene (**2**), prepared from 500mL of a solution of *n*-butyl lithium (1.6 M in *n*-hexane), 92.97g (0.80 mol) of TMEDA, and 16.4 g (0.136 mol) of mesitylene, was filtered off from the reaction mixture (P3) and washed with *n*-pentane. After drying in vacuo, **2** was suspended in 200 mL of *n*-pentane and added to a solution of 123.6 g (0.614 mol) of 1,3-dibrompropane in 500 mL *n*-pentane at –78 °C. The resulting mixture was stirred at –78 °C for 2 h and then allowed to warm slowly to room temperature. The reaction mixture was neutralized, and the organic phase was separated, and the aqueous phase extracted with dichlormethane. Combined organic extracts was dried over Na_2SO_4 and the volatile materials were removed in vacuum. The product was purified by column chromatography. Yield 11.5 g (18%), colorless oil. ^{1}H-NMR ($CDCl_3$): δ = 1.68 (m, 6H, $CH_2C\mathit{H}_2CH_2CH_2Br$), 1.73 (m, 6H, $CH_2CH_2C\mathit{H}_2CH_2Br$), 2.50 (t, $^{3}J_{HH} = 7.4$ Hz, 6H, $C\mathit{H}_2CH_2CH_2CH_2Br$), 3.33 (t, $^{3}J_{HH} = 6.6$ Hz, 6H, $CH_2CH_2CH_2C\mathit{H}_2Br$), 6.74 (s, 3H, aromatic CH). $^{13}C\{1H\}$-NMR ($CDCl_3$): δ = 28.6 ($CH_2\mathit{C}H_2CH_2CH_2Br$), 31.1 ($CH_2CH_2CH_2\mathit{C}H_2Br$), 32.5($CH_2CH_2\mathit{C}H_2CH_2Br$), 33.6 ($\mathit{C}H_2CH_2CH_2CH_2Br$), 125.0 (s, aromatic CH), 140.5 (s, aromatic C). EI-MS (*m/z*) (%): 480 (2), 482 (8), 484 (8), 486 (2) $[M]^+$.

1,3,5-Tris[4'-(diphenylphosphoryl)butyl]benzene (4): Literature proced-ure was applied[8]. Yield 86%, colorless solid (mp 155-156 °C) ^{1}H-NMR ($CDCl_3$): δ = 1.57 (br m, 12H, $CH_2CH_2C\mathit{H}_2C\mathit{H}_2P$), 2.19 (m, 6H, $CH_2C\mathit{H}_2CH_2CH_2P$), 2.39 (br s, 6H, $C\mathit{H}_2CH_2CH_2CH_2P$), 6.59 (s, 3H, C_6H_3), 7.23 (m, 6H, *p*-C_6H_5), 7.34(m, 12H, *o*-C_6H_5), 7.62 (m, 12H, *m*-C_6H_3). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ = 21.7 (d, $^{3}J_{PC} = 2.9$ Hz, $CH_2\mathit{C}H_2CH_2CH_2P$), 29.9 (d, $^{1}J_{PC} = 73.3$ Hz, $CH_2CH_2CH_2\mathit{C}H_2P$), 33.2 (d, $^{2}J_{PC}$ = 14.2 Hz, $CH_2CH_2\mathit{C}H_2CH_2P$), 35.7 (s, $CH_2CH_2CH_2\mathit{C}H_2P$), 126.0 (s, *tert*-$C_6H_3$), 129.0 (d, $^2J_{PC}$ = 11.4 Hz, *o*-C_6H_5), 131.1 (d, $^3J_{PC}$ = 9.3 Hz, *m*-C_6H_5), 132.1 (d, $^4J_{PC}$ = 2.1 Hz, *p*-C_6H_5), 133.3 (d, $^1J_{PC}$ = 97 Hz, *quat*-C_6H_5), 142.3 (s, *quat*-C_6H_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 34.1. EI-MS (*m/z*): 847 $[M]^+$.

1,3,5-Tris[4'-(diphenylphosphanyl)butyl]benzene (4): A modification of literature procedure$^{(8)}$ was used. Trichlorosilane (1.83 g, 13.5 mmol) was carefully added through a septum to a suspension of 3 (1.27 g, 1.5 mmol) in 30 mL *o*-dichlorobenzene in three-necked 100-mL round bottom flask equipped with a reflux condenser at 120 °C. After 1 h the reaction mixture was cooled to 0 °C. Degassed aqueous NaOH (40 mL, 4 M) was carefully added through a septum. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and dried in vacuo to give analytically pure 3 as colorless oil. Yield: 1,14 g (95%). ^1H-NMR ($CDCl_3$): δ = 1.42 (m, 6H, $CH_2CH_2C\mathit{H}_2CH_2P$), 1.62 (m, 6H, $CH_2C\mathit{H}_2CH_2CH_2P$), 1.98 (m, 6H, $CH_2CH_2CH_2C\mathit{H}_2P$), 2.42 (t, $^3J_{HH}$ = 7.7 Hz, $C\mathit{H}_2CH_2CH_2CH_2P$), 6.64 (s, 3H, C_6H_3), 7.22 - 7.32 (m, 30H, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 24.8 (d, $^1J_{PC}$ = 18.9 Hz, $CH_2CH_2CH_2\mathit{C}H_2P$), 26.9 (d, $^3J_{PC}$ = 6.3 Hz, $CH_2\mathit{C}H_2CH_2CH_2P$), 32.0 (d, $^2J_{PC}$ = 12.6 Hz, $CH_2CH_2\mathit{C}H_2CH_2P$), 34.4 (s, $\mathit{C}H_2CH_2CH_2CH_2P$), 124.8 (s, *tert*-$C_6H_3$), 127.3 (d, $^3J_{PC}$ = 6.3 Hz, *m*-C_6H_5), 127.4 (s, *p*-C_6H_5), 131.7 (d, $^2J_{PC}$ = 18.9 Hz, *o*-C_6H_5), 137.8 (d, $^1J_{PC}$ = 12.6 Hz *quat*-C_6H_5), 141.2 (s, *quat*-C_6H_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = -15.0. EI-MS (*m/z*): 799 $[M]^+$.

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