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Synthesis and Characterization of Platina-β-diketones†

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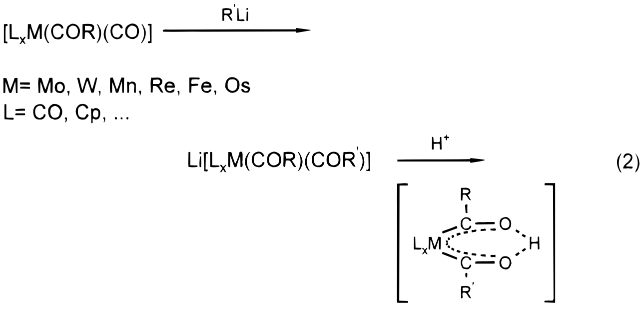
Summary: Hexachloroplatinic acid reacts with *n*-butanol to give the but-2-ene complex $H[PtCl_3(\eta^2\text{-}C_4H_8)]$ (**3**) as intermediate, which reacts with trimethylsilyl-substituted acetylenes $R'C{\equiv}CSiMe_3$ (R' = H, Me, $SiMe_3$) with cleavage of the silyl groups to form platina-β-diketones $[Pt_2(\mu\text{-}Cl)_2\{(COR)_2H\}_2]$ [R = Me (**2a**), Et (**2b**)]. The constitution of **2** was determined by microanalysis, NMR (^1H, ^{13}C) spectroscopy, IR, Raman, and mass spectroscopy. The structure of **2a** was determined by X-ray diffraction.

Introduction

Hexachloroplatinic acid is a very effective precatalyst for acetal formation $MeCH(O^nBu)_2$ by the reaction of acetylene with *n*-butanol.[1] Apart from this catalytic formation of ketals, alkynes with an internal triple bond, $RC{\equiv}CR'$, react with hexachloroplatinic acid to form monomeric (cyclobutadiene)platinum(II) complexes, $[PtCl_2(C_4R_2R'_2)]$ (**1**) (eq 1).[2,3]

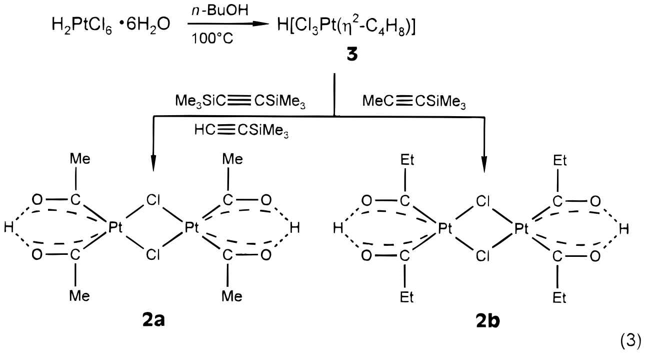
$$H_2PtCl_6\cdot 6\,H_2O \xrightarrow[75\text{-}100^\circ C]{RC\equiv CR'/{}^nBuOH} \underset{\mathbf{1}}{[PtCl_2(C_4R_2R'_2)]} + RCH_2CR'(O^nBu)_2 \qquad (1)$$

We report here on the analogous reaction of trimethylsilyl-substituted alkynes, which affords platina-β-diketones $[Pt_2(\mu\text{-}Cl)_2\{(COR)_2H\}_2]$ (R = Me, Et) (**2**). Metalla-β-diketones, prepared for the first time by Lukehart, were synthesized according to eq 2 by the protonation of diacylmetalate complexes (metalla-β-diketonate anions), which were obtained by the reaction of acylmetal carbonyl complexes with strong bases, such as organolithium or Grignard reagents.[4]



Results and Discussion

Hexachloroplatinic acid was reduced in *n*-butanol at 75−100 °C to form the trichloro(butene)platinate(II) complex (**3**), which is analogous to Zeise's acid. On addition of bis(trimethylsilyl)acetylene at ambient temperature, light yellow-colored needles of $[Pt_2(\mu\text{-}Cl)_2\{(COMe)_2H\}_2]$ (**2a**) were obtained within 10 h (eq 3).



The trimethylsilyl groups were cleaved, forming $Me_3SiOSiMe_3$. Quite analogously (trimethylsilyl)acetylene reacted to give **2a**. By the reaction with the methyl-substituted alkyne $MeC{\equiv}CSiMe_3$, the corresponding ethyl derivate $[Pt_2(\mu\text{-}Cl)_2\{(COEt)_2H\}_2]$ (**2b**) was obtained.

The platina-β-diketone complexes **2** decompose within 1 day when in contact with air. Both complexes show an astonishing thermal stability: **2a**,**b** melt with decomposition at 183 and 176 °C (dta), respectively. The NMR spectra of **2a**,**b** exhibit the equivalence of all C−O groups as well as of the methyl and ethyl substitutents, respectively. The resonances of the carbonyl carbon atoms [$\delta(^{13}C)$ 228.1 ppm (**2a**) and 231.0 ppm (**2b**)] are in the range of those in acyl and carbene platinum complexes.[5−8] However, the values of $^1J_{Pt-C}$ = 1457 Hz

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† Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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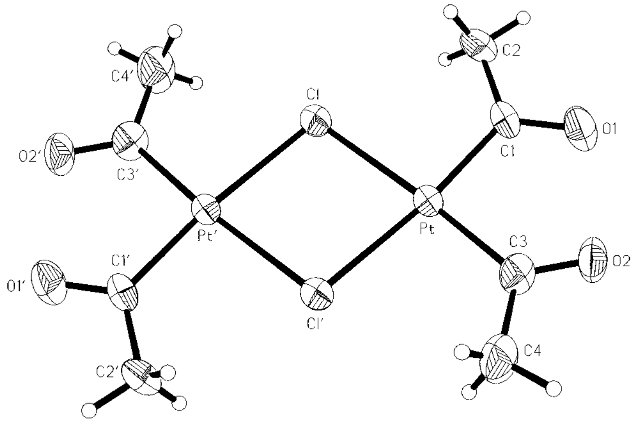

Figure 1. ORTEP plot of the molecule **2a**, showing atom numbering (thermal ellipsoids at 50% probability).

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $[Pt_2(\mu\text{-}Cl)_2\{(COMe)_2H\}_2]$ (2a)

Pt−C(1)	1.95(1)	C(3)−O(2)	1.23(1)
Pt−C(3)	1.95(1)	C(1)−C(2)	1.48(2)
Pt−Cl	2.430(3)	C(3)−C(4)	1.48(2)
Pt−Cl′	2.430(4)	O(1)−O(2)	2.37(1)
C(1)−O(1)	1.26(1)		

C(1)−Pt−C(3)	91.4(5)	O(1)−C(1)−Pt	123.9(8)
C(1)−Pt−Cl	93.6(3)	C(2)−C(1)−Pt	121.7(7)
C(3)−Pt−Cl	174.1(3)	O(2)−C(3)−C(4)	114.6(10)
C(1)−Pt−Cl′	173.8(3)	O(2)−C(3)−Pt	124.9(8)
C(3)−Pt−Cl′	94.2(3)	C(4)−C(3)−Pt	120.5(8)
Cl−Pt−Cl′	80.7(1)	C(1)−O(1)−O(2)	99.8(7)
Pt−Cl−Pt′	99.3(1)	C(3)−O(2)−O(1)	99.7(7)
O(1)−C(1)−C(2)	114.3(9)		

(**2a**) and 1459 Hz (**2b**) are significantly larger (about 300−500 Hz) than those measured in acyl and carbene complexes.[6−8] The chemical shifts of the enolic protons of about $\delta(^1H)$ 16 ppm (**2a**) and 18 ppm (**2b**) are approximately 2−5 ppm at higher field than the resonances of ferra-, tungstena-, and rhena-β-diketones, indicating a higher electron density at the enolic H atom in **2**.[9−11] The mass spectrum of **2a** shows the presence of the molecular ion $[M]^+$ (*m/e* 634; <1%), followed by successive elimination of a methyl group $[M - 15]^+$, HCl $[M - 51]^+$, and CO $[M - 79]^+$. The base peak represents the acetyl fragment $[MeCO]^+$. In the case of **2b** the base peak is the $[EtCO]^+$ fragment. The molecular ion was not observed, but the peaks $[M - 30]^+$, $[M - 66]^+$, and $[M - 94]^+$ indicate successive elimination of an ethyl group, HCl, and CO analogous to **2a**.

The molecular structure of **2a** was determined by single-crystal X-ray crystallography (Figure 1). Selected bond lengths and angles are listed in Table 1. The molecule has an imposed crystallographic C_i symmetry. The idealized molecular structure belongs to the symmetry point group D_{2h}. The Pt_2Cl_2 unit has an exactly rhombic constitution. The Pt−Cl distances [*d*(Pt−Cl) = 2.430(3) and *d*(Pt−Cl′) = 2.430(4) Å] are in the range of those known for chloro-bridged platinum compounds.[12−14] The Pt−C distances [*d*(Pt−C1)/*d*(Pt−C3) = 1.95(1) Å] are equivalent within one esd. They are in the range of platinum carbene complexes, whereas the Pt−C bond distances in acylplatinum complexes are generally somewhat longer.[12−17] The C−O bond lengths [*d*(C1−O1) = 1.26(1) Å and *d*(C3−O2) 1.23(1) Å] are equivalent within the 3σ limit. Thus the C−O bond lengths correspond to those in the rhena-β-diketone, *cis*-$[Re\{(COMe)_2H\}(CO)_4]$ (**4**) [1.28(2) and 1.25(2) Å, respectively].[18] The O1−O2 distance of 2.37(1) Å in **2a** is in accordance with a hydrogen bridge bond and is similar to that observed in the rhena complex **4** [*d*(O1−O2) = 2.40(2) Å].[9,18] The hydrogen atom itself could not be located.

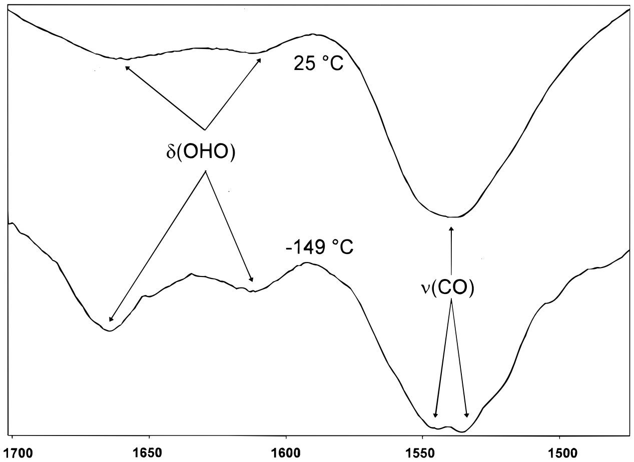

Figure 2. IR spectra (25, −149 °C) of **2b** in the region of the O−H−O deformation and C−O stretching vibration.

The IR and Raman spectra of **2** confirm the results of the X-ray structure determination. In accordance with the inversion symmetry of the molecule, the asymmetric stretching vibration of the Pt_2Cl_2 unit only appears in the IR spectra [238 cm^{-1} (**2a**), 251 cm^{-1} (**2b**)], and the symmetrical one, only in the Raman spectra [262 cm^{-1} (**2a**), 278 cm^{-1} (**2b**)]. An indication of the equivalence of the Pt−C bonds is a moderately strong absorption in the Raman spectra at 501 cm^{-1} (**2a**) and at 476 cm^{-1} (**2b**), respectively, caused by the symmetrical Pt−C vibration. Two very weak O−H−O deformation vibrations [1665, 1632 cm^{-1} (**2a**); 1662, 1611 cm^{-1} (**2b**)] and one C−O stretching vibration [1548 cm^{-1} (**2a**); 1539 cm^{-1} (**2b**)] were observed IR spectroscopically at room temperature; cf. Figure 2. At −149 °C the absorption of the O−H−O deformation vibrations increases from a very weak to a moderately strong band. Furthermore, two C−O stretching vibrations [1549 (s), 1559 (sh) cm^{-1} (**2a**); 1536 (s), 1544 (s) cm^{-1} (**2b**)] appear at low temperature, which points to a slight asymmetry of the molecules.

In order to characterize the bonding in the platina-β-diketones **2**, some *ab initio* Hartree−Fock MO calculations were carried out. For that purpose, the anion $[PtCl_2\{(COMe)_2H\}]^-$ (**I**) was used as a simplified model of **2**; see Figure 3 and Table 2. The resulting structure **I** was found to have C_{2v} symmetry, which is in ac-

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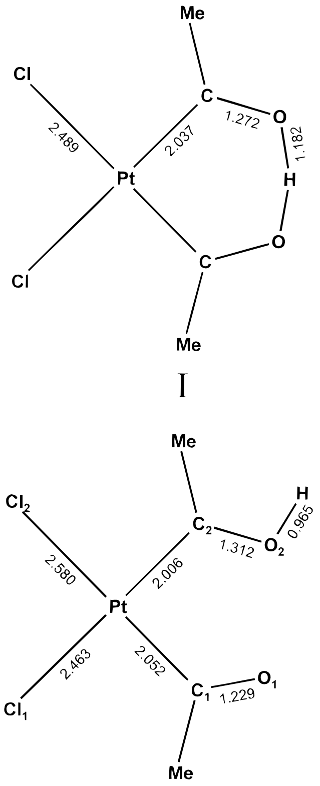
Table 2. Mulliken Net Atomic and Overlap Populations: Total Values and Irreducible Representations in C_{2v} and C_s, Respectively, Contributing to the π-System

	I		II	
	total	A_2, B_1	total	A″
Pt d_1/Pt d_2	1.9150/1.9340	1.9150/1.9340	1.8850/1.9240	1.8850/1.9240
C_1/C_2	5.1895	0.2803	5.0230/5.3379	0.4380/0.2339
O_1/O_2	8.3797	1.4871	8.1301/8.0800	1.2051/1.6755
H	0.2431		0.3970	
Cl_1/Cl_2	7.5740	1.9846	7.5412/7.6849	1.9769/1.9924
$Pt-C_1/Pt-C_2$	0.2798	0.0701	0.3453/0.0955	0.0278/0.1235
$Pt-Cl_1/Pt-Cl_2$	0.3003	-0.0022	0.3462/0.2413	0.0063/−0.0099
C_1-O_1/C_2-O_2	0.5856	0.1466	0.9757/0.4891	0.4067/0.1970
O_1-H/O_2-H	0.3180		−/0.5549	



I

II

Figure 3. Geometry of $[PtCl_2\{(COMe)_2H\}]^-$ (**I**) and $[PtCl_2(COMe)\{C(OH)Me\}]^-$ (**II**) (distances in Å).

cordance with the observed molecular structure of **2a**. It was impossible to determine any structure having a similar ring formation with lower symmetry, especially with an explicitly localized O−H bond. The calculated noncyclic arrangement **II** (see Figure 3 and Table 2) is about 37 kcal/mol higher in energy and shows slightly different Pt−C bonds. Furthermore, this results in a localized C−O single and double bond, respectively, corresponding to a hydroxycarbene and an acyl ligand.

The irreducible representations A_2/B_1 in C_{2v} symmetry (including the π-bonding system) consists of 16 electrons. The 12 electrons of interest (4 electrons centered at the methyl groups, will not be discussed further) at the Pt, Cl, C, and O centers are composed of a system of mainly localized C−O π-bonds and lone pairs at Pt ($5d_{xz}/d_{yz}$) and Cl; hence, only weak π-Pt−C bonds were obtained. Thus, the calculations agree with the observed D_{2h} symmetry for **2a** and the use of the term platina-β-diketone for this type of compound is justified. In contrast to that, **II** exhibits another distribution of π-electrons (as expected for a complex with a separated hydroxycarbene and acyl ligand); cf. Table 2.

Although the mechanism of the reaction 3 has not been investigated, as yet, a plausible intermediate is an anionic or a neutral platinum(II)−alkyne complex, $H[PtCl_3(\eta^2\text{-}RC{\equiv}CSiMe_3)]$ or $[PtCl_2(\eta^2\text{-}RC{\equiv}CSiMe_3)]_2$, respectively, which can undergo nucleophilic attack by water ($H_2PtCl_6{\cdot}6H_2O$ was used as starting material) resulting in a hydroxycarbene complex. Similar cleavages of Si−C bonds by nucleophilic attack of alcohol leading to stable alkoxycarbene complexes were observed in the reactions of *trans*-$[PtX(PR_3)_2(R'OH)]^+$ (R = alkyl, aryl; R′ = Me, Et) with (trimethylsilyl)acetylenes in R′OH.[19]

Reactions according to eq 3 establish the simplest access to metalla-β-diketones known to date. Investigations on the reactivity of complexes **2**, which represent the first platina-β-diketones as well as the first binuclear metalla-β-diketones, are in progress.

Experimental Section

General Comments. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemeni 300 or Varian Unity 500 NMR spectrometer. Chemical shifts are relative to $C\mathit{H}Cl_3$ (δ 7.24) and $\mathit{C}DCl_3$ (δ 77.0) as internal references. IR and Raman spectra were recorded on a Bruker IFS 66 FT-spectrometer (with Raman unit) using CsI pellets. Mass spectra were recorded on an Intectra AMD 402 mass spectrometer (electron impact, 70 eV). $H_2PtCl_6{\cdot}6H_2O$ was obtained from Degussa.

Synthesis of $[Pt_2(\mu\text{-}Cl)_2\{(COR)_2H\}_2]$ (2). A solution of hexachloroplatinic acid, $H_2PtCl_6{\cdot}6H_2O$ (0.51 g, 1.05 mmol), in *n*-butanol (3 mL, 33 mmol) was kept at 100 °C for 3 h. Then bis(trimethylsilyl)acetylene (2.5 g, 15 mmol) was added at room temperature. On standing overnight, deep yellow needles of **2a** were formed, which were washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 0.13 g (40%, based on $H_2PtCl_6{\cdot}6H_2O$). Mp: 183 °C (dec). Anal. Calcd for $C_8H_{14}Cl_2O_4Pt_2$: C, 15.16; H, 2.23; Cl, 11.18. Found: C, 15.26; H, 2.24; Cl, 11.16. IR (CsI, in cm^{-1}): ν_{OHO} 1665 (m), 1632 (m), ν_{CO} 1548 (s), ν_{PtCl} 238. ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 2.43 (s, 6H, $C\mathit{H}_3$, $^3J_{PtH}$ = 21 Hz), ca. 16 (bs, 1H, O*H*O). ^{13}C NMR (125.70 MHz, $CDCl_3$): δ 38.5 ($^2J_{PtC} = 161$ Hz), 228.1 ($^1J_{PtC} = 1457$ Hz). MS: *m*/*e* (%) 634 (<1) [M]$^+$, 619 (12), 583 (10), 555(11), 85 (31), 59 (44), 43 (100) [MeCO]$^+$.

The corresponding ethyl compound **2b** was sythesized in the same way using $MeC{\equiv}CSiMe_3$ (2.0 g, 18 mmol) instead of $Me_3SiC{\equiv}CSiMe_3$. Yield: 0.22 g (64%, based on $H_2PtCl_6{\cdot}6H_2O$). Mp: 176 °C (dec). Anal. Calcd for $C_{12}H_{22}Cl_2O_4Pt_2$: C, 20.85; H, 3.21; Cl, 10.26. Found: C, 21.04; H, 3.20; Cl, 10.37. IR (CsI, in cm^{-1}): ν_{OHO} 1662 (m), 1611 (m), ν_{CO} 1539 (s), ν_{PtCl} 251. ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 1.10 (t, 6H, $C\mathit{H}_3$), 2.80 (q, 4H, $C\mathit{H}_2$), 18.4 (bs, 1H, O*H*O). ^{13}C NMR (125.70 MHz, $CDCl_3$): δ 9.0 ($^3J_{PtC}$ = 14 Hz), 44.7 ($^2J_{PtC}$ = 154 Hz), 231.0 ($^1J_{PtC}$ = 1459 Hz). MS: *m*/*e* (%) 661 (6) [M − Et]$^+$, 625 (4), 597 (7), 57 (100) [EtCO]$^+$.

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Table 3. Crystal Data and Structure Refinement for 2a

empirical formula	$C_4H_7ClO_2Pt$
fw	317.64
T, K	203(2)
λ, Å	0.710 73
cryst system	monoclinic
space group	$P2_1/n$
a, Å	4.527(5)
b, Å	10.571(5)
c, Å	13.707(14)
β, deg	92.81(9)
V, Å^3	655.2(10)
Z	4
ρ_{calc}, g/cm^3	3.220
μ(Mo Kα), mm^{-1}	21.731
F(000)	568
scan range, deg	$2.43 < \theta < 25.01$
reflcns collcd	1162
indepdt reflcns	1162
refinement method	full-matrix least-squares on F^2
params refined	75
goodness-of-fit on F^2	1.074
final R [$I > 2\sigma(I)$]	$R_1 = 0.0308$, w$R_2 = 0.0774$
R, all data	$R_1 = 0.0411$, w$R_2 = 0.0831$
largest diff peak and hole, e Å^{-3}	1.884 and −1.255

X-ray Structure Determination of 2a. Geometry and intensity data were collected on a Stoe Stadi IV diffractometer with Mo Kα radiation (0.7173 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 3. An empirical absorption correction was applied using ψ scans. The structure was solved by direct methods with the SHELXS-86 program and refined with the SHELXS-93 program.[20,21] In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl H atoms were added to the model in the calculated position and refined isotropically.

Quantum Chemical Calculation. The calculations were carried out with the TURBOMOLE program.[22] Bases in standard DZ quality for main group elements except chlorine and ECPs for platinum and chlorine were employed.[23]

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Supporting Information Available: Complete tables of X-ray parameters, atomic coordinates and U values, H atom parameters, bond distances, bond angles, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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