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# SYNTHESIS AND CYCLOPALLADATION OF A MACROCYCLIC TRIAMINE, 7-METHYL-3,7,11-TRIAZABICYCLO[11,3,1]HEPTADECA-1(17),13,15-TRIENE[1)]

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A macrocyclic triamine, 7-methyl-3,7,11-triazabicyclo[11,3,1]-heptadeca-1(17),13,15-triene was treated with palladium(II) acetate and subsequently with $NaClO_4 \cdot H_2O$ to give [7-methyl-3,7,11-triazabicyclo[11,3,1]heptadeca-1(17),13,15-trienato-$C^{17}$,*N*,*N*',*N*'']palladium(II) perchlorate-water(1/1).

Organocobalt and -rhodium complexes coordinated with a macrocyclic tetradentate ligand have been investigated extensively in connection with the chemistry of vitamin $B_{12}$.[2)] In the course of the researches, a few organocobalt complexes which have an intramolecularly-bridged methine-,[3)] methylene-,[4)] or vinyl-metal bond[5)] have been reported. However, there has been no organometallic compound in which one carbon of a macrocyclic multidentate ligand is bonded directly to metal. In this letter, we wish to report synthesis of a 14-membered triamine and a novel type of organometallic compound, in which an aromatic carbon in the triamine is bonded to palladium atom and the triamine serves as a $CN_3$-type tetradentate ligand.

Isophthaloyl chloride was treated with *N*,*N*-bis(3-aminopropyl)methylamine in benzene in a high dilution method. The resulting suspension was filtered to remove a polymeric by-product. After the solvent was distilled, the remaining materials were washed with water and dried to give a white solid (1).[6,7)] The IR spectrum of 1 showed characteristic bands of secondary amide; a $\nu_{NH}$ band at 3330 $cm^{-1}$ and two $\nu_{C=O}$ ones at 1638 and 1660 $cm^{-1}$. Its mass spectrum gave a parent peak at m/e 275 (Calcd for $C_{15}H_{21}N_3O_2$: M, 275.1634 ). These data, its $^1H$ NMR spectrum (Table 1), and the elemental analysis disclose that 1 is a macrocyclic diamide, 7-methyl-3,7,-11-triazabicyclo[11,3,1]heptadeca-1(17),13,15-triene-2,12-dione. It is noted that

Table 1. $^1$H NMR data[a)]

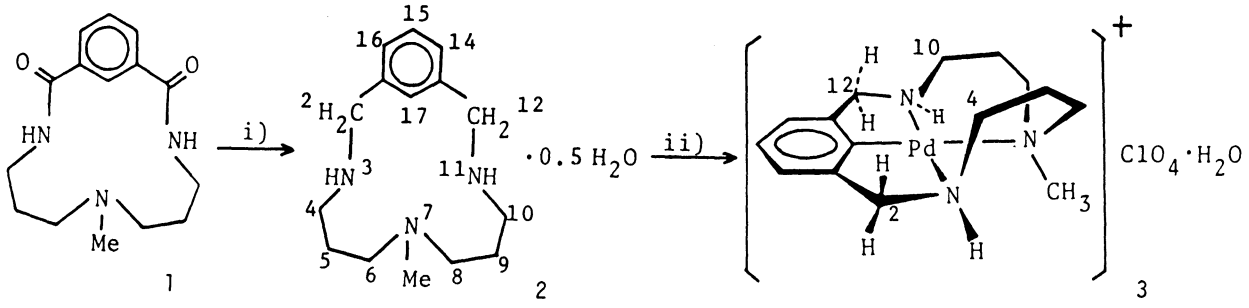
| Compound | 2,12-C$\underline{H}_2$ | 4,10-C$\underline{H}_2$ | 5,9-C$\underline{H}_2$ | 6,8-C$\underline{H}_2$ | N$\underline{H}$ | C$\underline{H}_3$ | H-14,16 | H-15 | H-17 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | - | 3.54qa[b)] | 1.94qi[c)] | 2.63t[d)] | 2.3 | 2.18s | 7.83d[e)] | 7.55t[e)] | 7.99s |
| 2 | 3.92s | 2.60t[d)] | 1.59qi[c)] | 2.42t[d)] | 1.90s | 2.02s | 6.96d[d)] | 7.16t[d)] | 7.58s |
| 3[f)] | 3.99dd[g)] 4.50dd[g)] | 2.34 ~3.24m | -[h)] | 2.34 ~3.24m | 4.92br | 2.50s | 6.79d[d)] | 6.90t[d)] | - |

a) δ value from TMS. In $CDCl_3$ unless noted elsewhere. b) qa=quartet. $^3J$= 6 Hz. c) qi=quintet. $^3J$= 6 Hz. d) $^3J$= 6 Hz. e) $^3J$= 7 Hz. f) In $CD_3CN$. $H_2O$; δ 2.20s. g) Doublets of AB-type quartet. $^2J$= 15 Hz, $^3J$= 3 Hz. h) Overlapping with the solvent signal.

the $^1$H NMR spectrum exhibited a quartet at δ 3.54 (4- and 10-C$\underline{H}_2$), implying that these protons coupled with the amide proton as well as with 5- or 9-methylene protons, respectively. However, the amide proton appeared as a singlet near δ 2.3, owing to rapid exchange with water protons coexisting in the solvent.[8)]

A THF suspension of 1 was treated with an excess amount of THF-borane(1/1) to afford a white waxy solid (2).[6,7)] The IR spectrum of 2 lacked the bands characteristic of secondary amide. Its mass spectrum gave a parent peak m/e 247 (Calcd for $C_{15}H_{25}N_3$, M= 247.2048 ). $^1$H NMR spectrum of 2 showed a singlet at δ 3.92 assignable to 2- and 12-methylene protons. On the basis of these facts and the $^{13}C\{^1H\}$ NMR data shown in Table 2, 2 was assigned to the macrocyclic triamine, 7-methyl-3,7,11-triazabicyclo[11,3,1]heptadeca-1(17),13,15-triene-water(2/1).

The triamine 2 was treated with palladium(II) acetate in benzene at ambient temperature for 15 h and subsequently twice with excess amounts of $NaClO_4 \cdot H_2O$ to afford a khaki solid (3).[6,7)] The electric conductivity of a $1.0\times10^{-3}$ mol dm$^{-3}$ solution of 3 in $CH_3CN$ was 131 S cm$^2$ mol$^{-1}$, supporting a 1:1 electrolyte. The $^1$H-NMR spectrum of 3 in $CD_3CN$ showed doublets of AB-type quartet near δ 4.20 (2- and




Scheme 1. i) $BH_3 \cdot THF$. ii) $Pd(CH_3CO_2)_2$ + $NaClO_4 \cdot H_2O$.

Table 2. $^{13}C\{^{1}H\}$ NMR data[a)]

| Compound | C-1,13 | C-2,12 | C-4,10 | C-5,9 | C-6,8 | $\underline{C}H_3$ | C-14,16 | C-15 | C-17 |
|---|---|---|---|---|---|---|---|---|---|
| 2[b)] | 140.49 | 55.86[c)] | 44.97 | 27.42 | 52.77[c)] | 40.80 | 126.29 | 125.56 | 127.98 |
| 3[d)] | 144.77 | 61.55[c)] | 51.41 | 23.62 | 60.02[c)] | 39.99 | 116.54 | 122.66 | 156.53 |

a) δ value from TMS. Every signal is a singlet. b) In $CDCl_3$. c) Assigned tentatively. d) In a DMSO + $CDCl_3$ mixed solvent (9:1).

12-$C\underline{H}_2$), implying that the eleven-membered chain from C-2 to C-12 was fixed through the coordination of the three nitrogens to palladium. Moreover, 3 lacked a singlet near δ 7.6 for H-17. In the $^{13}C$ NMR off-resonance spectrum, C-17 resonated as a singlet at δ 156.53, shifting downfield by about 28.5 ppm as compared with that of 2. These facts indicate that C-17 is directly palladated and the macrocyclic triamine acts as a $CN_3$-type tetradentate ligand. The $^{13}C\{^{1}H\}$ NMR spectrum of 3 showed nine singlets, as seen in Table 2. This indicates unambiguously that 3 consists of only one component possessing a σ symmetry, excluding the possibility of the other isomer. Accordingly, 3 is assigned to [7-methyl-3,7,11-triazabicyclo[11,3,1]heptadeca-1(17),13,15-trienato-$C^{17}$,*N*,*N'*,*N''*]palladium(II) perchlorate-water(1/1) and is the first example of the macrocyclic organometallics, in which one carbon atom of the macrocyclic multidentate ligand is directly metallated.

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6) 1: Yield 31%; mp 192-194 °C. 2: Yield 69%; mp 66-70 °C. 3: Yield 32%; mp 169 °C.

7) The elementary analyses of 1, 2, and 3 are satisfactory.

8) On adding $D_2O$ to the $CDCl_3$ solution of 1, the quartet changed to a triplet at $\delta$ 3.58 ($^3J_{HH}$ = 6 Hz).

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