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Binding of Pt^{II} via a σ-Pt–C Bond to a Novel Type of Macrocyclic Monoanionic Carbodiaza Ligand: X-ray Crystal Structure of *trans*-[2,6-(2,13-Dimethyl-2,13-diazatetradecanediyl)phenyl-*N*,*N*′]platinum(II) Iodide[1a]

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The macrocyclic monoanionic carbodiaza ligand 3,14-diaza-20-bromo-3,14-dimethylbicyclo[14.3.1]eicosane-1(20),16,18-triene has been prepared from 2-bromo-1,3-bis(bromomethyl)benzene and 1,10-bis[(*p*-tolylsulfonyl)amino]decane in the presence of Cs_2CO_3. A 55% yield of pure product was obtained after workup. Detosylation with HBr and methylation with formaldehyde/formic acid afforded the new macrocyclic ligand **4**. The organoplatinum complex **6** is the first example of an organometallic cage compound. Its preparation involved reaction of $[PtCl_2(SEt_2)_2]$ with the lithium derivative of **4**, followed by halide exchange with NaI in acetone. This novel complex contains a divalent platinum center with the N donor atoms positioned trans as a result of the geometric constraints of the terdentate coordination. A single-crystal X-ray study established the structure of **6**, $C_{20}H_{33}N_2PtI$: orthorhombic, space group *Pbca* with unit cell dimensions $a = 15.533$ (2) Å, $b = 25.630$ (3) Å, $c = 10.671$ (1) Å, and $Z = 8$. The crystal structure was solved by standard Patterson and Fourier techniques. Anisotropic full-matrix least-squares refinement with 2291 observed reflections converged at $R = 0.040$. An interesting feature is the long hydrocarbon chain bending away from the coordination plane.

Introduction

Multidentate ligand systems, cyclic[1] or acyclic,[2] can be designed to bind transition metals in a predictable manner. The steric constraints of such ligands as well as the nature of the donor atoms determine to a large extent the stability and properties of the metal complexes. We have been interested in the use of the terdentate monoanionic ligand **1**, which is bonded to a metal site via at least one σ metal–carbon bond. Stable complexes of this ligand with Sn^{IV},[3] Pt^{II} and Pd^{II},[4] Li^{I},[5] and Ni^{II},[6] have been prepared. Several of these complexes exhibited unanticipated properties, e.g., a stable σ carbon–Ni^{III} (d^7) interaction, a stable R_3Sn^+ cation, and specific reactivity, e.g., binding of small molecules such as SO_2 and MeI and a reversible 1,2-methyl shift over a σ carbon–Pt bond.

In these complexes the terdentate o,o'-$(Me_2NCH_2)_2C_6H_3$ (= NCN′) ligand (see Figure 1a) through its specific coordination restricts the number of available coordination sites for binding of additional ligands at the metal to those positions in a plane perpendicular to that of the NCN′–metal grouping. Our study revealed that, depending on the actual coordination sites occupied, the two five-membered chelate rings in the NCN′–metal part show a distinct type of puckering, i.e., for the square-planar and octahedral complexes a "twofold axis" puckering and for the square-pyramidal arrays a mirror-type of puckering. Figure 1b shows that as a result of this puckering the methyl groups at the N donor atoms take up distinct axial and equatorial orientations with respect to the plane defined by the NCN′–metal grouping.

To investigate the influence of the steric requirements of these amino substituents on the reactivity of the metal centers, we developed analogous ligands in which one of the methyl groups in each of the NMe_2 side arms of **1** is replaced by one other R group, e.g., ethyl isopropyl,

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[1] (a) This name will be used to emphasize the organometallic nature of this compound: Chemical Abstracts name is 3,14-diaza-20-platina-iodide-3,14-dimethylbicyclo[14.3.1]eicosane-1(20),16,18-triene. (b) Lotz, T. J.; Kaden, T. A. *Helv. Chim. Acta* **1978**, *61*, 1376. (c) Bencini, A.; Fabrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544. (d) Lecomte, J. P.; Lehn, J. M.; Parker, D.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1983**, 296. (e) Lemaire, M.; Buter, J.; Vriesema, B. K.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1984**, 309.

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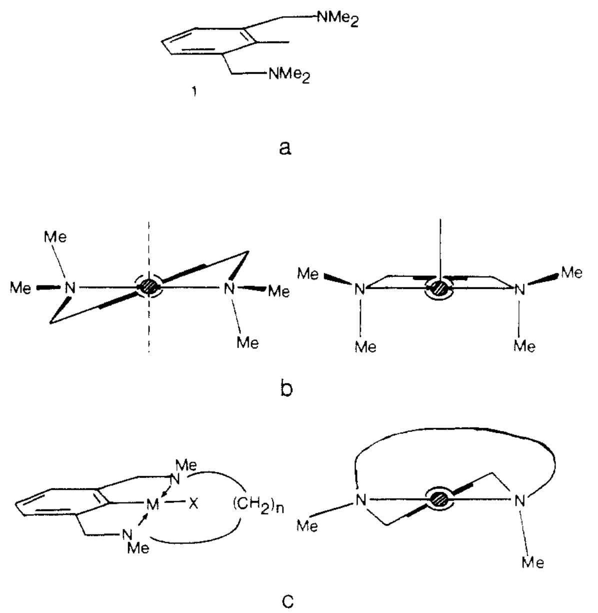

Figure 1. a. Monoanionic NCN′ ligand. b. Square-planar (or octahedral) and square-pyramidal configurations. c. Square-planar complex containing the macrocyclic monoanionic carbodiaza ligand.

tert-butyl, or phenyl or by an α,ω-alkanediyl, which interconnects the two N centers. In the latter case a new macrocyclic diaza system arises in which the metal may be screened on one side of the NCN′–metal plane from attack by a reactant. The effectiveness of the steric screening will be determined by the length, steric bulk, and conformation of the chain.

In fact in such a ligand a "cage" is created in which the metal is not only bonded via a metal–carbon σ bond but also via two N centers, which are now stereogenic,[7] see Figure 1c. Reactions at a metal center contained in such a cage should occur stereospecifically from the least hindered side.

In this paper we report the first results of this study involving the syntheses of the macrocyclic system with $n = 10$ and the platinum(II) complex thereof.

Experimental Section

All reactions with organolithium compounds were performed under a nitrogen atmosphere by using Schlenk tube techniques. Solvents were freshly distilled before use and were stored over molecular sieves (3 Å). The 2-bromo-1,3-bis(bromomethyl)benzene was prepared from 2-bromo-1,3-xylene and 2.2 equiv of *N*-bromosuccinimide in CCl_4.[8] 1,10-Bis[(*p*-tolylsulfonyl)amino]decane was synthesized from 1,10-diaminodecane and *p*-tolylsulfonyl chloride. $PtCl_2(SEt_2)_2$ was prepared according to literature methods.[9] All other materials were obtained commercially. The general technique and apparatus for the syntheses of macrocycles were described earlier.[10]

Melting points were determined on a Mettler FP-2 melting point apparatus, equipped with a FP-21-microscope. ^{1}H NMR spectra were recorded on a Varian T60, Varian XL 100-MHz, or Bruker WM 250-MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP 80 (22.1 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are relative to Me_4Si (0 ppm). Mass spectra were obtained on a AEI MS-902 mass spectrometer. Elemental analyses and osmometric molecular weight determinations of the organic compounds were performed by the Analytical Department, University of Groningen. Elemental analyses of the organometallic complexes were carried out by the Analytical Department of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands.

Synthesis of 3,14-Diaza-20-bromo-3,14-bis[(4-methylphenyl)sulfonyl]bicyclo[14.3.1]eicosane-1(20),16,18-triene (2). A 2-L round-bottomed flask was filled with 1 L of dry DMF and 25 mmol of Cs_2CO_3. To the magnetically stirred suspension was added dropwise a mixture of 10 mmol of 2-bromo-1,3-bis(bromomethyl)benzene and 10 mmol of 1,10-bis[(*p*-tolylsulfonyl)amino]decane in 200 mL of DMF at 50 °C over a period of 3–4 h.[10] The mixture was stirred for an additional 12 h. The DMF was removed under vacuum. The residue was taken up in CH_2Cl_2, and the solution then was washed with a NaCl–water solution (half-saturated) and dried over $MgSO_4$. The crude product was taken up in a small amount of dry CH_2Cl_2 and put on a flash column (100 g of Kieselgel 60, 230–400 mesh), with a mixture of *n*-hexane/ethyl acetate (7/3, v/v) as eluent (pure monomer R_f is 0.95), which gave 3.66 g (55%) of analytically pure product: white crystals: mp 150–152 °C; mol wt (osmometric in $CHCl_3$) 654.0, 658.0 (theory 661.7). ^{1}H NMR ($CDCl_3$) δ 1.12 (br, 16 H), 2.46 (s, 6 H), 3.10 (br, 4 H), 4.45 (s, 4 H), 7.33 (m, 11 H). EI mass spectrum: exact mass of the parent peak m/z 660.169 (theory for 2 m/z 660.163). Anal. Calcd for $C_{32}H_{41}BrN_2O_4S_2$: C, 58.06; H, 6.25; Br, 12.08; N, 4.23; S, 9.69. Found: C, 58.36; H, 6.25; Br, 12.11; N, 4.24; S, 9.70.

Synthesis of 3,14-Diaza-20-bromobicyclo[14.3.1]eicosane-1(20),16,18-triene (3). Compound 2 (3 mmol), 45% hydrogen bromide in glacial acetic acid (22 mL), and phenol (2 g) were mixed and stirred at 50–60 °C for 5 h.[11] The mixture was poured into dry diethyl ether (150 mL), and the resulting precipitate was filtered off. This precipitate was put into a mixture of 50 mL of H_2O and 50 mL of $CHCl_3$ and made basic (pH >10) with sodium hydroxide. The chloroform layer was separated, and the water layer was extracted two more times with 50-mL portions of $CHCl_3$. The combined chloroform layers were washed twice with 25-mL portions of NaCl water solution (half-saturated) and then dried over $MgSO_4$. After filtration the solvent was removed from the filtrate under reduced pressure leaving a colorless oil: 1.005 g (2.84 mmol, 95% yield). EI mass spectrum: m/z 352 and 354 (theory m/z 352 and 354), exact mass of the parent peak m/z 352.151 (theory m/z 352.151). ^{1}H NMR $CDCl_3$, δ): 0.92–1.73 (br m, 16 H), 1.93 (br s, 2 H), 2.46 (br t, 4 H), 3.98 (br s, 4 H), 7.23 (apparent s, 3 H). ^{13}C NMR ($CDCl_3$, δ): 139.71, C(1), C(16); 130.12, C(19), C(17); 126.42, C(18); 125.87, C(20); 53.96, C(2), C(15); 45.77, C(4), C(13); 28.35, 27.68, 26.59, 25.50, C(5)–C(12) (numbering according to IUPAC names).

Synthesis of 3,14-Diaza-20-bromo-3,14-bromo-3,14-dimethylbicyclo[14.3.1]eicosane-1(20),16,18-triene (4). Compound 3 (4 mmol), 8 mL of HCOOH, and 4 mL of H_2CO (36% in water) were refluxed for one night. After the solution had cooled to room temperature, 10.5 mL of concentrated HCl was added and the resulting mixture was stirred for 1 h. Thereafter 25 mL of $CHCl_3$ was added to the mixture, which was then cooled to 0 °C. The mixture was made basic (pH >10) with sodium hydroxide. The water layer was extracted three times with chloroform. The chloroform layers were extracted twice with a NaCl–water solution (half-saturated), dried over $MgSO_4$, and the $CHCl_3$ then was removed under vacuum. The product (1.4 g, 3.67 mmol, 92% yield) was obtained as a colorless oil. EI mass spectrum: exact mass of the parent peak m/z 380.183 (theory m/z 380.182). ^{1}H NMR ($CDCl_3$, δ): 0.83–1.50 (br m, 16 H), 2.28 (br m, 4 H), 2.42 (s, 6 H), 3.63 (br s, 4 H), 7.33 (m, 3 H). ^{13}C NMR ($CDCl_3$, δ): 139.04, C(1), C(16); 130.18, 126.00, C(17)–C(20); 62.15, C(2), C(15); 54.20, C(4), C(13); 43.46, (CH_3); 27.56, 27.02, 25.74, 25.38, C(5)–C(12) (numbering according to IUPAC names).

Synthesis of *trans*-[2,6-(2,13-Dimethyl-2,13-diazatetradecanediyl)phenyl-*N*,*N*′]platinum(II) Iodide (6).[1a] Compound 4 (1 mmol) in diethyl ether (10 mL) was allowed to react with *n*-Buli (0.8 mL of a 1.25 M solution in hexane) at –56 °C to give a clear yellow solution after reaching room temperature. This solution was added to a stirred suspension of $[PtCl_2(SEt_2)_2]$ (0.7

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Table I. Crystal Data and Details of the Structure Determination of 6

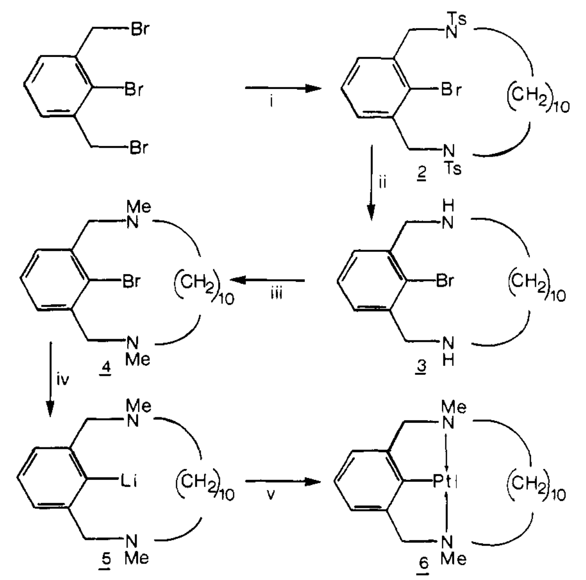
a. Crystal Data	
formula	$C_{20}H_{33}N_2IPt$
mol wt	623.47
space group	*Pbca*
crystal system	orthorhombic
a/Å	15.533 (2)
b/Å	25.630 (3)
c/Å	10.671 (1)
V/Å^3	4248 (1)
D(calcd)/g cm^{-1}	1.95
Z	8
F(000)/electrons	2384
μ(Mo Kα)/cm^{-1}	81.2
crystal size/mm	0.30 × 0.30 × 0.13
b. Data Collection	
θ min, max	1.1, 25.0
radiation/Å	Mo Kα, λ = 0.71069
ref reflctns	021
total reflctns data	4190
total unique reflctns	4190
obsd data ($I > 2.5\sigma(I)$)	2291
c. Refinement	
no. of refined parameters	107
weighting scheme	$w = (4.3 + 0.032F_o^2)^{-1}$
final R_F and R_{wF}	0.040 and 0.092

mmol, 312.2 mg) in diethyl ether (10 mL). After 5 min a white solid formed. Then the reaction mixture was stirred for another 3 h. The ether was evaporated, and acetone was added to the white residue followed by an excess of NaI (10 mmol, 1.5 g). The resulting mixture was stirred for 19 h and then evaporated. The off-white solid was washed with hexane (3 × 5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined yellow CH_2Cl_2 extracts were reduced in volume to 3 mL followed by addition of hexane (10 mL). The resulting light yellow precipitate was filtered off and dried in vacuo: yield 50%. The product was recrystallized from CH_2Cl_2/hexane. ^1H NMR (C_6D_6): δ 1.18 (br m, 2 H), 1.38 (br m, 4 H), 1.65 (br m, 6 H), 2.03 (br m, 2 H), 2.30 (br m, 2 H), 2.54 (br m, 2 H), 3.10 (br m, 2 H), 2.93 (s, 6 H, $^3J(^{195}Pt-^1H)$ = 37 Hz), 3.24 and 3.56 (AB pattern, ^2J(H-H) = 15 Hz, $^3J(^{195}Pt-^1H)$ = 46 Hz), 6.63 (d, 2 H), 7.08 (t, 1 H) (AB_2 pattern, J = 7.5 Hz). Anal. Calcd for $C_{20}H_{33}N_2PtI$: C, 38.53; H, 5.34; N, 4.49. Found: C, 38.10; H, 5.47; N, 4.18.

Data Collection and Structure Determination of 6.[12a] Crystals of 6 are orthorhombic, space group *Pbca*, with eight molecules in a unit cell of dimensions a = 15.533 (2) Å, b = 25.630 (3) Å, c = 10.671 (1) Å, V = 4248 (1) Å, D(calcd) = 1.95 g cm^{-3}, F(000) = 2384, and μ(Mo Kα) = 81.2 cm^{-1}; crystal dimensions 0.30 × 0.30 × 0.13 mm. From the total of 4190 reflections measured on a Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation, 1899 reflections were less than $2.5\sigma(I)$ and were treated as unobserved. The positions of Pt and I were derived from an E^2 Patterson synthesis, and the remaining non-hydrogen atoms were found from subsequent ΔF syntheses. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied.[12b]

Continued refinement, anisotropic for Pt and I and isotropic for C and N, converged to R = 0.040. The H atoms were introduced at their calculated positions and not refined. A weighting scheme, $w = (4.3 + 0.032F_o^2)^{-1}$, was applied.[12c] The anomalous dispersion of Pt and I was taken into account, and an extinction correction was applied.[12d] The programs used were from X-Ray 76.[13] Details concerning the data collection and refinement are given in Table I.

Scheme I



i, in the presence of $TsN(H)(CH_2)_{10}N(H)Ts$, 2.5 equiv of Cs_2CO_3, DMF, 323 K, 4–5 h; ii, detosylation with 45% HBr in glacial acetic acid and phenol, 323 K, 5 h; iii, methylating reaction with formic acid and formaldehyde, 373 K, 19 h; iv, lithiation with n-BuLi; v, in the presence of $[PtCl_2(Et_2S)_2]$, Et_2O, room temperature, followed by reaction with NaI in acetone.

Results and Discussion

Syntheses. The preparation of 2,6-(2,13-dimethyl-2,13-diazatetradecanediyl)phenyl bromide (**4**) followed the route presented in Scheme I. The method using Cs_2CO_3 and dimethylformamide (DMF) is especially useful for the preparation of compounds in which the chain component is mainly of hydrocarbon composition.[10,14] An equimolar amount of Cs_2CO_3 is required for each tosylamide deprotonated: $CsHCO_3$ fails to react further. Reaction times were 4–5 h, and a 55% yield of pure product was obtained after workup. The tosyl groups were removed with hydrogen bromide (45%) in glacial acetic acid after which the resulting HBr salt was neutralized with sodium hydroxide. Formic acid with formaldehyde was used to methylate the amines in an Eschweiler–Clarke reaction. The final product **4** could be obtained as a colorless oil in about 90% yield. The macrocycle **4** is slightly soluble in CCl_4, $CHCl_3$, and CH_2Cl_2 and is sensitive toward CO_2.[15] Products from each step of the synthesis of the ligand as shown in Scheme I have been fully characterized by ^1H NMR, ^{13}C NMR, and mass spectrometry (determination of the exact mass of the parent peak). The preparation of the lithium compound **5** proceeded well when n-butyllithium was used.[16] The light yellow organoplatinum(II) complex **6** was synthesized via the reaction of $[PtCl_2(SEt_2)_2]$ with **5** in diethyl ether, followed by halide exchange with NaI in acetone. Compound **6** is air-stable and soluble in $CHCl_3$, CH_2Cl_2, and C_6H_6.

Molecular Geometry of *trans*-[2,6-(2,13-Dimethyl-2,13-diazatetradecanediyl)phenyl-*N*,*N*′]platinum(II) Iodide (6).[1a] The structure in the solid state of **6** has been established by a single-crystal X-ray structure determi-

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[12] (a) See supplementary material for full data. (b) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158. (c) Cruickshank, D. W. J. In *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*; Pergamon: Oxford 1961; p 41. (d) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

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[15] Solid material is formed: these compounds must be stored under nitrogen atmosphere; see: Blauwhoff, P. W. N.; Versteeg, G. F.; van Swaaij, W. P. M. *Chem. Eng. Soc.* **1984**, *39*, 207.

[16] When lithium shavings are used to lithiate **4**, it is necessary to initiate the reaction with a few drops of freshly distilled MeI. The reaction of **4** with MeLi was unsuccessful; van Beek, J. A. M.; van Koten, G., unpublished results.

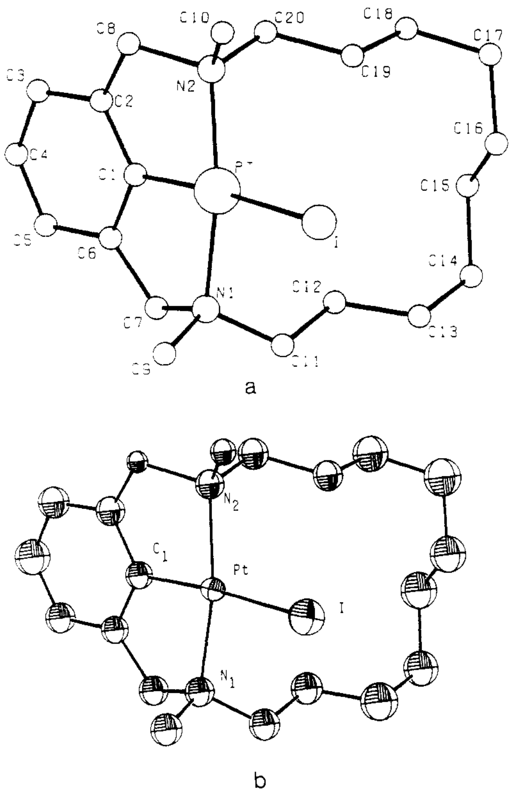

Figure 2. a. PLUTO drawing of the molecular structure of **6**. b. ORTEP drawing of **6** showing the thermal vibration ellipsoids (48% probability).

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for 6

	a. Bond distances		
Pt-I	2.7338 (9)	N(1)-C(11)	1.47 (2)
Pt-N(1)	2.132 (9)	N(2)-C(8)	1.56 (1)
Pt-N(2)	2.09 (1)	N(2)-C(10)	1.47 (1)
Pt-C(1)	1.94 (1)	N(2)-C(20)	1.51 (2)
N(1)-C(7)	1.54 (2)	C(6)-C(7)	1.44 (2)
N(1)-C(9)	1.49 (2)	C(19)-C(20)	1.56 (2)
	b. Bond angles		
I-Pt-N(1)	95.6 (4)	Pt-N(2)-C(8)	107.2 (7)
I-Pt-N(2)	100.0 (3)	Pt-C(1)-C(2)	119.2 (9)
I-Pt-C(1)	173.4 (3)	Pt-C(1)-C(6)	119.5 (9)
N(1)-Pt-N(2)	164.1 (4)	N(1)-C(7)-C(6)	114 (1)
N(1)-Pt-C(1)	81.9 (6)	N(2)-C(8)-C(2)	109 (1)
N(2)-Pt-C(1)	82.8 (6)	N(1)-C(11)-C(12)	115 (1)
Pt-N(1)-C(7)	107.2 (8)	N(2)-C(20)-C(19)	112 (1)
Pt-N(1)-C(9)	108.4 (8)	Pt-N(1)-C(11)	111.8 (8)

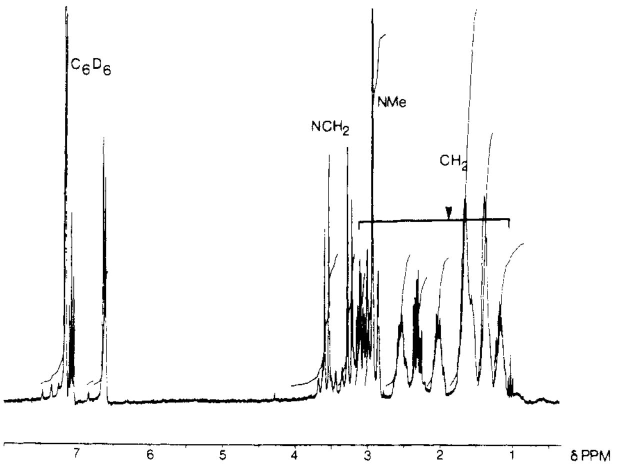

Figure 3. ^{1}H NMR spectrum of complex **6** in C_6D_6 at room temperature.

nation. Crystal data and details of the structure determination and refinement are summarized in Table I. The crystal structure of **6** consists of eight discrete molecules in an orthorhombic unit cell. The molecular geometry of complex **6** along with the adopted numbering scheme is shown in the PLUTO drawing and an ORTEP plot in Figure 2. Interatomic bond distances and angles are listed in Table II.

The four-coordinate platinum center has a distorted square-planar coordination geometry whereby the platinum is bonded to the NCN′ donor atoms of the terdentate macrocycle and the iodine atom. The principal distortion of the geometry results from the N-Pt-N angle of 164.1 (4)°, which is due to the intrinsically small N-Pt-C(1) bite angles of the two neighboring five-membered chelate rings. The puckering in the cyclometalated rings is typical for square-planar and octahedral metal complexes with the NCN′ ligand (see Introduction). As a result of the "twofold axis" type of puckering of the five-membered chelate rings, the N and methyl C atoms are at opposite sides of the plane containing the aryl-Pt portion of the molecule. This conformation is similar to the one found for PtBr(NCN′).[17] As a result of the hydrocarbon chain situated at one side of the coordination plane the iodine atom in **6** is tilted out of this plane [0.41 (4) Å; C(1)-Pt-I = 173.4 (3)°], whereas in PtBr(NCN′) the bromine atom is almost in the coordination plane [0.03 (0) Å; C(1)-Pt-Br = 177.4 (4)°]. The Pt-C distance in **6** and in [PtBr(NCN′)] are 1.94 (1) and 1.90 (1) Å, respectively, which are relatively short compared to such bonds in other organoplatinum(II) compounds (average Pt-phenyl 2.03 Å).[18] The Pt-N distances [Pt-N(1) = 2.132 (9) Å and Pt-N(2) = 2.09 (1) Å] are typical for mutually trans-coordinated N atoms.

Solution Structures. The ^{1}H NMR spectra ($CDCl_3$, 250 MHz) of the free ligand **4** showed a multiplet pattern for the three aryl protons centered at 7.33 ppm. The protons of the hydrocarbon chain were found at high field as broad multiplets in the range 0.83–1.50 and at 2.28 ppm, and the benzylic protons and the NMe protons were found as singlets at 3.63 and 2.42 ppm, respectively. These observations indicate that a single tetrahedral configuration of the N centers in **4** is not maintained on the NMR timescale. At room temperature a fast process occurs involving inversion at N. However, at 233 K this process is slow on the NMR time scale: the methylene groups are indeed observed as diastereotopic as indicated by the observation of an AB pattern for the benzylic protons.[19a]

Evidence for a rigid donor atom–platinum interaction on the NMR time scale in complex **6** comes from the ^{1}H NMR (C_6D_6, 250 MHz) patterns of the prochiral methylenes and the NMe groups. Both resonances show sharp ^{195}Pt ($I = {}^1/_2$, 34% abundance) satellites of significant magnitudes with $^3J(^{195}\text{Pt}-^1\text{H})$ of 46 and 37 Hz, respectively. These values for the $^3J(^{195}\text{Pt}-^1\text{H})$ are characteristic for

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[18] (a) Gee, R. J. D.; Powell, H. M. *J. Chem. Soc. A* 1971, 1956. (b) Crociani, B.; Clemente, D. A.; Bandoli, G. *J. Organomet. Chem.* **1973**, *49*, 249. (c) Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevato, V.; Romeo, R.; Belluco, U. *Inorg. Chim. Acta* **1978**, *31*, 171.

[19] (a) Earlier studies have shown that at 183 K the inversion of configuration at N in $C_6H_5CH(Me)NMe_2$-2-(*S*) is still fast on the NMR time scale. Slow or blocked inversion would render the NMe groups diastereotopic because of the neighboring stereogenic benzylic center: van der Ploeg, A. F. M. J.; van der Kolk, C. E. M.; van Koten, G. *J. Organomet. Chem.* **1981**, *212*, 283. (b) Cf. van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021. van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Verhoeckx, G. J.; Spek, A. L.; Kroon, J. *J. Chem. Soc., Dalton Trans.* **1980**, 1352.

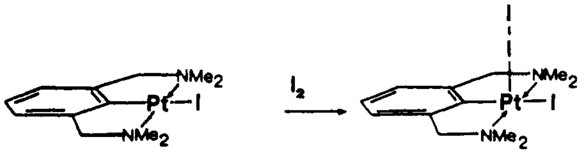
trans positioned N atoms bonded to Pt^{II}.[20] The benzylic protons of **6** (Figure 3) are diastereotopic and appear as an AB pattern at 3.56 and 3.24 ppm, which establishes that in **6** the N atoms are stereogenic centers with a stable configuration. This stability arises from the strong Pt–N coordination, which blocks efficiently the inversion process at the N centers. It is interesting to note that Figure 2 shows clearly that in the solid state the NMe groups take different positions, i.e., one axial and one equatorial. Down to a temperature of 223 K only one singlet is observed for these methyl groups, which indicates that the axial/equatorial exchange process is still fast on the NMR time scale. The possibility of accidentally equivalent chemical shifts is excluded by the observation that decoalescence of both the methyl singlet and the single AB pattern of the benzylic protons occurs at lower temperatures. Below 203 K (in CD_2Cl_2) two singlets (at δ 3.12 and 3.00) appear for the NMe protons. The AB pattern of the benzylic protons decoalesces below 173 K into two AB patterns (δ 4.47, 3.78 and 4.10, 3.54 with ^2J(H–H) of 14 and 13 Hz, respectively). These observations are in line with a process involving inversion of the five-membered chelate ring conformations by oscillation of the aryl plane about the C(4)C(1)Pt axis.[19] A reason for the fact that also the two benzylic CH_2 groups become nonequivalent in the slow-exchange limit is revealed by Figure 2a and more schematically by the Newman projection along the IPtC(1) axis in Figure 1c. These figures show that the macrocyclic ring including the $(CH_2)_{10}$ chain and the N–Pt–N unit is dissymmetric when the ring inversion process is blocked on the NMR time scale. At the fast-exchange limit this process creates an apparent molecular symmetry plane which contains the IPtC(1)C(4) axis and is perpendicular to the N–Pt–N axis, thus causing coalescence of the NMe and NCH_2 resonances.

The assignment of the remaining part of the ^{1}H NMR spectrum (C_6D_6, 250 MHz) of **6** is straightforward through the use of homodinuclear decoupling techniques. The aryl protons show an AB_2 multiplet at 7.08 and 6.63 ppm with a relative intensity ratio of 1:2 and ^3J(H–H) = 7.5 Hz. The methylene protons of the hydrocarbon chain, which are directly bonded to the N atoms, appear as multiplets at 3.10 and 2.54 ppm, whereas the other CH_2 protons were found as broad signals in the range 1.18–2.30 ppm.

From the above results it can be concluded that the novel macrocyclic carbodiaza ligand **4** can be bonded as a monoanionic terdentate ligand to Pt(II) via a σ Pt–C(ipso) bond. The structure of this novel organometallic cage compound in the solid state as well as in solution comprises an inert Pt–N coordination leading to N centers with a stable configuration.

The results of recent studies indicate that it is very interesting to establish the requirements which the hydrocarbon chain must fulfill in order to influence or steer reactions taking place at the metal center. It can be anticipated that processes, which involve occupation of additional coordination sites at the metal, e.g., during a change in the formal oxidation state of the metal as in oxidative addition processes, will be particularly sensitive to the properties of such α,ω chains interconnecting the N-donor atoms. Furthermore, it is interesting to compare these results with those obtained for the parent compounds $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$, which are known to give rise to compounds with unusual reactivity (see Introduction).

A striking example of the latter point is the similarity of the reactivity toward iodine of $[PtI\{C_6H_5\text{-}(CH_2NMe_2)_2\text{-}o,o'\}]$ (**7**) and of the novel organometallic cage compound **6** presented here. In both cases it is not the formation of the expected platinum(IV) oxidative addition product that has been observed. Instead unique examples of η^1-coordination of the highly reactive iodine molecule to the respective Pt(II) centers in these compounds were isolated, which is shown for the reaction of **7** with iodine in eq 1.[21] The structure in the solid state of the η^1-iodine complex of **7**, which contains a linear Pt–I–I arrangement, was reported recently.[21] Further comparative studies are now underway of reactions of these species with other electrophiles.



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Registry No. **2**, 104779-46-6; **3**, 104779-47-7; **4**, 104779-48-8; **5**, 104779-49-9; **6**, 104779-50-2; $TsN(H)(CH_2)_{10}N(H)Ts$, 79130-37-3; $[PtCl_2(Et_2S)_2]$, 14873-92-8; 2-bromo-1,3-bis(bromomethyl)benzene, 25006-88-6.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and all bond distances and angles (8 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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