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Reactivity of diacetylplatinum(II) complexes: Oxidative addition of halogens and hydrogen halides

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ABSTRACT

Diacetylplatinum(II) complexes [Pt(COMe)$_2$(N⌒N)] (N⌒N = bpy, **3a**; 4,4′-*t*-Bu$_2$-bpy, **3b**), obtained by the reaction of [Pt(COMe)$_2$X(H)(N⌒N)] with NaOH in CH_2Cl_2/H_2O, were found to undergo oxidative addition reactions with halogens (Br_2, I_2) yielding the platinum(IV) complexes (*trans*, *OC*-6-13)/(*cis*, *OC*-6-32) [Pt(COMe)$_2$X$_2$(N⌒N)] (N⌒N = bpy, X = Br, **4a**/**4b**; I, **4c**/**4d**; N⌒N = 4,4′-*t*-Bu$_2$-bpy, X = Br, **4e**/**4f**; I, **4g**/**4h**). The diastereoselectivity of the reactions proved to be strongly dependent on the solvent. The oxidative addition of $(SCN)_2$ resulted in the formation of (*OC*-6-13)-[Pt(COMe)$_2$(SCN)$_2$(N⌒N)] (N⌒N = bpy, **4i**; 4,4′-*t*-Bu$_2$-bpy, **4j**). In a reaction the reverse of their formation, the diacetylplatinum(II) complexes **3** underwent oxidative addition with anhydrous HX (X = Cl, Br, I), prepared *in situ* from Me_3SiX/H_2O, yielding diacetyl(hydrido)platinum(IV) complexes [Pt(COMe)$_2$X(H)(N⌒N)] (N⌒N = bpy, X = Cl, **5a**; Br, **5b**; I, **5c**; N⌒N = 4,4′-*t*-Bu$_2$-bpy, X = Cl, **5d**; Br, **5e**; I, **5f**). Furthermore, diacetyldihaloplatinum complexes **4** were found to undergo reductive elimination reactions in boiling methanol yielding acetylplatinum(II) complexes [Pt(COMe)X(N⌒N)] (N⌒N = bpy, X = Br, **6b**; I, **6c**; N⌒N = 4,4′-*t*-Bu$_2$-bpy, X = Br, **6e**; I, **6f**). All complexes were characterized by microanalysis, IR and ^{1}H and ^{13}C NMR spectroscopy. Additionally, the bis(thiocyanato) complex **4j** was characterized by single-crystal X-ray diffraction analysis.

1. Introduction

Dinuclear platina-β-diketones [Pt$_2${(COR)$_2$H}$_2$(μ-Cl)$_2$] (**1**), synthesized from hexachloroplatinic acid and trimethylsilyl substituted alkynes, exhibit a unique reactivity due to their electronic unsaturation and their kinetically labile ligand sphere [1]. They were found to react with bidentate donors L⌒L, in general, as shown for [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1a**) in Scheme 1: After the cleavage of the Pt–Cl–Pt bridges and the formation of mononuclear platina-β-diketones (i) oxidative addition reactions take place yielding acetyl(hydrido)platinum(IV) complexes (**2**) (ii). The thermal stability of these complexes has a pronounced dependence on the nature of the bidentate donor. In the case of N⌒N donors like bipyridine, complexes **2** were found to be thermally stable up to 150 °C [2], whereas P⌒P donors undergo reductive C–H elimination reactions even at room temperature yielding acetyl(chloro)platinum(II) complexes and acetaldehyde (Scheme 1, iii) [3]. The treatment of complexes **2** with a base resulted in the formation of diacetylplatinum(II) complexes **3** (Scheme 1, iv) [4].

As reported earlier [4], the resulting diacetylplatinum(II) complexes (**3**) could be synthesized in good yields as air and moisture stable substances. The analogous dialkylplatinum(II) complexes with N⌒N donor ligands were found to readily undergo oxidative addition reactions with halogens and HX yielding the corresponding platinum(IV) complexes [PtR$_2$X$_2$(N⌒N)] and [PtR$_2$(H)X(N⌒N)], respectively [5]. Since acetyl ligands are weaker σ donors than methyl ligands but have the ability to act as weak π acceptors [6], a different reactivity towards oxidation addition reactions between complexes [PtR$_2$(N⌒N)] with R = Me and R = COMe (**IV**) can be expected. Here we report such reactions starting from type **3** complexes.

2. Results and discussion

2.1. Oxidative addition of halogens and $(SCN)_2$

2.1.1. Synthesis

To investigate the reactivity of diacetylplatinum(II) complexes with N⌒N donors, a solution of the complex [Pt(COMe)$_2$(bpy)] (**3a**) in CH_2Cl_2 was treated with equimolar amounts of bromine and iodine, respectively, dissolved in the same solvent. Microanalyses and NMR (^{1}H, ^{13}C) spectroscopic investigations of the resulting products verifies the formation of a mixture of

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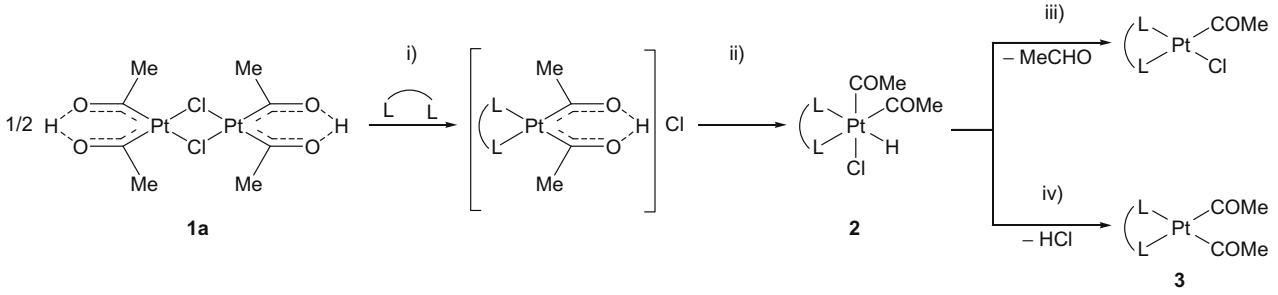


Scheme 1.

the *cis* (*OC*-6-32) and *trans* (*OC*-6-13) complexes $[Pt(COMe)_2X_2(bpy)]$ (X = Br, **4a**/**4b**; I, **4c**/**4d**) in 90% yield (Scheme 2). As revealed by ^1H NMR spectroscopy, in the case of the oxidation with iodine the two distereomers (*cis*/*trans*) were formed in a 1:1 ratio, whereas in the reaction with bromine they were formed in a 2:1 ratio. Attempts to separate the diastereomers failed by recrystallisation due to similar solubilities and by chromatography due to decomposition on Al_2O_3. Unexpectedly, the reactions proved to be strongly influenced by the solvent. In acetonitrile (instead of methylene chloride) the *trans* complexes (*OC*-6-13)–$[Pt(COMe)_2X_2(bpy)]$ (X = Br, **4b**; I, **4d**) were formed exclusively (Scheme 2). Both complexes were obtained in good yields (85%) as air and moisture stable powders. Their identities were confirmed by NMR (^1H, ^{13}C) and IR spectroscopy and by microanalysis. Furthermore, the isomerically pure *trans*-diiodoplatinum(IV) complex **4d** (obtained in acetonitrile solution) did not undergo isomerization in $CDCl_3$ solution over several days at room temperature.

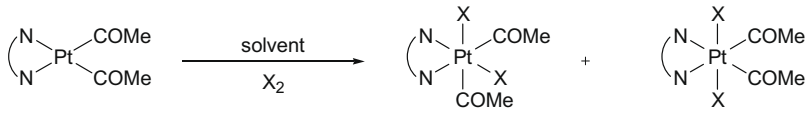
To gain further insight into the diastereoselectivity of oxidative addition reactions of this type, the analogous complex $[Pt(COMe)_2(4,4'\text{-}t\text{-}Bu_2\text{-}bpy)]$ (**3b**) was treated with bromine and iodine in CH_2Cl_2 and CH_3CN, respectively. In all cases the expected diacetyldihaloplatinum(IV) complexes were obtained (Scheme 2). The oxidative addition of bromine resulted in both solvents in the formation of (*OC*-6-32)–$[Pt(COMe)_2Br_2(t\text{-}Bu_2\text{-}bpy)]$ (**4e**), whereas in the reactions with iodine mixtures of the *cis* (*OC*-6-32) and *trans* (*OC*-6-13) complexes $[Pt(COMe)_2I_2(bpy)]$ (**4g**/**4h**) in 3:1 (CH_2Cl_2) and 1:1 ratio (CH_3CN) were formed. All complexes were isolated in good yields (90%) and characterized by NMR (^1H, ^{13}C) and IR spectroscopy and by microanalysis.

To investigate whether pseudohalogens undergo analogous oxidative addition reactions, the diacetylplatinum(II) complexes **3a**/**3b** were reacted with $(SCN)_2$. The reaction of KSCN and Br_2 in methanol at −78 °C (Scheme 3) [7] resulted in a methanolic solution of $(SCN)_2$ which was added to a solution of $[Pt(COMe)_2(N\frown N)]$ ($N\frown N$ = bpy, **3a**; 4,4′-*t*-Bu_2-bpy, **3b**) in methanol at −78 °C. Within a few seconds the color of the reaction mixtures went from red to light yellow and after conventional work-up procedures the platinum(IV) complexes (*OC*-6-13)–$[Pt(COMe)_2(SCN)_2(N\frown N)]$ ($N\frown N$ = bpy, **4i**; 4,4′-*t*-Bu_2-bpy, **4j**) were obtained as white powders in good yields (85/75%) (Scheme 3). The identities of the complexes were confirmed by microanalysis, NMR (^1H, ^{13}C) and IR spectroscopy and for **4j** also by single-crystal X-ray diffraction analysis.

2.1.2. Spectroscopic characterization

Characteristic ^1H and ^{13}C NMR spectroscopic parameters of complexes **4** are given in Table 1. All signals were found to be in the expected range. The substituents on the 4,4′ position (H, *t*-Bu) of the bipyridine ligands proved to have no significant influence on the NMR parameters. The configuration of the complexes was unambiguously determined by the chemical equivalence and non-equivalence of the two acetyl ligands in the *trans* (*OC*-6-13) and *cis* (*OC*-6-32) complexes giving rise to one and two sets of signals in ^1H and ^{13}C NMR spectra, respectively.

The hydrogen and carbon chemical shifts of the methyl groups of the acetyl ligands were found to be low-field shifted in the order SCN < Br < I for *trans* complexes **4**. Compared with the spectra of the diacetylplatinum(II) complexes **3**, in the platinum(IV) complexes **4** the chemical shifts of the directly platinum bound C atoms

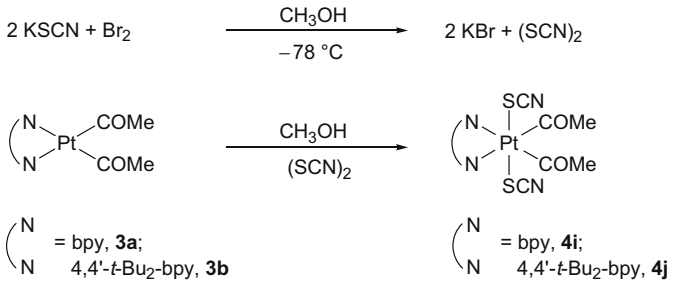


N⌒N = bpy	X = Br **4a** : **4b**	X = I **4c** : **4d**
CH_2Cl_2	2 : 1	1 : 1
CH_3CN	0 : 1	0 : 1

3b — X = Br (**4e**), X = I (**4g**) — X = Br (**4f**), X = I (**4h**)

N⌒N = 4,4'-*t*-Bu_2-bpy	X = Br **4e** : **4f**	X = I **4g** : **4h**
CH_2Cl_2	1 : 0	3 : 1
CH_3CN	1 : 0	1 : 1

Scheme 2.



Scheme 3.

Table 1
Characteristic NMR spectroscopic parameters of [Pt(COMe)$_2$X$_2$(N⌒N)] (**4**) (δ in ppm, J in Hz).

	CH_3		Pt–C
	δ_H ($^3J_{Pt,H}$)	δ_C ($^2J_{Pt,C}$)	δ_C ($^1J_{Pt,C}$)
[Pt(COMe)$_2$Br$_2$(bpy)]	2.61 (13.9)	[a]	[a]
(*OC*-6-32, **4a**)	3.44 (10.5)		
[Pt(COMe)$_2$Br$_2$(bpy)]	2.91 (12.2)	39.5 (122)	186.2
(*OC*-6-13, **4b**)			
[Pt(COMe)$_2$I$_2$(bpy)]	2.76 (15.6)	[a]	[a]
(*OC*-6-32, **4c**)	3.79 (12.0)		
[Pt(COMe)$_2$I$_2$(bpy)]	3.09 (13.7)	48.2 (119)	187.7
(*OC*-6-13,**4d**)			
[Pt(COMe)$_2$Br$_2$(4,4′-*t*-Bu$_2$-bpy)]	2.60 (15.2)	35.8 (125)	185.3 (687)
(*OC*-6-32, **4e**)	3.42 (12.5)	43.6 (71)	198.0
[Pt(COMe)$_2$I$_2$(4,4′-*t*-Bu$_2$-bpy)]	2.75 (14.8)	37.6 (139)	187.4 (668)
(*OC*-6-32, **4g**)	3.77 (11.2)	52.6 (87)	196.9 (856)
[Pt(COMe)$_2$I$_2$(4,4′-*t*-Bu$_2$-bpy)]	3.06 (14.5)	48.2 (121)	188.5
(*OC*-6-13, **4h**)			
[Pt(COMe)$_2$(SCN)$_2$(bpy)]	2.83 (13.9)	39.1 (125)	190.7 (672)
(*OC*-6-13, **4i**)			
[Pt(COMe)$_2$(SCN)$_2$(4,4′-*t*-Bu$_2$-bpy)]	2.82 (12.3)	39.2 (124)	191.5
(*OC*-6-13, **4j**)			

[a] Not measured due to low solubility.

were found to be high-field shifted by ca. 40 ppm and the $^1J_{Pt,C}$ coupling constants were lowered by ca. 500 Hz [4].

2.1.3. Structural characterization

Crystals of [Pt(COMe)$_2$(SCN)$_2$(4,4′-*t*-Bu$_2$-bpy)] (**4j**) suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a $CHCl_3$ solution of **4j**. Complex **4j** crystallized in the orthorhombic space group *Pcab* as isolated molecules. The molecular structure of **4j** is shown in Fig. 1. Selected bond lengths and angles are collected in Table 2. The methyl groups of one of the two *tert*-butyl groups were found to be disordered over two positions with an occupancy of 55/45.

Table 2
Interatomic distances (in Å) and angles (in °) of (*OC*-6-13)–[Pt(COMe)$_2$(SCN)$_2$(4,4′-*t*-Bu$_2$-bpy)] (**4j**).

Pt–C1	2.052(6)	Pt–C2	2.057(6)
Pt–S1	2.381(2)	Pt–S2	2.386(2)
C1–O1	1.211(8)	C2–O2	1.189(8)
C1–Pt–C2	90.1(2)	C2–Pt–N1	96.2(2)
N1–Pt–N2	75.7(2)	N2–Pt–C1	98.0(2)
C1–Pt–S1	87.1(2)	C1–Pt–S2	92.6(2)
$\gamma(E_{acetylC1}/E_{CP})$[a]	43.7(6)	$\gamma(E_{acetylC2}/E_{CP})$[a]	55.6(6)

[a] Interplanar angle between the mean complex plane CP (Pt, C1, C2, N1, N2) and the acetyl ligand.

The primary donor set [$C_2N_2S_2$] of the octahedrally coordinated platinum atom is made up by two acetyl ligands, the 4,4′-di-*tert*-butylbipyridine ligand and two thiocyanato-κ*S* ligands in the configuration *OC*-6-13. The bipyridine ligand shows a remarkable twist (interplanar angle between the mean planes of the two pyridine units: 17.2(3)°). The carbonyl oxygen atoms of the acetyl ligands were located on different sides of the Pt,N1,N2,C1,C2 complex plane exhibiting interplanar angles of 43.7(6)° (MeC1=O1) and 55.6(6)° (MeC2=O2), see Table 2. The Pt–C (2.052(6)/2.057(6) Å), C=O (1.189(8)/1.211(8) Å) and Pt–S (2.381(2)/2.386(2) Å) bond lengths were found to be in the same range of those of other structurally characterized acyl and thiocyanato platinum(IV) complexes, respectively (Pt–C min./max. 1.989/2.093 Å, n = 7; C=O min./max. 1.176/1.212 Å, n = 7; Pt–S lower/upper quartile 2.337/2.375 Å, n = 45; n = number of observations [8]). As shown in Fig. 1, C–H···O hydrogen bonds were found in which the carbonyl oxygen atoms act as hydrogen acceptors and the aromatic *o*-C–H groups (C3, C4) as hydrogen donors. The C···O distances (O1···C3 3.118(7)/O2···C4 3.224(7) Å) lie in the typical range of such intramolecular hydrogen bonds [9]. The torsion angle N3···S1···S2···N4 (−150.1(2)°), characterizing the relative orientation of the two thiocyanato ligands, is slightly deviated from the *antiperiplanar* conformation.

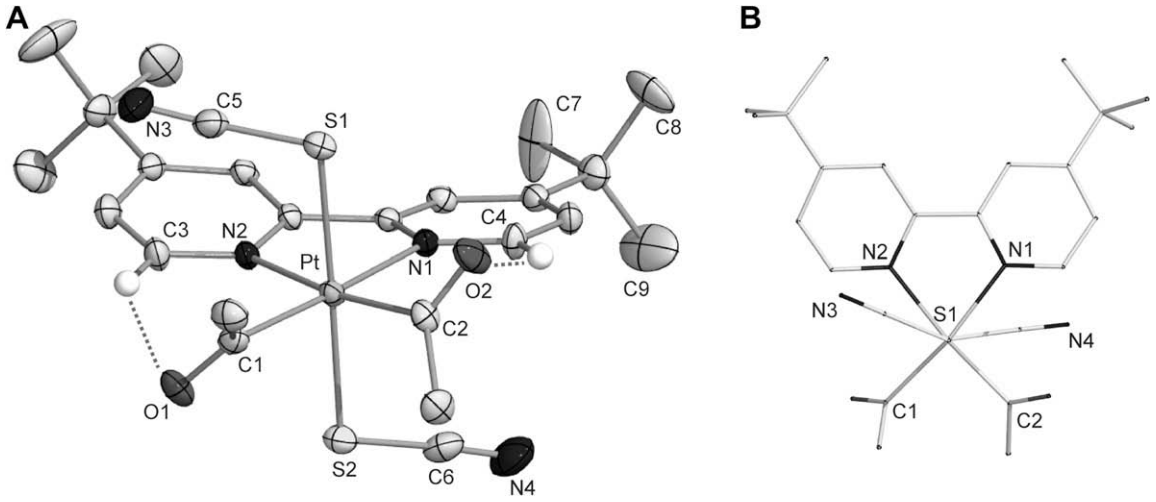


Fig. 1. (A) Molecular structure of [Pt(COMe)$_2$(SCN)$_2$(4,4′-*t*-Bu$_2$-bpy)] in crystals of **4j**. Only the major occupied positions of the methyl groups C7–C9 are shown. The thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms are omitted for clarity, except those involved in hydrogen bonds. (B) Wire model, view along S1–Pt–S2.

2.2. Oxidative addition of HX

2.2.1. Synthesis

The diacetylplatinum(II) complexes (**3**) were obtained in good yields by a straightforward reaction of the diacetyl(hydrido)platinum(IV) complexes with a base such as NaOH in a two phase mixture (CH_2Cl_2/H_2O) (Scheme 1, iv) [4]. Here, we investigated whether – in a reverse reaction – HX can be oxidatively added to complexes **3**. Thus, the complex [Pt(COMe)$_2$(bpy)] (**3a**) was reacted with aqueous hydrochloric acid in methylene chloride. Although, as confirmed by NMR investigations, the diacetyl(hydrido)platinum(IV) complex **5a** was formed, we failed to obtain **5a** in a pure state. Due to the moisture sensitivity of **5a**, approximately 50–75% [Pt(COMe)Cl(bpy)] (**6a**) was also formed depending on the reaction conditions (Scheme 4).

To avoid this decomposition, a solution of [Pt(COMe)$_2$(N⌒N)] (**3**) was treated with equimolar amounts of Me_3SiX (X = Cl, Br, I) and water thus preparing anhydrous HX *in situ*. Within a few seconds the red reaction mixtures discolored and the complexes (*OC*-6-34)–[Pt(COMe)$_2$(H)X(N⌒N)] (N⌒N = bpy, X = Cl, **5a**, Br, **5b**, I, **5c**; N⌒N = 4,4′-*t*-Bu$_2$-bpy, X = Cl, **5d**, Br, **5e**, I, **5f**) were obtained as colorless air and moisture sensitive powders in good yields (70–90%) (Scheme 5). Their identities were unambiguously confirmed by NMR (^{1}H, ^{13}C) and IR spectroscopy and by microanalysis. The NMR data of complexes **5a** and **5d** were found to be identical with those complexes obtained from the reaction of the platina-β-diketone **1a** with bpy and 4,4′-*t*-Bu$_2$-bpy, respectively (cf. Scheme 1, path i and ii) [2].

2.2.2. Spectroscopic characterization

Characteristic spectroscopic parameters of complexes **5** are collected in Table 3. The IR spectra of complexes **5** exhibit a band between 2227 and 2249 cm^{-1}, which is assigned to the Pt–H stretching vibration [10]. As was found for complexes **4**, the substitution pattern of the bipyridine ligand at the 4,4′ position (H vs. *t*-Bu) had almost no influence on the NMR (^{1}H, ^{13}C) chemical shifts and coupling constants. Both in the ^{1}H and ^{13}C NMR spectra, two sets of signals were found for the acetyl ligands confirming the (*OC*-6-34) configuration of complexes **5**. The chemical shifts of the Pt–*C* carbon atoms were observed in a narrow range (191.9–199.9 ppm) indicating only a marginal influence of the halo (Cl vs. Br vs. I) and bipyridine ligand (bpy vs. 4,4′-*t*-Bu$_2$-bpy). The chemical shifts of the hydrido ligands lie in the range of other hydridoplatinum(IV) complexes [10]. The $^1J_{Pt,H}$ coupling constants were found to decrease in the order X = Cl > Br > I by approximately 40 Hz both for the bpy (**5a**–**c**) and the 4,4′-*t*-Bu$_2$-bpy complexes (**5d**–**f**). The large value of the $^1J_{Pt,H}$ coupling constant for the hydride (1504–1564 Hz) is a good indication for a hydrido ligand *trans* to a nitrogen ligand in Pt^{IV} complexes [11].

2.3. Reductive elimination yielding acetylhaloplatinum(II) complexes

2.3.1. Synthesis

Complexes [Pt(COMe)$_2$(H)Cl(N⌒N)] (N⌒N = bpy, **5a**; 4,4′-*t*-Bu$_2$-bpy, **5d**) proved to be highly thermally stable. In the solid state, at temperatures of 174/180 °C (**5a**/**5b**) reductive elimination of acetaldehyde took place yielding complexes of the type [Pt(COMe)Cl(N⌒N)] (N⌒N = bpy, **6a**; 4,4′-*t*-Bu$_2$-bpy, **6d**) (cf. Scheme 1, iii) [2]. The bromo and iodo complexes exhibited a lower thermal stability. In both series the thermal stability was found to decrease in the order X = Cl (150/155 °C, **5a**/**5d**) > Br (98/145 °C, **5b**/**5e**) > I (72/130 °C, **5c**/**5f**).

Analogous to the chloro complexes **5a** and **5d** [2], heating at 140 °C for 30 min of the bromo complex **5e** resulted in a reductive elimination of acetaldehyde giving [Pt(COMe)Br(4,4′-*t*-Bu$_2$-bpy)] (**6e**) (Scheme 6) in a pure state and in good yields (75%). The other bromo and iodo complexes **5b**, **5c** and **5f** reacted in the same way, but along with the expected complexes [Pt(COMe)X(N⌒N)] (**6**) up to 50% of non-identified side products were formed. The side products could not be separated from the type **6** complexes.

Refluxing a suspension of diacetyldihaloplatinum(IV) complexes [Pt(COMe)$_2$X$_2$(N⌒N)] (N⌒N = bpy, X = Br, **4a**/**4b**; I, **4c**/**4d**; N⌒N = 4,4′-*t*-Bu$_2$-bpy; X = Br, **4e**; I, **4g**/**4h**) in methanol for approximately 30 min led to the formation of the corresponding acetylhaloplatinum(II) complexes [Pt(COMe)X(N⌒N)] (N⌒N = bpy, X = Br, **6b**; I, **6c**; N⌒N = 4,4′-*t*-Bu$_2$-bpy; X = Br, **6e**; I, **6f**) as air and moisture stable powders in good yields (60–70%) (Scheme 7). These reductive elimination reactions of acetyl halides proceeded irrespective of whether the *cis* or *trans* complexes were used as starting compounds. Complexes **6** were identified spectroscopically (^{1}H, ^{13}C NMR, IR) and by microanalysis.

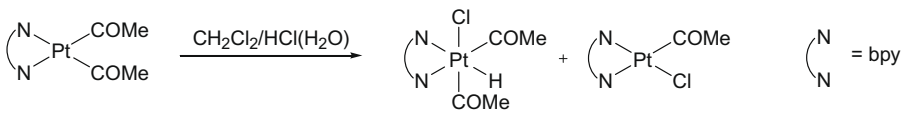
2.3.2. Spectroscopic characterization

In Table 4 characteristic spectroscopic parameters of complexes **6** are collected. The signals of Pt–*C* carbon atoms and of the methyl protons of the acetyl ligands lie in a very narrow range (δ_C(Pt–*C*) ≈ 220 ppm; δ_H(C*H*$_3$) ≈ 2.55 ppm). On the other hand, the C atoms of the methyl ligands were found to be high-field shifted by about 5 ppm and the $^2J_{Pt,C}$ coupling constants were decreased by 20–30 Hz in the order X = Cl (**6a**/**6d**), X = Br (**6b**/**6e**), X = I (**6c**/**6f**). Compared with the diacetylplatinum(II) complexes **3** ([Pt(COMe)$_2$(bpy)], **3a**: $^2J_{Pt,C}$ = 371 Hz; [Pt(COMe)$_2$(4,4′-*t*-Bu$_2$-bpy)], **3b**: $^2J_{Pt,C}$ = 374 Hz) the $^2J_{Pt,C}$ coupling constants in the acetylhaloplatinum(II) complexes **6** (82–111 Hz) are reduced by more than 260 Hz.

2.4. Conclusion

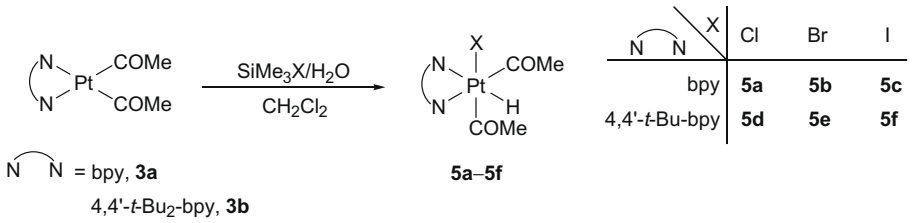
The present investigations show that diacetylplatinum(II) complexes **3** having a bipyridine type coligand (bpy, 4,4′-*t*-Bu$_2$-bpy) undergo oxidative addition reactions with halogens (Br_2, I_2), pseudohalogens ($(SCN)_2$) and hydrogen halides (HCl, HBr, HI) yielding the corresponding platinum(IV) complexes **4** and **5**. The analogous dialkyl complexes [PtR$_2$(bpy)] (**7**) undergo, in general, corresponding reactions. Oxidative addition reactions of type **7** complexes with halogens resulted predominantly in the formation of the *trans* addition products [PtR$_2$X$_2$(bpy)] (*OC*-6-13) [12] whereas analogous reactions of type **3** complexes gave rise to the formation of diastereomeric mixtures of *cis* (*OC*-6-32) and *trans* (*OC*-6-13) addition products. The diastereomeric ratio proved to be strongly solvent dependent.

The most pronounced difference in the reactivity of type **3** and **7** complexes was found in the oxidative addition reactions of hydrogen halides. The acetyl complexes **3** gave rise to the formation of



3a **5a** **6a**

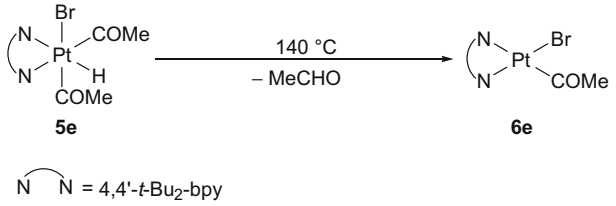
Scheme 4.



Scheme 5.

Table 3
Selected spectroscopic parameters of [Pt(COMe)$_2$(H)X(N⌒N)] (**5a**–**f**) (δ in ppm; J in Hz; ν in cm^{-1}).

N⌒N	X	*CH*$_3$		Pt–*C*	Pt–*H*	
		δ_H ($^3J_{Pt,H}$)	δ_C ($^2J_{Pt,C}$)	δ_C ($^1J_{Pt,C}$)	δ_H ($^1J_{Pt,H}$)	ν (Pt–H)
bpy	Cl (**5a**)	2.28 (27.4)	43.3 (290)	192.0 (886)	−18.30	2249
		2.90 (30.5)	47.2 (225)	198.2 (843)	(1564.3)	
	Br (**5b**)	2.28 (27.8)	42.9 (314)	192.5	−18.27	2227
		2.93 (31.5)	48.6 (236)	196.6	(1554.3)	
	I (**5c**)	2.28 (27.5)	41.5 (321)	194.3	−18.10	2237
		3.01 (33.0)	50.2 (238)	199.9	(1526.0)	
4,4′-*t*-Bu$_2$-bpy	Cl (**5d**)	2.28 (28.0)	44.4 (288)	193.1 (897)	−18.17	2233
		2.95 (29.5)	47.9 (220)	199.6 (856)	(1541.2)	
	Br (**5e**)	2.27 (27.5)	42.6 (299)	191.9	−18.11	2229
		2.91 (30.7)	48.3 (236)	196.5	(1532.6)	
	I (**5f**)	2.26 (27.1)	41.6 (318)	193.9	−18.00	2229
		2.91 (32.3)	50.8 (226)	198.2	(1504.4)	



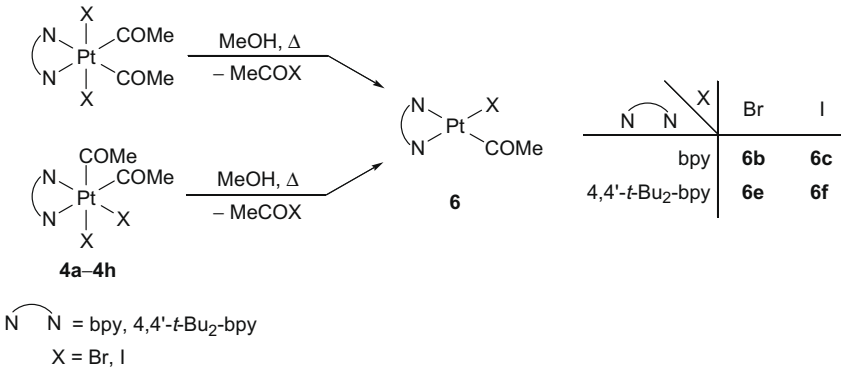
Scheme 6.

thermally stable diacetyl(hydrido)haloplatinum(IV) complexes **5**. Even the iodo complexes are stable in the solid state up to 70 °C. The analogous dialkyl(hydrido)chloroplatinum(IV) complexes [PtR$_2$(H)Cl(bpy)] proved to be remarkably less stable. Even with R = Me, Bn, they could only be characterized by NMR spectroscopy in solution at temperatures below −30 °C [13]. Reductive elimination of alkanes occurred readily at room temperature. A dimethyl(hydrido)chloroplatinum(IV) complex being stable at room temperature was obtained when the bpy ligand was substituted by a di-2-pyridylketone ligand [14].

3. Experimental

3.1. General comments

All reactions were performed under an argon atmosphere using the standard Schlenk techniques. Solvents were dried (Et_2O over Na/benzophenone, CH_2Cl_2 over CaH_2) and distilled prior to use. NMR spectra were recorded on Varian spectrometers Gemini 200, VXR 400 and Unity 500 operating at 200, 400 and 500 MHz for ^{1}H, respectively. Solvent signals (^{1}H, ^{13}C) were used as internal references. When necessary, assignments were revealed by running ^{1}H–^{1}H and ^{1}H–^{13}C COSY NMR experiments. IR spectra were recorded on a Galaxy Mattson 5000 FT-IR spectrometer using KBr pellets. Microanalyses were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL



Scheme 7.

Table 4
Characteristic NMR spectroscopic parameters (δ in ppm, J in Hz) of [Pt(COMe)X(N⌒N)] **(6a–f)**.

N⌒N	X		δ_H	CH_3	Pt–C
				δ_C ($^2J_{Pt,C}$)	δ_C
bpy	Cl	(**6a**)	2.52	42.0 (103)	220.2
	Br	(**6b**)	2.52	44.3 (99)	218.5
	I	(**6c**)	2.58	47.2 (84)	220.1
4,4′-*t*-Bu$_2$-bpy	Cl	(**6d**)	2.53	43.1 (111)	221.8
	Br	(**6e**)	2.55	44.1 (90)	220.0
	I	(**6f**)	2.57	48.0 (82)	221.9

(Elementaranalysensysteme) elemental analysers. The complexes [Pt(COMe)$_2$(N⌒N)$_2$] (N⌒N = bpy, **3a;** N⌒N = 4,4′-t-Bu$_2$-bpy, **3b**) were prepared according to a published method [4].

3.2. Oxidative addition of X_2 to [Pt(COMe)$_2$(bpy)] (**3a**)

To a solution of [Pt(COMe)$_2$(bpy)] (**3a**) (100 mg, 0.23 mmol) in methylene chloride (5 ml) and acetonitrile (5 ml), respectively, a solution of X_2 (X = Br, I; 0.23 mmol) in the same solvent (10 ml) was added. In vacuum the volume of the reaction mixture was reduced to approximately 1 ml and diethyl ether (10 ml) was added. The resulting precipitate was filtered, washed with *n*-pentane and dried in vacuum.

3.2.1. Reaction with Br_2 in methylene chloride

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(bpy)] (**4a**)*/(OC-6-13)–[Pt(COMe)$_2$Br$_2$-(bpy)]* (**4b**). Diastereomeric ratio 2:1 (^{1}H NMR). Yield: 125 mg (90%). Anal. Calc. for $C_{14}H_{14}Br_2N_2O_2Pt$ (597.16): C, 28.16; H, 2.36; N, 4.69. Found: C, 27.99; H, 2.52; N, 4.84%.

3.2.2. Reaction with I_2 in methylene chloride

(OC-6-32)–[Pt(COMe)$_2$I$_2$(bpy)] (**4c**)*/(OC-6-13)–[Pt(COMe)$_2$I$_2$-(bpy)]* (**4d**). Diastereomeric ratio 1:1 (^{1}H NMR). Yield: 145 mg (90%). Anal. Calc. for $C_{14}H_{14}I_2N_2O_2Pt$ (691.16): C, 24.33; H, 2.04; N, 4.05. Found: C, 24.21; H, 2.21; N, 4.32%

3.2.3. Reaction with Br_2 in acetonitrile

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(bpy)] (**4a**)*/(OC-6-13)–[Pt(COMe)$_2$Br$_2$-(bpy)]* (**4b**). Diastereomeric ratio 0:1 (^{1}H NMR). Yield: 115 mg (85%). Anal. Calc. for $C_{14}H_{14}Br_2N_2O_2Pt$ (597.16): C, 28.16; H, 2.36; N, 4.69. Found: C, 28.02; H, 2.45; N, 4.80%.

3.2.4. Reaction with I_2 in acetonitrile

(OC-6-32)–[Pt(COMe)$_2$I$_2$(bpy)] (**4c**)*/(OC-6-13)–[Pt(COMe)$_2$I$_2$(bpy)]* (**4d**): Diastereomeric ratio 0:1 (^{1}H NMR). Yield: 135 mg (85%). Anal. Calc. for $C_{14}H_{14}I_2N_2O_2Pt$ (691.16): C, 24.33; H, 2.04; N, 4.05. Found: C, 24.18; H, 2.25; N, 4.11%.

3.2.5. Spectroscopic data

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(bpy)] (**4a**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.61 (s + d, $^3J_{Pt,H}$ = 13.9 Hz, 3H, COCH_3), 3.44 (s + d, $^3J_{Pt,H}$ = 10.5 Hz, 3H, COCH_3), 7.65 (m, 2H, H^5/$H^{5'}$ bpy), 8.00–8.20 (m, 4H, H^3/$H^{3'}$/H^4/$H^{4'}$ bpy), 9.06 + 9.63 (m, 2H, H^6/$H^{6'}$-bpy).

(OC-6-13)–[Pt(COMe)$_2$Br$_2$(bpy)] (**4b**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.91 (s + d, $^3J_{Pt,H}$ = 12.2 Hz, 6H, COCH_3), 7.63 (m, 2H, H^5/$H^{5'}$ bpy), 8.03 (m, 2H, H^4/$H^{4'}$ bpy), 8.20 (m, 2H, H^3/$H^{3'}$ bpy), 9.12 (m, 2H, H^6/$H^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.5 (s + d, $^2J_{Pt,C}$ = 122 Hz, $COCH_3$), 123.0 (s, C^3/$C^{3'}$ bpy), 127.9 (s, C^5/$C^{5'}$ bpy), 138.9 (s, C^4/$C^{4'}$ bpy), 151.0 (s, C^2/$C^{2'}$ bpy), 152.1 (s, C^6/$C^{6'}$ bpy), 186.2 (s, Pt–COMe). IR: ν (cm^{-1}) 3113(w), 3055(w), 2910(w), 1721(s), 1689(s), 1601(s), 1497(w), 1473(m), 1444(s), 1316(s), 1179(w), 1076(s), 1020(m), 941(m), 801(w), 767(s), 724(w), 675(w), 644(w), 588(w), 570(m).

(OC-6-32)–[Pt(COMe)$_2$I$_2$(bpy)] (**4c**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (s + d, $^3J_{Pt,H}$ = 15.6 Hz, 3H, COCH_3), 3.79 (s + d, $^3J_{Pt,H}$ = 12.0 Hz, 3H, COCH_3), 7.65 (m, 2H, H^5/$H^{5'}$ bpy), 8.00–8.25 (m, 4H, H^3/$H^{3'}$/H^4/$H^{4'}$ bpy), 8.87 + 9.60 (m, 2H, H^6/$H^{6'}$ bpy).

(OC-6-13)–[Pt(COMe)$_2$I$_2$(bpy)] (**4d**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.09 (s + d, $^3J_{Pt,H}$ = 13.7 Hz, 6H, COCH_3), 7.62 (m, 2H, H^5/$H^{5'}$ bpy), 8.02 (m, 2H, H^4/$H^{4'}$ bpy), 8.21 (m, 2H, H^3/$H^{3'}$ bpy), 9.25 (m, 2H, H^6/$H^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 48.2 (s + d, $^2J_{Pt,C}$ = 119 Hz, $COCH_3$), 123.3 (s, C^3/$C^{3'}$ bpy), 126.4 (s, C^5/$C^{5'}$ bpy), 139.5 (s, C^4/$C^{4'}$ bpy), 150.9 (s, C^2/$C^{2'}$ bpy), 153.5 (s, C^6/$C^{6'}$ bpy), 187.7 (s, Pt–COMe). IR: ν (cm^{-1}) 3106(w), 2925(w), 2899(w), 1679(s), 1596(m), 1492(w), 1471(m), 1442(m), 1314(m), 1087(m), 1022(w), 941(w), 871(w), 767(m), 727(w), 634(w), 590(w), 572(w).

3.3. Oxidative addition of X_2 to [Pt(COMe)$_2$(4,4′-t-Bu$_2$-bpy)] (**3b**)

To a solution of [Pt(COMe)$_2$(4,4′-*t*-Bu$_2$-bpy)] (**3b**) (100 mg, 0.18 mmol) in methylene chloride (5 ml) and acetonitrile (5 ml), respectively, a solution of X_2 (X = Br, I; 0.18 mmol) in the same solvent (10 ml) was added. In vacuum the volume of the reaction mixture was reduced to approximately 1 ml and *n*-pentane (10 ml) was added. The resulting precipitate was filtered, washed with *n*-pentane and dried in vacuum.

3.3.1. Reaction with Br_2 in methylene chloride

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(4,4′-t-Bu$_2$-bpy)] (**4e**)*/(OC-6-13)–[Pt (COMe)$_2$ Br$_2$(4,4′-t-Bu$_2$-bpy)]* (**4f**): Diastereomeric ratio 1:0 (^{1}H NMR). Yield: 125 mg (90%). Anal. Calc. for $C_{22}H_{30}Br_2N_2O_2Pt$ (904.45): C, 29.21; H, 3.34; N, 3.10. Found: C, 28.99; H, 3.45; N, 3.21%.

3.3.2. Reaction with I_2 in methylene chloride

(OC-6-32)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)] (**4g**)*/(OC-6-13)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)]* (**4h**): Diastereomeric ratio 3:1 (^{1}H NMR). Yield: 125 mg (90%). Anal. Calc. for $C_{22}H_{30}I_2N_2O_2Pt$ (998.45): C, 26.46; H, 3.03; N, 2.81. Found: C, 26.21; H, 3.13; N, 2.96%.

3.3.3. Reaction with Br_2 in acetonitrile

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(4,4′-t-Bu$_2$-bpy)] (**4e**)*/(OC-6-13)–[Pt (COMe)$_2$Br$_2$(4,4′-t-Bu$_2$-bpy)]* (**4f**): Diastereomeric ratio 1:0 (^{1}H NMR). Yield: 125 mg (90%). Anal. Calc. for $C_{22}H_{30}Br_2N_2O_2Pt$ (904.45): C, 29.21; H, 3.34; N, 3.10. Found: C, 28.85; H, 3.51; N, 3.25%.

Table 5
Crystallographic and data collection parameters of complex **4j**.

	4j
Empirical formula	$C_{24}H_{30}N_4O_2PtS_2$
M_r	665.7
Crystal system/space group	orthorhombic/*Pcab*
a (Å)	12.3278(9)
b (Å)	21.018(2)
c (Å)	21.205(1)
V (Å^3)	5494.4(7)
Z	8
D_{calc} (g cm^{-1})	1.610
μ(Mo Kα) mm^{-1}	5.286
θ Range (°)	2.14–25.82
Number of reflections collected	40628
Number of reflections observed [$I > 2\sigma(I)$]	5321
Number of independent reflections	3845
Number of data/restraints/parameters	5321/0/338
Goodness-of-fit on F^2	1.008
R_1, wR_2 [$I > 2\sigma(I)$]	0.0369, 0.0727
R_1, wR_2 (all data)	0.0596, 0.0795
Largest difference in peak and hole (e Å^{-3})	1.115/−1.397

3.3.4. Reaction with I_2 in acetonitrile

(OC-6-32)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)] (**4g**)/*(OC-6-13)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)]* (**4h**): Diastereomeric ratio 1:1 (^{1}H NMR). Yield: 125 mg (90%). Anal. Calc. for $C_{22}H_{30}I_2N_2O_2Pt$ (998.45): C, 26.46; H, 3.03; N, 2.81. Found: C, 26.33; H, 3.10; N, 2.76%.

3.3.5. Spectroscopic data

(OC-6-32)–[Pt(COMe)$_2$Br$_2$(4,4′-t-Bu$_2$-bpy)] (**4e**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.42 (s, 18H, C(CH_3)$_3$), 2.60 (s + d, $^3J_{Pt,H}$ = 15.2 Hz, 3H, COCH_3), 3.42 (s + d, $^3J_{Pt,H}$ = 12.5 Hz, 3H, COCH_3), 7.53 + 7.61 (m, 2H, $H^5/H^{5'}$ bpy), 8.10 (m, 2H, $H^3/H^{3'}$ bpy), 8.96 + 9.46 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.3 + 30.4 (s, C(CH_3)$_3$), 35.6 + 35.7 (s, C(CH$_3$)$_3$), 35.8 (s + d, $^2J_{Pt,C}$ = 125 Hz, COCH$_3$), 43.6 (s + d, $^2J_{Pt,C}$ = 71 Hz, COCH$_3$), 119.7 + 121.1 (s, $C^3/C^{3'}$ bpy), 123.9 + 124.4 (s, $C^5/C^{5'}$ bpy), 148.2 + 148.3 (s, $C^4/C^{4'}$ bpy), 153.1 + 154.7 (s, $C^6/C^{6'}$ bpy), 164.4 + 165.3 (s, $C^2/C^{2'}$ bpy), 185.4 (s + d, $^1J_{Pt,C}$ = 687 Hz, Pt–COMe), 198.0 (s, Pt–COMe). IR: ν (cm^{-1}) 3047(w), 2960(m), 2870(w), 1707(m), 1675(s), 1610(m), 1548(w), 1481(w), 1466(w), 1411(m), 1367(w), 1336(w), 1251(w), 1105(w), 1081(m), 1025(w), 943(w), 896(w), 865(w), 605(w), 574(w), 550(w).

(OC-6-32)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)] (**4g**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 18H, C(CH_3)$_3$), 2.75 (s + d, $^3J_{Pt,H}$ = 14.8 Hz, 3H, COCH_3), 3.77 (s + d, $^3J_{Pt,H}$ = 11.2 Hz, 3H, COCH_3), 7.55 + 7.57 (m, 2H, $H^5/H^{5'}$ bpy), 8.09 (m, 2H, $H^3/H^{3'}$ bpy), 8.91 + 9.80 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.2 + 30.3 (s, C(CH_3)$_3$), 35.5 + 35.6 (s, C(CH$_3$)$_3$), 37.6 (s + d, $^2J_{Pt,C}$ = 139 Hz, COCH$_3$), 52.6 (s + d, $^2J_{Pt,C}$ = 87 Hz, COCH$_3$), 119.9 + 121.1 (s, $C^3/C^{3'}$ bpy), 123.7 + 124.5 (s, $C^5/C^{5'}$ bpy), 148.2 + 149.8 (s, $C^4/C^{4'}$ bpy), 153.1 + 154.6 (s, $C^6/C^{6'}$ bpy), 163.9 + 164.9 (s, $C^2/C^{2'}$ bpy), 187.4 (s + d, $^1J_{Pt,C}$ = 668 Hz, Pt–COMe), 196.9 (s + d, $^1J_{Pt,C}$ = 856 Hz, Pt–COMe).

(OC-6-13)–[Pt(COMe)$_2$I$_2$(4,4′-t-Bu$_2$-bpy)] (**4h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 18H, C(CH$_3$)$_3$), 3.06 (s + d, $^3J_{Pt,H}$ = 14.5 Hz, 6H, COCH_3), 7.58 (m, 2H, $H^5/H^{5'}$ bpy), 8.10 (m, 2H, $H^3/H^{3'}$ bpy), 9.08 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.2 (s, C(CH_3)$_3$), 35.3 (s, C(CH$_3$)$_3$), 48.2 (s + d, $^2J_{Pt,C}$ = 121 Hz, COCH$_3$), 119.8 (s, $C^3/C^{3'}$ bpy), 123.7 (s, $C^5/C^{5'}$ bpy), 150.1 (s, $C^4/C^{4'}$ bpy), 153.4 (s, $C^6/C^{6'}$ bpy), 164.0 (s, $C^2/C^{2'}$ bpy), 188.5 (s, Pt–COMe).

3.4. Oxidative addition of $(SCN)_2$ to [Pt(COMe)$_2$(N⌒N)] (**3**)

To a solution of KSCN (100 mg, 1 mmol) in methanol (10 ml) bromine (32 mg, 0.2 mmol) in methanol (5 ml) was slowly added at −78 °C [7]. After 30 min the resulting reaction mixture was added to a solution of [Pt(COMe)$_2$(N⌒N)] (N⌒N = bpy, **3a**; 4,4′-*t*-Bu$_2$-bpy, **3b**; 0.2 mmol) in methanol (5 ml) at −78 °C. After stirring for further 30 min, the reaction mixture was warmed to room temperature and the solvent was removed in vacuum. The residue was extracted with methylene chloride (10 ml). In vacuum the volume of the extract was reduced to approximately 2 ml and *n*-pentane (10 ml) was added. The precipitate was filtered, washed with *n*-pentane (2 ml) and dried in vacuum.

(OC-6-13)–[Pt(COMe)$_2$(SCN)$_2$(bpy)] (**4i**): Yield: 95 mg (85%). Anal. Calc. for $C_{16}H_{14}N_4O_2PtS_2$ (553.52): C, 34.72; H, 2.55; N, 10.12; S, 11.59. Found: C, 34.83; H, 2.65; N, 10.42; S, 11.23%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (s + d, $^3J_{Pt,H}$ = 13.9 Hz, 6H, COCH_3), 7.74 (m, 2H, $H^5/H^{5'}$ bpy), 8.15 (m, 2H, $H^4/H^{4'}$ bpy), 8.30 (m, 2H, $H^3/H^{3'}$ bpy), 8.74 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.1 (s + d, $^2J_{Pt,C}$ = 125 Hz, COCH$_3$), 114.3 (s, SCN), 123.8 (s, $C^3/C^{3'}$ bpy), 127.6 (s, $C^5/C^{5'}$ bpy), 140.5 (s, $C^4/C^{4'}$ bpy), 150.1 (s, $C^6/C^{6'}$ bpy), 153.4 (s, $C^2/C^{2'}$ bpy), 190.7 (s + d, $^1J_{Pt,C}$ = 672 Hz, Pt–COMe). IR: ν (cm^{-1}) 3110(w), 2961(w), 2870(w), 2127(m), 2065(m), 1689(s), 1598(s), 1560(w), 1542(w), 1490(w), 1473(m), 1442(m), 1419(m), 1342(w), 1315(w), 1089(m), 1069(m), 1024(w), 1014(w), 948(w), 898(w), 809(w), 771(m), 728(w), 635(w), 588(w), 572(w).

(OC-6-13)–[Pt(COMe)$_2$(SCN)$_2$(4,4′-t-Bu$_2$-bpy)] (**4j**): Yield: 100 mg (75%). . Anal. Calc. for $C_{24}H_{30}N_4O_2PtS_2$ (665.73): C, 43.30; H, 4.54; N, 8.42; S, 9.63. Found: C, 43.36; H, 4.55; N, 8.66; S, 9.45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (s + d, $^3J_{Pt,H}$ = 12.3 Hz, 6H, COCH_3), 7.67 (m, 2H, $H^5/H^{5'}$ bpy), 8.17 (m, 2H, $H^4/H^{4'}$ bpy), 8.58 (m, 2H, $H^3/H^{3'}$ bpy), 8.72 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.5 (s, C(CH_3)$_3$), 36.2 (s, C(CH$_3$)$_3$), 39.2 (s + d, $^2J_{Pt,C}$ = 124 Hz, COCH$_3$), 114.5 (s, SCN), 120.5 (s, $C^3/C^{3'}$ bpy), 124.9 (s, $C^5/C^{5'}$ bpy), 149.3 (s, $C^4/C^{4'}$ bpy), 153.4 (s, $C^2/C^{2'}$ bpy), 165.4 (s, $C^6/C^{6'}$ bpy), 191.5 (s, Pt–COMe). IR: ν (cm^{-1}) 3056(w), 2966(m), 2869(w), 2117(s), 2022(w), 1687(s), 1614(s), 1548(w), 1490(w), 1465(w), 1413(m), 1365(w), 1340(w), 1255(w), 1105(w), 1078(m), 1022(w), 944(w), 898(w), 852(w), 592(w), 578(w), 551(w).

3.5. Synthesis of [Pt(COMe)$_2$(H)X(N⌒N)] (**5**)

At −78 °C a solution of [Pt(COMe)$_2$(N⌒N)] (N⌒N = bpy, **3a**; 4,4′-*t*-Bu$_2$-bpy, **3c**; 0.23 mmol) in methylene chloride (5 ml) was treated with Me_3SiX (X = Cl, Br, I; 0.25 mmol) and water (4.5 mg, 0.25 mmol). Then, the reaction mixture was slowly warmed to 0 °C. The volume was reduced to 1/3, diethylether (5 ml) was added and the precipitate formed was filtered, washed with diethyl ether (2 × 2 ml) and dried in vacuum.

(OC-6-34)–[Pt(COMe)$_2$(H)Cl(bpy)] (**5a**): Yield: 95 mg (90%). Anal. Calc. for $C_{14}H_{15}Cl_1N_2O_2Pt$ (473.81): C, 35.49; H, 3.19; N, 5.91. Found: C, 35.21; H, 3.04; N, 6.02%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ *−18.30* (s + d, $^1J_{Pt,H}$ = 1564.3 Hz, 1H, Pt–*H*), 2.28 (s + d, $^3J_{Pt,H}$ = 27.4 Hz, 3H, COCH_3), 2.90 (s + d, $^3J_{Pt,H}$ = 30.5 Hz, 3H, COCH_3), 7.60 + 7.72 (m, 2H, $H^5/H^{5'}$ bpy), 8.10 (m, 2H, $H^4/H^{4'}$ bpy), 8.22 (m, 2H, $H^3/H^{3'}$ bpy), 9.05 + 9.56 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 43.3 (s + d, $^1J_{Pt,H}$ = 290 Hz, COCH$_3$), 47.2 (s + d, $^1J_{Pt,H}$ = 225 Hz, COCH$_3$), 123.3 + 123.5 (s, $C^3/C^{3'}$ bpy), 126.4 + 126.8 (s, $C^5/C^{5'}$ bpy), 139.2 + 139.3 (s, $C^4/C^{4'}$ bpy), 149.6 + 152.2 (s, $C^6/C^{6'}$ bpy), 154.0 + 154.5 (s, $C^2/C^{2'}$ bpy), 192.0 (s + d, $^1J_{Pt,C}$ = 886 Hz, Pt–COMe), 198.2 (s + d, $^1J_{Pt,C}$ = 843 Hz, Pt–COMe).

(OC-6-34)–[Pt(COMe)$_2$(H)Br(bpy)] (**5b**): $T_{dec.}$ = 98 °C. Yield: 100 mg (85%). Anal. Calc. for $C_{14}H_{15}BrN_2O_2Pt$ (518.26): C, 32.44; H, 2.92; N, 5.41. Found: C, 32.31; H, 2.85; N, 5.51%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ *−18.27* (s + d, $^1J_{Pt,H}$ = 1554.3 Hz, 1H, Pt–*H*), 2.28 (s + d, $^3J_{Pt,H}$ = 27.8 Hz, 3H, COCH_3), 2.93 (s + d, $^3J_{Pt,H}$ = 31.5 Hz, 3H, COCH_3), 7.58 + 7.60 (m, 2H, $H^5/H^{5'}$ bpy), 8.11 (m, 2H, $H^4/H^{4'}$ bpy), 8.22 (m, 2H, $H^3/H^{3'}$ bpy), 9.06 + 9.62 (m, 2H, $H^6/H^{6'}$ bpy). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 42.9 (s + d, $^1J_{Pt,H}$ = 314 Hz, COCH$_3$), 48.6 (s + d, $^1J_{Pt,H}$ = 236 Hz, COCH$_3$), 123.7 + 123.8 (s, $C^3/C^{3'}$ bpy), 126.8 + 127.5 (s, $C^5/C^{5'}$ bpy), 139.8 + 139.9 (s, $C^4/C^{4'}$ bpy), 150.7 + 152.9 (s, $C^6/C^{6'}$ bpy), 154.6 + 154.8 (s, $C^2/C^{2'}$ bpy), 192.5 (s, Pt–COMe), 196.6 (s, Pt–COMe). IR: ν (cm^{-1}) 3068(w), 3035(w), 2962(w), 2227(m), 1706(s), 1656(s), 1599(m), 1492(w), 1473(w), 1448(m), 1415(w), 1336(w), 1317(w), 1114(s), 1090(s), 1030(m), 941(m), 775(m), 728(w), 607(w), 582(w).

(OC-6-34)–[Pt(COMe)$_2$(H)I(bpy)] (**5c**): $T_{dec.}$ = 72 °C. Yield: 110 mg (85%). Anal. Calc. for $C_{14}H_{15}IN_2O_2Pt$ (565.26): C, 29.75; H, 2.67; N, 4.96. Found: C, 29.51; H, 2.71; N, 5.12%. ^{1}H NMR (400 MHz, $CDCl_3$): δ *−18.10* (s + d, $^1J_{Pt,H}$ = 1526.0 Hz, 1H, Pt–*H*), 2.28 (s + d, $^3J_{Pt,H}$ = 27.5 Hz, 3H, COCH_3), 3.01 (s + d, $^3J_{Pt,H}$ = 33.0 Hz, 3H, COCH_3), 7.56 + 7.71 (m, 2H, $H^5/H^{5'}$ bpy), 8.10 (m, 2H, $H^4/H^{4'}$ bpy), 8.21 (m, 2H, $H^3/H^{3'}$ bpy), 9.07 + 9.75 (m, 2H, $H^6/H^{6'}$ bpy).^{13}C NMR (100 MHz, CD_2Cl_2): δ 41.5 (s + d, $^1J_{Pt,H}$ = 321 Hz, COCH$_3$), 50.2 (s + d, $^1J_{Pt,H}$ = 238 Hz, COCH$_3$), 123.8 + 123.9 (s, $C^3/C^{3'}$ bpy), 126.5 + 127.6 (s, $C^5/C^{5'}$ bpy), 140.2 + 140.5 (s, $C^4/C^{4'}$ bpy), 151.2 + 152.5 (s, $C^6/C^{6'}$ bpy), 154.9 + 155.2 (s, $C^2/C^{2'}$ bpy), 194.3 (s, Pt–COMe), 199.9 (s, Pt–COMe). IR: ν (cm^{-1}) 3031(w), 2971(w), 2237(m), 1702(s), 1660(s), 1598(m), 1490(w), 1473(w), 1444(m),

1414(w), 1338(w), 1315(w), 1247(w), 1155(w), 1110(s), 1085(s), 1027(m), 945(m), 770(m), 728(w), 600(w), 582(m).

(OC-6-34)–[Pt(COMe)$_2$(H)Cl(4,4′-t-Bu$_2$-bpy)] (**5d**): Yield: 100 mg (75%). Anal. Calc. for $C_{22}H_{31}ClN_2O_2Pt$ (586.03): C, 45.09; H, 5.33; N, 4.78. Found: C, 44.80; H, 5.18; N, 4.66%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −18.17 (s + d, $^1J_{Pt,H}$ = 1541.2 Hz, 1H, Pt–*H*), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$), 2.28 (s + d, $^3J_{Pt,H}$ = 28.0 Hz, 3H, COC*H*$_3$), 2.95 (s + d, $^3J_{Pt,H}$ = 29.5 Hz, 3H, COC*H*$_3$), 7.50 + 7.61 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 8.10 (m, 2H, *H*^{4}/*H*$^{4'}$ bpy), 8.88 + 9.37 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 31.3 (s, C(*C*H$_3$)$_3$), 36.4 (s, *C*(CH$_3$)$_3$), 36.5 (s, *C*(CH$_3$)$_3$), 44.4 (s + d, $^1J_{Pt,H}$ = 288 Hz, COCH$_3$), 47.9 (s + d, $^1J_{Pt,H}$ = 220 Hz, COCH$_3$), 120.9 + 121.0 (s, *C*^{3}/*C*$^{3'}$ bpy), 124.9 + 125.4 (s, *C*^{5}/*C*$^{5'}$ bpy), 150.7 + 153.2 (s, *C*^{4}/*C*$^{4'}$ bpy), 155.5 + 155.6 (s, *C*^{6}/*C*$^{6'}$ bpy), 165.0 + 165.2 (s, *C*^{2}/*C*$^{2'}$ bpy), 193.1 (s + d, $^1J_{Pt,C}$ = 897 Hz, Pt–*C*OMe), 199.6 (s + d, $^1J_{Pt,C}$ = 856 Hz, Pt–*C*OMe).

(OC-6-34)–[Pt(COMe)$_2$(H)Br(4,4′-t-Bu$_2$-bpy)] (**5e**): $T_{dec.}$ = 145 °C. Yield: 100 mg (70%). Anal. Calc. for $C_{22}H_{31}BrN_2O_2Pt$ (630.48): C, 41.91; H, 4.96; N, 4.44. Found: C, 41.80; H, 4.88; N, 4.53%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ *−18.11* (s + d, $^1J_{Pt,H}$ = 1532.6 Hz, 1H, Pt–*H*), 1.44 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 2.27 (s + d, $^3J_{Pt,H}$ = 27.5 Hz, 3H, COC*H*$_3$), 2.91 (s + d, $^3J_{Pt,H}$ = 30.7 Hz, 3H, COC*H*$_3$), 7.57 + 7.71 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 8.16 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.93 + 9.47 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 30.2 (s, C(*C*H$_3$)$_3$), 35.6 (s, *C*(CH$_3$)$_3$), 35.7 (s, *C*(CH$_3$)$_3$), 42.6 (s + d, $^1J_{Pt,H}$ = 299 Hz, COCH$_3$), 48.3 (s + d, $^1J_{Pt,H}$ = 236 Hz, COCH$_3$), 119.9 + 120.0 (s, *C*^{3}/*C*$^{3'}$ bpy), 123.7 + 124.3 (s, *C*^{5}/*C*$^{5'}$ bpy), 149.6 + 152.0 (s, *C*^{4}/*C*$^{4'}$ bpy), 154.1 + 154.3 (s, *C*^{6}/*C*$^{6'}$ bpy), 164.0 + 164.2 (s, *C*^{2}/*C*$^{2'}$ bpy), 191.9 (s, Pt–*C*OMe), 196.5 (s, Pt–*C*OMe). IR: ν (cm^{-1}) 3050(w), 2960(m), 2872(w), 2229(m), 1693(s), 1660(s), 1612(m), 1550(w), 1481(w), 1468(w), 1411(m), 1367(w), 1334(w), 1252(w), 1112(m), 1091(m), 1026(w), 944(w), 898(w), 870(w), 603(w), 586(w).

(OC-6-34)–[Pt(COMe)$_2$(H)I(4,4′-t-Bu$_2$-bpy)] (**5f**): $T_{dec.}$ = 130 °C. Yield: 115 mg (75%). Anal. Calc. for $C_{22}H_{31}IN_2O_2Pt$ (677.48): C, 39.00; H, 4.61; N, 4.13. Found: C, 38.76; H, 4.55; N, 4.24%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ *−18.00* (s + d, $^1J_{Pt,H}$ = 1504.4 Hz, 1H, Pt–*H*), 1.44 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 2.26 (s + d, $^3J_{Pt,H}$ = 27.1 Hz, 3H, COC*H*$_3$), 2.91 (s + d, $^3J_{Pt,H}$ = 32.3 Hz, 3H, COC*H*$_3$), 7.59 + 7.70 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 8.15 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.95 + 9.58 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 30.3 (s, C(*C*H$_3$)$_3$), 35.7 (s, *C*(CH$_3$)$_3$), 35.8 (s, *C*(CH$_3$)$_3$), 41.6 (s + d, $^1J_{Pt,H}$ = 318 Hz, COCH$_3$), 50.8 (s + d, $^1J_{Pt,H}$ = 226 Hz, COCH$_3$), 118.2 + 119.5 (s, *C*^{3}/*C*$^{3'}$ bpy), 122.5 + 124.6 (s, *C*^{5}/*C*$^{5'}$bpy), 150.0 + 152.2 (s, *C*^{4}/*C*$^{4'}$ bpy), 154.4 + 154.9 (s, *C*^{6}/*C*$^{6'}$ bpy), 164.2 + 164.4 (s, *C*^{2}/*C*$^{2'}$ bpy), 193.9 (s, Pt–*C*OMe), 198.2 (s, Pt–*C*OMe). IR: ν (cm^{-1}) 3050(w), 2962(m), 2870(w), 2229(m), 1691(s), 1659(s), 1612(m), 1548(w), 1483(w), 1463(w), 1411(s), 1365(w), 1332(w), 1252(w), 1110(m), 1090(m), 1024(w), 943(w), 899(w), 850(w), 603(w), 588(w).

3.6. Synthesis of [Pt(COMe)X(N⌒N)] (6)

(a) (*OC*-6-34)–[Pt(COMe)$_2$(H)Br(4,4′-*t*-Bu$_2$-bpy)] (100 mg, 0.16 mmol, **5e**) was heated in vacuum to 140 °C for 30 min. After cooling to room temperature, the resulting solid was extracted with methylene chloride (5 ml). The volume of the extract was reduced to approximately 1/3 and *n*-pentane (5 ml) was added. The resulting precipitate (**6e**) was filtered, washed with *n*-pentane (5 ml) and dried in vacuum.

(b) A suspension of [Pt(COMe)$_2$X$_2$(N⌒N)] (N⌒N = bpy; X = Br, **4a**/**4b**; I, **4c**/**4d;** 4,4′-*t*-Bu$_2$-bpy; X = Br, **4e**; I, **4g**/**4h**, 0.16 mmol) in methanol (5 ml) was refluxed for 30 min. After cooling to room temperature the volume of the reaction mixture was reduced to 1 ml in vacuum. The resulting precipitate was filtered, washed with diethyl ether (2 × 2 ml) and dried in vacuum.

[Pt(COMe)Br(bpy)] (**6b**): Yield: 55 mg (70%) (b). Anal. Calc. for $C_{12}H_{11}BrN_2OPt$ (474.21): C, 30.39; H, 2.34; N, 5.91. Found: C, 30.21; H, 2.45; N, 5.87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s(br), 3H, COC*H*$_3$), 7.34 + 7.52 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 8.06 (m, 2H, *H*^{4}/*H*$^{4'}$ bpy), 8.14 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.70 + 9.28 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.3 (s + d, $^2J_{Pt,C}$ = 99 Hz, COCH$_3$), 122.3 + 123.5 (s, *C*^{3}/*C*$^{3'}$ bpy), 126.5 + 127.3 (s, *C*^{5}/*C*$^{5'}$ bpy), 138.1 + 139.2 (s, *C*^{4}/*C*$^{4'}$ bpy), 149.1 + 150.6 (s, *C*^{6}/*C*$^{6'}$ bpy), 153.7 + 155.3 (s, *C*^{2}/*C*$^{2'}$ bpy), 218.5 (s, Pt–COCH$_3$). IR: ν (cm^{-1}) 3073(w), 2921(w), 1617(s), 1602(s), 1490(w), 1467(m), 1444(s), 1315(w), 1261(w), 1243(w), 1159(w), 1106(m), 1070(w), 1016(w), 931(w), 759(s), 721(w), 640(w), 603(w).

[Pt(COMe)I(bpy)] (**6c**): Yield: 60 mg (70%) (b). Anal. Calc. for $C_{12}H_{11}IN_2OPt$ (521.21): C, 27.65; H, 2.13; N, 5.37. Found: C, 27.45; H, 2.31; N, 5.27%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s(br), 3H, COC*H*$_3$), .7.41 + 7.51 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 8.04 (m, 2H, *H*^{4}/*H*$^{4'}$ bpy), 8.19 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.63 + 9.56 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.2 (s + d, $^2J_{Pt,C}$ = 84 Hz, COCH$_3$), 124.3 + 126.5 (s, *C*^{3}/*C*$^{3'}$ bpy), 127.5 + 127.9 (s, *C*^{5}/*C*$^{5'}$ bpy), 139.1 + 140.0 (s, *C*^{4}/*C*$^{4'}$ bpy), 149.4 + 150.9 (s, *C*^{6}/*C*$^{6'}$ bpy), 154.2 + 155.5 (s, *C*^{2}/*C*$^{2'}$ bpy), 220.1 (s, Pt–COCH$_3$). IR: ν (cm^{-1}) 3046(w), 2962(w), 1621(s), 1600(s), 1490(w), 1470(m), 1444(s), 1317(w), 1241(w), 1159(w), 1105(m), 1070(w), 1018(w), 929(w), 755(s), 721(m), 642(w), 601(w).

[Pt(COMe)Br(4,4′-t-Bu$_2$-bpy)] (**6e**): Yield: 70 mg (75%) (a); 65 mg (70%) (b). Anal. Calc. for $C_{20}H_{27}BrN_2OPt$ (586.42): C, 40.96; H, 4.64; N, 4.78. Found: C, 40.76; H, 4.75; N, 4.69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 18H, C(C*H*$_3$)$_3$), 2.55 (s(br), 3H, COC*H*$_3$), 7.41 + 7.58 (m,2H, *H*^{5}/*H*$^{5'}$ bpy), 7.88 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.80 + 9.36 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.0 (s, C(*C*H$_3$)$_3$), 30.3 (s, C(*C*H$_3$)$_3$), 35.7 (s, *C*(CH$_3$)$_3$), 35.8 (s, *C*(CH$_3$)$_3$), 44.4 (s + d, $^1J_{Pt,H}$ = 90 Hz, COCH$_3$), 118.1 + 119.2 (s, *C*^{3}/*C*$^{3'}$ bpy), 123.9 + 124.8 (s, *C*^{5}/*C*$^{5'}$ bpy), 149.2 + 150.6 (s, *C*^{4}/*C*$^{4'}$ bpy), 154.2 + 155.6 (s, *C*^{6}/*C*$^{6'}$ bpy), 162.9 + 163.8 (s, *C*^{2}/*C*$^{2'}$ bpy), 220.0 (s, Pt–COCH$_3$). IR: ν (cm^{-1}) 3046(w), 2964(m), 2906(w), 2871(w), 1617(s), 1542(w), 1484(m), 1467(m), 1415(m), 1371(w), 1324(w), 1251(w), 1203(w), 1103(m), 1024(w), 927(w), 900(w), 879(w), 848(m), 737(w), 600(m), 555(w).

[Pt(COMe)I(4,4′-t-Bu$_2$-bpy)] (**6f**): Yield: 60 mg (60%) (b). Anal. Calc. for $C_{20}H_{27}IN_2OPt$ (633.42): C, 37.92; H, 4.43; N, 4.42. Found: C, 38.22; H, 4.58; N, 4.33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 18H, C(C*H*$_3$)$_3$), 2.57 (s(br), 3H, COC*H*$_3$), 7.44 + 7.52 (m, 2H, *H*^{5}/*H*$^{5'}$ bpy), 7.90 (m, 2H, *H*^{3}/*H*$^{3'}$ bpy), 8.64 + 9.54 (m, 2H, *H*^{6}/*H*$^{6'}$ bpy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.1 (s, C(*C*H$_3$)$_3$), 30.4 (s, C(*C*H$_3$)$_3$), 35.6 (s, *C*(CH$_3$)$_3$), 35.8 (s, *C*(CH$_3$)$_3$), 48.0 (s + d, $^1J_{Pt,H}$ = 82 Hz, COCH$_3$), 118.3 + 119.5 (s, *C*^{3}/*C*$^{3'}$ bpy), 124.1 + 124.7 (s, *C*^{5}/*C*$^{5'}$ bpy), 148.2 + 149.5 (s, *C*^{4}/*C*$^{4'}$ bpy), 154.4 + 154.9 (s, *C*^{6}/*C*$^{6'}$ bpy), 163.6 + 164.9 (s, *C*^{2}/*C*$^{2'}$ bpy), 221.9 (s, Pt–COCH$_3$). IR: ν (cm^{-1}) 3046(w), 2962(m), 2904(w), 2869(w), 1625(s), 1614(s), 1542(m), 1479(w), 1465(m), 1411(m), 1367(w), 1324(w), 1252(w), 1201(w), 1097(m), 1020(w), 927(w), 900(w), 883(w), 844(m), 738(w), 599(m), 550(w).

3.7. X-ray crystallography

Single crystals of the complex [Pt(COMe)$_2$(SCN)$_2$(4,4′-*t*-Bu$_2$-bpy)] (**4j**) suitable for X-ray diffraction measurements were obtained by recrystallisation from chloroform/diethyl ether (1/2). Intensity data were collected on a STOE IPDS at 220(2) K with Mo Kα radiation (λ = 0.71073 Å, plane graphite monochromator). Details on crystallographic and data collection parameters are given in Table 5. Absorption correction was applied numerically ($T_{min.}/T_{max.}$ = 0.075/0.232). The structure was solved by direct methods with SHELXS-97 and refined using full-matrix least-square routines against F^2 with SHELXL-97 [15]. Non-hydrogen atoms were

refined with anisotropic and hydrogen atoms with isotropic displacement parameters. Hydrogen atoms were refined according to the "riding model". The methyl groups of one of the two *tert*-butyl groups were found to be disordered over two positions with an occupancy of 55/45. The occupancy was refined without restraints.

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Appendix A. Supplementary material

CCDC 692986 contains 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.

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