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Reactivity of platina-β-diketones towards chelating nitrogen and sulfur donors: formation of acyl(hydrido)platinum(IV) and acyl(chloro)platinum(II) complexes

Tushar Gosavi, Eduard Rusanov, Harry Schmidt, Dirk Steinborn *

Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, Halle D-06120, Germany

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday

Abstract

The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) was found to react with chelating *N*,*N*-ligands $2(R'N{=}CR)C_5H_4N$ (R/R′ = Ph/OH, H/Ph, Me/Ph) to form acyl(hydrido)platinum(IV) complexes $[Pt(COMe)_2Cl(H)\{2\text{-}(R'N{=}CR)C_5H_4N\}]$ (R/R′ = Ph/OH **2a**; H/Ph **2b**; Me/Ph (**2c**)). Reactions of complex **1** with chelating *S*,*S*- and *N*,*S*-donors ($RS{-}CH_2{-}CH_2{-}SR$, $2\text{-}(RSCH_2)C_5H_4N$, R = Et, Ph, *t*-Bu) afforded acyl(chloro)platinum(II) complexes $[Pt(COMe)Cl(RSCH_2CH_2SR)]$ (R = Et, **3a**; Ph, **3b**; *t*-Bu, **3c**) and $[Pt(COMe)Cl\{2\text{-}(RSCH_2)C_5H_4N\}]$ (R = Et, **4a**; Ph, **4b**; *t*-Bu, **4c**), respectively. All complexes were fully characterized by microanalysis, IR and NMR (^1H, ^{13}C) spectroscopy. Furthermore, molecular structures of complexes **3b** and **4b** were determined by single-crystal X-ray diffraction analyses revealing close to square-planar configuration. In complex **4b** the acetyl ligand is *trans* to pyridine N atom (configuration index *SP*-4-2). The reactions are discussed in terms of consecutive oxidative addition and reductive elimination reactions.

Keywords: Platina-β-diketones; Platinum complexes; Acyl complexes; Hydroxycarbene complexes; Hydrido complexes

1. Introduction

Metalla-β-diketones are (formally) derived from enolic forms of 1,3-diketones by replacing the central methine group by a transition metal fragment L_xM (Scheme 1). Just as 1,3-diketones are hydrogen-bridged vinyl alcohol/ketone species, so metalla-β-diketones may be regarded as hydroxycarbene complexes intramolecularly stabilized by hydrogen bridges to acyl ligands. Stability and reactivity of metalla-β-diketones cover a wide range: Lukehart' s metalla-β-diketones [1,2] (**A**, Scheme 1) having carbonyl and cyclopentadienyl co-ligands are electronically saturated and kinetically inert complexes. They can be easily deprotonated and nucleophiles attack typically the carbene carbon atoms as in the case of Fischer' s carbene complexes. On the other hand, dimeric platina-β-diketones (**B**, Scheme 1) being electronically unsaturated (16 ve), kinetically labile complexes exhibit completely different reactivity than Lukehart' s complexes **A** [3,4].

Typically, the platina-β-diketone **1** (**B**, R = Me) reacts with chelating N and P nucleophiles in an oxidative addition forming acetyl(hydrido)platinum(IV) complexes followed by reductive elimination of acetaldehyde yielding acetyl(chloro)platinum(II) complexes (**1** → **C** → **D**, Scheme 2). In the case of N⌒N donors of the bipyridine and phenanthroline type the platinum(IV) complexes **C** are thermally extraordinarily stable and undergo reductive eliminations (**C** → **D**) only at temperatures above 140 °C in the solid state [5]. On the other hand, with diphosphines P⌒P the intermediate complexes **C** could not be observed, not even at −30 °C [6]. With bipyridine in the presence of $TlPF_6$, new types of hydroxycarbene complexes *inter*molecularly stabilized by hydrogen bridges to

* Corresponding author. Tel.: +49-345-55-25620; fax: +49-345-55-27028.
E-mail address: steinborn@chemie.uni-halle.de (D. Steinborn).

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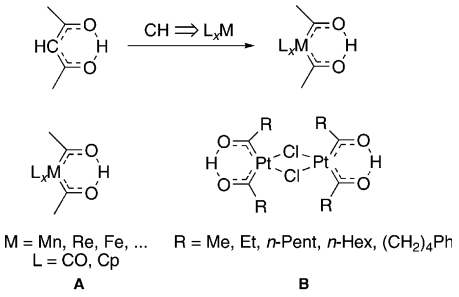
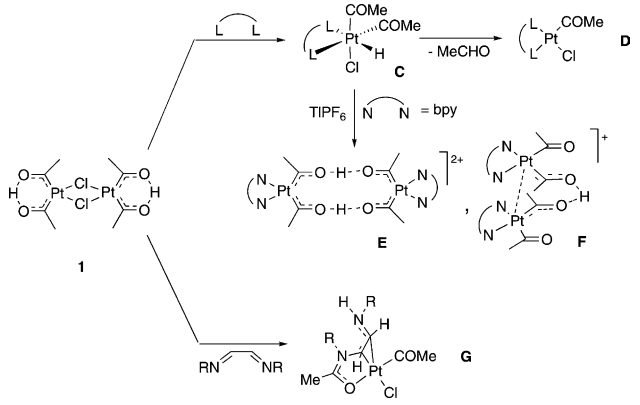


Scheme 1.



Scheme 2.

acetyl ligands were obtained (**E**, **F**; Scheme 2) [7]. Reactions with diazadiene type ligands RN=CR′–CR′=NR afforded in dependence on substituents R and R′ either type **D** complexes (via intermediates of type **C**) or complexes **G**. These complexes contain en-amine-amide type ligands that are formally obtained by 1,4-addition of MeC(O)–H (a tautomer of hydroxycarbene Me–C–OH that is a building block of platina-β-diketone **1**) to diazadienes [8].

To get further insight into the reactivity, we investigated reactions of the platina-β-diketone **1** with bidentate donors having hard/hard, soft/soft and hard/soft donor centers. We used here chelating *N*,*N*-donors 2-($R'N{=}CR)C_5H_4N$ (R/R′ = Ph/OH, H/Ph, Me/Ph) having a pyridine type and a Schiff base/oxime donor site, chelating *S*,*S*-donors $RS–CH_2–CH_2–SR$ (R = Et, Ph, *t*-Bu) being bis(thioethers) and chelating *N*,*S*-ligands 2-($RSCH_2)C_5H_4N$ (R = Et, Ph, *t*-Bu). These are "mixed" ligands of the former two types having a pyridine N atom and a thioether S atom as donor sites. The results gave evidence that hard donors like N tend to react yielding stable platinum(IV) type **C** complexes whereas soft donors like S tend to react yielding platinum(II) type **D** complexes. Part of this work has been prepublished in a Conference Issue [9].

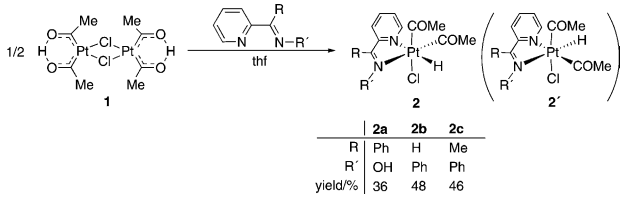
2. Results and discussion

2.1. Reactions of platina-β-diketone with chelating N,N-ligands

The platina-β-diketone **1** was found to react with chelating *N*,*N*-ligands (*E*)-2-($R'N{=}CR)C_5H_4N$ (R/R′ = Ph/OH, H/Ph, Me/Ph) having pyridine type and Schiff base/oxime donor centers in a molar ratio 1:2 in tetrahydrofuran as solvent to give acyl(hydrido)platinum(IV) complexes [$Pt(COMe)_2Cl(H)${2-($R'N{=}CR)$ C_5H_4N}](**2a–c**) in yields between 36% and 48% (Scheme 3). Under the same reaction conditions, the analogous reaction with an aldoxime, (*E*)-2-($HO–N{=}CH)C_5H_4N$, did not proceed so selective: The acyl(hydrido)platinum(IV) complex [$Pt(COMe)_2Cl(H)${2-($HO–N{=}CH)$ C_5H_4N}] and platinum(II) complexes (most likely [$Pt(COMe)Cl${2-($HO–N{=}CH)$C_5H_4N$}] and [$Pt(COMe)_2${2-($HO–N{=}CH)C_5H_4N}]) were obtained in various amounts in an erratic manner.

The platinum(IV) complexes **2a–c** were isolated as slightly air-sensitive off-white (**2a**) or pale yellow (**2b/c**) microcrystalline substances. In the solid state they decompose with melting between 104 and 168 °C while in chloroform solution they undergo decomposition within several hours at room temperature. Identities of complexes **2a–c** were confirmed by microanalysis as well as by IR and NMR (^1H, ^{13}C) spectroscopy.

The presence of hydrido ligand in **2a–c** is clearly confirmed by their ^1H NMR and IR spectra, showing highfield Pt–H resonances from −17.50 to −18.67 ppm and sharp IR absorption bands between 2225 and 2264 cm^{-1}, being consistent with data in analogous complexes [$Pt(COMe)_2Cl(H)(N^{\frown}N)$] (**5**, $N^{\frown}N$ = bipyridine/phenanthroline type ligand) [5] and with data of other complexes with terminal hydrido ligands [10]. The large values of the $^1J(Pt,H)$ coupling constant (1563–1585 Hz) are characteristic for hydrido ligands *trans* to nitrogen ligands in platinum(IV) complexes [5,11–13]. The two acetyl groups are NMR spectroscopically non-equivalent, ^1H and ^{13}C chemical shifts of acetyl ligands in complexes **2** ($\delta(^1H_{Me})$ 2.22–2.96 ppm; $\delta(^{13}C_{Me})$ 43.8–46.5 ppm; $\delta(^{13}C_{CO})$ 190.3–206.6 ppm) are in the expected range as compared with other Pt(IV) complexes of this type [5]. By means of HMBC experiments it was shown for complexes **2b** and **2c** that acetyl group pro-



Scheme 3.

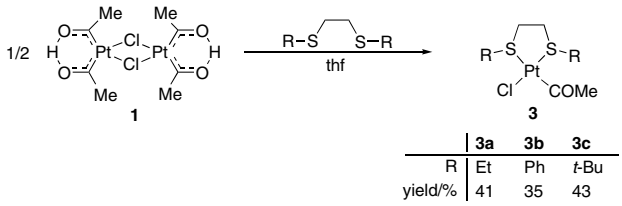
tons which are higher shifted in ^{1}H NMR spectra correspond to higher-field shifted methyl and acyl carbon atoms in ^{13}C NMR spectra as it is also the case in analogous complexes [Pt(COMe)$_2$Cl(H)(N⌒N)] (**5**, N⌒N = bipyridine/phenanthroline type ligand) [5]. ^3J(Pt,H) coupling constants of acetyl hydrogens are in the range of 26–34 Hz. ^1J(Pt,C) and ^2J(Pt,C) coupling constants are in the range of 836–895 and 209–305 Hz, respectively. Differences in coupling constants between the two acetyl groups (*trans* to N versus *trans* to Cl) amount to Δ^1J(Pt,C) 17–43 Hz and Δ^2J(Pt,C) 55–77 Hz. On the basis of the well-known dependence of the magnitudes of ^1J(Pt,C) and ^2J(Pt,C) coupling constants on *trans* influence of ligands [14] the acetyl groups with lower carbon–platinum coupling constants are *trans* to N atom and those with higher carbon–platinum coupling constants *trans* to chloro ligand. The Pt–Cl and C=O stretching vibrations were found in the range of 252–264 and 1592–1702 cm^{-1}, respectively.

Thus, from NMR investigations it follows undoubtless that the hydrido ligand is *trans* to N and the chloro ligand *trans* to an acetyl ligand. The narrow range of hydride chemical shifts (−17.50 to −18.67 ppm) and ^1J(Pt,H) coupling constants (1563–1585 Hz) and the close correspondence of these values to those in complexes **5** (δ(Pt*H*) −17.50 to −18.77 ppm; ^1J(Pt,H) 1474–1582 Hz [5]) indicates that the hydrido ligand is *trans* to the pyridine N atom (**2** in Scheme 1) but the diastereomer **2′** in Scheme 3 (H ligand *trans* to Schiff base/oxime N atom) cannot strictly be ruled out. Reactions according to Scheme 3 proved to be strongly regioselective as in all cases only one diastereomer (probably **2**, Scheme 3) was obtained. In contrast, analogous reactions with non-symmetrically substituted bipyridine/phenanthroline ligands yielding complexes [Pt(COMe)$_2$Cl(H)(N⌒N)] (**5**) proved to be regioselective only with *ortho*-substituted bipyridine/phenanthroline ligands [5].

2.2. Reactions of platina-β-diketone with chelating S,S-ligands

Reactions of the platina-β-diketone **1** with chelating *S*,*S*-ligands RS–CH$_2$–CH$_2$–SR (R = Et, Ph, *t*-Bu) in a molar ratio 1:2 in tetrahydrofuran as solvent afforded acyl(chloro)platinum(II) complexes [Pt(COMe)Cl(RS-CH$_2$CH$_2$SR)] (**3**) in yields of 35–43% (Scheme 4). The platinum(II) complexes **3a**–**c** were isolated as slightly air-sensitive off-white microcrystalline substances. They melt with decomposition between 110 and 133 °C. Their identities were confirmed by microanalysis, IR (ν(Pt–Cl) 316–325 cm^{-1}, ν(C=O) 1633–1657 cm^{-1}), and NMR (^{1}H, ^{13}C) spectroscopic measurements and for **3b** by X-ray structure analysis, too.

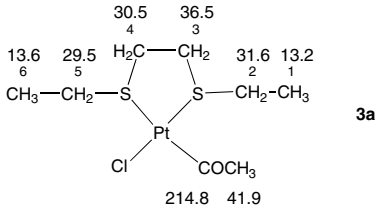
^{1}H and ^{13}C chemical shifts of the acetyl ligands in complexes **3** (δ(^{1}H$_{Me}$) 2.36–2.47 ppm; δ(^{13}C$_{Me}$) 41.4–42.1 ppm; δ(^{13}C$_{CO}$) 209.1–214.8 ppm) are in the expected range as compared with other Pt(II) complexes of the type [Pt(COMe)(Cl)L$_2$] (L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 2, 3 (**6**) [6]; L$_2$ = 4,4′-R$_2$bpy, R = H, Me, *t*-Bu (**7**)) [5,15]. The donor capability of sulfur atoms in ligands RS–CH$_2$–CH$_2$–SR is expected to be R = *t*-Bu > Et > Ph but the magnitudes of ^1J(Pt,C) and ^2J(Pt,C) coupling constants (844–869 and 114–122 Hz, respectively) in complexes **3a**–**c** are not clearly dependent on that.



	3a	3b	3c
R	Et	Ph	*t*-Bu
yield/%	41	35	43

Scheme 4.

Full assignment of all hydrogen and carbon atoms in complex **3a** (R = Et) was done by means of COSY (^{1}H,^{1}H; ^{1}H,^{13}C) and NOE experiments (see formula, chemical shifts δ_C are given, δ_H, see Section 3).



Formula 3a

Irradiation in the resonance frequency of acetyl protons led to distinguish between the two methyl groups (nos. 1 and 6, see formula; positive NOE for C$^1H_3$) of the ethyl substituents which was confirmed by irradiation in the resonances of these protons. Irradiation in the resonances of methyl protons of ethyl groups led to distinguish between the methylene protons 2/3 and 4/5. ^{1}H,^{1}H COSY experiments made clear which methylene protons belong to the ethyl substituents (2 and 5) and which ones to the ethylene bridge CH$_2$–CH$_2$ (3 and 4). Finally, ^{1}H,^{13}C COSY experiments gave the assignments of the carbon atoms. The highly electronegative chloro ligand gives rise to lowfield shift of carbon atoms attached to S *trans* to Cl by 2.1 ppm (2 versus 5) and 6.0 ppm (3 versus 4).

Molecular structure of complex **3b** was determined by single-crystal X-ray diffraction analysis, see Fig. 1. Selected bond lengths and angles are listed in Table 1. The complex crystallizes as discrete molecules without unusual intermolecular contacts (shortest intermolecular contact between non-hydrogen atoms: O···C7′ 3.327(6) Å).

The geometry at platinum center is close to square planar (angles at Pt: 87.3(1)–93.09(3) °; sum of angles 360.0 °; greatest deviation of the mean square plane Pt,S1,S2,Cl,C1 for the Pt atom by 0.0195(2) Å). The Pt–C1 bond length (2.012(4) Å) as well as the C–O bond

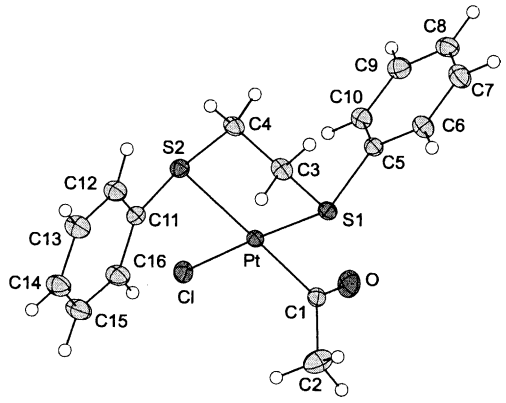


Fig. 1. Molecular structure of [Pt(COMe)Cl(PhSCH$_2$CH$_2$SPh)] (**3b**) showing the numbering scheme (displacement ellipsoids at 30% probability).

Table 1
Selected bond lengths (Å) and angles (°) for [Pt(COMe)Cl(PhSCH$_2$CH$_2$SPh)] (**3b**)

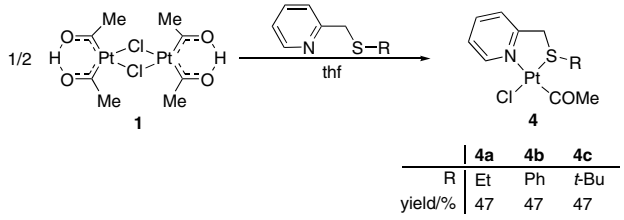
Pt–C1	2.012(4)	Pt–S1	2.2563(9)
Pt–Cl	2.3207(9)	Pt–S2	2.457(1)
C1–O	1.188(5)		
C1–Pt–S1	90.1(1)	C1–Pt–Cl	87.3(1)
S1–Pt–S2	89.50(3)	S2–Pt–Cl	93.09(3)
S1–Pt–Cl	177.08(3)	S2–Pt–C1	178.8(1)

length (1.188(5) Å) are in the range of those found in other acylplatinum(II) complexes (Pt–C: median 2.029 Å, lower/higher quartile 1.988/2.056 Å; C–O 1.221 Å, lower/higher quartile 1.193/1.242 Å; 37 observations) [16]. The five-membered PtS_2C_2-ring has a half-chair conformation twisted on C3–C4; the phenyl substituents occupy axial positions. The plane of the acetyl ligand is nearly perpendicular to the complex plane (interplanar angle: 86.9(5)°). In accord with the *trans* influence Cl ≪ COMe, the Pt–S bond *trans* to chloro ligand is distinctly shorter than that *trans* to the acetyl ligand (2.2563(9) versus 2.457(1) Å).

2.3. Reactions of platina-β-diketone with chelating N,S-ligands

Finally, we investigated the reactivity of the platina-β-diketone **1** with chelating *N*,*S*-ligands 2-(RSCH$_2$)-C$_5$H$_4$N (R = Et, Ph, *t*-Bu) built up of a pyridine type and a thioether donor center, thus being the "mixed" ligands between the former two chelate ligands. The reactions proceeded in a molar ratio 1:2 in tetrahydrofuran yielding acyl(chloro)platinum(II) complexes [Pt(COMe)Cl{2-(RSCH$_2$)C$_5$H$_4$N}] (**4**) in yields of 47% (Scheme 5).

The platinum(II) complexes **4a**–**c** were isolated as slightly air-sensitive off-white (**4a/c**) or pale yellow (**4b**)



	4a	4b	4c
R	Et	Ph	*t*-Bu
yield/%	47	47	47

Scheme 5.

microcrystalline substances that melt with decomposition between 110 and 144 °C. Their identities were confirmed by microanalysis, IR, and NMR (^{1}H, ^{13}C) spectroscopy and for **4b** also by X-ray structure analysis.

The Pt–Cl and C=O stretching vibrations were observed at 318–320 and 1634–1642 cm^{-1}, respectively. The methylene protons of the py–CH$_2$–S bridge are not chemical shift equivalent. They show AB spin patterns with magnitudes of $^2J(H_A,H_B)$ coupling constants between 16 and 17 Hz. The lines of the highfield shifted protons (H_A) are flanked by platinum satellites ($^{3+4}J(Pt,H_A)$ 66–71 Hz). The carbon chemical shifts $\delta(^{13}C_{CO})$ (207.3–209.7 ppm) and the couplings $^1J(Pt,C)$ (867/890 Hz) in complexes **4** with *N*,*S* co-ligands show greater differences both to the corresponding values in the analogous complexes with *S*,*S* co-ligands (**3**) and to those with the bipyridine complex [Pt(COMe)Cl(bpy)] (**8**) [15] chosen as a representative for *N*,*N* co-ligands: $\delta(^{13}C_{CO})$ N⌒S (**4**) < S⌒S (**3**) < N⌒N (**8**); $^1J(Pt,C)$ S⌒S (**3**) < N⌒S (**4**) ≪ N⌒N (**8**). Thus, from these measurements it cannot be decided unambiguously whether the acetyl ligand in complexes **4** is *trans* to N (configuration index *SP*-4-2) or to S (configuration index *SP* -4-3). For **4b** X-ray diffraction analysis revealed that the acetyl ligand is *trans* to N. Furthermore, in no experiment was found any indication of formation of isomeric mixtures.

The molecular structure of complex **4b** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The complex crystallizes as discrete molecules without unusual intermolecular contacts between them (shortest intermolecular contact between non-hydrogen atoms: O···C7′ 3.16(2) Å). The complex exhibits a square-planar geometry (angles at Pt: 83.2(1)–94.5(1)°, sum of angles 360.1°; greatest deviation of the mean square plane Pt,N,S,Cl,C1 for the S atom by 0.057(2) Å) with the acetyl ligand *trans* to the pyridine N atom. The five-membered $PtNSC_2$-ring has an envelope conformation on S; the phenyl substituent is axially oriented. The interplanar angle between the acetyl ligand and the complex plane is 65.9(8)°.

As for complex **3b**, in complex **4b** the Pt–C1 and C–O bond lengths (1.997(6) and 1.185(8) Å, respectively) are in the expected range. As expected, the Pt–S bond in complex **4b** has the same length as the Pt–S bond *trans* to Cl in complex **3b** (2.257(2) versus 2.2563(9) Å). On the other hand, the Pt–C1 bond length is not strongly

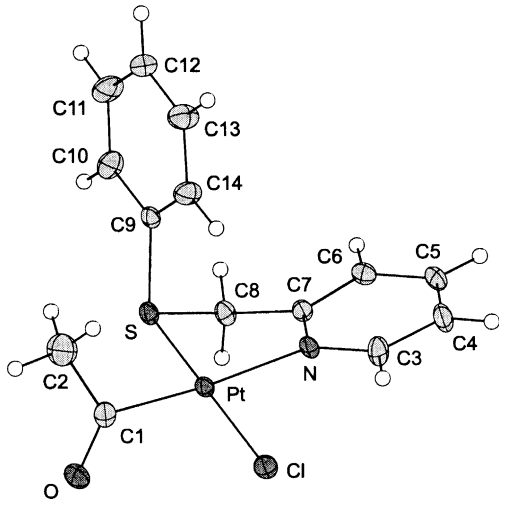


Fig. 2. Molecular structure of [Pt(COMe)Cl{2-PhSCH$_2$)C$_5$H $_4$N}](**4b**) showing the numbering scheme (displacement ellipsoids at 30% probability).

Table 2
Selected bond lengths (Å) and angles (°) for [Pt(COMe)Cl{2-PhSCH$_2$)C$_5$H$_4$N}](**4b**)

Pt–C1	1.997(6)	Pt–N	2.190(5)
Pt–Cl	2.320(2)	Pt–S	2.257(2)
C1–O	1.185(8)		
C1–Pt–S	92.8(2)	C1–Pt–Cl	89.6(2)
N–Pt–S	83.2(1)	N–Pt–Cl	94.5(1)
S–Pt–Cl	176.15(6)	N–Pt–C1	175.2(2)

dependent on the *trans* ligand: Pt–C$_{trans\ to\ py}$ 1.997(6) Å (**4b**) ≈ Pt–C$_{trans\ to\ SPh}$ 2.012(4) Å (**3b**).

In many reactions, platina-β-diketones were found to react as hydroxycarbene complexes stabilized by hydrogen bridges. Thus, formation of acyl(hydrido)platinum(IV) complexes **2** can be understood as ligand induced oxidative addition reaction of a hydroxycarbene ligand. Likely, formation of acylplatinum(II) complexes **3** and **4** using chelating S⌒S and N⌒S ligands proceeded via (unseen) platinum(IV) intermediates that underwent readily reductive elimination of acetaldehyde analogously to Scheme 2 (**1** → **C** → **D**; L⌒L = RS–CH$_2$–CH$_2$–SR, 2-(RSCH$_2$)C$_5$H$_4$N). The marked contrast of reactions using N⌒N ligands on the one side and S⌒S/N⌒S ligands on the other side gives further support for the generalization that platinum(IV) complexes are more stable with hard co-ligands than with soft ones [17].

3. Experimental

3.1. General

All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Solvents were dried (Et$_2$O and thf over Na–benzophenone) and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200 and Varian VXR 400 NMR spectrometers. Chemical shifts are relative to C*H*Cl$_3$ (δ 7.24) and *C*DCl$_3$ (δ 77.0) as internal references. Assignments of NMR signals were partly revealed by COSY experiments (^{1}H,^{1}H; ^{1}H,^{13}C) and by running spectra in APT mode. IR spectra were recorded on a Galaxy FT-IR spectrometer Mattson 5000 using CsBr pellets. Microanalysis were performed by the University of Halle microanalysis laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. The complex [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) was synthesized according to a published method [3]. Phenyl(pyridin-2-yl)ketone-(*E*)-oxime, 2-pyridine aldoxime and 1,2-bis(phenylthio)ethane were commercially available, the other N⌒N [18–20], S⌒S [21] and N⌒S ligands [22,23] were prepared according to published methods.

3.2. Syntheses

3.2.1. Preparation of complexes [Pt(COMe)$_2$Cl(H){2-(R′N=CR)C$_5$H$_4$N)}] (**2**)

To a suspension of [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) (50 mg, 0.08 mmol) in thf (4 ml) cooled down to −40 °C ligand 2-(R′N=CR)C$_5$H$_4$N (0.16 mmol) was added. The pale yellow suspension immediately changed the color to intense yellow colored solution. The reaction mixture was warmed up to room temperature. Seventy percent of total volume of thf was removed in vacuo. Then diethyl ether (10–15 ml) was added resulting in an off-white/pale yellow precipitate that was filtered off, washed with diethyl ether (5 ml) and dried briefly in vacuo.

Complex ***2a*** (R = Ph, R′ = OH). Yield: 30 mg (36%); m.p. 166–168 °C (dec.). *Anal*. Calc. for C$_{16}$H$_{17}$ClN$_2$O$_3$Pt (515.87): C, 37.25; H, 3.32; N, 5.43. Found: C, 36.08; H, 3.49; N, 5.24%. IR(CsBr): *ν*(Pt–H) 2260, *ν*(C=O) 1702, 1679, *ν*(Pt–Cl) 264 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = −17.50 (s + d, ^1J(Pt,H) = 1566.92 Hz, 1H, Pt*H*), 2.34 (s + d, ^3J(Pt,H) = 26.29 Hz, 3H, COC*H*$_3$), 2.96 (s + d, ^3J(Pt,H) = 33.84 Hz, 3H, COC*H*$_3$), 7.46–7.58 (m, 7H, *o*,*m*,*p*-*H*$_{Ph}$ + 3-C*H*$_{py}$ + 5-C*H*$_{py}$), 7.91 (ddd, ^3J(H4,H5) = ^3J(H4,H3) = 7.85 Hz, ^4J(H4,H6) = 1.54 Hz, 1H, 4-C*H*$_{py}$), 8.93 (dd, ^3J(H6,H5) = 5.36 Hz, ^4J(H6,H4) = 0.97 Hz, 1H, 6-C*H*$_{py}$), 13.28 (s + d, ^3J(Pt,H) = 20.93 Hz, 1H, N–O*H*). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 43.8 (s + d, ^2J(Pt,C) = 283.1 Hz, CO*C*H$_3$), 46.2 (s + d, ^2J(Pt,C) = 208.7 Hz, CO*C*H$_3$), 126.8/126.9 (s/s, 3/5-*C*$_{py}$), 128.9 (s, *i*-*C*$_{Ph}$), 129.0/130.8 (s/s, *o*,*m*,*p*-*C*$_{Ph}$), 139.6 (s, 4-*C*$_{py}$), 152.6 (s, 2-*C*$_{py}$), 152.7 (s, 6-*C*$_{py}$), 157.4 (s, *C*=NOH), 190.3 (s + d, ^1J(Pt,C) = 835.9 Hz, *C*OCH$_3$), 206.6 (s + d, ^1J(Pt,C) = 872.8 Hz, *C*OCH$_3$).

Complex ***2b*** (R = H, R′ = Ph). Yield: 38 mg (48%); m.p. 104–106 °C (dec.). *Anal*. Calc. for C$_{16}$H$_{17}$ClN$_2$O$_2$Pt

(499.87): C, 38.45; H, 3.43; N, 5.60. Found: C, 38.55; H, 3.44; N, 5.23%. IR(CsBr): ν(Pt–H) 2264, ν(C=O) 1663, 1592, ν(Pt–Cl) 257 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = -18.54$ (s + d, $^1J(Pt,H) = 1584.59$ Hz, 1H, Pt*H*), 2.22 (s + d, $^3J(Pt,H) = 30.36$ Hz, 3H, COCH_3), 2.95 (s + d, $^3J(Pt,H) = 30.69$ Hz, 3H, COCH_3), 7.37–7.44 (m, 3H, *o,p*-H_{Ph}), 7.64–7.67 (m, 3H, *m*-H_{Ph} + 5-CH_{py}), 7.96–8.02 (m, 2H, 3-CH_{py} + 4-CH_{py}), 8.80 (s + d, $^{3+4}J(Pt,H) = 24.05$ Hz, 1H, C*H*=N), 9.42 (d, $^3J(H6,H5) = 5.05$ Hz, 1H, 6-CH_{py}). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 43.9$ (s + d, $^2J(Pt,C) = 294.1$ Hz, CO*C*H_3), 46.3 (s + d, $^2J(Pt,C) = 239.0$ Hz, CO*C*H_3), 122.8 (s, *m*-C_{Ph}), 128.8 (s, 5-C_{py}), 129.3/129.5 (s, *o,p*-C_{Ph} + 3-C_{py}), 139.5 (s, 4-C_{py}), 147.4 (s, *i*-C_{Ph}), 150.7 (s, 6-C_{py}), 154.1 (s, 2-C_{py}), 163.7 (s, *C*H=N), 191.2 (s + d, $^1J(Pt,C) = 885.8$ Hz, *C*OCH$_3$), 194.9 (s + d, $^1J(Pt,C) = 869.0$ Hz, *C*OCH$_3$). Overnight measurement at room temperature to identify Pt–C coupling constants resulted in partly decomposition due to restricted stability of complex.

Complex ***2c*** (R = Me, R′ = Ph). Yield: 38 mg (46%); m.p. 128–130 °C (dec.). *Anal.* Calc. for $C_{17}H_{19}ClN_2O_2Pt$ (513.90): C, 39.73; H, 3.73; N, 5.45. Found: C, 39.87; H, 3.72; N, 5.48%. IR(CsBr): ν(Pt–H) 2225, ν(C=O) 1663, 1594, ν(Pt–Cl) 252 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = -18.67$ (s + d, $^1J(Pt,H) = 1562.67$ Hz, 1H, Pt*H*), 2.24 (s + d, $^3J(Pt,H) = 32.21$ Hz, 3H, COCH_3), 2.42 (s, 3H, C(CH_3)=N), 2.88 (s + d, $^3J(Pt,H) = 28.63$ Hz, 3H, COCH_3), 7.22 (broad, 2H, *o*-H_{Ph}), 7.28–7.32 (m, 1H, *p*-H_{Ph}), 7.41–7.45 (m, 2H, *m*-H_{Ph}), 7.76 (ddd, ^3J(H5, H4) = 7.58 Hz, $^3J(H5,H6) = 5.37$ Hz, $^4J(H5,H3) = 1.37$ Hz, 1H, 5-CH_{py}), 8.01 (d, $^3J(H3,H4) = 7.37$ Hz, 1H, 3-CH_{py}), 8.13 (ddd, $^3J(H4,H5) = {}^3J(H4,H3) = 7.79$ Hz, $^4J(H4,H6) = 1.54$ Hz, 1H, 4-CH_{py}), 9.50 (ddd, ^3J(H6, H5) = 4.21 Hz, $^4J(H6,H4) = 2.64$ Hz, $^5J(H6,H3) = 1.16$ Hz, 1H, 6-CH_{py}). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.5 (s, C(*C*H_3)=N), 44.2 (s + d, $^2J(Pt,C) = 304.7$ Hz, CO*C*H_3), 46.5 (s + d, $^2J(Pt,C) = 227.4$ Hz, CO*C*H_3), 121.3 (s, *o*-C_{Ph}), 127.2 (s, *p*-C_{Ph}), 127.6 (s, 3-C_{py}), 128.1 (s, 5-C_{py}), 129.4 (s, *m*-C_{Ph}), 139.5 (s, 4-C_{py}), 148.1 (s, *i*-C_{Ph}), 150.6 (s, 6-C_{py}), 154.7 (s, 2-C_{py}), 172.3 (s, *C*(CH$_3$)=N), 191.9 (s + d, $^1J(Pt,C) = 894.9$ Hz, *C*O-CH$_3$), 197.5 (s + d, $^1J(Pt,C) = 852.2$ Hz, *C*OCH$_3$). Overnight measurement resulted in partly decomposition, see **2b**.

3.2.2. Preparation of complexes [Pt(COMe)Cl(RS-CH$_2$CH$_2$SR)] (*3*)

To a suspension of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) (50 mg, 0.08 mmol) in thf (4 ml) cooled down to −40 °C ligand RS–CH$_2$–CH$_2$–SR (0.16 mmol) was added. The pale yellow suspension immediately changed the color to colorless. The reaction mixture was warmed up to room temperature. Seventy percent of total volume of thf was removed in vacuo. Then diethyl ether (10–15 ml) was added. Stirring the reaction mixture for two days (**3b**, R = Ph) and one day (**3c**, R = *t*-Bu), respectively, resulted in formation of a white powdery precipitate (**3b/c**) that was filtered off, washed with diethyl ether (5 ml) and dried briefly in vacuo. In the case of **3a** (R = Et) an oily mass sticked on the walls of the Schlenk tube was obtained. The mixture was kept at −40 °C for 3 days yielding a white powdery precipitate that was isolated as described above.

Complex ***3a*** (R = Et). Yield: 28 mg (41%); m.p. 110–112 °C (dec.). *Anal.* Calc. for $C_8H_{17}ClOPtS_2$ (423.90): C, 22.67; H, 4.04. Found: C, 22.55; H, 3.87%. IR(CsBr): ν(C=O) 1633, ν(Pt–Cl) 320 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (t, 3H, H1), 1.40 (t, 3H, H6), 2.40 (s, 3H, COCH_3), 2.60–2.68 (m, 1H, H4a), 2.71–2.79 (m, 1H, H4b), 2.82–2.91 (m, 3H, H5a/5b, H2a), 2.93–2.99 (m, 1H, H3a), 3.00–3.05 (m, 1H, H3b), 3.07–3.13 (m, 1H, H2b). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.2 (s + d, $^3J(Pt,C) = 69.9$ Hz, C1, one of the two platinum satellites is partially overlapped with neighboring signal at δ 13.6), 13.6 (s, C6), 29.5 (s, C5), 30.5 (s, C4), 31.6 (s, C2), 36.5 (s, C3), 41.9 (s + d, $^2J(Pt,C) = 121.7$ Hz, CO*C*H_3), 214.8 (s + d, $^1J(Pt,C) = 869.2$ Hz, *C*OCH$_3$). Assignments were additionally verified by NOE experiments. Numbering scheme see formula on p. xx.

Complex ***3b*** (R = Ph). Yield: 29 mg (35%); m.p. 131–133 °C (dec.). *Anal.* Calc. for $C_{16}H_{17}ClOPtS_2$ (519.99): C, 36.96; H, 3.30. Found: C, 35.90; H, 3.48%. IR(CsBr): ν(C=O) 1657, ν(Pt–Cl) 325 cm^{-1}. ^1H NMR (400 Hz, $CDCl_3$): $\delta = 2.36$ (s, 3H, COCH_3), ca. 2.6/3.0/3.2 (m/m/m, 1H/2H/1H, CH_2CH_2), 7.40–7.49 (m, 6H, H_{Ph}), 7.93–7.99 (m, 4H, H_{Ph}). ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 36.4$ (s, *C*H$_2$), 41.4 (s + d, $^2J(Pt,C) = 114.1$ Hz, CO*C*H$_3$), 44.8 (s, *C*H$_2$), 128.9 (s, *i*-C_{Ph}), 129.0 (s, *i*-C_{Ph}), 129.7/132.7/133.1 (s/s/s, 2 × *o,m-C*), 130.0/131.3 (s/s, 2 × *p-C*), 209.1 (s + d, $^1J(Pt,C) = 851.1$ Hz, *C*OCH$_3$).

Complex ***3c*** (R = *t*-Bu). Yield: 33 mg (43%); m.p. 120–122 °C (dec.). *Anal.* Calc. for $C_{12}H_{25}ClOPtS_2$ (480.00): C, 30.03; H, 5.25. Found: C, 29.86; H, 5.27%. IR(CsBr): ν(C=O) 1638, ν(Pt–Cl) 316 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (s, 9H, C(CH_3)$_3$), 1.55 (s, 9H, C(CH_3)$_3$), 2.47 (s, 3H, COCH_3), 2.58–2.70 (broad, 2H, CH_2), 2.83–2.97 (broad, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 28.9$ (s, *C*Me$_3$), 30.0 (s, C(*C*H$_3$)$_3$), 30.6 (s, C(*C*H$_3$)$_3$), 35.6 (s + d, $^2J(Pt,C) = 28.6$ Hz, *C*Me$_3$), 42.1 (s + d, $^2J(Pt,C) = 120.2$ Hz, CO*C*H$_3$), 50.8 (s, *C*H$_2$), 52.8 (s, *C*H$_2$), 212.7 (s + d, $^1J(Pt,C) = 843.7$ Hz, *C*OCH$_3$).

3.2.3. Preparation of complexes [Pt(COMe)Cl{2-(RSCH$_2$)C$_5$H$_4$N}] (*4*)

To a suspension of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) (50 mg, 0.08 mmol) in thf (4 ml) cooled down to −40 °C ligand 2-(RSCH$_2$)C$_6$H$_4$N (0.16 mmol) was added. The

pale yellow suspension immediately changed the color to colorless. The reaction mixture was warmed up to room temperature. Seventy percent of total volume of thf was removed in vacuo. Then diethyl ether (10–15 ml) was added resulting in formation of an oily mass. The mixture was kept at −40 °C for 3 days yielding an off-white/pale yellow powdery precipitate that was filtered off, washed with diethyl ether (5 ml) and dried briefly in vacuo.

Complex ***4a*** (R = Et). Yield: 32 mg (47%); m.p. 110–112 °C (dec.). *Anal.* Calc. for $C_{10}H_{14}ClNOPtS$ (426.84): C, 28.14; H, 3.31; N, 3.28. Found: C, 28.05; H, 3.34; N, 3.34%. IR(CsBr): ν(C=O) 1634, ν(Pt–Cl) 320 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (t, $^3J(H,H) = 7.42$ Hz, 3H, CH_2CH_3), 2.42 (s, 3H, $COCH_3$), 2.84 (m, 2H, S–CH_2CH_3), 4.14 (H_A)/4.43 (H_B) (AB pattern + dd for H_A,$^2J(H_A,H_B) = 16.60$ Hz, $^{3+4}J(Pt,H_A) = 68.06$ Hz, 2H, CH_AH_BSEt), 7.41 (t, $^3J(H,H) = 6.54$ Hz, 1H, 5-CH_{py}), 7.50 (d, $^3J(H,H) = 7.62$ Hz, 1H, 3-CH_{py}), 7.86 (td, $^3J(H,H) = 7.71$ Hz, $^4J(H,H) = 1.69$ Hz, 1H, 4-CH_{py}), 9.28 (dd, $^3J(H,H) = 5.47$, $^4J(H,H) = 0.98$ Hz, 1H, 6-CH_{py}). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 13.2$ (s + d, $^3J(Pt,C) = 63.2$ Hz, CH_2CH_3), 34.0 (s + d, $^2J(Pt,C) = 25.4$ Hz, CH_2CH_3), 42.7 (s, CH_2SEt), 43.2 (s + d, $^2J(Pt,C) = 109.8$ Hz, $COCH_3$), 123.1 (s, 3-C_{py}), 124.1 (s, 5-C_{py}), 138.8 (s, 4-C_{py}), 149.4 (s, 6-C_{py}), 157.1 (s + d, $^2J(Pt,C) = 64.7$ Hz, 2-C_{py}), 208.5 (s + d, $^1J(Pt,C) = 889.9$ Hz, $COCH_3$).

Complex ***4b*** (R = Ph). Yield: 36 mg (47%); m.p. 142–144 °C (dec.). *Anal.* Calc. for $C_{14}H_{14}ClNOPtS$ (474.88): C, 35.41; H, 2.97; N, 2.95. Found: C, 35.40; H, 3.15; N, 3.04%. IR(CsBr): ν(C=O) 1642, ν(Pt–Cl) 319 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.35$ (s, 3H, $COCH_3$), 4.31 (H_A)/4.74 (H_B) (AB pattern + dd for H_A, $^2J(H_A,H_B) = 16.30$ Hz, $^{3+4}J(Pt,H_A) = 66.45$ Hz, 2H, CH_AH_BSPh), 7.31–7.44 (m, 5H, *m,p*-H_{Ph} + 3-CH_{py} + 5-CH_{py}), 7.74 (d, $^3J(H,H) = 7.10$ Hz, 2H, *o*-H_{Ph}), 7.84 (td, $^3J(H,H) = 7.73$, $^4J(H,H) = 1.25$ Hz, 1H, 4-CH_{py}), 9.34 (d,$^3J(H,H) = 5.02$ Hz, 1H, 6-CH_{py}). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 43.5$ (s + d, $^2J(Pt,C) = 98.9$ Hz, CH_2S), 50.4 (s, $COCH_3$), 123.4 (s, 3-C_{py}), 124.7 (s, 5-C_{py}), 130.1 (s, *m*-C_{Ph}), 130.8 (s, *i*-C_{Ph}), 131.5 (s, *p*-C_{Ph}), 132.3 (s + d, $^3J(Pt,C) = 79.6$ Hz, *o*-C_{Ph}), 139.3 (s, 4-C_{py}), 150.0 (s, 6-C_{py}), 156.9 (s + d, $^2J(Pt,C) = 67.1$ Hz, 2-C_{py}), 207.3 (s, $COCH_3$).

Complex ***4c*** (R = *t*-Bu). Yield: 34 mg (47%); m.p. 140–142 °C (dec.). *Anal.* Calc. for $C_{12}H_{18}ClNOPtS$ (454.89): C, 31.69; H, 3.99; N, 3.08. Found: C, 31.12; H, 4.28; N, 3.03%. IR(CsBr): ν(C=O) 1637, ν(Pt–Cl) 318 cm^{-1}.^1H NMR (400 Hz, $CDCl_3$): $\delta = 1.25$ (s, 9H, $C(CH_3)_3$), 2.43 (s, 3H, $COCH_3$), 4.19 (H_A)/4.49 (H_B) (AB pattern + dd for H_A, $^2J(H_A,H_B) = 17.19$ Hz, $^{3+4}J(Pt,H_A) = 71.10$ Hz, 2H, CH_AH_BS(*t*-Bu)), 7.38 (t, $^3J(H,H) = 6.55$ Hz, 1H, 5-CH_{py}), 7.52 (d,$^3J(H,H) = 7.81$ Hz, 1H, 3-CH_{py}), 7.85 (td, $^3J(H,H) = 7.72$ Hz, $^4J(H,H) = 1.49$ Hz, 1H, 4-CH_{py}), 9.25 (d, $^3J(H,H) =$ 4.88 Hz, 1H, 6-CH_{py}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 29.9 (s + d, $^3J(Pt,C) = 32.5$ Hz, $C(CH_3)_3$), 42.0 (s + d, $^2J(Pt, C) = 23.6$ Hz, CH_2S), 43.9 (s + d, $^2J(Pt,C) = 103.8$ Hz, CMe_3), 53.6 (s, $COCH_3$), 122.7 (s, 3-C_{py}), 124.3 (s, 5-C_{py}), 139.4 (s, 4-C_{py}), 149.5 (s, 6-C_{py}), 158.4 (s + d, $^3J(Pt,C) = 72.6$ Hz, 2-C_{py}), 209.7 (s + d, $^1J(Pt,C) = 866.9$ Hz, $COCH_3$).

Table 3
Crystallographic and data collection parameters for compounds **3b** and **4b**

	3b	**4b**
Empirical formula	$C_{16}H_{17}ClOPtS_2$	$C_{14}H_{14}ClNOPtS$
M_r	519.96	474.86
Crystal size (mm)	0.18 × 0.10 × 0.04	0.20 × 0.20 × 0.10
Crystal system	monoclinic	monoclinic
Space group	$P2_1c$	$C2/c$
a (Å)	14.3497(15)	21.855(3)
b (Å)	8.8594(10)	8.670(1)
c (Å)	13.3439(14)	15.770(2)
β (°)	90.131(2)	90.42(3)
V (Å^3)	1696.1(3)	2988.1(7)
Z	4	8
D_{calc} (g cm^{-1})	2.036	2.111
μ(Mo Kα) (mm^{-1})	8.672	9.700
$F(000)$	992	1792
θ range (°)	1.42–28.01	2.84–25.94
Reflections collected	10757	8517
Reflections observed [$I > 2\sigma(I)$]	3277	2601
Reflections independent (R_{int})	3989 (0.0379)	2845 (0.0728)
Data/restraints/parameters	3850/0/190	2805/0/172
Goodness-of-fit on F^2	0.968	0.984
R_1, $wR_2[I > 2\sigma(I)]$	0.0234, 0.0484	0.0464, 0.1195
R_1, wR_2 (all data)	0.0336, 0.0515	0.0499, 0.1262
Largest difference peak and hole (e Å^{-3})	0.908 and −0.886	3.592 and −2.624 (near Pt atom)

3.3. X-ray structure determinations

Crystals suitable for X-ray diffraction analyses were grown from mother liquor at room temperature (**3b**) and by slow diffusion of diethyl ether into a solution of **4b** in chloroform, respectively. Intensity data were collected on a Siemens SMART CCD area-detector diffractometer at 218(2) K (**3b**) and on a STOE IPDS diffractometer at 203(2) K (**4b**) using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 3. The structures were solved by direct methods with SHELXS 86 [24] and refined using full-matrix least-squares routines against F^2 with SHELXL 93 [25]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were found in the difference Fourier maps and refined isotropically with fixed $U_{iso} = 0.08$ Å^2 according to the riding model.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-223982 (**3b**) and No. CCDC-223983 (**4b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax (internat.): +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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