How Strong Are Hydrogen Bonds in Metalla-β-diketones?

Dirk Steinborn* and Sebastian Schwieger[a]

Abstract: The energies of the kinetically inert, electronically saturated Lukehart-type metalla-β-diketone [Re-{(COMe)$_2$H}(CO)$_4$] (**9a**) and of the kinetically labile, electronically unsaturated platina-β-diketones [Pt-{(COMe)$_2$H}Cl$_2$]$^-$ (**10a**), [Pt$_2$-{(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**11a**), and [Pt-{(COMe)$_2$H}(bpy)]$^+$ (**12a**) have been calculated by DFT at the B3LYP/6-311++G(d,p) level using effective core potentials with consideration of relativistic effects for the transition metals. Analogously, energies of the requisite open (non-hydrogen-bonded) equilibrium conformers (**9b**, **10c**, **11b**, **12b**) and energies which were obtained from the hydrogen-bonded conformers by rigid rotation of the OH group around the C–O bond by 180° followed by relaxation of all bond lengths and angles (**9c**, **10d**, **11c**, **12d**) have been calculated. These energies were found to be higher by 14.7/27.2 (**9b/9c**), 20.7/27.2 (**10c/10d**), 19.2/25.7 (**11b/11c**), and 9.4/19.6 kcal mol^{-1} (**12b/12d**) than those of the intramolecularly O–H···O hydrogen-bonded metalla-β-diketones **9a**, **10a**, **11a**, and **12a**, respectively. In acetylacetone (Hacac), the generic organic analogue of metalla-β-diketones, the energies of the most stable non-hydrogen-bonded enol isomer (**6b**) and of the conformer derived from the H-bonded form by rigid rotation of the OH group by 180° followed by subsequent relaxation of all bond lengths and angles (**6k**) were found to be 10.9/16.1 kcal mol^{-1} (**6b/6k**) higher compared to the intramolecularly O–H···O bonded isomer **6a**. Thus, the hydrogen bonds in metalla-β-diketones must be regarded as strong and were found to be up to twice as strong as that in acetylacetone. A linear relationship was found between the hydrogen-bond energies based on the rigidly rotated structures and the O···O separation in the hydrogen-bonded structures. Furthermore, these energies were also found to be correlated with the electron densities at the O···H bond critical points (ρ_{bcp}) in the O–H···O bonds of metalla-β-diketones **9a**, **10a**, **11a**, and **12a** (calculated using the AIM theory). The comparison of the energies of the doubly intermolecularly hydrogen-bonded dinuclear platina-β-diketone [{Pt{(COMe)$_2$H}-(bpy)}$_2$]$^{2+}$ (**14**) with that of the mononuclear intramolecularly hydrogen-bonded cation [Pt{(COMe)$_2$H}(bpy)]$^+$ (**12a**) showed that the intermolecular hydrogen bonds in **14** are weaker than the intramolecular hydrogen bond in **12**.

Keywords: density functional calculations · hydrogen bonds · metalla-β-diketones · platinum · rhenium

Introduction

Although hydrogen bonds are among the weaker chemical forces, they are crucial to understanding structure, molecular association, and reactivity of numerous classes of compounds in which a hydrogen atom in a quite polar $^{\delta-}$X–H$^{\delta+}$ bond interacts with another electronegative, electron-rich atom Y. Because of the frequent occurrence of hydrogen donors (O–H, N–H) and hydrogen acceptors (O, N) in biomolecules, hydrogen bonding is not only of fundamental importance in chemistry but also in bioprocesses of living organisms.[1] The strength of hydrogen bonds ΔH_{hb} is usually defined as the enthalpy of the reaction in Equation (1).

$$X-H\cdots Y \longrightarrow X-H + |Y \qquad (1)$$
$$\mathbf{1} \qquad\qquad \mathbf{2} \qquad \mathbf{3}$$
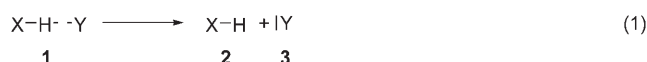
Analogous to the general definition of bond enthalpies, within intermolecularly hydrogen-bonded systems ΔH_{hb} is the difference in energy between **1** and **2**+**3** when **1**–**3** are in their equilibrium conformations and **2** and **3** at infinite distance. Thus, in general, the reference state is well defined.

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The ΔH_{hb} values can be calculated by means of quantum chemical methods with high accuracy, but corrections for basis set superposition errors (BSSE) must be made. On the other hand, in intramolecularly hydrogen-bonded systems **4** [Eq. (2)], the problem is complicated by the definition of a reference structure **5**, an isomer of **4** in which the hydrogen bond is absent.

$$(2)$$

There may be more than one "open" conformer having no hydrogen bond. Thus for acetylacetone (**6**), which is a typical example of a strongly intramolecularly hydrogen-bonded molecule (**6a**),[2,3] seven non-hydrogen-bonded enol conformers (**6b–6h**) must be taken into consideration (Scheme 1).[4] Regardless of the structure of the open con-
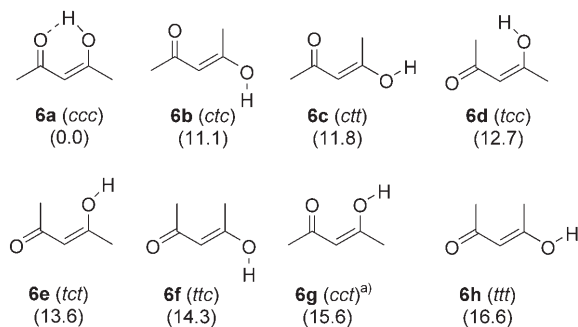

Scheme 1. Hydrogen-bonded (**6a**) and non-hydrogen-bonded (**6b–6h**) enol forms of acetylacetone. "*c*" and "*t*" stand for *cis* and *trans* character, respectively, relative to the C–C, C=C, and C–O bonds. Energies [kcal mol^{-1}, B3LYP/6-311++G(2d,2p)] relative to **6a** are given in parentheses.[4] a) Compounds **6i–6k** are nonequilibrium *cct* isomers (see Table 2).

former, the energy difference between **4** and **5** (for Hacac: **6a** versus **6b–6h**) reflects not only the strength of the intramolecular hydrogen bond but also comprises other terms resulting from different attractive and/or repulsive interactions in the two compared structures, such as different X⋯Y repulsion and different conjugation in the backbone of **4** and **5**. Furthermore, these quantum chemical calculations cannot be corrected for BSSE. Thus, the reference state for intramolecularly hydrogen-bonded systems is not well defined, and the interpretation that enthalpies of type 2 reactions reflect the strength of (intramolecular) hy-

drogen bonds may be misleading. Particularly problematic is the comparison of systems with large structural differences in the open conformations.

In β-diketones and related compounds the hydrogen-bond energies of the cyclic enols **6a** can be defined relative to the open *cct* conformers **6g** or to the most stable non-hydrogen-bonded enol conformers (for Hacac: **6b**). Furthermore, a "rigid" rotation (without optimization of the open structure and thus maintaining the structural parameters of the hydrogen-bonded structure) of the XH group around the C–X bond (in Hacac: X=O) by 180° has also been proposed.[5] Thus, a clearly defined reference structure for the conformation having no hydrogen bond was defined. However, it may be a drawback that this is not an equilibrium structure, especially since comparisons with intermolecular hydrogen bonds [based on equilibrium structures, see Eq. (1)] are made.

Metalla-β-diketones **7** are formally derived from hydrogen-bonded enol forms of organic 1,3-diketones **8** by replacing the central methine group by a transition metal fragment L_xM (Scheme 2). Just as a β-diketone **8** may be regarded as a vinyl alcohol stabilized by an intramolecular hydrogen bond to a ketone, so can a metalla-β-diketone **7** be understood as a hydroxycarbene complex whose OH group is intramolecularly hydrogen-bonded to an acyl ligand (**7a/7b**). This gives rise to strong stabilization of the hydroxycarbene moiety. There are different types of metalla-β-diketones: In the mid-1970s Lukehart prepared complexes of type **A** (M= Mn, Re, Fe, etc.) having carbonyl/cyclopentadienyl coligands.[6] All of them are electronically saturated complexes (18 ve) that are kinetically inert towards ligand substitution reactions. On the other hand, we observed that reactions of hexachloroplatinic acid in butanol with alkynylsilanes R′C≡ CSiMe₃ resulted in the formation of dinuclear platina-β-diketones **B** as electronically unsaturated complexes (16 ve) that readily undergo addition and ligand substitution reactions. Thus, platina-β-diketones **B** exhibit completely different reactivity to Lukehart's complexes **A**.[7] Cleavage reactions of the Pt–Cl–Pt bridge led to the synthesis of neutral and anionic mononuclear platina-β-diketones **C** (L=py, quin: $z=0$; L=Cl: $z=1$; Scheme 2). Furthermore, irida-β-diketones of type **D** (L=Cl, OTs, OTf, ..: $z=0$; L=py,
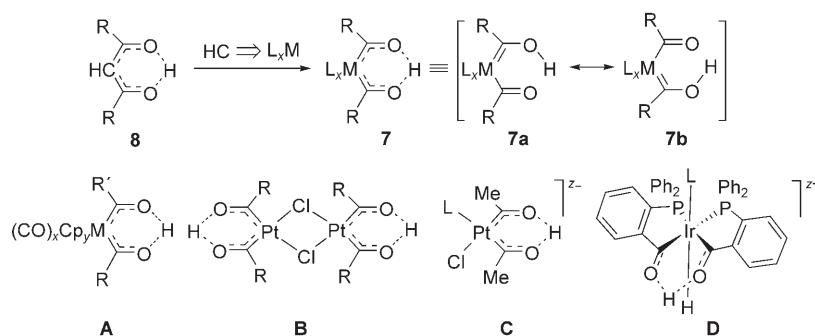
Scheme 2. Relationship between enols of 1,3-diketones (**8**) and metalla-β-diketones (**7**), as well as different types of metalla-β-diketones **A–D** (see text).

PPh$_3$: $z=1$) have recently been synthesized by Garralda et al.[8]

In all metalla-β-diketones that have been structurally investigated so far, very short O···O distances (median: 2.405 Å, lower/upper quartile: 2.391/2.411; number of observations $n=16$)[9] in the O−H···O bridges suggest strong intramolecular hydrogen bonds. In the organic analogues **8** the longer O···O distances (ca 2.50 Å) that were found indicate weaker hydrogen bonds. Based on quantum-chemical calculations at the DFT level of theory, here we seek to answer the question of the strength of the O−H···O bonds in metalla-β-diketones compared to those in 1,3-diketones.

Results and Discussion

Acetylacetone: For metalla-β-diketones the "generic" organic analogue is the intramolecularly hydrogen-bonded isomer of acetylacetone **6a** (Scheme 1). All isomers of acetylacetone have been carefully calculated before,[3,4,10–12] and **6a** is used here as reference compound. To calculate metalla-β-diketones **A**–**C** of the third transition series with good accuracy at reasonable computational costs, the DFT method was applied using the B3LYP functional, and for the core orbitals of the transition metals (Pt, Re), effective core potentials with consideration of relativistic effects were used. The appropriateness of such calculations for reliable interpretation of structural and energetic aspects of platina-β-diketones and related complexes has been demonstrated.[13] Thus, the same functional was used for calculations on acetylacetone. Energies obtained for the non-hydrogen-bonded *cct* (**6g**) and *tct* (**6e**) isomers relative to the hydrogen-bonded isomer (**6a**) are given in Table 1. Density func-

Table 1. Calculated energies of non-hydrogen-bonded acetylacetone isomers (*cct*, **6g**; *tct*, **6e**; see Scheme 1). Energies [kcal mol^{-1}] are relative to hydrogen-bonded isomer **6a** (in parentheses: ZPE-corrected values).

Basis set	*cct* (**6g**)	*tct* (**6e**)	Reference
B3LYP/6-31G(d)	17.2 (16.8)	15.4 (15.2)	[a]
B3LYP/6-31G(d,p)	17.4 (17.2)	15.6 (15.5)	[a]
B3LYP/6-311G(d,p)	16.5 (16.2)	14.6 (14.3)	[a]
B3LYP/6-311++G(d,p)	15.9 (15.4)	13.7 (13.3)	[a]
B3LYP/6-311++G(2d,2p)	15.6	13.6	[4]
CR-CCSD(T)/6-31++G(d,p)	14.7	12.0	[4]
MP2/D95(d,p)		12.5 (12.2)	[3]
MP4/6-311+G(2d,2p)	14.3		[11a]

[a] This work.

tional calculations using a triple-zeta basis set augmented with diffuse and polarization functions both on the heavy and hydrogen atoms were found to be very close to calculations using post-HF methods, which explicitly include electron correlation (Table 1). Thus, in the present study the high-quality basis set 6-311++G(d,p) was employed for all DFT(B3LYP) calculations.

Taking the *cct* isomer **6g** as the reference structure for non-hydrogen-bonded acetylacetone, the strength of the O−H···O bond amounts to 15.9 kcal mol^{-1}. Due to the reso-

nance-assisted stabilization of the hydrogen bond in **6a**,[14] its cleavage results in severe shortening of the double bonds (C=O, C=C) and lengthening of the single bonds (C−O, C−C) (Table 2). Furthermore, in the open form **6g** the angles in the O=C−C=C−O backbone are widened. Thus, the O···O distance is enlarged (2.804 versus 2.543 Å) and hence repulsive (Pauli) O···O interactions are weaker.

Table 2. Selected distances [Å] of acetylacetone *ccc* (**6a**) and *cct* isomers (**6g**: equilibrium structure; **6j**: rotated OH group, relaxed bond lengths) and energies [kcal mol^{-1}] relative to **6a**.

	6a	**6g**	**6j**
O−H/O···H	1.003/1.633	0.963/–	0.965/–
C−O/C=O	1.326/1.246	1.351/1.219	1.354/1.220
C=C/C−C	1.370/1.444	1.352/1.474	1.356/1.482
O···O	2.543	2.804	2.565
ΔE	0.0 (20.0)[a]	15.9 (16.1)[b]	17.9

[a] Energy of the *cct* isomer **6i** (rotated OH group) is given in parentheses. [b] Energy of the *cct* isomer **6k** (rotated OH group, relaxed bond lengths and angles) is given in parentheses.

On the other hand, based on the discussions in references [5,15], we can define as reference a molecule **6i** which is obtained by rigid rotation of the OH group around the C−O bond in **6a** by 180°. The energy of **6i** was found to be 20.0 kcal mol^{-1} higher than that of **6a**, and 4.1 kcal mol^{-1} higher than that of **6g**. The latter is a consequence of the retention of the geometry of **6a** along the backbone. If we allow the relaxation of all bond lengths in **6i**, structure **6j** is obtained, which is 17.9 kcal mol^{-1} higher in energy than **6a**. All bond lengths in the backbones of **6j** and **6g** are very similar (Table 2). Additional relaxation of the bond angles resulted in **6k**, which has essentially the same structure as **6g**. The marginally higher energy of **6k** relative to equilibrium structure **6g** (0.2 kcal mol^{-1}) is due to the fixed torsion angles in the geometry optimization.

In the case of metalla-β-diketones it was found that the structures of the non-hydrogen-bonded and hydrogen-bonded conformers are very different (see below). Thus, we decided to additionally calculate the energy of a reference structure, derived, as described above, from the hydrogen-bonded conformer by rigid rotation of the OH group around the C−O bond by 180° and subsequent relaxation of all bond lengths and angles.

Lukehart's rhena-β-diketone [Re{(COMe)$_2$H}(CO)$_4$]: The rhena-β-diketone [Re{(COMe)$_2$H}(CO)$_4$] (**9**), prepared by Lukehart and co-workers,[6] is a typical representative for an electronically saturated (18 ve), kinetically inert metalla-β-diketone. As the comparison (Table 3) reveals, the calculated structure (**9a**, Figure 1) is in very good agreement with that obtained by neutron diffraction measurements (**9$_{exp}$**).[16] In particular, the calculated structural parameters of the hydrogen bond (C−O, O−H, and O···O distances, see numbering scheme in formula **E**)[17] match
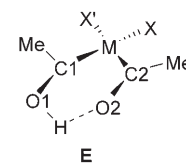

E

Table 3. Selected distances [Å], angles [°], and energies [kcal mol⁻¹] for calculated hydrogen-bonded (**9a**) and non-hydrogen-bonded (**9b**) equilibrium structures of the rhena-β-diketone [Re{(COMe)₂H}(CO)₄], as well as open conformation **9c** (rotated OH group, relaxed bond lengths and angles). For comparison, structural parameters of the experimentally measured structure **9exp** are given.

	9a	9b	9c	9exp
Re−C[a]	2.212/2.230	2.128/2.306	2.160/2.305	2.13(2)/2.18(2)
C−O[a]	1.266/1.253	1.325/1.214	1.301/1.210	1.28(2)/1.25(2)
O−H/O···H[a]	1.132/1.273	0.968/−	0.974/−	1.15(4)/1.26(4)
O1···O2	2.395	4.234	2.683	2.40(2)
$\phi_{carbene}/\phi_{acetyl}$[b]	0/0	+115/−49	0/0	+9/+11
ΔE	0.0	14.7 (16.4)[c]	27.2	

[a] The first value refers to the hydroxycarbene moiety (C1, O1 in Figure 1) and the second to the acyl moiety (C2, O2 in Figure 1). [b] Interplanar angles between the plane of the complex and the hydroxycarbene and acyl moieties, respectively. [c] ZPE-corrected value.
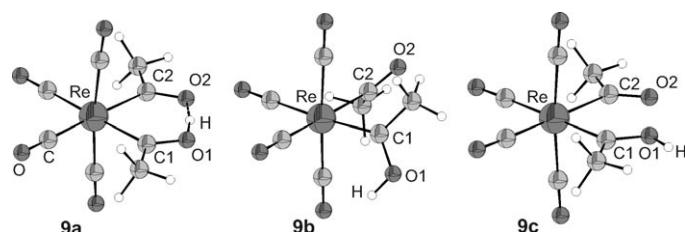

Figure 1. Calculated structures of [Re{(COMe)₂H}(CO)₄] (**9**): Equilibrium hydrogen- and non-hydrogen-bonded structures **9a** and **9b**, respectively. Open conformation **9c** (rotated OH group, relaxed bond lengths and angles).

very well (within the limit of the standard deviation) to the experimentally found parameters. The most obvious difference between these two structures is the essentially planar rhena-β-diketone unit ReC₂O₂ (interplanar angles: $\phi_{carbene}/\phi_{acetyl}=0/0°$) in the calculated structure, whereas in **9exp** the ReC₂O₂ unit adopts a slightly envelopelike conformation ($\phi_{carbene}/\phi_{acetyl}=+9/+11°$). As shown for platina-β-diketones (see below) the energies associated with such transformations are very small.

The non-hydrogen-bonded structure **9b** (Figure 1) is characterized by a severe conrotatorylike motion of the hydroxycarbene and acyl ligands out of the plane of the complex. The interplanar angles of $\phi_{carbene}/\phi_{acetyl}=+115/−49°$ result in

a O1···O2 separation of 4.2 Å. As expected, opening of the H-bond leads to formation of typical Fischer carbene (shortening/lengthening of the Re−C1/C1−O1 bonds) and acetyl ligands (shortening/lengthening of the C2−O2/Re−C2 bonds). The non-hydrogen-bonded structure **9c** (Figure 1) was obtained by rotation of the OH group by 180°, followed by relaxation of all bond lengths and angles. As for **9a→9b**, cleavage of the H-bond (**9a→9c**) results in a typical hydroxycarbene acetyl complex (Table 3).

The rhena-β-diketone **9a** is 14.7 and 27.2 kcal mol⁻¹ more stable than the hydroxycarbene acetyl complexes **9b** and **9c**, respectively. A structure analogous to **9c** but without relaxed bond lengths and bond angles is 13.9 kcal mol⁻¹ less stable than **9c**. About 60% of this is lost solely on relaxation of the O−H bond length, and a further 20% each on relaxation of the other bond lengths and all angles.

Anionic mononuclear platina-β-diketone [Pt-{(COMe)₂H}Cl₂]⁻: The molecular structure of the mononuclear anionic platina-β-diketone complex [PPh₄][Pt-{(COMe)₂H}Cl₂] ([PPh₄][**10**]), prepared from dinuclear platina-β-diketone **11** by cleavage of the Pt−Cl−Pt bridges with [PPh₄]Cl [Eq. (3)], was determined by single-crystal X-ray diffraction (Table 4).[18] The calculated structure of the anion **10a** (Figure 2, Table 4) is in very good agreement with that experimentally found in [PPh₄][**10**]. Both in the calculated and in the experimental structures the PtC₂O₂ units exhibit envelopelike conformations at Pt. Furthermore, an equilibrium structure **10b** was found having an O−H···Cl instead of an O−H···O hydrogen bond (Figure 2). While the hydroxycarbene ligand remains in the plane of the complex ($\phi_{carbene}=+178°$), the acetyl ligand forms an angle of −58° with this plane. Compared with **10a** the Pt−C1 and C1−O1 bonds in **10b** are slightly shorter and longer, respectively, that is, the carbene character in **10b** is more pronounced. In the non-hydrogen-bonded equilibrium structure **10c** (Figure 2) neither of the two organo ligands lies in the plane of the complex ($\phi_{carbene}/\phi_{acetyl}=+40/−62°$), and this results in an O1···O2 separation of 3.2 Å. The open conformation **10d** (Figure 2) was obtained from **10a** by rotation the O−H bond by 180° around the C−O bond and subsequent optimization of all bond lengths and angles.
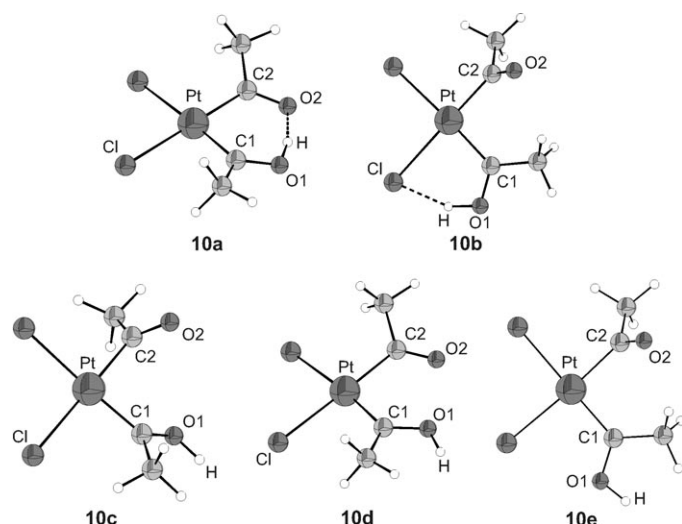
Table 4. Selected distances [Å], angles [°], and energies [kcal mol⁻¹] for calculated O−H···O (**10a**) and O−H···Cl (**10b**) hydrogen-bonded and for non-hydrogen-bonded (**10c**) equilibrium structures of [Pt{(COMe)₂H}Cl₂]⁻, as well as open conformations (rotated OH bond, relaxed bond lengths and angles; **10d** derived from **10a**; **10e** derived from **10b**). For comparison, structural parameters of the anion in the experimentally determined structure [PPh₄][Pt-{(COMe)₂H}Cl₂] (**10exp**) are given. Furthermore, structural parameters of the transition states for rotation of the acetyl ligand with respect to the coordination plane (**10f**) and for H transfer from the hydroxycarbene to the acetyl moiety (**10g**) are given.

	10a	10b	10c	10d	10e	10exp	10f	10g
Pt−C[a]	1.965/1.999	1.951/2.006	1.908/2.028	1.927/2.054	1.921/2.032	1.952(5)/1.947(5)	1.977/2.000	1.983/1.983
C−O[a]	1.286/1.254	1.304/1.215	1.333/1.214	1.325/1.212	1.329/1.220	1.262(6)/1.250(6)	1.279/1.259	1.269/1.269
O−H/O···H[a]	1.080/1.352	1.018/1.906[d]	0.971/−	0.970/−	0.970/−	1.05(6)/1.38(7)	1.113/1.283	1.192/1.192
O1···O2	2.405	2.862[e]	3.188	2.594	3.029[e]	2.424(6)	2.379	2.365
$\phi_{carbene}/\phi_{acetyl}$[b]	+19/+22	+178/−58	+40/−62	+19/+22	+178/−58	+26/+36	0/0	+16/+16
ΔE	0.0	2.2 (2.7)[c]	20.7 (21.0)[c]	27.2	26.7		0.2	0.1
Q[f]	−0.066	−0.144	−0.239	−0.240	−0.220	−0.017	−0.043	0.000

[a]–[c] See footnotes in Table 3. [d] Cl···H. [e] O1···Cl. [f] Delocalization parameter; see text.

Figure 2. Calculated structures of $[Pt\{(COMe)_2H\}Cl_2]^-$ (**10**): Equilibrium O−H⋯O (**10a**) and O−H⋯Cl (**10b**) hydrogen-bonded structures. Equilibrium non-hydrogen-bonded structure **10c**. Open conformations (rotated OH group, relaxed bond lengths and angles) **10d** (derived from **10a**) and **10e** (derived from **10b**).

$$^1/_2 \quad \text{(11)} \quad \xrightarrow{[PPh_4]Cl} \quad [PPh_4]\text{[10]} \quad (3)$$
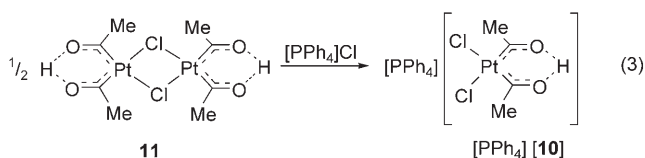
The energies of the O−H⋯O and O−H⋯Cl hydrogen-bonded structures **10a** and **10b**, respectively, differ only by 2.2 kcal mol^{-1} in favor of **10a**. The non-hydrogen-bonded isomer **10c** lies 20.7 kcal mol^{-1} above **10a**. Rigid rotation of the OH group in **10a** by 180° requires 36.9 kcal mol^{-1}, with subsequent relaxation of the bond lengths 29.1 kcal mol^{-1}, and with subsequent relaxation of the bond lengths and angles (yielding **10d**) 27.2 kcal mol^{-1}. Thus, the open *cis* isomer **10d** having the hydroxycarbene and acyl ligands in the same relative positions as in the hydrogen-bonded platina-β-diketone **10a** is 6.5 kcal mol^{-1} higher in energy than the (fully optimized) isomer **10c**, in which the hydroxycarbene and acyl ligands are rotated in conrotatorylike fashion.

To estimate the strength of the O−H⋯Cl hydrogen bond the OH group in **10b** was rotated by 180° around the C−O bond and then the bond lengths and angles were relaxed to give **10e** (Figure 2, Table 4). Due to repulsive (Pauli) O⋯Cl interactions in **10e**, the O⋯Cl separation is increased by 0.167 Å compared with **10b**. The fully and partially optimized non-hydrogen-bonded structures are 18.5 (**10c**) and 24.5 kcal mol^{-1} (**10e**) higher in energy than **10b**, that is, the O−H⋯Cl hydrogen bond is quite strong. This is in accord with the metrical properties of the O−H⋯Cl hydrogen bond in **10b** (O−H 1.018 Å, H⋯Cl 1.906 Å, O−H⋯Cl 155.1°). For chloride–alcohol complexes RO−H⋯Cl$^-$ hydrogen-bond energies between 15 and 20 kcal mol^{-1} were both experimen-

tally measured and calculated for even longer (compared with **10b**) H⋯Cl distances (2.079/2.190 Å, R = Me/*i*Pr).[19]

Geometric and electronic features of the hydrogen bond in $[Pt\{(COMe)_2H\}Cl_2]^-$: We have analyzed the energetic barrier for rotation of the acetyl ligand into the coordination plane and beyond, corresponding to inversion of the "envelope". The transition state **10f** (Figure 3) of this rotation is
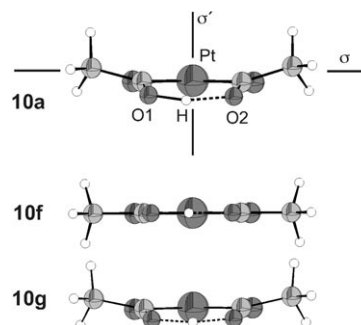

Figure 3. Front views of the transition states **10f** and **10g** and of the starting equilibrium structure **10a**. The transition states **10f** ($\nu_{imag} = 36$ cm^{-1}) and **10g** ($\nu_{imag} = 408$ cm^{-1}) describe ring inversion (**10a**→**10f**→**10a'**) and hydrogen transfer from the hydroxycarbene to the acetyl ligand (**10a**→**10g**→**10a''**), respectively. **10a'**/**10a''** are mirror images of **10a** obtained by mirroring **10a** on σ and σ', respectively.

completely planar ($\phi_{carbene}/\phi_{acetyl} = 0/0°$) and energetically only 0.2 kcal mol$^{-1[20]}$ above the corresponding equilibrium structure **10a** (Table 4). In the transition state, the delocalization in the π system of the O=C−Pt=C−O moiety is even more apparent. This can be seen in the almost vanishing structural differences between the carbene and acetyl moieties. The resonance in organic β-diketones is often described by the parameter $Q = q_1 + q_2$, where $q_1 = d_{C=O} - d_{C-O}$ and $q_2 = d_{C=C} - d_{C-C}$ (for acetylacetone (**6a**): $Q = -0.154$ Å).[14a] A value of $Q = 0$ Å describes full delocalization, whereas $|Q| = 0.320$ Å corresponds to the completely localized forms. Comparing this parameter for **10a** and **10f** (−0.066 and −0.043, respectively) clearly shows that π delocalization is more pronounced, but still not complete, in the planar transition state **10f**.

Furthermore, a comparative orbital analysis of the π systems of acetylacetone and of the anionic platina-β-diketone $[Pt\{(COMe)_2H\}Cl_2]^-$ (**10**), both hydrogen-bonded in idealized C_{2v} symmetry, exhibited analogies. As metalla-β-diketones are formally derived from hydrogen-bonded enol forms of organic 1,3-diketones by replacing the central methine group with a transition metal fragment (see Scheme 2), we chose exactly those fragments to construct the MO diagrams (Figure 4). Besides the p$_z$ orbitals of C and O atoms and the d$_{xz}$/d$_{yz}$ orbitals of Pt, the analyses revealed that methyl substituents in the central fragment **I** and chloro ligands in fragment **III** also account for symmetry-relevant a$_2$/b$_1$ orbitals. As the delocalization of the π system of acetylacetone is mediated by the p$_z$ orbital of the methine C atom, the delocalization in **10** is realized by d$_{xz}$/d$_{yz}$ orbitals
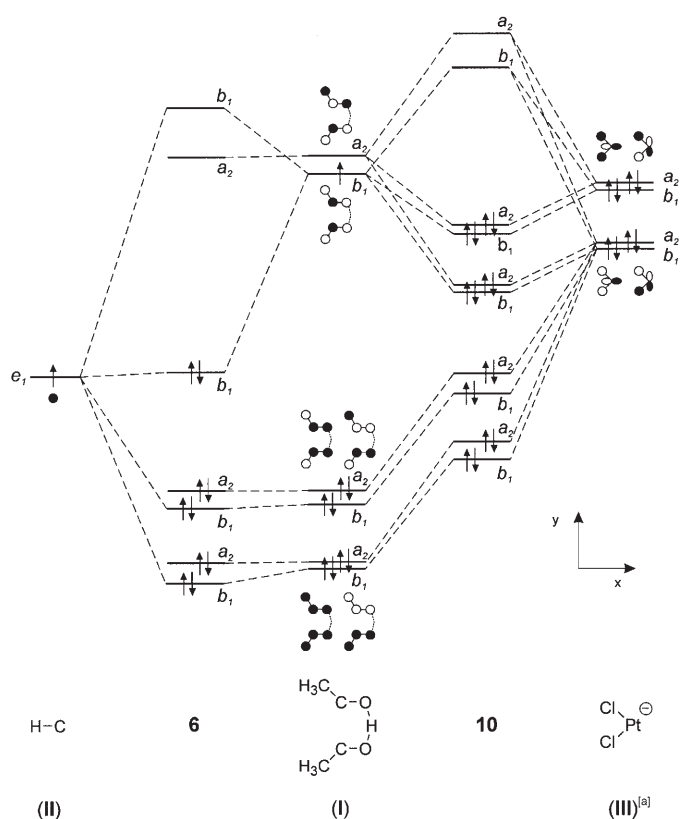
Figure 4. Qualitative molecular orbital diagrams of the π systems of acetylacetone (**6**) and of the anionic platina-β-diketone [Pt{(COMe)₂H}Cl₂]⁻ (**10**), both hydrogen-bonded in idealized C_{2v} symmetry. The formation of **6** and **10** is shown from the [C₄O₂H₇] fragment (**I**) and HC (**II**, left) and PtCl₂⁻ fragments (**III**, right), respectively. a) One fragment π electron is shifted into an orbital of σ symmetry.

of platinum. Thus, there is structural and electronic evidence of resonance-assisted hydrogen bonding in both **6**[14] and **10**.

To determine the ease of hydrogen transfer from the hydroxycarbene moiety to the acetyl moiety, the associated transition state was calculated (complex **10g**, Figure 3). As for transition state **10f**, the energy difference relative to **10a** is very small ($\Delta E = 0.1$ kcal mol⁻¹[20]), which suggests very fast hydrogen transfer. Since the transition state **10g** describes the mutation of the hydroxycarbene into an acetyl ligand and vice versa, the delocalization parameter was found to be $Q = 0$. Notably, the transition state **10g** is not planar ($\phi_{carbene}/\phi_{acetyl} = 16/16°$), as might be expected for electronic reasons in the fully delocalized structure. We believe this deviation is caused by steric hindrance, either between the two organo ligands or between the CH₃ groups and the chloro ligands.

Dinuclear platina-β-diketone [Pt₂{(COMe)₂H}₂(μ-Cl)₂]: The structure of the dinuclear platina-β-diketone **11a** was calculated in C_i symmetry, as was also experimentally found;[21] the calculated (**11a**) and experimental (**11exp**) structures are in a good agreement (Figure 5, Table 5). As for the other metalla-β-diketones, cleavage of the hydrogen bond forms a hydroxycarbene acyl complex (**11b**), in which the Pt−C and
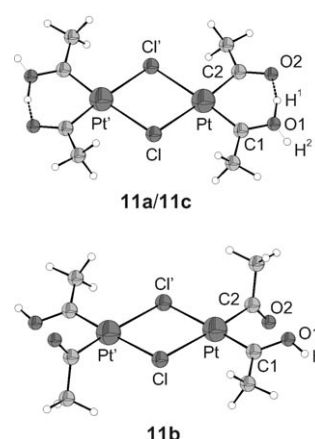

Figure 5. Calculated structures of [Pt₂{(COMe)₂H}₂(μ-Cl)₂] (**11**): Equilibrium hydrogen-bonded structure **11a** and equilibrium non-hydrogen-bonded structure **11b**. Because the structure of the open conformation **11c** (rotated OH groups, relaxed bond lengths and angles) is very close to that of **11a**, the isomer is not drawn; H¹ (top) shows the position of the H atom in **11a**, and H² that in **11c**.

Table 5. Selected distances [Å], angles [°], and energies [kcal mol⁻¹] for calculated hydrogen-bonded (**11a**) and non-hydrogen-bonded (**11b**) equilibrium structures of the platina-β-diketone [Pt₂{(COMe)₂H}₂(μ-Cl)₂], as well as open conformation **11c** (rotated OH group, relaxed bond lengths and angles). For comparison, structural parameters of the experimentally determined structure **11exp** are given.

	11a	**11b**	**11c**	**11exp**
Pt−C[a]	1.968/1.995	1.918/2.024	1.937/2.064	1.95(1)/1.95(1)
C−O[a]	1.268/1.240	1.319/1.199	1.302/1.200	1.26(1)/1.23(1)
O−H/O···H[a]	1.090/1.329	0.972/–	0.971/–	
O1···O2	2.394	3.189	2.422	2.37(1)
$\phi_{carbene}/\phi_{acetyl}$[b]	+8/+9	+18/−74	+8/+9	+2/+4
ΔE	0.0	38.3 (38.8)[c]	51.3	

[a]–[c] See footnotes in Table 3.

C−O bond lengths are more strongly differentiated (Δ(Pt−C) 0.11 versus 0.03 Å; Δ(C−O) 0.12 versus 0.03 Å) and the two organo ligands do not lie in the plane of the complex. Similar values (Δ(Pt−C) 0.13 Å; Δ(C−O) 0.10 Å) were found for the hydroxycarbene acyl complex **11c** obtained by rigid rotation of the OH group and subsequent relaxation of the bond lengths and angles.

Complexes **11b** and **11c** are higher in energy by 38.3 and 51.3 kcal mol⁻¹, respectively, than **11a**. These values are about twice as large as in the mononuclear platina-β-diketones **10c/10d** and thus indicate hydrogen bonds of approximately the same strength.

Cationic mononuclear platina-β-diketone [Pt{(COMe)₂H}(bpy)]⁺: Dinuclear platina-β-diketone **11** was found to react with 2,2′-bipyridine in an oxidative addition reaction yielding hydrido acetyl platinum(IV) complex **13**, which proved to have high thermal stability (Scheme 3).[22] As an intermediate, the formation of the (unseen) cationic mononuclear platina-β-diketone [Pt{(COMe)₂H}(bpy)]⁺ (**12**) by Pt−Cl−Pt bridge cleavage can be assumed. The reaction
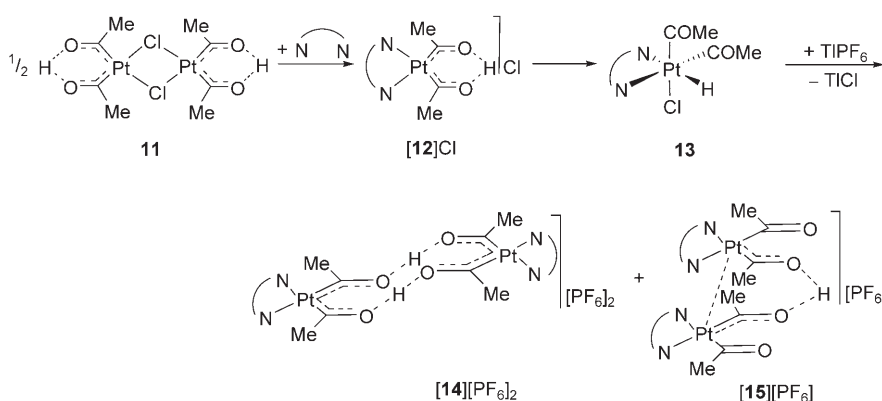
Scheme 3.

[12]Cl→13 occurs with a transition from an acidic to a hydridic hydrogen atom. The abstraction of chloride from 13 by means of Tl[PF$_6$] afforded the intermolecularly hydrogen-bonded platina-β-diketones [14][PF$_6$]$_2$ and [15][PF$_6$] having acidic protons as in 11/12 (Scheme 3).[23] Here we calculated the hydrogen-bonded and the non-hydrogen-bonded conformations of the cationic mononuclear complex 12 to evaluate the strength of its hydrogen bond (Figure 6, Table 6). Structural parameters and energies were obtained at the same level as before [B3LYP/6-311++G(d,p)], but frequency calculations were done at a lower level because of the size of the molecule.
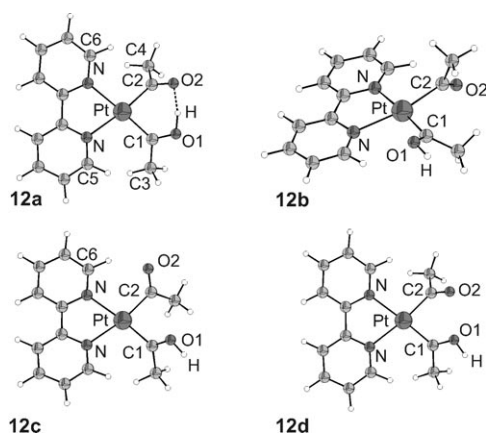
(2.500 Å) than in all other metalla-β-diketones described before (2.394–2.405 Å). Thus, the conformation can be understood as a compromise, on the one habnd, to minimize steric repulsion between the bpy ligand and the methyl groups of the platina-β-diketone unit and, on the other hand, to strengthen the O−H···O bond.

Two non-hydrogen-bonded equilibrium structures were found, namely, 12b and 12c

Table 6. Selected distances [Å], angles [°], and energies [kcal mol^{-1}] for calculated hydrogen-bonded (12a) and non-hydrogen-bonded (12b, 12c) equilibrium structures of the cationic platina-β-diketone [Pt{(COMe)$_2$H}-(bpy)]$^+$, as well as open conformation 12d (rotated OH group, relaxed bond lengths and angles).

	12a	12b	12c	12d
Pt−C[a]	1.970/2.017	1.942/2.050	1.936/2.051	1.975/2.021
C−O[a]	1.281/1.226	1.313/1.206	1.309/1.206	1.298/1.202
O−H/O···H[a]	1.023/1.571	0.975/–	0.975/–	0.973/–
O1···O2	2.500	4.845	3.975	2.507
$\phi_{carbene}/\phi_{acetyl}$[b]	+44/+52	+48/-68	+65/+45	+44/+52
ΔE	0.0	9.4	11.3	19.6

[a], [b] See footnotes in Table 3.

having the O atoms of the hydroxycarbene and acyl ligands on different sides and on the same side of the plane of the complex, respectively (Figure 6). As for the metalla-β-diketones described before, cleavage of the hydrogen bond is incidental to shortening of the Pt−C bond and lengthening of the C−O bond in the hydroxycarbene ligand, and vice versa in the acyl ligand.

The non-hydrogen-bonded structures 12b and 12c are 9.4 and 11.3 kcal mol^{-1}, respectively, less stable than the hydrogen-bonded one. Complex 12c may be stabilized by a weak C6−H···O2 hydrogen bond; the geometrical parameters (H···O2 2.108 Å, C6−H···O2 137.4°) fall into the expected range.[25] The open conformer 12d (derived from 12a by rigid rotation of the OH group followed by optimization of all bond lengths and angles) is 19.6 kcal mol^{-1} higher in energy than 12a.

Figure 6. Calculated structures of [Pt{(COMe)$_2$H}(bpy)]$^+$ (12): Equilibrium hydrogen-bonded structure 12a. Equilibrium non-hydrogen-bonded structures having the O atoms on different sides (12b) and on the same side (12c) of the plane of the complex, respectively. Open conformation 12d (rotated OH group, relaxed bond lengths and angles).

The hydrogen-bonded structure 12a (Figure 6) is far from being planar. Likely for steric reasons (C3···C5/C4···C6 ca. 3.4 Å; cf. r_{vdW}(CH$_3$)=2.00 Å;[24] the hypothetical planar structure would have C3···C5/C4···C6 distances of about 3.0 Å) the planes of the hydroxycarbene and acetyl ligands form angles of 44 and 52°, respectively, with the plane of the complex. This gives rise to a much larger O···O separation

Intermolecularly hydrogen-bonded platina-β-diketone [{Pt-{(COMe)$_2$H}(bpy)}$_2$]$^{2+}$: Complexes [14][PF$_6$]$_2$ and [15][PF$_6$] (Scheme 3) represent two new structural motifs in metalla-β-diketones, one of which has two O−H···O bonds (14), and the other (15) one O−H···O bond and a Pt···Pt (d^8–d^8) closed-shell interaction.[23] Thus, the first complex provides the possibility to compare the strength of the intermolecular hydrogen bonds in the dinuclear cation [{Pt{(COMe)$_2$H}-(bpy)}$_2$]$^{2+}$ (14) with that of the intramolecular hydrogen bond in the mononuclear cation [Pt{(COMe)$_2$H}(bpy)]$^+$

(**12a**). The large molecular size and limited computational capacity forced us to optimize the molecule of **14** in C_i symmetry (as was also found in the experimental structure [**14**$_{exp}$][PF$_6$]$_2$) and to use a smaller basis set [B3LYP/6-311++G(d,p)//B3LYP/6-31G(d)].[26] Despite that, the calculated structure (Figure 7) fits quite well with that of the cation **14**$_{exp}$ (Table 7). Both in the experimental and in the calculated structure the hydroxycarbene and the acyl ligands lie nearly perpendicular to the plane of the complex. This con-
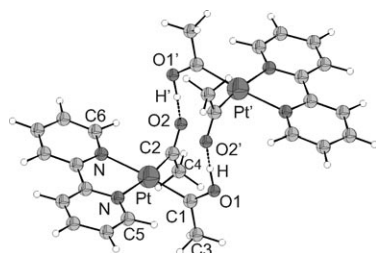

Figure 7. Calculated structure of the platina-β-diketone [{Pt{(COMe)$_2$H}(bpy)}$_2$]$^{2+}$ (**14**) intermolecularly stabilized by O–H···O bonds.

Table 7. Selected distances [Å] and angles [°] for the calculated structure of platina-β-diketone [{Pt{(COMe)$_2$H}(bpy)}$_2$]$^{2+}$ (**14**), intermolecularly stabilized by O–H···O bonds. For comparison, structural parameters of the experimentally determined structure of [{Pt{(COMe)$_2$H}(bpy)}$_2$][PF$_6$]$_2$ ([**14**$_{exp}$][PF$_6$]$_2$) are given.

	14	**14**$_{exp}$
Pt–C[a]	1.971/2.022	1.967(6)/1.968(6)
C–O[a]	1.287/1.237	1.281(8)/1.253(8)
O–H[a]	1.026/1.565	
O1···O2′/O1···O2	2.561/3.920	2.455(5)/4.085
$\phi_{carbene}/\phi_{acetyl}$[b]	+85/+75	+87/+71

[a], [b] See footnotes in Table 3.

formation gives rise to C3···C5/C4···C6 distances of about 4.0 Å (Figure 7) and thus avoids close contacts between the bpy ligand and the methyl groups of the hydroxycarbene/acetyl ligands (see preceding discussion for **12a**). Breaking the hydrogen bonds and optimizing the geometry of the mononuclear monocationic complexes resulted in formation of the intramolecularly hydrogen-bonded complex **12a** [Eq. (4)].

The reaction according to Equation (4) proved to be exothermic by 21.7 kcal mol^{-1}. Due to the newly formed (intramolecular) hydrogen bond in **12a**, this energy cannot be interpreted as the strength of the intermolecular hydrogen bonds in **14**. The exothermicity indicates only that the intramolecular hydrogen bond in **12a** is more stable than the intermolecular one in **14**. Thus, the usual way
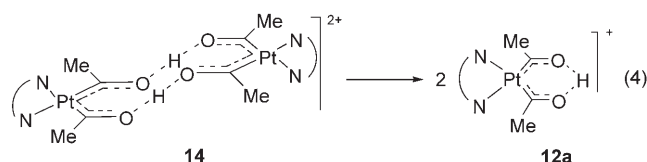
to estimate the strength of intermolecular hydrogen bonds [see Eq. (1) in the Introduction] fails in this special case.

Finally, the intermolecularly hydrogen-bonded complex **14** was used to estimate the BSSE. It was calculated to be only 0.4 kcal mol^{-1} per hydrogen bond. Due to the large (high-quality) basis sets to expand the wave functions, this relatively low value meets the expectations.[27] Thus, it seems to be justified to neglect the BSSE also in the intramolecularly hydrogen-bonded metalla-β-diketones discussed before.

Strength of hydrogen bonds in metalla-β-diketones and their geometrical and topological properties: Based on the preceding calculations the strength of the hydrogen bonds in metalla-β-diketones can be given as energy differences between the (hydrogen-bonded) metalla-β-diketones and the requisite (non-hydrogen-bonded) hydroxycarbene acetyl complexes, both in their equilibrium states, and those obtained by rigid rotation of the OH group around the C–O bond by 180° followed by relaxation of all bond lengths and angles (Table 8). The higher energies of the latter series (6.5–12.5 kcal mol^{-1} compared with the equilibrium hydroxycarbene acyl complexes) may be caused to a considerable extent by a strong repulsive (Pauli) O···O interaction. The O···O separation in these structures (2.42–2.68 Å) is much smaller than twice the van der Waals radius of oxygen (2 × 1.50 Å[24]).

In intermolecular X–H···Y hydrogen bonds the X···Y distances are a well-accepted measure to estimate hydrogen-bond strengths.[2, 12, 14, 28] To investigate whether such a relationship also exists for the intramolecular O–H···O hydrogen bonds in metalla-β-diketones (including acetylacetone), we investigated the correlation between the O···O distances and the energies given in Table 8. Figure 8a shows that a linear relationship ($R = 98.6\%$) exists between the hydrogen-bond energies based on the rigidly rotated structures and the O···O distance in the hydrogen-bonded structures.

Table 8. Summary of the energies [kcal mol^{-1}] of non-hydrogen-bonded metalla-β-diketones (equilibrium structures and those obtained by rigid rotation of the OH group around the C–O bond by 180° with subsequent relaxation of the bond lengths and angles) relative to the hydrogen-bonded structures, as well as O···O distances [Å] and electron densities at the O···H bond critical points (ρ_{bcp} [a.u.]) of the hydrogen-bonded structures. For comparison, the requisite values of acetylacetone are given.

	Open conformation (equilibrium structure)	Open conformation (rotated OH group)	O···O	ρ_{bcp}
Hacac (**6**)	10.9 (**6b**)	16.1/15.9[a] (**6k/6g**)	2.543	0.057
[Re{(COMe)$_2$H}(CO)$_4$] (**9**)	14.7 (**9b**)	27.2 (**9c**)	2.395	0.145
[Pt{(COMe)$_2$H}Cl$_2$]$^-$ (**10**)	20.7 (**10c**)	27.2 (**10d**)	2.405	0.118
[Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**11**)	19.2[b] (**11b**)	25.7[b] (**11c**)	2.394	0.124
[Pt{(COMe)$_2$H}(bpy)]$^+$ (**12**)	9.4 (**12b**)	19.6 (**12d**)	2.500	0.065

[a] The value for the requisite equilibrium structure (**6g**, *cct* isomer) is additionally given. [b] Per O–H···O bond.
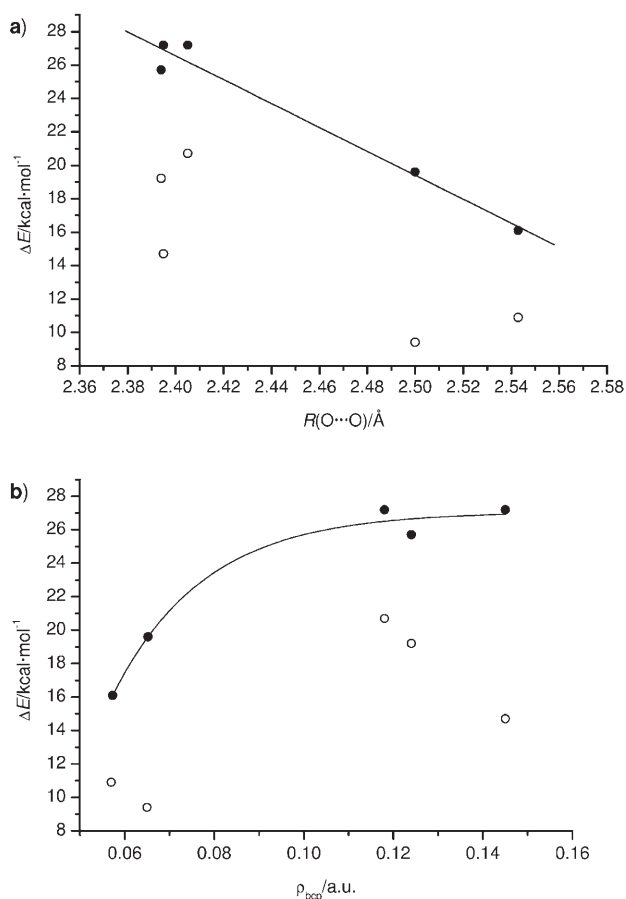
Figure 8. Correlation of O···O distances (a) and electron densities (b) at the O···H bond critical point (ρ_{bcp}) with ΔE_{hb}. Reference structures are the most stable non-hydrogen-bonded conformers (open circles) and the conformers obtained by rigid rotation of the OH group by 180° with subsequent relaxation of the bond lengths and angles (filled circles).

Previously, in particular in structurally very similar systems, topological properties of O−H···O fragments have been correlated with hydrogen-bond energies.[15b,29] Here we calculated, using the AIM theory,[30] the electron densities at the O···H bond critical points (ρ_{bcp}) in the metalla-β-diketones and for comparison in acetylacetone (Table 8). As shown in Figure 8b only the hydrogen-bond energies based on the rigidly rotated structures can be correlated with ρ_{bcp} (first-order exponential decay, $R^2 = 98.6\%$).

Conclusions

Deviations between experimental and calculated structures of metalla-β-diketones, as well as between energies of various acetylacetone isomers calculated with the model used here [B3LYP/6-311++G(d,p)] and with ab inito post-HF methods (see Table 1) were found to be, in general, very small. Thus, the calculations performed in this work can be regarded to be reliable.

Cleavage of hydrogen bonds in metalla-β-diketones yielding hydroxycarbene acyl complexes resulted in shortening of the M−C and lengthening of the C−O bonds of the hydroxycarbene ligands, and vice versa for the acyl ligands. This differentiation of M−C and C−O bond lengths is in accord with a resonance-assisted hydrogen bonding in metalla-β-diketones similar to that found in cyclic enols of organic β-diketones.

Furthermore, the cleavage of hydrogen bonds in metalla-β-diketones is accompanied by a severe conrotatorylike motion of the hydroxycarbene and acyl ligands. Thus, the O atoms of the two ligands come to lie on different sides of the plane of the complex, which results in a marked increase in the O···O separation. In contrast, π conjugation in enols of organic β-diketones gives rise to planar O=C−C=C−O backbones in both the hydrogen- and non-hydrogen-bonded conformers.

When structurally different intramolecularly hydrogen-bonded systems are compared, difficulties in defining a (non-hydrogen-bonded) reference state allow only estimates of relative hydrogen-bond energies. In the case of organic cyclic enols of β-diketones and metalla-β-diketones it seems to be justified either to refer to the most stable open conformer (Table 8, column 2) or to the open conformer in which the relative positions of the hydroxycarbene (enol) and acyl (keto) groups are retained (Table 8, column 3). The hydrogen-bond energies based on the rigidly rotated structures (Table 8, column 3) were found to correlate with geometrical (O···O distances in the hydrogen-bonded structures; Table 8, column 4) and topological properties (electron densities at the O···H bond critical points; Table 8, column 5). Thus, the plots shown in Figure 8 may open up a way to determine the hydrogen-bond strength of other metalla-β-diketones without having to calculate the energy of a non-hydrogen-bonded reference structure.

Although there is no clear definition of the strength of intramolecular hydrogen bonds (vide supra), comparative analysis of the energies given in Table 8 clearly shows that the hydrogen bonds in metalla-β-diketones are much stronger than that in acetylacetone, the "generic" organic β-diketone. The comparative weakness of the hydrogen bond in the bipyridine-substituted platina-β-diketone **12b** can be rationalized in terms of steric repulsion between the methyl groups of the platina-β-diketone unit and the *ortho*-hydrogen atoms of the bipyridine ligand, which gives rise to a nonplanar platina-β-diketone unit having a relatively large O···O distance.

With the limitations discussed in the introduction that the energy values given in Table 8 may comprise other stabilizing or destabilizing factors, it is clear that all these intramolecular O−H···O bonds are much stronger than those in gaseous water dimer (5.0 kcal mol^{-1}),[27] which is a benchmark for hydrogen bonds. Hydrogen bonds can be classified with respect to their energies into weak (< 4 kcal mol^{-1}), moderate (4–15 kcal mol^{-1}), and strong (14–40 kcal mol^{-1}).[1b,31] Thus, the intramolecular hydrogen bonds discussed here must be regarded as strong; those in metalla-β-diketones

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were found to be up to twice as strong as that in acetylace-tone.

Computational Details

All DFT calculations were carried out with the Gaussian 98/Gaussian 03 program package[32] using the hybrid functional B3LYP.[33] For the main group atoms the basis set 6-311++G(d,p) (unless otherwise explicitly stated) was employed as implemented in the Gaussian program. The valence shells of rhenium and platinum were approximated by split valence basis sets, too; for their core orbitals effective core potentials in combination with consideration of relativistic effects were used.[34] All systems were fully optimized without any symmetry restrictions, except for the dinuclear platinum complexes, which were calculated in C_i symmetry. The resulting geometries were characterized as equilibrium structures by analysis of the force constants of the normal vibrations. Due to the large molecular size of complexes **12**, for geometry optimizations (without any symmetry restrictions) and frequency computations the B3LYP functional and the 6-31G(d) basis set were used. Then the structures were fully optimized again using the same model as for all other complexes [B3LYP/6-311++G(d,p)]. The structural parameters of structures obtained with the two different basis sets proved to be very close. Basis-set superposition errors (BSSE) were estimated with counterpoise-type calculations.[35] The AIM analyses were performed using the program package AIMPAC, as provided by Bader et al.[36]

Energies and Cartesian coordinates of atom positions of all calculated structures are available as Supporting Information.

Acknowledgement

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