contains delocalized electrons. However, NdI_2 is known to transform to a metallic compound with the same $MoSi_2$-type structure under pressure.[19] Therefore NdI_2 can be regarded as a potentially metallic compound and may be a borderline case of the generalization. The distinctly smaller amount of reaction of hydrogen with molten NdI_2 (Figure 2) is appropriate to the greater localization of the valence electrons implied by the low electronic conductivity of liquid NdI_2 compared with LaI_2.[13]

Registry No. LaI_2H, 65530-51-0; NdI_2H, 75600-19-0; LaI_2, 19214-98-3; NdI_2, 61393-36-0; H_2, 1333-74-0.

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Synthesis and Crystal Structure of a Methoxy-Bridged Binuclear Organoplatinum Complex: Di-μ-methoxy-bis[1,4,5-η-(8-methoxy-4-cycloocten-1-yl)]diplatinum(II)

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Alkoxy and/or hydroxy complexes of platinum(II) are thought to be probable intermediates in the preparation of various hydridoplatinum complexes[1] and in some catalytic processes such as the hydration of nitriles.[2] However, stable alkoxyplatinum complexes are rare, probably owing to the "hard" character of the oxygen donor atom, and only a limited number of them have been reported, including mononuclear[3] and binuclear (methoxy-bridged) complexes.[4]

We report here the preparation and the crystal structure of a methoxy-bridged organoplatinum complex. To our knowledge this one represents the first structural characterization of an alkoxyplatinum compound.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in Nujol mulls. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer in $CDCl_3$ solution using Me_4Si as internal standard. All solvents and chemicals were of AR grade purity.

The complex $PtCl_2COD$ (COD = cycloocta-1,5-diene) was prepared by known procedures.[5]

Preparation of the Complex $[Pt(OMe)(C_8H_{12}OMe)]_2$. A suspension of 374 mg (0.100 mmol) of finely powdered $PtCl_2COD$ and 340 mg (0.200 mmol) of $AgNO_3$ in 10 mL of methanol was stirred for 30 min at room temperature in the dark. Then 212 mg (0.200 mmol) of finely powdered Na_2CO_3 was added, and the mixture was further stirred for 30 min. The resulting suspension was evaporated in vacuo, and the residue was extracted twice with 10 mL of CH_2Cl_2. The solution was concentrated to small volume, and the product was crystallized as white needles by addition of a few milliliters of MeOH and cooling at 0 °C (65% yield). The compound decomposes on heating, giving a dark powder above 140 °C.

Table I. Crystal data for $[Pt(OMe)(C_8H_{12}OMe)]_2$

mol formula	$(C_{10}H_{18}O_2Pt)_2$	β, deg	113.0 (1)
mol wt	730.6	V, Å^3	1097
cryst system	monoclinic	Z	2
space group	$P2_1/c$	d_{calcd}, g cm^{-3}	2.21
a, Å	6.67 (1)	d_{exptl}, g cm^{-3}	2.19
b, Å	14.26 (2)	$F(000)$	688
c, Å	12.53 (2)	μ(Mo Kα), cm^{-1}	134

Table II. Atomic Fractional Coordinates (×10^4) for $[Pt(OMe)(C_8H_{12}OMe)]_2$

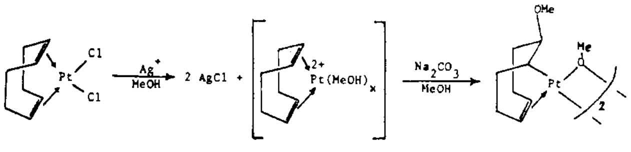
atom	x/a	y/b	z/c
Pt	1697.8 (6)	5895.4 (3)	5439.1 (3)
O(1)	449 (12)	4838 (5)	6090 (6)
O(2)	7308 (16)	6517 (8)	8497 (9)
C(1)	3583 (18)	6508 (8)	6974 (10)
C(2)	3218 (24)	7577 (9)	6873 (13)
C(3)	2922 (26)	7946 (10)	5700 (17)
C(4)	2183 (20)	7192 (8)	4762 (11)
C(5)	3601 (21)	6504 (9)	4642 (11)
C(6)	6037 (22)	6404 (10)	5298 (12)
C(7)	7046 (21)	6683 (10)	6582 (14)
C(8)	6004 (19)	6228 (9)	7317 (11)
C(9)	1421 (28)	4436 (12)	7233 (13)
C(10)	7129 (35)	5927 (16)	9384 (16)

Table III. Thermal Parameters (×10) for $[Pt(OMe)(C_8H_{12}OMe)]_2$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	26.5 (2)	35.0 (2)	37.0 (2)	−3.8 (3)	29.2 (3)	−3.5 (3)
O(1)	38 (3)	45 (4)	33 (3)	−21 (6)	27 (5)	0 (5)
O(2)	52 (5)	87 (7)	51 (5)	−23 (9)	21 (8)	−36 (9)
C(1)	35 (5)	41 (5)	45 (5)	−22 (8)	49 (8)	−31 (8)
C(2)	58 (7)	50 (7)	70 (8)	−5 (11)	76 (13)	−52 (11)
C(3)	58 (8)	38 (6)	105 (11)	−6 (11)	91 (15)	−19 (13)
C(4)	48 (6)	32 (5)	53 (6)	3 (9)	53 (10)	8 (9)
C(5)	47 (6)	41 (6)	53 (6)	−9 (9)	45 (10)	20 (9)
C(6)	44 (6)	47 (6)	69 (7)	−10 (10)	66 (11)	−26 (11)
C(7)	35 (5)	53 (7)	73 (8)	−28 (9)	45 (10)	−35 (11)
C(8)	32 (5)	45 (5)	51 (6)	−10 (8)	36 (9)	−20 (9)
C(9)	62 (8)	66 (8)	51 (7)	−13 (13)	12 (12)	29 (13)
C(10)	66 (10)	132 (17)	51 (8)	−51 (19)	24 (14)	2 (17)

[a] The temperature factors are in the form $\exp\{-0.25[B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl]\}$.

Scheme I



1 2

IR (cm^{-1}): 1092 (vs), 1078 (vs), 1064 (s) (ν_{C-O}); 530 (s) (ν_{Pt-O}). ^1H NMR: δ 1.0–2.9 (m, 9 H), 3.25 (s, C–OMe), 3.55 (s, Pt–OMe, the expected four ^{195}Pt satellite peaks are observable, $^3J_{H-Pt}$ = 14 Hz), 3.3–3.7 (m, 1 H), 4.17 (m, CH=CH, $^2J_{H-Pt}$ = 82 Hz).

X-ray Data Collection. Crystals were grown by slow evaporation of a CH_2Cl–MeOH solution of the compound as thin, colorless needles elongated along *a*. A crystal of small dimensions, 0.05 × 0.05 × 0.3 mm, was selected for X-ray analysis in order to minimize absorption effects. All measurements were made on a Siemens AED automatic

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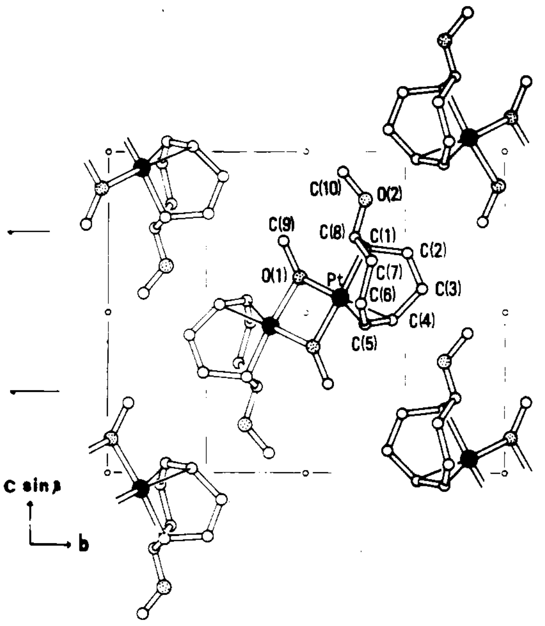

Figure 1. Crystal structure of $[Pt(OMe)(C_8H_{12}OMe)]_2$ as viewed along the *a* axis.

diffractometer using Mo Kα radiation. Cell constants were determined by a least-square refinement of the 2θ values of 12 reflections. The crystal data are summarized in Table I. A total of 1809 independent reflections were measured out to $(\sin \theta)/\lambda = 0.58$ Å^{-1} by the θ–2θ scan technique. Of them, 1447 having $I \geq 2.5\sigma(I)$ were used for the analysis. The intensity of a standard reflection, recorded every 20 reflections, showed a crystal deterioration, linearly dependent on irradiation. Its value dropped by about 20% during the whole data collection. Intensities were corrected for Lorentz and polarization effects, crystal deterioration, and absorption by using the cylindrical approximation ($\mu r = 0.33$).

The structure was solved by a straightforward application of the heavy-atom method. The position of Pt was readily determined from the Patterson function and refined by a cycle of least squares. The subsequent Fourier synthesis revealed all of the remaining nonhydrogen atoms. Refinement of the atomic parameters, allowing thermal parameters to vary initially isotropically and then anisotropically, was carried out by block-diagonal least-squares procedures. The *R* index $(\sum||F_o| - |F_c||/\sum|F_o|)$ was 0.030. A difference Fourier synthesis, calculated at this stage, showed a number of peaks with height lower than 1.4 e Å^{-3}, some of which could be interpreted as hydrogen atoms. Because of their poor localization in the electron density map, the positions of the 12 nonmethylic hydrogen atoms were stereochemically derived and included in the calculations of the structure factors but not refined. The last two cycles of refinement resulted in a final *R* value of 0.028. The weighting scheme used was $w = (40 + F_o + 0.08F_o^2)^{-1}$. The atomic scattering factors were taken from ref 6 for the nonhydrogen atoms and from ref 7 for H. Those for Pt were corrected for real and imaginary components of the anomalous dispersion. The final positional and thermal parameters of the nonhydrogen atoms are listed in Tables II and III.

Results and Discussion

A simple way to obtain the title compound involves chloride displacement from the cycloocta-1,5-diene starting complex $PtCl_2COD$ by silver ions in methanol and successive base-induced methoxidation, a well-known reaction of dienes coordinated to Pt(II).[5,8] In absence of chloride ions, the methoxide nucleophilic addition occurs both on the coordinated double bond and on the metal ion (Scheme I). We found that the methoxy-bridged complex **2** is obtained also as a byproduct in the synthesis of the corresponding chloride-bridged complex, with yields that are highly variable and scarcely reproducible. A strictly related and possibly identical compound was reported earlier by Chatt et al.[5] without characterization and referred by the authors as "α-dimethoxide". The title compound appears to be rather peculiar, since some attempts to prepare analogous methoxy-bridged derivatives starting from other $PtCl_2$(diene) complexes (diene = dicyclopentadiene or norbornadiene) failed, leading to complex mixtures of products and/or extensive decomposition.

Table IV. Bond Distances and Bond Angles for $[Pt(OMe)(C_8H_{12}OME)]_2$[a]

Distances, Å			
Pt–O(1)	2.040 (9)	C(3)–C(4)	1.526 (20)
Pt–O(1)*	2.161 (7)	C(4)–C(5)	1.411 (20)
Pt–C(1)	2.038 (11)	C(5)–C(6)	1.514 (18)
Pt–MP	1.977 (15)	C(6)–C(7)	1.534 (21)
Pt–C(4)	2.111 (13)	C(7)–C(8)	1.501 (24)
Pt–C(5)	2.088 (16)	C(8)–C(1)	1.552 (18)
O(1)–C(9)	1.440 (17)	C(8)–O(2)	1.452 (16)
C(1)–C(2)	1.541 (18)	O(2)–C(10)	1.435 (26)
C(2)–C(3)	1.500 (26)		
Angles, Deg			
O(1)–Pt–O(1)*	76.3 (4)	Pt–C(1)–C(8)	110.0 (11)
O(1)–Pt–C(1)	97.9 (7)	C(8)–C(1)–C(2)	113.0 (19)
C(1)–Pt–MP	86.2 (9)	C(1)–C(2)–C(3)	112.5 (22)
MP–Pt–O(1)*	99.6 (8)	C(2)–C(3)–C(4)	112.8 (23)
O(1)*–Pt–C(1)	174.1 (7)	C(3)–C(4)–C(5)	122.9 (27)
O(1)–Pt–MP	175.2 (7)	C(4)–C(5)–C(6)	129.1 (28)
O(1)–Pt–C(4)	163.4 (7)	C(5)–C(6)–C(7)	118.8 (21)
O(1)–Pt–C(5)	156.7 (7)	C(6)–C(7)–C(8)	114.4 (24)
Pt–O(1)–Pt*	103.7 (4)	C(7)–C(8)–C(1)	113.7 (23)
Pt–O(1)–C(9)	126.6 (18)	O(2)–C(8)–C(1)	110.7 (16)
Pt*–O(1)–C(9)	125.0 (15)	O(2)–C(8)–C(7)	105.4 (20)
Pt–C(1)–C(2)	109.1 (12)	C(8)–O(2)–C(10)	115.2 (26)

[a] MP defines the midpoint of the olefinic double bond. Asterisked atoms belong to the half of the molecule related by the inversion center at 0, $^1/_2$, $^1/_2$. Values in parentheses are the estimated standard deviations in units of the least significant figure.

The X-ray diffraction analysis showed the complex to be a dimeric ($\bar{1}$ symmetry) oxygen-bridged binuclear Pt(II) complex with a trans configuration. Each platinum atom displays the usual square-planar arrangement of the ligands and links the organic octamembered ring through a σ and a π-olefinic bond. A perspective view of the crystal structure along the *a* axis together with the atom numbering scheme is shown in Figure 1. Bond lengths and angles are given in Table IV. The equation of the plane through the central dimeric unit, including Pt, O(1), C(1), and their centrosymmetricals, was calculated by a least-square analysis using weights equal to reciprocals of the atomic σ^2's. It is listed in Table V together with atomic displacements. The central unit is planar within experimental error. The bridging oxygen has a rather flat pyramidal configuration that leaves the methyl carbon 0.50 Å out of the coordination plane. The Pt–O(1) bond length of 2.040 (9) Å falls in the expected range[9] and compares well with the values reported for hydroxy-bridged platinum(II) complexes.[10] This result agrees with the known weak trans influence of π-bonded olefins.[11,12] In turn, the longer Pt–O(1)* bond (2.161 (7) Å) reflects the large trans

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Table V

Weighted Least-Squares Planes and Atomic Displacements (Å × 10^3)[b]

atom	plane 1	plane 2
Pt	0[a]	0[a]
O(1)	2[a]	20[a]
C(1)	−20[a]	−19[a]
MP	86	69
Pt*	−18	0[a]
O(1)*	−20[a]	−20[a]
C(1)*	3	19[a]
MP*	−104	−69
C(9)*	−495	−505

Equations of the Planes Referred to Crystallographic Axes

plane 1: $5.371x - 8.434y - 3.367z = -5.892$
plane 2: $5.341x - 8.515y - 3.285z = -5.900$
plane 3: $2.443x + 3.551y + 8.545z = 7.156$

Dihedral Angles (Deg) between the Planes:
1-2, 0.5; 1-3, 78.9; 2-3, 78.8

[a] Distances refer to atoms defining the plane. [b] See footnote to Table IV. Plane 3 is defined by Pt, C(4), and C(5).

influence of a σ-bonded carbon atom.[12,13] The difference of 0.12 Å in the platinum–oxygen bond lengths is comparable to that between the two platinum–chlorine bond lengths trans to a σ-bonded carbon and to a π-bonded olefin in other platinum(II) complexes.[14]

The cyclo-olefinic ring has the same distorted boat conformation found in the complex chloro(2-methoxycyclo-octa-1,5-dienyl)(pyridine)platinum(II).[12] The slight lengthening of the double bond (1.411 Å) is a common feature observed upon coordination and compares well with the values quoted by Mason et al.[11,15] The Pt–C(1) σ-bond length (2.038 Å) and the Pt–C(olef) distances (mean value 2.10 Å) are among the shortest observed in other σ-alkyl[13] and π-olefin[16] complexes. The C═C bond makes an angle of 78.4° with the metal coordination plane and its midpoint is 0.07 Å out of it. As the dihedral angle between the coordination plane and the plane containing Pt and the olefinic carbon atoms has nearly the same value, the deviation of the double bond from the perpendicularity to the coordination plane consists in a tilt around the $\mathrm{Pt}\text{-}\genfrac{}{}{0pt}{}{\mathrm{C}}{\mathrm{C}}$ axis, as found for similar compounds.[17] This distortion optimizes the nonbonding distances (3.57 and 3.52 Å, respectively) between the olefinic carbon atoms and the methyl C(9). All the intermolecular contacts fall in the normal range.

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Registry No. $[\mathrm{Pt(OMe)(C_8H_{12}OMe)}]_2$, 75534-44-0; $\mathrm{PtCl_2COD}$, 12080-32-9.

Supplementary Material Available: Table of the observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Some New Cobalt and Chromium Carbonyl Derivatives of 1,4-Bis(dimethylsilyl)benzene

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Although there are numerous silyltetracarbonylcobalt compounds known, very few of these contain more than one cobalt center.[2] A relatively stable derivative containing two tetracarbonylcobalt entities joined by a bridging $\mathrm{SiH_2}$ group has been reported;[3] however systems in which two $\mathrm{SiMe_2Co(CO)_4}$ moieties are joined by a bridging oxygen (O),[4] nitrogen, (NH),[5] or alkyl ($\mathrm{CH_2}$ or $\mathrm{CH_2CH_2}$)[4,6] grouping are much less stable than comparable compounds that contain one tetracarbonylcobalt grouping. For example, solid $\mathrm{Me_3SiCo(CO)_4}$ decomposes slowly at room temperature (87% of a sample held at room temperature in vacuo for 3 months was recovered unchanged)[7] whereas the bridged bis((tetracarbonylcobaltio)dimethylsilyl) systems $\mathrm{(CO)_4CoSiMe_2\text{-}X\text{-}SiMe_2Co(CO)_4}$ (X = O, $\mathrm{CH_2}$) decompose readily at −78 °C in a nitrogen atmosphere.[4] In the present project we have undertaken a study of the synthesis and properties of some bis((tetracarbonylcobaltio)dimethylsilyl) derivatives which contain an aromatic bridging group.

Experimental Section

All synthetic work was done in nitrogen-purged drybags and/or glassware suitably modified for inert-atmosphere work. Infrared spectra of complexes were obtained on Perkin-Elmer spectrometers (Models 457 or 580). Cyclohexane was used as a solvent. Proton NMR spectra were recorded with use of a Hitachi-Perkin-Elmer R20 spectrometer. Spectra were obtained at ambient temperature on dilute solutions (ca. 5%) in deuteriochloroform with a cyclohexane reference. 1,4-Bis(dimethylsilyl)benzene (Silar Laboratories) and fresh samples of $\mathrm{Co_2(CO)_8}$ and $\mathrm{Cr(CO)_6}$ (Pressure Chemical Co.) were obtained commercially and used as received. Analyses were performed by Geller Microanalytical Laboratory.

Synthesis of η^6-[1,4-Bis(dimethylsilyl)benzene]chromium Tricarbonyl. A mixture of 1,4-bis(dimethylsilyl)benzene (17.2 g, 88 mmol) and $\mathrm{Cr(CO)_6}$ (6.3 g, 29 mmol) in a glyme (15 mL)/diglyme (30 mL) solution was allowed to reflux for 28 h in a Strohmeier-type reactor.[8] After removal of the solvents and unreacted starting materials by vacuum distillation, a black oil remained. This oil was passed through a 3 × $1^1/_2$ in. alumina column with pentane as eluant. Upon cooling of the product-containing eluant to −78 °C, crude η^6-$\mathrm{[1,4\text{-}(HSiMe_2)_2C_6H_4]Cr(CO)_3}$ (4.0 g, 12 mmol, 41% yield) precipitated. The pure product, obtained as yellow crystals (mp 46.5–48.5 °C), was obtained after further purification by recrystallization from pentane and sublimation onto a cold finger held at 0 °C. Anal. Calcd for $\mathrm{C_{13}H_{18}O_3Si_2Cr}$: C, 47.2; H, 5.5. Found: C, 47.1; H, 5.5. Spectral characterization data are given in the discussion.

Synthesis of η^6-[1,4-Bis((tetracarbonylcobaltio)dimethylsilyl)benzene]chromium Tricarbonyl. A solution of η^6-$\mathrm{[1,4\text{-}(HSiMe_2)_2C_6H_4]Cr(CO)_3}$ (2.27 g, 6.87 mmol) in methylene chloride

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