ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Reactivity of Quinoline-8-carbaldehyde toward Platina-β-diketone and Acetyl(amine)platinum(II) Complexes. Formation of Acyl(hydroxyalkyl)platinum(IV)

Itziar Zumeta,[†] Tim Kluge,[‡] Claudio Mendicute-Fierro,[†] Cristoph Wagner,[‡] Lourdes Ibarlucea,[†] Tobias Rüffer,[§] Virginia San Nacianceno,[†] Dirk Steinborn,*[,‡] and María A. Garralda*[,†]

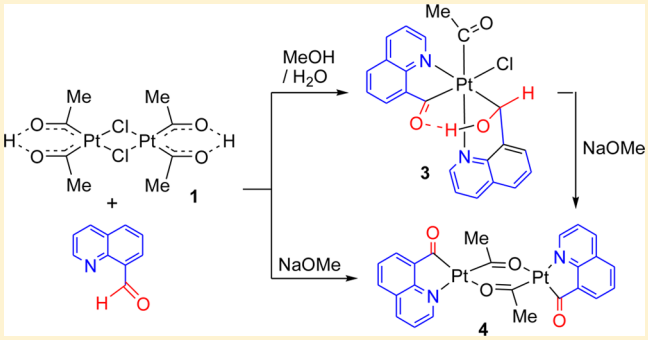
[†]Faculty of Chemistry at San Sebastian, University of the Basque Country, UPV/EHU, P° Manuel Lardizábal, 3, 20018 San Sebastián, Spain

[‡]Institute of Chemistry, Martin Luther University Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany

[§]Institute of Chemistry, Chemnitz University of Technology, Straße der Nationen 62, D-09111 Chemnitz, Germany

Supporting Information

ABSTRACT: The reaction of the platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with quinoline-8-carbaldehyde (C_9H_6NCHO) in MeOH/H_2O (Pt/C_9H_6NCHO = 1/2) leads to the cleavage of the chloride bridges in **1** with acetaldehyde displacement and to the formation of the acetylacyl-(hydroxyalkyl)platinum(IV) complex $[Pt(COMe)Cl(C_9H_6NCO\text{-}\kappa N,\kappa C)(C_9H_6NCHOH\text{-}\kappa N,\kappa C)]$ (**3**) as a single diastereomer (*OC*-6-46). Water-assisted activation of the OC−H bond of one aldehyde and H transfer to the oxygen atom of the second aldehyde occurs. In the presence of sodium methoxide, dehydrochlorination of the platinum starting material affords the dinuclear $[Pt_2(C_9H_6NCO\text{-}\kappa N,\kappa C)_2(\mu\text{-}COMe)_2]$ (**4**) with acetyl bridges in a head-to-tail fashion. Pyridine or tetrahydrofuran fail to cleave the acetyl bridges, which are readily cleaved by triphenylphosphane to afford the mononuclear $[Pt(C_9H_6NCO\text{-}\kappa N,\kappa C)(COMe)(PPh_3)]$ (**5**) with the two acyl groups in cis positions. The reaction of the diacetylbis(amine)platinum(II) complexes $[Pt(COMe)_2(NH_2R)_2]$ (R = CH_2Ph (**2a**), Et (**2b**)) with quinoline-8-carbaldehyde produced the Schiff base products $[Pt(COMe)_2(C_9H_6NCH{=}NR\text{-}\kappa N,\kappa N')]$ (R = CH_2Ph (**6a**), Et (**6b**)). The complexes have been fully characterized, and X-ray diffraction structures of **3** and **4** are reported.



INTRODUCTION

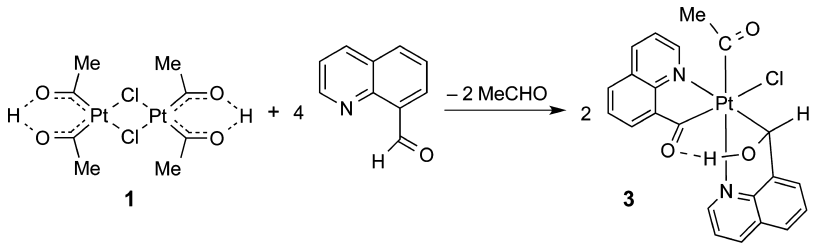
Aldehydes are useful reagents that can undergo different types of transformations. Among others, the activation of the OC−H bonds mediated by late-transition-metal complexes is involved in many stoichiometric and catalytic reactions and has long been an attractive subject in organometallic and organic chemistry.[1,2] Aldehydes are also widely used for the condensation reaction with primary amines, often coordinated to transition metals, to afford imines. A large number of Schiff bases, including chiral and macrocyclic ligands, have thus been prepared.[3] Tethered aldehydes, such as phosphino-aldehydes[4] or quinoline-8-carbaldehyde (C_9H_6NCHO),[5] have proved useful to stabilize the intermediates in the reactions of aldehydes involving metal atoms, and quinoline-8-carbaldehyde has been recently used to prepare polydentate ligands used in the synthesis of platinum complexes for chemotherapeutic drug design.[6]

When metals in low oxidation states are used, the activation of the OC−H bond is generally assumed to proceed via classical oxidative addition pathways, leading to acyl hydrido metal complexes. The zerovalent platinum complexes $[Pt(PR_3)_x(C_2H_4)_{3-x}]$ (x = 1, 2) react with $PPh_2(o\text{-}C_6H_4CHO)$ or C_9H_6NCHO to afford the square-planar acylhydridoplatinum(II) derivative $[PtH\{PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C\}(PPh_3)]$ or $[PtH(C_9H_6NCO\text{-}\kappa N,\kappa C)(PR_3)]$.[7,8] The iridium(III) complex $[IrHCl\{PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C\}(Cod)]$ (Cod = 1,5-cyclooctadiene) is also believed to undergo the oxidative addition of C_9H_6NCHO, followed by an Ir to O hydrogen transfer, to afford the coordinatively saturated hydrido irida-β-diketone $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C)(C_9H_6NCO\text{-}\kappa N,\kappa C)H\}]$.[9] In contrast, the reaction of halo- or alkylplatinum(II) compounds with tethered aldehydes affords complexes with P- or N-coordinated monodentate ligands such as $[NBu_4][Pt(C_6F_5)_3\{PPh_2(o\text{-}C_6H_4CHO)\text{-}\kappa P\}]$,[10] *cis*-$[PtX_2\{PPh_2(o\text{-}C_6H_4CHO)\text{-}\kappa P\}_2]$ (X = Me, Cl),[4a,11] or *trans*-$[PtCl_2(C_9H_6NCHO\text{-}\kappa N)(PR_3)]$.[12] The neutral complexes may afford the acyl derivatives $[PtX\{PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C\}\{PPh_2(o\text{-}C_6H_4CHO)\text{-}\kappa P\}]$ (X = Me, Cl),[4a] $[Pt\{PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C\}_2]$,[11] and $[PtCl(C_9H_6NCO\text{-}\kappa N,\kappa C)(PR_3)]$,[12]

Received: December 5, 2013

 © XXXX American Chemical Society dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1



and proposed mechanisms for their formation have been the oxidative addition of OC−H followed by reductive elimination of HX or direct electrophilic attack on the formyl group by platinum(II) with displacement of a proton.[4a,11,13] The hydridoplatinum(II) derivative [PtH{$(PPh_2O)_2H$}(PPh_2OH)], containing hydrogen-bonded secondary phosphane oxide, reacts with $PPh_2(o\text{-}C_6H_4CHO)$ to undergo the insertion of the aldehyde into the Pt−H bond to give the cyclic platinum alkoxide [Pt{$(PPh_2O)_2H$}{$PPh_2(o\text{-}C_6H_4CH_2O)$-$\kappa P,\kappa O$}].[14]

Platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ are unsaturated acyl(hydroxycarbene) complexes stabilized by an intramolecular O−H···O hydrogen bond. They show unique reactivity in comparison to 18-valence-electron metalla-β-diketones due to their electronic unsaturation and their kinetically labile ligand sphere.[15] The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) reacts with mono- or bidentate L/(LL) donors to yield the acetylhydridoplatinum(IV) complexes $[PtHCl(COMe)_2(LL)]$, which are highly stable when they contain hard bidentate N donors.[16] Furthermore, oxidative addition of halogens and halides to diacetylplatinum(II) results in the requisite platinum(IV) complexes.[17] In the presence of a base, a reductive HCl elimination on $[PtHCl(COMe)_2(LL)]$ can be enforced to selectively yield the diacetylplatinum(II) complexes $[Pt(COMe)_2(LL)]$.[18] Recently we have reported that $PPh_2(o\text{-}C_6H_4CHO)$ reacts with **1** to produce [PtCl{$PPh_2(o\text{-}C_6H_4CO)$-$\kappa P,\kappa C$}{$PPh_2(o\text{-}C_6H_4CHO)$-$\kappa P$}], while in the reactions with the diacetylbis(amine)platinum(II) complexes $[Pt(COMe)_2(NH_2R)_2]$ (**2**), the Schiff base reaction products [Pt$(COMe)_2$\{$PPh_2(o\text{-}C_6H_4CH{=}NR)$-$\kappa P,\kappa N$}] and the intermediate hemiaminal-containing species [Pt$(COMe)_2$(PPh_2\{$o\text{-}C_6H_4CH(OH)(NHR)$\}-$\kappa P,\kappa N$)] are obtained, depending on the reaction conditions.[19] We report now on the reaction of **1** with quinoline-8-carbaldehyde leading to unprecedented acyl(hydroxyalkyl)platinum(IV) derivatives or to dinuclear acetyl-bridged platinum(II) complexes, depending on the reaction conditions. The reaction of C_9H_6NCHO with **2** is also reported.

RESULTS AND DISCUSSION

The reaction of complex **1** with quinoline-8-carbaldehyde in $MeOH/H_2O$ at room temperature (Pt/C_9H_6NCHO = 1/2) leads to the cleavage of the chloride bridges in **1** and the formation of the acetylacyl(hydroxyalkyl)platinum(IV) complex [Pt$(COMe)Cl(C_9H_6NCO$-$\kappa N,\kappa C)(C_9H_6NCHOH$-$\kappa N,\kappa C$)] (**3**), shown in Scheme 1 ,with displacement of acetaldehyde. Complex **3** was isolated as a colorless powder in moderate yield (53%). It is stable at room temperature in the solid state and decomposes in chloroform or methylene chloride solution within 1 day. Complex **3** was characterized by NMR (^1H, $^{13}C\{^1H\}$, $^{195}Pt\{^1H\}$) as well as by microanalysis and single-crystal X-ray diffraction analysis.

For complex **3** the ^1H NMR spectrum shows a resonance at 2.68 ppm, in the range expected for an acetyl ligand,[16,20,21] and the $^3J_{Pt,H}$ = 11.4 Hz coupling constant is also characteristic of this type of acetylplatinum(IV) complex. The hydroxyl proton of the formed hydroxyalkyl group appears at 6.27 ppm as a doublet with satellites. The pattern observed is due to coupling to platinum ($^3J_{Pt,H}$ = 39.2 Hz) and to the alkyl CH ($^3J_{H,H}$ = 11.4 Hz) proton, which appears at 7.22 ppm also as doublet with platinum satellites ($^2J_{Pt,H}$ = 107.2 Hz). By addition of 1 drop of CD_3OD to a CD_2Cl_2 solution of **3**, the signal at 6.27 ppm disappears due to H/D exchange and the resonance at 7.22 ppm becomes a singlet with platinum satellites. In the $^{13}C\{^1H\}$ NMR spectrum the carbon atom of the hydroxyalkyl group appears at 62.6 ppm coupled with platinum ($^1J_{Pt,C}$ = 841 Hz). The $^{13}C\{^1H\}$ NMR spectrum also contains resonances at 196.4 and 197.6 ppm, indicating the presence of ligands, with characteristic $^1J_{Pt,C}$ coupling constants of 1142 and 901 Hz, respectively.[16] The platinum chemical shift, −1421 ppm, is as expected for a platinum(IV) complex.[21] Complex **3** contains a newly formed asymmetric sp^3 carbon atom. This complex could exist in several diastereomeric forms because the platinum atom is also stereogenic, but the reaction is highly diastereoselective.

Single crystals of **3**·$2CHCl_3$ for X-ray diffraction analysis were grown overnight, at room temperature, from a chloroform solution. Complex **3**·$2CHCl_3$ was found to crystallize in the triclinic system with two crystallographically identical molecules in the unit cell and four molecules of chloroform. Selected bond lengths and angles are given in Figure 1.

The geometry around the metal atom is a slightly distorted octahedron (configuration index *OC*-6-46), with the three organyl ligands trans to N and Cl ligands, thus avoiding an energetically unfavorable trans arrangement of two strong σ-donor ligands. The highest deviation from linearity corresponds to the C3−Pt−Cl angle of 173.4(2)°. The Pt atom is displaced from the best least-squares C1C13N2N1 plane by 0.065 Å toward the chlorine atom. The Pt−N1 bond length trans to the hydroxyalkyl fragment (2.179(6) Å) is equal to the Pt−N2 bond length trans to the acetyl ligand (2.187(4) Å), as expected. The Pt−C13 distance trans to nitrogen is longer than the Pt−C3 distance trans to chlorine (2.068(7) and 2.005(5) Å, respectively). This difference may be viewed as a consequence of the differences in the trans influence (N > Cl) and of the different hybridization for both carbon atoms: sp^3 for C13 and sp^2 for C3.[22] Both distances are longer than the Pt−C bonds in **1** (1.95(1) Å), which have substantial double-bond character.[23] The C3−O2 distance (1.213(8) Å) in complex **3** is similar to that observed for [PdCl(C_9H_6NCO-$\kappa N,\kappa C$)(PPh_3)]·PPh_3[12b] and shorter than the C13−O3 distance (1.411(8) Å), as expected. An intramolecular O3−H···O2 hydrogen bond between the hydroxyalkylquinoline and the acylquinoline units is observed, with an O3···O2 distance of 2.708(7) Å (O2···H, 1.90 Å; O3−H···O2, 155°). π−π interactions

dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

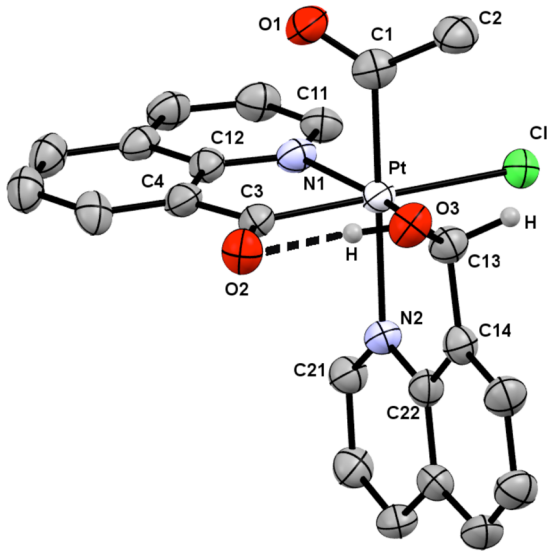


Figure 1. ORTEP view of **3** in crystals of **3**·2$CHCl_3$ (30% probability ellipsoids; H atoms omitted for clarity, except those of the hydrogen bond and of the chiral C atom). Selected bond lengths (Å) and angles (deg): Pt−N1, 2.179(6); Pt−N2, 2.187(4); Pt−Cl 2.481(1); Pt−C1, 2.052(6); Pt−C13, 2.068(7); Pt−C3, 2.005(5); C3−O2, 1.213(8); C13−O3, 1.411(8); C1−O1, 1.196(8); C1−Pt−C3, 89.2(2); C1−Pt−C13, 91.9(2); C1−Pt−N1, 91.4(2); C1−Pt−N2, 174.0(2); C1−Pt−Cl, 93.6(2); C3−Pt−C13, 94.2(2); C3−Pt−N1, 82.0(2); C3−Pt−N2, 88.1(2); C3−Pt−Cl, 173.4(2); C13−Pt−N1, 174.9(2); C13−Pt−N2, 82.9(2); C13−Pt−Cl, 91.7(2); N1−Pt−N2, 93.6(2); N1−Pt−Cl, 92.1(1); N2−Pt−Cl, 89.6(1); C14−C13−O3, 110.6(5); C4−C3−O2, 122.5(5); C2−C1−O1, 122.5(6).

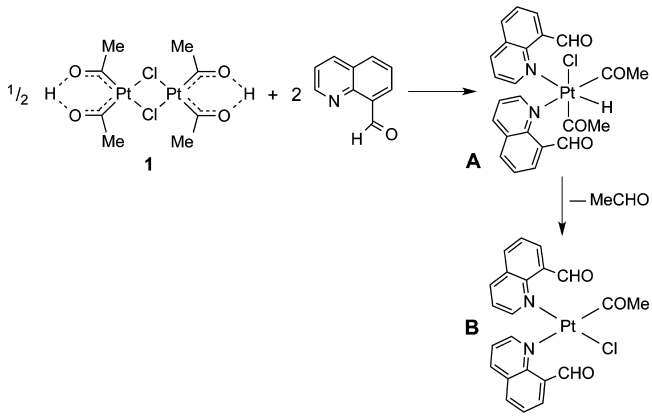
involving adjacent molecules between the hydroxyalkylquinoline moieties (3.356 Å) and between the carboxyquinoline moieties (3.612 Å) are also observed.[24]

DFT calculations show that, out of the 20 possible diastereomers, the most stable one is that which was found in crystals of **3**·2$CHCl_3$ (configuration index *OC*-6-46) with a *C*-configured platinum atom[25] and the asymmetric C atom in an *R* configuration (abbreviated *CR*) or the other way a round, the *AS* enantiomer (for more details see the Supporting Information)

The reaction of the platina-*β*-diketone **1** with C_9H_6NCHO to afford the Pt(IV) derivative **3** requires a Pt/(C_9H_6NCHO) = 1/2 ratio and the presence of water. Complex **1** is known to react with quinoline (quin) with cleavage of the chloride bridges to give the mononuclear platina-*β*-diketone [PtCl{$(COMe)_2H$}(quin)],[26] and C_9H_6NCHO has been reported to behave as a monodentate ligand in [$PtCl_2$(C_9H_6NCHO-*κN*)(PEt_3)].[12a] **1** also reacts with bidentate N-donor ligands (N^N) such as 2,2′-bipyridine and 1,4-diazabuta-1,3-dienes to afford, among others, [PtCl(COMe)(N^N)] compounds with acetaldehyde displacement.[16,20] To gain insight into the mechanism of the reaction shown in Scheme 1, we performed several experiments using the deuterated aldehyde C_9H_6NCDO. When a Pt/C_9H_6NCDO = 1/2 ratio was used, in a CD_3OD/D_2O mixture, the deuterated derivative [Pt(COMe)Cl(C_9H_6NCO-*κN*,*κC*)(C_9H_6NCDOD-*κN*,*κC*)] (**3DD**) was obtained, as shown by the ^1H NMR spectrum lacking the resonances of the CHOH fragment. When the reaction with a Pt/C_9H_6NCDO = 1/2 ratio was performed in a CH_3OH/H_2O mixture, the only partially deuterated [Pt(COMe)Cl(C_9H_6NCO-*κN*,*κC*)(C_9H_6NCDOH-*κN*,*κC*)] (**3DH**) was obtained, due to the easy H/D exchange between the hydroxyl group and the solvents. The corresponding ^1H NMR spectrum in $CDCl_3$ contains a singlet, instead of a doublet, with satellites at 6.41 ppm and no resonance at 7.22 ppm. From these deuteration experiments we conclude that activation of the aldehyde OC−H bond occurs in only half of the molecules of C_9H_6NCHO, while in the other half this bond remains unaltered and protonation of the oxygen occurs. As expected, when using a Pt/C_9H_6NCDO/C_9H_6NCHO = 1/1/1 ratio, in a CH_3OH/H_2O mixture, an equimolar mixture of **3** and **3DH** was obtained.

According to this evidence we believe that the reaction of **1** with C_9H_6NCHO starts with cleavage of the chloride bridges, N coordination of two molecules of the ligand, and O to Pt hydrogen transfer to form **A**, followed by acetaldehyde elimination, leading to **B**, as shown in Scheme 2.

Scheme 2



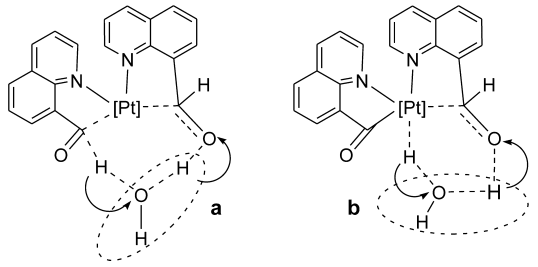
Possible paths for the transformation of the monodentate C_9H_6NCHO ligands in **B** into the acylquinoline and the hydroxyalkylquinoline fragments observed in **3** are an electrophilic activation of one aldehyde OC−H by the metal to generate a positively charged hydrogen that would be transferred to the other aldehyde to form the hydroxyalkyl fragment[13,27] and the chelate-assisted oxidative addition of one of the two aldehydes followed by insertion of the second aldehyde into the Pt−H bond, as in the reaction of *o*-(diphenylphosphino)benzaldehyde with rhodium(I) complexes.[4c]

Both types of mechanisms could be assisted by the presence of water, which may form a hydrogen bond with the oxygen atom of aldehydes. Transfer of a water proton to one of the aldehydes and electrophilic OC−H activation of the other aldehyde, with transfer of proton to the oxygen of water (see **a** in Chart 1), appears feasible. Transfer of a proton from water to an oxygen atom doubly bonded to carbon plays a role in the selective hydrogenation of the C═O bond of *α*,*β*-unsaturated aldehydes[28] and in the hydrogenation of CO_2 promoted by Ir(III) complexes through heterolysis of H_2.[29] The oxidative addition of one aldehyde to afford an acyl−hydrido intermediate followed by transfer of the water proton to the other aldehyde and hydrogen transfer from platinum to the oxygen atom of water via a six-centered transition state (see **b** in Chart 1) can also afford **3**. The ability of late-transition-metal hydrides to transfer a hydride or a proton is well known.[30]

When the reaction of complex **1** with quinoline-8-carbaldehyde is performed in dichloromethane in the presence

dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

Chart 1. [a]



[a]C(O)Me and Cl ligands omitted for clarity.

of sodium methoxide, dehydrochlorination and activation of the OC−H bonds occurs with formation of the dinuclear complex $[Pt_2(C_9H_6NCO\text{-}\kappa N,\kappa C)_2(\mu\text{-}COMe)_2]$ (**4**) and displacement of acetaldehyde, irrespective of the Pt/C_9H_6NCHO ratio employed (1/1 or 1/2) (Scheme 3). Complex **4** could be isolated as a yellow powder in moderate yield (63%). Complex **4** is also formed in the reaction of **3** with NaOMe, which occurs with displacement of C_9H_6NCHO, as shown in Scheme 3. It is stable at room temperature in the solid state but decomposes in chloroform or dichloromethane solution within 1 day. Complex **4** was characterized by microanalysis, high-resolution ESI mass spectrometry, and NMR and IR spectroscopy as well as by single-crystal X-ray diffraction analysis.

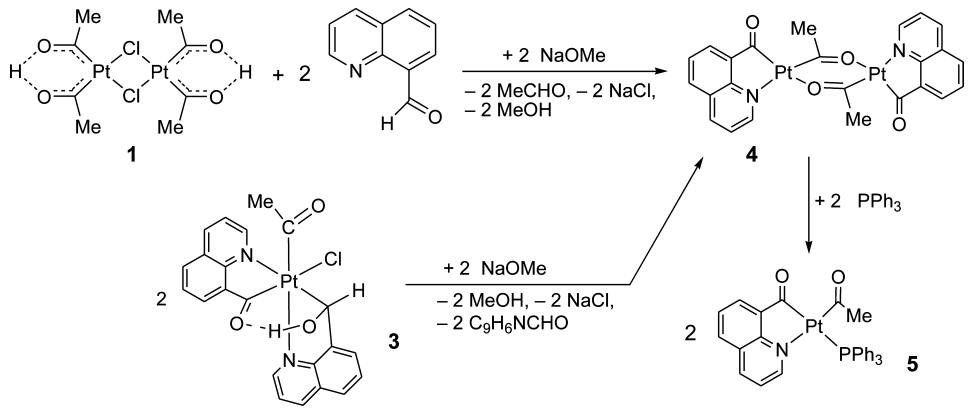
In the ESI mass spectra signals due to dinuclear protonated ($[Pt(C_9H_6NCO\text{-}\kappa N,\kappa C)(\mu\text{-}COMe)]_2 + H^+$) or aggregated with Na^+ ($[Pt(C_9H_6NCO\text{-}\kappa N,\kappa C)(\mu\text{-}COMe)]_2 + Na^+$) were identified. In the IR spectrum of complex **4**, absorptions due to acyl groups were observed. The signals at lower wavenumbers (1499, 1512 cm^{-1}) are in accord with the presence of bridging acyl groups.[31] Bridging acetyl ligands in platina-β-diketonates of platina-β-diketones show absorptions in the 1514−1534 cm^{-1} range.[32] The signal at 1629 cm^{-1} can be assigned to terminal acyl groups. In line with these observations, the $^{13}C\{^1H\}$ NMR spectrum shows a resonance at very low field, 261.6 ppm, characteristic of bridging acyl groups, and a singlet with platinum satellites ($^1J_{Pt,C}$ = 1523 Hz) at 194.7 ppm due to terminal acyl groups.[33] The platinum chemical shift, −3143 ppm, is as expected for a platinum(II) complex.[34]

Acetyl groups are well-known as bridging ligands in platinum dinuclear complexes, while the acylquinoline ligand behaves as a bridge in the heterodinuclear Rh−Ir derivative $[IrCl\{PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa N,\kappa C\}(\mu\text{-}H)(\mu\text{-}C_9H_6NCO\text{-}\kappa N,\kappa C\text{:}\kappa O)Rh(Cod)]$, which also contains a terminal acylphosphane ligand, or as a terminal in the dinuclear Ir complex $[\{Ir(C_9H_6NCO\text{-}\kappa N,\kappa C)(py)\{\mu\text{-}PPh_2(o\text{-}C_6H_4CO)\text{-}\kappa P,\kappa C\text{:}\kappa O\}\}_2](ClO_4)_2$, which also contains a bridging acylphosphane ligand.[35] To ascertain which acyl group behaves as a bridge, an X-ray diffraction study was undertaken. Single crystals of **4**·0.5H_2O suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether onto a dichloromethane solution. The complex **4**·0.5H_2O crystallizes with two crystallographically independent dimers, namely **A** and **B**, and a molecule of water. No significant differences are observed in the molecular geometries of **A** and **B**. An ORTEP view of **4A** and selected bond lengths and angles are shown in Figure 2.

Complex **4** consist of dimers with two bridging acetyl ligands in a head-to-tail fashion, forming a six-membered ring in a slightly twisted boat conformation with the two Pt atoms at the apexes. The coordination around the platinum can be described as square planar and deviates only slightly from planarity in all cases. The deviation of the platinum atom from the corresponding least-squares best-fit mean plane formed by its coordinated atoms is between 0.016 and 0.056 Å. The bond distances involving the metal are as expected, and the C−O bond lengths are equal within the 3σ criterion, regardless of the acyl groups belonging to an acetyl bridge (mean 1.25(2) Å) or to a terminal chelating ligand (mean 1.22(2) Å). The coordination planes are bent at an angle of 102.2(6)°, larger than in the related platina-β-diketonates of platina-β-diketones $[\{X_2Pt(\mu\text{-}COMe)_2Pt\{(COMe)_2H\}\}_2]^z$ (X/X = Cl/NH_2Ph', z = 0; X/X = Cl/Cl, z = 2−; X/X = bpy, z = 2+) with a head-to-head arrangement of the bridging acetyl ligands, where the angles are 76.3(4)−89.6(4)°.[32,36] The platinum−platinum distances, Pt1···Pt2 = 3.462(1) Å for **4A** and Pt3···Pt4 = 3.438(1) Å for **4B**, are longer than those in platina-β-diketonates of platina-β-diketones (3.160(1)−3.358(1) Å). Two kinds of intermolecular interactions can be detected. Hydrogen bonds are observed between the O1w atom of the water molecule, the O1 atom of one of the acylquinoline ligands of an **A** dimer, and the O5 atom of one of the acylquinoline ligands of a **B** dimer, so that the water molecule bridges both types of dimers (O1···O1w = 2.861(3) Å, O5···O1w = 2.951(2) Å; O1w−H2···O1 = 154°, O1w−H1···O5 = 151°) to form [**A**···H−O−H···**B**] units. Additionally, the quinoline rings form a net of $\pi-\pi$ interactions with distances in the range 3.33−3.40 Å.

DFT calculations give proof that complex **4** (configuration index *SP*-4-3) found in crystals of **4**·0.5H_2O is the most stable isomer. The diastereomer having two acyl ligands in mutually

Scheme 3



dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

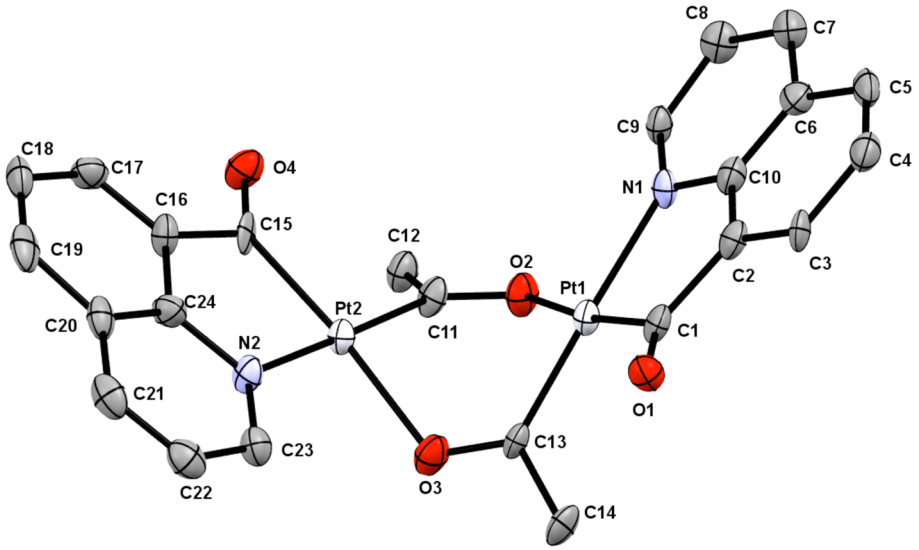


Figure 2. ORTEP view of **4A** in crystals of **4**·0.5H_2O (30% probability ellipsoids; H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg) (the values of the two crystallographically independent molecules are given separated by a slant): Pt1−C1, 1.96(2)/1.98(1); Pt2−C15, 1.97(2)/1.95(1); Pt1−N1, 2.092(9)/2.09(1); Pt2−N2, 2.11(1)/2.12(2); Pt1−C13, 1.97(1)/1.96(2); Pt2−C11, 1.98(2)/1.97(2); Pt1−O2, 2.15(2)/2.15(1); Pt2−O3, 2.13(1)/2.135(9); C1−O1, 1.20(2)/1.21(2); C15−O4, 1.21(2)/1.24(2); C11−O2, 1.26(2)/1.27(2); C13−O3, 1.25(2)/1.23(2); C1−Pt1−N1, 83.9(6)/83.6(5); C15−Pt2−N2, 84.1(6)/83.4(6); N1−Pt1−O2, 88.5(5)/88.6(5); N2−Pt2−O3, 88.1(5)/87.3(5); C13−Pt1−O2, 92.6(6)/91.5(6); C11−Pt2−O3, 92.3(6)/92.8(7); C1−Pt1−C13, 95.0(7)/96.3(6); C15−Pt2−C11, 95.5(7)/96.4(8); C1−Pt1−O2, 172.3(6)/172.2(5); C15−Pt2−O3, 172.1(6)/170.6(6); C13−Pt1−N1, 178.4(6)/178.2(6); C11−Pt2−N2, 177.4(6)/174.9(7); O1−C1−C2, 117(2)/119(1); O4−C15−C16, 118(1)/199(2); O3−C13−C14, 115(1)/115(2); O2−C11−C12, 115(2)/113(1).

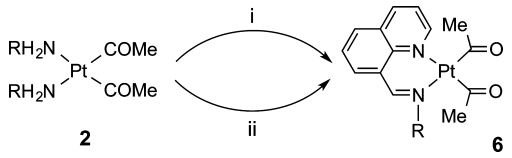
trans positions (configuration index *SP*-4-2) is 43.9 kcal/mol higher in energy. The configurational isomer with bridging acylquinoline ligands (μ-C_9H_6NCO-$\kappa N,\kappa C$:κO) proved to be also 43.6 kcal/mol higher in energy (for details see the Supporting Information).

As shown in Scheme 3, complex **4** reacts with triphenylphosphane to undergo acyl bridge cleavage to give the mononuclear complex [Pt(C_9H_6NCO-$\kappa N,\kappa C$)(COMe)(PPh_3)] (**5**) with cis acyl groups. Complex **5** was isolated as a red powder in 55% yield. At room temperature, the solid is stable, but after 2 days in chloroform solution decomposition products appear. The IR spectrum shows absorptions due to terminal acyl groups and the $^{13}C\{^1H\}$ NMR spectrum shows resonances at 231.7 (d) ppm, due to the acylquinoline fragment trans to phosphorus ($^2J_{P,C}$ = 120 Hz),and at 222.8 (d) ppm, due to the acetyl group cis to phosphorus ($^2J_{P,C}$ = 8 Hz). The ^{31}P NMR spectrum of complex **5** contains a singlet with satellites at 28.1 ppm, and the $^1J_{Pt,P}$ = 1755 Hz coupling constant agrees with a phosphorus atom trans to an acyl group.[13,26,37] The platinum chemical shift, −3630 (d) ppm, is as expected for a platinum(II) complex.[34] Other donors such as pyridine and tetrahydrofuran are unable to cleave the acetyl bridges in **4** under the same reaction conditions. In line with this behavior, complex **4** fails to react with C_9H_6NCHO to afford **3**.

Finally the reaction of the diacetylbis(amine)platinum(II) complexes [Pt$(COMe)_2(NH_2R)_2$] (R = CH_2Ph (**2a**), Et (**2b**))[38] with quinoline-8-carbaldehyde, either in dichloromethane at −78 °C or in methanol at room temperature, affords the Schiff base products [Pt$(COMe)_2$(C_9H_6NCH═NR-$\kappa N,\kappa N'$)] (R = CH_2Ph (**6a**), Et (**6b**)), shown in Scheme 4i.

At variance with the reaction of **2** with *o*-(diphenylphosphino)benzaldehyde, where the imine−phosphane complexes and the intermediate hemiaminal−phosphane complexes could be isolated and characterized,[19] in the present case intermediate hemiaminal derivatives could be neither

Scheme 4. [a]



[a]Legend: (i) C_9H_6NCHO; (ii) C_9H_6NCH═NEt. R = CH_2Ph (**a**), Et (**b**).

obtained nor detected by NMR, thus showing that the condensation reaction is much faster when using quinoline-8-carbaldehyde than when using the more flexible *o*-(diphenylphosphino)benzaldehyde. Complexes **6a**,**b** could both be isolated as a brown or red powder in a yield of 35−85%. Complexes **6** show resonances due to two nonequivalent acetyl groups. The chemical shifts of the acetyl ligands in the $^{13}C\{^1H\}$ NMR spectra, in the 227−238 ppm range, agree with acetyl groups trans to nitrogen ligands in acetylplatinum(II) complexes.[34] The appearance of new resonances at 163.4 (**6a**) and 161.5 (**6b**) ppm confirms the formation of a new C═N bond. The platinum chemical shifts are in the range of typical platinum(II) complexes. Furthermore, high-resolution ESI mass spectra (cationic mode) of complexes **6** showed the molecular peaks of **6** ([M + H]$^+$). Complex **6b** can also be easily prepared by the reaction of **2b** with the iminoacylquinoline C_9H_6NCH═NEt (**7**) (Scheme 4ii), which leads to displacement of the ethylamine.

CONCLUSIONS

The reaction of quinoline-8-carbaldehyde with platina-β-diketones leads to metal-mediated and water-assisted carbon to oxygen proton transfer between two aldehydes and to the formation of new (acylquinoline)(hydroxyalkylquinoline)-platinum(IV) species. In the presence of bases dehydrochlori-

dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

nation occurs to afford dinuclear platinum(II) derivatives with preferred acetyl bridges and chelating acylquinoline ligands. In the solid state these dimers are connected via hydrogen bonds involving the acylquinoline oxygen atoms. Pyridine or THF fails to cleave the acetyl bridges, while triphenylphosphane easily affords mononuclear Pt(II) species. The reaction of quinoline-8-carbaldehyde with diacetylbis(amine)platinum(II) leads readily to new diacetyl(iminoacylquinoline)platinum(II) complexes.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere using the standard Schlenk techniques. Solvents were dried (Et_2O and *n*-pentane over Na/benzophenone; MeOH over Mg; $CHCl_3/CH_2Cl_2$ over CaH_2) and distilled prior to use. NMR spectra were, unless otherwise specified, recorded at 27 °C on Varian Gemini 200, VXR 400, and Unity 500 NMR spectrometers. TMS (^1H, $^{13}C\{^1H\}$) was used as internal reference and H_2PtCl_6 ($\delta(^{195}Pt)$ 0 ppm) or H_3PO_4 ($\delta(^{31}P)$ 0 ppm) as external reference. IR spectra were recorded on a Bruker Tensor 27 spectrometer with a Platinum ATR unit. The positive ion high-resolution ESI mass spectra were measured with a Bruker Apex III Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Microanalyses were performed by the University of Halle microanalytical laboratory using a CHNS-932 (LECO) elemental analyzer. The platinum complexes $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) and $[Pt(COMe)_2(NH_2R)_2]$ (**2**) as well as C_9H_6NCHO and C_9H_6NCDO were prepared according to literature methods.[13,23,38,39]

Preparation of [Pt(COMe)Cl(C_9H_6NCO-κ*N*,κ*C*)(C_9H_6NCHOH-κ*N*,κ*C*)] (3). To a freshly prepared suspension of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**; 80 mg, 0.13 mmol) in methanol/water (3/0.75 mL) was added C_9H_6NCHO (79 mg, 0.50 mmol), whereupon dissolution of **1** and precipitation of a colorless product occurred. The solid was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 88 mg (53%). Finally, the complex was recrystallized from chloroform/diethyl ether. Anal. Calcd for $C_{22}H_{17}ClN_2O_3Pt\cdot CHCl_3$ (707.31): C, 39.06; H, 2.57; N, 3.96. Found: C, 38.71; H, 2.67; N, 3.77. ^1H NMR (500 MHz, CD_2Cl_2): δ 2.68 (s+d, $^3J_{Pt,H}$ = 11.4 Hz, 3H, $COCH_3$), 6.27 (d+d, $^3J_{H,H}$ = 11.4 Hz, $^3J_{Pt,H}$ = 39.2 Hz, 1H, O*H*), 7.22 (d+d, $^3J_{H,H}$ = 11.5 Hz, $^2J_{Pt,H}$ = 107.2 Hz, 1H, C*H*(OH)), 7.03, 7.44, 7.66, 7.84, 8.16, 8.24, 8.66, and 10.01 (m, 12H, aromatic protons). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 37.7 (s+d, $^2J_{Pt,C}$ = 168 Hz, $COCH_3$), 62.6 (s+d, $^1J_{Pt,C}$ = 841 Hz, *C*H(OH)), 121.8, 123.9, 126.5, 128.7, 128.8, 128.9, 129.0, 129.5, 131.7, 133.1, 138.8, 139.4, 140.9, 146.4, 147.6, 148.2, and 150.6 (s, 18C, aromatic carbon atoms), 196.4 (s+d, $^1J_{Pt,C}$ = 1142 Hz, *C*OMe), 197.6 (s+d, $^1J_{Pt,C}$ = 901 Hz, CO_{quin}). $^{195}Pt\{^1H\}$ NMR (107 MHz, CD_2Cl_2): δ −1421 (s). IR: 1697 (m), 1673 (s), 1638 (s) cm^{-1}.

Preparation of [Pt_2(C_9H_6NCO-κ*N*,κ*C*)$_2$(μ-COMe)$_2$] (4). To a methylene chloride (3 mL) solution of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**; 90 mg, 0.14 mmol) at −78 °C were added C_9H_6NCHO (44.5 mg, 0.28 mmol) and NaOMe (15.3 mg, 0.28 mmol). The resulting orange solution became a black suspension after it was stirred overnight at room temperature. The precipitate was filtered off, and the solution was concentrated under vacuum (0.5 mL). Addition of diethyl ether (3 mL) gave a yellow precipitate that was filtered off, washed with diethyl ether (5 mL), and dried under vacuum. Yield: 71 mg (63%). Anal. Calcd for $C_{24}H_{18}N_2O_4Pt_2$ (788.60): C, 36.55; H, 2.30; N, 3.55. Found: C, 36.43; H, 1.86; N, 3.77. HRMS (ESI): *m*/*z* calcd $[C_{24}H_{18}N_2O_4Pt_2 + H]^+$ 789.0634, found 789.0646; calcd $[C_{24}H_{18}N_2O_4Pt_2 + Na]^+$ 811.0448, found 811.0465. ^1H NMR (400 MHz, $CDCl_3$): δ 2.87 (s +d, $^3J_{Pt,H}$ = 23.5 Hz, 3H, $COCH_3$), 7.59, 7.97, 8.11, 8.45, and 9.03 (m, 6H, aromatic protons). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 41.6 (s +d, $^2J_{Pt,C}$ = 260 Hz, $COCH_3$), 122.6, 124.0, 128.2, 128.9, 129.4, 137.4, 145.8, 149.0, and 150.9 (s, 9C, aromatic carbon atoms), 194.7 (s+d, $^1J_{Pt,C}$ = 1523 Hz, CO_{quin}), 261.6 (s, *C*OMe). $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$): δ −3143 (s). IR: 1629 (m), 1576 (m), 1512 (m), 1499 (m) cm^{-1}.

Reaction of Complex 3 with NaOMe. To a methylene chloride (3 mL) solution of complex **3** (10 mg, 0.02 mmol) was added NaOMe (0.9 mg, 0.02 mmol) to afford a yellow solution. After the mixture was stirred for 1 h at room temperature, the addition of diethyl ether (3 mL) gave a yellow precipitate, which was filtered off, washed with diethyl ether (5 mL), and dried under vacuum. The ^1H NMR spectrum shows the solid to be a mixture of **4** and C_9H_6NCHO.

Preparation of [Pt(C_9H_6NCO-κ*N*,κ*C*)(COMe)(PPh_3)] (5). To a methylene chloride (3 mL) solution of $[Pt_2(C_9H_6NCO\text{-}\kappa N,\kappa C)_2(\mu\text{-}COMe)_2]$ (**4**; 40 mg, 0.05 mmol) was added a stoichiometric amount of PPh_3 (27 mg, 0.10 mmol) to afford a red solution. After the mixture was stirred for 1.5 h at room temperature, the addition of diethyl ether (3 mL) gave a red precipitate, which was filtered off, washed with diethyl ether (5 mL), and dried under vacuum. Yield: 36 mg (55%). Anal. Calcd for $C_{30}H_{24}NO_2PPt$ (656.60): C, 54.88; H, 3.68; N, 2.13. Found: C, 55.07; H, 3.96; N, 2.35. HRMS (ESI): *m*/*z* calcd $[C_{30}H_{24}NO_2PPt + Na]^+$ 679.1085, found 679.1090. ^1H NMR (200 MHz, $CDCl_3$): δ 1.97 (s+d, $^3J_{Pt,H}$ = 19.0 Hz, 3H, $COCH_3$), 6.94, 7.39, 7.70, 7.95, 8.11, and 8.34 (m, 21H, aromatic protons). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 28.1 (s+d, $^1J_{Pt,P}$ = 1755 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 42.1 (s+d, $^2J_{Pt,C}$ = 310 Hz, 3H, $COCH_3$), 121.9 (s), 123.8 (s), 128.7 (d, $^3J_{P,C}$ = 10 Hz), 129.1 (s), 130.4 (s), 130.7 (d, $^4J_{P,C}$ = 2 Hz), 131.4 (s), 131.8 (s), 134.5 (d, $^2J_{P,C}$ = 13 Hz), 138.0 (s), 146.9 (d, $^1J_{P,C}$ = 25 Hz), 151.7 (s), 152.9 (d, $^3J_{P,C}$ = 3 Hz), (13 nonequivalent aromatic C atoms), 222.8 (d, $^2J_{P,C}$ = 8 Hz, *C*OMe), 231.7 (d, $^2J_{P,C}$ = 120 Hz, CO_{quin}). $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$): δ −3630 (d, $^1J_{Pt,P}$ = 1764 Hz). IR: 1636 (m), 1619 (m) cm^{-1}.

Preparation of [Pt(COMe)$_2$(C_9H_6NCH=NR-κ*N*,κ*N*′)] (R = CH_2Ph (6a), Et (6b)). *Method a.* To a methanol (3 mL) solution of $[Pt(COMe)_2(NH_2R)_2]$ (R = CH_2Ph (**2a**), Et (**2b**); 0.11 mmol) or to a methylene chloride (3 mL) solution of **2a** or **2b** at −78 °C was added C_9H_6NCHO (16.9 mg, 0.11 mmol) to afford a red solution at room temperature. After the mixture was stirred for 4.5 h at room temperature, the addition of *n*-hexane for **6a** and diethyl ether for **6b** gave a brown or a red precipitate, which was filtered off, washed with *n*-hexane or diethyl ether, and dried under vacuum. Data for **6a** (R = CH_2Ph) are as follows. Yield: 21 mg (36%). Anal. Calcd for $C_{21}H_{20}N_2O_2Pt\cdot CH_2Cl_2$ (612.43); C, 43.15; H, 3.62; N, 4.57. Found: C, 43.28; H, 3.39; N, 4.85. HRMS (ESI): *m*/*z* calcd $[C_{21}H_{20}N_2O_2Pt + H]^+$ 528.1256, found 528.1254 (in addition to other signals). ^1H NMR (200 MHz, $CDCl_3$): δ 2.06 (s+d, $^3J_{Pt,H}$ = 22.7 Hz, 6H, $COCH_3$), 5.19 (s+d, $^3J_{Pt,H}$ = 21.5 Hz, 2H, CH_2), 7.29, 7.52, 7.70, 7.87, 8.12, and 8.37 (m, 10H, aromatic protons), 8.33 (s+d, $^3J_{Pt,H}$ = 30 Hz, 1H, N=C*H*), 9.45 (m+d, $^3J_{Pt,H}$ = 23.3 Hz, 1H, *CH* H^2 quinoline). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 43.5 (s, $COCH_3$), 43.9 (s, $COCH_3$), 68.2 (s, CH_2), 122.7, 127.0, 128.0, 128.6, 128.9, 129.4, 130.1, 135.1, 135.9, 139.9, 140.5, 141.1, and 156.8 (s, 13 nonequivalent aromatic C atoms), 163.4 (s, N=*C*H), 227.9 (s, *C*OMe), 236.9 (s, *C*OMe). $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$): δ −3199 (s). IR: 1574 (m), 1551 (m) cm^{-1}. Data for **6b** (R = Et) are as follows. Yield: 44 mg (85%). Anal. Calcd for $C_{16}H_{18}N_2O_2Pt\cdot CH_2Cl_2$ (549.06); C, 37.10; H, 3.66; N, 5.09. Found: C, 36.27; H, 4.05; N, 5.21. HRMS (ESI): *m*/*z* calcd $[C_{16}H_{18}N_2O_2Pt + H]^+$ 466.1100, found 466.1104. ^1H NMR (200 MHz, $CDCl_3$): δ 1.37 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_2CH_3), 2.07 (s+d, $^3J_{Pt,H}$ = 23.5 Hz, 3H, $COCH_3$), 2.34 (s+d, $^3J_{Pt,H}$ = 24.0 Hz, 3H, $COCH_3$), 3.94 (m, 2H, CH_2CH_3), 7.50, 7.70, 7.93, 8.09, and 8.38 (m, 5H, aromatic protons), 8.38 (s+d, $^3J_{Pt,H}$ = 30.6 Hz, 1H, N=C*H*), 9.39 (s+d, $^3J_{Pt,H}$ = 26.9 Hz, 1H, aromatic proton). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 17.1 (s, CH_2CH_3), 43.7 (s, $COCH_3$), 43.8 (s, $COCH_3$), 60.9 (s, CH_2CH_3), 122.7, 127.0, 129.3, 130.3, 134.8, 139.8, 140.0, 141.1, and 156.7 (s, 9C, aromatic carbon atoms), 161.5 (s, N=*C*H), 227.1 (s, *C*OMe), 237.4 (s, *C*OMe). $^{195}Pt\{^1H\}$ NMR (86 MHz, $CDCl_3$): δ −3194 (s). IR: 1617 (m), 1579 (m) cm^{-1}.

Method b. To a methanol (3 mL) solution of $[Pt(COMe)_2(NH_2Et)_2]$ (**2b**; 100 mg, 0.27 mmol) was added C_9H_6NCH=NEt (**7**; 50 mg, 0.27 mmol) to afford an orange solution. After the mixture was stirred for 3 h at room temperature, the addition of diethyl ether gave an orange precipitate of **6b**, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 106 mg (85%). Analytical data are as given above.

dx.doi.org/10.1021/om4011774 | *Organometallics* XXXX, XXX, XXX−XXX

Preparation of $C_9H_6NCH{=}NEt$ (7). To a solution of C_9H_6NCHO in methanol (100 mg, 0.64 mmol) cooled to −78 °C was added ethylamine. The reaction mixture was warmed to room temperature and stirred for 4 h. The reaction mixture was concentrated under vacuum to afford an oil that was identified spectroscopically. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_2CH_3), 3.79 (m, 2H, CH_2CH_3), 7.39 (dd, $^3J_{2,3}$ = 4.2 Hz, $^3J_{4,3}$ = 8.3 Hz, H^3_{quin}), 7.56 (dd, $^3J_{5,6}$ = 8.1 Hz, $^3J_{7,6}$ = 7.3 Hz, H^6_{quin}), 7.84 (dd, $^4J_{7,5}$ = 1.2 Hz, H^5_{quin}), 8.12 (dd, $^4J_{2,4}$ = 1.7 Hz, H^4_{quin}), 8.39 (dd, H^7_{quin}), 8.93 (dd, H^2_{quin}), 9.64 (s, N=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.4 (s, CH_2CH_3), 56.2 (s, CH_2CH_3), 121.2 (s, C^3_{quin}), 126.5 (s, C^6_{quin}), 127.3 (s, C^7_{quin}), 128.2 (s, C^{10}_{quin}), 130.1 (s, C^5_{quin}), 133.3 (s, C^8_{quin}), 136.3 (s, C^4_{quin}), 146.6 (s, C^9_{quin}), 149.9 (s, C^2_{quin}), 158.1 (s, N=CH).

X-ray Structure Determination of $[Pt(COMe)Cl(C_9H_6NCO\text{-}\kappa N,\kappa C)(C_9H_6NCHOH\text{-}\kappa N,\kappa C)]\cdot 2CHCl_3$ (3·2CHCl$_3$) and $[Pt_2(C_9H_6NCO\text{-}\kappa N,\kappa C)_2(\mu\text{-}COMe)_2]\cdot 0.5H_2O$ (4·0.5H$_2$O). Data for X-ray diffraction analyses were collected on Stoe-IPDS 2T (3·2CHCl$_3$) and Oxford Gemini S (4·0.5H$_2$O) diffractometers using Mo Kα and Cu Kα radiation, respectively (λ = 0.71073/1.54184 Å, 3/4, graphite monochromator). A summary of the crystallographic data, the data collection parameters, the refinement parameters, and details of the absorption corrections is given in Table S1 in the Supporting Information. The structures were solved with direct methods using SHELXS-97[40] and refined using full-matrix least-squares routines against F^2 with SHELXL-97.[41] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic ones. H atoms were placed in calculated positions according to the riding model, except that of the O−H···O hydrogen bond in 3·2CHCl$_3$ and those of the solvate molecule in 4·0.5H$_2$O, which were located in the electron density map.

■ ASSOCIATED CONTENT

Supporting Information

A table, figures, and a CIF file giving crystallographic data for complexes **3** and **4** and details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mariaangeles.garralda@ehu.es (M.A.G.); dirk.steinborn@chemie.uni-halle.de (D.S.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Partial financial support by the Ministerio de Economía y Competitividad (CTQ2011-24859), Gobierno Vasco, and Universidad del País Vasco (UPV/EHU) are gratefully acknowledged. I.Z. is grateful to Gobierno Vasco for a scholarship. We also thank Dr. Jürgen Schmidt (Leibniz Institute of Plant Biochemistry, Halle, Germany) and Dr. Martin Bette (University of Halle) for ESI-MS determinations and discussions.

■ REFERENCES

(1) For decarbonylation reactions see for example: (a) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 5269−5270. (b) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 2130−2143. (c) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340−1348. (d) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Rubio, L. *Organometallics* **2008**, *27*, 799−802. (e) Iwai, T.; Fujihara, T.; Tsuji, Y. *Chem. Commun.* **2008**, 6215−6217. (f) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P. O.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206−5215. (g) Beck, R.; Flörke, U.; Klein, H. F. *Inorg. Chem.* **2009**, *48*, 1416−1422. (h) Adams, J. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2012**, *31*, 1439−1447. (i) Roa, A. E.; Salazar, V.; López-Serrano, J.; Oñate, E.; Paneque, M.; Poveda, M. L. *Organometallics* **2012**, *31*, 716−721.

(2) For hydroacylation reactions see for example: (a) Roy, A. H.; Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 2082−2093. (b) Jun, C. H.; Jo, E. A.; Park, J. W. *Eur. J. Org. Chem.* **2007**, 1869−1881. (c) Shen, Z.; Khan, H. A.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2916−2917. (d) Omura, S.; Fukuyama, T.; Horiguchi, J.; Murakami, Y.; Ryu, I. *J. Am. Chem. Soc.* **2008**, *130*, 14094−14095. (e) Moxham, G. L.; Randell-Sly, H.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C. *Chem. Eur. J.* **2008**, *14*, 8383−8397. (f) Pawley, R. J.; Huertos, M. A.; Lloyd-Jones, G. C.; Weller, A. S.; Willis, M. C. *Organometallics* **2012**, *31*, 5650−5659.

(3) (a) Che, C. M.; Huang, J. S. *Coord. Chem. Rev.* **2003**, *242*, 97−113. (b) Garralda, M. A. *C. R. Chim.* **2005**, *8*, 1413−1420. (c) Vigato, P. A.; Tamburini, S.; Bertolo, L. *Coord. Chem. Rev.* **2007**, *251*, 1311−1492. (d) Shibasaki, M.; Kanai, M.; Matsunaga, S.; Kumagai, N. *Top. Organomet. Chem.* **2011**, *37*, 1−30. (e) Pradeep, C. P.; Das, S. K. *Coord. Chem. Rev.* **2013**, *257*, 1699−1715.

(4) (a) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045−1047. (b) Lorenzini, F.; Moiseev, D.; Patrick, B. O.; James, B. R. *Inorg. Chem.* **2010**, *49*, 2111−2122. (c) El Mail, R.; Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Organometallics* **2000**, *19*, 5310−5317.

(5) (a) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640−641. (b) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101−1107.

(6) (a) Goldsworthy, D. H.; Kite, K. *J. Organomet. Chem.* **1987**, *319*, 257−264. (b) Castor, K. J.; Mancini, J.; Fakhoury, J.; Weill, N.; Kieltyka, R.; Englebienne, P.; Avakyan, N.; Mittermaier, A.; Autexier, C.; Moitessier, N.; Sleiman, H. F. *ChemMedChem* **2012**, *7*, 85−94. (c) Kenche, V. B.; Hung, L. W.; Perez, K.; Volitakes, I.; Ciccotosto, G.; Kwok, J.; Critch, N.; Sherratt, N.; Cortes, M.; Lal, V.; Masters, C. L.; Murakami, K.; Cappai, R.; Adlard, P. A.; Barnham, K. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 3374−3378.

(7) Koh, J. J.; Lee, W. H.; Williard, P. G.; Risen, W. M. *J. Organomet. Chem.* **1985**, *284*, 409−419.

(8) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1988**, 1833−1836.

(9) (a) Ciganda, R.; Garralda, M. A.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Dalton Trans.* **2009**, 4227−4235. (b) Garralda, M. A. *Dalton Trans* **2009**, 3635−3645 and references therein.

(10) Casas, J. M.; Forniés, J.; Martín, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1559−1563.

(11) Vaughan, T. P.; Koedyk, D. J.; Spencer, J. L. *Organometallics* **2011**, *30*, 5170−5180.

(12) (a) Albinati, A.; Anklin, C. G.; Pregosin, P. S. *Inorg. Chim. Acta* **1984**, *90*, L37−L38. (b) Albinati, A.; Anklin, C. G.; Ganazzoli, F.; Rüegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 503−508.

(13) Anklin, C. G.; Pregosin, P. S.; Wombacher, F. J.; Rüegg, H. *Organometallics* **1990**, *9*, 1953−1958.

(14) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Orpen, A. G. *Organometallics* **1990**, *9*, 2179−2181.

(15) Steinborn, D. *Dalton Trans.* **2005**, 2664−2671.

(16) Gerisch, M.; Bruhn, C.; Vyater, A.; Davies, J. A.; Steinborn, D. *Organometallics* **1998**, *17*, 3101−3104.

(17) (a) Werner, M.; Wagner, C.; Steinborn, D. *J. Organomet. Chem.* **2009**, *694*, 190−198. (b) Werner, M.; Bruhn, C.; Steinborn, D. *Trans. Met. Chem.* **2009**, *34*, 61−74. (c) Bette, M.; Schmidt, J.; Steinborn, D. *Eur. J. Inorg. Chem.* **2013**, 2395−2410.

(18) (a) Werner, M.; Bruhn, C.; Steinborn, D. *J. Organomet. Chem.* **2008**, *693*, 2369−2376. (b) Albrecht, C.; Wagner, C.; Steinborn, D. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2858−2866.

(19) Kluge, T.; Mendicute-Fierro, C.; Bette, M.; Rodríguez-Diéguez, A.; Garralda, M. A.; Steinborn, D. *Eur. J. Inorg. Chem.* **2013**, 5418−5427.

(20) Vyater, A.; Wagner, C.; Merzweiler, K.; Steinborn, D. *Organometallics* **2002**, *21*, 4369−4376.
(21) Bette, M.; Rüffer, T.; Bruhn, C.; Schmidt, J.; Steinborn, D. *Organometallics* **2012**, *31*, 3700−3710.
(22) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422. (b) Clark, G. R.; Greene, T. R.; Roper, W. R. *J. Organomet. Chem.* **1985**, *293*, C25−C28. (c) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, 435−440.
(23) Steinborn, D.; Gerisch, M.; Merzweiler, K.; Schenzel, K.; Pelz, K.; Bögel, H.; Magull, J. *Organometallics* **1996**, *15*, 2454−2457.
(24) (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534. (b) Janiak, C. *Dalton Trans.* **2000**, 3885−3896.
(25) For the chirality symbols *C*/*A* for stereogenic octahedral central atoms, cf.: International Union of Pure and Applied Chemistry. *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005*; RSC Publishing: Cambridge, U.K., 2005.
(26) Gerisch, M.; Heinemann, F. W.; Bruhn, C.; Scholz, J.; Steinborn, D. *Organometallics* **1999**, *18*, 564−572.
(27) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564. (b) Oxgaard, J.; Tenn, W. J., III; Nielsen, R. J.; Periana, R. A.; Goddard, W. A., III *Organometallics* **2007**, *26*, 1565−1567.
(28) (a) Joubert, J.; Delbecq, F. *Organometallics* **2006**, *25*, 854−861. (b) Rossin, A.; Kovács, G.; Ujaque, G.; Lledós, A.; Joó, F. *Organometallics* **2006**, *25*, 5010−5023. (c) Comas-Vives, A.; Ujaque, G.; Lledós, A. *Adv. Inorg. Chem.* **2010**, *62*, 231−260.
(29) Wang, W. H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *ACS Catal.* **2013**, *3*, 856−860.
(30) (a) Aresta, M.; Dibenedetto, A.; Pápai, I.; Schubert, G.; Macchioni, A.; Zuccaccia, D. *Chem. Eur. J.* **2004**, *10*, 3708−3716. (b) Bullock, R. M. In *Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. *1*, pp 153−197. (c) Fu, X.; Wayland, B. B. *J. Am. Chem. Soc.* **2005**, *127*, 16460−16467.
(31) (a) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1990**, *9*, 2101−2105. (b) Doherty, S.; Hogarth, G.; Elsegood, M. R. J.; Clegg, W.; Rees, N. H.; Waugh, M. *Organometallics* **1998**, *17*, 3331−3345.
(32) Gerisch, M.; Bruhn, C.; Porzel, A.; Steinborn, D. *Eur. J. Inorg. Chem.* **1998**, 1655−1659.
(33) (a) Acha, F.; Ciganda, R.; Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Dalton Trans.* **2008**, *34*, 4602−4611. (b) Ciganda, R.; Garralda, M. A.; Ibarlucea, L.; Mendicute, C.; Pinilla, E.; Torres, M. R. *Eur. J. Inorg. Chem.* **2010**, 3167−3173.
(34) Schwieger, S.; Heinemann, F. W.; Wagner, C.; Kluge, R.; Damm, C.; Israel, G.; Steinborn, D. *Organometallics* **2009**, *28*, 2485−2493.
(35) Ciganda, R.; Garralda, M. A.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Dalton Trans.* **2009**, 4227−4235.
(36) (a) Steinborn, D.; Gerisch, M.; Heinemann, F. W.; Bruhn, C. *Chem. Commun.* **1997**, 843−844. (b) Gerisch, M.; Bruhn, C.; Steinborn, D. *Polyhedron* **1999**, *18*, 1953−1956.
(37) Albrecht, C.; Wagner, C.; Merzweiler, K.; Lis, T.; Steinborn, D. *Appl. Organomet. Chem.* **2005**, *19*, 1155−1163.
(38) Kluge, T.; Bette, M.; Vetter, C.; Schmidt, J.; Steinborn, D. *J. Organomet. Chem.* **2012**, *715*, 93−101.
(39) Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101−109.
(40) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1998.
(41) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.