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Synthesis and characterization of diacetyl platinum(II) complexes with two primary and secondary amine ligands

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ABSTRACT

[Pt(COMe)$_2$(bpy)] (**2**; bpy = 2,2′-bipyridine) and [Pt(COMe)$_2${H(Me)dmg}] (**5**; H(Me)dmg = MeO–N=C(Me)–C(Me)=N–OH) were found to react with primary and secondary amines yielding diacetyl platinum(II) complexes with two monodendate amine ligands [Pt(COMe)$_2$(NH$_2$R)$_2$] (R = Bn, **3a**; CH$_2$CH$_2$Ph, **3b**; Et, **3c**; *i*-Pr, **3d**; CH$_2$CH=CH$_2$, **3e**; Cy, **3f**; Bn = benzyl, Cy = cyclohexyl) and [Pt(COMe)$_2$(NHR$_2$)$_2$] (R = Me, **6a**; Et, **6b**), respectively. The equilibrium of these ligand exchange reactions was investigated by NMR experiments and DFT calculations showing that complex **5** is the more preferable starting complex and a large excess of the amine has to be used. The sterically demanding diisopropylamine was found to react with **5** yielding a thermally highly unstable dinuclear bis(acetyl) bridged complex [{Pt(COMe){NH(*i*-Pr)$_2$}}$_2$(μ-COMe)$_2$] (**7**). Analogous reactions with ethylenediamine derivatives resulted in the formation of [Pt(COMe)$_2$(N^N)] (N^N = ethylenediamine, en, **8a**; *N*,*N*′-dimethylethylenediamine, **8b**; *N*,*N*-dimethylethylenediamine, **8c**; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, TMEDA, **8d**). All complexes were fully characterized by microanalysis/high-resolution ESI mass spectrometry, by NMR (^{1}H, ^{13}C, ^{195}Pt) and IR spectroscopies as well as by single-crystal X-ray diffraction measurements (**3a**/**3d**). Due to the high trans influence of the acetyl ligands, the Pt–N bonds were found to be relatively long (2.164(2)–2.182(3) Å). The resulting weak coordination of the amines gave rise to a decomposition of complexes **3** under CO extrusion yielding carbonyl–methyl complexes.

1. Introduction

Dinuclear platina-β-diketones such as the parent complex **1** (Scheme 1), which can be regarded as hydroxycarbene complexes stabilized by intramolecular O–H···O hydrogen bonds, are easily accessible from hexachloroplatinic acid and silylated alkynes [1]. Complex **1** proved to be a versatile starting complex for the syntheses both of diacetyl platinum(II) and platinum(IV) complexes. Thus, reactions with bidentate N^N donors such as 2,2′-bipyridine led to extraordinarily stable diacetylhydridoplatinum(IV) complexes **I** (Scheme 1, reaction path **A**) [2] from which, with bases, under cleavage of HCl diacetyl platinum(II) complexes **II** were obtained (Scheme 1, **B**) [3]. In contrast to this, reactions of the platina-β-diketone **1** with monodentate amines, irrespective whether primary, secondary, or tertiary amines (such as NH$_2$(*n*-Bu), NH(*i*-Pr)$_2$, NEt$_3$) were used, resulted in the formation of platina-β-diketonates of platina-β-diketones **III** (Scheme 1, **C**) [4], which resemble, due to their tetranuclear solid-state structures, to platinum blue complexes with central Pt···Pt (d^8···d^8) closed shell interactions [5]. The only exception proved to be the reaction of **1** with hexamethyldisilazane which resulted under deprotonation of O–H···O bridges and cleavage of chloride to the formation of a coordination polymeric diacetyl platinum(II) complex **IV** (Scheme 1, **D**) [6]. Due to its very weak Pt–O bonds, complex **IV** undergoes readily ligand exchange reactions with formation of [Pt(COMe)$_2$L$_2$] complexes, among them the formation of type **II** complexes (Scheme 1, **E**) and of the diacetylbis(benzylamine) complex **3a** (Scheme 1, **F**) [6].

Organyl platinum(II) complexes with bidentate amine ligands are very well known, whereas those with two monodentate amine ligands are rare; examples are [Pt(C$_6$X$_5$)$_2$(NH$_2$R)$_2$] (R = Ph, Bn; X = F, Cl) [7] and [PtCl(L-κC^5)(NH$_2$Me)$_2$] (HL = 1,3-dimethyluracil) [8]. Here, we report on a straightforward synthesis and characterization of diacetyl platinum(II) complexes with two monodentate primary or secondary amine ligands (or, alternatively, with one ethylenediamine derivative as ligand) via ligand substitution starting from type **II** complexes. Furthermore, DFT calculations give an insight into which factors affect the substitution of the bidentate N^N ligand by two monodentate amines.

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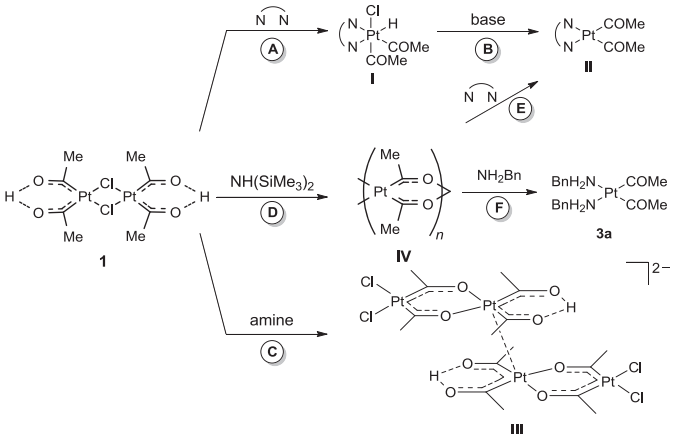


Scheme 1. Reactivity of the platina-β-diketone **1** toward *N,N* donors and amines.

2. Results and discussion

2.1. Syntheses and characterization

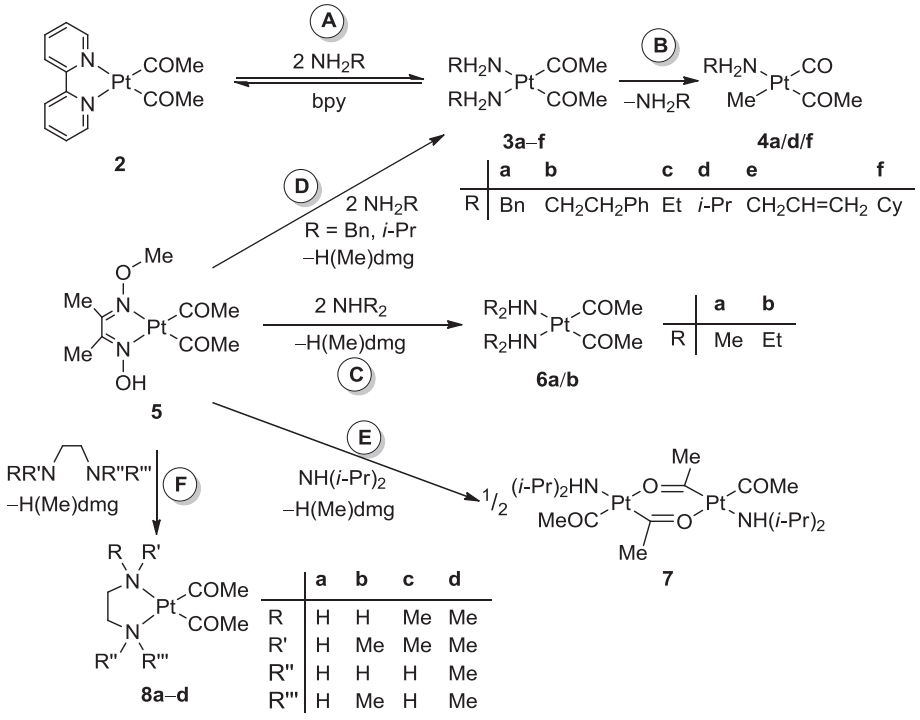
The diacetyl(2,2′-bipyridine)platinum(II) complex **2** was found to react in neat primary amines NH_2R (R = Bn, CH_2CH_2Ph, Et, *i*-Pr, $CH_2CH{=}CH_2$, Cy) with substitution of the bidentate bipyridine ligand by two amine ligands (Scheme 2, **A**). The resulting diacetylbis(amine) platinum(II) complexes **3a**–**f** could be isolated as colorless powders in yields between 40 and 95%. The excess of the amines as realized in the neat liquids is crucial for the success of these substitution reactions: As exemplified with NH_2R (R = Bn, *i*-Pr), in solution (such as chloroform or methylene chloride) even with a 10-fold excess of the amine, no complexes **3a**/**3d** could be isolated. An equilibrium between **2** and **3a**/**3d** could be detected ^{1}H NMR spectroscopically (see Paragraph 2.3). In contrast, secondary and tertiary alkyl amines ($NHEt_2$, $NH(i\text{-}Pr)_2$, $NHBu_2$, NEt_3) and aromatic amines (NH_2Ph, $NH_2(p\text{-}Et\text{-}C_6H_4)$) did not react at all with $[Pt(COMe)_2(bpy)]$ (**2**), even not in the neat liquids.

The complexes **3a**–**f** were fully characterized by NMR (^{1}H, ^{13}C, ^{195}Pt) and IR spectroscopy, by microanalysis and high-resolution ESI mass spectrometry, respectively, as well as by single-crystal X-ray diffraction analyses (**3a**/**3d**). The solids proved to be stable at −40 °C at least for several months but at room temperature for few hours only. A thermoanalysis (TG) of complex **3a** revealed that the decomposition starts at 120 °C yielding Pt (mass loss found 61.1%, calc. 60.6%). At room temperature, solutions of complexes **3a**–**f** in methylene chloride or THF decompose within 2–6 h with the formation of platinum black.

In the case of complexes **3a**, **3d** and **3f**, as intermediates carbonyl–methyl complexes, $[Pt(COMe)Me(NH_2R)(CO)]$ (R = Bn, **4a**; *i*-Pr, **4d**; Cy, **4f**; Scheme 2, **B**), were identified by NMR and IR spectroscopy as well as by high-resolution ESI mass spectrometry. Likely, complexes **4** were formed after cleavage of one amine ligand by CO extrusion from an acetyl ligand. Although there is no experimental proof, DFT calculations made clear that the configuration (*SP*-4-3) given in Scheme 2 is the most stable one. Thus, for the model complex $[Pt(COMe)Me(NH_2Me)(CO)]$ this configuration showed a preference in the ΔG° values (in CH_2Cl_2 as solvent) over the other two configurations (*SP*-4-4/*SP*-4-2) by 4.9/5.5 kcal/mol (see Supplemental material).

The diacetyl platinum(II) complex $[Pt(COMe)_2\{H(Me)dmg\}]$ (**5**) having coordinated instead of the 2,2′-bipyridine ligand the weaker coordinating diacetyldioxime mono methyl ether ligand, was found to react in neat secondary amines NHR_2 (R = Me, Et) yielding the complexes $[Pt(COMe)_2(NHR_2)_2]$ (**6a**/**b**) (Scheme 2, **C**). As shown in reactions with benzyl and isopropyl amine, $[Pt(COMe)_2\{H(Me)dmg\}]$ (**5**) also reacts with primary amines yielding complexes **3a** and **3d**, respectively, even in methylene chloride and chloroform solutions (Scheme 2, **D**). With the tertiary amine NEt_3 only decomposition under formation of platinum black was observed.

Complexes **6a**/**b** were isolated as colorless powders in moderate yields (70/45%). At room temperature, the solids decompose within



Scheme 2. Synthesis routes to acetyl platinum(II) complexes bearing amine and diamine ligands.

10–60 min and solutions in chloroform and methylene chloride within few minutes under formation of platinum black. The identities of the complexes **6a**/**b** were confirmed by NMR (^{1}H, ^{13}C, ^{195}Pt) and IR spectroscopy and by microanalysis or high-resolution ESI mass spectrometry, respectively.

A special case is the reaction of complex **5** with neat diisopropylamine, which resulted in the formation of the complex [{Pt(COMe){NH(*i*-Pr)$_2$}}$_2$(μ-COMe)$_2$] (**7**) in 85% yield (Scheme 2, **E**). Complex **7** proved to be highly temperature sensitive. At room temperature, even the solid was found to decompose within 1 h and $CHCl_3$/CH_2Cl_2 solutions within 5 min. Analytical and NMR (^{1}H, ^{13}C, ^{195}Pt) spectroscopical data exhibited that complex **7** is an bis(acetyl) bridged dimer. NMR spectroscopically, complex **7** was shown to react with 2,2′-bipyridine and pyridine under bridge cleavage to yield the well known mononuclear complexes **2** and [Pt(COMe)$_2$(py)$_2$] [6], respectively. On the other hand, with DMSO or D_2O no reactions were observed.

Ethylenediamine (en) and its methylated derivatives (*N*,*N*′-dimethylethylenediamine; *N*,*N*-dimethylethylenediamine; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, TMEDA) were also found to react with the precursor complex **5** (Scheme 2, **F**). By cleavage of the H(Me)dmg ligand, complexes [Pt(COMe)$_2$(N^N)] (**8a**–**d**) were formed. They were isolated as colorless products in moderate yields (30–90%) and fully characterized by the established analytical and spectroscopical methods. At room temperature, all complexes are stable in the solid state. The diacetyl–TMEDA complex **8d** proved also to be stable in chloroform solution, whereas the other complexes **8a**–**c** undergo decomposition within a few hours. A solution of complex **2** with ethylenediamine became immediately colorless (**8a**), with the doubly methylated derivatives in several minutes (**8b**–**c**) and with TMEDA only after one day (**8d**), which indicates a reaction, but in all cases no isolation was attempted.

2.2. Spectroscopic characterization

Characteristic ^{1}H, ^{13}C and, ^{195}Pt NMR spectroscopic data of the mononuclear diacetyl platinum complexes with amine ligands (**3a**–**f**, **6a**/**b**, **8a**–**d**) were compiled in Table 1. In order to accommodate the restricted thermal stability of complexes **6a**/**b**, the NMR spectra were measured at −40 °C. The ^{1}H and ^{13}C NMR spectra of all complexes confirmed their identities; all signals were found in the expected shift range with correct intensities in the ^{1}H NMR spectra. As in other diacetyl platinum(II) complexes with trans standing nitrogen ligands [3], the acetyl ligands showed characteristic $^3J_{Pt,H}$ (19.1–26.8 Hz) and $^2J_{Pt,C}$ (351–397 Hz) coupling constants. Only in the case of complex **8c** bearing the unsymmetrically substituted *N*,*N*-dimethylethylenediamine ligand, two sets of signals for the acetyl ligands were found. The platinum chemical shifts δ_{Pt} (−3272 to −3439) are in the range of typical diacetyl platinum(II) complexes [6].

Table 1
Selected NMR[a] spectroscopic parameters of the complexes [Pt(COMe)$_2$L$_2$] (**3a**–**f**, **6a**/**b**, **8a**–**d**) and [{Pt(COMe){NH(*i*-Pr)$_2$}}$_2$(μ-COMe)$_2$] (**7**) (δ in ppm, *J* in Hz).

	Amine ligand	δ_H ($^3J_{Pt,H}$)	δ_C ($^2J_{Pt,C}$)	δ_C ($^1J_{Pt,C}$)	δ_{Pt}
		COC*H*$_3$	COCH$_3$	*C*O	
3a	NH_2Bn	2.15 (22.0)	44.1 (372)	232.6	−3329
3b	$NH_2CH_2CH_2Ph$	2.21 (19.1)	44.3 (356)	233.8 (1275)	−3299
3c	NH_2Et	2.21 (23.2)	44.5	234.5	−3274
3d	NH_2(*i*-Pr)	2.21 (23.0)	44.3 (367)	233.7	−3304
3e	$NH_2CH_2CHCH_2$	2.18 (22.7)	44.2 (362)	233.6 (1295)	−3272
3f	NH_2Cy	2.20	44.3 (351)	234.0	−3296
6a[b]	$NHMe_2$	2.05 (25.0)	43.5	229.5	−3439
6b[b]	$NHEt_2$	2.04 (20.7)	43.4	230.0	−3399
8a	$H_2NCH_2CH_2NH_2$	2.22 (22.4)	44.5	240.6	−3337
8b	$MeHNCH_2CH_2NHMe$	2.31 (19.3)	44.9 (351)	238.7 (1233)	−3293
8c	$Me_2NCH_2CH_2NH_2$	2.05 (25.7); 2.19 (20.8)	43.8 (397); 44.1 (363)	224.3; 234.3	−3347
8d	$Me_2NCH_2CH_2NMe_2$	2.10 (26.8)	43.6 (393)	228.5 (1283)	−3430
7[c]	NH(*i*-Pr)$_2$	1.90; 2.05	42.2; 43.7	214.6; 253.4	−3138

[a] If not otherwise noted, in $CDCl_3$ at room temperature.
[b] In CD_2Cl_2 at −40 °C.
[c] In CD_2Cl_2 at −70 °C.

NMR spectra of the thermally less stable dinuclear complex **7** were measured at −40 and −70 °C in CD_2Cl_2. For the acetyl ligands, both in the ^{1}H and ^{13}C NMR spectra two sets of signals were found (Table 1). In accord with data given for an iridium complex [9], likely, the carbonyl carbon atom signals at lower (253.4 ppm) and higher (214.6 ppm) field had to be assigned to the bridging and the terminal acetyl ligands, respectively. The presence of only one signal in the ^{195}Pt NMR spectra (δ_{Pt} −3138 ppm), both at −40 and at −70 °C, gave proof of a symmetric structure of the complex. At −70 °C, in the ^{1}H and ^{13}C NMR spectra for the methyl groups of the diisopropylamine ligand four sets of signals (δ_H = 1.07/1.12/1.37/1.83; δ_C = 19.6/20.1/23.0/23.4) were found and for the two CH groups two sets (δ_H = 3.25, br, overlapping with N*H*; δ_C = 47.2/47.4).

At −40 °C, signal broadening along with a reduction of the number of signals (see Experimental) exhibits a dynamic process. This could be (with respect to the NMR time scale) a fast ligand exchange (NH(*i*-Pr)$_2$) reaction and/or an inversion of the six-membered $Pt_2C_2O_2$ ring. In other diacetyl-bridged metal complexes, rings of this type have a boat conformation [9]. DFT calculations on the model complex [{Pt(COMe)(NHMe$_2$)}$_2$(μ-COMe)$_2$], in which the isopropyl groups in complex **7** were replaced by methyl groups, showed that the boat conformation is energetically favored by ΔG° = 5.9 kcal/mol over the planar conformation and by ΔG° = 6.8 kcal/mol over the chair conformation. Furthermore, the *SP*-4-4 configuration (as depicted in Scheme 2) is energetically favored over the *SP*-4-3 isomer by more than 40 kcal/mol. Thus, the latter one must not be taken into account.

At room temperature, ^{1}H and ^{195}Pt NMR spectroscopically, a decomposition of **7** into the coordination polymer [{Pt(COMe)$_2$}$_n$] (**IV**) [6] and noncoordinated diisopropylamine was found, which is an indication for the fast ligand exchange reaction discussed before.

In the IR spectrum of complex **7**, two strong C=O bands (ν_{CO} = 1514, 1608 cm^{-1}) were observed. The vibration with the lower wavenumber (1514 cm^{-1}) is in accord with those of the bridging acetyl ligands in platina-β-diketonates of platina-β-diketones, [Cl_2Pt(μ-COMe)$_2$Pt{(COMe)$_2$H}]$^-$ (ν_{CO} = 1524–1534 cm^{-1}) [4] and in the iridium complex [Ir_2H_2{PPh$_2$(*o*-C_6H_4CO)}$_2${μ-PPh$_2$(*o*-C_6H_4CO)}$_2$] (ν_{CO} = 1504 cm^{-1}) [9]. The vibration at 1608 cm^{-1} has to be assigned to the terminal acetyl ligands.

The methyl–carbonyl complexes, [Pt(COMe)Me(NH_2R)(CO)] (**4a**,**d**,**f**), being identified as intermediates of the decomposition of complexes **3** (Scheme 2), showed chemical shifts characteristic for the methyl ligand Pt–CH_3 (δ_H = 0.24–0.29; δ_C = 3.4) and IR bands characteristic for carbonyl ligands (ν_{CO} = 2048–2061 cm^{-1}). Furthermore, high-resolution ESI mass spectra (cationic mode) of the corresponding complexes **3** showed, apart from the molecular peaks of **3** ([M + H]$^+$) and other peaks, also the molecular peaks of **4** ([M′ + H]$^+$) with the correct isotopic pattern. Likely, these findings can be explained in terms of the restricted thermal stability of **3** and the thermal load during the ESI measurements.

2.3. On the equilibrium between complexes 2/5 and the amine complexes 3/6/8/9

The formation of the diacetylbis(amine) complexes **3** from the diacetyl(2,2′-bipyridine) complex **2** according to Scheme 2 (pathway **A**) proved to be an equilibrium reaction. With the benzylamine ligand, the equilibrium constant (**2** + 2NH_2Bn ⇌ **3a** + bpy) was estimated ^{1}H NMR spectroscopically to be in the order of

Table 2
Selected bond lengths (in Å) and angles (in deg) of the calculated equilibrium structures **2*** and **3a*** (gas phase) in comparison with data obtained by X-ray diffraction measurements of complexes **2**[a] and **3a**.

	2*	**2**	**3a***	**3a**
Pt–C	1.991	1.991(8)/1.986(8)	1.989	1.979(2)
	1.991	1.99(1)/2.011(9)	1.989	
Pt–N	2.194	2.099(7)/2.119(7)	2.232	2.164(2)
	2.194	2.138(8)/2.116(7)	2.232	
C=O	1.219	1.22(1)/1.21(1)	1.226	1.210(3)
	1.219	1.22(1)/1.23(1)	1.226	
C–Pt–C	90.6	91.7(4)/88.2(4)	98.1	91.8(1)
C–Pt–N	97.7	95.6(3)/96.7(3)	84.1	87.8(1)
	97.7	95.9(3)/97.8(3)	84.0	
N–Pt–N	74.7	76.8(3)/77.0(3)	93.9	92.7(1)
ε(Pt,C,C,N,N)/ε(C,C,O)	47.9	54.3(4)/73.9(3)	32.4	53.9(1)
	47.9	78.4(5)/84.3(6)	32.4	

[a] Taken from Ref. [3].

Table 3
Standard Gibbs free energies (in kcal/mol) in the gas phase (ΔG°) and with consideration of CH_2Cl_2 as solvent (ΔG°_{solv}) of the reactions according to Scheme 3.

Starting complex	**2*** (N^N = bpy)		**5*** (N^N = H(Me)dmg)	
2 L in $[Pt(COMe)_2L_2]$	ΔG°	ΔG°_{solv}	ΔG°	ΔG°_{solv}
$2NH_2Bn$ (**3a***)	2.3	4.7	2.3	0.6
$2NH_2Me$ (**3g***)	2.2	4.1	2.2	0.0
$2NHMe_2$ (**6a***)	4.7	8.7	4.7	4.6
$2NMe_3$ (**9***)	22.8	25.0	22.8	20.9
en (**8a***)	−3.0	−4.7	−2.9	−8.8
$MeHNCH_2CH_2NHMe$ (**8b***)	−2.4	−3.5	−2.3	−7.6
$Me_2NCH_2CH_2NH_2$ (**8c***)	−1.3	−2.1	−1.3	−6.2
TMEDA (**8d***)	0.8	0.3	0.8	−3.8

magnitude of 10^{-3}–10^{-4} L/mol, thus corresponding to a Gibbs free energy ΔG of about 4–6 kcal/mol. In accordance with that, synthesis of **3a** required a large excess of the amine as realized in neat NH_2Bn.

To get further insight into ligand substitution reactions according to Scheme 2, DFT calculations using the mPW1PW91 functional [10] and highly qualitative basis sets as well as an ECP for Pt have been performed. The comparison of structural data of the calculated complexes **2*** and **3a***[1] (representing structures in the gas phase) with those obtained by X-ray diffraction measurements of crystals of **2** and **3a** exhibited a good agreement (Table 2).

Table 3 shows the calculated standard Gibbs free energies in the gas phase (ΔG°) and in methylene chloride solution (ΔG°_{solv}) for reactions according to Scheme 3. Noteworthy, the ΔG° values are essentially the same, irrespective whether **2*** (N^N = bpy) or **5*** (N^N = H(Me)dmg) is used as starting complex. Considering solvent effects (CH_2Cl_2), in all cases, in full accord with the experimental findings, the substitution of the H(Me)dmg ligand in complex **5*** proved to be thermodynamically more favorable than that of the bpy ligand in complex **2*** ($\Delta\Delta G^\circ_{solv}$ ca. 4.1 kcal/mol). In the following, only the ΔG°_{solv} values will be discussed.

Ligand exchange reactions according to Scheme 3 will be thermodynamically more feasible in the order tertiary amine < secondary amine < primary amine < diamine. Thus, for instance, starting from complex **5***, the reactions with NMe_3 and $NHMe_2$ are strongly and weakly endergonic, those with primary amines (NH_2Bn, NH_2Me) are thermoneutral and those with diamines are exergonic. In good agreement with the experiment (4–6 kcal/mol), for the reaction of **2*** with benzylamine $\Delta G^\circ_{solv} = 4.7$ kcal/mol was calculated. Obviously, this endergonicity could be overcome in the experiments by a large excess of the amine. Thus, starting from **2**, in neat primary amines (NH_2Bn, NH_2Me) and starting from **5** even in neat secondary amines ($NHMe_2$) the diacetylbis(amine) complexes could be prepared (cf. Scheme 2). Furthermore, on the one hand, neither starting from **2** nor from **5**, the tertiary amine NMe_3 underwent a ligand substitution reaction and all ethylenediamine derivatives were prone to ligand exchange both with **2** and **5** as starting complex on the other.

2.4. Structural characterization

$[Pt(COMe)_2(NH_2Bn)_2]$ (**3a**) and $[Pt(COMe)_2(NH_2i\text{-}Pr)_2]$ (**3d**) were found to crystallize in the monoclinic crystal system in the space group $I2/a$ and $P2_1/c$, respectively. Molecules of **3a** exhibit crystallographically imposed C_2 symmetry. Their structure is shown in Fig. 1 along with selected structural parameters in the figure caption. The asymmetric unit of complex **3d** contains two symmetry independent molecules with very similar structures. One of them is shown in Fig. 2, selected distances and angles are given in the figure caption.

The platinum centers in the two complexes are square-planar coordinated by two nitrogen and two carbon atoms (sum of angles around Pt: 360.1°, **3a**; 360.1/360.0°,[2] **3d**) in mutual cis position (configuration index: *SP*-4-2). The acetyl ligands include an angle with the complex plane of 53.9° (**3a**) as well as 52.4/72.1° and 74.2/75.3°, respectively (**3d**). They are oriented in a "transoid" conformation, meaning that the oxygen atoms of the two acetyl ligands are lying on different sides of the complex plane.

While the C=O bond lengths (1.210(3)–1.224(5) Å) are in the range of other structurally characterized acetyl platinum(II) complexes (median: 1.214 Å; lower/upper quartile 1.193/1.228 Å; number of observations $n = 29$ [11]), the Pt–C bonds (1.976(4)–1.985(4) Å) are relatively short (median: 2.003 Å; lower/upper quartile 1.986/2.019 Å; $n = 29$ [11]). In accord with the high trans influence of the acetyl ligands, the Pt–N bonds are relatively long (2.164(2)–2.182(3) Å). Thus, in platinum(II) complexes with halido and phosphane ligand trans to a primary amine ligand, Pt–N bond lengths of 2.041 Å (median; lower/upper quartile 2.030/2.057 Å; $n = 268$, [11]) and 2.108 Å (median; lower/upper quartile 2.095/2.121 Å; $n = 50$; [11]), respectively, were found. Organyl ligands in trans position give rise to Pt–N bond lengths of 2.127 Å (median; lower/upper quartile 2.098/2.136 Å; $n = 30$, [11]).

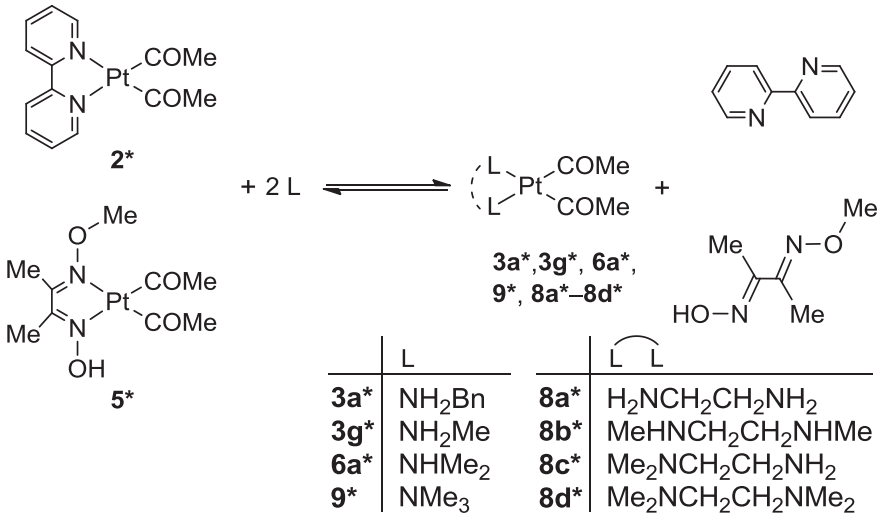
In crystals of **3a** intermolecular interactions were found (Fig. 3). The phenyl rings of the benzylamine ligands are π stacked as indicated by the centroid–centroid distance of the phenyl rings (3.724(2) Å) and the angle between the centroid–centroid vector and the normal to the plane (10.3°) [12]. Furthermore, intermolecular N–H···O″ hydrogen bonds (N···O″ 2.926(3) Å; N–H···O″ 153°) were observed [13]. In crystals of **3d**, the molecules are connected by a two-dimensional network of weak intermolecular N–H···O′ hydrogen bonds (N···O′ 2.939(5)–3.190(5) Å; N–H···O′ 134–177°). The two protons in the NH_2 groups act as hydrogen donors and the carbonyl oxygen atoms as hydrogen acceptors such that bifurcated hydrogen bonds are formed.

2.5. Conclusion

The present investigation shows that diacetylbis(amine)platinum(II) complexes bearing two monodendate and bidendate primary and secondary amine ligands can be synthesized by ligand exchange reactions according to Scheme 2. Due to the higher purity

[1] Here and in the following, calculated complexes are marked with a star.

[2] Here and in the following the values for the two symmetry independent molecules are given separated by a slash.



Scheme 3. Equilibrium between the precursor complexes **2***/**5*** and amine complexes **3***, **6***, **8***, and **9***.

of the products and the easier accessibility of the starting complexes, this method is superior to the synthesis route starting from the coordination polymer **IV** (Scheme 1, **F**).

Both the experimental results and DFT calculations gave proof that the starting complex with the diacetyldioxime mono methyl ether ligand (**5**) is more prone to ligand substitution than that with the bipyridine ligand (**2**), indicating a weaker coordination of the H(Me)dmg ligand than the bpy ligand. Interestingly, calculation of the dissociation process $[Pt(COMe)_2(N\hat{}N)]$ (**2**/**5**) → $[Pt(COMe)_2]$ + N^N made clear, that this is caused by solvent effects: Whereas the dissociation energies for the two processes are nearly identical (ΔE = 32.0/32.7 kcal/mol, **2**/**5**), the Gibbs free energies in CH_2Cl_2 as solvent are significantly different (ΔG_{solv} = 10.1/6.0 kcal/mol, **2**/**5**). The order $NH_2R > NHR_2 \gg NR_3$ for the readiness of the substitution reactions might be primarily caused by an increasing sterical hindrance in the complexes.

The weakness of the amine coordination ($NHR_2 > NH_2R$) will also be obvious in a fast decomposition reaction, whereas for primary amines an extrusion of CO from an acetyl ligand yielding acetyl–carbonyl–methyl complexes could be proved. This is preceded by the cleavage of one amine ligand which is favored in all these complexes by the high trans influence of the acetyl ligand [14].

The formation of the dinuclear twofold acetyl-bridged complex **7** in the reaction of **5** with diisopropylamine is unique. As the Gibbs free energies shown in Scheme 4 exhibit, the formation of the (hypothetical) mononuclear complex $[Pt(COMe)_2L_2]$ (L = NH(*i*-Pr)$_2$) is energetically much more disfavored than that with L = $NHMe_2$ ($\Delta\Delta G^\circ_{solv}$ = 9.3 kcal/mol; solvent: CH_2Cl_2), likely due to steric reasons (see above). On the other hand, in the case of diisopropylamine, the formation of the dinuclear acetyl-bridged complex **7** is strongly favored over the corresponding (hypothetical) complex with L = $NHMe_2$ ($\Delta\Delta G^\circ_{solv}$ = 18.3 kcal/mol).

Summing up, complexes $[Pt(COMe)_2L_2]$ (L = amine), which are easily accessible, have two substitutionally labile ligands at their disposal and might be envisioned as suitable starting complexes for synthesizing other diacetyl platinum complexes as has been shown

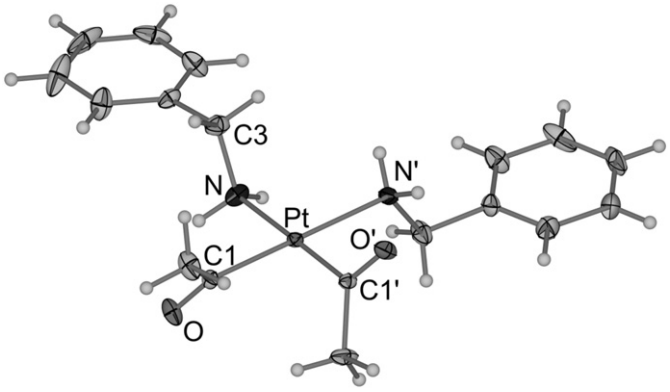


Fig. 1. Molecular structure of $[Pt(COMe)_2(NH_2Bn)_2]$ (**3a**). Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Pt–C1 1.979(2), Pt–N 2.164(2), C1–O 1.210(3), N–C3 1.459(4), C1–Pt–C1′ 91.8(1), C1–Pt–N 87.8(1), N–Pt–N′ 92.7(1), C3–N–Pt 115.2(2).

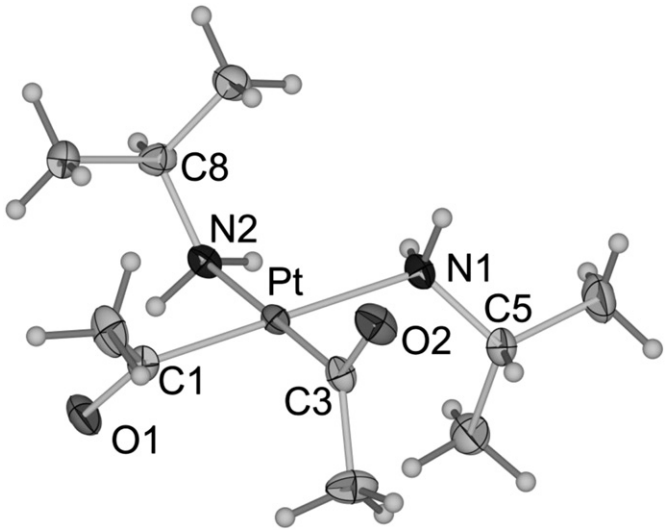


Fig. 2. Molecular structure of one of the two symmetry independent molecules of $[Pt(COMe)_2(NH_2i\text{-}Pr)_2]$ (**3d**) (displacement ellipsoids at 30% probability). Selected distances (Å) and angles (deg); the values for the two symmetry independent molecules are given separated by a slash: Pt–C1 1.985(4)/1.982(4), Pt–C3 1.976(4)/1.977(4), Pt–N1 2.176(3)/2.174(3), Pt–N2 2.177(3)/2.182(3), N1–C5 1.476(6)/1.477(6), N2–C8 1.489(6)/1.471(6), C1–O1 1.224(5)/1.222(5), C3–O2 1.219(5)/1.224(5), C1–Pt–C3 89.1(2)/87.5(2), C1–Pt–N2 91.3(2)/93.8(2), N2–Pt–N1 88.3(1)/87.7(1), N1–Pt–C3 91.4(2)/91.0(2), Pt–N1–C5 117.3(3)/118.6(3), Pt–N2–C8 119.9(2)/121.1(3).

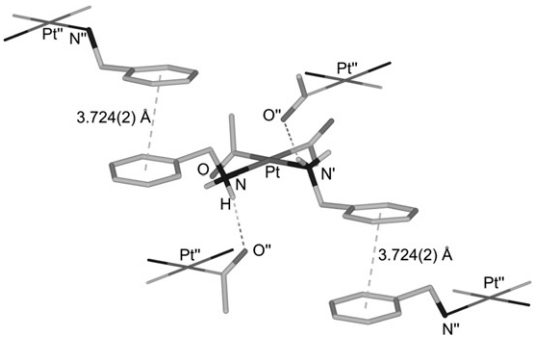


Fig. 3. Solid-state structure of $[Pt(COMe)_2(NH_2Bn)_2]$ (**3a**) showing the π–π stacking and hydrogen bonds by dashed lines. H atoms have been omitted for clarity, except those of the NH_2 group.

in reactions with tris- and tetrakis(pyrazolyl)borates yielding in new diacetyl platinum(II) and platinum(IV) complexes with hemilabile scorpionate ligands [15].

3. Experimental section

3.1. General remarks

All reactions were performed in an argon atmosphere using the standard Schlenk techniques. Solvents were dried (Et_2O and *n*-pentane over Na/benzophenone, CH_2Cl_2 over CaH_2) and distilled prior to use. NMR spectra were, unless otherwise specified, recorded at 27 °C on Varian Gemini 200, VXR 400 and Unity 500 NMR spectrometers. Solvent signals (^1H, ^{13}C) were used as internal references and H_2PtCl_6 ($\delta(^{195}Pt) = 0$ ppm) as external reference. IR spectra were recorded on a Bruker Tensor 27 spectrometer with a Platinum ATR unit. The positive ion high-resolution ESI mass spectra were measured at a Bruker Apex III Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, Billerica, USA), which is equipped with an infinity cell, a 7.0 T superconducting magnet (Bruker), an RF-only hexapole ion guide, and an external electron spray ion source (Agilent, off axis spray, voltages: endplate, −3.700 V; capillary, −4.200 V; capillary exit, 100 V; skimmer 1, 15.0 V; skimmer 2, 12.0 V). Nitrogen was used as drying gas at 150 °C. The sample solutions (in MeOH) were introduced continuously via a syringe pump with a flow rate of 120 μL h^{-1}. The data were acquired with 512K data points and zero filled to 2048K by averaging 32 scans. The data were evaluated by the Bruker XMASS 7.0.8 software. Thermal gravimetric analysis was performed on a Netzsch STA449 unit under argon (heating rate 10 K/min). Microanalyses were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) elemental analyzer. The complex $[Pt(COMe)_2(bpy)]$ (**2**) was prepared according to literature methods [3], whereas the synthesis of $[Pt(COMe)_2\{H(Me)dmg\}]$ (**5**) is unpublished yet [16].

3.2. Synthesis of $[Pt(COMe)_2(NH_2R)]$ (**3a–f**)

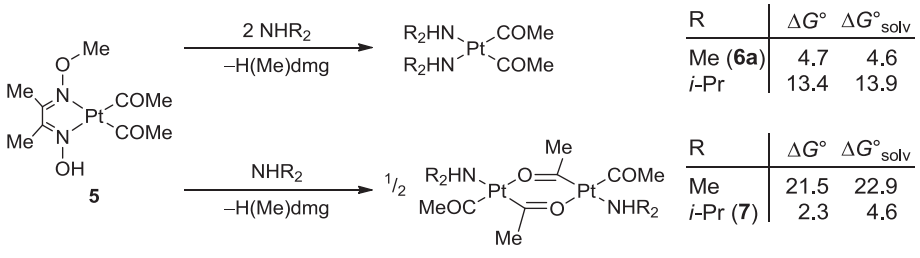
To $[Pt(COMe)_2(bpy)]$ (**2**) (150 mg, 0.3 mmol) the respective primary amine NH_2R (1 mL, ca. 10 mmol) was added with stirring. The resulting red solutions became colorless within 10–20 min. Further stirring for 1 h resulted in the precipitation of complexes $[Pt(COMe)_2(NH_2R)_2]$ (R = Bn, **3a**; CH_2CH_2Ph, **3b**; Cy, **3f**). To complete the precipitation and to precipitate the other complexes (R = Et, **3c**; *i*-Pr, **3d**; $CH_2CH{=}CH_2$ **3e**), respectively, diethyl ether (3 mL) was added. Then, the solids were filtered off, washed with cold (−10 °C) diethyl ether (2 × 1 mL), and dried in vacuo. Analogously, instead of complex **2**, $[Pt(COMe)_2\{H(Me)dmg\}]$ (**5**) can be used as starting material.

3a (R = Bn). Yield: 153 mg (90%). Found (Calc.): $[C_{18}H_{25}N_2O_2Pt]$ (495.46); C 43.79 (43.63), H 4.99 (4.88). HRMS (ESI) *m/z* calc. for $[C_{18}H_{25}N_2O_2^{194}Pt + H]^+$ 495.1537; found 495.1551 (in addition to other signals). ^1H NMR (200 MHz, $CDCl_3$): δ 2.15 (s + d, $^3J_{Pt,H} = 22.0$ Hz, 6H, $COCH_3$), 3.68 (s(br), 8H, $NH_2{+}CH_2$), 7.28–7.31 (m, 10H, C_6H_5). ^{13}C NMR (50 MHz, $CDCl_3$): δ 44.1 (s + d, $^2J_{Pt,C} = 372$ Hz, $COCH_3$), 49.2 (s, CH_2), 127.9 (s, *p*-CH), 128.1 (s, *o*-CH), 128.8 (s, *m*-CH), 139.2 (s + d, $^3J_{Pt,C} = 19$ Hz, *i*-C), 232.6 (s, CO). ^{195}Pt NMR (107 MHz, THF-d_8): δ −3329 (s). DTA: $T_{dec.} = 125$ °C, mass loss at 200 °C: 61.1% (calc. for residual Pt: 60.6%). IR: ν 3285 (m), 3225 (m), 3121 (m), 3026 (m), 2968 (m), 1547 (s), 1495 (m), 1455 (m), 1406 (m), 1359 (m), 1330 (m), 1208 (w), 1159 (m), 1147 (m), 1122 (s), 1099 (s), 1070 (w), 1025 (w), 995 (s), 929 (w), 749 (m), 695 (s), 610 (m), 595 (w), 530 (w), 491 (w), 441 (w), 354 (w) cm^{-1}.

To estimate the equilibrium constant between complex **3a** and its starting complex **2**, in an NMR tube a solution of **2** (8.9 mg, 0.02 mmol) and benzylamine (13.2 μL) in CD_2Cl_2 (0.9 mL) was prepared and measured ^1H NMR spectroscopically. Then, stepwise a defined amount of benzylamine (6 times 4.4 μL) was added and from the ^1H NMR spectra the ratio of complexes **2**:**3a** were calculated.

3b (R = CH_2CH_2Ph). Yield: 170 mg (95%). Found (Calc.): $[C_{20}H_{28}N_2O_2Pt]$ (523.53); C 45.57 (45.88), H 5.29 (5.39). ^1H NMR (500 MHz, $CDCl_3$): δ 2.21 (s + d, $^3J_{Pt,H} = 19.1$ Hz, 6H, $COCH_3$), 2.75 (m, 4H, NH_2CH_2), 2.81 (m, 4H, CH_2Ph), 3.45 (m(br), 4H, NH_2), 7.09–7.30 (m, 10H, C_6H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.3 (s, CH_2Ph), 44.3 (s + d, $^2J_{Pt,C} = 356$ Hz, $COCH_3$), 46.1 (s, NH_2CH_2), 126.7 (s, *p*-CH), 128.7 (s(br), *o* + *m*-CH), 138.0 (s, *i*-C), 233.8 (s + d, $^1J_{Pt,C} = 1275$ Hz, CO). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3299 (s). IR: ν 3307 (m), 3259 (m), 3136 (m), 3062 (m), 3028 (m), 2960 (m), 2946 (m), 1610 (s), 1537 (s), 1454 (m), 1411 (m), 1337 (m), 1202 (w), 1155 (w), 1123 (s), 1090 (m), 1039 (m), 1008 (m), 941 (w), 912 (w), 749 (s), 701 (s), 612 (m), 549 (w), 507 (m) cm^{-1}.

3c (R = Et). Yield: 57 mg (45%). Found (Calc.): $[C_8H_{20}N_2O_2Pt]$ (371.35); C 25.93 (25.88), H 5.21 (5.43). ^1H NMR (200 MHz, $CDCl_3$): δ 1.24 (t, $^3J_{H,H} = 7.2$ Hz, 6H, CH_2CH_3), 2.21 (s + d, $^3J_{Pt,H} = 23.2$ Hz, 6H, $COCH_3$), 2.73 (m, 4H, CH_2), 3.46 (m(br), 4H, NH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.1 (s, CH_2CH_3), 40.4 (s, CH_2), 44.5 (s, $COCH_3$), 234.5 (s, CO). ^{195}Pt NMR (86 MHz, $CDCl_3$): δ −3274 (s). IR: ν 3276 (w), 3219



R	ΔG°	ΔG°solv
Me (**6a**)	4.7	4.6
i-Pr	13.4	13.9

R	ΔG°	ΔG°solv
Me	21.5	22.9
i-Pr (**7**)	2.3	4.6

Scheme 4. Differences in the reactivity of **5** with dimethyl- and diisopropylamine and the corresponding Gibbs free energies (in kcal/mol) obtained by DFT calculations.

(w), 3116 (w), 2974 (w), 2958 (w), 2883 (w), 1732 (m), 1554 (s), 1471 (w), 1446 (w), 1404 (m), 1329 (m), 1194 (m), 1117 (s), 1093 (m), 1057 (s), 922 (m), 881 (w), 812 (w), 609 (m), 596 (m), 349 (s) cm^{-1}.

3d (R = *i*-Pr). Yield: 130 mg (95%). Found (Calc.): $[C_{10}H_{28}N_2O_2Pt]$ (399.15); C 29.86 (30.07), H 6.03 (6.06). ^1H NMR (200 MHz, $CDCl_3$): δ 1.24 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, $NH_2CH(CH_3)_2$), 2.21 (s + d, $^3J_{Pt,H}$ = 23.0 Hz, 6H, $COCH_3$), 2.91 (m, 2H, $NH_2CH(CH_3)_2$), 3.40 (d(br), $^3J_{H,H}$ = 6.4 Hz, 4H, $NH_2CH(CH_3)_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.3 (s, $NH_2CH(CH_3)_2$), 44.3 (s + d, $^2J_{Pt,C}$ = 367 Hz, $COCH_3$), 46.9 (s, $NH_2CH(CH_3)_2$), 233.7 (s, CO). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3304 (s). IR: ν 3285 (m), 3244 (s), 3159 (m), 2968 (m), 2926 (w), 2880 (w), 1564 (s), 1442 (w), 1384 (m), 1329 (m), 1214 (w), 1164 (w), 1104 (m), 928 (w), 819 (w), 775 (w), 608 (w), 549 (w) cm^{-1}.

3e (R = $CH_2CH{=}CH_2$). Yield: 54 mg (40%). Found (Calc.): $[C_{10}H_{20}N_2O_2Pt]$ (395.15); C 30.02 (30.38), H 4.84 (5.10). ^1H NMR (500 MHz, $CDCl_3$): δ 2.18 (s + d, $^3J_{Pt,H}$ = 22.7 Hz, 6H, $COCH_3$), 3.27 (m, 4H, NH_2CH_2), 3.67 (m(br), 4H, NH_2), 5.15 (d(br), $^3J_{H,H}$ = 10.2 Hz, 2H, $=CH^{(Z)}H$), 5.22 (d(br), $^3J_{H,H}$ = 17.2 Hz, 2H, $=CHH^{(E)}$), 6.03 (m, 2H, $CH{=}CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 44.2 (s + d, $^2J_{Pt,C}$ = 362 Hz, $COCH_3$), 47.6 (s, NH_2CH_2), 117.4 (s, $=CH_2$), 136.0 (s, $CH{=}CH_2$), 233.6 (s + d, $^1J_{Pt,C}$ = 1295 Hz, CO). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3272 (s). IR: ν 3264 (w), 3218 (w), 3104 (w), 2976 (w), 2903 (w), 2868 (w), 1648 (w), 1552 (s), 1456 (m), 1409 (m), 1331 (m), 1147 (w), 1118 (s), 1110 (s), 1025 (m), 994 (m), 924 (s), 694 (w), 609 (m), 602 (m), 529 (m), 411 (m), 352 (s) cm^{-1}.

3f (R = Cy). Yield: 156 mg (95%). Found (Calc.): $[C_{16}H_{32}N_2O_2Pt]$ (479.52); C 39.24 (40.08), H 6.61 (6.73). HRMS (ESI) *m*/*z* calc. for $[C_{16}H_{33}N_2O_2^{194}Pt + H]^+$ 479.2163; found 479.2174 (in addition to other signals). ^1H NMR (200 MHz, $CDCl_3$): δ 1.08 (m, 6H, C_6H_{11}), 1.23 (m, 6H, C_6H_{11}), 1.61 (m, 4H, C_6H_{11}), 1.74 (m, 4H, C_6H_{11}), 2.20 (s, 6H, $COCH_3$), 2.46 (m, 2H, NH_2CH), 3.34 (d(br), $^3J_{H,H}$ = 6.0 Hz, 4H, NH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.0 (s, C^4 Cy), 25.3 (s, $C^{3/5}$ Cy), 35.9 (s, $C^{2/6}$ Cy), 44.3 (s + d, $^2J_{Pt,C}$ = 351 Hz, $COCH_3$), 54.1 (s, NH_2CH), 234.0 (s, CO). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3296 (s). IR: ν 3285 (m), 3109 (w), 2933 (m), 2854 (w), 1589 (w), 1545 (s), 1449 (w), 1401 (w), 1334 (m), 1232 (m), 1122 (m), 1100 (m), 1055 (m), 615 (m) cm^{-1}.

3.3. On the decomposition of complexes **3a**, **3d**, and **3f** in solution

Solutions of the requisite complex $[Pt(COMe)_2(NH_2R)_2]$ (**3a**, **3d**, **3f**; 20 mg) in $CDCl_3$ or THF-d_8 (0.7 mL) were transferred in an NMR tube and spectra were measured from the freshly prepared solutions after 3 h. In addition to signals of the starting complex (**3a**, **3d**, **3f**, see below) and of non-identified decomposition products, those of complexes $[Pt(COMe)Me(CO)(NH_2R)]$ (**4a**, **4d**, **4f**) were observed. Then, the solvent was removed in vacuo and IR spectra were recorded.

4a (R = Bn). HRMS (ESI) *m*/*z* calc. for $[C_{11}H_{16}N_1O_2^{194}Pt + H]^+$ 388.0807; found 388.0802 (in addition to other signals). ^1H NMR (500 MHz, THF-d_8): δ 0.29 (s + d, $^2J_{Pt,H}$ = 69.8 Hz, 3H, $PtCH_3$), 2.20 (s + d, $^3J_{Pt,H}$ = 18.9 Hz, 3H, $COCH_3$), 3.96 (m, 2H, CH_2), 4.24 (s(br), 2H, NH_2), 7.14–7.35 (m, 5H, C_6H_5). ^{13}C NMR (125 MHz, THF-d_8): δ 3.4 (s + d, $^1J_{Pt,C}$ = 708.7 Hz, $PtCH_3$), 45.3 (s, $COCH_3$), 51.6 (s, CH_2), 128.3 (s, *p*-CH), 128.9 (s, *o*-CH), 129.3 (s, *m*-CH), 141.5 (s, *i*-C), 180.9 (s + d, $^1J_{Pt,C}$ = 1125.5 Hz, PtCO), 214.0 (s, $COCH_3$). ^{195}Pt NMR (107 MHz, THF-d_8): δ −3455 (s). IR: ν(CO) 2052 (m) cm^{-1}.

4d (R = *i*-Pr). ^1H NMR (200 MHz, $CDCl_3$): δ 0.24 (s + d, $^2J_{Pt,H}$ = 67.7 Hz, 3H, $PtCH_3$), 2.33 (s + d, $^3J_{Pt,H}$ = 20.4 Hz, 3H, $COCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 3.4 (s, $PtCH_3$). IR: ν(CO) 2061 (w) cm^{-1}.

4f (R = Cy). HRMS (ESI) *m*/*z* calc. for $[C_{10}H_{19}N_1O_2^{194}Pt + H]^+$ 380.1115; found 380.1122 (in addition to other signals). ^1H NMR (500 MHz, $CDCl_3$): δ 0.28 (s + d, $^3J_{Pt,H}$ = 66.8 Hz, 3H, $PtCH_3$), 2.34 (s, 3H, $COCH_3$). ^{195}Pt NMR (107 MHz, THF-d_8): δ −3484 (s). IR: ν(CO) 2048 (s) cm^{-1}.

3.4. Synthesis of $[Pt(COMe)_2(NHR_2)_2]$ (**6a**/**b**) and $[\{Pt(COMe)\{NH(i\text{-}Pr)_2\}\}_2(\mu\text{-}COMe)_2]$ (**7**)

$[Pt(COMe)_2\{H(Me)dmg\}]$ (**5**) (150 mg, 0.4 mmol) and the respective secondary amine NHR_2 (1 mL) were stirred for 1 h at −78 °C (R = Me) and 0 °C (R = Et), respectively, resulting in a change of color (from red to colorless) and precipitation of a fine white solid. Then, diethyl ether (3 mL) was added and, in the case of $NHEt_2$, the reaction mixture was immediately cooled down to −78 °C. The solid was filtered off at about −10 °C, washed with cooled (−78 °C) diethyl ether (2 × 1 mL), and dried in vacuo. The solid complexes **6** proved to be stable at −70 °C over several weeks, but decomposition occurred at temperatures above −20 °C within few days. Complex **7** was synthesized analogously by adding diisopropylamine (1 mL) to the starting complex **5** (150 mg, 0.4 mmol) and stirred for 1 h at −78 °C.

6a (R = Me). Yield: 95 mg (70%). HRMS (ESI) *m*/*z* calc. for $[C_8H_{20}N_2O_2Pt + H]^+$ 372.1259; found 372.1245 (in addition to other signals). ^1H NMR (200 MHz, CD_2Cl_2, −40 °C): δ 2.05 (s + d, $^3J_{Pt,H}$ = 25.0 Hz, 6H, $COCH_3$), 2.42 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, $NH(CH_3)_2$), 3.63 (m(br), 2H, NH). ^{13}C NMR (50 MHz, CD_2Cl_2, −40 °C): δ 41.3 (s + d, $^2J_{Pt,C}$ = 149 Hz, NCH_3), 43.5 (s, $COCH_3$), 229.5 (s, CO). ^{195}Pt NMR (107 MHz, CD_2Cl_2, −40 °C): δ −3439 (s). IR: ν 3228 (m), 2968 (w), 2901 (w), 1608 (s), 1572 (s), 1462 (m), 1402 (m), 1325 (m), 1211 (w), 1086 (s), 1020 (w), 901 (s), 590 (m), 530 (w), 443 (w), 361 (w), 341 (s) cm^{-1}.

6b (R = Et). Yield: 69 mg (45%). Found (Calc): $C_{12}H_{28}N_2O_2Pt$ (427.44); C 33.29 (33.72), H 6.37 (6.60). ^1H NMR (500 MHz, CD_2Cl_2, −40 °C): δ 1.32 (t, $^3J_{H,H}$ = 7.0 Hz, 12H, CH_2CH_3), 2.04 (s + d, $^3J_{Pt,H}$ = 20.7 Hz, 6H, $COCH_3$), 2.56 (m(br), 4H, CH_2CH_3), 2.79 (m(br), 4H, CH_2CH_3), 3.33 (s(br), 2H, NH). ^{13}C NMR (125 MHz, CD_2Cl_2, −40 °C): δ 14.5 (s, CH_2CH_3), 43.4 (s, $COCH_3$), 47.3 (s, CH_2CH_3), 230.0 (s, CO). ^{195}Pt NMR (107 MHz, CD_2Cl_2, −40 °C): δ −3399 (s). IR: ν 3240 (m), 3167 (m), 2968 (m), 2898 (m), 1616 (s), 1562 (s), 1472 (m), 1377 (m), 1151 (m), 1107 (m), 1080 (s), 1055 (m), 1026 (m), 910 (m), 851 (w), 829 (w), 783 (w), 606 (w), 588 (w), 540 (w), 430 (w), 370 (m) cm^{-1}.

7. Yield: 115 mg (85%). Found (Calc): $C_{20}H_{42}N_2O_4Pt_2$ (764.71); C 30.99 (31.41), H 5.15 (5.54). ^1H NMR (500 MHz, CD_2Cl_2, −70 °C): δ 1.07 (s(br), 6H, $CHCH_3$), 1.12 (s(br), 6H, $CHCH_3$), 1.37 (s(br), 6H, $CHCH_3$), 1.83 (s(br), 6H, $CHCH_3$), 1.90 (s, 6H, $COCH_3$), 2.05 (s, 6H, $COCH_3$), 3.25 (s(br), 6H, CH + NH). ^1H NMR (500 MHz, CD_2Cl_2, −40 °C): δ 1.16 (s(br), 12H, $CHCH_3$), 1.58 (s(br), 12H, $CHCH_3$), 1.96 (s, 6H, $COCH_3$), 2.07 (s, 6H, $COCH_3$), 3.29 (s(br), 6H, CH + NH). ^1H NMR (500 MHz, CD_2Cl_2, 27 °C after ca. 5 min): uncoordinated amine (ca. 30%): δ 0.99 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3), 2.87 (sept, $^3J_{H,H}$ = 6.2 Hz, 2H, CH), complex **7** (ca. 70%): 1.26 (d, $^3J_{H,H}$ = 6.0 Hz, 12H, $CHCH_3$), 1.62 (d, $^3J_{H,H}$ = 6.1 Hz, 12H, $CHCH_3$), 2.05 (s, 6H, $COCH_3$), 2.13 (s, 6H, $COCH_3$), 3.34 (m, 6H, CH + NH), complex **IV** (ca. 30%): 2.38 (s, $COCH_3$). ^{13}C NMR (125 MHz, CD_2Cl_2, −70 °C): δ 19.6 (s, $CHCH_3$), 20.1 (s, $CHCH_3$), 23.0 (s, $CHCH_3$), 23.4 (s, $CHCH_3$), 42.2 (s, $COCH_3$), 43.7 (s, $COCH_3$), 47.2 (s, CH), 47.4 (s, CH), 214.6 (s, CO terminal), 253.4 (s, CO bridged). ^{13}C NMR (125 MHz, CD_2Cl_2, −40 °C): δ 22.0 (s(br), $CHCH_3$), 42.6 (s, $COCH_3$), 43.7 (s, $COCH_3$), 47.7 (s, CH), 214.0 (s, CO terminal), 253.1 (s, CO bridged). ^{195}Pt NMR (107 MHz, CD_2Cl_2, −70/−40 °C): δ −3138 (s). IR: ν 3209 (w), 2974 (w), 2962 (w), 1608 (s), 1514 (s), 1460 (m), 1381 (m), 1331 (m), 1165 (m), 1130 (s), 1093 (s), 1045 (s), 984 (w), 941 (m), 808 (w), 648 (m), 600 (m), 416 (m), 358 (s) cm^{-1}.

At −40 °C, to a solution of complex **7** (35 mg, 0.05 mmol) in CD_2Cl_2 (0.7 mL), bpy (0.18 mmol) or pyridine (ca. 0.5 mmol) was added and ^1H NMR spectra (−40 °C) were recorded. Apart from residual signals of bpy/py, the diacetyl platinum(II) complex **2a** and $[Pt(COMe)_2(py)_2]$ [6], respectively, were identified. Performing these reactions with DMSO and D_2O, no reactions were observed.

3.5. Synthesis of [Pt(COMe)$_2$(N^N)] (**8a**–**d**)

[Pt(COMe)$_2${H(Me)dmg}] (**5**) (150 mg, 0.4 mmol) and the respective ethylenediamine derivative (0.5 mL) were stirred for about 1 h at room temperature resulting in a colorless solution of [Pt(COMe)$_2$(N^N)] (N^N = $H_2NCH_2CH_2NH_2$, en, **8a**; $MeHNCH_2CH_2NHMe$, **8b**; $Me_2NCH_2CH_2NH_2$, **8c**; $Me_2NCH_2CH_2NMe_2$, TMEDA, **8d**). Addition of diethyl ether (1 mL) yielded a precipitation which was filtered off, washed with diethyl ether (2 × 0.5 mL), and dried in vacuo.

8a (N^N = $H_2NCH_2CH_2NH_2$). Yield: 36 mg (30%). Found (Calc): $C_6H_{14}N_2O_2Pt$ (341.27); C 21.57 (21.12), H 4.21 (4.13). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.22 (s + d, $^3J_{Pt,H}$ = 22.4 Hz, 6H, $COCH_3$), 2.79 (s(br), 4H, CH_2), 3.87 (s(br), 4H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.5 (s, $COCH_3$), 45.5 (s, CH_2), 240.6 (s, *C*O). ^{195}Pt NMR (86 MHz, $CDCl_3$): δ −3337 (s). IR: ν 3242 (m), 3128 (w), 2949 (w), 2889 (w), 1579 (m), 1539 (s), 1404 (m), 1327 (m), 1111 (s), 1084 (s), 1045 (s), 981 (w), 927 (m), 866 (w), 758 (w), 607 (m), 592 (m), 559 (m) 347 (s) cm^{-1}.

8b (N^N = $MeHNCH_2CH_2NHMe$). Yield: 120 mg (90%). Found (Calc): $C_8H_{18}N_2O_2Pt$ (369.32); C 25.94 (26.02), H 4.61 (4.91). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s + d, $^3J_{Pt,H}$ = 19.3 Hz, 6H, $COCH_3$), 2.40 (m, 2H, *CH*H), 2.54 (d(br), $^3J_{H,H}$ = 6.0 Hz, 6H, $NHCH_3$), 2.91 (m, 2H, CH*H*), 5.51 (s(br), 2H, $NHCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.1 (s, $NHCH_3$), 44.9 (s + d, $^2J_{Pt,C}$ = 351 Hz, $COCH_3$), 53.8 (s, CH_2), 238.7 (s + d, $^1J_{Pt,C}$ = 1233 Hz, *C*O). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3293 (s). IR: ν 3250 (m), 3145 (w), 2932 (w), 2878 (w), 1587 (m), 1458 (m), 1406 (m), 1325 (m), 1151 (m), 1090 (s), 1003 (w), 920 (m), 895 (m), 785 (m), 602 (m), 492 (m), 372 (m) cm^{-1}.

8c (N^N = $Me_2NCH_2CH_2NH_2$). Yield: 105 mg (80%). Found (Calc): $C_8H_{18}N_2O_2Pt$ (369.32); C 25.86 (26.02), H 4.55 (4.91). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (s + d, $^3J_{Pt,H}$ = 25.7 Hz, 3H, $COCH_3$), 2.19 (s + d, $^3J_{Pt,H}$ = 20.8 Hz, 3H, $COCH_3$), 2.62 (s + d, $^3J_{Pt,H}$ = 20.6 Hz, 8H, $CH_2N(CH_3)_2$), 2.94 (m, 2H, CH_2NH_2), 3.57 (m, 2H, NH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.3 (s, CH_2NH_2), 43.8 (s + d, $^2J_{Pt,C}$ = 397 Hz, $COCH_3$), 44.1 (s + d, $^2J_{Pt,C}$ = 363 Hz, $COCH_3$), 49.4 (s, NCH_3), 64.7 (s, CH_2NCH_3), 224.3 (s, *C*O), 234.3 (s, *C*O). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3347 (s). IR: ν 3186 (w), 3147 (m), 2934 (m), 1603 (m), 1566 (s), 1448 (m), 1412 (m), 1325 (m), 1286 (w), 1059 (m), 983 (m), 912 (m), 860 (m), 839 (m), 592 (m), 420 (m), 341 (s) cm^{-1}.

8d (N^N = $Me_2NCH_2CH_2NMe_2$). Yield: 85 mg (60%). Found (Calc): $C_{10}H_{22}N_2O_2Pt$ (397.37); C 30.99 (30.23), H 5.27 (5.58). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.10 (s + d, $^3J_{Pt,H}$ = 26.8 Hz, 6H, $COCH_3$), 2.52 (s + d, $^3J_{Pt,H}$ = 12.1 Hz, 4H, CH_2), 2.61 (s + d, $^3J_{Pt,H}$ = 22.2 Hz, 12H, NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.6 (s + d, $^2J_{Pt,C}$ = 393 Hz, $COCH_3$), 49.2 (s + d, $^2J_{Pt,C}$ = 10 Hz, CH_3), 61.1 (s, CH_2), 228.5 (s + d, $^1J_{Pt,C}$ = 1283 Hz, *C*O). ^{195}Pt NMR (86 MHz, CD_2Cl_2, −40 °C): δ −3430 (s). IR: ν 3493 (w), 2996 (w), 2972 (w), 2896 (w), 1612 (m), 1585 (s), 1456 (m), 1323 (m), 1103 (m), 1082 (s), 1024 (m), 954 (m), 904 (w), 802 (s), 771 (m), 590 (m), 484 (w), 347 (s) cm^{-1}.

3.6. X-ray crystallography

Crystals of [Pt(COMe)$_2$(NH_2i-Pr)$_2$] (**3d**) suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3d** which contained a few drops of isopropyl amine to reduce the decomposition of the complex. Crystals of [Pt(COMe)$_2$(NH_2Bn)$_2$] (**3a**) were obtained from a methylene chloride/diethyl ether (1:2) solution containing a thioglycoside (per-benzylated 4-(pyridin-2-yl)thiazol-2-yl thioglucopyranoside) for stabilization [17]. Data for X-ray diffraction analyses of **3a** were collected on a CCD Oxford Xcalibur S diffractometer at 130 K and of **3d** on a Stoe-IPDS 2T diffractometer at 200 K using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 4. Absorption corrections were applied empirically using the PLATON program package [18] (**3a**, T_{min}/T_{max} 0.49/1.00) or numerically (**3d**, T_{min}/T_{max} 0.19/0.50). The structures were solved by direct methods using SHELXS-97 [19] and refined using full-matrix least-square routines against F^2 with SHELXL-97 [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic ones. H atoms were placed in calculated positions according to the riding model.

Table 4
Crystal data, data collection, and refinement parameters of [Pt(COMe)$_2$(NH_2Bn)$_2$] (**3a**) and [Pt(COMe)$_2$(NH_2i-Pr)$_2$] (**3d**).

	3a	**3d**
Empirical formula	$C_{18}H_{24}N_2O_2Pt$	$C_{10}H_{24}N_2O_2Pt$
Formula weight	495.48	399.40
Crystal system/space group	Monoclinic/*I*2/*a*	Monoclinic/$P2_1/c$
Z	4	8
a/Å	9.3628(2)	11.6904(5)
b/Å	20.0751(2)	13.7554(6)
c/Å	9.6263(1)	19.7478(8)
β/°	96.049(1)	116.154(3)
V/Å^3	1799.28(5)	2850.4(2)
D_{calc}/g cm^{-3}	1.829	1.861
μ(Mo *K*α)/mm^{-1}	7.809	9.833
F(000)	960	1536
Scan range θ/°	3.53–28.28	2.70–26.00
Reciprocal lattice segments *h*, *k*, *l*	−11 → 12, −26 → 26, −12 → 12	−14 → 14, −16 → 16, −22 → 24
Reflections collected	22,854	18,342
Reflections independent	2236 (R_{int} = 0.0277)	5589 (R_{int} = 0.0399)
Data/restrains/parameters	2236/0/106	5589/1/283
Goodness-of-fit on *F* [2]	1.065	0.968
R_1, wR_2 [$I > 2\sigma(I)$]	0.0153, 0.0380	0.0215, 0.0496
R_1, wR_2 [all data]	0.0174, 0.0383	0.0289, 0.0524
Largest diff. peak and hole/e Å^{-3}	1.213 and −0.679	1.268 and −1.193

3.7. Computational details

DFT calculations were performed by the Gaussian09 program package [21] using the functional mPW1PW91 [10]. The 6-311++G** basis sets as implemented in Gaussian09 were employed for main group elements. For platinum, the ECP by Hay and Wadt [22] and concomitant basis set (LanL2DZ) were used. All systems were fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. Solvent effects were considered according to Tomasi's polarized continuum model [23] as implemented in Gaussian 09.

Appendix A. Supplementary material

CCDC 875056 (**3a**) and CCDC 875057 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.05.043.

References

[1] D. Steinborn, Dalton Trans. (2005) 2664.
[2] M. Gerisch, C. Bruhn, A. Vyater, J.A. Davies, D. Steinborn, Organometallics 17 (1998) 3101.

[3] M. Werner, C. Bruhn, D. Steinborn, J. Organomet. Chem. 693 (2008) 2369.
[4] (a) M. Gerisch, C. Bruhn, A. Porzel, D. Steinborn, Eur. J. Inorg. Chem. (1998) 1655;
(b) D. Steinborn, M. Gerisch, F.W. Heinemann, C. Bruhn, Chem. Commun. (1997) 843.
[5] (a) K. Matsumoto, M. Ochiai, Coord. Chem. Rev. 231 (2002) 229;
(b) P. Pyykkö, Chem. Rev. 97 (1997) 597.
[6] S. Schwieger, F.W. Heinemann, C. Wagner, R. Kluge, C. Damm, G. Israel, D. Steinborn, Organometallics 28 (2009) 2485.
[7] (a) G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J.M. Marti, J.A. Hermoso, A. Vegas, M. Martinez-Ripoll, J. Chem. Soc. Dalton Trans. (1992) 53;
(b) J.M. Casas, J. Fornies, A. Martin, B. Menjon, M. Tomas, J. Chem. Soc. Dalton Trans. (1995) 2949.
[8] M. Höpp, A. Erxleben, I. Rombeck, B. Lippert, Inorg. Chem. 35 (1996) 397.
[9] F. Acha, R. Ciganda, M.A. Garralda, R. Hernandez, L. Ibarlucea, E. Pinilla, M.R. Torres, Dalton Trans. (2008) 4602.
[10] (a) C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664;
(b) J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533.
[11] Cambridge Structural Database (CSD), Cambridge University Chemical Laboratory, Cambridge, 2011.
[12] C. Janiak, J. Chem. Soc. Dalton Trans. (2000) 3885.
[13] T. Steiner, Angew. Chem. Int. Ed. 41 (2002) 48.
[14] (a) S.P. Dent, C. Eaborn, A. Pidcock, B. Ratcliff, J. Organomet. Chem. 46 (1972) C68;
(b) A. Albinati, U. von Gunten, P.S. Pregosin, H.J. Ruegg, J. Organomet. Chem. 295 (1985) 239.
[15] M. Bette, T. Rüffer, C. Bruhn, J. Schmidt, D. Steinborn, Organometallics 31 (2012) 3700.
[16] T. Kluge, unpublished.
[17] C. Vetter, PhD thesis, Martin-Luther-Universität Halle-Wittenberg, Halle 2010.
[18] (a) MULscanABS, PLATON for Windows Taskbar v1.15, University of Glasgow, Glasgow, 2008;
(b) A.L. Spek, J. Appl. Cryst. 36 (2003) 7.
[19] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1998.
[20] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc, Wallingford CT, 2009.
[22] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[23] (a) E. Cances, B. Mennucci, J. Tomasi, J. Chem. Phys. 107 (1997) 3032;
(b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, Chem. Phys. Lett. 286 (1998) 253;
(c) B. Mennucci, J. Tomasi, J. Chem. Phys. 106 (1997) 5151.