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# Synthesis, characterization and decomposition behavior of novel acyl(hydrido)platinum(IV) complexes

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Dedicated to Professor Stanislaw Pasynkiewicz on the occasion of his 70th birthday.

**Abstract**

The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) easily reacts with chelating nitrogen ligands NN (2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) derivatives) to form novel acyl(hydrido)platinum(IV) complexes $[Pt(COMe)_2Cl(H)(NN)]$ (NN = bpy **2a**, 6-*n*-Bubpy **2b**, 6-*sec*-Bubpy **2c**, 6-Phbpy **2d**, 4,4′-$Me_2$bpy **2e**, 4,4′-*tert*-$Bu_2$bpy **2f**, 4,4′-*tert*-$Bu_2$-6-*n*-Bubpy **2g**, phen **2h**, 5-Mephen **2i**, 4-Mephen **2j**, 5-Phphen **2k**) with good to excellent yields (55–95%). The identities of **2a**–**k** were determined by microanalysis, NMR ($^1H$, $^{13}C$) and IR spectroscopies. The crystal structure of $[Pt(COMe)_2Cl(H)(4,4'\text{-}tert\text{-}Bu_2\text{-}6\text{-}n\text{-}Bubpy)]$ (**2g**) has been determined. The Pt–H bond distance was found to be 1.79(2) Å. Complexes **2a**–**k** show an astonishing thermal stability in the solid state ($T_{dec}$ 140–180°C) and decompose with cleavage of acetaldehyde to form acylplatinum(II) complexes [Pt(COMe)Cl(NN)] (**3**). For **2f** it was shown that in boiling solvents (chloroform, methylene chloride, acetone, methanol, toluene, dimethyl sulfoxide, tetrahydrofuran) this decomposition reaction proceeds as well. In boiling chlorinated solvents $[PtCl_2(NN)]$ (**4**) is formed as a side product. 

*Keywords:* Platinum; Acyl complexes; Hydrido complexes; X-ray diffraction

## 1. Introduction

Acyl(hydrido)metal complexes have been proposed as key intermediates in homogeneously catalyzed hydroformylation and aldehyde decarbonylation reactions, as well as in Fischer–Tropsch synthesis. Furthermore, they might be involved as intermediates in the protolysis of metal–acyl bonds and C–H activation reactions of aldehydes [1]. Stable acyl(hydrido)metal complexes with acyl ligands that lack stabilization through chelation are rare and only known with iridium or rhodium as the metal [2]. They are obtained in most cases by oxidative addition of RCHO to low-valent metal complexes. Synthesis of acyl(hydrido)metal complexes starting from the tautomeric hydroxycarbene complexes is not known to date. In an isolated case, Casey et al. described an equilibrium between a hydroxycarbene complex and its tautomeric acyl(hydrido)metal complex [3].

Recently we reported the synthesis of the first acyl(hydrido)platinum(IV) complexes [4] by the reaction of the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) [5] with bpy, 4,4′-$Me_2$bpy and 4,4′-*tert*-$Bu_2$bpy. Here we present the extension of this work, as well as further investigations of the physico-chemical properties of acyl(hydrido)platinum(IV) complexes.

## 2. Results and discussion

The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) reacts with a wide range of bpy and phen derivatives in methylene chloride or tetrahydrofuran to form acyl(hydrido)platinum(IV) complexes $[Pt(COMe)_2Cl(H)(NN)]$ (**2a**–**k**) (Scheme 1). Whereas for bpy complexes **2a**–**g**, there is no distinct influence of the solvent, phen derivatives **2h**–**k** obtained in dichloromethane were found to be more pure than those obtained in tetrahydrofuran.

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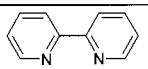
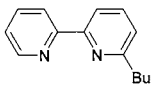
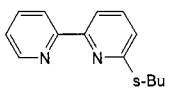
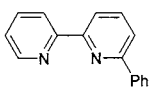
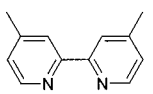
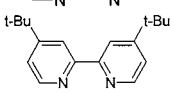
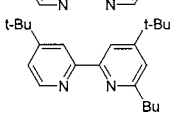
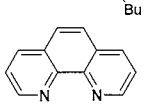
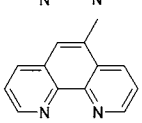
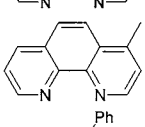
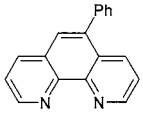
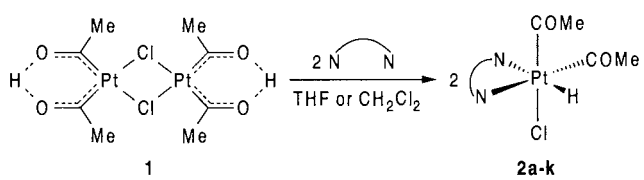
Table 1
Isolated yields, decomposition temperatures and selected $^1$H-NMR ($\delta$ in ppm, $J$ in Hz) and IR ($\nu$ in cm$^{-1}$) data for **2**

| Complex | N N | Isolated yield, % | $T_{dec.}$, °C | $^1$H NMR | | IR | |
|---|---|---|---|---|---|---|---|
| | | | | δ(Pt*H*) | $^1J$(Pt,H) | ν(Pt-Cl) | ν(Pt-H) |
| **2a** |  | 90 | 174 | -18.32 | 1566 | 246 | 2249 |
| **2b** |  | 81 | 150 | -17.67 | 1496 | 241 | 2256 |
| **2c** [a] |  | 79 | 150 | -17.62<br>-17.55 | 1484<br>1485 | 243 | 2267 |
| **2d** |  | 59 | 140 | -18.77 | 1513 | 250 | 2270 |
| **2e** |  | 95 | 175 | -17.83 | 1552 | 241 | 2215 |
| **2f** |  | 85 | 150 | -18.07 | 1541 | 246 | 2233 |
| **2g** |  | 77 | 160 | -17.50 | 1474 | 246 | 2233 |
| **2h** |  | 95 | 180 | -18.08 | 1582 | 246 | 2245 |
| **2i** [a] |  | 55 | 180 | -18.09<br>-17.99 | 1578<br>1570 | 243 | 2232 |
| **2j** [a] |  | 84 | 150 | -18.01<br>-17.92 | 1574<br>1564 | 246 | 2238 |
| **2k** [a] |  | 73 | 140 | -18.05<br>-17.97 | 1579<br>1574 | 251 | 2236 |

[a] Complexes **2c**, **2i**, **2j** and **2k** are isolated as mixture of two isomers in a ratio about 1:1 (see text.).

The platinum(IV) complexes **2a**–**k** were isolated as slightly air-sensitive off-white or pale yellow microcrystalline substances. Yields, decomposition temperatures as well as selected NMR and IR spectroscopic data are compiled in Table 1. The presence of a hydrido ligand in **2a**–**k** is confirmed by their $^1$H-NMR and IR spectra that show high-field Pt–H resonances from −17.50 to −18.77 ppm and sharp absorption bands between 2215 and 2270 cm$^{-1}$, being consistent with literature data for terminal hydrido ligands [6]. The large values of the $^1J$(Pt, H) coupling constants (1474–1582 Hz) are characteristic for hydrido ligands *trans* to nitrogen ligands in platinum(IV) complexes [7]. The two acetyl groups are not chemical shift equivalent ($\Delta\delta(^1H) = 0.6–0.8$ ppm, $\Delta\delta(^{13}C_{Me}) = 2.0–3.5$ ppm, $\Delta\delta(^{13}C_{CO}) = 5–7$ ppm). By means of COSY- and HETCOR-NMR experiments it was shown for complex **2b** that acyl group protons, which are higher shifted in $^1$H-NMR spectra,




Scheme 1. Synthesis of acyl(hydrido)platinum(IV) complexes **2a**–**k**. The ligands NN are shown in Table 1.

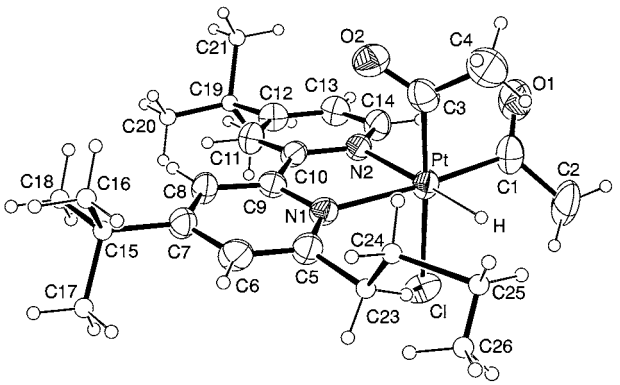



Fig. 1. ORTEP-III plot [9] of $[Pt(COMe)_2Cl(H)(4,4'\text{-}tert\text{-}Bu_2\text{-}6\text{-}n\text{-}Bubpy)]$ (**2g**) showing atom numbering (displacement ellipsoids at 30% probability).

correspond to higher-field-shifted methyl and acyl carbons in $^{13}$C-NMR spectra. There is no systematic dependence of the magnitude of $^3J$(Pt, H) coupling constants of acetyl protons (27–33 Hz) on the NN ligand. However, $^1J$(Pt, C) and $^2J$(Pt, C) coupling constants for higher-field-shifted acetyl group carbons are in all cases significantly higher than for low-field-shifted carbons ($\Delta^2J = 39$–$68$ Hz and $\Delta^1J = 14$–$41$ Hz for methyl and acyl carbons, respectively). On the basis of the well-known dependence of the magnitudes of $^1J$(Pt, C) and $^2J$(Pt, C) coupling constants on *trans* influence [8] the acetyl groups with lower carbon–platinum coupling constants are *trans* to N atom and *cis* to chloro ligand.

The formation of the acyl(hydrido)platinum(IV) complexes according to Scheme 1 is highly regioselective. In all complexes the hydrido and chloro ligands are *trans* and *cis*, respectively, to the nitrogen ligand. With symmetrically substituted ($C_{2v}$ symmetry) NN ligands only one isomer is formed (complexes **2a**, **e**, **f**, **h**). As the doubling of the Pt*H* resonances shows, in positions 4 and 5 non-symmetrically substituted phen ligands give rise to the formation of two isomers (complexes **2i**, **j**, **k**). They are formed in about 1:1 ratio, revealing that there is no directing influence of the methyl and phenyl substituents in these positions.

In the case of asymmetrically 6-substituted bpy ligands only one isomer is formed (complexes **2b**, **d**, **g**), which can be seen from the single Pt*H* resonance. Obviously for steric reasons the phenyl and butyl group, respectively, and hydrido ligand are in neighboring position, as was shown by X-ray structure analysis of **2g** (see below). In the 6-*n*-Bu-substituted bpy complexes **2b** and **2g**, the two protons of the β-$CH_2$ group ($NN\text{–}CH_2CH_2CH_2CH_3$) are chemically non-equivalent in $CDCl_3$ (shift difference $\Delta\delta$ 0.20 and 0.24 ppm, respectively) but no splitting is observed in acetone-$d_6$.

Using 6-*sec*-Bubpy (**2c**) two isomers are formed in about 1:1 ratio. As the doubling of C*H* resonances of *sec*-Bu protons and of the Pt*H* resonance in $^1$H-NMR spectrum shows, this diastereoisomerism results from the two asymmetric centers of the molecule, namely the chiral carbon atom of the *sec*-Bu group and the asymmetrically substituted platinum atom.

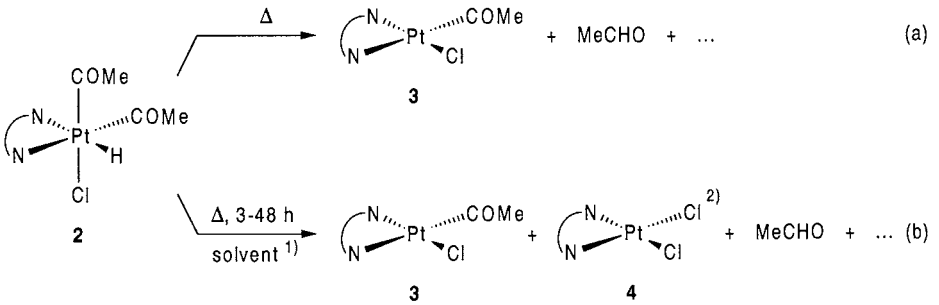
The molecular structure of complex **2g** is shown in Fig. 1. Selected bond lengths and angles are compiled in Table 2. The complex crystallizes as discrete molecules; there are no unusual intermolecular contacts. The platinum center is nearly octahedrally coordinated by 4,4′-*tert*-$Bu_2$-6-*n*-Bubpy ligand, two acetyl ligands and by one chloro and one hydrido ligand. Deviations from the octahedral coordination seem to be mainly due to the restricted bite (N1–Pt–N2 76.3(2)°) of the bpy ligand. Each of the rings of the bpy ligand is planar, but they are tilted from each other by 13.0(5)° (torsion angle N1–C9–C10–N2 8(1)°). These two ring planes of the bpy ligand are tilted from the complex plane PtN1N2C1[1] by 10.0(5)° and 7.7(5)°, respectively. The plane of the acetyl ligand *trans* to the bpy ligand (C1C2O1) and the complex plane form an angle of 48(2)°. Thus, there is no C14–H···O1 hydrogen bond as it was found in the corresponding *tert*-$Bu_2$bpy complex **2f** where the angle is only 24.9(6)° [4].

The hydrido ligand in **2g** could be located in the difference Fourier map and the Pt–H distance was determined to be 1.79(2) Å. Similar values were found in other platinum complexes with terminal hydrido ligands [6], among them complex **2f** (1.72(5) Å). Within the experimental error ($3\sigma$), there are no significant differences in the geometrical parameters either between the two acetyl ligands (mean values: Pt–C 2.00 Å, C–O 1.20 Å, C–C 1.50 Å; all angles between 118(1) and 121.4(9)°) or from those in complex **2f** [4].

Table 2
Selected bond lengths and angles for $[Pt(COMe)_2Cl(H)(4,4'\text{-}tert\text{-}Bu_2\text{-}6\text{-}n\text{-}Bubpy)]$ (**2g**)

| | | | |
|---|---|---|---|
| *Bond distances* (Å) | | | |
| Pt–N(1) | 2.194(7) | Pt–C(3) | 2.00(1) |
| Pt–N(2) | 2.151(7) | C(1)–O(1) | 1.20(1) |
| Pt–Cl | 2.479(3) | C(3)–O(2) | 1.21(1) |
| Pt–H | 1.79(2) | C(1)–C(2) | 1.50(2) |
| Pt–C(1) | 2.00(1) | C(3)–C(4) | 1.50(2) |
| *Bond angles* (°) | | | |
| C(1)–Pt–C(3) | 89.2(5) | C(3)–Pt–Cl | 177.1(3) |
| C(1)–Pt–N(2) | 98.7(3) | C(1)–Pt–H | 85(3) |
| C(3)–Pt–N(2) | 92.1(3) | C(3)–Pt–H | 86(3) |
| C(1)–Pt–N(1) | 174.7(4) | N(1)–Pt–H | 100(3) |
| C(3)–Pt–N(1) | 89.3(3) | N(2)–Pt–H | 176(3) |
| N(1)–Pt–N(2) | 76.3(2) | N(1)–Pt–Cl | 88.1(2) |
| C(1)–Pt–Cl | 93.2(4) | N(2)–Pt–Cl | 86.0(2) |
| | | Cl–Pt–H | 95(3) |

[1] Although the H-ligand was found in the difference Fourier map, the calculation of the complex plane around the Pt atom (PtN1N2C1H) was performed without the H atom due to the relative uncertainty in the location of H atoms in heavy atom structures.




Scheme 2. Thermal decomposition of **2a**, **e**, **f**, **h** in the solid state (a) and of **2f** in solution (b). (1) Solvent: chloroform, methylene chloride, acetone, methanol, toluene, dimethyl sulfoxide, tetrahydrofuran. (2) Side product in chlorinated solvents.

Complexes **2a**–**k** exhibit an astonishing thermal stability. In solid state they do not decompose until 140°C (**2d**, **k**) to 180°C (**2h**, **i**) (Table 1). In case of **2a**, **e**, **f**, **h**, it was shown that the first step is the reductive elimination of acetaldehyde (GC-MS) and the formation of acyl(chloro)platinum(II) complexes [Pt(COMe)Cl(NN)] (**3**) (Scheme 2).

Thermogravimetric analysis (TG) of complexes **2f** and **2h** (Fig. 2) exhibits that the reductive elimination (step I; **2f**: $\Delta m$ 8.1% (obs.), 7.5% (calcd.); **2h**: $\Delta m$ 9.9% (obs.), 8.8% (calcd.)) is quite well separated from the further decomposition of **3**, which in the end (ca. 600°C) leads nearly to metallic platinum (**2f**: $\Delta m$ 53.9% (obs.), 66.7% (calcd.); **2h**: $\Delta m$ 59.9% (obs.), 60.8% (calcd.)).

Decomposition of the acyl(hydrido)platinum(IV) complex **2f** in a range of different solvents (Scheme 2) resulted in reductive elimination to give **3**. Using chlorinated solvents, dichloroplatinum(II) complex **4** is formed as the second product, with **3**:**4** ratio from about 10:1 (in $CH_2Cl_2$) and 3:1 (in $CHCl_3$), respectively, to 1:1 depending on reaction time and temperature. For example, **2f** decomposes in boiling $CHCl_3$ within 1 h, leading to a mixture of **3** and **4** in ratio about 1:1. At room temperature the full conversion of **2f** into **3** and **4** is much slower and takes up to 1 month with ratio **3**:**4** ca. 3:1. Toluene and dimethyl sulfoxide were found to be the only solvents that cause a clean ($>95\%$) reductive elimination to give **3** without major side products. The lowest rate of conversion was observed in acetone and tetrahydrofuran.

The investigations contribute to a deeper understanding of a reaction sequence which is relevant to homogenously catalyzed reactions, namely (i) rearrangement in the sense of oxidative addition of hydroxycarbene ligands (intramolecularly stabilized by hydrogen bonds) in platinum(II) complexes to give acyl(hydrido)-platinum(IV) complexes followed by (ii) a reductive elimination of aldehydes yielding acyl platinum(II) complexes.

## 3. Experimental

All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Solvents were dried prior to use: $Et_2O$ and THF over Na–benzophenone, $CH_2Cl_2$ over $CaH_2$. $^1$H- and $^{13}$C-NMR spectra were recorded on Varian Gemini 200 and Varian VXR 400 NMR spectrometers. Chemical shifts are relative to $CHCl_3$ ($\delta$ 7.24) and $CDCl_3$ ($\delta$ 77.0) as internal references. Assignment of NMR signals for **2b** revealed by $^1$H-$^1$H COSY- and $^1$H-$^{13}$C HETCOR-NMR experiments. IR spectra were recorded on a Galaxy FT-IR spectrometer Mattson 5000 using CsBr pellets. Microanalyses (C, H, N, Cl) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. Thermogravimetric investigations were accomplished with a NETZSCH STA 409 C thermal analysis system. The complex $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) was prepared according to the literature method [5a].

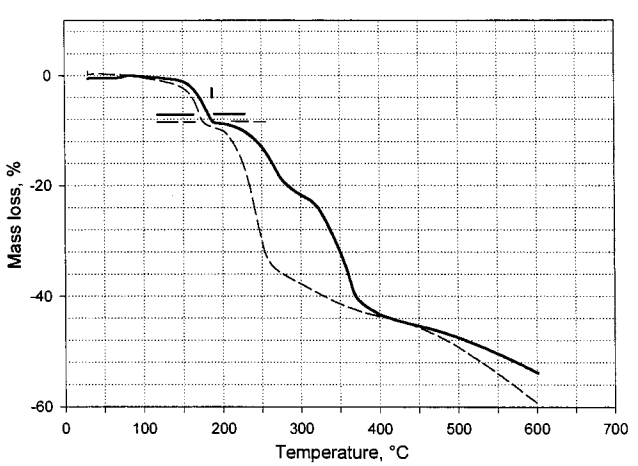



Fig. 2. TG curves for the decomposition of **2f** (solid line) and **2h** (broken line) under helium. Theoretical mass loss for the reductive elimination step (I) is marked by horizontal bars.

### 3.1. Preparation of complexes [Pt(COMe)$_2$Cl(H)(NN)] (2)

In a typical synthesis, to a suspension of [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (50 mg, 0.08 mmol) in methylene chloride or THF (4 ml), cooled down to −50°C, NN ligand (0.16 mmol) was added. In most cases the pale yellow suspension immediately changed color to orange–red. The reaction mixture was warmed up to 0°C over 10 min yielding a clear pale yellow solution. After adding diethyl ether (10–15 ml) an off-white, microcrystalline product was filtered off, washed with diethyl ether and dried briefly in vacuo. The solid substances are stable on air for 5–15 min. Complexes **2a**, **2e** and **2f** are fully characterized in [4].

**2b** (NN = 6-*n*-Bubpy): Yield: 81%. Anal. Found: C, 39.84; H, 4.62; N, 5.13; Cl, 6.97. $C_{18}H_{23}ClN_2O_2Pt$ (529.93). Anal. Calc.: C, 40.80; H, 4.37; N, 5.29; Cl, 6.69. IR (CsBr): *ν*(Pt–Cl) 241, *ν*(C=O) 1670, 1702, *ν*(Pt–H) 2256 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 500 MHz): *δ* = −17.67 (s + d, 1H, $^1J$(Pt, H) = 1496.1 Hz, Pt*H*), 1.04 (t, 3H, $CH_2CH_3$), 1.56 (m, 2H, $CH_2CH_3$), 1.73 (m, 1H, NN–$CH_2CH$*H*), 1.93 (m, 1H, NN–$CH_2CH$*H*), 2.30 (s + d, 3H, $^3J$(Pt, H) = 29.5 Hz, $COCH_3$), 3.02 (s + d, 3H, $^3J$(Pt, H) = 28.2 Hz, $COCH_3$), 3.37 ('t', 2H, NN–$CH_2$), 7.46 (d, 1H, C$^5$*H*), 7.60 (t, 1H, C$^{5'}$*H*), 7.91 (t, 1H, C$^4$*H*), 8.00 (d, 1H, C$^3$*H*), 8.04 (t, 1H C$^{4'}$*H*), 8.13 (d, 1H, C$^{3'}$*H*), 9.40 (d, 1H, C$^{6'}$*H*). $^{13}$C-NMR ($CDCl_3$, 125 MHz,): *δ* = 13.92 ($CH_2CH_3$), 22.76 ($CH_2CH_3$), 31.45 (NN–$CH_2CH_2$), 42.51 (s + d, $^3J$(Pt, C) = 37.9 Hz, NN–$CH_2$), 43.23 (s + d, $^2J$(Pt, C) = 291.2 Hz, $COCH_3$), 46.84 (s + d, $^2J$(Pt, C) = 242.4 Hz, $COCH_3$), 120.78 (C$^{4'}$H), 123.54 (C$^{3'}$H), 125.40 (C$^{5'}$H), 126.07 (C$^5$H), 139.17 (C$^3$H), 139.32 (C$^4$H), 149.86 (C$^{6'}$H), 154.79 (C$^2$), 156.06 (C$^{2'}$), 164.25 (C$^6$), 191.64 (s + d, $^1J$(Pt, C) = 892.4 Hz, $COCH_3$), 197.03 (s + d, $^1J$(Pt, C) = 877.8 Hz, $COCH_3$).

**2c** (NN = 6-*sec*-Bubpy, mixture of two isomers): Yield: 79%. Anal. Found: C, 40.83; H, 4.71; N, 5.30; Cl, 6.96. $C_{18}H_{23}ClN_2O_2Pt$ (529.93). Anal. Calc.: C, 40.80; H, 4.37; N, 5.29; Cl, 6.69. IR (CsBr): *ν*(Pt–Cl) 243, *ν*(C=O) 1659, 1681, 1697, *ν*(Pt–H) 2267 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 400 MHz): *δ* = −17.62/−17.55 (s + d, 1H/1H, $^1J$(Pt, H) = 1484.4/1484.8 Hz, Pt*H*), 0.92/1.02 (t, 3H/3H, $CH_2CH_3$), 1.28/1.48 (d, 3H/3H, $CHCH_3$), 1.62–1.76 (m, 3H, $CH_2CH_3$ + $CHCH_3$), 2.00–2.07 (m, 1H, $CHHCH_3$), 2.28/2.30 (s + d, 3H/3H, $^3J$(Pt ,H) = 29.4/29.8 Hz, $COCH_3$), 3.01/3.02 (s + d, 3H/3H, $^3J$(Pt, H) = 28.6/28.0 Hz, $COCH_3$) 3.95/3.95 (m, 1H/1H, $CHCH_3$), [7.45 (m, 2H), 7.55 (m, 2H), 7.91 (m, 2H), 7.98 (m, 4H), 8.12 ('d', 2H), 9.33 (m, 2H)][2]. $^{13}$C-NMR ($CDCl_3$, 101 MHz): *δ* = 11.96/11.98 ($CH_2CH_3$), 20.22/20.97 (NN–$CHCH_3$), 29.91/30.00 ($CH_2CH_3$), 43.15/43.20 (s + d, $^2J$(Pt, C) = 291.7/291.7 Hz, $COCH_3$), 46.50/46.60 (s + d, $^2J$(Pt, C) = 242.4/242.4 Hz, $COCH_3$), 47.66/48.15 (s + d, $^3J$(Pt, C) = 38.5/39.8 Hz, NN–$CHCH_3$), [121.09, 121.22, 123.02 (2 ×), 123.65, 125.99, 126.00, 126.03, 139.28 (2 ×), 139.62 (2 ×), 139.66 (2 ×), 149.82, 149.94, 154.48, 156.53, 156.63, 169.18], 191.44/191.85 (s + d, $^1J$(Pt, C) = 899.2/900.0 Hz, $COCH_3$), 196.66/196.86 (s + d, $^1J$(Pt, C) = 885.9/885.9 Hz, $COCH_3$).

**2d** (NN = 6-Phbpy): Yield: 59%. Anal. Found: C, 43.25; H, 3.56; N, 4.76; Cl, 6.67. $C_{20}H_{19}ClN_2O_2Pt$ (549.92). Anal. Calc.: C, 43.68; H, 3.48; N, 5.09; Cl, 6.45. IR (CsBr): *ν*(Pt–Cl) 250, *ν*(C=O) 1662, 1695, *ν*(Pt–H) 2270 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 500 MHz): *δ* = −18.77 (s + d, 1H, $^1J$(Pt, H) = 1512.7 Hz, Pt*H*), 1.96 (s + d, 3H, $^3J$(Pt, H) = 33.2 Hz, $COCH_3$), 2.77 (s + d, 3H, $^3J$(Pt, H) = 28.2 Hz, $COCH_3$), [7.57 (m, 5H), 7.79 (m, 2H), 8.02 (m, 2H), 8.17 (m, 2H), 9.29 (m, 1H)]. $^{13}$C-NMR ($CDCl_3$, 101 MHz): 43.89 (s + d, $^2J$(Pt, C) = 281.4 Hz, $COCH_3$), 46.36 (s + d, $^2J$(Pt, C) = 214.7 Hz, $COCH_3$), [122.23, 124.05, 126.40, 126.54, 128.13, 129.88, 130.00, 139.17, 139.56, 142.13, 149.93, 154.86, 155.80, 162.87 (s + d, *J*(Pt, C) = 20.8 Hz)], 191.47 (s + d, $^1J$(Pt, C) = 910.8 Hz, $COCH_3$), 196.80 (s + d, $^1J$(Pt, C) = 893.8 Hz, $COCH_3$).

**2g** (NN = 4,4′-*tert*-Bu$_2$-6-*n*-Bubpy): Yield: 77%. Anal. Found: C, 49.08; H, 6.14; N, 4.18; Cl, 5.68. $C_{26}H_{39}ClN_2O_2Pt$ (642.14). Anal. Calc.: C, 48.63; H, 6.12; N, 4.36; Cl, 5.52. IR (CsBr): *ν*(Pt–Cl) 246, *ν*(C=O) 1663, 1693, *ν*(Pt–H) 2233 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 200 MHz): *δ* = −17.50 (s + d, 1H, $^1J$(Pt, H) = 1474.2 Hz, Pt*H*), 1.04 (t, 3H, $CH_2CH_3$), 1.38 (s, 9H, $3CH_3$), 1.40 (s, 9H, $3CH_3$), 1.51 (m, 2H, $CH_2CH_3$), 1.68 (m, 1H, NN–$CH_2CH$*H*), 1.92 (m, 1H, NN–$CH_2CH$*H*), 2.30 (s + d, 3H, $^3J$(Pt, H) = 29.4 Hz, $COCH_3$), 3.00 (s + d, 3H, $^3J$(Pt, H) = 27.0 Hz, $COCH_3$) 3.31 (m, 2H, NN–$CH_2$), [7.40 ('d', 1H), 7.57 (m, 1H), 7.93 ('d', 1H), 8.06 ('d', 1H), 9.23 (dd, 1H)]. $^{13}$C-NMR ($CDCl_3$, 50 MHz): *δ* = 13.76 ($CH_2CH_3$), 22.65 ($CH_2CH_3$), 30.23 ($C(CH_3)_3$), 30.26 ($C(CH_3)_3$), 31.49 (NN–$CH_2CH_2$), 35.15 ($C(CH_3)_3$), 35.34 ($C(CH_3)_3$), 42.55 (s + d, $^3J$(Pt, H) = 36.9 Hz, NN–$CH_2$), 43.17 (s + d, $^2J$(Pt, C) = 290.9 Hz, $COCH_3$), 46.78 (s + d, $^2J$(Pt, C) = 236.2 Hz, $COCH_3$), [117.84, 120.26, 122.55, 123.47, 149.26, 154.89, 156.04, 163.62, 163.75, 163.80], 191.83 (s + d, $^1J$(Pt, C) = 906.3 Hz, $COCH_3$), 198.25 (s + d, $^1J$(Pt, C) = 876.0 Hz, $COCH_3$).

**2h** (NN = phen): Yield: 95%. Anal. Found: C, 38.63; H, 3.23; N, 5.59; Cl, 7.06. $C_{16}H_{15}ClN_2O_2Pt$ (497.84). Anal. Calc.: C, 38.60; H, 3.04; N, 5.63; Cl, 7.12. IR (CsBr): *ν*(Pt–Cl) 246, *ν*(C=O) 1661, 1698, ν(Pt–H) 2245 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 200 MHz): *δ* = −18.08 (s + d, 1H, $^1J$(Pt, H) = 1582.4 Hz, Pt*H*), 2.32 (s + d, 3H, $^3J$(Pt, H) = 29.1 Hz, $COCH_3$), 3.03 (s + d, 3H, $^3J$(Pt, H) = 29.9 Hz, $COCH_3$), [7.92 (m, 4H), 8.51 (m, 2H), 9.30 (m, 1H), 9.84 (m, 1H)]. $^{13}$C-NMR ($CDCl_3$,

[2] Aromatic hydrogen and carbon atoms are given in square brackets.

101 MHz): δ = 43.66 (s + d, $^2J$(Pt, C) = 294.2 Hz, CO*C*H$_3$), 46.84 (s + d, $^2J$(Pt, C) = 232.1 Hz, CO*C*H$_3$), [125.37, 125.62 (s + d, $J$(Pt, C) = 16.6 Hz), 127.30, 128.01, 130.91, 131.31, 138.44, 138.54, 145.76, 146.38, 150.50, 152.13 (s + d, $J$(Pt, C) = 31.9 Hz)], 191.95 (s + d, $^1J$(Pt, C) = 886.4 Hz, *C*OCH$_3$), 197.31 (s + d, $^1J$(Pt, C) = 862.8 Hz, *C*OCH$_3$).

**2i** (NN = 5-Mephen, mixture of two isomers): Yield: 55%. Anal. Found: C, 39.73; H, 3.69; N, 5.30; Cl, 7.24. $C_{17}H_{17}ClN_2O_2Pt$ (511.86). Anal. Calc.: C, 39.89; H, 3.35; N, 5.47; Cl, 6.93. IR (CsBr): $\nu$(Pt–Cl) 243, $\nu$(C=O) 1660, 1695, $\nu$(Pt–H) 2232 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta = -18.09/-17.99$ (s + d, 1H/1H, $^1J$(Pt, H) = 1578.0/1569.6 Hz, Pt*H*), 2.31/2.31 (s + d, 3H/3H, $^3J$(Pt, H) = 28.4/28.4 Hz, COC*H*$_3$), 2.80/2.80 (3H/3H, NN–C*H*$_3$), 3.03/3.03 (s + d, 3H/3H, $^3J$(Pt, H) = 29.6/29.6 Hz, COC*H*$_3$), [7.87 (m, 6H), 8.40 (m, 2H), 8.63 (m, 2H), 9.27 (m, 2H), 9.80 (m, 2H)]. $^{13}$C-NMR ($CDCl_3$, 125 MHz): $\delta$ = 18.71/19.95 (NN–*C*H$_3$), 43.51/43.69 (s + d, $^2J$(Pt, C) = 286.2/291.2 Hz, CO*C*H$_3$), 46.88/46.92 (s + d, $^2J$(Pt, C) = 233.4/225.4 Hz, CO*C*H$_3$), [125.12, 125.31, 125.32, 125.59 (s + d, $J$(Pt, C) = 15.9 Hz), 126.14, 126.78, 130.68, 130.98, 131.12, 131.53, 134.73, 135.12, 135.17, 135.52, 137.45, 137.58, 144.99, 145.59, 145.84, 146.46, 149.44, 149.90, 151.14 (s + d, $J$(Pt, C) = 29.92 Hz), 151.63 (s + d, $J$(Pt, C) = 31.9 Hz)], 191.65/191.79 (*C*OCH$_3$)[3], 197.17/197.59 (*C*OCH$_3$).

**2j** (NN = 4-Mephen, mixture of two isomers): Yield: 84%. Anal. Found: C, 40.10; H, 3.66; N, 5.35; Cl, 7.29. $C_{17}H_{17}ClN_2O_2Pt$ (511.86). Anal. Calc.: C, 39.89; H, 3.35; N, 5.47; Cl, 6.93. IR (CsBr): $\nu$(Pt–Cl) 246, $\nu$(C=O) 1660, 1698, $\nu$(Pt–H) 2238 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta = -18.01/-17.92$ (s + d, 1H/1H, $^1J$(Pt, H) = 1573.6/1563.5 Hz, Pt*H*), 2.33/2.34 (s + d, 3H/3H, $^3J$(Pt, H) = 28.1/28.1 Hz, COC*H*$_3$), 2.88/2.88 (s, 3H/3H, NN–C*H*$_3$), 3.04/3.05 (s + d, 3H/3H, $^3J$(Pt, H) = 29.0/29.0 Hz, COC*H*$_3$), [7.69 ('d', 1H), 7.83 (m, 2H), 7.95 (m, 3H), 8.11 (m, 2H), 8.51 ('t', 1H), 8.52 ('t', 1H), 9.19 (m, 1H), 9.33 (m, 1H), 9.72 (m, 1H), 9.87 (m, 1H)]. $^{13}$C-NMR ($CDCl_3$, 100 MHz): $\delta$ = 19.03/19.03 (s, NN–*C*H$_3$), 43.37/43.52 (s + d, $^2J$(Pt, C) = 265.0/265.0 Hz, CO*C*H$_3$), 46.84/46.90 (s + d, $^2J$(Pt, C) = 226.7/226.7 Hz, CO*C*H$_3$), [123.67, 124.40, 125.17, 125.46 (s + d, $J$(Pt, H) = 17.0 Hz), 126.19, 126.51 (s + d, $J$(Pt, H) = 17.0 Hz), 126.92, 127.55, 130.60, 130.91, 130.96, 138.31, 138.44, 145.28, 145.82, 145.97, 146.52, 148.46, 148.54, 149.73, 150.40, 151.63 (s + d, $J$(Pt, H) = 31.9 Hz), 152.22 (s + d, $J$(Pt, H) = 31.9 Hz)][4], 191.75/191.87 (s + d, $^1J$(Pt, C) = 886.8/889.5 Hz, *C*OCH$_3$), 197.64/197.95 (*C*OCH$_3$).

**2k** (NN = 5-Phphen, mixture of two isomers): Yield: 73%. Anal. Found: C, 45.91; H, 3.90; N, 4.88; Cl, 6.17. $C_{22}H_{19}ClN_2O_2Pt$ (573.94). Anal. Calc.: C, 46.04; H, 3.34; N, 4.88; Cl, 6.18. IR (CsBr): $\nu$(Pt–Cl) 251, $\nu$(C=O) 1663, 1698, $\nu$(Pt–H) 2236 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta = -18.05/-17.97$ (s + d, 1H/1H, $^1J$(Pt, H) = 1579.5/1573.8 Hz, Pt*H*), 2.35/2.35 (s + d, 3H/3H, $^3J$(Pt, H) = 28.9/28.9 Hz, COC*H*$_3$), 3.04/3.04 (s + d, 3H/3H, $^3J$(Pt, H) = 29.1/29.1 Hz, COC*H*$_3$), [7.51 (m, 10H), 7.80 (m, 6H), 8.51 (m, 4H), 9.31 (m, 2H), 9.86 (m, 2H)]. $^{13}$C-NMR ($CDCl_3$, 100 MHz): $\delta$ = 43.61/43.65 (s + d, $^2J$(Pt, C) = 289.7/289.7 Hz, CO*C*H$_3$), 46.77/46.83 (s + d, $^2J$(Pt, C) = 231.6/231.6 Hz, CO*C*H$_3$), [125.16, 125.42, 125.58, 125.88, 126.88, 127.48, 129.01, 129.11, 129.12, 129.89, 129.93, 129.96, 130.37, 130.53, 130.69, 130.93, 136.83, 136.97, 137.21, 137.34, 137.40, 138.39, 138.50, 140.44, 141.14, 145.12, 145.76, 145.94, 146.64, 150.17, 151.90, 152.03], 191.96/192.01 (s + d, $^1J$(Pt, C) = 886.4/884.6, *C*OCH$_3$), 197.43/197.72 (s + d, $^1J$(Pt, C) = 862.7/864.4, *C*OCH$_3$).

### 3.2. Thermal decomposition of [Pt(COMe)$_2$(Cl)H(NN)]

Method A: a solution of **2f** was heated in a solvent (see Scheme 2) for 3–72 h. After that, the solvent was evaporated and the residue was dried briefly in vacuo. Method B: **2f**, **h** were heated in a closed tube for 10 min at 150°C under Ar. The residue was dissolved in $CDCl_3$ and investigated by $^1$H-NMR spectroscopy. Acetaldehyde was detected qualitatively in the gas phase (GC–MS) and to a small extend also in solution ($^1$H-NMR). Thermal decomposition of **2a**, **e**, **f** (see Ref. [4]).

**3h**: $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.07 (s, 3H, C*H*$_3$), [7.75 (m, 1H), 7.92 (m, 3H), 8.51 (d, 1H), 8.61 (d, 1H), 9.33 (m, 1H), 9.50 (d, 1H)].

**4f**: $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.46 (s, 18H, C*H*$_3$), [7.51 (d, 2H), 7.87 (s, 2H), 9.57 (d, 2H)]. The spectrum is identical with that of a reference substance prepared by reaction of $K_2[PtCl_4]$ with 4,4′-*tert*-Bu$_2$bpy [10].

### 3.3. X-ray structure determination of **2g**

Intensity data were collected on a Stoe Stadi4 four-circle diffractometer with Mo–K$_\alpha$ radiation (0.71073 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 3. Absorption correction was applied semi-empirically via ψ-scans ($T_{min}/T_{max}$ 0.24/0.33). The structures were solved by direct methods with SHELXS-86 [11] and refined using full-matrix least-squares routines against $F^2$ with SHELXL-93 [11]. Non-hydrogen atoms were refined with anisotropic displacement parameters, H atoms were added to the model in their calculated positions and refined isotropically. The hydrido ligand was found in

[3] Due to restricted solubility and stability of phen derivatives, the $J$(Pt, C) coupling constants could not be measured in all cases.

[4] 23 of 24 aromatic carbons were found.

Table 3
Crystal data and structure refinement for **2g**

| | |
|---|---|
| Empirical formula | $C_{26}H_{39}ClN_2O_2$ Pt |
| Formula weight | 642.13 |
| $T$ (K) | 298(2) |
| Crystal system | Monoclinic |
| Space group | $C2/c$ (no. 15) |
| $a$ (Å) | 23.095(2) |
| $b$ (Å) | 10.865(1) |
| $c$ (Å) | 27.041(2) |
| $\beta$ (°) | 122.906(6) |
| $V$ (Å$^3$) | 5696.8(8) |
| $Z$ | 8 |
| $\rho_{calc.}$ (g cm$^{-3}$) | 1.497 |
| $\mu$ (Mo–K$_\alpha$) (mm$^{-1}$) | 5.042 |
| $F$(000) | 2560 |
| Crystal size (mm) | $0.20 \times 0.20 \times 0.10$ |
| Scan range (°) | 1.79 to 24.97 |
| Reciprocal lattice segments $h$, $k$, $l$ | $-27 \rightarrow 26$, $0 \rightarrow 12$, $-32 \rightarrow 32$ |
| Reflections collected | 5087 |
| Independent reflections | 4990 [$R_{int} = 0.0369$] |
| Data/restraints/parameters | 4990/1/293 |
| Goodness-of-fit on $F^2$ | 1.188 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0436$, $wR_2 = 0.0903$ |
| $R$ indices (all data) | $R_1 = 0.0735$, $wR_2 = 0.1149$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.902 and −0.813 |

the difference Fourier map and refined isotropically although certainty in its location may be compromised by residual electron density near the Pt atom. The methyl groups of *tert*-Bu substituents and two carbon atoms (C(25), C(26)) of *n*-Bu group show large displacement ellipsoids pointing to uncertainty of their location in the crystal due to high flexibility in the packing.

## 4. Supplementary material

Atomic coordinates, equivalent isotropic displacement parameters, hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, all bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Center (CCDC). They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, citing the deposition no. CCDC-128516, the authors and the reference.

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