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Synthesis of Cyclometalated (8-Methoxynaphthyl)- and {8-(Dimethylamino)naphthyl}platinum Compounds and Their Reactivity toward Electrophiles. X-ray Molecular Structures of Square-Planar (8-Methoxynaphthyl)platinum(II) Chloride Bis(diethyl sulfide) and Bis(8-methoxynaphthyl)platinum(II) Diethyl Sulfide and Octahedral *fac*-Bis(8-methoxynaphthyl)methylplatinum(IV) Iodide

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The syntheses and characterization (^{1}H NMR and FD mass spectroscopy) of cyclometalated platinum complexes containing 8-methoxynaphthyl and 8-(dimethylamino)naphthyl groups are described. Both mono- and disubstituted naphthylplatinum derivatives were prepared from the reactions of lithiated naphthyl compounds with either $[PtCl_2(Et_2S)_2]$ or $[PtCl_2(COD)]$ in various stoichiometries (Schemes I and II). Reaction of the new compounds with electrophiles (methyl iodide and iodine) smoothly affords Pt(IV) oxidative-addition products whose stereochemistry is dependent on the nature of the cyclometalated ligand and the electrophile (Scheme III). From the reaction with iodine trans iodide products were always isolated, though in the case of bis(8-methoxynaphthyl)platinum(II) diethyl sulfide the cis isomer was also identified in the reaction mixture by ^{1}H NMR. With methyl iodide the N-metallacycles gave trans products, whereas the O-metallacycles afforded exclusively the cis product *fac*-bis(8-methoxynaphthyl)methylplatinum(IV) iodide (**15**). Other stereoisomers could not be detected in the reaction mixture. For (8-methoxynaphthyl)platinum(II) chloride bis(diethyl sulfide) (**6**) and bis(8-methoxynaphthyl)platinum(II) diethyl sulfide (**7**) the X-ray crystal structures were determined and these show square-planar coordination geometry around platinum for both **6** and **7** (**6**, monoclinic, $P2_1/c$, a = 8.035 (3) Å, b = 16.277 (4) Å, c = 16.926 (3) Å, β = 103.77 (2)°, Z = 4; **7**, monoclinic, $P2_1/n$, a = 9.298 (5) Å, b = 21.107 (4) Å, c = 11.677 (6) Å, β = 92.62 (3)°, Z = 4). In **6** the methoxy substituent does not coordinate to platinum, whereas **7** contains one coordinated and one uncoordinated methoxy substituent. The X-ray structure of **15** confirmed the cis arrangement of the methyl and iodide ligands (monoclinic, $P2_1/n$, a = 10.931 (3) Å, b = 24.167 (6) Å, c = 18.301 (3) Å, β = 91.67 (2)°, Z = 8).

Introduction

Cyclometalated organoplatinum and particularly organopalladium compounds have been extensively studied because of their potential utility in organic synthesis; several reviews on their synthesis and characterization have appeared[2] as well as one concerning their organic chemistry.[3]

Whereas reaction of organopalladated compounds with electrophiles often leads to cleavage of the palladium–carbon bond and formation of a coupling product, reaction of analogous platinum compounds generally yields a Pt(IV) species.[4] In studies concerning the mechanistic aspects of the oxidative-addition reactions, those involving alkyl iodide and halogens have in particular attracted much interest. Some notable complexes that are models for the reactive, transient intermediates formed in these reactions are *fac*-$[Me_3Pt(CD_3CN)(SMe_2)_2]I$,[5b] $[\{MeC_6H_3(CH_2NMe_2)_2\}PtI]^+BF_4^-$,[6c] and $[\{C_6H_3(CH_2NMe_2)_2\text{-}o,o\}Pt(I)(\eta^1\text{-}I_2)]$.[6d] Isolation of the last two and recent calculations by Hoffmann et al. on the formation of the second of these, the ionic arenonium Pt(II) species, have provided further insights into the oxidative-addition reaction,[7] though many mechanistic aspects remain a point of discussion.[5]

During our investigations of N-metallacycles[6] corresponding cyclometalated Pt and Pd compounds with O substituents were also synthesized.[8,9] O substituents should have a much lower affinity toward Pt and Pd than their N-substituent counterparts, i.e. much weaker coordination. This was confirmed both by the fluxional behavior of the various O-chelated compounds prepared and by the easy replacement of the intramolecular O coordination by external ligands such as CO.[9] This behavior prompted us to study the reactivity of related {8-(dimethylamino)naphthyl}- and (8-methoxynaphthyl)platinum(II) derivatives toward electrophilic reagents (MeI and I_2). The results, reported in this paper, are used to compare the effect of N vs O coordination and to determine the influence exerted by the fixed stereochemistry of the C and N or O donor atoms in the naphthyl ligands on the course of these reactions.

Experimental Section

Syntheses were conducted using standard Schlenk techniques under an atmosphere of purified nitrogen. The solvents were dried prior to use. $[Li(DMAN)Et_2O]$[10] (DMAN = 8-(dimethylamino)naphthyl), $[PtCl_2(Et_2S)_2]$,[11] $PtCl_2(COD)$[12] (COD = 1,5-cyclooctadiene), Li(DMBA)[13]

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(DMBA = 2-{(dimethylamino)methyl}phenyl), Li(MXN)[9] (MXN = 8-methoxynaphthyl), and $[(MXN)_2Pt(Et_2S)]$[9] (7) were prepared by literature methods.

^1H NMR spectra were obtained on Bruker AC 100, Bruker SY 200, and Bruker WM 250 spectrometers (see Table V). The field desorption (FD) mass spectra were obtained with a Varian MAT 711 double-focusing mass spectrometer with a combined EI/FI/FD source. Tungsten-wire FD emitters (10 μm) containing carbon microneedles with an average length of 30 μm were used. The samples were dissolved in chloroform and the solutions then loaded onto the emitter with the dipping technique. The emitter currents used to desorb the samples are given in parentheses. The ion source temperature was generally 80 °C.[14] Elemental analyses were obtained from the Elemental Analyses section of ITC, Zeist, The Netherlands, and from the Service de Microanalyses du CNRS, Lyon, France.

Synthesis of Bis{8-(dimethylamino)naphthyl}platinum (3). To a suspension of 1.00 g of $[Li(DMAN)Et_2O]$ (4 mmol) in 100 mL of diethyl ether was added 750 mg of $[PtCl_2(COD)]$ (2 mmol). The white suspension was stirred for 24 h and then evaporated to dryness and the residue subsequently extracted with $CHCl_3$ (200 mL). Evaporation of the $CHCl_3$ afforded a yellowish solid, which was washed twice with diethyl ether (15 mL) and then dried in vacuo to afford **3**, as an off-white powder, yield 850 mg (80%). Anal. Calcd for $C_{24}H_{24}N_2Pt$: C, 53.83; H, 4.49; N, 5.23. Found: C, 53.61; H, 4.46; N, 5.09. FD-MS ($CHCl_3$, 5 mA): *m/z* 535 (M_r = 535).

Synthesis of {8-(Dimethylamino)naphthyl}platinum Chloride Diethyl Sulfide (4). A solution of 800 mg of $[PtCl_2(Et_2S)_2]$ (1.8 mmol) in toluene (20 mL) was added to a solution of 480 mg of $[Li(DMAN)Et_2O]$ (1.8 mmol) in toluene (20 mL) at −30 °C. The temperature of the reaction mixture was slowly raised to 25 °C, followed by stirring the white suspension for another 1.5 h. The solvent was removed in vacuo and the residue extracted with 100 mL of $CHCl_3$. Removing the $CHCl_3$ in vacuo and washing the residue with hexane afforded **4** as a white powder, yield 0.8 g (85%). Anal. Calcd for $C_{26}H_{22}ClNSPt$: C, 39.14; H, 4.53; N, 2.85; Cl, 7.22. Found: C, 39.05; H, 4.53; N, 2.77; Cl, 7.38. FD-MS ($CHCl_3$, 9 mA): *m/z* 491 (M_r = 490).

Synthesis of [2-{(Dimethylamino)methyl}phenyl]{8-(dimethylamino)-naphthyl}platinum (5). To a suspension of $[(DMAN)PtCl(Et_2S)]$ (250 mg, 0.5 mmol) in diethyl ether (50 mL) was added [Li(DMBA)] (70 mg, 0.5 mmol) dissolved in THF (5 mL). After the suspension was stirred for 24 h, the solvent was removed in vacuo and the resulting residue was extracted with $CHCl_3$. Evaporating the $CHCl_3$ and washing the residue with 10 mL of hexane afforded **5** as a white solid, which was dried in vacuo; yield 175 mg (70%). Anal. Calcd for $C_{21}H_{24}N_2Pt$: C, 50.49; H, 4.85; N, 5.61. Found: C, 50.31; H, 4.82; N, 5.43. FD-MS ($CHCl_3$, 0 mA): *m/z* 499 (M_r = 499).

Synthesis of (8-Methoxynaphthyl)platinum Chloride Bis(diethyl sulfide) (6). A solution of 200 mg of [Li(MXN)] (1.21 mmol) in THF (50 mL) was added to 400 mg of $[PtCl_2(Et_2S)_2]$ (1.03 mmol) in THF (20 mL) at 0 °C. The resulting orange solution was filtered through a column of alumina (dimension 5 cm × 10 cm) and subsequently evaporated to dryness. The orange residue was recrystallized from THF (10 mL)/pentane (20 mL) at −20 °C, affording 0.085 g of yellow-orange $[(MXN)PtCl(Et_2S)_2]$ (**6**), yield 15%. Anal. Calcd for $C_{19}H_{10}OClS_2Pt$: C, 40.17; H, 5.11. Found: C, 41.00; H, 5.06.

Synthesis of Bis(8-methoxynaphthyl)platinum (8). To a solution of 200 mg of $[(MXN)_2Pt(Et_2S)]$ (**7**; 0.33 mmol) in toluene (10 mL) was added 1 mL of benzonitrile. The solution was stirred for 24 h, after which time the solvent was carefully removed in vacuo. The residue thus obtained was dissolved in THF (15 mL) to which pentane (45 mL) was added, affording 130 mg of a yellow crystalline precipitate of $[(MXN)_2Pt]$ (**8**), which was separated by filtration, washed with pentane (2 × 15 mL), and dried in vacuo; yield 76%. Anal. Calcd for $C_{22}H_{18}O_2Pt$: C, 51.85; H, 3.53. Found: C, 51.61; H, 3.75.

Synthesis of [2-{(Dimethylamino)methyl}phenyl]platinum Chloride Diethyl Sulfide (9). [Li(DMBA)] (130 mg, 1 mmol) was dissolved in THF (10 mL), and this solution was slowly added to a solution of $[PtCl_2(Et_2S)_2]$ (446 mg, 1 mmol) in diethyl ether (75 mL) at −30 °C. The reaction mixture was allowed to warm slowly to 25 °C, and the resulting white suspension was stirred for 1.5 h. The residue obtained by removal of the solvent in vacuo was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ gave rise to an oily residue, which solidified upon the addition of diethyl ether (5 mL). Filtering the suspension followed by drying in vacuo afforded **9** as a pale gray solid, yield 100 mg (22%). Anal. Calcd for $C_{13}H_{22}NClSPt$: C, 34.32; H, 4.88; N, 3.08; Cl, 7.79. Found: C, 33.98; H, 5.01; N, 3.00; Cl, 8.26. FD-MS ($CHCl_3$, 0 mA): *m/z* 454 (M_r = 454).

Synthesis of Bis{8-(dimethylamino)naphthyl}platinum Diiodide (10). To a solution of 200 mg of $[(DMAN)_2Pt]$ (**3**; 0.37 mmol) in $CHCl_3$ (15 mL) was added 100 mg of I_2 (0.39 mmol) dissolved in $CHCl_3$ (5 mL). The solution was left overnight without stirring, affording an orange solid. The supernatant liquid was decanted and the residue washed with two portions of hexane (15 mL each) and then dried in vacuo; yield 250 mg of orange **10** (85%). Anal. Calcd for $C_{24}H_{24}N_2PtI_2$: C, 36.51; H, 3.07; N, 3.35. Found: C, 36.45; H, 2.97; N, 3.34. FD-MS ($CHCl_3$, 20 mA): *m/z* 789 (M_r = 789).

Synthesis of [2-{(Dimethylamino)methyl}phenyl]{8-(dimethylamino)-naphthyl}platinum Diiodide (11). The reaction of [(DMAN)(DMBA)Pt] (**5**) and I_2 was conducted by the above procedure for $[(DMAN)_2Pt(I)_2]$, affording 80% of orange **11**. Anal. Calcd for $C_{21}H_{24}N_2I_2Pt$: C, 33.48; H, 3.22; N, 3.72. Found: C, 33.52; H, 3.04; N, 3.47. FD-MS ($CHCl_3$, 20 mA): *m/z* 752 (M_r = 752).

Synthesis of *fac*-[2-{(Dimethylamino)methyl}phenyl]{8-(dimethylamino)naphthyl}methylplatinum Iodide (12). To a solution of 200 mg of [(DMAN)(DMBA)Pt] (**5**; 0.40 mmol) in $CHCl_3$ (10 mL) was added 50 μL of MeI (0.80 mmol) with a microsyringe. The solution was left overnight without stirring. The resulting white solid **12** was separated by decanting the supernatant liquid, washed with two portions of hexane (15 mL each), and then dried in vacuo; yield 180 mg (70%). Anal. Calcd for $C_{22}H_{27}N_2IPt$: C, 41.19; H, 4.25; N, 4.37. Found: C, 40.87; H, 4.00; N, 3.59. FD-MS ($CHCl_3$, 0 mA): *m/z* 640 (M_r = 641).

Synthesis of *fac*-Bis{8-(dimethylamino)naphthyl}methylplatinum Iodide (13). To a solution of 200 mg of $[(DMAN)_2Pt]$ (**3**; 0.37 mmol) in $CHCl_3$ (5 mL) was added acetone until **3** started to precipitate, and a small amount of $CHCl_3$ was then added to regain a clear solution. To this solution was added 25 μL of MeI (0.37 mmol) by means of a microsyringe. The solution was left overnight without stirring. The supernatant liquid was decanted from the white solid, which was washed with two portions of hexane (15 mL each) and dried in vacuo. This afforded 200 mg of **13**, yield 80%. Anal. Calcd for $C_{25}H_{25}N_2PtI$: C, 44.32; H, 4.02; N, 4.14. Found: C, 44.31; H, 4.21; N, 4.14.

Synthesis of Bis(8-methoxynaphthyl)platinum Diiodide (14). To a solution of 500 mg of $[(MXN)_2Pt(Et_2S)]$ (**7**; 0.08 mmol) in toluene (8 mL) was added 250 mg of I_2 (0.1 mmol), and this mixture was stirred for 10 min. The resulting orange precipitate was filtered, washed with pentane (10 mL), and dried in vacuo; yield 400 mg of orange **14** (60%). Anal. Calcd for $C_{22}H_{18}O_2I_2Pt$: C, 34.60; H, 2.36. Found: C, 34.99; H, 2.34.

Synthesis of Bis(8-methoxynaphthyl)methylplatinum Iodide (15). To a solution of $[(MXN)_2Pt(Et_2S)]$ (**7**; 300 mg, 0.5 mmol) in toluene (20 mL) was added 60 μL of MeI (1 mmol) with a microsyringe. The solution was stirred for 10 min, and subsequently the white precipitate was filtered. The solid was washed with pentane (15 mL) and then dried in vacuo to afford 230 mg of **15** (70%). Anal. Calcd for $C_{23}H_{21}O_2IPt$: C, 42.39; H, 3.22. Found: C, 42.20; H, 3.10.

Synthesis of Acetylbis(8-methoxynaphthyl)platinum Chloride (16). To a solution of 540 mg of $[(MXN)_2Pt(Et_2S)]$ (**7**; 0.9 mmol) in toluene (5 mL) was added 0.2 mL of CH_3COCl (2.7 mmol). After 10 min, a white precipitate formed and this was filtered and washed with pentane (10 mL). Drying in vacuo afforded 350 mg of white **16** (60%). Anal. Calcd for $C_{24}H_{21}O_3ClPt$: C, 49.01; H, 3.57. Found: C, 49.48; H, 3.69.

X-ray Structure Determination and Refinement of 6, 7, and 15. Crystal data and numerical details of the structure determination of **6**, **7**, and **15** are collected in Table I. X-ray data were collected on an Enraf-Nonius CAD4F diffractometer (θ_{max} = 25°; Mo Kα (Zr-filtered) radiation, λ = 0.71073 Å) for pale brownish crystals mounted on a glass fiber. Lattice parameters with standard deviations were determined from least-squares treatment of the setting angles of 13 reflections in the range $11 < \theta < 14°$ for **6**, 21 reflections in the range 5–15° for **7**, and 19 reflections in the range $7 < \theta < 12°$ for **15**. The space groups were derived from observed extinctions. The data were corrected for linear decay and Lp effects. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the variance of the reference reflections:[15] $\sigma^2(I) = \sigma^2_{cs}(I) + (PI)^2$. The structures were solved by Patterson and Fourier techniques (SHELXS84).[16] Empirical absorption

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Table I. Crystal Data and Details of the Structure Determination for **6**, **7**, and **15**

	6	**7**	**15**
	(a) Crystal Data		
empirical formula	$C_{19}H_{29}ClOPtS_2$	$C_{26}H_{28}O_2PtS$	$C_{23}H_{21}IO_2Pt\cdot{}^3/_4CDCl_3$
mol wt	568.09	599.64	741.68
cryst syst	monoclinic-*b*	monoclinic-*b*	monoclinic-*b*
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	8.035 (3)	9.298 (5)	10.931 (3)
b, Å	16.277 (4)	21.107 (4)	24.167 (6)
c, Å	16.926 (3)	11.677 (6)	18.301 (3)
β, deg	103.77 (2)	92.62 (3)	91.67 (2)
V, Å^3	2150 (1)	2289 (2)	4833 (2)
Z	4	4	8
D(calc), g/cm^3	1.755	1.740	2.038
F(000), e	1112	1176	2796
μ(Mo K*α*), cm^{-1}	69.1	63.0	73.6
cryst size, mm	0.30 × 0.38 × 0.50	0.23 × 0.25 × 0.53	0.20 × 0.25 × 0.80
	(b) Structure Determination		
no. of reflns	3012	3290	4559
no. of params	233	284	556
R^a	0.0307	0.0296	0.054
$R_w{}^a$	0.0266	0.0338	0.041
w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$	$\sigma^2(F)$
S	2.36	2.38	6.72
$(\Delta/\sigma)_{av}$	0.1	0.1	0.1
min and max dens, e/Å^3	−1.00, 0.78	−1.37, 1.12	−1.09, 1.14

[a] $R = \sum(F_o - |F_c|)/\sum F_o$; $R_w = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$.

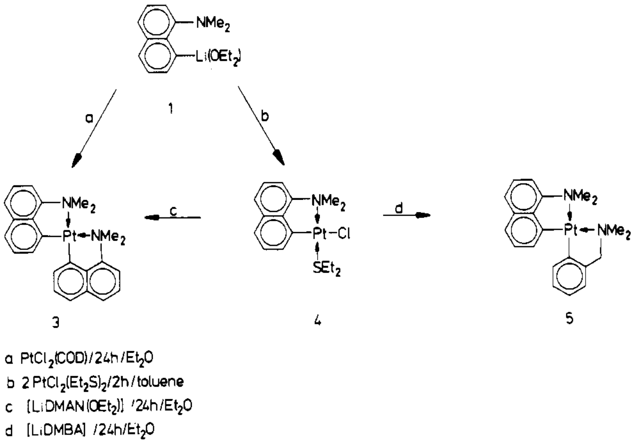
Table II. Final Positional Parameters for the Non-Hydrogen Atoms of **6** and Equivalent Isotropic Temperature Factors[a]

atom	*x*	*y*	*z*	*U*(eq), Å^2
Pt	0.06225 (3)	0.16875 (2)	0.26917 (1)	0.0356 (1)
Cl	0.2843 (2)	0.1038 (1)	0.3686 (1)	0.0539 (6)
S(1)	0.2218 (2)	0.1862 (1)	0.1751 (1)	0.0532 (6)
S(2)	−0.1268 (2)	0.1535 (1)	0.3497 (1)	0.0502 (6)
O	−0.1180 (6)	0.0605 (3)	0.1474 (3)	0.063 (2)
C(1)	−0.1236 (8)	0.2292 (4)	0.1888 (4)	0.043 (2)
C(2)	−0.142 (1)	0.3121 (4)	0.2037 (4)	0.059 (2)
C(3)	−0.262 (1)	0.3606 (5)	0.1470 (5)	0.067 (2)
C(4)	−0.3587 (9)	0.3276 (5)	0.0784 (4)	0.061 (2)
C(5)	−0.3446 (8)	0.2439 (5)	0.0606 (4)	0.047 (2)
C(6)	−0.448 (1)	0.2115 (6)	−0.0113 (4)	0.072 (2)
C(7)	−0.434 (1)	0.1312 (6)	−0.0281 (5)	0.088 (2)
C(8)	−0.323 (1)	0.0778 (5)	0.0227 (4)	0.070 (2)
C(9)	−0.2225 (9)	0.1094 (4)	0.0934 (4)	0.048 (2)
C(10)	−0.2271 (7)	0.1945 (4)	0.1154 (3)	0.033 (2)
C(11)	−0.083 (1)	−0.0189 (5)	0.1267 (5)	0.098 (2)
C(12)	0.274 (1)	0.2916 (5)	0.1738 (5)	0.090 (2)
C(13)	0.374 (1)	0.3251 (5)	0.2543 (5)	0.102 (2)
C(14)	0.4278 (9)	0.1360 (6)	0.2063 (5)	0.091 (2)
C(15)	0.409 (1)	0.0471 (6)	0.1864 (5)	0.114 (2)
C(16)	−0.1288 (9)	0.0426 (4)	0.3690 (4)	0.065 (2)
C(17)	−0.2527 (9)	0.0189 (5)	0.4195 (4)	0.082 (2)
C(18)	−0.0190 (9)	0.1915 (4)	0.4496 (4)	0.057 (2)
C(19)	0.011 (1)	0.2828 (5)	0.4450 (4)	0.078 (2)

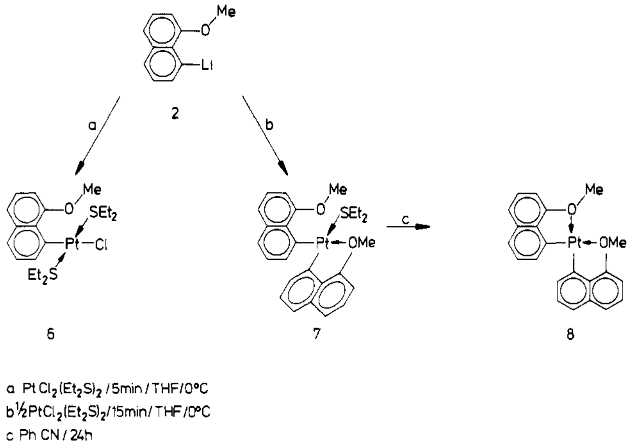
[a] In this and the following tables the number in parentheses is the estimated standard deviation in the least significant digit. U_{eq} = one-third of the trace of the orthogonalized anisotropic temperature factor.

corrections were applied with the Walker and Stuart procedure[17] after isotropic refinement. Hydrogen atoms were introduced at calculated positions (except for those on the disordered $CDCl_3$ in **15**) and refined with fixed geometries (*d*(C–H) = 1.08 Å) with respect to their carrier atoms and one common isotropic thermal parameter. Weights were introduced in the final cycles of blocked full-matrix least-squares refinement on *F* including anisotropic thermal parameters for the non-hydrogen atoms (except for the disordered atoms in the $CDCl_3$ molecules in **15** that were refined with isotropic parameters). The final coordinates of the non-hydrogen atoms are given in Tables II–IV. Scattering factors were taken from ref 18 and 19 and anomalous dispersion corrections from ref 20.

Scheme I. Synthesis of {8-(Dimethylamino)naphthyl}platinum Derivatives



Scheme II. Synthesis of (8-Methoxynaphthyl)platinum Derivatives



The data collection was done with a modified CAD4F software package.[21] The calculations were conducted on an in-house DG-Eclipse S/230 minicomputer using a locally modified SHELX-76[22] implementation

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(17) Walker, N.; Stewart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(18) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

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(21) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

Table III. Final Positional Parameters for the Non-Hydrogen Atoms of **7** and Equivalent Isotropic Temperature Factors

atom	*x*	*y*	*z*	*U*(eq), Å^2
Pt	0.22951 (3)	0.14126 (1)	0.04826 (2)	0.0375 (1)
S	0.0353 (2)	0.15725 (9)	−0.0869 (2)	0.0542 (6)
O(11)	0.1055 (5)	0.0775 (2)	0.1596 (4)	0.060 (1)
O(21)	0.3950 (5)	0.0670 (2)	−0.0985 (4)	0.054 (1)
C(1)	0.0904 (8)	0.1825 (3)	−0.2278 (6)	0.061 (2)
C(2)	0.1374 (9)	0.1273 (4)	−0.2961 (6)	0.075 (2)
C(3)	−0.0475 (8)	0.2312 (4)	−0.0390 (7)	0.071 (2)
C(4)	−0.1357 (8)	0.2184 (5)	0.0620 (7)	0.089 (2)
C(101)	0.3680 (7)	0.1283 (3)	0.1779 (6)	0.043 (2)
C(102)	0.5119 (7)	0.1509 (3)	0.1940 (6)	0.048 (2)
C(103)	0.5957 (8)	0.1408 (4)	0.2952 (6)	0.061 (2)
C(104)	0.5443 (9)	0.1057 (4)	0.3868 (7)	0.067 (2)
C(105)	0.4004 (8)	0.0815 (3)	0.3742 (6)	0.054 (2)
C(106)	0.344 (1)	0.0449 (4)	0.4650 (7)	0.074 (2)
C(107)	0.206 (1)	0.0215 (4)	0.4498 (8)	0.083 (2)
C(108)	0.1247 (9)	0.0300 (4)	0.3498 (7)	0.066 (2)
C(109)	0.1801 (7)	0.0657 (3)	0.2634 (6)	0.047 (2)
C(110)	0.3200 (7)	0.0920 (3)	0.2724 (6)	0.047 (2)
C(111)	−0.0326 (9)	0.0511 (4)	0.1377 (8)	0.090 (2)
C(201)	0.3612 (6)	0.1971 (3)	−0.0334 (5)	0.034 (2)
C(202)	0.3550 (7)	0.2605 (3)	−0.0127 (6)	0.046 (2)
C(203)	0.4471 (7)	0.3049 (3)	−0.0619 (6)	0.055 (2)
C(204)	0.5441 (8)	0.2849 (3)	−0.1367 (6)	0.056 (2)
C(205)	0.5558 (6)	0.2200 (3)	−0.1658 (5)	0.042 (2)
C(206)	0.6579 (7)	0.2007 (4)	−0.2454 (6)	0.055 (2)
C(207)	0.6703 (8)	0.1400 (4)	−0.2726 (7)	0.071 (2)
C(208)	0.5838 (7)	0.0927 (4)	−0.2239 (6)	0.063 (2)
C(209)	0.4835 (7)	0.1102 (3)	−0.1479 (6)	0.048 (2)
C(210)	0.4658 (6)	0.1754 (3)	−0.1134 (5)	0.032 (2)
C(211)	0.4086 (8)	0.0022 (3)	−0.1268 (7)	0.070 (2)

Table IV. Final Positional Parameters for the Non-Hydrogen Atoms of **15** and Equivalent Isotropic Temperature Factors

atom	*x*	*y*	*z*	*U*(eq), Å^2
		Molecule 1		
Pt(1)	0.03497 (5)	0.24802 (3)	0.36129 (3)	0.0387 (2)
I(1)	−0.1298 (1)	0.17221 (5)	0.40504 (7)	0.0729 (5)
O(11)	0.0387 (8)	0.2049 (4)	0.2542 (5)	0.056 (3)
O(21)	0.1973 (8)	0.2055 (4)	0.4090 (6)	0.067 (4)
C(1)	0.025 (1)	0.2897 (6)	0.4570 (7)	0.064 (4)
C(101)	−0.090 (1)	0.2882 (6)	0.3039 (8)	0.045 (4)
C(102)	−0.155 (1)	0.3365 (6)	0.3294 (9)	0.052 (4)
C(103)	−0.247 (1)	0.3582 (7)	0.281 (1)	0.067 (4)
C(104)	−0.272 (1)	0.3342 (8)	0.216 (1)	0.070 (5)
C(105)	−0.215 (1)	0.2869 (8)	0.191 (1)	0.073 (5)
C(106)	−0.246 (1)	0.2604 (8)	0.123 (1)	0.082 (5)
C(107)	−0.181 (2)	0.2164 (8)	0.104 (1)	0.097 (5)
C(108)	−0.087 (1)	0.1950 (8)	0.145 (1)	0.079 (5)
C(109)	−0.056 (1)	0.2202 (7)	0.2103 (8)	0.050 (4)
C(110)	−0.122 (1)	0.2657 (6)	0.2367 (8)	0.050 (4)
C(111)	0.094 (1)	0.1535 (7)	0.2428 (9)	0.075 (5)
C(201)	0.168 (1)	0.3001 (6)	0.3330 (7)	0.036 (4)
C(202)	0.162 (1)	0.3482 (6)	0.2971 (8)	0.045 (4)
C(203)	0.266 (1)	0.3783 (6)	0.2851 (8)	0.057 (4)
C(204)	0.381 (1)	0.3648 (6)	0.3113 (9)	0.056 (4)
C(205)	0.392 (1)	0.3163 (7)	0.3506 (8)	0.043 (4)
C(206)	0.504 (1)	0.2987 (7)	0.3780 (8)	0.055 (4)
C(207)	0.517 (1)	0.2502 (8)	0.4160 (7)	0.058 (4)
C(208)	0.414 (1)	0.2184 (7)	0.4290 (9)	0.068 (4)
C(209)	0.305 (1)	0.2356 (6)	0.4018 (7)	0.045 (4)
C(210)	0.286 (1)	0.2844 (6)	0.3604 (7)	0.042 (4)
C(211)	0.202 (1)	0.1506 (7)	0.4427 (9)	0.080 (4)
		Molecule 2		
Pt(2)	0.53026 (5)	0.05352 (3)	0.17736 (3)	0.0378 (2)
I(2)	0.3623 (1)	0.04078 (5)	0.28348 (6)	0.0642 (5)
O(31)	0.5416 (7)	0.1425 (4)	0.2070 (5)	0.052 (3)
O(41)	0.6900 (8)	0.0275 (4)	0.2480 (5)	0.065 (4)
C(2)	0.512 (1)	−0.0260 (5)	0.1427 (8)	0.054 (4)
C(301)	0.408 (1)	0.0848 (5)	0.1090 (7)	0.037 (4)
C(302)	0.341 (1)	0.0579 (6)	0.0551 (8)	0.046 (4)
C(303)	0.250 (1)	0.0860 (7)	0.0120 (8)	0.058 (4)
C(304)	0.224 (1)	0.1401 (7)	0.0238 (8)	0.061 (4)
C(305)	0.288 (1)	0.1689 (7)	0.0803 (8)	0.052 (4)
C(306)	0.265 (2)	0.2265 (8)	0.099 (1)	0.076 (5)
C(307)	0.329 (2)	0.2519 (8)	0.153 (1)	0.079 (5)
C(308)	0.427 (1)	0.2268 (7)	0.1915 (9)	0.065 (4)
C(309)	0.446 (1)	0.1721 (6)	0.1756 (8)	0.048 (4)
C(310)	0.382 (1)	0.1419 (6)	0.1220 (8)	0.042 (4)
C(311)	0.616 (1)	0.1645 (7)	0.2667 (8)	0.074 (4)
C(401)	0.667 (1)	0.0625 (6)	0.1054 (8)	0.040 (4)
C(402)	0.659 (1)	0.0804 (6)	0.0368 (8)	0.048 (4)
C(403)	0.764 (1)	0.0840 (7)	−0.0047 (9)	0.066 (5)
C(404)	0.874 (1)	0.0663 (7)	0.023 (1)	0.070 (4)
C(405)	0.887 (1)	0.0474 (6)	0.0933 (9)	0.047 (4)
C(406)	1.001 (1)	0.0308 (7)	0.121 (1)	0.069 (4)
C(407)	1.011 (1)	0.0119 (6)	0.192 (1)	0.061 (4)
C(408)	0.909 (1)	0.0102 (7)	0.238 (1)	0.065 (4)
C(409)	0.797 (1)	0.0266 (6)	0.2075 (9)	0.053 (4)
C(410)	0.783 (1)	0.0449 (6)	0.1358 (8)	0.046 (4)
C(411)	0.693 (1)	0.0125 (7)	0.3232 (8)	0.080 (5)

and on the CDC-Cyber/855 computer of the University of Utrecht with programs of the EUCLID package[23] (calculation of geometrical data and preparation of illustrations including an extended version of PLUTO).

Results

Synthesis of the Platinum(II) Compounds.[24] Reaction of either {8-(dimethylamino)naphthyl}lithium (**1**), [Li(DMAN)],[10] or (8-methoxynaphthyl)lithium (**2**), [Li(MXN)], with [PtCl$_2$(Et$_2$S)$_2$] or [PtCl$_2$(COD)] affords a series of new cyclometalated organoplatinum compounds (see Schemes I and II). Their formulation as [(DMAN)$_2$Pt] (**3**), [(DMAN)PtCl(Et$_2$S)] (**4**), [(DMAN)(DMBA)Pt] (**5**), [(MXN)PtCl(Et$_2$S)$_2$] (**6**), [(MXN)$_2$Pt(Et$_2$S)] (**7**), and [(MXN)$_2$Pt] (**8**) was based on their ^{1}H NMR spectra, elemental analyses, and FD mass spectra.[14] For **6** and **7**, the X-ray crystal structures were determined.

The selective formation of monoarylated **4**, [(DMAN)PtCl(Et$_2$S)] (85%), instead of diarylated [(DMAN)$_2$Pt] in the 1:1 reaction of [Li(DMAN)] with [PtCl$_2$(Et$_2$S)$_2$] (Scheme I, reaction b) was unexpected since a second chloride is usually easier to replace than the first one.[25,26] A similar selectivity was found for the formation of [(MXN)PtCl(Et$_2$S)$_2$] (**6**) from the 1:1 molar reaction of [Li(MXN)] with [PtCl$_2$(Et$_2$S)$_2$] (Scheme II, reaction a), though here the yield was rather low (about 15%). In contrast to the case for **4**, in which one diethyl sulfide is replaced by NMe$_2$ coordination to Pt, **6** contains two molecules of coordinated Et$_2$S in addition to the C-bonded 8-methoxynaphthyl ligand and a chlorine atom.

As expected, the remaining chloride in [(DMAN)PtCl(Et$_2$S)] (**4**) can easily be replaced in a subsequent reaction with [Li(DMAN)] by a second DMAN group to afford *cis*-[(DMAN)$_2$Pt] (**3**), which could also be obtained directly from the 2:1 reaction of [Li(DMAN)] with either [PtCl$_2$(Et$_2$S)$_2$] or [PtCl$_2$(COD)]. Mixed diarylated [Pt(DMAN)(DMBA)] (**5**) was synthesized in good yield by reacting **4** with [Li(DMBA)] (Scheme I, reaction d). In the ^{1}H NMR spectra of both **3** and **5**, the $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ value of 14 Hz for the NMe$_2$ signals indicates that the Pt–C bonds are mutually cis (vide infra). A cis configuration is commonly encountered for this kind of compound[27] and arises from the large trans influence of the anionic carbon donor atoms.[28]

The exclusive formation of *cis*-[(DMAN)$_2$Pt] from the 2:1 [Li(DMAN)]/[PtCl$_2$(Et$_2$S)$_2$] reaction contrasts with the mixture

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(23) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon: Oxford, England, 1982; p 528.

(24) Throughout this paper the following abbreviations will be used for the cyclometalated ligands: DMAN = 8-(dimethylamino)naphthyl; MXN = 8-methoxynaphthyl; DMBA = 2-{[(dimethylamino)methyl]phenyl.

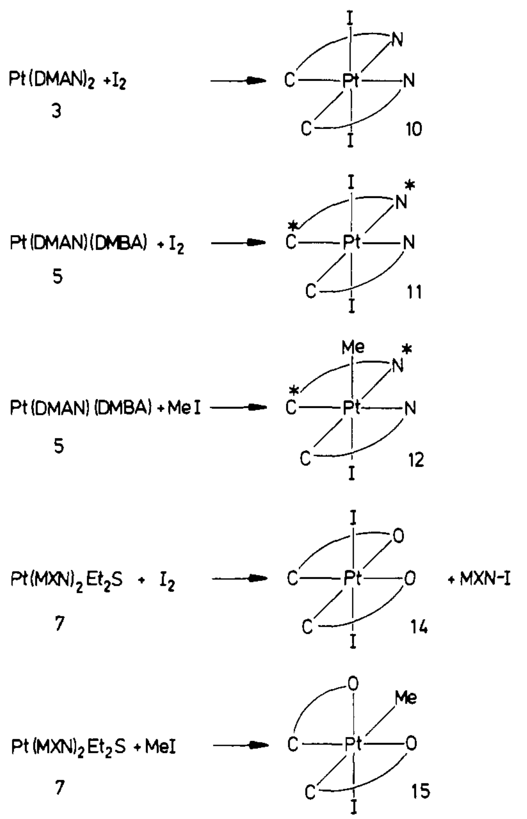
(25) (a) Ertl, J.; Graft, D.; Brune, H. A. *Z. Naturforsch.* **1982**, *37B*, 1082. (b) Bayer, U.; Brune, H. A. *Z. Naturforsch.* **1983**, *38B*, 226.

(26) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501.

(27) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155.

(28) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1981; Vol. 6, Chapter 39, p 471.

Scheme III



of *cis*-$[(MXN)_2Pt(Et_2S)]$ (7) and *trans*-$[(MXN)_2Pt(Et_2S)]$ initially generated from the corresponding 2:1 $[LiMXN]/[PtCl_2(Et_2S)_2]$ reaction.[9] However, in solution *trans*-$[(MXN)_2Pt(Et_2S)]$ isomerized slowly to the cis isomer, 7.

In contrast to the easy formation of mixed MXN/DMAN palladium compounds (e.g. [(DMAN)(MXN)Pd][9]) attempts to synthesize the mixed platinum analogue were unsuccessful; $[(DMAN)PtCl(Et_2S)]$ (4) reacted with [Li(MXN)] to afford the diarylated MXN compound $[(MXN)_2Pt(Et_2S)]$ (7). Further study of this reaction may provide insight into the factors governing the transmetalation reaction between cyclometalated compounds and organolithium species.

Reactions with Electrophiles. Reaction of *cis*-$[(DMAN)_2Pt]$ (3), *cis*-[(DMAN)(DMBA)Pt] (5), and *cis*-$[(MXN)_2Pt(Et_2S)]$ (7) with MeI or I_2 in all cases resulted in oxidative-addition products (see Scheme III), which were characterized by elemental analyses and FD mass spectra.[14] The stereochemistry of the products could, in most cases, be deduced from their ^1H NMR spectra. Since the isolated Pt(IV) products were only sparingly soluble in common organic solvents, their NMR spectra were obtained in situ from a $CDCl_3$ solution of the Pt(II) compound to which a known amount of MeI or I_2 had been added.

Reaction of I_2 with *cis*-$[(DMAN)_2Pt]$ (3) and *cis*-[(DMAN)(DMBA)Pt] (5) in $CHCl_3$ resulted in the formation of orange complexes that were analyzed as $[(DMAN)_2PtI_2]$ (10) and $[(DMAN)(DMBA)PtI_2]$ (11), respectively, in good yield. All the ^1H NMR spectra show, compared to the spectra of the Pt(II) starting materials, a downfield shift of the single NMe_2 signal and a decrease of $^3J(^{195}Pt,^1H)$ from 14 to 11 Hz for these signals. These data indicate that Pt(II) to Pt(IV) oxidation has occurred[29] and, since a *cis*-diiodide product would give rise to diastereotopic NMe_2 signals, that the product formed has a *trans*-I_2 geometry.

$[(MXN)_2Pt(Et_2S)]$ was treated with I_2 in toluene to afford an orange precipitate of *trans*-$[(MXN)_2PtI_2]$ (14), whose ^1H NMR spectrum shows only one signal for the OMe groups. This geometry is confirmed by the absence of an upfield-shifted H(2) naphthyl group proton, a feature that is characteristic for a cis addition product where H(2) is positioned in the shielding region of a second, perpendicularly positioned, naphthyl ring (vide infra). As in the case of 7, the OMe signal did not show $^3J(^{195}Pt,^1H)$. Finally, it is worth noting that during the oxidative reaction in which $[(MXN)_2PtI_2]$ was formed, partial reductive elimination of this product to (MXN)I and PtI_2 with liberation of Et_2S also occurred. Evaporation of the mother liquor afforded a dark oil whose ^1H NMR spectrum suggests the presence of a cis addition product. However, until now this product, which will be the subject of further investigations,[30] could not be isolated in a pure form.

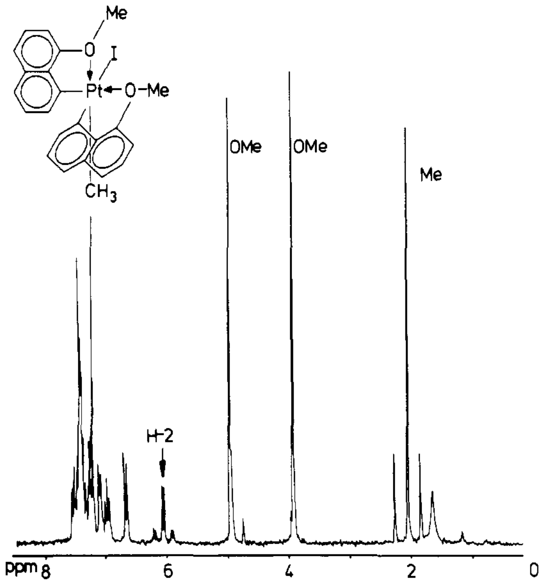


Figure 1. ^1H NMR spectrum (200 MHz) of $[(MXN)_2MePtI]$ (15; $CDCl_3$, room temperature).

Compared to I_2, methyl iodide and acetyl chloride show a different reactivity pattern with $[(MXN)_2Pt(Et_2S)]$ (7) and they afford white solids (in ca. 70% yield) that are sparingly soluble in common organic solvents. Elemental analysis of these products indicated $[(MXN)_2MePtI]$ (15) and $[(MXN)_2(MeCO)PtCl]$ (16) stoichiometries, respectively. The ^1H NMR spectra showed two OMe signals, indicating a molecule with a dissymmetric structure that does not have the Me or MeCO group trans to the halide. Furthermore, the spectra showed a very characteristic, high-field shift of the H(2) naphthyl proton at 6.10 ppm ($^3J(^{195}Pt,^1H)$ = 56 Hz) for 15 and 6.51 ppm ($^3J(^{195}Pt,^1H)$ = 58 Hz) for 16 (see Figure 1). This shift can be explained by a shielding of this proton as a result of being placed in the shielding cone of the second naphthyl group. These NMR data suggest that 15 and 16 have a cis arrangement for the carbon and halogen ligand of the electrophile and are therefore *fac*-$[(MXN)_2MePtI]$ and *fac*-$[(MXN)_2(MeCO)PtCl]$, respectively. Since only one resonance pattern is observed for the two naphthyl groups, these compounds appear to be formed in only one isomeric form, though each reaction could, in principle, afford 11 stereoisomers, of which 5 are enantiomeric pairs.[31]

Reaction of the N-metallocycle [(DMAN)(DMBA)Pt] (5) with MeI afforded the Pt(IV) oxidative-addition product [(DMAN)(DMBA)MePtI] (12), which was identified by its ^1H NMR spectral and elemental analysis data. The ^1H NMR spectrum showed four signals for the NMe_2 groups with, compared to those of the starting Pt(II) compound 5, decreased $^3J(^{195}Pt,^1H)$ values (see Table I), and an AB pattern for the DMBA CH_2. The coupling constant values indicate that each NMe_2 is trans to a Pt–C bond, which can only be realized by cis positioning of the cyclometalated ligands (if one of the C ligands had been the Me

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[29] Oxidation of Pt(II) to Pt(IV) causes a decrease of $^3J(^{195}Pt,^1H)$ of ca. 30%: Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1466. Clegg, D. E.; Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1972**, *38*, 403.

[30] van Beek, J. A. M.; Wehman, E.; Ooyevaar, I. C. M.; van Koten, G., unpublished results.

[31] Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; p 635.

Table V. ^{1}H NMR Data[a]

compd	NMe$_2$	OMe	naphthyl	other groups
(DMAN)$_2$Pt (**3**)	3.41 [13.5][b]		7.80–7.20	
(DMAN)PtCl(Et$_2$S) (**4**)	3.57 [34][b]		7.80–7.20	1.44 (t, CH$_3$)[e]
(DMAN)(DMBA)Pt (**5**)	3.30 [14];[b] 2.74 [14][b]		7.70–6.80	3.93 [18][b] (CH$_2$; DMBA)
(MXN)PtCl(Et$_2$S)$_2$ (**6**)		4.00	7.65–6.72	2.68 (b, CH$_2$–S); 1.26 (t, CH$_3$)
(MXN)$_2$Pt(Et$_2$S) (**7**)		4.42; 3.64	7.43–6.78	2.99 (q, CH$_2$–S); 1.30 (t, CH$_3$)
(MXN)$_2$Pt(PhCN)		4.27 [14];[b] 4.94	7.79–6.82; 6.09 [30][b]	
(MXN)$_2$Pt (**8**)		4.67	7.85–6.95	
(DMBA)PtCl(Et$_2$S) (**9**)	2.97		7.40–6.80	3.90 [41][b] (CH$_2$; DMBA); 1.38 (t, CH$_3$)[e]
(DMAN)$_2$PtI$_2$ (**10**)	3.78 [11][b]		7.90–7.20	
(DMAN)(DMBA)PtI$_2$ (**11**)	3.81 [11];[b] 3.27 [11][b]		7.90–6.80	4.37 [15][b] (CH$_2$; DMBA)
(DMAN)(DMBA)MePtI (**12**)	3.59 [8];[b] 3.35;[c] 3.29 [11];[b] 2.78 [11][b]		7.90–6.90	5.17, 3.66 (CH$_2$, J(AB) = 13 Hz); 1.10 [67][d] (CH$_3$–Pt)
(MXN)$_2$PtI$_2$ (**14**)		4.76	7.60–6.90	
Me(MXN)$_2$PtI (**15**)		5.01; 3.98	7.60–6.68; 6.10 [56][b] (H$_2$)	2.12 [87][d] (CH$_3$–Pt)
(MeCO)(MXN)$_2$PtCl (**16**)		4.90; 3.87	7.90–6.70; 6.51 [58][b] (H$_2$)	2.54 (MeCO)

[a] In ppm relative to TMS (internal), recorded in CDCl$_3$; J in Hz given in brackets. [b] $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$. [c] $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ could not be observed. [d] $^2J(^{195}\mathrm{Pt},^1\mathrm{H})$. [e] CH$_2$ of the Et$_2$S group could not be observed.

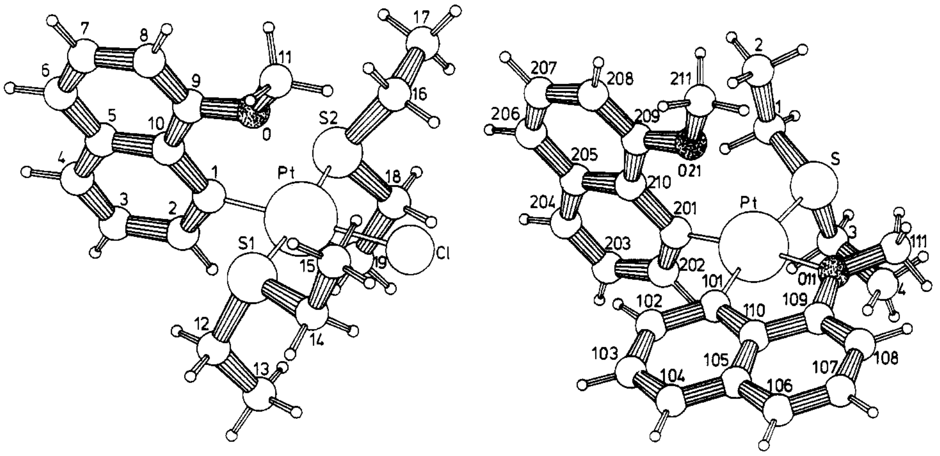

Figure 2. Molecular structures of (left) [(MXN)PtCl(Et$_2$S)$_2$] (**6**) and (right) [(MXN)$_2$Pt(Et$_2$S)] (**7**) along with the adopted numbering schemes.

Table VI. Relevant Bond Distances (Å) and Angles (deg) of [(MXN)PtCl(Et$_2$S)$_2$] (**6**)

Pt–Cl	2.388 (2)	Pt–C(1)	2.020 (7)
Pt–S(1)	2.287 (2)	Pt···O	2.834 (5)
Pt–S(2)	2.283 (2)		
Cl–Pt–S(1)	95.57 (6)	Pt–S(1)–C(12)	107.6 (3)
Cl–Pt–S(2)	91.30 (6)	Pt–S(1)–C(14)	111.5 (3)
Cl–Pt–C(1)	176.9 (2)	Pt–S(2)–C(16)	104.4 (2)
S(1)–Pt–S(2)	172.72 (6)	Pt–S(2)–C(18)	106.3 (2)
S(1)–Pt–C(1)	85.3 (2)	Pt–C(1)–C(10)	125.0 (5)
S(2)–Pt–C(1)	88.0 (2)	C(9)–O–C(11)	120.8 (6)

Table VII. Relevant Bond Distances (Å) and Angles (deg) of [(MXN)$_2$Pt(Et$_2$S)] (**7**)

Pt–S	2.367 (2)	Pt–C(101)	1.961 (7)
Pt–O(11)	2.229 (5)	Pt–C(201)	1.976 (6)
Pt···O(21)	2.829 (5)		
S–Pt–O(11)	94.3 (1)	C(101)–Pt–C(201)	93.2 (3)
S–Pt–C(101)	171.2 (2)	Pt–S–C(1)	113.9 (2)
S–Pt–C(201)	93.7 (2)	Pt–O(11)–C(111)	128.5 (5)
O(11)–Pt–C(101)	78.7 (2)	C(109)–O(11)–C(111)	120.0 (6)
O(11)–Pt–C(201)	171.9 (2)	C(209)–O(21)–C(211)	118.8 (5)

group, the second NMe$_2$ group would have inevitably been trans to the iodide). The $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ value of 67 Hz observed for the Me group attached to platinum is consistent with this group being trans to I,[32] and the proposed structure for **12** having all these features is shown in Scheme III. The ^{1}H NMR spectrum obtained from a CDCl$_3$ solution of *fac*-[(DMAN)(DMBA)MePtI] that had been left for some days at room temperature was complicated even though an FD mass spectrum of a sample isolated from this solution was still consistent with the Pt(IV) species. The complexity of the ^{1}H NMR spectrum can be explained by a rearrangement of the Pt(IV) species to various stereoisomers with the methyl group now being cis to iodide. Scrambling of methyl groups in Pt(IV) complexes has been observed before, for example, in [PtXMe$_2$(CD$_3$)(AsMe$_2$Ph)$_2$].[33]

Reaction of MeI with [(DMAN)$_2$Pt] (**3**) proceeded less straightforewardly than the reactions with **5**, **7**, and **8** described above. Whereas MeI does not react with **3** in CHCl$_3$ (unlike **5**, which reacts smoothly), in an acetone/CHCl$_3$ mixture it does react to afford the insoluble compound **13**, which was analyzed as [(DMAN)$_2$MePtI]. A full characterization of **13** was hampered due to its insolubility, but it is likely that it is also an oxidative-addition product.

Structural Characterization of the Compounds. The ^{1}H NMR spectrum of [(DMAN)$_2$Pt] (**3**) showed a single resonance for the dimethylamino group with $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 14 Hz (see Table V). This small coupling constant is in accordance with the nitrogen being trans to a carbon, and consequently the naphthyl groups are mutually cis; for example, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ for the *N*-methyl groups in *trans*-[(DMBA)$_2$Pt] is 43 Hz whereas it amounts to 14 Hz in the cis isomer.[34] For the mixed-ligand [(DMAN)(DMBA)Pt] (**5**) similar small platinum coupling constants were observed on both NMe$_2$ signals and accordingly the aryl groups here are also cis. The small $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ values in **3** and **5** contrast sharply with the value of 33 Hz found for the monoarylated compounds

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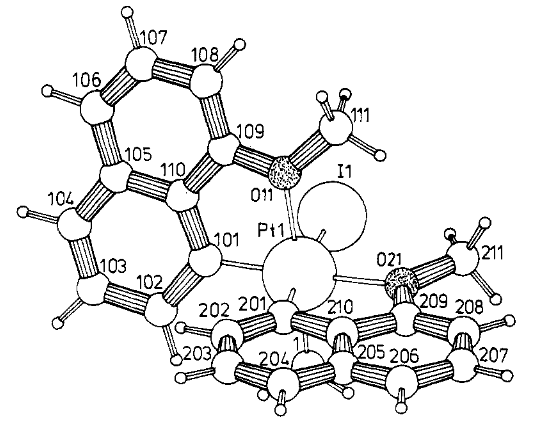

Figure 3. Molecular structure of $[(MXN)_2MePtI]$ (**15**) along with the adopted numbering scheme.

$[(DMAN)PtCl(Et_2S)]$ (**4**) and $[(DMBA)PtCl(Et_2S)]$ (**9**). A similar high value was found for the related $[\{CH(SiMe_3)C_6H_4NMe_2\text{-}2\}PtCl(Et_2S)]$, which likewise contains one cyclometalated N ligand.[35] An X-ray structure determination of the latter established the trans positioning of the Pt–C and Pt–Cl bonds, which is also proposed for **4**. The Pt–Cl IR absorption at 275 cm^{-1} is in agreement with the proposed trans configuration.[36a,37]

The stereochemistry of $[(MXN)PtCl(Et_2S)_2]$ (**6**) and $[(MXN)_2Pt(Et_2S)]$ (**7**) could not be conclusively derived from their ^1H NMR spectra. Therefore, X-ray crystal structures were determined.

Figure 2 shows the molecular structures of **6** and **7** along with the adopted numbering schemes. Both crystallize with four molecules in a monoclinic unit cell with no unusually short intermolecular contacts. Relevant bond distances and angles of the complexes are assembled in Tables VI and VII.

The X-ray structure of the monosubstituted $[(MXN)PtCl(Et_2S)_2]$ reveals a slightly distorted square-planar coordination geometry for platinum, comprising two Pt–S bonds, a Pt–Cl bond, and a Pt–C bond. The MXN group is attached to the platinum(II) center via a Pt–C bond (2.020 (7) Å), with the naphthyl group perpendicular to and the methoxy group situated above the coordination plane. The long Pt···O distance of 2.834 (5) Å indicates that the oxygen atom does not coordinate. The Pt–Cl bond (2.388 (2) Å) is trans to the Pt–C bond, and the remaining two coordination sites at the platinum center are occupied by two S-bonded diethyl sulfide groups (Pt–S = 2.287 (2) and 2.283 (2) Å).

In $[(MXN)_2Pt(Et_2S)]$ the platinum center had a square-planar coordination geometry with two Pt–C bonds, a Pt–O bond with a methoxy substituent, and a Pt–S bond. The methoxynaphthyl groups, which are both bound to platinum via a Pt–C bond (Pt–C = 1.961 (7) and 1.976 (6) Å) are cis (C–Pt–C = 93.2 (3)°) and mutually perpendicular. One of these ligands is also coordinated via the methoxy oxygen to platinum (Pt–O = 2.229 (5) Å), whereas the methoxy group of the second MXN is, as in $[(MXN)PtCl(Et_2S)_2]$, situated above the coordination plane of the complex with a long Pt···O distance of 2.829 (5) Å. The coordination around platinum is completed by a S-coordinated diethyl sulfide group with a Pt–S bond length of 2.367 (2) Å.

The Pt–C bond lengths in both **6** and **7** are close to the value expected for a Pt–C(sp^2) interaction[28] and are in the range expected for cyclometalated compounds.[38] The Pt–S distances are consistent with those reported previously.[39]

Table VIII. Relevant Bond Distances (Å) and Angles (deg) of $[(MXN)_2MePtI]$ (**15**) (Molecule 1)

Pt(1)–I(1)	2.707 (1)	Pt(1)–C(1)	2.03 (1)
Pt(1)–O(11)	2.221 (9)	Pt(1)–C(101)	1.96 (1)
Pt(1)–O(21)	2.208 (9)	Pt(1)–C(201)	2.00 (1)
I(1)–Pt(1)–O(11)	88.4 (2)	O(11)–Pt(1)–C(201)	92.0 (4)
I(1)–Pt(1)–O(21)	95.9 (2)	O(21)–Pt(1)–C(1)	87.3 (4)
I(1)–Pt(1)–C(1)	91.6 (4)	O(21)–Pt(1)–C(101)	169.6 (5)
I(1)–Pt(1)–C(101)	92.0 (4)	O(21)–Pt(1)–C(201)	79.3 (4)
I(1)–Pt(1)–C(201)	175.1 (4)	C(1)–Pt(1)–C(101)	99.4 (6)
O(11)–Pt(1)–O(21)	95.5 (4)	C(1)–Pt(1)–C(201)	88.2 (5)
O(11)–Pt(1)–C(1)	177.2 (4)	C(101)–Pt(1)–C(201)	92.9 (5)
O(11)–Pt(1)–C(101)	77.9 (5)		

The structure of *fac*-$[(MXN)_2MePtI]$ (**15**) was confirmed by a single-crystal X-ray diffraction analysis. The unit cell contains eight molecules of **15** and six disordered $CDCl_3$ molecules of crystallization. Both crystallographically independent molecules of **15** have a slightly distorted octahedral geometry around platinum. Figure 3 shows the molecular structure along with the adopted numbering scheme.

Some relevant bond distances and bond angles are given in Table VIII. A complete list of distances and angles is available as supplementary material. The iodide and methyl groups originating from the electrophile are cis on Pt(IV), while both MXN groups are chelate-coordinated via C-1 and the 8-methoxy group. The three coordinating carbon atoms of the organic groups occupy facial positions within the octahedral array.

The Pt–I bond length (2.707 (1) Å) is in accordance with Pt–I distances trans to a Pt–C bond.[40] The Pt–C and Pt–O bond lengths have the expected values[40] and are similar to those relating to the chelate-bonded MXN ligand in the structure of the Pt(II) compound $[(MXN)_2Pt(Et_2S)]$ (**7**).

Discussion

Selective monoarylations of platinum(II) chlorides by (methoxyphenyl)- and (*N*,*N*-dimethylanilino)lithium species related to [Li(DMAN)] and [Li(MXN)] have been reported.[36] Although the factors influencing mono- or diarylation are not completely understood, it has been suggested that electronic factors are more important than steric ones.[41] In general aryl groups with strong σ-donor substituents favor diarylation whereas with the same substrates, aryl groups with π-acceptor capacity give monoarylation or no reaction at all. The fact that with DMBA (σ-donor group $-CH_2NMe_2$) it is difficult to synthesize the monoaryl product $[(DMBA)PtCl(Et_2S)]$ (**9**) from the reaction of [Li(DMBA)] and $[PtCl_2(Et_2S)_2]$ supports this idea. Compound **9** could only be isolated, and then in a very low yield, when [Li(DMBA)] was slowly added to $[PtCl_2(Et_2S)_2]$ at low temperature; when the order of addition was reversed, *cis*-$[(DMBA)_2Pt]$ was obtained exclusively. The monoarylation found when $[PtCl_2(Et_2S)_2]$ is reacted with [Li(DMAN)] and [Li(MXN)] can be explained similarly. The 8-substituted naphthyl groups DMAN and MXN are likely to be electronically similar to the unsubstituted naphthyl unit, which on the basis of $^1J(^{195}Pt,^{31}P)$ in the ^{31}P NMR spectra of $[Pt(naph)_2DPPM]$ (naph = naphthyl, DPPM = $Ph_2PCH_2PPh_2$)[26] has been indicated as being a group with the largest electronegativity in the series 1-naph > Ph > C_6H_4Me-2.

On the basis of the fluxional behavior of the O coordination (vide infra) that was observed in the ^1H NMR spectrum of **7** it was concluded that the Et_2S group was only weakly bonded to the platinum atom.[9] This was confirmed by the synthesis of Et_2S-free $[(MXN)_2Pt]$ (**8**) by dissolution of **7** in toluene with excess benzonitrile and subsequent evaporation of all volatiles (see

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Experimental Section). This synthesis can be explained by assuming the equilibria

$$\underset{\mathbf{7}}{[(MXN)_2Pt(Et_2S)]} + PhCN \rightleftharpoons [(MXN)_2Pt(PhCN)] + Et_2S \quad (1)$$

$$[(MXN)_2Pt(PhCN)] \rightleftharpoons \underset{\mathbf{8}}{[(MXN)_2Pt]} + PhCN \quad (2)$$

Due to the lower boiling point of Et_2S compared to that of PhCN, equilibria 1 and 2 are shifted to the side of $[(MXN)_2Pt]$ upon evaporation of solvent. Support for the formation of the intermediate product $[(MXN)_2Pt(PhCN)]$ was obtained from ^1H NMR measurements of the in situ reaction of PhCN with $[(MXN)_2Pt]$ in $CDCl_3$ solution. The ^1H NMR spectrum obtained, which is completely different from that of $[(MXN)_2Pt]$, shows two OMe peaks at positions characteristic for noncoordinated and coordinated OMe groups, respectively (vide infra), at 4.94 and 4.27 ppm ($^3J(^{195}Pt,^1H)$ = 14 Hz). The coupling to platinum seen for the latter signal is remarkable since similar couplings were not found for other (8-methoxynaphthyl)platinum derivatives, and a convincing explanation for this has not been found. Furthermore, the spectrum shows an upfield-shifted naphthyl proton at 6.08 ppm with $^3J(^{195}Pt,^1H)$ = 30 Hz characteristic for perpendicularly positioned MXN groups. Since, unfortunately, all attempts to isolate $[(MXN)_2Pt(PhCN)]$ afforded $[(MXN)_2Pt]$, it can be concluded that the PhCN in the former compound is only weakly coordinated.

The cyclometalated Pt(II) species described in the present paper possess some interesting features that have not been encountered in previously studied compounds. For example, the rigid flat naphthyl skeleton in N-cyclometalated *cis*-$[(DMAN)_2Pt]$ keeps the dimethylamino substituent fixed in the square-planar coordination plane of platinum and ring puckering, as generally found in cyclometalated compounds,[6a,42,43] is not allowed. Furthermore, the very stable Pt to N coordination makes rearrangements of the metallacycle positioning unlikely. However, it can be expected that the protons ortho to the Pt–C bond in the two naphthyl rings experience an unfavorable steric interaction, which makes a rearrangement more attractive. This steric hindrance is confirmed in the recently determined X-ray crystal structure of $[(DMAN)_2Pt]$,[30] in which there is a significant bending of the planes of the naphthyl groups (cf. also the X-ray crystal structure of *cis*-bis[(2-phenylpyridine)platinum][38a]). A different situation is met in $[(MXN)_2Pt(Et_2S)]$, where the Pt–O coordination is weaker so that a naphthyl rearrangement is easier. Moreover, approach to the Pt center from one side of the coordination plane is hindered because one of the MXN ligands is now perpendicular to it. This situation allows attack of an electrophile from only one side of the molecule, with the uncoordinated OMe substituent almost ideally situated for coordination in a six-coordinate Pt(IV) compound. Finally, in [(DMAN)(DMBA)Pt] (**5**) the rigid DMAN ligand is combined with the more flexible DMBA chelate, for which rearrangements have shown to be highly probable (see for example in $[(DMBA)_2PtHg(O_2CCH_3)_2]$[6a]). Moreover, dissociation of a Pt–N bond is more facile in **5**.

Oxidative-Addition Reactions. Oxidative addition of alkyl halides or halogens on Pt(II) can proceed via several mechanisms. Depending on the metal substrate, the alkyl halide, the halogen, and the reaction conditions, both S_N2 and free-radical reactions (chain and nonchain) have been identified. The S_N2 mechanism is dominant in reactions of primary alkyl halides and halogens and for square-planar d^8 complexes with ligands that do not block the coordination sites above and below the coordination plane.[44a]

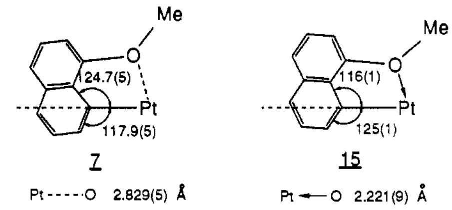
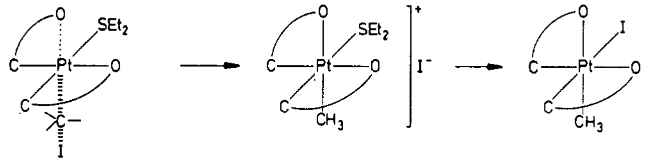


Figure 4. Structural detail for the naphthylplatinum moiety with (**15**) and without (**7**) intramolecular Pt- - -O coordination. Note the tilting of the naphthyl system with respect to the C_{ipso}–Pt axis.

Scheme IV



For methyl iodide the most likely mechanism for the S_N2 reaction is nucleophilic attack by platinum on the carbon atom to give $[MeR_2PtL_2]^+I^-$, which rapidly rearranges to $[MeR_2PtIL_2]$. Recently, Puddephatt et al. detected the cationic $[Me_3Pt(CD_3CN)(SMe_2)_2]I$ species,[5b] which strongly supports the above route.

The selective formation of oxidative-addition products in one isomeric form, from the reaction of [(DMAN)(DMBA)Pt] and $[(MXN)_2Pt(Et_2S)]$ with MeI or I_2, points to an S_N2 mechanism for these reactions. The nature of the cyclometalated ligands clearly determines the Pt–heteroatom interactions and in combination with steric factors has an important influence on the course of the oxidative-addition reaction. A proposed scheme for these reactions with methyl iodide will be discussed.

In the first step attack of the Pt(II) species on methyl iodide will probably lead to formation of the anion–cation intermediate $[(DMAN)_2MePt]I$. In the second step I^- attacks this intermediate trans to the methyl C atom. The stereochemistry of this attack is determined by the nature of the cyclometalated ligands. For [(DMAN)(DMBA)MePt]I the trans product **10** is formed (Scheme III). A different situation is met in the (8-methoxynaphthyl)platinum compounds. In the case of $[(MXN)_2MePt(Et_2S)]I$ it still contains a site with a labile Et_2S group, and this seems a reasonable place for attack of I^-. Displacement of this group by the nucleophile I^- gives directly the cis oxidative-addition product *fac*-$[(MXN)_2MePtI]$. Attack of I^- on $[(MXN)_2MePt]^+$ must involve a coordination rearrangement of the cyclometalated groups. Most likely in the initially formed product the Me and the I are trans to each other. Rearrangement of the groups on platinum then affords the final product *fac*-$[(MXN)Me_2PtI]$. The formation of *cis*-$[(MXN)_2MePtI]$ upon reaction of both $[(MXN)_2Pt(Et_2S)]$ and $[(MXN)_2Pt]$ with methyl iodide indicates that this stereoisomer with cis Me and I positioning is thermodynamically preferred.

From this study it can be concluded that the nature of the coordinating heteroatom has mainly an influence on the stereochemistry of the formed products. Further investigations, involving kinetic measurements on these reactions, into the influence of the nature of the cyclometalated ligand on the oxidative-addition reactions are currently in progress.[30] It is interesting to observe that the reaction of methyl iodide with $[(MXN)_2Pt(Et_2S)]$ proceeds much faster than with $[(MXN)_2Pt]$, though both afford the same compound. This difference in rate may be the result of anchimeric assistance of the initially uncoordinated OMe group in $[(MXN)_2Pt(Et_2S)]$, which is ideally positioned to assist nucleophilic attack of the Pt center on the methyl iodide carbon atom (Scheme IV).

The off/on coordination of the methoxy group on the naphthyl ligand perpendicular to the coordination plane, depending on the platinum oxidation state, is nicely illustrated when the structural details of the noncoordinated $(MXN)Pt^{II}$ moieties in **7** and **15** are compared (see Figure 4).[45] In addition to the dramatic

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decrease of the platinum–oxygen bond lengths from 2.829 (5) to 2.221 (9) Å it can be seen in Figure 4 that the naphthyl ligand in **7** is pivoted about an axis through carbon, C(201), normal to the ligand plane, such as to move the methoxy oxygen somewhat away from the platinum, presumably to minimize nonbonding repulsions. This is reflected by the inequivalent bond angles about the carbon bonded to platinum. With the coordination of this oxygen in compound **15**, the naphthyl ligand appears to pivot about the Pt-bonded carbon atom, C(101), again but this time in the opposite sense to bring the oxygen of the methoxy group much closer to the platinum, and the bond angles about this carbon atom are now reversed from those in **7**.

Only a few other structurally characterized cis addition products have previously been reported. Reaction of $[Pt\{2\text{-}C_6H_4N(O)O\}_2]$ with MeI and halogens afforded $[Pt\{2\text{-}C_6H_4N(O)O\}_2Me(I)]$ and $[Pt\{2\text{-}C_6H_4N(O)O\}_2X_2]$ (X = Cl, Br, I), respectively, which were characterized by ^{1}H NMR spectroscopy.[46] Interestingly these complexes also contain oxygen donor atoms in the cyclometalating ring, pointing to an important influence of the nature of the donor atom on the stereochemistry of the formed products. A photochemically induced cis oxidative addition was observed in the reaction of MeI, CH_2Cl_2, or (*E*)-ClCH=CHCl with *cis*-bis(2-phenylpyridine)platinum(II) and *cis*-bis{2-(2-thienyl)pyridine}platinum(II), respectively.[47] On the basis of their ^{1}H NMR spectra, it was concluded that all these complexes were formed in only one isomeric form.

Acknowledgment. The Commission of the European Communities (Contract No. ST2J-0090-1-F(CD)) is thanked for its financial support. This work was also supported (A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank A. J. M. Duisenberg for collecting the diffraction data and Prof. K. Vrieze and Dr. D. M. Grove for their interest in this research.

Registry No. **1**, 86526-70-7; **2**, 51179-24-9; **3**, 116840-82-5; **4**, 116840-83-6; **5**, 116840-84-7; **6**, 116840-85-8; **7**, 87370-33-0; **8**, 116840-86-9; **9**, 116840-87-0; **10**, 116840-88-1; **11**, 116840-89-2; **12**, 116840-90-5; **13**, 116840-91-6; **14**, 116840-92-7; **15**, 116840-93-8; **16**, 116840-94-9; $[PtCl_2(COD)]$, 12080-32-9; $[PtCl_2(Et_2S)_2]$, 14873-92-8; [Li(DMBA)], 60528-57-6; *cis*-bis(8-methoxynaphthyl)platinum diiodide, 116908-91-9.

Supplementary Material Available: A full table of crystallographic data, listings of thermal parameters, hydrogen atom positions, thermal parameters, and all bond distances and bond angles for **6** and **7**, listings of disordered solvate positions, thermal parameters, hydrogen atom positions, and all bond distances and angles for **15**, and ORTEP projections for **6**, **7**, and **15** (21 pages); listings of observed and calculated structure factors (102 pages). Ordering information is given on any current masthead page.

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Synthetic and Structural Studies on the Formation of a Tetradecametallic Yttrium Oxide Alkoxide Chloride Complex: An Example of How Molecular Yttrium Oxygen Frameworks Form Extended Arrays[1]

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YCl_3 reacts with 2 equiv of $NaOCMe_3$ in THF to form $Y_3(OCMe_3)_7Cl_2(THF)_2$ (**1**) in 80% yield. The yttrium atoms in this molecule form a triangle that has doubly bridging alkoxide groups along each edge, a μ_3-$OCMe_3$ group on one side of the Y_3 plane, and a μ_3-Cl ligand on the other side. One metal is coordinated to a terminal chloride ion and a terminal alkoxide group. Each of the other metals is coordinated to a terminal alkoxide group and a molecule of THF. Both chloride ions lie on the same side of the Y_3 plane as the two THF ligands. In toluene under nitrogen over a period of 2 weeks, **1** converts to $Y_{14}(OCMe_3)_{28}Cl_{10}O_2(THF)_4$ (**2**) in quantitative yield. **2** is comprised of four trimetallic $Y_3(\mu_3\text{-}OR)(\mu_3\text{-}X)(\mu\text{-}Z)_3$ units (where X = Cl, O; Z = Cl, $OCMe_3$) that have structures similar to the $Y_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_3Cl(THF)_2$ structure of **1**. The four trimetallic subunits in **2** are connected by two μ-Cl ions, a μ_4-O ion and a $[(\mu\text{-}OR)_2Y(\mu\text{-}Cl)]_2$ group. Complex **2** is a dimer, $\{[Y_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_3(THF)_2](\mu\text{-}Cl)[Y_3(\mu_3\text{-}OR)(\mu\text{-}OR)_2(\mu\text{-}Cl)(OR)_2](\mu_4\text{-}O)[(\mu\text{-}OR)_2Y(\mu\text{-}Cl)]\}_2$, which contains a center of inversion. **1** crystallizes from THF in the space group $P2_1/c$ with unit cell dimensions $a = 18.102$ (7) Å, $b = 15.871$ (6) Å, $c = 21.084$ (5) Å, $\beta = 104.87$ (3)° and $Z = 4$ for $D_{calcd} = 1.291$ g cm^{-3}. Least-squares refinement on the basis of 2435 observed reflections led to a final R value of 0.136. **2** crystallizes from toluene in the space group $P\bar{1}$ with unit cell dimensions $a = 17.373$ (14) Å, $b = 18.343$ (11) Å, $c = 19.278$ (10) Å, $\alpha = 99.75$ (5)°, $\beta = 92.26$ (6)°, $\gamma = 114.15$ (5)° for $Z = 2$ and $D_{calcd} = 1.313$ g cm^{-3}. Least-squares refinement on the basis of 3830 observed reflections led to a final R value of 0.114.

Introduction

The conversion of alkoxide compounds to oxides via sol–gel processes has been studied extensively as a route to high-purity oxides and thin-film coatings.[2–11] Much of this research has centered on silicon alkoxides, although some transition-metal systems have also been studied.[9–18] The transition-metal systems

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(1) Reported in part at the 2nd International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements, Lisbon, Portugal, April 1987; paper L(II)1.

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