Journal of Organometallic Chemistry 739 (2013) 57–62

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, structure and characterization of adenine-based aminocarbene complexes of platinum(II)

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ARTICLE INFO

Article history:
Received 17 March 2013
Accepted 19 April 2013

Keywords:
Platinum complexes
Aminocarbene complexes
Platina-β-diketones
Adenine-based ligands

ABSTRACT

The reaction of the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with two equivalents of adenine and its methylated derivatives N^6-R,9-R′Ade$_{-H}$ resulted in adenine-based aminocarbene platinum(II) complexes [Pt(COMe)Cl{CMe(N^6-R,9-R′Ade$_{-H}$)-κ*C*,κ*N*}] (R/R′ = Me/Me, **2**; H/Me, **3**; H/H, **4**) whose identities were confirmed by NMR and IR spectroscopies as well as by high-resolution mass spectrometric investigations. Single-crystal X-ray diffraction analyses of complexes **2** and **4**·THF revealed relatively short Pt–C and N–C bonds in the aminocarbene–platinum units, which is in accord with a substantial double bond character of these bonds. The electronic structure of these complexes will be further confirmed by DFT calculations as also the course of reaction.

1. Introduction

At the end of 70ies, C. M. Lukehart was the first, who synthesized and characterized metalla-β-diketones $[M\{(COR)_2H\}(CO)_x(C_5H_5)_y]$ (**I**; M = Mo, Re, Fe, Mn, W, Os; R = alkyl, aryl) [1]. Formally, they are derived from enol forms of organic β-diketones by replacing the central methine unit by a metal fragment. Thus, they can be understood as hydroxycarbene complexes stabilized by an intramolecular O–H···O hydrogen bond to a neighbored acyl ligand. Due to the way of synthesis, which starts from *cis*-acyl–carbonyl metal complexes (Scheme 1), all these complexes are electronically saturated (18 *ve*; *ve* = valence electrons) having kinetically inert ligand spheres. The chemistry of Lukehart's metalla-β-diketones is dominated by two typical reactions (Scheme 1), namely *i*) the deprotonation of the O–H–O bridge re-forming anionic *cis*-diacyl complexes (**I** → **a**) or yielding metal complexes bearing metalla-β-diketonato ligands (**I** → **b**) and *ii*) the attack of the carbene C atom by nucleophiles such as ammonia or primary amines (**I** → **c**). Although 18 *ve* complexes too, irida-β-diketones such as $[IrH(\{PPh_2(o\text{-}C_6H_4CO)\}_2H)Cl]$ differ in their reactivity due to the reactive hydrido and chlorido ligands [2].

In contrast to Lukehart's metalla-β-diketones, the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) and its derivatives are electronically unsaturated 16 *ve* complexes having kinetically labile ligand spheres [3]. Due to that, their reactivity is completely different from Lukehart's metalla-β-diketones. Typically, the platina-β-diketone **1** undergoes easily ligand induced oxidative addition yielding (sometimes thermally extraordinarily stable) diacetyl(hydrido) platinum(IV) complexes which are prone to reductive C–H elimination with formation of acetyl platinum(II) complexes (Scheme 2a). On the other side, reactions of **1** with amines result in the formation of platina-β-diketonates of platina-β-diketones (Scheme 2b) which can be considered to be organometallic analogs of platinum blue complexes. One of the few reactions in which a nucleophile attacks the carbene C atom, as it is frequently the case for Lukehart's metalla-β-diketones, proved to be reactions with 2-aminopyridines resulting in the formation of aminocarbene complexes (Scheme 2c) [4]. Here we report reactions of the platina-β-diketone **1** with adenine and its methylated derivatives which lead to adenine-based aminocarbene platinum(II) complexes.

2. Results and discussion

2.1. Synthesis and characterization

The platina-β-diketone **1** was found to react in tetrahydrofuran with two equivalents of adenine and its methylated derivatives yielding new aminocarbene platinum(II) complexes (Scheme 3). The orange-red complexes **2**–**4** were obtained in good yields (79–84%). The complexes are only moderately soluble

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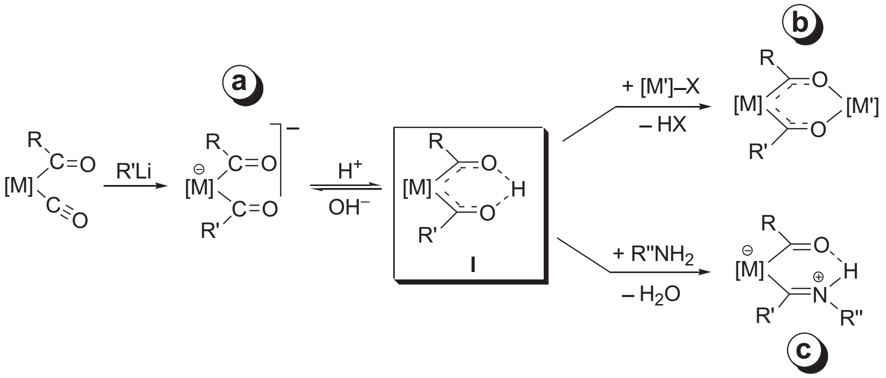
http://dx.doi.org/10.1016/j.jorganchem.2013.04.030



Scheme 1. Synthesis (a) and typical reactivity (b, c) of Lukehart's metalla-β-diketones **I**. The square brackets around M denote the coligands (CO/Cp) which are not directly involved in these reactions.

in common solvents or even insoluble in them. They were characterized by IR and ^{1}H NMR spectroscopy. Furthermore, the identities of all complexes were proved by high-resolution mass spectrometric (HRMS-ESI) investigations and for complexes **2** and **4**·THF, additionally, by a single-crystal X-ray diffraction measurement.

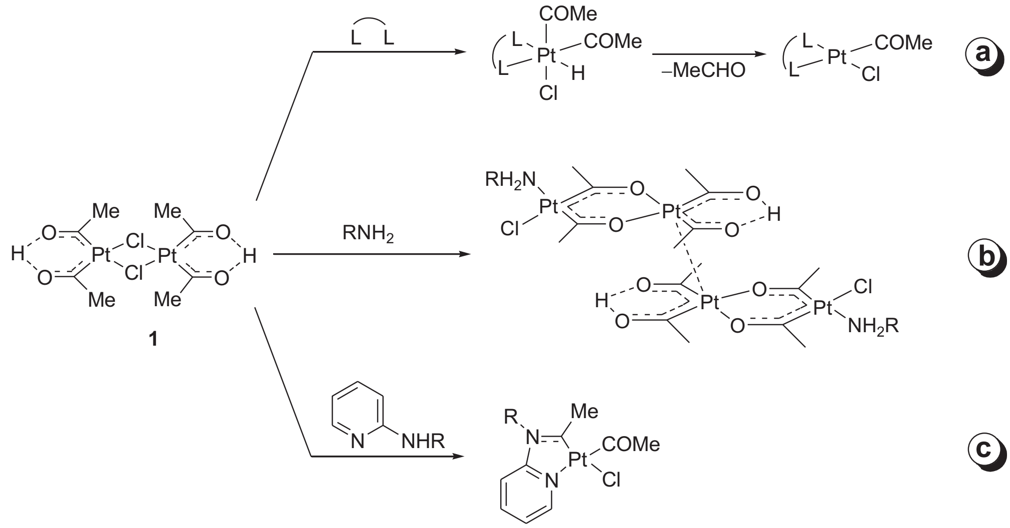
In the ^{1}H NMR spectra the signals of all protons were found in the expected range with correct intensities (Table 1). The acetyl protons were found between 2.42 and 2.50 ppm with $^3J_{Pt,H}$ coupling constants between 13.4 and 14.2 Hz, as typical for acetyl platinum(II) complexes [5,6]. Moreover, a strong carbonyl vibration (ν(C═O) = 1579–1627 cm^{-1}) is indicative for an acetyl ligand. In the ^{1}H NMR spectra, the coordination of the adenine type ligands gives rise to a downfield shift of resonances of H^2 and H^8. The protons of the methyl group bonded to the carbene C atom are in a shift range from 1.23 to 2.24 ppm with $^3J_{Pt,H}$ couplings of 59.7 Hz (**2**) and 58 Hz (**4**). Analogous values (δ_H 2.26/2.32 ppm; $^3J_{Pt,H}$ = 57.6/60.4 Hz) were observed in similar aminocarbene platinum(II) complexes (Scheme 2c) [4].

High-resolution mass spectrometric (HRMS-ESI) measurements in the cationic mode showed peaks [M − Cl]$^+$ (**2**–**4**) as base peak. Both the *m*/*z* values and the isotope distribution experimentally observed were found in a good agreement with the calculated values, thus giving further proof for the identities of the complexes. Further signals of smaller intensities (see Experimental) are due to decomposition during the ionization process.

2.2. Structures of complexes 2 and 4·THF

Single crystals of complexes **2** and **4**·THF suitable for X-ray structure analyses were obtained from CH$_2$Cl$_2$/*n*-pentane and THF solutions, respectively. The molecular structures are shown in Fig. 1, selected bond lengths and angles are listed in Table 2.

In the two complexes the platinum atoms are square-planar coordinated by the chelating κ*C*,κ*N* bound aminocarbene ligand, as well as by an acetyl and a chlorido ligand. Thus, the platinum atoms adopt a primary C$_2$NCl donor set. The five-membered PtC$_2$N$_2$ rings are nearly planar (greatest deviation from the mean plane: 0.041 Å for N1, **2**; 0.014 Å for N6, **4**). Furthermore, these rings are practically coplanar to the C$_5$N$_4$ adenine planes (interplanar angle: 4.8(2)/1.1(2)°, **2**/**4**). The Pt–C bonds to the carbene C atoms (Pt–C11 1.928(4)/1.924(4) Å, **2**/**4**) are significantly shorter than that to the acetyl C atoms (Pt–C13 2.001(4)/1.978(4) Å, **2**/**4**). Furthermore, in the complexes **2**/**4** the N6–C11 bonds (1.354(6)/1.346(5) Å) are even shorter than the N6–C6 bonds (1.399(5)/1.393(5) Å) and in the same order of magnitude as those in noncoordinated *N*^{6},9-Me$_2$Ade (1.3342(3) Å) [7] and Ade (1.349(5)/1.343(5) Å) [8], respectively, where a substantial p$_\pi$–p$_\pi$ bonding character is well



Scheme 2. Typical reactivity of the platina-β-diketone **1**.