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A Bis(acetyl)-Bridged Platinum(II) Coordination Polymer as a Building Block for Diacetylplatinum(II) Complexes and Platina-*β*-diketones

Sebastian Schwieger,[†] Frank W. Heinemann,[‡] Christoph Wagner,[†] Ralph Kluge,[†]
Cornelia Damm,[†] Gunter Israel,[†] and Dirk Steinborn*[,†]

*Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Strasse 2,
06120 Halle (Saale), Germany, and Lehrstuhl für Anorganische Chemie, Universität Erlangen-Nürnberg,
Egerlandstrasse 1, 91058 Erlangen, Germany*

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The bis(acetyl)-bridged complex [{Pt(COMe)$_2$}$_n$] (**2**) has been prepared from the platina-β-diketone [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) with hexamethyldisilazane. Reactions of complex **2** with the monodentate P and N donors PPh$_3$, pyrazole (Hpz), pyridine (py), 4-methylpyridine (4-Mepy), and benzylamine (BnNH$_2$) resulted in the formation of the *cis*-diacetylplatinum(II) complexes *cis*-[Pt(COMe)$_2$L$_2$] (L = PPh$_3$, **3**; Hpz, **5**; py, **6a**; 4-Mepy, **6b**; BnNH$_2$, **7**). Reactions with the bidentate N donors 2,2′-bipyridine (bpy), dimethylglyoxime (H$_2$dmg), and pyridazine (pydz) resulted in formation of the complexes *cis*-[Pt(COMe)$_2$(L∩L)] (L∩L = bpy, **4**; H$_2$dmg, **8**) and [Pt$_2$(COMe)$_4$(μ-pydz)$_2$] (**9**), respectively. Furthermore, complex **2** has been found to react with acids such as HX (X = Cl, Br), generated in situ from Me$_3$SiX/H$_2$O, acetylacetone (Hacac), and hexafluoroacetylacetone (Hhfacac) to yield the known platina-β-diketone **1**, the new dinuclear bromo-bridged platina-β-diketone [Pt$_2${(COMe)$_2$H}$_2$(μ-Br)$_2$] (**10**), and new mononuclear platina-β-diketones [Pt{(COMe)$_2$H}(L∩L)] (L∩L = acac, **11**; hfacac, **12**). All complexes were characterized by means of microanalysis and IR and NMR spectroscopy. X-ray diffraction analyses were performed for complexes **10**−**12**, showing a two-dimensional network built up by closed-shell Pt···Pt (d^8−d^8) interactions and bifurcated hydrogen bonds in crystals of complex **10** as well as infinite platinum chains built up by closed-shell Pt···Pt (d^8−d^8) interactions in crystals of complexes **11** and **12**. Complexes **8**, **11**, and **12** have further been analyzed by UV/vis and luminescence spectroscopy in solution and in the solid state as well as time-resolved photo-emf measurements. Additionally, quantum chemical studies on the DFT level of theory revealed very strong O−H···O hydrogen bonds in the platina-β-diketones **10**−**12** (25.6−27.9 kcal/mol).

Introduction

Metalla-β-diketones can be regarded as organometallic analogues of the enol form of hydrogen-bonded β-diketones. Formally they are obtained by replacing the central methine group of a β-diketone with a metal fragment. The first metalla-β-diketone—a Re(I) complex—has been synthesized by Lukehart in 1976 by alkylation of an acetyl(carbonyl) complex and its subsequent protonation.[1] Other octahedral metalla-β-diketones are known with iron,[2] manganese,[3] tungsten,[4] and iridium.[5] In contrast to the aforementioned metalla-β-diketones, platina-β-diketones are coordinatively and electronically unsaturated square-planar 16 valence electron (VE) complexes that are kinetically labile toward ligand substitution reactions. They can be obtained from the reaction of hexachloroplatinic acid with *n*-butanol and 1-trimethylsilylalkynes and have been found to undergo unique sequences of oxidative addition and reductive elimination processes.[6] Furthermore, the catalytic activity of the thoroughly investigated platina-β-diketone [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) in hydrosilylation reactions has been demonstrated.[7] Typical reactivities of **1** toward P and N donors include ligand-induced bridge cleavage (**1** → **A**, Scheme 1) and oxidative addition followed by reductive C−H and/or Cl−H elimination reactions (**A** → **B** → **C/D**).[6,8,9] Reactions with a broad variety of amines as well as with [NMe$_4$]OH and a Proton Sponge led to platina-β-diketonates of platina-β-diketones that can be considered as analogues to platinum-blue complexes (**1** → **E**, Scheme 1).[10] In these reactions only one moiety of the dinuclear

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* To whom correspondence should be addressed. E-mail: steinborn@chemie.uni-halle.de.

[†] Universität Halle.

[‡] Universität Erlangen.

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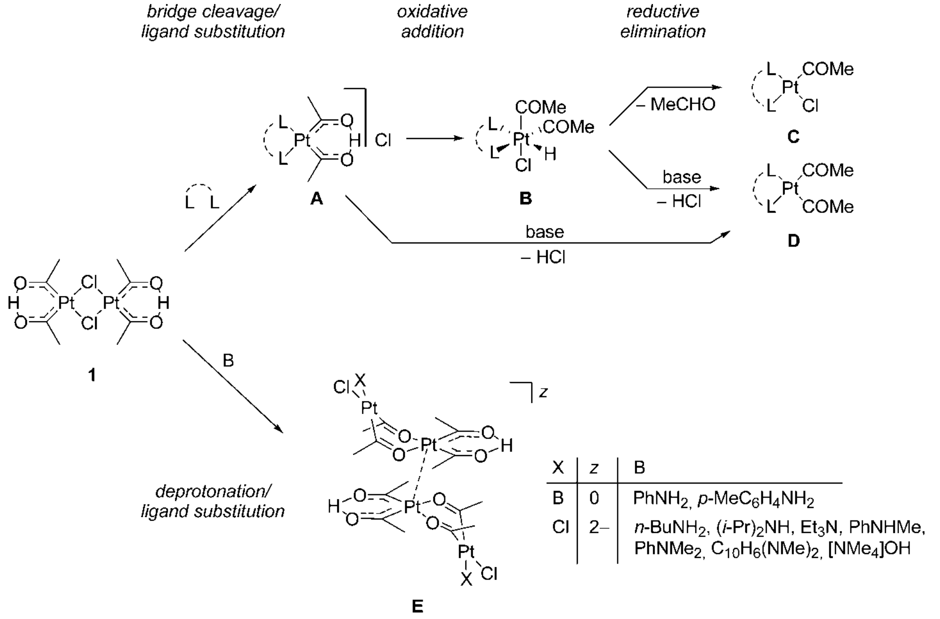
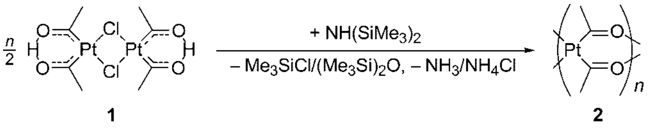
Scheme 1. Reactivity of the Platina-*β*-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (1) toward P and N Donors with and without the Presence of a Base (1 → A/B/D and 1 → A/B/C) and toward Bases B (1 → E)



X	z	B
B	0	$PhNH_2$, $p\text{-}MeC_6H_4NH_2$
Cl	2–	$n\text{-}BuNH_2$, $(i\text{-}Pr)_2NH$, Et_3N, $PhNHMe$, $PhNMe_2$, $C_{10}H_6(NMe)_2$, $[NMe_4]OH$

Scheme 2. Formation of the Diacetylplatinum(II) Coordination Polymer 2



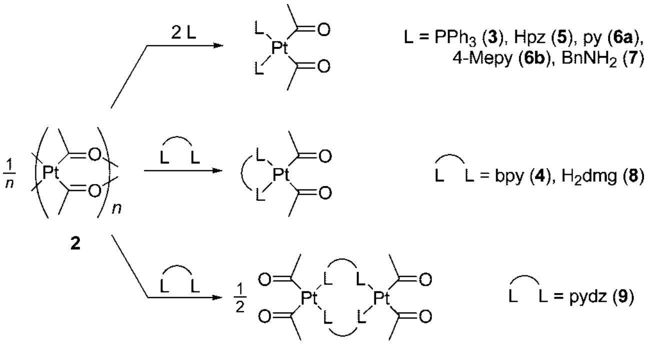
platina-*β*-diketone **1** is deprotonated, while the other one remains intact. The use of an excess of amines did not lead to identifiable products. In this work we report on the synthesis of a new bis(acetyl)-bridged platinum(II) coordination polymer, **2**, that was obtained by complete deprotonation of the platina-*β*-diketone **1** using hexamethyldisilazane. The reactivity of this complex was explored, showing pathways to new platina-*β*-diketones with interesting structural properties and diacetyl platinum(II) complexes.

Results and Discussion

Formation of $[\{Pt(COMe)_2\}_n]$ (2). Reaction of the dinuclear platina-*β*-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with hexamethyldisilazane in dichloromethane resulted in the precipitation of a colorless powder, **2** (Scheme 2). The variation of the ratio of educts from 1:1 to 1:100 did not have any effect on the product obtained. The coordination polymer **2** was formed by formal cleavage of HCl from **1**; thus hexamethyldisilazane acted both as a Brønsted base and as a chloride acceptor. In accordance with that, chlorotrimethylsilane and its hydrolysis product (hexamethyldisiloxane) were found as further products (NMR, GC-MS). Complex **2** was found to react with PPh_3 and 2,2′-bipyridine (bpy), forming the known complexes *cis*-$[Pt(COMe)_2(PPh_3)_2]$ (**3**) and *cis*-$[Pt(COMe)_2(bpy)]$ (**4**) in 86% and 93% isolated yield, respectively (Scheme 3).

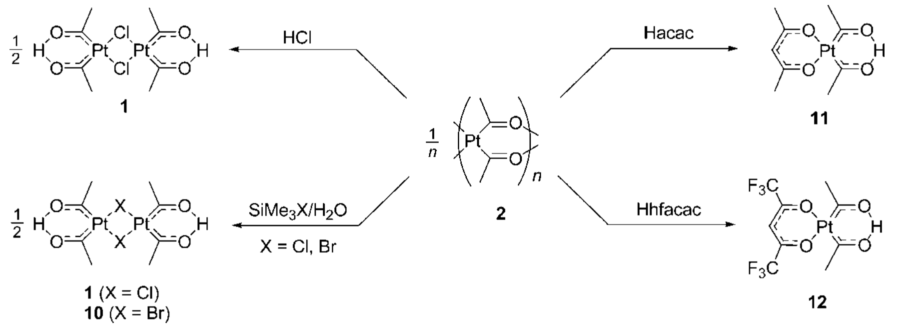
Complex **2** proved to be only barely soluble in all common solvents, thus preventing the recrystallization and its precise characterization. From freshly prepared solutions in $CDCl_3$ it was possible to obtain NMR spectra (^1H, ^{13}C) showing that the two acetyl ligands are NMR spectroscopically identical. In ESI mass spectra a tetranuclear aggregate with Na^+ ($[\{Pt(COMe)_2\}_4] + Na^+$) was identified. Since there were no end groups found, it can be assumed that it is a cyclotetramer. Thus, the results of both characterizations are in agreement but reflect only the solute part of **2**. Microanalyses of all batches of **2** exhibited minor residues of Cl and N (ca. 2%). This might be due to residual amounts of NH_4Cl and/or end groups of linear oligomers.

Scheme 3. Complex 2 as a Building Block for the *cis*-Diacetylplatinum(II) Complexes 3−9



Reactivity of $[\{Pt(COMe)_2\}_n]$ (2). Apart from the two above-mentioned complexes **3** and **4** further diacetylplatinum(II) complexes (**5**−**9**) could be obtained in the reactions of complex **2** with pyrazole (Hpz), pyridine (py), 4-methylpyridine (4-Mepy), benzylamine ($BnNH_2$), dimethylglyoxime (H_2dmg), and pyridazine (pydz) (Scheme 3). Complexes **6a** and **6b** have been found to be unstable in solution due to ligand loss and subsequent CO extrusion from an acetyl ligand, yielding $[Pt(COMe)Me(CO)L]$ (L = py, 4-Mepy). This reaction proceeded faster with **6b**, thus preventing its isolation in a pure state. Both complexes proved to be stable at room temperature over a period of several days in the presence of a 3-fold excess of the pyridine ligand. This finding supports the proposed mechanism that a ligand is eliminated prior to CO extrusion. An analogous decomposition behavior has been observed for L = $BnNH_2$ (complex **7**). As the bipyridine complex,[8] the dimethylglyoxime-coordinated complex **8** is highly stable in the solid state (fp: 192−194 °C) as well as in solution. No decomposition has been observed in dichloromethane solution over a period of several days.

Scheme 4. Complex 2 as a Building Block for the Platina-*β*-diketones 1 and 10−12



The identities of all isolated complexes were confirmed by microanalyses as well as NMR (^{1}H, ^{13}C, ^{195}Pt) and IR spectroscopically. The ^{1}H and ^{13}C NMR spectra clearly gave proof of the constitution (see Experimental Section) of complexes **5**−**9**. Their $^3J_{\mathrm{Pt,H}}$ (22.7−25.5 Hz) and $^2J_{\mathrm{Pt,C}}$/$^1J_{\mathrm{Pt,C}}$ (308.2−378.2/1268.4−1323.5 Hz) coupling constants are in the same ranges as those of other *cis*-diacetylplatinum(II) complexes.[8] This indicates in complexes **5**−**9** a *cis* arrangement of the two acetyl ligands, as also expected because of their high *trans* influence. The dinuclear structure of the pyridazine-bridged complex **9** was proved by ESI-MS measurements showing $[M + H]^+$ and $[M + Na]^+$ peaks in methanol solution. Complex **9** was found to be only barely soluble in common organic solvents but, interestingly, easily soluble in water, where it decomposes within several hours at room temperature.

Furthermore, complex **2** was found to react with HCl in a reverse reaction (with respect to the formation of **2**), yielding the dinuclear platina-*β*-diketone **1** (Scheme 4). The analogous reaction with HBr was not successful and resulted in decomposition of the reaction solution to platinum black. However, the reaction with stoichiometric amounts of HX, generated in situ from an excess of the corresponding $SiMe_3X$ (X = Cl, Br) and H_2O ($n(Me_3SiX)$:$n(H_2O)$ = 4:1), resulted in the formation of the known platina-*β*-diketone **1** and the bromo-bridged platina-*β*-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Br)_2]$ (**10**, Scheme 4). Complex **10** was found to decompose much faster in air than the chloro-bridged complex **1** (2 min vs >30 min). Thus, the synthesis of **10** has to be performed under strictly water-free conditions as realized with an excess of Me_3SiBr. The identity of complex **10** was proved by microanalysis, NMR spectroscopy, and an X-ray crystal structure determination.

Treatment of complex **2** with acetylacetone (Hacac) resulted within 1^1/$_2$ days in a dichroic violet-green precipitate, which could be identified as the mononuclear platina-*β*-diketone $[Pt\{(COMe)_2H\}(acac)]$ (**11**). Likewise, the reaction of complex **2** with hexafluoroacteylacetone (Hhfacac) in dichloromethane resulted in the formation of $[Pt\{(COMe)_2H\}(hfacac)]$ (**12**) as a red crystalline substance (Scheme 4). Both complexes could be characterized by microanalyses, NMR, IR and UV/vis spectroscopy, and X-ray crystal structure determinations.

Structure of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Br)_2]$ (10). The molecular structure of complex **10** is shown in Figure 1; selected distances and angles are given in the caption. The dinuclear molecule exhibits crystallographically imposed C_i symmetry. The platinum atom is square-planar coordinated (sum of angles around Pt: 359.9°), and overall the molecule is planar (largest deviation of a non-hydrogen atom (C2) from the complex plane: 0.34(2) Å). The bond lengths in the platina-*β*-diketone moieties in the bromo- and chloro-bridged complexes **10** and **1** do not significantly differ. The C−O distances (1.26(2)/1.27(3) Å) are between typical C═O double bond (median in ketones: 1.21 Å)[11] and C−O single bond lengths (median in ethers: 1.42 Å),[11] reflecting a partial C−O double bond character, as expected for a hydrogen-bonded hydroxycarbene-acyl system. The intramolecular O1···O2 distance (2.42(2) Å) indicates strong hydrogen bonds. In addition, relatively short intermolecular O2···O2′ and O1···O2′ distances (2.99(2)/3.36(2) Å) show that these are actually part of a pair of bifurcated hydrogen bonds (O1, O2, O2′ and O1′, O2′, O2, Figure 1), thus forming one-dimensional ribbons in crystals of **10**. Because the hydrogen atoms involved in the hydrogen bonds could not be located in the electron density map, the discussion has to be restricted to the positions of the oxygen atoms. Furthermore, Pt···Pt closed-shell d^8−d^8 interactions (d(Pt···Pt) = 3.601(1) Å) give rise to a staircase-like packing of the dinuclear platina-*β*-diketone molecules **10**, thus connecting the hydrogen-bonded ribbons in a second dimension (Figure 2). In crystals of the analogous chloro-bridged platina-*β*-diketone **1** only a packing via Pt···Pt closed-shell d^8−d^8 interactions was found, however being stronger than those in **10**, as indicated by shorter Pt···Pt distances (3.352(1) Å).[12]

Structures of $[Pt\{(COMe)_2H\}(acac)]$ (11) and $[Pt\{(COMe)_2H\}(hfacac)]$ (12). The molecular structures of complexes **11** and **12** are given in the Figures 3 and 4. Selected distances and angles are given in the figure captions. Complex **11** exhibits crystallographically imposed C_{2v} symmetry. The backbone of complex **12** (Pt, O3, O4, C1−C9) was found to be planar, and due to crystal symmetry all atoms above and below that plane are disordered over two equally occupied positions (see Experimental Section). In both complexes the platinum atoms are coordinated in a square-planar manner (sum of angles around Pt: 360.0/360.0°, **11**/**12**). In complex **11** all non-hydrogen atoms are situated in the molecular plane. In complex **12** the largest deviation of non-hydrogen atoms (except F atoms) from the coordination plane is realized by O2 (0.225(9) Å). The Pt−C distances (1.936(4)−1.956(4) Å) are within the typical range for Pt−C distances of other platina-*β*-diketones (median: 1.956 Å, lower/upper quartile: 1.938/1.967 Å, n = 20).[13] The C−O bond lengths in the platina-*β*-diketone as well as in the acetylacetonato moieties (1.263(6)−1.293(5) Å) are between typical lengths of C−O single (median in ethers: 1.42 Å)[11] and C═O double bonds (median in ketones: 1.21 Å),[11] indicating a partial double-bond character in these bonds. Compared to other structurally characterized acetylacetonato platinum(II) complexes (median: 2.019 Å, lower/upper quartile: 2.000/2.033 Å, n = 186),[13] the Pt−O distances in **11** (2.108(3) Å) and in **12** (2.122(2)/2.132(3) Å) are significantly longer. Those in **12** are

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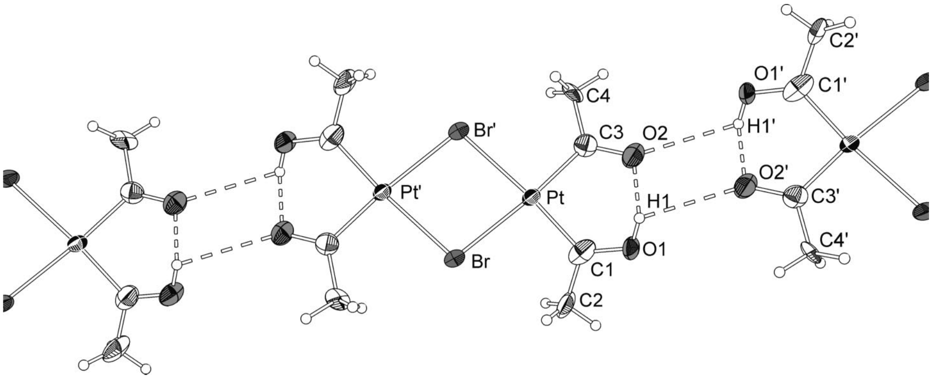

Figure 1. Molecular structure of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Br)_2]$ (**10**). Ellipsoids are shown at the 50% probability level. Selected distances (Å) and angles (deg): Pt−Br 2.580(2), Pt−Br′ 2.575(2), Pt−C1 1.96(2), Pt−C3 1.98(2), C1−O1 1.27(2), C3−O2 1.26(2), O1···O2 2.42(2), O2···O2′ 2.99(2), O1···O2′ 3.36(2), Br−Pt−Br′ 81.22(6), C1−Pt−C3 91.0(8), Pt−Br−Pt′ 98.78(6).

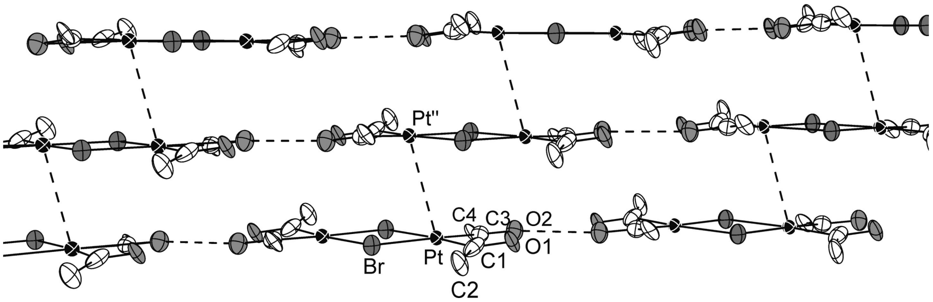

Figure 2. Packing of molecules with closed-shell platinum d^8-d^8 interactions in crystals of **10**. $d(Pt\cdots Pt'') = 3.601(1)$ Å. Distance between coordination planes: 3.48 Å.

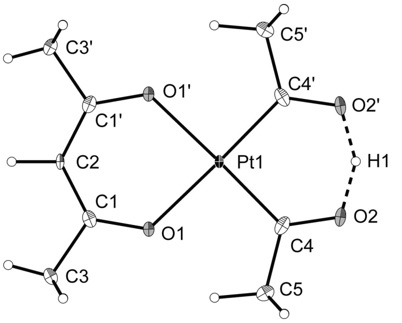

Figure 3. Molecular structure of $[Pt\{(COMe)_2H\}(acac)]$ (**11**). Ellipsoids are shown at the 50% probability level. Selected distances (Å) and angles (deg): Pt−C4 1.943(5), Pt−O1 2.108(3), C4−O2 1.263(6), C1−O1 1.293(5), C1−C2 1.391(5), O2···O2′ 2.408(5), C4−Pt−C4′ 91.5(2), O1−Pt−O1′ 87.9(1).

even the longest ones known up to now. As for other platina-β-diketones, the O···O distance of 2.408(5) Å in complex **11** indicates a strong O−H···O hydrogen bond. Due to disordered O1 and O2 atoms in complex **12**, two values have to be considered (2.389(4)/2.419(5) Å), pointing also to strong hydrogen bonds.

Molecules of complexes **11** and **12** are stacked in the crystals via Pt···Pt closed-shell d^8-d^8 interactions (Figure 5), forming one-dimensional platinum chains. Neighbored molecules are related by an inversion center positioned on the Pt···Pt′ axis. The Pt···Pt′ distances (3.1601(6) Å, **11**; 3.2855(1) Å, **12**) are within the typical range of closed-shell interactions of Pt(II) (in Krogmann's salts: 3.09−3.60 Å).[14] As found in Krogmann's salts, the arrangements of the Pt atoms in the chains are nearly linear (Pt···Pt′···Pt″ angles: 179.41° and 175.32° for **11** and **12**, respectively).

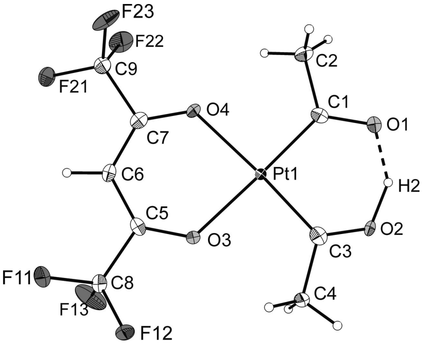

Figure 4. Molecular structure of $[Pt\{(COMe)_2H\}(hfacac)]$ (**12**). Ellipsoids are shown at the 50% probability level. All F-atoms, all H-atoms of the methyl groups, and O1 and O2 are disordered over two equally occupied positions due to a mirror plane identical to the complex plane. In all cases only one of the two disordered atoms is shown. Selected distances (Å) and angles (deg): Pt−C1 1.956(4), Pt−C3 1.936(4), Pt−O3 2.122(2), Pt1−O4 2.132(3), C1−O1 1.265(6), C3−O2 1.288(5), C5−O3 1.271(5), C7−O4 1.269(5), O1···O2 2.389(4), O1···O2′ 2.419(5), O3−Pt−O4 86.6(1), C1−Pt−C3 92.0(2).

UV/Vis Characterization. Previously we have reported on the UV/vis properties of dinuclear platina-β-diketones of the type $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (R = Me, Et, *n*-Pent, *n*-Hex, $(CH_2)_4Ph$)[12] showing in the solid state an absorption band in the visible light region that is absent in solution spectra. It was concluded that this is due to the staircase-like packing of the dinuclear platina-β-diketone molecules in crystals (analogous to that in crystals of **10**) containing alternating intermolecular Pt···Pt d^8-d^8 interactions and intramolecular Pt−Cl−Pt bridges.

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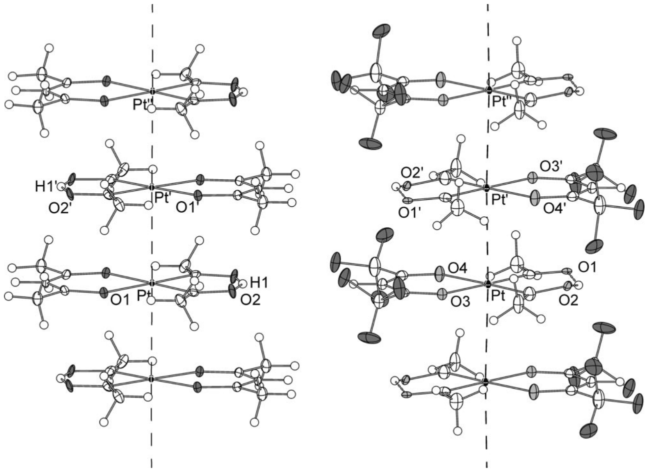

Figure 5. Packing of molecules in crystals of **11** (left) and **12** (right). $d(\mathrm{Pt\cdots Pt}) = 3.1601(6)$ Å (**11**) and 3.2855(1) Å (**12**), Pt···Pt···Pt: 179.41° (**11**) and 175.32° (**12**).

Furthermore, the emissions at $\lambda_{\max} = 555$ nm after excitation of the platina-β-diketones were ascribed to ligand field (d^8-d^8) electronic excited states of the isolated intermolecular Pt···Pt interactions. The structural characteristics and the intensive colors of complexes **8** (blue), **11** (dichroic green-violet), and **12** (red) in the solid state prompted us to perform UV/vis analyses, showing broad absorption bands in the visible light region in solid state spectra but no requisite absorptions in solution spectra (Table 1). Furthermore, as shown in Table 1 in complexes **1** (for comparison), **11**, and **12** $\lambda_{\max}$ of the longest wavelength absorption was found to correlate with the structurally determined intermolecular Pt···Pt distance. In contrast to the platina-β-diketones mentioned above, no emissions were found in the visible light region for complexes **8**, **11**, and **12**. On the other hand, all three complexes show photo-emf signals and thus a spatial separation of the charge carriers e^-/h^+ in the solids after pulse exposure (Figure 6). The principle for the origin of a photo-emf with the measurement arrangement is given in ref 15. While complexes **8** and **11** behave like *n*-type photoconductors (large positive photo-emf signals $U_{\max}$), complex **12** behaves like a *p*-type photoconductor (small negative photo-emf signal $U_{\max}$). The efficiency of the charge separation decreases in the following sequence: complex **8** ≫ **11** > **12** ($U_{\max}$, Table 1). Additionally, the rate of charge carrier recombination is lower in complex **8** as compared to complex **11** (k_1/k_2, Table 1). From the electronic properties of complex **8**, whose solid state structure is unknown until now, it can be concluded that in crystals infinite ···Pt···Pt··· chains are found that are broken up in dichloromethane solutions. The maximum of absorption in the visible light region ($\lambda_{\max} = 637$ nm) indicates that the Pt···Pt distance may be shorter (<3.16 Å) than those in complexes **11** and **12**.

Hydrogen Bond Strength in the Platina-*β*-diketones. High-level DFT calculations (B3LYP/6-311++G(d,p)) of the dinuclear bromo-bridged platina-β-diketone **10** as well as of the mononuclear acetylacetonato-coordinated platina-β-diketones **11** and **12** were performed to determine the strength of the intramolecular hydrogen bonds (ΔE_{hb}) according to the method introduced in ref 16. There it was shown that in enol forms of organic β-diketones and in metalla-β-diketones the hydrogen bond energies can be adequately described by comparing the electronic energies of the equilibrium structure of the hydrogen-bonded system with an "open" structure that was obtained by rigid rotation of the O−H hydrogen atom around the C−O bond by 180° and subsequent relaxation of all bond lengths and angles (but dihedral angles kept frozen). In all cases the calculated equilibrium structures (**10**$_{\mathbf{calc}}$−**12**$_{\mathbf{calc}}$) are in good agreement with the experimentally found structures (see Table 2), thus proving the validity of the quantum chemical model used. In Figure 7 the calculated hydrogen-bonded and the non-hydrogen-bonded ("open") structures **11**$_{\mathbf{calc}}$/**11***$_{\mathbf{calc}}$ are shown as an example. The hydrogen bonds in all three platina-β-diketones **10**−**12** are very strong (25.6−27.9 kcal/mol, see Table 2), being nearly twice as strong as that in acetylacetone (16.1 kcal/mol).[16] Essentially the same values were found in the dinuclear platina-β-diketones **1** and **10** (25.7 vs 25.6 kcal/mol); thus no influence of the bridging halogen atoms (Cl vs Br) was observed. Furthermore, the hydrogen bonds in the neutral mononuclear complexes **11** and **12** (27.9/26.6 kcal/mol) proved to be as strong as that in the mononuclear anionic platina-β-diketone ($[\mathrm{Pt}\{(\mathrm{COMe})_2\mathrm{H}\}\mathrm{Cl}_2]^-$, 27.2 kcal/mol) and significantly stronger as that in the mononuclear cationic platina-β-diketone ($[\mathrm{Pt}\{(\mathrm{COMe})_2\mathrm{H}\}(\mathrm{bpy})]^+$, 19.6 kcal/mol).[16]

Concluding Remarks. In this work the reactivity of the chloro-bridged platina-β-diketone **1** toward hexamethyldisilazane was shown forming a new platinum coordination polymer **2** having bis(acetyl)-bridged $\mathrm{Pt^{II}}(\mu\text{-COMe})_2\mathrm{Pt^{II}}$ building blocks. This reaction requires not only the deprotonation of the platina-β-diketone unit but also the formation of two free coordination sites on the platinum fragment. Thus, the substrate ($\mathrm{NH(SiMe_3)_2}$) has to be a Brønsted base, a chloride acceptor, and may only be a weak donor to prevent the cleavage of the weak $\mathrm{Pt-O_{acetyl}}$ bonds in **2**. Obviously, hexamethyldisilazane fulfills all these three requirements. Additionally, the formation of the oligomeric/polymeric complex **2** is also favored by its insolubility. On the other hand, the analogous reactions with alkyl and aryl amines being stronger nucleophiles and—if any—weaker chloride acceptors resulted in a partial deprotonation of **1** only (**1** → **E**, Scheme 1) and a decomposition by using an excess of amines, respectively.[10]

The deprotonation of **1** yielding the bis(acetyl)-bridged coordination polymer **2** is, in general, reversible, as shown in the reaction of **2** with HCl, $\mathrm{Me_3SiX/H_2O}$ (X = Cl, Br), and Hacac/Hhfacac. These reactions opened up a way to synthesize the new platina-β-diketones **10**−**12**. The bromo-bridged complex **10** is the first dinuclear platina-β-diketone having bridge atoms other than Cl. It is worth mentioning that other ways to synthesize **10** failed: (i) Reactions of $\mathrm{H_2[PtX_6]\cdot}x\mathrm{H_2O}$ in *n*-BuOH with $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ resulted for X = Cl in the formation of complex **1** but for X = Br in the decompostion with formation of platinum black.[17] (ii) Reactions of *cis*-$[\mathrm{PtX_2\{C(OMe)Me\}_2}]$ with water were found for X = Cl to result in the quantitative formation of the platina-β-diketone **1**, whereas for X = Br a slow decomposition occurred.[18] Complexes **11** and **12** are the first platina-β-diketones having *O* donors as coligands. Interestingly, the synthesis of **11** starting from **1** and Hacac failed, most likely because the nucleophilicity of Hacac is too low for cleavage of the Pt−Cl−Pt bridges.

All these reactions as well as the synthesis of $[\mathrm{Pt}\{(\mathrm{COMe})_2\mathrm{H}\}(\mathrm{dppe})][\mathrm{BF_4}]$ from $[\mathrm{Pt(COMe)_2(dppe)}]/\mathrm{H[BF_4]}$[9]

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Table 1. UV/Vis and Luminescence Spectroscopic Data as well as Kinetic Parameters from Photo-emf Measurements[a] of Complexes $[Pt(COMe)_2L_2]$ (8) and $[Pt\{(COMe)_2H\}L_2]$ (1, 11, 12)

complex	L_2	$d(Pt\cdots Pt)$ [Å]	color	absorption (solid state) λ_{max} [nm]	absorption (solution) λ_{max} [nm]	emission (solid state) λ_{max} [nm]	U_{max}	U_1^0/U_2^0 [mV]	k_1/k_2 [s^{-1}]
8	H_2dmg		blue	637 (m, br), 369 (s)	424, 355, 321	[c]	10.3	28.6/−18.3	49.4/30.4
11	acac	3.160(1)	green-violet	591 (m, br), 506 (sh), 327 (s)	341, 307	[c]	2.3	10.2/−7,9	154.6/110.7
12	hfacac	3.2855(1)	red	514 (m, br), 349 (sh), 303 (s)	323, 299	[c]	−0.4	≈0	
1[b]	μ-Cl/μ-Cl	3.352(1)	yellow	412	334, 305	555	0		

[a] Evaluated according to a biexponential decay: $U(t) = U_1^0 \exp(-k_1t) + U_2^0 \exp(-k_2t)$. [b] From ref 12. [c] No emission was observed.

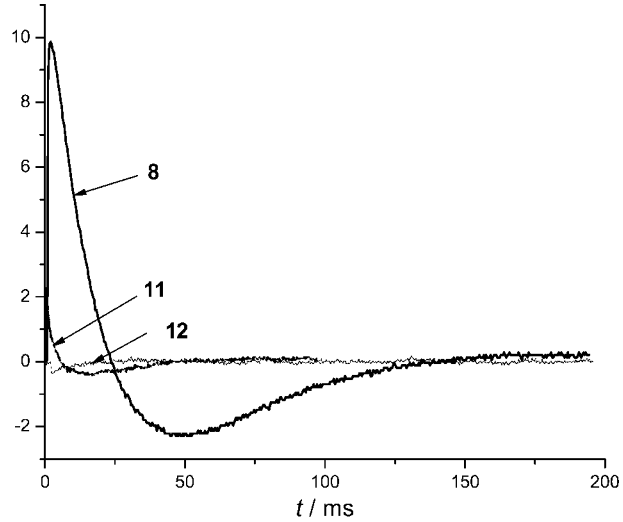

Figure 6. Time-resolved photo-emf signals for the complexes $[Pt(COMe)_2(H_2dmg)]$ (**8**) and $[Pt\{(COMe)_2H\}(L\cap L)]$ ($L\cap L$ = acac, **11**; hfacac, **12**).

give proof that via protonation of diacetyl platinum complexes platina-β-diketones are accessible. The analogous reaction, the protonation of anionic diacetyl complexes $[M(COMe)_2L_x]^-$ (M = Re, Fe; L = CO, Cp) having carbonyl and cyclopentadienyl coligands, is the general (and only) way how metalla-β-diketones $[M\{(COMe)_2H\}L_x]$ were obtained by Lukehart.[19] Due to the electronic saturation (18 VE) of Lukehart's complexes, the attack of the proton is expected to occur directly on the oxygen atoms of the acetyl ligands. In the case of the electronically nonsaturated (16 VE) diacetyl platinum(II) complexes the protonation of the platinum atom in the sense of an oxidative addition reaction followed by a proton shift in the sense of a reductive elimination forming the platina-β-diketone moiety appears to be an alternative. On grounds of the experimental data neither of these two reaction ways can be favored.

Although in crystals of platina-β-diketones $Pt\cdots Pt$ (d^8–d^8) closed-shell interactions were frequently found,[12] so far no infinite $\cdots Pt\cdots Pt\cdots$ chains were observed as in Krogmann's salts.[14] The first examples for this are the mononuclear acetylacetonato-coordinated platina-β-diketones **11** and **12** described herein. Both optical and photoelectrical properties of the complexes do agree with the polymeric $Pt\cdots Pt$ chain structure. Thus, the bis(acetyl)-bridged platinum(II) coordination polymer **2** proved to be a suitable starting complex for the synthesis not only of *cis*-diacetylplatinum(II) complexes having N donors as coligands (**4**–**9**) but also—in the formal reverse of its building reaction—of new platina-β-diketones (**10**–**12**) that have not been accessible in "conventional" ways.

Experimental Section

General Comments. All reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried prior to use ($CHCl_3$, CH_2Cl_2 over CaH_2, diethyl ether, benzene, toluene, *n*-pentane over Na/benzophenone, and acetone over 4 Å molecular sieves) and freshly distilled. NMR spectra (^1H, ^{13}C, ^{19}F, ^{31}P, ^{195}Pt) were recorded at 27 °C on Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to solvent signals ($CDCl_3$, δ_H 7.24, δ_C 77.0; CD_2Cl_2, δ_H 5.32, δ_C 53.8; C_6D_6, δ_H 7.15, δ_C 128.0) as internal references; $\delta(^{19}F)$, $\delta(^{31}P)$, and $\delta(^{195}Pt)$ are relative to external $CFCl_3$ (δ_F 0.0), H_3PO_4 (85%) (δ_P 0.0), and $H_2[PtCl_6]$ in D_2O (δ_{Pt} 0.0), respectively. When necessary, assignments of signals were verified by $^1H,^1H$ and $^{13}C,^1H$ COSY experiments. Microanalyses (C, H, N, Cl, Br) were performed in the Microanalytical Laboratory of the University of Halle using a CHNS-932 (LECO) as well as a VARIO EL (Elementaranalysensysteme) elemental analyzer for C, H, and N and a volumetric analysis (Schöninger) for Cl and Br. IR spectra were recorded on a Mattson 5000 Galaxy FT-IR spectrometer using CsBr or KBr pellets and a Tensor 27 FT-IR spectrometer using an ATR sampler, respectively. Hexachloroplatinic acid was commercially available (m&k GmbH, 47.4% Pt). The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) was prepared according to a previously published procedure.[20] Positive and negative ESI-MS were obtained from a Finnigan Mat. LCQ. The sample solutions were introduced continuously via a syringe pump (flow: 8 μL/min, sheath gas: N_2, ESI spray voltage: 4.1 kV, capillary temperature: 200 °C, capillary voltage: 34 kV). GC-MS analysis was performed on an HP 5890 Series II/HP-5972 MSD (Hewlett-Packard) (column: HP5-MS; 30 m). UV/vis spectra of complexes in dichloromethane solution were performed on a Varian Cary 4E. Reflection data of the complexes in the solid state were collected on a Perkin-Elmer Lambda 19 and recalculated to transmission data following the Kubelka–Munk function.[21] Emission measurements were taken on a Perkin-Elmer LS 50B fluorescence spectrometer ($\lambda_{exc.}$ = 400 nm). Photo-emf measurements were performed using a home-built apparatus consisting of a nitrogen pumped dye laser UDL 210 (Lasertechnik Berlin, > 30 μJ per pulse, $\lambda_{exc.}$ = 337 nm, 2.7 × 10^{13} quanta/flash, $\tau_{1/2}$ = 0.5 ns, registration via 200 MHz digital storage oscilloscope Philips PM3394).[15] For photo-emf measurements pellets were prepared from powdered samples by applying high pressure.

Synthesis of $[\{Pt(COMe)_2\}_n]$ (2). At −78 °C hexamethyldisilazane (0.375 g, 2.323 mmol) was added to a solution of **1** (1.475 g, 2.323 mmol) in dichloromethane (5 mL) with stirring. Then, the reaction mixture was stirred at room temperature for an additional 10 min, whereupon **2** precipitated as colorless powder. The volume of the reaction mixture was reduced in vacuo up to half. Then, the precipitate was filtered at −50 °C and washed with acetone (5 × 10 mL) at the same temperature. Finally, the product was dried in vacuo. Yield: 1.084 g (83%). T_{dec}: 140 °C. Anal. Found: C, 16.74; H, 2.81; Cl, 2.29; N, 2.24. $C_4H_6O_2Pt$ (281.17) requires: C, 17.09; H, 2.15. ^1H NMR (200 MHz, $CDCl_3$): δ 2.40 (s+d, $^3J_{Pt,H}$ = 17.6

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Table 2. Atom Distances (in Å) and Angles (in deg) as well as Relative Electronic Energies of the Calculated Equilibrium Structures $\mathbf{10_{calc}}$−$\mathbf{12_{calc}}$ and the Requisite "Open" Conformers $\mathbf{10^{*}_{calc}}$−$\mathbf{12^{*}_{calc}}$ in Comparison with Crystal Structure Data of Complexes 10−12

	10	10_{calc}	10^{*}_{calc}	11	11_{calc}	11^{*}_{calc}	12	12_{calc}	12^{*}_{calc}
Pt−C	1.96(2)/1.98(2)	1.972/2.003	1.947/2.037	1.943(5)	1.960/1.989	1.964/2.002	1.936(4)/1.956(4)	1.960/1.988	1.961/2.029
C−O	1.27(2)/1.26(2)	1.271/1.238	1.302/1.201	1.266(5)	1.273/1.244	1.302/1.209	1.288(5)/1.265(6)	1.267/1.240	1.296/1.203
O−H/O···H		1.075/1.361	0.971/−		1.087/1.343	0.972/−		1.090/1.339	0.972/−
O···O	2.42(2)	2.405	2.413	2.407(4)	2.406	2.421	2.389(4)/2.419(5)[a]	2.405	2.436
$\varphi_{\text{carbene}}/\varphi_{\text{acetyl}}$	12/9	18/22	18/22	3	9/8	9/8	6/4	1/1	1/1
ΔE		0.0	51.1		0.0	27.9		0.0	26.6

[a] Two values are possible due to disorders of O1 and O2 (see text).

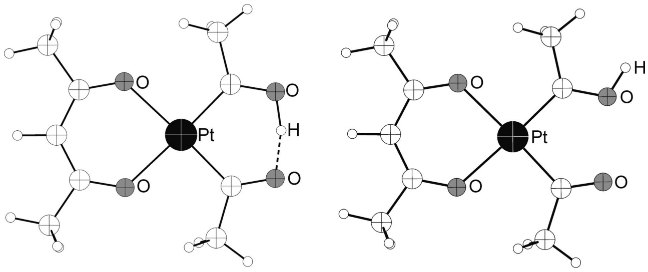

Figure 7. Structures of calculated hydrogen-bonded platina-β-diketone $\mathbf{11_{calc}}$ (left) and non-hydrogen-bonded "open" conformer $\mathbf{11^{*}_{calc}}$ (right).

Hz, 6H, COCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.7 (s, COCH_3), 242.0 (s, $COCH_3$). IR (CsBr): ν 3420 (w), 3153 (m), 3052 (m), 2983 (m), 1607 (s), 1563 (vs), 1409 (s), 1339 (m), 1151 (m), 1121 (s), 651 (w), 344 (w) cm^{-1}. ESI-MS (negative mode, MeOH): *m*/*z* (obsd/calcd %) {[{Pt(COMe)$_2$}$_4$]+Cl}$^-$: 1156 (8/23), 1157 (17/51), 1158 (36/81), 1159 (100/100), 1160 (98/100), 1161 (61/88), 1162 (17/67), 1163 (9/47). MS/MS (1161): *m*/*z* 1131, 1103, 1073, 879, 851. ESI-MS (positive mode, MeOH): *m*/*z* (obsd/calcd %) {[{Pt(COMe)$_2$}$_4$]+Na}$^+$: 1143 (10/9), 1144 (33/27), 1145 (36/56), 1146 (53/83), 1147 (100/100), 1148 (75/89), 1149 (48/72), 1150 (29/50).

Synthesis of *cis*-[Pt(COMe)$_2$(PPh$_3$)$_2$] (3). Triphenylphosphine (150 mg, 0.570 mmol) was added to a suspension of complex **2** (80 mg, 0.285 mmol) in dichloromethane (5 mL) and stirred for 20 min at 0 °C. After an additional hour of stirring at room temperature the volume of the reaction mixture was reduced in vacuo (2 mL). Addition of *n*-pentane/diethyl ether (3:1, 15 mL) resulted in the formation of a light yellow precipitate that was filtered, washed with *n*-pentane (10 mL), and dried in vacuo. Yield: 198 mg (86%). T_{dec}: 64 °C. Anal. Found: C, 59.06; H, 4.76; $C_{40}H_{36}O_2P_2Pt$ (805.74) requires C, 59.63; H, 4.50. ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra were found as reported in ref 9b.

Synthesis of *cis*-[Pt(COMe)$_2$(bpy)] (4). 2,2′-Bipyridine (33 mg, 0.21 mmol) was added at 0 °C to a suspension of complex **2** (60 mg, 0.21 mmol) in dichloromethane (5 mL), and the resulting mixture was stirred for 1 h at room temperature. Then the volume of the red solution was reduced in vacuo (2 mL), and diethyl ether (10 mL) was added slowly. The resulting red precipitate was filtered, washed with diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 86 mg (93%). Anal. Found: C, 37.86; H, 3.63; N, 6.25. $C_{14}H_{14}O_2N_2Pt$ (437.3) requires: C, 38.45; H, 3.23; N, 6.41. IR, ^{1}H NMR, and ^{13}C NMR spectra were found as reported in ref 8.

Synthesis of *cis*-[Pt(COMe)$_2$(Hpz)$_2$] (5). A mixture of complex **2** (140 mg, 0.498 mmol) and pyrazole (Hpz, 68 mg, 0.996 mmol) was dissolved in cold (−70 °C) dichloromethane (5 mL) and warmed to room temperature with stirring within 30 min. Afterward, the volume of the reaction mixture was reduced in vacuo (2.5 mL), and diethyl ether (10 mL) was added slowly. The resulting colorless precipitate was filtered, washed with diethyl ether (10 mL), and dried in vacuo. Yield: 135 mg (65%). T_{dec}: 141 °C. Anal. Found: C, 27.72; H, 3.67; N, 13.66. $C_{10}H_{14}N_4O_2Pt$ (417.32) requires: C, 28.78; H, 3.38; N, 13.43. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.18 (s+d, $^{3}J_{\text{Pt,H}}$ = 23.0 Hz, 6H, COCH_3), 6.12 (s, 2H, H^4-Hpz), 7.11 (s, 2H, H^3-Hpz), 7.23 (s, 2H, H^5-Hpz), 14.68 (s (br), 2H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 43.7 (s+d, $^{2}J_{\text{Pt,C}}$ = 331.7 Hz, COCH_3), 105.3 (s, C^4-Hpz), 129.8 (s, C^3-Hpz), 139.8 (s+d, $^{2}J_{\text{Pt,C}}$ = 34.9 Hz, $C^{5\text{NPt}}$), 234.2 (s+d, $^{1}J_{\text{Pt,C}}$ = 1293.4 Hz, COMe). ^{195}Pt NMR ($CDCl_3$, 107 MHz): δ −3194 (s). IR (CsBr): ν 3116 (m), 3049 (m), 2962 (m), 2794 (w), 2627 (w), 1565 (s), 1431 (w), 1404 (s), 1366 (m), 1330 (m), 1151 (m), 1119 (s), 1102 (s), 1057 (s), 941 (m), 905 (m), 878 (m), 757 (s), 618 (s), 363 (m), 309 (m) cm^{-1}. UV/vis (solid): $\lambda_{\max}$ 561 (w), 365 (s), 293 (s, br), 230 (s, br) nm. UV/vis (in CH_2Cl_2): $\lambda_{\max}$ (ϵ/L mol^{-1} cm^{-1}) 350 (900), 279 (2800), 246 (5000), 230 (7000) nm.

Synthesis of *cis*-[Pt(COMe)$_2$(py)$_2$] (6a). At −70 °C pyridine (131 μL, 1.624 mmol) was added to complex **2** (114 mg, 0.406 mmol) in dichloromethane (5 mL) with stirring. The reaction mixture was warmed to room temperature with stirring within 30 min. Afterward, the volume of the reaction mixture was reduced in vacuo (2.5 mL) and diethyl ether (10 mL) was added. The resulting colorless precipitate was filtered, washed with diethyl ether (10 mL), and dried in vacuo. Yield: 117 mg (66%). T_{dec}: 77−79 °C. Anal. Found: C, 37.52; H, 3.84; N, 6.50. $C_{14}H_{16}N_2O_2Pt$ (439.09) requires: C, 38.26; H, 3.67; N, 6.38. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.15 (s+d, $^{3}J_{\text{Pt,H}}$ = 25.5 Hz, 6H, COCH_3), 7.24−7.32 (m, 4H, H^3-py), 7.72 (t, $^{3}J_{\text{H,H}}$ = 7.7 Hz, 2H, H^4-py), 8.61 (d, $^{3}J_{\text{H,H}}$ = 4.9 Hz, 4H, H^2-py). ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.4 (s+d, $^{2}J_{\text{Pt,C}}$ = 378.2 Hz, COCH_3), 125.2 (s, C^3-py), 137.9 (s, C^4-py), 151.2 (s, C^2-py), 228.5 (s+d, $^{1}J_{\text{Pt,C}}$ = 1268.4 Hz, COCH$_3$). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3376.5 (s). IR (CsBr): ν 3148 (m), 3048 (m), 1613 (s), 1590 (s), 1446 (m), 1410 (w), 1323 (w), 1111 (m), 1093 (m), 1063 (m), 1013 (w), 916 (w), 770 (m), 704 (m), 639 (w), 601 (w), 351 (w) cm^{-1}.

***cis*-[Pt(COMe)$_2$(4-Mepy)$_2$] (6b).** A reaction in an NMR tube analogous to the previous one using 4-methylpyridine (4-Mepy) instead of pyridine afforded complex **6b** in a mixture with excess 4-Mepy. ^{1}H NMR (200 MHz, THF-d_8) δ 1.92 (s+d, $^{3}J_{\text{Pt,H}}$ = 24.6 Hz, 6H, COCH_3), 2.30 (s, 12H, pyCH_3), 7.08 (d, $^{3}J_{\text{H,H}}$ = 5.5 Hz, 4H, H^3-py, free ligand), 7.17 (d, $^{3}J_{\text{H,H}}$ = 6.0 Hz, 4H, H^3-py), 8.38 (d, $^{3}J_{\text{H,H}}$ = 5.6 Hz, 4H, H^2-py, free ligand), 8.50 (d, $^{3}J_{\text{H,H}}$ = 6.4 Hz, 1H, H^2-py). ^{13}C NMR (125 MHz, THF-d_8): δ 20.8/20.9 (s, pyCH_3/pyCH_3 free ligand), 44.8 (s+d, $^{2}J_{\text{Pt,C}}$ = 351.2 Hz, COCH_3), 125.0 (s, C^3-py, free ligand), 126.4 (s+d, $^{3}J_{\text{Pt,C}}$ = 17.3 Hz, C^3-py), 147.1 (s, C^4-py, free ligand), 150.4 (s, C^2-py, free ligand), 151.8 (s+d, $^{2}J_{\text{Pt,H}}$ = 15.1 Hz, C^2-py), 221.7 (s, COCH$_3$).

Synthesis of *cis*-[Pt(COMe)$_2$(NH$_2$Bn)$_2$] (7). At −70 °C benzylamine (580 μL, 5.305 mmol) was added to complex **2** (150 mg, 0.534 mmol) in dichloromethane (4 mL) with stirring. The reaction mixture was warmed to room temperature with stirring within 30 min, and the volume reduced in vacuo (1 mL). The resulting colorless precipitate was filtered, washed with *n*-pentane (2 mL), and dried in vacuo. Yield: 235 mg (89%). T_{dec}: 92−94 °C. Anal. Found: C, 43.79; H, 4.99; N, 5.45. $C_{18}H_{24}N_2O_2Pt$ (495.47) requires: C, 43.63; H, 4.88; N, 5.65. ^{1}H NMR (500 MHz, THF-d_8): δ 2.10 (s+d, $^{3}J_{\text{Pt,H}}$ = 22.7 Hz, 6H, COCH_3), 3.73−3.78 (m, 4H, CH_2), 4.02 (s (br), 4H, NH_2), 7.19−7.22 (m, 2H, *p*-CH), 7.28 (t, $^{3}J_{\text{H,H}}$ = 7.6 Hz, 4H, *m*-CH), 7.43 (d, $^{3}J_{\text{H,H}}$ = 7.5 Hz, 4H, *o*-CH). ^{13}C NMR (125 MHz, THF-d_8): δ 43.8 (s, COCH_3), 49.9 (s, CH_2), 128.0 (s, *p*-CH), 128.9 (s, *o*-CH), 129.2 (s, *m*-CH), 141.9 (s, *i*-C), 227.3 (s, COCH$_3$). IR (KBr): ν 3116 (w), 3026 (w), 1551 (s), 694 (m) cm^{-1}.

Synthesis of *cis*-[Pt(COMe)$_2$(H$_2$dmg)] (8). Dimethylglyoxime (27 mg, 0.23 mmol) was added to a suspension of complex **2** (65 mg, 0.23 mmol) in dichloromethane and stirred for 10 h at room temperature. The reaction mixture was filtered, and the solvent of the red filtrate was removed in vacuo. The residue was recrystallized from dichloromethane/diethyl ether. Yield: 60 mg (65%). Fp: 192−194 °C. Anal. Found: C, 24.34; H, 3.90; N, 6.96. $C_8H_{14}N_2O_4Pt$ (397.29) requires: C, 24.19; H, 3.55; N, 7.05. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.17 (s, 6H, NCCH_3), 2.42 (s+d, $^3J_{Pt,H} = 25.3$ Hz, 6H, COCH_3), 14.16 (s (br), 2H, NOH). ^{13}C NMR (50 MHz, $CDCl_3$): 12.9 (s, NCCH$_3$), 43.0 (s+d, $^2J_{Pt,C} = 308.2$ Hz, COCH$_3$), 156.9 (s+d, $^2J_{Pt,C} = 30.2$ Hz, CN), 236.8 (s+d, $^1J_{Pt,C} = 1323.5$ Hz, COCH$_3$). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3461 (s). IR (ATR): ν 1817 (w), 1651 (w), 1624 (m), 1424 (m), 1363 (s), 1326 (s), 1130 (s), 1070 (m), 938 (m), 819 (m), 710 (m), 656 (m), 527 (w), 490 (m), 358 (m), 239 (m), 216 (m) cm^{-1}. DTA (argon, 10 K/min): T 190−210 (−30.74%), 210−720 (−20.75%) °C. UV/vis (solid): λ_{max} 637 (m, br), 369 (s, br), 275 (sh), 230 (sh), 212 (vs) nm. UV/vis (CH_2Cl_2): λ_{max} 424 (w), 355 (sh), 321 (m), 262 (s) nm.

Synthesis of [Pt$_2$(COMe)$_4$(μ-pydz)$_2$] (9). At −70 °C pyridazine (36 mg, 0.448 mmol) was added to complex **2** (126 mg, 0.448 mmol) in dichloromethane (5 mL) by means of a syringe. Then the reaction mixture was warmed to room temperature within 30 min and kept at this temperature for 15 min with stirring. The resulting orange precipitate was filtered, washed with diethyl ether (3 × 7 mL), and dried in vacuo. Yield: 27 mg (78%). T_{dec}: 100−102 °C. Anal. Found: C, 26.00; H, 3.47; N, 7.97. $C_{16}H_{20}N_4O_4Pt_2$ (722.51) requires: C, 26.60; H, 2.79; N, 7.75. ^{1}H NMR (200 MHz, D_2O): δ 2.32 (s+d, $^3J_{Pt,H} = 23.0$ Hz, 12H, COCH_3), 7.90 (m, 4H, NCCH), 9.17 (m, 4H, NCH). ^{13}C NMR (50 MHz, D_2O): δ 43.6 (s+d, $^2J_{Pt,C} = 337.0$ Hz, COCH$_3$), 133.5 (s, NC), 157.2 (s, NCC), 235.0 (s+d, $^1J_{Pt,C} = 1296.0$ Hz, COCH$_3$). ^{195}Pt NMR (107 MHz, $CDCl_3$): δ −3393 (s). IR (KBr): ν 3142 (w), 3082 (m), 3050 (m), 2977 (m), 2899 (w), 1617 (s), 1596 (s), 1573 (s), 1442 (w), 1413 (s), 1329 (m), 1292 (w), 1114 (s), 1094 (s), 1062 (w), 982 (w), 929 (w), 789 (w), 771 (w), 598 (w) cm^{-1}. ESI-MS (positive mode, MeOH): m/z 722.9 [M + H]$^+$; m/z (obsd/calcd %) [M + Na]$^+$: 741 (16/2), 742 (16/2), 743 (34/34), 744 (70/74), 745 (100/100), 746 (82/70), 747 (56/44), 748 (22/23). MS/MS (723): m/z 643, 585, 557, 541.

Synthesis of [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (1) via Complex 2. A. HCl (generated from NaCl and H_2SO_4) was bubbled over a period of 30 min through a suspension of complex **2** (139 mg, 0.49 mmol) in nitromethane (10 mL) with stirring. Afterward, the yellow reaction mixture was reduced in vacuo (2 mL), and after addition of *n*-pentane (8 mL) complex **1** precipitated. It was filtered, washed with *n*-pentane, and dried in vacuo. Yield: 66 mg (42%). **B.** To complex **2** (139 mg, 0.49 mmol) in benzene (5 mL) first chlorotrimethylsilane (122 μL, 1.00 mmol) and then water (4.5 μL, 0.25 mmol) were added with stirring. After 2 h of stirring at room temperature, the volume of the reaction mixture was reduced in vacuo (1 mL). Then, the yellow precipitate was filtered and recrystallized from dichloromethane (8 mL). Yield: 92 mg (60%). T_{dec}: 183 °C. ^{195}Pt NMR (CD_2Cl_2/C_6D_6, 107 MHz): δ −2756 (s)/ −2717 (s). ^{1}H and ^{13}C NMR spectra were found as reported in ref 6a.

Synthesis of [Pt$_2${(COMe)$_2$H}$_2$(μ-Br)$_2$] (10). To complex **2** (171 mg, 0.61 mmol) in toluene (15 mL) first bromotrimethylsilane (160 μL, 1.21 mmol) and then water (7 μL, 0.39 mmol) were added with stirring. After 2 h of stirring at room temperature, the reaction mixture was filtered and the volume of the yellow filtrate was reduced in vacuo (3 mL). At −40 °C complex **5** crystallized as yellow needles, which were filtered at this temperature, washed with *n*-pentane (2 mL), and dried in vacuo. Yield: 160 mg (72%). T_{dec}: 94 °C. Anal. Found: C, 13.67; H, 2.17; Br, 22.39. $C_8H_{14}Br_2O_4Pt_2$ (724.16) requires: C, 13.27; H, 1.95; Br, 22.07. ^{1}H NMR (500 MHz, C_6D_6): δ 2.17 (s+d, $^3J_{Pt,H} = 21.8$ Hz, 12H, COCH_3), 19.78 (s, 2H, OHO). ^{13}C NMR (125 MHz, C_6D_6): δ 39.7 (s+d, $^2J_{Pt,C} = 169.9$ Hz, COCH$_3$), 229.6 (s+d, $^1J_{Pt,C} = 1453.5$ Hz, COCH$_3$). ^{195}Pt NMR (107 MHz, C_6D_6): δ −2817 (s). IR (CsBr): ν 2376 (w), 1547 (m), 1365 (s), 1299 (s), 1087 (m) cm^{-1}.

Synthesis of [Pt{(COMe)$_2$H}(acac)] (11). A suspension of complex **2** (200 mg, 0.712 mmol) in acetylacetone was stirred for 32 h at room temperature. The resulting dichroic green-violet precipitate was filtered, washed with ethanol (5 mL) and diethyl ether (5 mL), and dried in vacuo. Yield: 225 mg (83%). T_{dec}: 129−132 °C. Anal. Found: C, 27.94; H, 3.93. $C_9H_{14}O_4Pt$ (381.28) requires: C, 28.35; H, 3.70. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.08 (s, 6H, CHCOCH_3), 2.43 (s+d, $^3J_{Pt,H} = 13.5$ Hz, 6H, PtCOCH_3), 5.60 (s, 1H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.9 (s, CHCOCH$_3$), 41.7 (s, PtCOCH$_3$), 100.4 (s, CH), 191.1 (s, CHCOCH$_3$), 242.0 (s, PtCOCH$_3$). Pt,C coupling constants could not be observed due to low solubility of **11**. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ −2729 (s). IR (ATR): ν 770 (w), 844 (w), 1027 (w), 1154 (m), 1201 (w), 1247 (w), 1268 (m), 1332 (m), 1359 (m), 1388 (m), 1532 (s), 1579 (s), 1618 (m), 1626 (m), 1680 (m), 2920 (w), 3143 (w) cm^{-1}. DTA (argon, 5 K/min): T 100 (−5.47%), 110−400 (−54.05%) °C. UV/vis (solid): λ_{max} 591 (s, br), 506 (sh), 327 (s), 284 (s), 222 (vs), 202 (sh) nm. UV/vis (in CH_2Cl_2): λ_{max} (ϵ/L mol^{-1} cm^{-1}) 341 (1400), 307 (7500), 279 (6100), 234 (5800) nm.

Synthesis of [Pt{(COMe)$_2$H}(hfacac)] (12). 1,1,1,5,5,5-Hexafluoroacetylacetone (Hhfacac, 148 mg, 0.712 mmol) was added to a suspension of complex **2** (100 mg, 0.356 mmol) in dichloromethane (5 mL). After a reaction time of 72 h the volume of the reaction mixture was reduced up to half in vacuo. The red precipitate was filtered, washed with diethyl ether, and dried in vacuo. Yield: 89 mg (51%). T_{dec}: 114−116 °C. Anal. Found: C, 22.30; H, 1.97. $C_9H_8F_6O_4Pt$ (489.23) requires: C, 22.10; H 1.65. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.50 (s+d, $^3J_{Pt,H} = 14.9$ Hz, 6H, CH_3), 6.40 (s, 1H, CH). ^{19}F NMR (188 MHz, $CDCl_3$): δ −75.8 (s, CF_3). ^{13}C NMR (125 MHz, C_6D_6): δ 34.3 (s+d, $^2J_{Pt,C} = 132.5$ Hz, COCH$_3$), 93.9 (m, CH), 117.9 (q, $^1J_{F,C} = 284.8$ Hz, CF$_3$), 175.5 q, $^2J_{F,C} = 35.3$ Hz, COCF$_3$), 229.6 (s+d, $^1J_{Pt,C} = 1487.7$ Hz, COCH$_3$). ^{195}Pt NMR (107 MHz, C_6D_6): δ −2764 (s). IR (ATR): ν 3152 (w), 1639 (m), 1617 (s), 1564 (s), 1453 (m), 1407 (w), 1347 (m), 1271 (s), 1203 (s), 1152 (s), 1101 (m), 815 (m), 685 (w) cm^{-1}. UV/vis (solid): λ_{max} 514 (s, br), 349 (sh), 303 (s), 223 (s) nm. UV/vis (in CH_2Cl_2): λ_{max} (ϵ/L mol^{-1} cm^{-1}) 323 (4500), 299 (5400), 264 (5600), 226 (6500) nm.

X-ray Crytal Structure Determinations. Suitable crystals for X-ray diffraction analyses of complex **10**, **11**, and **12** have been obtained from toluene solution at 5 °C (**10**), from recrystallization with hot acetylacetone (**11**), and from recrystallization with hot toluene (**12**). Intensity data were collected on STOE-IPDS and Kappa-CCD (Bruker-Nonius) diffractometers using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 220(2) K (**10**) and 100(2) K (**11**, **12**), respectively. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 3. Absorption corrections were applied semiempirically (**10**) and numerically (**11**, **12**), respectively ($T_{min.}$/$T_{max.}$: 0.04/0.39, **10**; 0.18/0.72, **11**; 0.32/079, **12**). The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against F^2 with SHELXL-97.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically, and their positions were determined from the difference Fourier map in the case of complex **11** or included in the models in calculated positions using the riding model in the cases of complexes **10** and **12**. As an exception in structure **12**, the position of H2 was taken from the difference Fourier map and kept frozen during further refinement. Complex **12** was found to crystallize in the space group $P2_1/m$ with the atoms Pt, O3, O4, and C1−C9 lying on the mirror plane. All F and H atoms above and below this plane are therefore equally

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[22] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Table 3. Crystallographic and Data Collection Parameters for Complexes 10−12

	10	**11**	**12**
empirical formula	$C_8H_{14}Br_2O_4Pt_2$	$C_9H_{14}O_4Pt$	$C_9H_8F_6O_4Pt$
M_r	724.19	381.29	489.24
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	*Imma*	$P2_1/m$
a/Å	4.5822(8)	16.725(3)	9.1107(6)
b/Å	8.930(2)	6.320(1)	6.5655(2)
c/Å	9.155(2)	9.620(2)	10.1263(7)
α/deg	73.43(2)	90	90
β/deg	83.11(2)	90	93.738(5)
γ/deg	75.47(2)	90	90
V/Å^3	347.1(1)	1016.8(3)	604.43(6)
Z	1	4	2
D_{calc}/g cm^{-1}	3.464	2.491	2.688
μ(Mo Kα)/mm^{-1}	25.881	13.785	11.696
F(000)	320	712	452
θ range/deg	2.32−25.48	3.86−29.50	3.70−27.09
no. of reflns collected	3049	13 940	14 165
no. of indep reflns	1199 (R_{int} = 0.096)	797 (R_{int} = 0.070)	1450 (R_{int} = 0.0430)
no. of reflns obsd [$I > 2\sigma(I)$]	1108	606	1297
no. of data/restraints/params	1199/0/74	797/0/45	1450/18/148
goodness-of-fit F^2	1.195	1.075	1.051
R_1/wR_2 ($I > 2\sigma(I)$)	0.0497/0.1426	0.0169, 0.0378	0.0136/0.0264
R_1/wR_2 (Σ)	0.0547/0.1610	0.0258, 0.0414	0.0184/0.0276
largest diff peak and hole/e Å^{-3}	3.33/−4.16	1.484/−1.409	0.450/−0.758

disordered over two positions. Atoms O1 and O2 have been found to lie slightly out of the plane and are consequently also equally disordered over two positions. It has been checked that the refinement of the data in the space group $P2_1$ resulted in identical disorders.

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-716311 (**10**), CCDC-716312 (**11**), and CCDC-716313 (**12**). 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).

Computational Details. All DFT calculations were carried out with the Gaussian03 program package[23] using the hybrid functional B3LYP.[24] For the main group atoms the basis set 6-311++G(d,p) was employed as implemented in the program. The valence shells of platinum were approximated by split valence basis sets, too; for their core orbitals effective core potentials in combination with consideration of relativistic effects were used.[25] All systems were fully optimized without any symmetry restrictions. Except for the open conformations (**10***$_{calc}$−**12***$_{calc}$), the resulting geometries were characterized as equilibrium structures by analysis of the force constants of the normal vibrations.

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Supporting Information Available: CIF files giving X-ray crystallographic data of structures **10**−**12** and nuclear coordinates as well as electronic energies of all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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