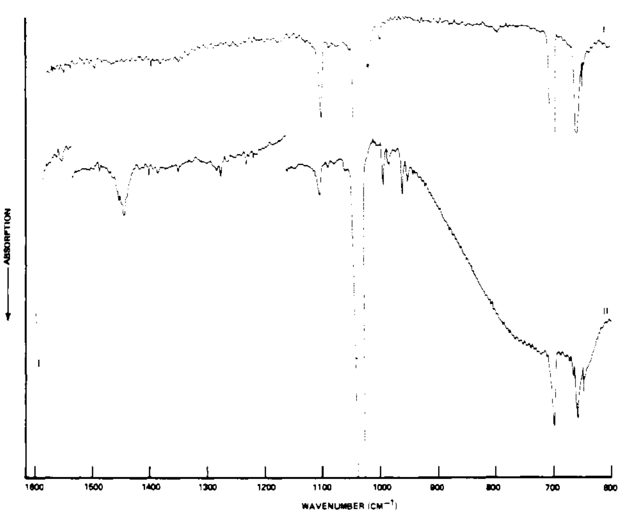


Figure 1. Infrared spectrum of the $Cl_2/O_3/Ar$ matrix prior to photolysis (I) and after 5 h of photolysis with $\lambda > 3300$ Å (II). In I, the only absorptions are due to ozone (1110, 1040, and 700 cm^{-1}). In II, the 1440-cm^{-1} absorption is ClOO, the 952- and 961-cm^{-1} absorptions are ClClO, and the 995-, 989-, and 983-cm^{-1} absorptions are due to $(ClO)_2$. The absorption near 1600 cm^{-1} is α-O_2.

Table I

ν, cm^{-1}	designation	time lapse,[a] h
961.3, 952.9	Cl-Cl-O (Cl-O stretch)	≃1
995.6, 989.4, 983.2	$(ClO)_2$ (Cl-O stretch)	≃2
1444	ClOO (O-O stretch)	≃4

[a] Between the start of photolysis and appearance.

photolysis of $Cl_2/O_3/Ar$ and $Cl_2/O_2/Ar$ mixtures.

Chlorine (Matheson, research grade) was further purified by trap to trap distillation to remove nitrogen. Chlorine/argon (1:50) mixtures were prepared by standard manometric techniques. Typically 2 mmol of Cl_2/Ar and 0.15 mmol of ozone (or oxygen) were simultaneously deposited onto a CsI window held at 10 K by an Air Products CS-202 refrigerator. A 1000-W Oriel mercury lamp, with water and glass filters ($\lambda > 3300$ Å), was employed for matrix photolysis. Spectral observations (4000–200 cm^{-1}) were made with a Beckman 4250X infrared spectrometer, with a frequency accuracy better than 1.5 cm^{-1} in the 1500–700-cm^{-1} region.

Figure 1 contrasts the prephotolysis and postphotolysis spectra of the region of interest (650–1500 cm^{-1}). The ClClO doublet at 961 and 953 cm^{-1}[3] was the first absorption to appear (after 1 h of photolysis). The ClOCl molecule was not observed. Further irradiation of the sample produced, after ≃2 h, a doublet at 995 cm^{-1}, indicating the presence of the ClO dimer.[3] After ≃5 h of photolysis, the ClOO molecule was observed (1444 cm^{-1}, see Table I).[2b]

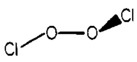
Warming the sample to ≃15 K resulted in an increase in the 995-cm^{-1} absorption (ClO dimer) and a decrease in the 961-cm^{-1} absorption (ClClO). There was a complete loss in intensity of the 1444-cm^{-1} absorption (ClOO) upon warming the sample to 40 K, and the ClOO absorption did not reappear upon recooling the sample, consistent with the expected $ClOO \xrightarrow{\Delta} Cl + O_2$ reaction.

The formation of ClClO is best explained by the mechanism

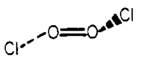
$$O_3 + h\nu \rightarrow O_2 + O \tag{1}$$

$$Cl_2 + O \rightarrow Cl_2O \tag{2}$$

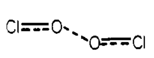
The Cl_2O molecule may further react with oxygen atoms to give the observed ClO dimer,[3,4] $(ClO)_2$. The ClO molecule (850 cm^{-1}) was not observed in our experiments, and the dimerization of ClO in a 10 K matrix is unlikely. The structure of the ClO dimer absorbing at 995 cm^{-1} may be inferred from the possible photolysis mechanisms. In $Cl_2O/O_3/Ar$ photolysis experiments,[2a] the 995-cm^{-1} band is very intense, and Chi and Andrews[2a] suggest that the structure is Cl=O···Cl=O (I), while Pimental et al.[3,4] have proposed five different structures (I–V). If the ClO dimer is formed



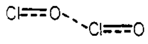
I



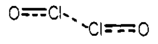
II



III



IV



V

by the reaction of ClClO and a migrating oxygen, then structures I–III require a (photolytic) intramolecular rearrangement in order to impose the two oxygen atoms between the two chlorine atoms. Structures IV and V require only the capture of migrating oxygen atom. However, the present growth data (Table I) suggests that the 995-cm^{-1} absorber is formed from the 962-cm^{-1} absorber which suggests that the 995-cm^{-1} band is due to structure V. Electronic structure calculations of the geometrical orientation of the ClO dimer are very desirable, inasmuch as they would provide information on the relative stabilities of the structures I–V.

The appearance of the ClOO molecule may be due to the direct reaction of ClO and O atoms, by the reaction of ClO and O atoms to produce OClO which undergoes intramolecular photochemical rearrangement to ClOO[2b] or by scission of a Cl‒‒O bond in structure IV to produce OClO which subsequently rearranges to give ClOO. The photolytic conversion of OClO to ClOO is complete,[2b] and thus the OClO molecule should not be observed in our experiments.

The in situ photolysis of $Cl_2/O_2/Ar$ matrices for 5 h, under conditions identical with the $Cl_2/O_3/Ar$ photolysis, produced no chlorine oxides, consistent with published data.[2b] Thus, the direct reaction of Cl and O_2 to produce ClOO is conclusively ruled out.

Acknowledgment. We gratefully thank the National Aeronautics and Space Administration (Grants NSG7289 and NSG8049) and the Minority Biomedical Sciences Program (Grant RR08006) for support of this research.

Registry No. Cl_2, 7782-50-5; O_3, 10028-15-6; ClClO, 7791-21-1; $(ClO)_2$, 12292-23-8; ClOO, 17376-09-9.

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Lanthanum and Neodymium Diiodide Hydride Phases and Their Hydrogen Dissociation Pressures

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Recently, lower halides of several early transition and lanthanide metals and thorium have been found to absorb hydrogen to form halohydrides,[2-5] and an empirical rule has been proposed to predict the composition limits of hydrogen in these compounds relative to those of the binary hydrides of the same element.[5] Little is known about the thermodynamic stability of many halohydrides, and hydrogen dissociation pressures have been measured only in three systems, ZrCl–H_2, ZrBr–H_2, and ThI_2–H_2.[3,4] In each system two discrete hydride phases are formed. For further definition of general trends of stability for these halohydrides the pressure isotherms of two more systems, LaI_2–H_2 and NdI_2–H_2, have been measured. Three of the metallic lanthanide diiodides, LaI_2, CeI_2, and PrI_2, have already been reported to absorb hydrogen.[4] However, the conversion to the apparent monohydrides was incomplete and pressures could not be measured because the trihalide vapor in equilibrium with the diiodide sample attacked the fused silica container at temperatures above 600 °C which were necessary to generate a measurable hydrogen pressure. In the present work these difficulties have been avoided through use of a sealed tantalum container as a semipermeable wall for hydrogen so that measurements can be made at higher temperatures.[6] Reaction of hydrogen with NdI_2 was also studied since this is a salt-type compound with a $SrBr_2$-type structure at normal pressure,[7,8] in contrast to the $MoSi_2$-type structure[9] exhibited by the metallic LaI_2 and the isostructural CeI_2 and PrI_2.[10,11]

Experimental Section

Materials. The diiodide samples were prepared by reduction of the vacuum-sublimed triiodides with the corresponding metal in a sealed Ta container.[7,11] Impurities in the metals in ppm by weight were as follows. La: O, 35; N, 55; H, 3; C 8. Nd: O, 42; N, 17; H, 6; C, 15. High-purity hydrogen (99.999%, Matheson) was further purified as previously described.[3]

The apparatus for the determination of the dissociation pressures was similar to that described elsewhere[6] except that only Hoke metal valves rather than glass stopcocks were used in the part where hydrogen was confined at >12 torr in order to prevent leakage.

Measurement Procedure. For each measurement 1–2 g of sample was welded under ~0.3 atm He into a Ta container (ca. 6 × 50 mm, 4–6 g). The amount of hydrogen absorbed by the Ta container at temperature was calculated with the equation given by Franzen, Khan, and Peterson.[12]

A slight leakage of hydrogen through the wall of the quartz tube together with a slow equilibration rate with the iodide made the exact determination of the stoichiometry (H/MI_2) somewhat difficult while the plateau pressure could be measured rather easily. The sample was first completely hydrogenated under 1–1.5 atm H_2 for >1 day, and then hydrogen was extracted stepwise through a succession of evacuations and pressure measurements until the dissociation pressure reached ~1 torr. Each step required more than 3 h to achieve equilibrium. The apparent amount of the hydrogen remaining at the last stage of the extraction (the amount absorbed by the first hydrogenation less the summation of the amounts extracted in each step) was greater than the true value which could be calculated by the extrapolation of the Sievert's law relation between $P^{1/2}$ and the hydrogen concentration in MI_2 in the dilute region, and the difference was the amount of hydrogen lost through the leakage. Most of the hydrogen lost certainly leaked during the initial hydrogenation step because the pressure was much higher than during the following extraction process. The largest possible error with this assumption is the amount of hydrogen lost during the entire process, H(leak). The ratio H(leak):MI_2, was 0.151 for the measurements on the LaI_2–H_2 system at 1179 K and 0.046 for the NdI_2–H_2 system at 1073 K. If the amount of leakage is proportional to pressure and time, the stoichiometry errors in these isotherms should be 10–20% of these ratios or 0.02–0.03 in H/LaI_2 and 0.005–0.01 in H/NdI_2. The value of H(leak) for the LaI_2–H_2 study at 1073 K could not be determined, and the isotherm was not corrected.

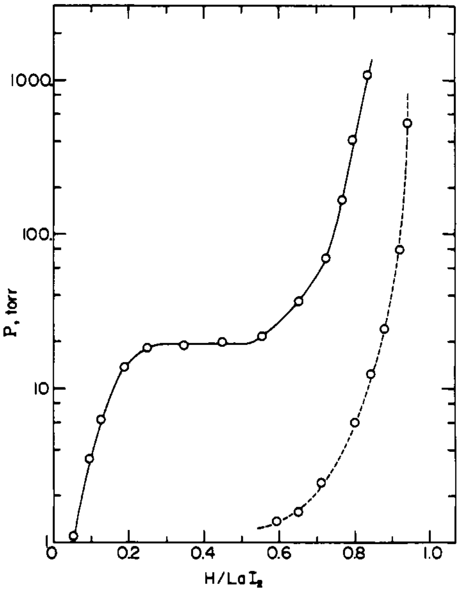

Figure 1. Dissociation pressure isotherms for the LaI_2–H_2 system: solid line, 1179 K; broken line, 1073 K.

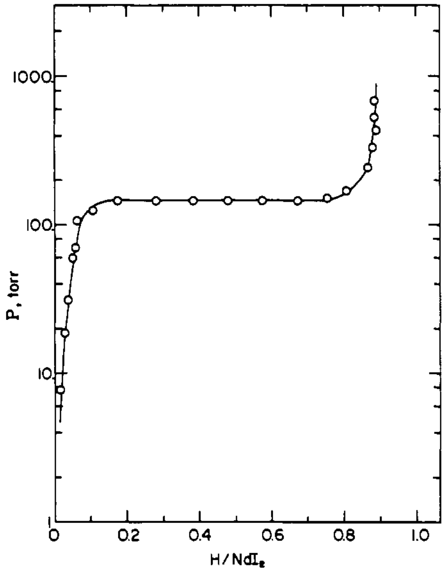

Figure 2. Dissociation pressure isotherm for the NdI_2–H_2 system at 1073 K.

X-ray Data. The stronger lines in the powder pattern of LaI_2H (Guinier, Cu Kα_1, internal Si standard) are, with relative intensities in parentheses, 3.56 (s), 3.305 (s), 2.981 (ms), 2.657 (ms), 2.109 (vs), 1.814 (m), 1.814 (m), 1.722 (m), 1.651 (m), 1.300 (m), and 1.217 (m) Å.

Results

The measured isotherms for LaI_2–H_2 and NdI_2–H_2, Figures 1 and 2, show that only the solution phase MI_2H_y (hydrogen in MI_2) and the nonstoichiometric product phase MI_2H_{1-x},

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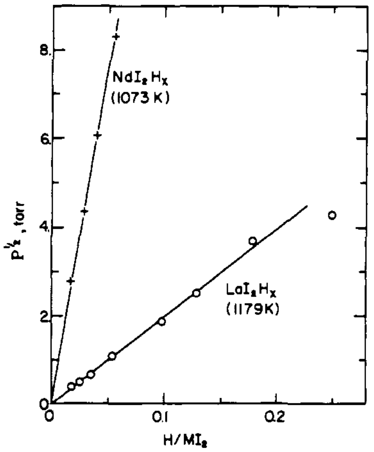

Figure 3. Dissociation pressure isotherms for hydrogen in liquid LaI_2 (1179 K) and NdI_2 (1073 K).

$0.05 \le x \le 0.5$, exist in these systems at ~800–900 °C. The initial solution phase has not been detected in previous studies.[3,4] Both MI_2H_y phases are liquid at the temperatures where the full isotherm is known since the melting points are 1103 K for LaI_2[11] and 835 K for NdI_2.[7] Figure 3 shows that Sievert's law holds well in the melt phases of both systems, which means hydrogen is completely dissociated in them. On the other hand, the hydride phase LaI_2H_{1-x} was found to be solid at 1163 K by rotating the sample from the horizontal to the vertical position after the hydrogenation. Therefore, the solid hydride MI_2H_{1-x} phase precipitates from the MI_2H_y melt with increasing hydrogen concentration.

Plateau pressures for the LaI_2–LaI_2H system measured at several temperatures were as follows [*T* in K, *P* in torr, standard deviations in parentheses]: 1123, 1.28 (2); 1173, 13.4 (3); 1179, 19.4 (5); 1223, 104 (4). These show a good linear relationship between log *P* and 1/*T*, and give enthalpy and entropy changes of −503 kJ/mol and −396 J/(K mol) for eq 1.

$$8.0LaI_2H_{0.27}(l) + H_2(1\ atm) \rightarrow 8.0LaI_2H_{0.52}(s) \quad (1)$$

These values are much larger than those usually observed for metal–hydrogen or reduced halide–hydrogen systems for the reason that reaction 1 is accompanied by a transition from the liquid to solid state. Thermodynamically the reaction can be considered in two steps, the solidification of the initial phase and the formation of the hydride phase from this hypothetical solid solution phase. The entropy of fusion of LaI_2 (=$La^{3+}(I^-)_2e^-$[10]) is probably close to that of a saltlike diiodide,[13] and the value for BaI_2, 27 J/(K mol),[14] may be a good approximation. Accordingly, the enthalpy change for solidification of the liquid LaI_2H_y phase is estimated to be −30 kJ/mol when its melting point is approximated with that of LaI_2. Therefore, the enthalpy and entropy changes of the hydride formation from the hypothetical solid solution phase are evaluated to be −265 kJ and −181 J/K per mole of H_2. These values are somewhat larger than those for other metallic halide–hydrogen systems;[3,4] in particular, the enthalpy change is 27% greater than for the formation of the dihydrides of the light rare-earth metals.[15]

Both LaI_2H and NdI_2H are gray in bulk and white when ground. The powder patterns show they are isomorphous; the stronger lines of the former are listed in the Experimental Section. A suitable structural interpretation has not been found. The melting point trend for La (920 °C), LaI_2 (830 °C), and LaI_3 (779 °C) vs. LaI_2H (>890 °C) is quite striking but is consistent with the effect of hydrogen on the metal, where it increases the melting point to above 1150 °C for LaH_2.[16]

Some preliminary reactions of SmI_2 with hydrogen (923 K, 680 torr, 3 days and 618 K, 1800 torr, 16 days) did not produce any hydride. An attempt to prepare $LaIH_2$ was unsuccessful; reaction of an equimolar mixture of LaI_2 and La (turnings) with ~800 torr H_2 for 5 days at 900 °C produced only LaI_2H and LaH_{2+x}.

Discussion

The authors have recently proposed the empirical rule that a halide MX_m of an early transition element for which the highest binary hydride is MH_n can absorb hydrogen to form MX_mH_x with $x \le n - m$, or in other words only when $n > m$.[5] This rule naturally leads to a comparison of the stabilities of MX_mH_x with those of MH_{m+x}. For LaI_2H and NdI_2H the dissociation pressures are much lower than those of LaH_{2+x} and NdI_{2+x}, and those for the trihydride would be even more disparate. For example, the dissociation pressure of $LaI_2H_{0.6}$ at 850 °C is only ~1 torr while that of $LaH_{2.6}$ is ca. 10^3 torr even at 400 °C.[17] Thorium iodide hydride ($ThI_2H_{1.75}$) also has much lower dissociation pressure than the corresponding binary hydride ($ThH_{3.75}$).[4] The dissociation pressure of $Nb_6I_{11}H$ should be lower than that of NbH_2 judging from the condition of the preparation.[2] On the other hand, $ZrClH_x$ and $ZrBrH_x$ ($x = 0.5, 1.0$) have higher dissociation pressures than does ZrH_2.[3]

The diversity of halohydride vs. hydride stabilities now known is clearly not consistent with the early, more heuristic prediction that halide would decrease hydride stability at the same composition. *If* the foregoing contrasts arise solely because of the halide ion present, they can be summarized in the tentative order of dissociation pressures $MI_mH_x < MH_{m+x} > MCl_mH_x \simeq MBr_mH_x$. One might imagine that hydrogen in MX_mH_x (X = halogen or hydrogen) should be more stable when X is less electronegative as this leaves more electron density on the metal for bonds or transfer to hydrogen. But this simple reasoning misplaces the binary hydride in the series, namely, $MH_{m+x} > MI_xH_x > MCl_mH_x \simeq MBr_mH_x$. The discrepancy may arise because of the difference in structures of iodide (MI_m) and hydride (MH_n). While the binary hydride has very extensive delocalization and metal–metal bonding, the iodides can have this only in a limited extent in their layered structures because of the large size of iodide ions, and bonding electrons may not be stabilized as well as in binary hydrides. Perhaps the large enthalpy of hydride formation by LaI_2, about 25% greater than for LaH_2 from the metal, is related, the large iodide ion opening up the structure considerably while still allowing a metallic conduction in the diiodide. There are no thermodynamic data available for any of the reduced halides considered above. Therefore it is impossible to judge whether the relative stabilities of their halohydrides follow the "rule of reversed stability" which has been applied to the stabilities of hydrides of closely related alloys.[18] However, the foregoing discussion has to do with much larger differences in H_2 pressures above MX_mH–MX_m systems which have different structures, and so any relationships of this character will be more complex.

The hydrogen absorption of NdI_2, a salt-type compound,[8] is an apparent exception of the generalization developed earlier[4] that hydrogen is taken up only by those halides which

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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 $[Pt(OMe)(C_8H_{12}OMe)]_2$

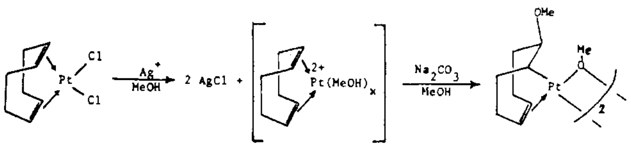
atom	x/a	y/b	z/c
Pt	1697.8 (6)	5895.4 (3)	5439.1 (3)
O(1)	449 (12)	4838 (5)	6090 (6)
O(2)	7308 (16)	6517 (8)	8497 (9)
C(1)	3583 (18)	6508 (8)	6974 (10)
C(2)	3218 (24)	7577 (9)	6873 (13)
C(3)	2922 (26)	7946 (10)	5700 (17)
C(4)	2183 (20)	7192 (8)	4762 (11)
C(5)	3601 (21)	6504 (9)	4642 (11)
C(6)	6037 (22)	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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