Synthesis and Characterization of Intermolecular Hydrogen Bond Stabilized Acyl(hydroxycarbene)platinum(II) Complexes

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The cationic acyl(hydroxycarbene)platinum(II) complexes [Pt$_2$(bpy)$_2${μ-(COMe)$_2$H}$_2$][PF$_6$]$_2$ (**4**) (bpy = 2,2′-bipyridine) and [Pt$_2$(COMe)$_2$(bpy)$_2${μ-(COMe)$_2$H}]PF$_6$ (**5**) have been prepared by reaction of the acyl(hydrido)-platinum(IV) complex [PtCl(H)(COMe)$_2$(bpy)] (**2a**) with TlPF$_6$. The complexes **4** and **5** have been shown to be stable in the solid state up to 160 °C. The identities of **4** and **5** were determined by microanalysis, NMR (^{1}H, ^{13}C), and IR spectroscopies. The crystal structures of **4**, **5** (with two independent molecules in the asymmetric unit), and of **5**·Me$_2$CO show that these are dinuclear complexes with square-planar platinum centers. In complex **4** these centers are bridged by two μ-acyl(hydroxycarbene) ligands. In complex **5** the dinuclear structure is supported by one bridging acyl(hydroxycarbene) ligand and an additional d^8–d^8 interaction between the two Pt centers [3.340(1)–3.542(1) Å]. The O···O distances were found to be 2.455(5) Å (**4**) and 2.42(1)–2.44(1) Å (**5**), corresponding to strong hydrogen bonds.

Introduction

Hydroxycarbene complexes are proposed as important intermediates in CO reduction reactions, including the Fischer–Tropsch process.[1] Calculations suggest that they are also key intermediates in hydroformylation and aldehyde decarbonylation reactions.[2] The first hydroxycarbene complex, [Re{=C(OH)-Me}(η^5-C$_5$H$_5$)(CO)$_2$] (**A**), was prepared by protonation of a rhenium acyl anion by Fischer (Scheme 1).[3]

Since then, hydroxycarbene complexes of Cr, Mo, W, Re, Mn, Fe, and Ru have been synthesized, in most cases by protonation of acyl anions.[4] Syntheses of hydroxycarbene complexes starting from the tautomeric acyl(hydrido) complexes have not yet been described. Only very recently, Casey et al. reported an equilibrium between both tautomeric forms **B** and

Scheme 1
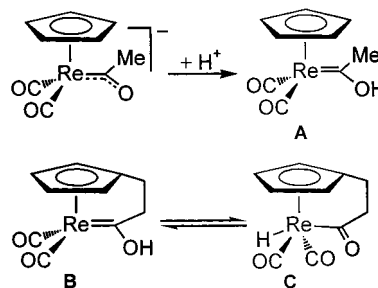
C (Scheme 1) as a consequence of ring strain perturbation in a system very similar to those of Fischer.[5] Overall, only few hydroxycarbene complexes have been structurally characterized.[4l–o]

We have found that the platina-β-diketone [Pt$_2${(COMe)$_2$H}$_2$-(μ-Cl)$_2$] (**1**), which can be regarded as an acyl(hydroxycarbene) complex intramolecularly stabilized by hydrogen bonds, reacts with bipyridines (NN = bpy, 4,4′-Me$_2$bpy, 4,4′-*t*-Bu$_2$bpy) via oxidative addition to yield acyl(hydrido)platinum(IV) complexes [PtCl(H)(COMe)$_2$(NN)] (**2**) (Scheme 2).[6] Complexes **2** decompose in the solid state (above 170 °C) nearly quantitatively via reductive elimination of acetaldehyde to form acylplatinum(II) complexes [PtCl(COMe)(NN)] (**3**) (Scheme 2).

Here we report the reaction of the complex [PtCl(H)(COMe)$_2$-(bpy)] (**2a**) with TlPF$_6$ to yield acyl(hydroxycarbene)platinum-(II) complexes stabilized by hydrogen bonds.

Experimental Section

General Considerations. All reactions were performed under Ar atmospheres using standard Schlenk techniques. Me$_2$CO was dried prior to use: over B$_2$O$_3$ followed by 4 Å molecular sieves. ^{1}H and ^{13}C NMR

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Scheme 2
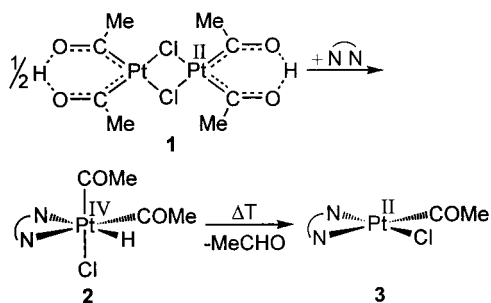
Scheme 3
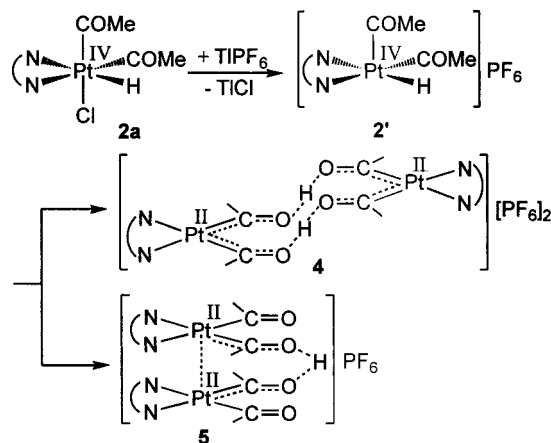
spectra were recorded on Varian Gemini 200 and Varian VXR 400 NMR spectrometers. Chemical shifts are relative to CHDCl$_2$ (δ 5.32) and CD$_2$Cl$_2$ (δ 53.8) as internal references. IR spectra were recorded on a Galaxy FT-IR spectrometer, Mattson 5000, using CsBr pellets. The complex [PtCl(H)(COMe)$_2$(bpy)] (**2a**) was prepared according to the literature method.[6]

Synthesis of [Pt$_2$(bpy)$_2${μ-(COMe)$_2$H}$_2$][PF$_6$]$_2$ (4) and [Pt$_2$(COMe)$_2$-(bpy)$_2${μ-(COMe)$_2$H}]PF$_6$ (5). To a colorless suspension of [PtCl-(H)(COMe)$_2$(bpy)] (**2a**) (200 mg, 0.42 mmol) in acetone (5 mL) at 10 °C was added TlPF$_6$ (293 mg, 0.84 mmol), producing within 1 min an orange suspension. After stirring for 30 min at ambient temperature, the suspension was filtered. On standing over 1−2 days, yellow crystals began to precipitate from solution, which were filtered and dried briefly in vacuo. After 4−5 days, red crystals were obtained from the filtrate, which were filtered and dried briefly in vacuo. **4**: yield, 37 mg (15%). Mp (dec): 162−164 °C. Anal. Calcd for C$_{28}$H$_{30}$F$_{12}$N$_4$O$_4$P$_2$Pt$_2$: C, 28.83; H, 2.60; N, 4.80. Found: C, 29.07; H, 2.84; N, 4.78. IR (CsBr): ν-(CO) 1606, 1582, ν(PF) 842 cm^{-1}. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ [8.49 (m, 2H), 8.15 (m, 4H), 7.55 (dt, 2H)], 2.48 (s + d, 6H, $^3J_{PtH}$ 24.8 Hz, CH_3), resonance for OHO not observed.

5: yield, 107 mg (50%). Mp (dec): 166−168 °C. Anal. Calcd for C$_{28}$H$_{29}$F$_6$N$_4$O$_4$PPt$_2$: C, 32.95; H, 2.86; N, 5.49. Found: C, 32.44; H, 2.87; N, 5.42. IR (CsBr): ν(CO) 1634, 1601, ν(PF) 839 cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ [8.45 (m, 2H), 8.02 (m, 4H), 7.47 (dt, 2H)], 2.43 (std, 6H, $^3J_{PtH}$ 23.5 Hz, CH_3), resonance for OHO not observed. ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ 240.8 (s + d, $^1J_{PtC}$ 1233 Hz, CO), [154.7, 151.3 (s + d, $^2J_{PtC}$ 36 Hz), 140.3, 127.4, 123.4], 44.1 (s + d, $^2J_{PtC}$ 301 Hz, CH$_3$). Resonances of the bipyridine ligands are given in square brackets.

X-ray Crystal Structure Determinations. Intensity data were collected on a Stoe IPDS diffractometer. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 1. Absorption corrections were carried out numerically, minimum/maximum transmission factors 0.08/0.15 for **5**·Me$_2$CO and 0.49/0.84 for **5'**. The structures were solved by direct methods using *SHELXS*-86[7] and refined with full-matrix least-squares routines against F^2 using *SHELXL*-93.[7] All non-H atoms were refined with anisotropic displacement parameters, except those belonging to

the solvate molecule in **5**·Me$_2$CO, which could only be refined isotropically. The H atoms were added to the model in their calculated positions and refined isotropically, except for the bridging H atom in **5**·Me$_2$CO, which was found in the difference Fourier map.

Results

Treatment of the acyl(hydrido)platinum(IV) complex **2a** with TlPF$_6$ in acetone solution results in rapid cleavage of the chloro ligand. Within 1−2 days, yellow crystals (15% yield) of [Pt$_2$(bpy)$_2${μ-(COMe)$_2$H}$_2$][PF$_6$]$_2$ (**4**) and, within 4−5 days, red crystals (50% yield) of [Pt$_2$(COMe)$_2$(bpy)$_2${μ-(COMe)$_2$H}]PF$_6$ (**5**) precipitate from the solution (Scheme 3). The complexes **4** and **5** exhibit an astonishing thermal stability; they melt with decomposition at 162−164 °C (**4**) and 166−168 °C (**5**).

The molecular structures of **4** and **5** were determined by X-ray diffraction. Complex **5** crystallizes in two different modifications: at low temperature (−30 °C) as an acetone solvate (**5**·Me$_2$CO) and at room temperature without solvent and with two independent molecules in the asymmetric unit (**5'**). ORTEP diagrams of the cation in **4** and of the cation in **5**·Me$_2$CO are shown in Figures 1 and 2. The representation of **5'** is not shown owing to the similarity to **5**·Me$_2$CO. Tables 2 and 3 contain selected atom distances, bond angles, and torsion angles. Bond lengths and bond angles of complexes **5**·Me$_2$CO and **5'** do not differ significantly.

The dinuclear complex **4** exhibits crystallographically imposed inversion symmetry. Platinum is square-planar and coordinated by two nitrogen atoms and two carbon atoms. Both planes are parallel for symmetry reasons. The Pt−C bond lengths [1.967(6)/1.968(6) Å] and the C−O bond lengths [1.281-(8)/1.253(8) Å] are in each case equivalent within 3σ and do not differ significantly from those in the platina-β-diketone **1** [d(Pt−C) = 1.95(1) Å; d(C−O) = 1.23(1)/1.26(1) Å].[8] The O···O distance in the "intermolecular" O···H···O bond is 2.455-(5) Å and is slightly longer than those in the intramolecularly bridged complex **1** [d(O···O) = 2.37(1) Å] that belongs to the strongest O···H···O bridges[9] known. The Pt···Pt distance of 4.725(1) Å rules out any direct interaction between these metal centers.

The cation in complex **5**·Me$_2$CO exhibits crystallographically imposed C_2 symmetry whereas both independent molecules of **5'** have C_1 symmetry only. As in complex **4**, the platinum centers in **5** are square-planar and coordinated by two nitrogen and two carbon atoms. As expected, the mean C−O distance in the μ-acyl(hydroxycarbene) unit is longer than those in the terminal acyl ligands (1.262 Å vs 1.204 Å, mean values of all three crystalline forms). In the case of the Pt−C bond lengths, the opposite trend is found (1.956 Å vs 2.010 Å, mean values of all three crystalline forms). The Pt···Pt distances [ranging from 3.340(1) to 3.542(1) Å] indicate closed-shell d^8−d^8 interactions.[10] Similar Pt···Pt distances (3.09−3.60 Å) were found in platinum(II) complexes with columnar structures.[11] The coordination planes around platinum are tilted relative to each other by 27.7/18.4° (**5'**) and 29.6° (**5**·Me$_2$CO) (mean values of the

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Table 1. Crystallographic Data for Complexes **4**, **5·Me₂CO**, and **5′**[a]

	4	**5·Me₂CO**	**5′**
empirical formula	$C_{14}H_{15}F_6N_2O_2PPt$	$C_{31}H_{35}F_6N_4O_5PPt_2$	$C_{56}H_{58}F_{12}N_8O_8P_2Pt_4$
fw	583.34	1078.78	2041.40
space group	$P\bar{1}$ (No. 2)	$I2/a$ (No. 15)	$P2_1/a$ (No. 14)
T/K	220(2)	220(2)	220(2)
$\lambda/\text{Å}$	0.710 73	0.710 73	0.710 73
$a/\text{Å}$	8.119(2)	13.813(3)	21.147(6)
$b/\text{Å}$	9.243(3)	16.641(4)	14.355(2)
$c/\text{Å}$	12.822(4)	15.722(4)	23.036(4)
α/deg	76.15(3)	90	90
β/deg	89.39(3)	96.73(2)	116.78(2)
γ/deg	69.63(3)	90	90
$V/\text{Å}^3$	873.0(4)	3589(2)	6243(2)
Z	2	4	4
$\rho_{calcd}/\text{g cm}^{-3}$	2.219	1.997	2.172
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	82.00	79.06	90.82
R	0.0339	0.0394	0.0363
R_w	0.0829	0.0984	0.0845

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, R based on reflections [$I > 2\sigma(I)$], R_w based on all data.
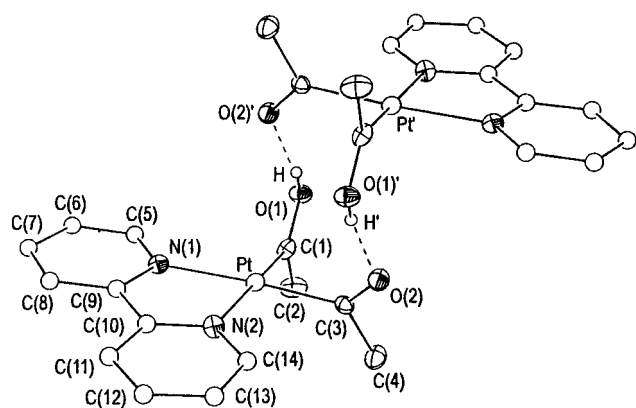
Figure 1. ORTEP-III plot[14] of the cation in [Pt₂(bpy)₂{μ-(COMe)₂H}₂]-[PF₆]₂ (**4**), showing atom numbering (displacement ellipsoids at 30% probability).
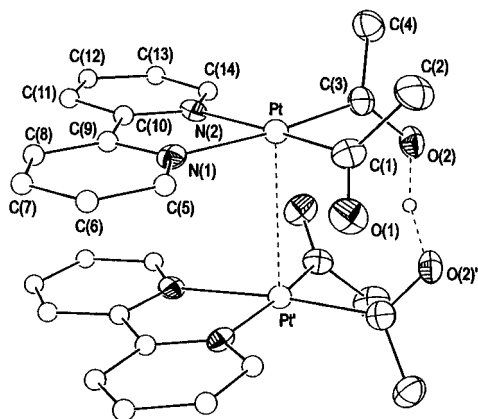
Figure 2. ORTEP-III plot of the cation in [Pt₂(COMe)₂(bpy)₂{μ-(COMe)₂H}]PF₆ (**5·Me₂CO**), showing atom numbering (displacement ellipsoids at 30% probability).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [Pt₂(bpy)₂{μ-(COMe)₂H}₂][PF₆]₂ (**4**)

Pt−N(1)	2.109(5)	C(1)−O(1)	1.281(8)
Pt−N(2)	2.111(5)	C(3)−O(2)	1.253(8)
Pt−C(1)	1.967(6)	O(1)···O(2′)[a]	2.455(5)
Pt−C(3)	1.968(6)	Pt···Pt′	4.725(1)

N(1)−Pt−N(2)	78.3(2)	Pt−C(3)−O(2)	124.4(4)
Pt−C(1)−O(1)	125.2(4)	Pt−C(3)−C(4)	120.6(5)
Pt−C(1)−C(2)	122.4(5)	C(4)−C(3)−O(2)	114.9(6)
C(2)−C(1)−O(1)	112.4(5)		

[a] Symmetry transformations used to generate equivalent atoms: (′) $-x$, $1 - y$, z.

Table 3. Selected Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for [Pt₂(COMe)₂(bpy)₂{μ-(COMe)₂H}]PF₆ (**5**)

	5·Me₂CO	**5′**[a]
Pt−C(1)	2.00(1)	2.00(1), 2.02(1)/2.02(1), 2.01(1)
Pt−C(3)	1.95(1)	1.96(1), 1.98(1)/1.94(1), 1.95(1)
Pt−N(1)	2.121(6)	2.111(6), 2.115(7)/2.142(7), 2.118(6)
Pt−N(2)	2.142(7)	2.142(6), 2.117(7)/2.127(7), 2.125(7)
C(1)−O(1)	1.20(1)	1.21(1), 1.16(1)/1.22(1), 1.23(1)
C(3)−O(2)	1.26(1)	1.28(1), 1.24(1)/1.27(1), 1.26(1)
O(2)···O(2′)[b]	2.44(1)	2.42(1)/2.43(1)
Pt···Pt′	3.340(1)	3.428(1)/3.542(1)
N(1)−Pt−N(2)	77.0(2)	77.4(2), 76.6(3)/76.0(3), 76.5(3)
Pt−C(1)−O(1)	122.8(6)	123.5(7), 122.8(8)/118.2(8), 118.8(7)
Pt−C(1)−C(2)	119.6(7)	118.3(7), 117.7(7)/120.3(8), 121.5(7)
C(2)−C(1)−O(1)	117.5(8)	118.3(8), 119.3(9)/122(1), 119.7(8)
Pt−C(3)−O(2)	125.0(6)	125.6(6), 125.9(7)/127.4(7), 125.3(6)
Pt−C(3)−C(4)	121.5(6)	120.2(7), 118.2(8)/121.0(7), 120.6(7)
C(4)−C(3)−O(2)	113.4(8)	114.2(7), 115.9(8)/111.6(8), 114.1(7)
C(1)−Pt−Pt′−C(3′)	31.0(4)	27.3(3), 30.2(4)/18.6(3), 19.2(4)
N(1)−Pt−Pt′−N(2′)	28.2(3)	26.2(2), 27.0(3)/18.4(3), 17.3(3)

[a] The values of the two crystallographically independent molecules are separated by a slash (/). Due to the lack of crystallographic symmetry, the number of values is doubled in most cases. [b] Symmetry transformations used to generate equivalent atoms: (′) $1/2 - x$, y, $-z$.

C(1)−Pt−Pt′−C(3′) and N(1)−Pt−Pt′−N(2′) torsion angles) where the smaller angles are associated with the longer Pt···Pt distances. These geometric parameters are likely associated with optimization of the strength of the hydrogen bond. This is supported by examination of the O···O distances, which do not differ significantly in the three forms of **5** [ranging from 2.42-(1) to 2.44(1) Å] or from those in **4** [2.455(5) Å] and only slightly from those in **1** [2.37(1) Å].

In accordance with the results of the X-ray structure determination, the four methyl groups in **4** are chemically equivalent in the ¹H NMR spectrum. The ¹H and ¹³C NMR spectra of **5** also exhibit chemical equivalence of all organic ligands, indicating a rapid exchange of the proton in the O−H···O bridge in solution. Even at −50 °C, no splitting of the methyl resonance is observed. In both complexes the proton resonances of the hydrogen-bonded hydrogen atoms could not be detected due to line broadening. The C−O stretching vibrations appear at higher wavenumbers (**4**, 1606, 1582 cm⁻¹; **5**, 1634, 1601 cm⁻¹) than those in the platina-β-diketone **1** (1548 cm⁻¹).[8]

Discussion

Both complexes **4** and **5** are cationic acyl(hydroxycarbene)-platinum(II) complexes, where the hydroxycarbene ligands are stabilized by hydrogen bonds to acyl ligands. Initial formation of a cationic diacyl(hydrido)platinum(IV) complex **2′** is likely, in which the sixth coordination site is probably occupied by a solvent molecule (Scheme 3). This intermediate can react further to give complexes **4** and **5** by a 1,3-hydrogen shift in the sense of an intramolecular reductive elimination reaction or by an intermolecular deprotonation/protonation reaction. Such reactions, induced by ligand abstraction, are fundamentally important in organometallic chemistry and homogeneously catalyzed processes.[12]

The presented results illustrate that hydroxycarbene ligands can be effectively stabilized by hydrogen bonding to acyl ligands. These hydrogen bonds can be formed not only intramolecularly, as in metalla-β-diketones,[8,13] but also intermolecularly, as shown for the first time in this work. Complexes **4** and **5** demonstrate that two of these bridges [μ-C(R)O$-$H$\cdots$OC(R)] or one of them with an additional weak metal$-$metal interaction are sufficient for the formation of stable dinuclear complexes.

Furthermore, it was shown that the decomposition of acyl-(hydrido) complexes can give hydroxycarbene complexes (stabilized by intermolecular hydrogen bonds) in reductive elimination reactions. Thus, acyl(hydrido) complexes **2** can be formed from (see Scheme 2) and decomposed to hydroxycarbene complexes (see Scheme 3) which are stabilized by hydrogen bridges in both cases.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **4**, **5**·Me$_2$CO, and **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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