# Reactivity of Dinuclear Platina-*β*-diketones toward Phosphines and Pyridines: Formation of Mononuclear Platina-*β*-diketones and Acyl(chloro)platinum(II) Complexes[†]

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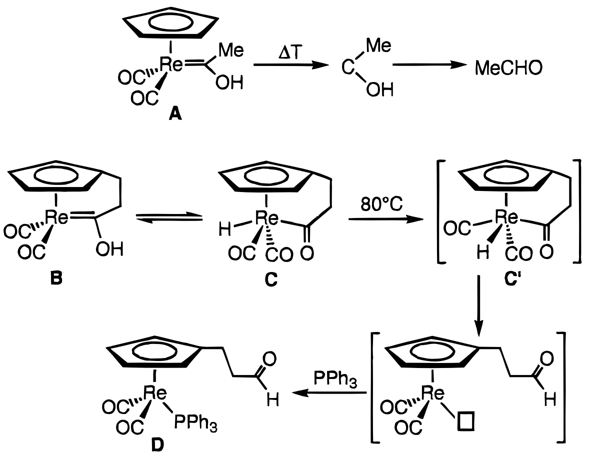
Dinuclear platina-*β*-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (R = Me (**1a**), Et (**1b**)) react with phosphines ($PPh_3$, $Ph_2P(CH_2)_nPPh_2$, $n = 1-3$) and triphenylarsine to form acylplatinum(II) complexes as well as acetaldehyde and propionaldehyde, respectively. Reaction of **1** with 4 equiv of $PPh_3$ and $AsPh_3$ leads to *trans*-[PtCl(COR)$L_2$] (L = $PPh_3$ (**4**), $AsPh_3$ (**5**); R = Me (**a**), Et (**b**)). Reaction of **1a** with $PPh_3$ in a 1:2 molar ratio results in formation of carbonyl(methyl)platinum complexes [PtCl(Me)(CO)($PPh_3$)] (**11**). Cationic A-frame complexes $[Pt_2(COR)_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]Cl$ (R = Me (**6a**), Et (**6b**)) were formed in reactions of **1** with 2 equiv of $Ph_2PCH_2PPh_2$ (dppm). Treatment of **1a** with $Ph_2P(CH_2)_2PPh_2$ (dppe) and $Ph_2P(CH_2)_3PPh_2$ (dppp) yields complexes $[PtCl(COMe)\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 2$ (**7**), 3 (**8**)). However, at low temperatures (−30 °C) reactions of **1a** with dppe and dppp afford mononuclear cationic platina-*β*-diketones $[Pt\{(COMe)_2H\}(Ph_2P(CH_2)_nPPh_2)]Cl$ ($n = 2$ (**9a**), 3 (**10**)). The reaction of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1a**) with pyridine (py) or quinoline (quin) results in cleavage of the Pt−Cl−Pt bridges, yielding mononuclear neutral platina-*β*-diketones $[PtCl\{(COMe)_2H\}L]$ (L = py (**13a**), quin (**13b**)). In the solid state complex **13b** reveals a nonplanar arrangement of the platina-*β*-diketone unit with a strong hydrogen bond (O···O 2.419(8) Å). From all these findings the mechanism of the aldehyde formation in the reactions of platina-*β*-diketones **1** with L ($PPh_3$, $AsPh_3$) and LL (dppm, dppe, dppp) is deduced.

## Introduction

Hydroxycarbene complexes are proposed as important intermediates in CO reduction reactions, including the Fischer−Tropsch process.[1] Calculations suggest that they are also key intermediates in hydroformylation and aldehyde decarbonylation reactions.[2] Since the synthesis of the first hydroxycarbene complex, $[Re\{=C(OH)Me\}(\eta^5\text{-}C_5H_5)(CO)_2]$ (**A**),[3] by Fischer, hydroxycarbene complexes of groups 6−8 have been synthesized.[4] Fischer proposed that aldehyde formation by thermal decomposition of **A** starts with the cleavage of the Re═C bond, producing free methylhydroxycarbene that is rearranged to acetaldehyde (Scheme 1).[3] Only very recently, Casey et al. reported an equilibrium between the tautomeric hydroxycarbene complex **B** and the acyl(hydrido) complex **C** (Scheme 1) as a consequence of ring strain perturbation in a system very similar to those of Fischer.[5] It is suggested that aldehyde formation occurs via reductive elimination from an unseen *cis*-acyl(hydrido) intermediate **C′**, because by thermolysis of **B** in the presense of $PPh_3$ a clean formation of the untethered aldehyde $[Re(\eta^5\text{-}C_5H_4CH_2CH_2CHO)(CO)_2(PPh_3)]$ (**D**) is observed (Scheme 1).[5b]

### Scheme 1



Dinuclear platina-*β*-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (R = Me (**1a**), R = Et (**1b**)), prepared by reaction of hexachloroplatinic(IV) acid with silyl-substituted acetylenes in *n*-butanol, proved to be electronically unsatur-

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[†] Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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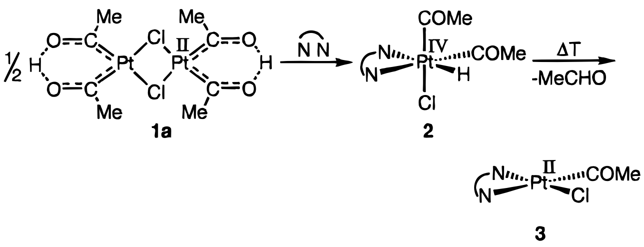
**Scheme 2**



ated complexes with a kinetically labile ligand sphere.[6] Complexes **1** can be regarded as acyl(hydroxycarbene) complexes intramolecularly stabilized by hydrogen bonds and exhibit a fundamentally different reactivity than Lukehart's mononuclear metalla-β-diketones [$L_xM$-{$(COR)_2H$}][7] (L = CO, Cp; M = Mo, W, Mn, Re, Fe, Os), which are electronically saturated and kinetically stable complexes.

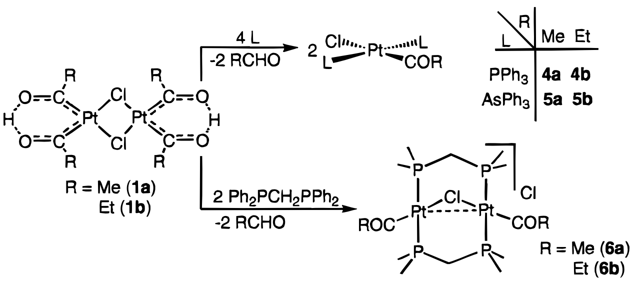
Previously, we have found that **1a** reacts with bipyridines (NN = bpy, 4,4′-$Me_2$bpy, 4,4′-*t*-$Bu_2$bpy) via oxidative addition to yield acyl(hydrido)platinum(IV) complexes [PtCl(H)$(COMe)_2$(NN)] (**2**) (Scheme 2).[8] Complexes **2** decompose in the solid state (above 150 °C) nearly quantitatively via reductive elimination of acetaldehyde to form acylplatinum(II) complexes [PtCl-(COMe)(NN)] (**3**) (Scheme 2).

We here report reactions of platina-β-diketones **1** with phosphines ($PPh_3$, dppm, dppe, dppp), with triphenylarsine, and with pyridine (py) and quinoline (quin) yielding acyl(chloro)platinum(II) complexes and mononuclear platina-β-diketones, respectively. The pathway of aldehyde formation in reactions of **1** with phosphines will be discussed.

## Results and Discussion

**Reactions of Platina-β-diketones with $PPh_3$, $AsPh_3$, and dppm.** Platina-β-diketones **1** react in methylene chloride at ambient temperature with 4 equiv of $PPh_3$ or $AsPh_3$ to give acyl(chloro)platinum(II) complexes *trans*-[PtCl(COR)$L_2$] (L = $PPh_3$ (**4**), $AsPh_3$ (**5**), R = Me (**a**), Et (**b**)) (Scheme 3). The reaction with 2 equiv of dppm (bis(diphenylphosphino)methane) affords the cationic A-frame complexes [$Pt_2(COR)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2$]-Cl (R = Me **6a**, Et **6b**) (Scheme 3). In all these reactions the formation of acetaldehyde or propionaldehyde is observed by NMR spectroscopy ($\delta(CHO)$ = 9.75 ppm for MeCHO; $\delta(CHO)$ = 9.77 ppm for EtCHO).

**Scheme 3**



All complexes **4**−**6** were obtained as off-white or pale yellow, air-stable crystals in good yields (68−85%) and identified by microanalyses and NMR and IR spectroscopy. The spectroscopic data of the triphenylphosphine complexes **4** agree with literature data.[9] Only the chemical shift of the methyl protons in complex **4b** (−0.13 ppm) shows a noticeable difference from the reported value (0.15 ppm).[9c] The resonances of the carbonyl carbon atoms in complexes **4**−**6** appear at 200.5−218.8 ppm. The $^1J(PtC)$ coupling constants were found to be 844−962 Hz.

The typical anisochronic behavior of the protons of the methylene bridges in A-frame complexes[10] is well observed in complexes **6**, too, whereas splitting of the resonances in **6a** appears only at low temperatures (−20 °C). Due to the nonzero value of the $^2J(PP)$ coupling and the superposition of three subspectra of the platinum isotopomers ($^{195}Pt$: $I = 1/2$, 33.8% abundance), the coupling constants $^2J(HH)$, $^3J(PtH)$, and $^2J(PH)$ could not be calculated in complexes **6**. The $^{31}P$ NMR chemical shifts in both complexes (**6a**, **6b**, 7.3 ppm) are very similar to those found in [$Pt_2(COPh)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2$]-Cl ($\delta$ = 5.9 ppm[11]). The $^{31}P$ NMR spectra result from superposition of $A_4$ (43.8%), AA′BB′X (44.8%), and AA′A″A‴XX′ subspectra (11.4%) (A, B = $^{31}P$; X = $^{195}Pt$). Coupling constants $^1J(PtP)$ (**6a**, 3447 Hz; **6b**, 3442 Hz), $^3J(PtP)$ (**6a**, 56 Hz; **6b**, 58 Hz), $^2J(PP)$ (**6a**, 30/48 Hz; **6b**, 31/42 Hz), $^2J(PtPt)$ (**6a**, 474 Hz), and $^4J(PP)$ (<1 Hz) were obtained by simulation of the experimental subspectra using the program PERCH.[12]

The carbonyl stretching frequencies in complexes **5** and **6** were found near 1650 $cm^{-1}$. These frequencies are characteristic for complexes *trans*-[PtCl(COR)-$(PPh_3)_2$].[13] Contrary to the A-frame complex **6b**, complex **6a** shows two $\nu(CO)$ (1650, 1656 $cm^{-1}$), indicating a slight asymmetry in the Pt−Cl−Pt bridge.

**Reactions of Platina-β-diketones with dppe and dppp.** Reaction of **1a** with 2 equiv of dppe (bis(1,2-

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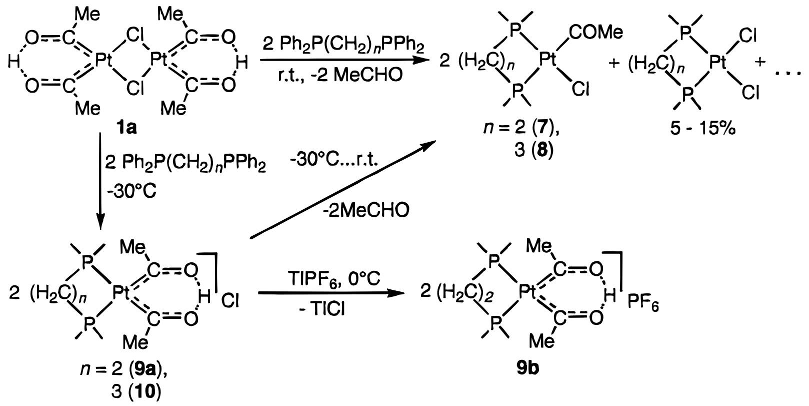
**Scheme 4**



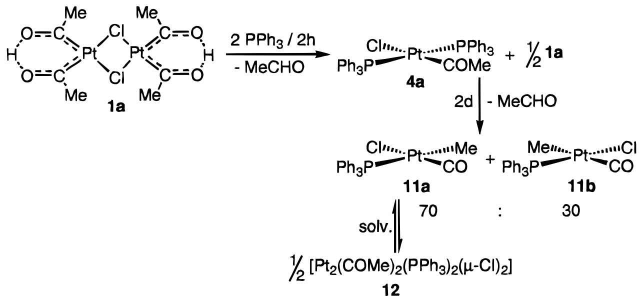
diphenylphosphino)ethane) and dppp (bis(1,3-diphenylphosphino)propane) at ambient temperature yields acyl(chloro)platinum(II) complexes [PtCl(COMe)(dppe)] (**7**) and [PtCl(COMe)(dppp)] (**8**), respectively (Scheme 4). As was shown by $^{31}$P NMR spectroscopy, dichloro(diphosphine)platinum complexes [$PtCl_2\{Ph_2P(CH_2)_n$-$PPh_2\}$] ($n = 2, 3$)[14] are formed as side products in low yields (ca. 5−15%). Both reactions reveal the formation of acetaldehyde. Complexes **7** and **8** were isolated as off-white, air-stable crystals. Separation of **7** and **8** from corresponding dichloro(diphosphine)platinum complexes was not carried out.

Carrying out the reaction of **1a** with dppe and dppp at −30 °C, cationic complexes [$Pt\{(COMe)_2H\}$(dppe)]Cl (**9a**) and [$Pt\{(COMe)_2H\}$(dppp)]Cl (**10**), respectively, are formed as intermediates (Scheme 4). These complexes decompose in solution ($CH_2Cl_2$, $CHCl_3$) at ambient temperature within 2 h (**9a**) and 20 min (**10**), respectively, under cleavage of acetaldehyde, yielding **7** and **8**, respectively, and the corresponding dichloro(diphosphine)platinum complexes in small amounts (<5%). In accord with the cationic structure, complex **9a** reacts with $TlPF_6$ at 0 °C producing the complex [$Pt\{(COMe)_2$-$H\}$(dppe)]$PF_6$ (**9b**) (Scheme 4). Attempts to isolate the cationic complexes **9** and **10** failed due to decomposition in the workup procedure, yielding acyl(chloro)platinum(II) complexes **7** and **8** as well as a number of unidentifiable products.

Complexes **7**−**10** were characterized by NMR ($^{1}$H, $^{13}$C, $^{31}$P) and IR spectroscopy. The $^{31}$P NMR spectroscopic data of [PtCl(COMe)(dppp)] (**8**) agree with literature data.[15] The resonance of the carbonyl carbon atom in **8** appears at 244.3 ppm as a doublet of doublets due to the two inequivalent P atoms, whereas in **7** only a doublet at 244.3 ppm is observed as a consequence of line broadening.

The cis geometry of **7** and **8** showing an AX pattern for **7** and an AB pattern for **8** flanked by platinum satellites is confirmed by $^{31}$P NMR spectra. The great difference in both couplings $^{1}J$(PtP) (**7**, 4439/1407 Hz; **8**, 4416/1326 Hz) is a consequence of the great difference between the trans influence of the chloro and the acyl ligand.

**Scheme 5**



The $^{1}$H NMR spectra of the cationic platina-$\beta$-diketones **9a**, **9b**, and **10** reveal a singlet for protons of the methyl groups of the platina-$\beta$-diketone unit, confirming the proposed structure shown in Scheme 4. The magnitudes for **9a** and **9b** are nearly identical. The chemical shift of the hydrogen-bonded hydrogen atoms in **9a** and **9b** is 14.4 and 14.6 ppm, respectively, indicating an upfield shift (ca. 2 ppm) with respect to those found in **1a**. The resonance for the hydrogen-bonded proton in complex **10** could not be detected due to line broadening. The $^{13}$C NMR spectrum of **9a** exhibits a pseudosextet for the methyl carbons at 27.7 ppm ($N = 49$ Hz). The chemical shifts of the carbonyl carbon atoms were determined by a HMBC spectrum and were found at 265.3 ppm, indicating a strong downfield shift of 37.2 ppm compared with those in **1a** (228.1 ppm).[6a] The $^{13}$C NMR spectrum of **10** could not be measured due to its low stability and solubility. The $^{31}$P NMR spectra show only singlet resonances with platinum satellites. The magnitudes of the $^{31}$P NMR chemical shifts (**9a**/**9b**, 39.5 ppm; **10**, −7.7 ppm) and of the $^{1}J$(PtP) coupling constants (**9a**/**9b**, 1725 Hz; **10**, 1696 Hz) confirm the structures proposed in Scheme 4, too.

**Carbonyl(methyl)platinum(II) Complexes.** Reaction of **1a** with triphenylphosphine in a 1:2 molar ratio affords within 2 h the acyl complex **4a** and acetaldehyde, whereas half of **1a** remains unchanged. Within 2 days, the reaction between **4a** and the unchanged platina-$\beta$-diketone **1a** goes on, yielding quantitatively the carbonyl(methyl) complexes [$PtCl(Me)(CO)(PPh_3)$] (**11**) (Scheme 5). NMR spectra indicate the presence of two isomers: the major product (ca. 70%) with the methyl ligand trans to $PPh_3$ (**11a**) and the minor product (ca. 30%) with the chloro ligand trans to $PPh_3$ (**11b**). The same reaction occurs between **1a** and 2 equiv of **4a** isolated in solid state, but nearly exclusive formation of isomer **11a** is observed.

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The diastereomeric structures of both complexes (Me/$PPh_3$ (**11a**) and Cl/$PPh_3$ (**11b**) in mutual trans positions) were established by the low and high value, respectively, of $^1J$(PtP) (**11a**, 1468 Hz; **11b**, 4093 Hz). In accord with this, the magnitudes of $\delta$(CO), $^2J$(PC), and $^1J$(PtC) are typical in complex **11a** ($\delta$ = 165.0 ppm, $^2J$(PC) = 7.0 Hz, $^1J$(PtC) = 1977 Hz) for a carbonyl ligand trans to a chloro ligand and cis to a phosphine and in complex **11b** ($\delta$ = 179.1 ppm, $^2J$(PC) = 5.5 Hz, $^1J$(PtC) = 958 Hz) for a carbonyl ligand trans to an organyl ligand (Ph) and cis to a phosphine.[16]

Adding pentane to a $CDCl_3$ solution of **11** or rapid removal of the solvent by evaporation yields the chloro-bridged acyl complex $[Pt_2(COMe)_2(PPh_3)_2(\mu\text{-}Cl)_2]$ (**12**) (Scheme 5), as can be seen by IR spectroscopy: Chloroform solutions of complexes **11** exhibit carbonyl stretching frequencies at 2077 $cm^{-1}$ (**11a**) and at 2107 $cm^{-1}$ (**11b**). The solid-state IR spectrum exhibits a very weak absorption at 2071 $cm^{-1}$, indicating a small amount of **11a**, and a strong one at 1668 $cm^{-1}$ due to the acyl complex **12**. The reaction **11a** $\rightleftharpoons$ **12** is reversible, shown by repeated dissolving of **12** and removal of the solvent by evaporation. An analogous CO insertion/deinsertion reaction has been described for complexes $[PtCl(Ph)(CO)(PMePh_2)]$ and $[Pt_2Cl(COPh)(PMePh_2)_2(\mu\text{-}Cl)_2]$.[17] Otherwise, complex **12** is reported to be prepared by reaction of $[PtCl_2(CO)(PPh_3)]$ with $HgMe_2$ and was identified by IR spectroscopy in the solid state ($\nu$(CO) = 1665 $cm^{-1}$) and by $^1H$ NMR spectroscopy in $CDCl_3$ ($\delta(CH_3)$ = 1.26 ppm, $^3J$(PH) = 7.5 Hz, $^3J$(PtH) = 57 Hz).[18] All these values are identical with those found for **12**/**11a** in this work, and thus, it is highly probable that equilibrium **11a** $\rightleftharpoons$ **12** was overlooked in the literature.[18]

**Molecular Structures of $[Pt_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (6a) and [PtCl(COMe)(dppe)] (7).** The molecular structures of **6a** and **7** are shown in Figures 1 and 2, respectively. Selected interatomic distances and bond angles are given in Tables 1 and 2.

The distortion of the molecular geometry of the cation in $[Pt_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (**6a**) from an idealized "A-frame" is high, characterized by the P1−Pt1−Pt2−P4 and P2−Pt1−Pt2−P3 torsion angles of −15.49(8)° and −16.84(8)°, respectively. Thus, the eight-membered dimetallacycle (Pt1, Pt2, P1, P2, P3, P4, C1, C2) shows a twisted boat conformation. The geometry at the platinum centers is close to square-planar (maximal deviation of 0.054(3) Å for Pt1Cl1C3P1P2 at Pt1 and of 0.033(3) Å for Pt2Cl1C5P3P4 at Pt2). Both planes are inclined at an angle of 76.8(1)°. The Pt−P distances on Pt1 (2.336(2)/2.339(2) Å) differ slightly from those on Pt2 (2.319(2)/2.329(2) Å) and point to a weak asymmetry. The Pt−Cl distances differ slightly from each other (2.556(2) vs 2.519(2) Å), too. The magnitudes of the Pt−C bond lengths as well as the C−O bond lengths ($d$(Pt−C) = 2.003(9)/2.010(9) Å, $d$(C−O) = 1.20(1)/1.21(1) Å) are in the range of those found in other acylplatinum(II) complexes.[19] The planes of the acyl ligands are nearly perpendicular to the complex planes (Pt1C4C3O1/Pt1P1P2Cl1C3 76.9(3)°; Pt2C5C6O2/Pt2P3P4C5Cl1 78.3(3)°). Thus, any $\pi$-bonding between the platinum centers and the acyl groups can be ruled out.

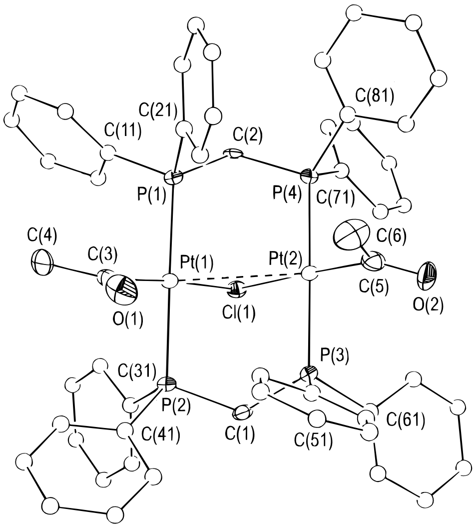

**Figure 1.** ORTEP−III plot[26] of the cation in $[Pt_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (**6a**), showing atom numbering (displacement ellipsoids at 30% probability); H atoms omitted for clarity.

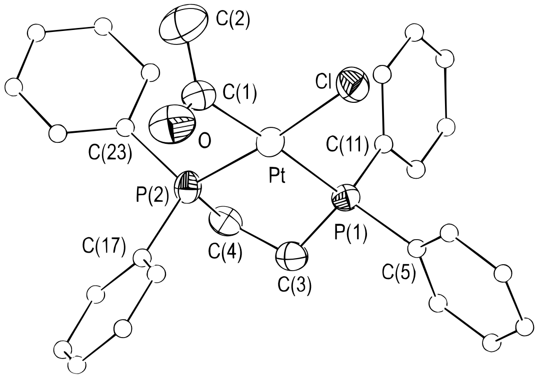

**Figure 2.** ORTEP−III plot of [PtCl(COMe)(dppe)] (**7**), showing atom numbering (displacement ellipsoids at 30% probability); H atoms omitted for clarity.

**Table 1. Selected Interatomic Distances [Å] and Bond Angles [deg] for $[Pt_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (6a)**

| | | | |
|---|---|---|---|
| Pt(1)−C(3) | 2.010(9) | Pt(2)−C(5) | 2.003(9) |
| Pt(1)−P(1) | 2.339(2) | Pt(2)−P(3) | 2.319(2) |
| Pt(1)−P(2) | 2.336(2) | Pt(2)−P(4) | 2.329(2) |
| Pt(1)−Cl(1) | 2.556(2) | Pt(2)−Cl(1) | 2.519(2) |
| C(3)−O(1) | 1.20(1) | C(5)−O(2) | 1.21(1) |
| P(1)−C(2) | 1.837(9) | P(2)−C(1) | 1.823(8) |
| P(4)−C(2) | 1.820(9) | P(3)−C(1) | 1.852(8) |
| Pt(1)···Pt(2) | 3.1130(5) | | |
| C(3)−Pt(1)−P(1) | 92.0(3) | C(5)−Pt(2)−P(3) | 87.7(3) |
| C(3)−Pt(1)−P(2) | 93.1(3) | C(5)−Pt(2)−P(4) | 96.2(3) |
| P(1)−Pt(1)−Cl(1) | 91.22(7) | P(3)−Pt(2)−Cl(1) | 91.26(7) |
| P(2)−Pt(1)−Cl(1) | 83.49(7) | P(4)−Pt(2)−Cl(1) | 84.73(7) |
| P(1)−C(2)−P(4) | 117.9(5) | P(2)−C(1)−P(3) | 119.7(4) |
| Pt(1)−Cl(1)−Pt(2) | 75.67(6) | | |

The bond angles at the methylene carbon atoms C1 and C2 of the chelating diphosphine ligands are each

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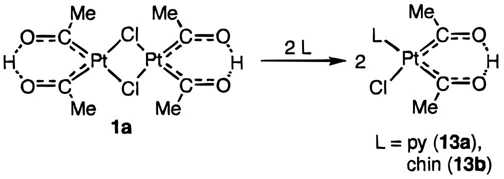
**Table 2. Selected Bond Distances [Å] and Angles [deg] for [PtCl(COMe)(dppe)] (7)**

| | | | |
|---|---|---|---|
| Pt−C(1) | 2.08(1) | Pt−Cl | 2.368(3) |
| Pt−P(1) | 2.356(3) | Pt−P(2) | 2.223(3) |
| P(1)−C(3) | 1.83(1) | P(2)−C(4) | 1.82(1) |
| C(1)−O | 1.17(1) | | |
| C(1)−Pt−P(2) | 90.3(3) | P(1)−Pt−P(2) | 86.1(1) |
| C(1)−Pt−Cl | 86.2(3) | P(1)−Pt−Cl | 97.5(1) |
| P(1)−C(3)−C(4) | 108.5(7) | P(2)−C(4)−C(3) | 109.1(7) |

**Scheme 6**



slightly increased (117.9(5)°/119.7(4)°) with respect to the tetrahedral one. The Pt···Pt distance (3.1130(5) Å) is comparable with those found in cationic A-frame complexes bridged by methylene, $\mu$-$\eta^1$-, or $\mu$-$\eta^2$-acetylenic groups ($d$(Pt···Pt) = 3.025−3.120 Å).[20]

There are weak cation−anion interactions: The chloride anions Cl2 are placed in the lattice such that short Cl···H−C contacts to hydrogen atoms of the methylene bridges (C1 and C2′) exist. Thus, a polymeric chainlike structure with alternating cations and chloride anions is formed. The interatomic distances and angles of the Cl···H−C hydrogen bonds ($d$(Cl···H) = 2.54/2.59 Å, $d$(Cl···C) = 3.42(1)/3.48(1) Å, ∠(Cl−H−C) = 152(1)°/152(1)°) are in the range of those dicussed in the literature ($d$(Cl···H) = 2.6−2.9 Å, $d$(Cl···C) ca. 3.5 Å, ∠(Cl−H−C) > 90°).[21] However, it should be noted that all hydrogen atoms are placed in calculated positions.

The geometry at Pt in [PtCl(COMe)(dppe)] (**7**) is close to square-planar (maximal deviation of 0.046(3) Å at P2). In accord with the trans influence Cl ≪ COR, the Pt−P bond distance trans to the chloro ligand (2.223(3) Å) is distinctly shorter than those trans to the acyl ligand (2.356(3) Å). The Pt−C bond length (2.08(1) Å) is comparable to those found for acyl ligands in trans-position to a phosphine ligand.[22] Pt−C−$\pi$ interactions should not play any role, because the plane PtC1C2O is nearly perpendicular to the molecular plane PtP1P2-C1Cl (78.3(4)°).

**Mononuclear Platina-$\beta$-diketones [PtCl{(COMe)$_2$H}L].** Treatment of **1a** with pyridine or quinoline in methylene chloride at ambient temperature in a 1:2 molar ratio results under cleavage of the Pt−Cl−Pt bridges in formation of mononuclear platina-$\beta$-diketones [PtCl{(COMe)$_2$H}L] (L = py (**13a**), quin (**13b**)) (Scheme 6). Complexes **13** were obtained as off-white (**13a**) or pale yellow (**13b**) crystals by condensation of pentane into methylene chloride solution at −30 °C. In solution ($CH_2Cl_2$, $CHCl_3$), complexes **13** decompose at room temperature within 2−4 days; however, at low temperatures (< −50 °C) the solutions are stable over a period of several weeks. Complex **13a** melts at 79−80 °C with the color changing from off-white to yellow followed by rapid decomposition at 92−94 °C, whereas **13b** decomposes without melting at 100−102 °C. Thus, both complexes are thermally distinctly less stable than the dinuclear complexes **1** (Mp (dec) = 183 °C (**1a**), 176 °C (**1b**)).[6a]

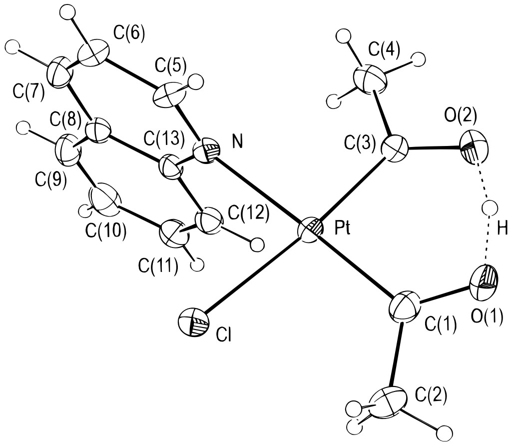


**Figure 3.** ORTEP−III plot of [PtCl{(COMe)$_2$H}(quin)] (**13b**), showing atom numbering (displacement ellipsoids at 30% probability).

**Table 3. Selected Interatomic Distances [Å] and Bond Angles [deg] for [PtCl{(COMe)$_2$H}(quin)] (13b)**

| | | | |
|---|---|---|---|
| Pt−Cl | 2.389(2) | Pt−N | 2.188(6) |
| Pt−C(1) | 1.996(7) | Pt−C(3) | 1.953(7) |
| C(1)−O(1) | 1.248(9) | C(3)−O(2) | 1.265(9) |
| O(1)···O(2) | 2.419(8) | | |
| C(3)−Pt−C(1) | 91.2(3) | C(1)−Pt−Cl | 93.6(2) |
| C(3)−Pt−N | 92.0(3) | N−Pt−Cl | 83.2(2) |

The identities of complexes **13** were confirmed by microanalyses and NMR and IR spectroscopy and for **13b** by X-ray structure analysis, too. The $^1$H NMR spectra exhibit two resonances for the methyl protons (**13a**, 1.81/2.62 ppm; **13b**, 1.62/2.72 ppm) as a consequence of the unsymmetrical coordination at platinum. Thus, a downfield and an upfield shift appear with respect to the chemical shift found for **1a** (2.43 ppm).[6a] The resonances of the protons in the O−H−O bridges (**13a**, 18.9 ppm; **13b**, 18.8 ppm) are shifted downfield by ca. 3 ppm with respect to that in **1a** (ca. 16 ppm). In agreement with the $^1$H NMR spectra two resonances for the carbonyl carbon atoms were also observed (**13a**, 236.9/245.0 ppm, **13b**, 234.2/243.8 ppm) exhibiting a downfield shift (6.1−16.9 ppm) with respect to that found in **1a** (228.1 ppm). The values of $^1J$(PtC) (**13a**, 1361/1295 Hz; **13b**, 1353/1290 Hz) are smaller by 96−167 Hz than in **1a** (1457 Hz),[6a] indicating a smaller s-electron density in the Pt−C bonds.

The C−O stretching vibrations appear at 1542/1536 cm$^{-1}$ in the pyridine complex **13a** and at 1539 cm$^{-1}$ in the quinoline complex **13b**. Thus, an essential decrease in wavenumbers of the C−O vibration with respect to that in **1a** (1548 cm$^{-1}$) is not observed. In both complexes **13a** and **13b** $\nu$(Pt−Cl) were found at 273 cm$^{-1}$.

**Molecular Structure of [PtCl{(COMe)$_2$H}(quin)] (13b).** The molecular structure of **13b** is shown in Figure 3. Selected interatomic distances and bond angles are given in Table 3. The crystal structure of **13b**

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(20) (a) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Pudephatt, R. J. *Organometallics* **1985**, *4*, 1400. (b) Hutton, A. T.; Shabanzadeh, B.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1984**, 549. (c) Alcock, N. W.; Kemp, T. J.; Pringle, P. G.; Bergamini, P.; Traverso, O. *J. Chem. Soc., Dalton Trans.* **1987**, 1659.

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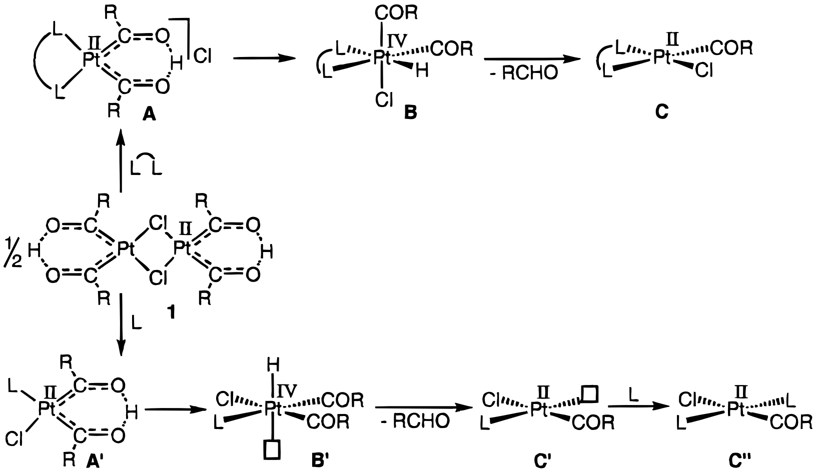
**Scheme 7**



consits of discrete molecules; no unusual short intermolecular contacts are observed. The closest Pt⋯Pt distance is 5.136(1) Å, ruling out any interaction between the metal centers. The coordination at Pt is close to square-planar (maximal deviation of 0.033(3) Å at Pt). The Pt−C bond lengths (1.996(7)/1.953(7) Å) and the C−O bond lengths (1.248(9)/1.265(9) Å) are in each case equivalent within 3$\sigma$ and do not differ significantly from those in **1a** ($d$(Pt−C) = 1.95(1) Å, $d$(C−O) = 1.23(1)/1.26(1) Å).[6a] The O⋯O distance in the O⋯H⋯O bond of **13b** (2.419(8) Å) is slightly longer than those in the dinulear complex **1a** (2.37(1) Å). The angle between the plane defined by the atoms of the quinoline ring and the complex plane PtNClC1C3 is close to 90° (88.1(2)°). The complex plane PtNClC1C3 and the planes of the acyl/hydroxycarbene ligands PtC1C2O1 and PtC3C4O2 are inclined at angles of 16.1(2)° and 13.0(4)°, respectively. Thus, the platina-β-diketone unit is not planar, in contrast to the exactly planar arrangement in the dinuclear complexes **1**.[6]

## Conclusions

It has been shown that monodentate donors L ($PPh_3$, $AsPh_3$) and bidentate donors LL (dppm, dppe, dppp, bpy, 4,4′-$Me_2$bpy, 4,4′-*t*-$Bu_2$bpy[8]) react with platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (R = Me **1a**, Et **1b**) under formation of acetaldehyde and propionaldehyde, respectively. A plausible pathway for these reactions includes the following steps (Scheme 7):

**1. Cleavage of the Pt−Cl−Pt Bridges.** The reactions of donors L or LL with platina-β-diketones **1** result in formation of mononuclear platina-β-diketones **A** and **A′**, respectively. In the case of LL = dppe and dppp the cationic complexes **A** were identified by NMR spectroscopy at low temperatures (−30 °C), whereas in the case of L = py and quin the neutral complexes **A′** were isolated. Complexes **A′** (L = py, quin) are stable at room temperature and do not react further to give **B′**.

**2. Formation of Acyl(hydrido)platinum(IV) Complexes B and B′.** This step involves oxidative addition reactions which may proceed in the sense of 1,3-hydrogen shifts or in the sense of deprotonation/reprotonation reactions. In the case of LL = bpy, 4,4′-$Me_2$bpy, and 4,4′-*t*-$Bu_2$bpy these complexes could be isolated and characterized.[8] In contrast, with diphosphines as coligands these intermediates could not be detected by NMR spectroscopy, not even at −30 °C. This is further support for the far greater versatility of nitrogen-donor ligands in stabilizing platinum(IV) than phosphine ligands.[23]

**3. Cleavage of Aldehydes.** The final step involves reductive elimination reactions, yielding acyl(chloro)platinum(II) complexes **C** and **C′**/**C″**, respectively. The vacant coordination sites in **B′** and **C′** might be occupied by solvent molecules. An indication for the coordinatively unsaturated intermediates **C′** is the formation of carbonyl(methyl) complexes **11** in the reaction of **1a** with 2 equiv of $PPh_3$. In the case of LL = bipyridines, the reactions **B** → **C** proceed in the solid state at temperatures above 150 °C only and in solution typically in boiling solvents (acetone, methanol, toluene).[24] In the case of phosphorus coligands the facile reductive elimination of aldehydes even at ambient temperature may be a consequence of higher trans influence of phosphines than those of pyridines and bipyridines.

To summarize, in all the reactions presented here the platina-β-diketones **1** behave as hydroxycarbene complexes that are stabilized intramolecularly by hydrogen bridges to acyl ligands. The results give strong evidence for an oxidative addition/reductive elimination sequence in the aldehyde formation from hydroxycarbene complexes. This is in accordance with studies by Casey[5] and quantum chemical calculations by Ziegler.[2]

## Experimental Section

**General Comments.** All reactions were performed under Ar atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. Infrared spectra were recorded on a Galaxy Mattson 5000 FT-IR spectrometer using CsBr pellets or on a Bruker IFS 66 FT spectrometer using cells (solution). NMR spectra were obtained on Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to $CHDCl_2$ ($\delta$ 5.32), $CD_2Cl_2$ ($\delta$ 53.8), $CHCl_3$ ($\delta$ 7.24), and $CDCl_3$ ($\delta$ 77.0) as internal references; $\delta(^{31}P)$ is relative to external $H_3PO_4$ (85%). Complexes $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) were prepared according to literature methods.[6a] Other chemicals were commercial materials used without further purification or after distillation.

***trans*-[PtCl(COR)L₂] (L = PPh₃ 4, AsPh₃ 5).** To a pale yellow suspension of $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) (0.16 mmol)

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(23) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735.
(24) Steinborn, D.; Vyater, A.; Gerisch, M. Unpublished results.

in methylene chloride (3 mL) was added triphenylphosphine (168 mg, 0.64 mmol) or triphenylarsine (196 mg, 0.64 mmol) at room temperature, affording a light green solution within 1 min. After 2 h diethyl ether (10 mL) was added and the precipitate so formed was filtered off, washed with diethyl ether, and dried briefly in vacuo. **4a** (L = PPh$_3$, R = Me): Yield: 221 mg, 85%. Mp (dec): 276−279 °C. Anal. Calcd for $C_{38}H_{33}ClOP_2Pt$ (798.16): C 57.18; H 4.17; Cl 4.44. Found: C 57.19; H 4.24; Cl 4.82. IR (CsBr): $\nu$(CO) 1654, $\nu$(PtCl) 255 cm$^{-1}$. $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.18 (s+d, 3H, $^{3}J$(PtH) = 13 Hz, C*H*$_3$), 7.40 (m, 18H, *m*-, *p*-C*H*), 7.76 (m, 12H, *o*-C*H*). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 44.2 (t, $^{3}J$(PC) = 6 Hz, *C*H$_3$), 128.2 ("t", *N* = 11 Hz, *m*-*C*H), 130.3 ("t", *N* = 28 Hz, *i*-C), 130.7 (*p*-*C*H), 134.9 ("t", *N* = 12 Hz, *o*-*C*H), 218.4 (t, $^{2}J$(PC) = 6 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 20.9 (s+d, $^{1}J$(PtP) = 3480 Hz). **4b** (L = PPh$_3$, R = Et): Yield: 228 mg, 78%. Mp (dec): 279−281 °C. Anal. Calcd for $C_{39}H_{35}ClOP_2Pt$ (812.19): C 57.68; H 4.34; Cl 4.56. Found: C 57.54; H 4.42; Cl 4.66. IR (CsBr): $\nu$(CO) 1658, $\nu$(PtCl) 253 cm$^{-1}$. $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ −0.13 (t, 3H, C*H*$_3$), 1.53 (q, 2H, C*H*$_2$), 7.39 (m, 18H, *m*-, *p*-C*H*), 7.75 (m, 12H, *o*-C*H*). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 8.2 (s+d, $^{3}J$(PtC) = 19 Hz, *C*H$_3$), 51.2 (t+d, $^{3}J$(PC) = 6 Hz, $^{2}J$(PtC) = 186 Hz, *C*H$_2$), 128.2 ("t", *N* = 11 Hz, *m*-*C*H), 130.4 ("t", *N* = 28 Hz, *i*-C), 130.6 (*p*-*C*H), 134.9 ("t", *N* = 12 Hz, *o*-*C*H), 218.8 (t+d, $^{2}J$(PC) = 6 Hz, $^{1}J$(PtC) = 917 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 21.1 (s+d, $^{1}J$(PtP) = 3505 Hz). **5a** (L = AsPh$_3$, R = Me): Yield: 234 mg, 84%. Anal. Calcd for $C_{38}H_{33}As_2ClOPt$ (886.06): C 51.51; H 3.75; Cl 4.00. Found: C 51.48; H 3.83; Cl 4.22. IR (CsBr): $\nu$(CO) 1650, $\nu$(PtCl) 256 cm$^{-1}$. $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.33 (s br, 3H, C*H*$_3$), 7.40 (m, 18H, *m*-, *p*-C*H*), 7.74 (m, 12H, *o*-C*H*). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 45.5 (s+d, $^{2}J$(PtC) = 157 Hz, *C*H$_3$), 128.8 (*m*-*C*H), 130.4 (*p*-*C*H), 131.9 (*i*-C), 134.1 (*o*-*C*H), 214.9 (s+d, $^{1}J$(PtC) = 844 Hz, *C*O). **5b** (L = AsPh$_3$, R = Et): Yield: 258 mg, 80%. Anal. Calcd for $C_{39}H_{35}As_2ClOPt$ (900.09): C 52.04; H 3.92; Cl 3.93. Found: C 52.24; H 4.08; Cl 4.29. IR (CsBr): $\nu$(CO) 1656, $\nu$(PtCl) 256 cm$^{-1}$. $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ −0.10 (t, 3H, C*H*$_3$), 1.63 (t, 2H, C*H*$_2$), 7.40 (m, 18H, *m*-, *p*-C*H*), 7.72 (m, 12H, *o*-C*H*). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 8.1 (s+d, $^{3}J$(PtC) = 22 Hz, *C*H$_3$), 52.6 (s+d, $^{2}J$(PtC) = 150 Hz, *C*H$_2$), 128.7 (*m*-*C*H), 130.3 (*p*-*C*), 132.1 (*i*-C), 134.1 (*o*-*C*H), 215.9 (s+d, $^{1}J$(PtC) = 854 Hz, *C*O).

**Reaction of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (1a) with PPh$_3$ in a 1:2 Molar Ratio.** To a suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (100 mg, 0.16 mmol) in CDCl$_3$ (5 mL) was added triphenylphosphine (84 mg, 0.32 mmol) at room temperature. NMR investigations of the resulting light green solution show a degree of conversion of **1a** of about 50% ($^{1}$H NMR), formation of [PtCl(COMe)(PPh$_3$)$_2$] (**4a**) after 2 h, and quantitative formation of complexes [PtCl(Me)(CO)(PPh$_3$)] (**11a**:**11b** ca. 7:3) after 2 days. **11a**: $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.24 (d+dd, 4.2H, $^{3}J$(PH) = 7.6 Hz, $^{3}J$(PtH) = 57 Hz, C*H*$_3$), 7.32−7.78 (m, CH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 2.7 (d+dd, $^{2}J$(PC) = 87 Hz, $^{1}J$(PtC) = 390 Hz, *C*H$_3$), 128.2−135.0 (phenyl−*C*), 165.0 (d+dd, $^{2}J$(PC) = 7 Hz, $^{1}J$(PtC) = 1977 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 25.2 (s+d, $^{1}J$(PtP) = 1468 Hz). **11b**: $^{1}$H NMR (200 MHz, CDCl$_3$): $\delta$ 0.72 (d+dd, 1.8H, $^{3}J$(PH) = 4.3 Hz, $^{3}J$(PtH) = 55 Hz, C*H*$_3$), 7.32−7.78 (m, CH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.7 (d+dd, $^{2}J$(PC) = 5.5 Hz, $^{1}J$(PtC) = 490 Hz, *C*H$_3$), 128.2−135.0 (phenyl−*C*), 179.1 (d+dd, $^{2}J$(PC) = 5.5 Hz, $^{1}J$(PtC) = 958 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 18.6 (s+d, $^{1}J$(PtP) = 4093 Hz).

**Reaction of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (1a) with [PtCl(COMe)(PPh$_3$)$_2$] (4a).** To a suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (100 mg, 0.16 mmol) in CDCl$_3$ (5 mL) was added [PtCl(COMe)(PPh$_3$)$_2$] (**4a**) (255 mg, 0.32 mmol) at ambient temperature. After 2 days the resulting light green solution was investigated by IR ($\nu$(CO) 2107 (**11b**), 2077 (**11a**), 1723 (MeCHO) cm$^{-1}$) and NMR spectroscopy ($^{1}$H NMR: quantitative formation of [PtCl(Me)(CO)(PPh$_3$)] (**11**), **11a**:**11b** ca. 99:1). The solvent was removed by evaporation, and the residue (complex **12**) was investigated by IR spectroscopy. IR (CsBr): $\nu$(CO) 2071vw (**11a**), 1668s (**12**), $\nu$(PtCl) 302vw, 281vw, 253vw, 245vw cm$^{-1}$.

**[Pt$_2$(COR)$_2$($\mu$-Cl)($\mu$-dppm)$_2$]Cl (6).** Complexes **6** were prepared according to the procedure described for **4** using 2 equiv of bis(diphenylphosphino)methane (123 mg, 0.32 mmol) instead of triphenylphosphine. **6a** (R = Me): Yield: 158 mg, 75%. Mp (dec): 217−219 °C. Anal. Calcd for $C_{54}H_{50}Cl_2O_2P_4Pt_2$ (1315.94): C 49.29; H 3.83; Cl 5.39. Found: C 48.83; H 3.87; Cl 5.43. IR (CsBr): $\nu$(CO) 1656, 1650 cm$^{-1}$. $^{1}$H NMR (200 MHz, 293 K, CDCl$_3$): $\delta$ 1.42 (s, 6H, C*H*$_3$), 3.96−4.38 (m, 4H, C*H*$_2$), 7.39 (m, 24H, *m*-, *p*-C*H*), 7.75 (m, 16H, *o*-C*H*). $^{1}$H NMR (500 MHz, 253 K, CD$_2$Cl$_2$): $\delta$ 1.38 (s, 6H, C*H*$_3$), 3.99 (m, 2H, C*H*$_2$), 4.25 (m, 2H, C*H*$_2$), 7.37−7.82 (m, C*H*, 40H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 29.9 ("q", *N* = 30 Hz, *C*H$_2$), 42.9 (t+d, $^{2}J$(PtC) = 225 Hz, $^{3}J$(PC) = 4 Hz, *C*H$_3$), 128.0−133.7 (phenyl−*C*), 200.5 (s+d, $^{1}J$(PtC) = 962 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 7.3 (s+m, $^{1}J$(PtP) = 3447 Hz, $^{3}J$(PtP) = 56 Hz, $^{2}J$(PP) = 30/48 Hz, $^{4}J$(PP) < 1 Hz, $^{2}J$(PtPt) = 474 Hz). **6b** (R = Et): Yield: 146 mg, 68%. Mp (dec): 214−216 °C. Anal. Calcd for $C_{56}H_{54}O_2Cl_2P_4Pt_2$ (1344.00): C 50.00; H 4.05; Cl 5.28. Found: C 49.83; H 3.93; Cl 5.41. IR (CsBr): $\nu$(CO) 1656 cm$^{-1}$. $^{1}$H NMR (200 MHz, 293 K, CDCl$_3$): $\delta$ −0.03 (t, 6H, C*H*$_3$), 1.62 (q, 4H, C*H*$_2$), 4.04 (s br, 2H, PC*H*$_2$), 4.23 (s br, 2H, PC*H*$_2$), 7.39 (m, 24H, *m*-, *p*-C*H*), 7.75 (m, 16H, *o*-C*H*). $^{1}$H NMR (500 MHz, 253 K, CD$_2$Cl$_2$): $\delta$ −0.03 (t, 6H, C*H*$_3$), 1.62 (q, 4H, C*H*$_2$), 4.03 (m, 2H, PC*H*$_2$), 4.22 (m, 2H, PC*H*$_2$), 7.26−7.80 (m, C*H*, 40H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 8.6 (s+d, $^{3}J$(PtC) = 22 Hz, *C*H$_3$), 30.5 (m, P*C*H$_2$), 50.0 (s+d, $^{2}J$(PtC) = 226 Hz, *C*H$_2$), 126.9−133.7 (phenyl-*C*), 202.9 ("t"+d, *N* = 3 Hz, $^{1}J$(PtC) = 951 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 7.3 (s+m, $^{1}J$(PtP) = 3472 Hz, $^{3}J$(PtP) = 58 Hz, $^{2}J$(PP) = 31/42 Hz).

**Reaction of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (1a) with dppe at Room Temperature.** To a suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (100 mg, 0.16 mmol) in CD$_2$Cl$_2$ (4 mL) was added bis(1,2-diphenylphosphino)ethane (127 mg, 0.32 mmol) at −30 °C, affording a pale yellow solution. The solution was slowly warmed to ambient temperature for 30 min and investigated by NMR spectroscopy (degree of conversion of **1a** 100%; ratio of [PtCl(COMe)(dppe)] (**7**):[PtCl$_2$(dppe)] ca. 85−95:15−5 detected by $^{31}$P NMR). To isolate **7** (in mixture with about 10% [PtCl$_2$(dppe)]), diethyl ether (10 mL) was added. After standing overnight the off-white crystals were filtered off and dried briefly in vacuo. IR (CsBr): $\nu$(CO) 1633, $\nu$(PtCl) 298 cm$^{-1}$. $^{1}$H NMR (200 MHz, CD$_2$Cl$_2$): $\delta$ 1.87 (d+dd, 3H, $^{4}J$(PH) = 1.6 Hz, $^{3}J$(PtH) = 14.2 Hz, C*H*$_3$), 2.15 (m, 2H, C*H*$_2$), 2.43 (m, 2H, C*H*$_2$), 7.39 (m, 12H, *m*-, *p*-C*H*), 7.69−7.84 (m, 8H, *o*-C*H*). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 24.3 (dd, $^{1}J$(PC) = 25 Hz, $^{2}J$(PC) = 7 Hz, *C*H$_2$), 28.5 (dd, $^{1}J$(PC) = 34 Hz, $^{2}J$(PC) = 8 Hz, *C*H$_2$), 41.9 (dd+d, $^{3}J$(P$_a$C) = 33 Hz, $^{3}J$(P$_b$C) = 4 Hz, $^{2}J$(PtC) = 124 Hz, *C*H$_3$), 127.2−133.2 (phenyl−*C*), 244.3 (d, $^{1}J$(PC) = 124 Hz, *C*O). $^{31}$P NMR (81 MHz, CDCl$_3$): $\delta$ 30.6 (d+dd, $^{1}J$(PtP) = 4439 Hz, $^{2,3}J$(P$_a$P$_b$) = 3 Hz), 32.2 (d+dd, $^{1}J$(PtP) = 1407 Hz, $^{2,3}J$(P$_a$P$_b$) = 3 Hz).

**Reaction of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (1a) with dppe at −30 °C.** To a pale yellow suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (100 mg, 0.16 mmol) in CD$_2$Cl$_2$ (3 mL) was added bis(diphenylphosphino)ethane (127 mg, 0.32 mmol) at −30 °C, affording a pale yellow solution of [Pt{(COMe)$_2$H}(dppe)]Cl (**9a**) that was investigated by NMR spectroscopy at −30 °C (degree of conversion of **1a** 100%). $^{1}$H NMR (300 MHz, 243 K, CD$_2$Cl$_2$): $\delta$ 2.02 (s+d, 6H, $^{3}J$(PtH) = 16.5 Hz, C*H*$_3$), 2.34 ("d", 4H, *N* = 17.0 Hz, C*H*$_2$), 7.51 (m, 12H, *m*-, *p*-C*H*), 7.74 (m, 8H, *o*-C*H*), 14.4 (s br, 1H, O*H*O). $^{13}$C NMR (75 MHz, 243 K, CD$_2$Cl$_2$): $\delta$ 27.7 ("sext", *N* = 49 Hz, *C*H$_2$), 43.4 ("t"+d, *N* = 21 Hz, $^{2}J$(PtC) = 206 Hz, *C*H$_3$), 129.2 ("t", *N* = 51 Hz, *i*-C), 129.3 ("t", *N* = 10.1 Hz, *m*-*C*H), 131.8 (*p*-*C*H), 133.4 ("t", *N* = 11.8 Hz, *C*H$_3$). HMBC (500 MHz, 243 K, CD$_2$Cl$_2$): $\delta$($^{1}$H)/($^{13}$C) = 2.02/265.3 (C*H*$_3$, *C*O). $^{31}$P NMR (81 MHz, CD$_2$Cl$_2$): $\delta$ 39.5 (s+d, $^{1}J$(PtP) = 1725 Hz).

A solution of [Pt{(COMe)$_2$H}(dppe)]Cl (**9a**), prepared as described above, was warmed to 0 °C for 10 min, and then

**Table 4. Crystal Data and Structure Refinement for 6a, 7, and 13b**

| | **6a** | **7** | **13b** |
|---|---|---|---|
| empirical formula | $C_{54}H_{50}Cl_2O_2P_4Pt_2$ | $C_{28}H_{27}ClOP_2Pt$ | $C_{13}H_{14}ClNO_2Pt$ |
| fw | 1315.90 | 671.98 | 446.79 |
| $T$, K | 293(2) | 293(2) | 293(2) |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ (no. 2) | $P2_1/n$ (no. 14) | $P2_1/n$ (no. 14) |
| $a$, Å | 11.364(1) | 9.289(1) | 12.899(3) |
| $b$, Å | 12.781(2) | 26.458(7) | 7.517(1) |
| $c$, Å | 18.694(2) | 12.018(2) | 14.751(4) |
| $\alpha, \beta, \gamma$, deg | 72.51(1), 88.01(1), 89.18(1) | 90, 103.51(1), 90 | 90, 106.49(3), 90 |
| $V$, Å$^3$ | 2588.1(5) | 2871.9(9) | 1371.5(5) |
| $Z$ | 2 | 4 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.689 | 1.554 | 2.164 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 5.665 | 5.107 | 10.418 |
| $F(000)$ | 1280 | 1312 | 840 |
| scan range, deg | $2.29 < \theta < 25.00$ | $1.91 < \theta < 22.50$ | $2.48 < \theta < 25.00$ |
| no. of reflns collected | 25 435 | 13 241 | 9362 |
| no. of indep reflns | 8579 ($R_{int} = 0.1123$) | 3674 ($R_{int} = 0.1252$) | 2318 ($R_{int} = 0.0501$) |
| no. of params refined | 590 | 299 | 180 |
| goodness-of-fit on $F^2$ | 1.086 | 0.971 | 0.997 |
| final $R$ ($I > 2\sigma(I)$) | $R1 = 0.0453$, $wR2 = 0.1232$ | $R1 = 0.0450$, $wR2 = 0.0751$ | $R1 = 0.0292$, $wR2 = 0.0657$ |
| $R$, all data | $R1 = 0.0630$, $wR2 = 0.1323$ | $R1 = 0.0960$, $wR2 = 0.0885$ | $R1 = 0.0408$, $wR2 = 0.0695$ |
| largest diff peak and hole, e Å$^{-3}$ | 1.669 and −3.178 | 0.585 and −0.504 | 2.537 and −1.120 |

$TlPF_6$ (112 mg, 0.32 mmol) was added. After stirring for 5 min, the precipitate of TlCl was filtered. The solution of [Pt{(COMe)$_2$H}(dppe)]$PF_6$ (**9b**) was characterized by NMR spectroscopy (degree of conversion of **9a** 100%). $^1$H NMR (300 MHz, 243 K, $CD_2Cl_2$): $\delta$ 2.03 (s+d, 6H, $^3J$(PtH) = 16.5 Hz, C*H*$_3$), 2.35 ("d", 4H, $N$ = 17.0 Hz, C*H*$_2$), 7.49 (m, 12H, *m*-, *p*-C*H*), 7.76 (m, 8H, *o*-C*H*), 14.6 (s br, 1H, O*H*O). $^{31}$P NMR (81 MHz, $CD_2Cl_2$): $\delta$ 39.5 (s+d, $^1J$(PtP) = 1725 Hz), −141.7 (sept, $^1J$(PF) = 711 Hz).

**Reaction of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (1a) with dppp.** To a pale yellow suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (100 mg, 0.16 mmol) in $CD_2Cl_2$ (4 mL) was added bis(1,3-diphenylphosphino)propane (132 mg, 0.32 mmol) at −30 °C, affording a pale yellow solution that was investigated by $^1$H and $^{31}$P NMR spectroscopy at −30 °C ($^1$H NMR: degree of conversion of **1a** yielding [Pt{(COMe)$_2$H}(dppp)]Cl (**10**) 100%). The solution was slowly warmed to ambient temperature for 30 min and investigated by NMR spectroscopy (ratio of [PtCl(COMe)(dppp)] (**8**):[PtCl$_2$(dppp)] ca. 85−90:15−10 detected by $^{31}$P NMR). To isolate **8** (in mixture with about 10% [PtCl$_2$(dppp)]), diethyl ether (10 mL) was added. After standing overnight the off-white crystals were filtered off and dried briefly in vacuo. **8**: IR (CsBr): $\nu$(CO) 1637, $\nu$(PtCl) 292 cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 1.74 (d, 3H, $^4J$(PH) = 1.0 Hz, C*H*$_3$), 1.86 (m, 2H, C*H*$_2$), 2.32 (m, 2H, C*H*$_2$), 2.63 (m, 2H C*H*$_2$), 7.36 (m, 12H, *m*-, *p*-C*H*), 7.67 (m, 8H, *o*-C*H*). $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 19.2 (PCH$_2$*C*H$_2$), 26.3 (dd, $^1J$(PC) = 20 Hz, $^3J$(PC) = 7 Hz, P*C*H$_2$), 26.9 (dd, $^1J$(PC) = 33 Hz, $^3J$(PC) = 12 Hz, P*C*H$_2$), 40.7 (dd, $^3J$(P$_a$C) = 27 Hz, $^3J$(P$_b$C) = 11 Hz, *C*H$_3$), 128.4−133.4 (phenyl−*C*), 244.3 (dd, $^2J$(P$_a$C) = 126 Hz, $^2J$(P$_b$C) = 9 Hz, *C*O). $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ −4.5 (d+dd, $^1J$(PtP) = 4416 Hz, $^2J$(P$_a$P$_b$) = 27.8 Hz), −4.7 (d+dd, $^1J$(PtP) = 1326 Hz, $^2J$(P$_a$P$_b$) = 27.8 Hz). **10**: $^1$H NMR (300 MHz, 243 K, $CD_2Cl_2$): $\delta$ 1.89 (s, 6H, C*H*$_3$), 2.82 (m, 6H, C*H*$_2$), 7.33 (m, 12H, *m*-, *p*-C*H*), 7.73 (m, 8H, *o*-C*H*), resonance for O*H*O not observed. $^{31}$P NMR (81 MHz, $CD_2Cl_2$): $\delta$ −7.7 (s+d, $^1J$(PtP) = 1696 Hz).

**[PtCl{(COMe)$_2$H}L] (13).** To a suspension of [Pt$_2${(COMe)$_2$H}$_2$($\mu$-Cl)$_2$] (**1a**) (200 mg, 0.32 mmol) in methylene chloride (3 mL) was added pyridine (53 $\mu$L, 0.66 mmol) or quinoline (86 $\mu$L, 0.66 mmol) at room temperature. After 30 min, the resulting green-yellow solution was layered with pentane (10 mL). After standing overnight at −30 °C off-white (**13a**) or pale yellow (**13b**) crystals that precipitated were filtered off, washed with pentane (5 mL), and dried briefly in vacuo. **13a** (L = py): Yield: 230 mg, 92%. Mp: 79−80 °C (dec 92−94 °C). Anal. Calcd for $C_9H_{12}ClNO_2Pt$ (396.73): C 27.25; H 3.05; Cl 8.94; N 3.53. Found: C 26.91; H 2.82; Cl 9.01; N 3.37. IR (CsBr): $\nu$(CO) 1542, 1536, $\nu$(PtCl) 273 cm$^{-1}$. $^1$H NMR (200 MHz, 253 K, $CD_2Cl_2$): $\delta$ 1.81 (s+d, 3H, $^3J$(PtH) = 19.3 Hz, C*H*$_3$), 2.62 (s+d, 3H, $^3J$(PtH) = 17.2 Hz, C*H*$_3$), 7.55 (m, 2H, *m*-C*H*), 7.94 (m, 1H, *p*-C*H*), 8.65 (m, 2H, *o*-C*H*), 18.9 (s br, 1H, O*H*O). $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 39.4 (s+d, $^2J$(PtC) = 174 Hz, *C*H$_3$), 40.8 (s+d, $^2J$(PtC) = 124 Hz, *C*H$_3$), 126.5 (*m*-*C*H), 139.1 (*p*-*C*H), 152.2 (*o*-*C*H), 236.9 (s+d, $^1J$(PtC) = 1361 Hz, *C*O), 245.0 (s+d, $^1J$(PtC) = 1295 Hz, *C*O). **13b** (L = quin): Yield: 220 mg, 78%. Mp (dec): 100−102 °C. Anal. Calcd for $C_{13}H_{14}ClNO_2Pt$ (446.79): C 34.95; H 3.16; Cl 7.93; N 3.13. Found: C 34.78; H 2.83; Cl 7.86; N 2.82. IR (CsBr): $\nu$(CO) 1539, $\nu$(PtN) 504, $\nu$(PtCl) 273 cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 1.62 (s+d, 3H, $^3J$(PtH) = 19.0 Hz, C*H*$_3$), 2.72 (s+d, 3H, $^3J$(PtH) = 17.9 Hz C*H*$_3$), [7.65 (dd, 1H, $^3J$(HH) = 8.4 Hz, $^4J$(HH) = 2.9 Hz), 7.72 (t, 1H, $^3J$(HH) = 7.3 Hz), 7.91 ("quin", 1H, $N$ = 16.5 Hz), 8.02 (d, 1H, $^3J$(HH) = 8.0 Hz), 8.48 (d, 1H, $^3J$(HH) = 8.0 Hz), 8.89 (d, 1H, $^3J$(HH) = 8.4 Hz), 9.10 (dd, 1H, $^3J$(HH) = 4.9 Hz, $^4J$(HH) = 1.1 Hz)], 18.8 (s br, 1H, O*H*O). $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 38.8 (s+d, $^2J$(PtC) = 166 Hz, *C*H$_3$), 40.6 (s+d, $^2J$(PtC) = 140 Hz, *C*H$_3$), [121.9 (s+d, $^2J$(PtC) = 25 Hz), 128.0 (s+d, $^2J$(PtC) = 36 Hz), 128.2, 128.6, 129.9, 131.6, 139.3, 146.4, 152.8], 234.2 (s+d, $^1J$(PtC) = 1353 Hz, *C*O), 243.8 (s+d, $^1J$(PtC) = 1290 Hz, *C*O). Resonances of the quinoline ligand are given in square brackets.

## Crystallographic Studies

Intensity data for **6a**, **7**, and **13b** were collected on a Stoe IPDS diffractometer with Mo K$\alpha$ radiation (0.710 73 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 4. **13b** was corrected for absorption numerically ($T_{min}/T_{max}$ 0.15/0.29). The structures were solved by direct methods with SHELXS-86[26] and refined using full-matrix least-squares routines against $F^2$ with SHELXL-93.[26] Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions of **6a**, **7**, and **13b** were calculated and allowed to ride on their corresponding carbon atoms. The isotropic displacement parameters

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(25) Sheldrick, G. M. *SHELXS-86, SHELXS-93, Programs for Crystal Structure Determination*; University of Göttingen, Göttingen, 1986, 1993.

(26) Burnett, M. N.; Johnson, C. K. *ORTEP−III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*; Oak Ridge National Laboratory Report ORNL-6895, 1996.

of **6a** and **7** were tied to those of the adjacent carbon atoms by a factor of 1.5 (**6a**) and 1.2 (**7**), respectively; those of **13b** were refined. The bridging H atom in **13b** was found in the difference Fourier map. The chloride anion in **6a** is disordered, lying on two positions with a major (Cl2, 83.8%) and a minor (Cl2a, 16.2%) site occupancy.

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**Supporting Information Available:** Complete tables of atomic coordinates, H atom parameters, bond distances, bond angles, and anisotropic displacement parameters for **6a**, **7**, and **13b** (23 pages). Ordering information is given on any current masthead page.

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