Anionic Tetranuclear Platina-β-diketonates of Platina-β-diketones – Organometallic Analogues of Platinum Blue Complexes

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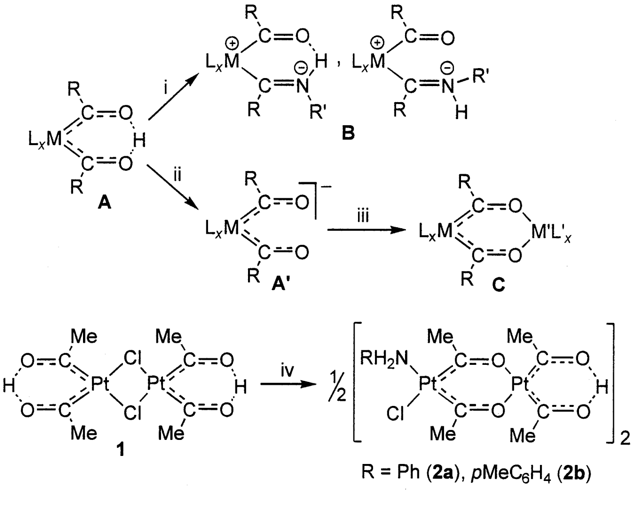
The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) reacts with aliphatic amines [nBuNH$_2$, (iPr)$_2$NH, NEt$_3$], *N*-methylaniline, and *N*,*N*-dimethylaniline, as well as with strong bases, such as a proton sponge or [NMe$_4$]OH, in an equimolar ratio to give the anionic platina-β-diketonato complexes of platina-β-diketones $[BH]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ (**3**) {B = nBuNH$_2$ (**3a**), (iPr)$_2$NH (**3b**), NEt$_3$ (**3c**), PhNHMe (**3d**), PhNMe$_2$ (**3e**), $C_{10}H_6(NMe_2)_2$ [1,8-bis(dimethylamino)naphthalene] (**3f**) and $[NMe_4]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ (**3g**)}. All complexes were characterized by microanalysis, and by ^{1}H-NMR and IR spectroscopy. X-ray structure analyses reveal that in the solid state the complexes **3a** · 0.5 CH$_2$Cl$_2$ and **3g** · 2 CH$_2$Cl$_2$ consist of tetranuclear dianions with zigzag Pt$_4$ chains [Pt–Pt–Pt angle: 122.92(3)° (**3a**), 119.30(6)° (**3g**)]. The central Pt···Pt distances [**3a**: 3.171(1) Å, **3g**: 3.176(1) Å] give evidence for closed shell d^8-d^8 interactions. Thus, these bis(acyl)-bridged complexes can be regarded as organometallic analogues of platinum blue complexes.

The dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**), prepared by the reaction of hexachloroplatinic(IV) acid with silyl-substituted acetylenes in *n*-butanol, proved to be an electronically unsaturated complex with a kinetically labile ligand sphere[1]. When compared to Lukehart's mononuclear metalla-β-diketones $[L_xM\{(COR)_2H\}]$ (**A**)[2] (L = CO, Cp; M = Mo, W, Mn, Re, Fe, Os), which are electronically saturated and kinetically stable complexes, the complex **1** exhibits a fundamentally different reactivity. These complexes **A** were shown to react with primary amines to give the corresponding metalla-β-ketoimines **B**[3] [Scheme 1(i)] and, after deprotonation (**A′**), with metal salts to give the metalla-β-diketonato metal complexes **C** [Scheme 1(ii) and (iii)][4]. Recently, we reported that the platina-β-diketone **1** reacts with aniline or *p*-toluidine to yield platina-β-diketonato complexes of platina-β-diketones $[\{(RNH_2)ClPt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ (R = Ph **2a**, pMeC$_6$H$_4$ **2b**) [Scheme 1(iv)][5]. These complexes are neutral complexes containing tetranuclear zigzag Pt$_4$ chains in the solid state.

Here we report on the reaction of the platina-β-diketone **1** with primary, secondary, and tertiary aliphatic amines, and with *N*-methyl- and *N*,*N*-dimethylaniline as well as with strong bases such as a proton sponge and [NMe$_4$]OH, to give anionic platina-β-diketonato complexes of platina-β-diketones.

Scheme 1. (i) RNH$_2$; (ii) − H$^+$; (iii) $[L'_xM']^+$; (iv) 2 RNH$_2$ (− [RNH$_3$]Cl)



R = Ph (**2a**), pMeC$_6$H$_4$ (**2b**)

Results and Discussion

Treatment of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with one equiv. of *n*-butylamine (nBuNH$_2$), diisopropylamine [(iPr)$_2$NH], triethylamine (NEt$_3$), *N*-methylaniline (PhNHMe), *N*,*N*-dimethylaniline (PhNMe$_2$), or the proton sponge 1,8-bis(dimethylamino)naphthalene [$C_{10}H_6(NMe_2)_2$] in dichloromethane at ambient temperature af-

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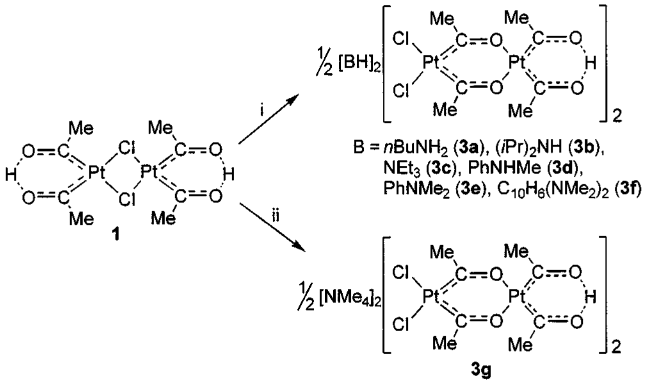
fords, in moderate to good yield (56−82%), the anionic platina-β-diketonato complexes of platina-β-diketones $[BH]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ [B = nBuNH$_2$ (**3a**), (iPr)$_2$NH (**3b**), NEt_3 (**3c**), PhNHMe (**3d**), $PhNMe_2$ (**3e**), $C_{10}H_6(NMe_2)_2$ (**3f**)] [Scheme 2(i)]. An analogous reaction carried out with tetramethylammonium hydroxide forms the complex $[NMe_4]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ (**3g**) in a yield of 60% [Scheme 2(ii)]. No well defined products could be obtained with an excess of amines or $[NMe_4]OH$.

Scheme 2. (i) nBuNH$_2$, (iPr)$_2$NH, NEt_3, PhNHMe, $PhNMe_2$ or $C_{10}H_6(NMe_2)_2$ (1:1); (ii) $[NMe_4]OH$ (1:1; − H_2O)

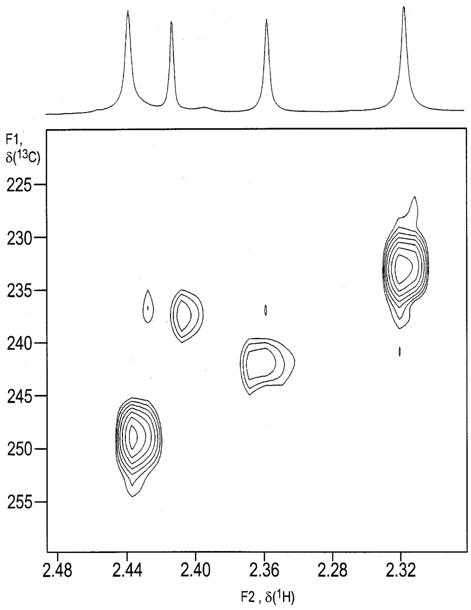


Complex **3a** was obtained as orange crystals and the complexes **3b**, **3c**, and **3f** were obtained as yellow, microcrystalline solids. The complexes **3d** and **3e** were isolated as orange rubberlike solids. After drying briefly, the complex **3g**·CH_2Cl_2 was obtained as orange crystals. All anionic platina-β-diketonato complexes of platina-β-diketones **3** are air-sensitive and decompose between 79 and 110°C. Thus, their thermal stability is similar to that of the neutral platina-β-diketonates of platina-β-diketones **2** [m.p. (dec) = 90−93°C][5], but smaller than that of the starting complex **1** [m.p. (dec) = 183 C][1]. In solution (CH_2Cl_2) complexes of **3** decompose at room temp. within less than 1 h, whereas at low temperatures (< −50°C) the solutions are stable over a period of one week.

Spectroscopic Investigations

At room temp. the ^{1}H-NMR spectra of the anionic complexes **3** show only one broad signal for the methyl protons (δ ≈ 2.4). With the exception of the complex **3d**, four methyl resonances are found at low temperatures (< −20°C). These methyl resonances form two pairs, the signals within each pair having the same intensity; and the ratio of intensities between the two pairs of signals being ca. 70:30 in all cases. Because all of the complexes are only slightly soluble in CD_2Cl_2 at −25°C, and due to the restricted thermal stability of these solutions, the carbonyl carbon atoms could not be detected by conventional ^{13}C-NMR spectroscopy. However, from the ^{1}H,^{13}C shift-correlation 2D-NMR spectra of **3g** via one (HMQC) and three bonds (HMBC), recorded at −25°C, the ^{13}C-chemical shifts of the four methyl groups and the corresponding four chemically inequivalent carbonyl carbon atoms (Figure 1) can be extracted and are found to be in in the range δ = 233.2−248.8.

Figure 1. HMBC spectrum of **3g** showing the range of the carbonyl carbon resonances



The temperature dependence of the ^{1}H-NMR spectra points to a dynamic process at room temp. and to the existence of two isomers at temperatures below −20°C. Taking into account the fact that the neutral complex **2b** is dinuclear in chloroform solution at room temp.[5], one isomer should be the dinuclear species **3′** (Scheme 3). **3′** could be in equilibrium with either the tetranuclear complex **3′′** (as was found in the solid state) or with the deprotonated starting complex **1′** (Scheme 3).

The proton resonances of the hydrogen-bonded hydrogen atoms in all anionic platina-β-diketonato complexes of platina-β-diketones **3** appear as a broad signal at δ ≈ 20, indicating a downfield shift of about 4 ppm with respect to the platina-β-diketone **1** (δ ≈ 16).

Two strong bands in the carbonyl region are found in the IR spectra of the complexes **3**: $\tilde{\nu}$ = 1524−1534 cm^{-1} for the bridging μ-acyl groups in the platina-β-diketonato unit and $\tilde{\nu}$ = 1552−1556 cm^{-1} for the platina-β-diketone unit. In the neutral complexes **2**, there were two bands observed at 1514 cm^{-1} and 1535 cm^{-1} for the bridging μ-acyl unit (the splitting is due to the unsymmetric coordination of the platinum centre) and one band at 1545 cm^{-1} (**2a**) and 1553 cm^{-1} (**2b**), for the platina-β-diketone unit. The C−O stretching vibration in the platina-β-diketone **1** also appears in this region ($\tilde{\nu}$ = 1548 cm^{-1}).

Crystal Structures

The crystal structures of **3a**·0.5 CH_2Cl_2 and **3g**·2 CH_2Cl_2 were obtained by X-ray diffraction analyses. The ORTEP diagram of the anion in **3g**·2 CH_2Cl_2 is shown in

Scheme 3. Possible isomers of the anion $[Cl_2Pt(\mu\text{-}COMe)_2Pt\{(COMe)_2H\}]^-$ (**3**) in solution

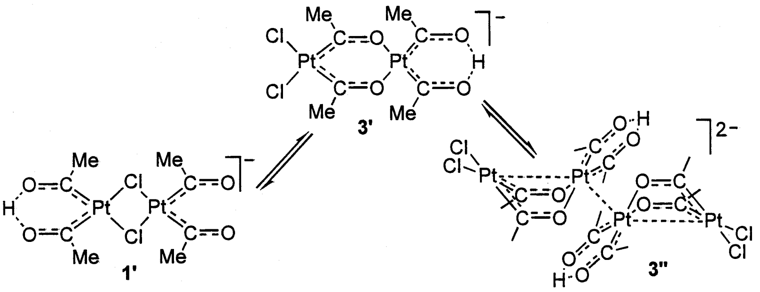
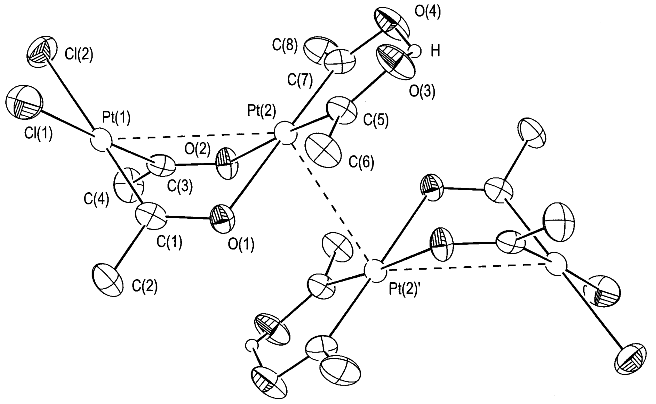


Figure 2. ORTEP-III plot[14] of the anion in **3g**·2 CH_2Cl_2[a], showing atom numbering (displacement ellipsoids at 30% probability); only the H atom in the hydrogen bridge is shown



[a] Selected interatomic distances [Å] and angles [°]; values concerning **3a**·0.5 CH_2Cl_2 are given in square brackets: Pt(1)−Cl(1) 2.412(2) [2.417(4)], Pt(1)−Cl(2) 2.408(2) [2.424(4)], Pt(1)−C(1) 1.940(8) [1.91(1)], Pt(1)−C(3) 1.941(8) [1.96(1)], Pt(2)−C(5) 1.94(1) [1.90(2)], Pt(2)−C(7) 1.939(8) [1.93(1)], Pt(2)−O(1) 2.148(5) [2.139(7)], Pt(2)−O(2) 2.138(5) [2.129(8)], C(1)−O(1) 1.25(1) [1.26(1)], C(3)−O(2) 1.27(1) [1.26(2)], C(5)−O(3) 1.25(1) [1.27(2)], C(7)−O(4) 1.26(1) [1.25(2)], O(3)···O(4) 2.397(8) [2.40(2)], Pt(1)···Pt(2) 3.358(1) [3.336(1)], Pt(2)···Pt(2′) 3.176(1) [3.171(1)]; Pt(1)−Pt(2)−Pt(2′) 119.30(6) [122.92(3)], [Pt(1)Cl(1)Cl(2)C(1)C(3)]/[Pt(2)O(1)O(2)C(5)C(7)] 89.1(2) [89.6(3)].

Figure 2. The representation of the anion in **3a**·0.5 CH_2Cl_2 is not shown due to the close similarities to **3g**·2 CH_2Cl_2. Both complexes exhibit crystallographically imposed inversion symmetry. Bond lengths and bond angles of complexes **3a**·0.5 CH_2Cl_2 and **3g**·2 CH_2Cl_2 do not differ significantly. Minor differences were found in the Pt(1)···Pt(2) distance [**3a**: 3.336(1) Å, **3b**: 3.358(1) Å] and in the Pt(1)−Pt(2)−Pt(2′) angle [**3a**: 122.92(3)°, **3b**: 119.30(6)°].

Platinum is square-planar coordinated by two Cl and two C atoms, and by two O and two C atoms, respectively. The Pt−C bond lengths [1.90(1)−1.96(1) Å] and the C−O bond lengths [1.25(1)−1.27(2) Å] are in each case equivalent to within 3σ, and do not differ significantly from those in the platina-β-diketone **1** and in the neutral platina-β-diketonato complexes of platina-β-diketones **2** [*d*(Pt−C) = 1.95(1)−2.00(2) Å; *d*(C−O) = 1.21(3)−1.26(1) Å][1][5]. The Pt−O distances [2.129(8)−2.148(5) Å] and the Pt−Cl distances [2.408(2)−2.424(4) Å] are in the range of those observed in **2** [*d*(Pt−O) = 2.15(1)−2.18(1) Å; *d*(Pt−Cl) = 2.409(6)/2.390(4) Å]. The O···O distances in the intramolecular O···H···O bonds [**3a**: 2.40(2) Å, **3g**: 2.397(8) Å] are essentially the same as those in the complexes **1** and **2** [2.28(4)−2.37(2) Å].

As for the complexes **2**[5], complexes **3a**·0.5 CH_2Cl_2 and **3g**·2 CH_2Cl_2 are "head-to-head" dimers forming Pt_4 "zigzag" chains. Analogous Pt_4 units are found in platinum blue complexes that were first prepared (1908) by treating an aqueous solution of $[PtCl_2(MeCN)_2]$ with silver nitrate[6] and were structurally characterized (1977) as amidato bridged complexes especially by Lippard[7].

The conformations of the zigzag Pt_4 chains are very similar in all four complexes **2** and **3**. The Pt···Pt distances between the two central platinum atoms [**3a**: 3.171(1)/**3g**: 3.176(1) Å] indicate relatively strong closed shell d^8-d^8 interactions[8]. Similar values are observed in the "classical" platinum blue complexes with platinum in the average oxidation state of 2.0 [*d*(Pt···Pt) = 2.87−3.24 Å][9], and in platinum(II) complexes with columnar structures [*d*(Pt···Pt) = 3.09−3.60 Å][10].

In complexes **2** and **3** the coordination planes of Pt(1) and Pt(2) are inclined at angles of 76.4(4)°−89.6(4)°[11]. In the classical platinum blue complexes these angles are markedly smaller (18−40°)[7][9][12]. This may be due to the different numbers of bridging atoms (two in complexes **2** and **3** vs. three in the platinum blue complexes). In accordance with this, the Pt(1)−Pt(2)−Pt(2′) angles in complexes **2** and **3** are distinctly smaller than in the platinum blues [119.30(6)−127.52(3)° vs. 158−170°][7][9][12]. Furthermore, in all complexes **2** and **3,** the central Pt···Pt distances {mean value *d*[Pt(2)···Pt(2′)] = 3.171 Å} are shorter than the distances between the ligand-bridged platinum atoms {mean value *d*[Pt(1)···Pt(2)] = 3.284 Å}. The reverse order is observed in the classical platinum blue complexes[7][9][12].

The comparison made between the platina-β-diketonato complexes of platina-β-diketones **2** and **3** and the classical platinum blue complexes reveals many structural similarities. Thus, the bis(acyl)-bridged complexes **2** and **3** can be regarded as organometallic analogues of platinum blue complexes. The investigations show that stable organometallics with Pt_4 chains can appear as neutral complexes **2**[5] or as anionic complexes **3**. Investigations are in progress to synthesize analogous cationic complexes.

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Experimental Section

All reactions were performed under an Ar atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. − IR: Galaxy Mattson 5000 FT-IR spectrometer using CsBr pellets. − NMR: Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to $\mathrm{C}H\mathrm{DCl_2}$ (δ_H = 5.32), $C\mathrm{D_2Cl_2}$ (δ_C = 53.8), $\mathrm{C}H\mathrm{Cl_3}$ (δ_H = 7.24), and $C\mathrm{DCl_3}$ (δ_C = 77.0) as internal references. − Microanalyses (C, H, N, Cl): University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. − The complex $[\mathrm{Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2}]$ (**1**) was prepared according to the literature method[1]. Other chemicals were commercial materials used after distillation or without further purification.

General Procedure for the Synthesis of $[BH]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ (**3**): The amine [*n*BuNH$_2$; (*i*Pr)$_2$NH; NEt$_3$; PhNHMe; PhNMe$_2$; $\mathrm{C_{10}H_6(NMe_2)_2}$] (0.32 mmol) was added to a stirred suspension of $[\mathrm{Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2}]$ (**1**) (200 mg, 0.32 mmol) in dichloro methane (3 ml) at ambient temp., producing a yellow/orange solution within 1 min. Diethyl ether (5 ml) was added and a precipitate was formed within 2 d at −40°C which was filtered off, washed with diethyl ether, and dried briefly in vacuo.

(*B* = *nBuNH*$_2$) (**3a**): Orange crystals. − M.p. (dec) 84−86°C. − Yield: 169 mg (76%). − IR: $\tilde{\nu}$ = 1556 cm^{-1} (sh, CO), 1531 (s, CO), 274 (w, PtCl), 249 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 0.92 [t, 3 H, $\mathrm{N(CH_2)_3C}H_3$], 1.42 [sext, 2 H, $\mathrm{N(CH_2)_2C}H_2$], 1.77 (quin, 2 H, $\mathrm{NCH_2C}H_2$), 2.36 [s(br), 6 H, $\mathrm{COC}H_3$], 2.38 [s(br), 6 H, $\mathrm{COC}H_3$], 3.10 (t, 2 H, $\mathrm{NC}H_2$), 7.53 [s(br), 3 H, $\mathrm{N}H_3$], ca 19.5 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$]. − ^{1}H NMR (248 K, CDCl$_3$): δ = 0.92 [t, 3 H, $\mathrm{N(CH_2)_3C}H_3$], 1.39 [sext, 2 H, $\mathrm{N(CH_2)_2C}H_2$], 1.77 (quin, 2 H, $\mathrm{NCH_2C}H_2$), 2.31 (s, 1.8 H, $\mathrm{COC}H_3$), 2.33 (s, 4.2 H, $\mathrm{COC}H_3$), 2.36 (s, 1.8 H, $\mathrm{COC}H_3$), 2.46 (s, 4.2 H, $\mathrm{COC}H_3$), 3.09 (sext, 2 H, $\mathrm{NC}H_2$), 7.54 (s, 3 H, $\mathrm{N}H_3$), 20.10 (s, 1 H, $\mathrm{O}H\mathrm{O}$). − $\mathrm{C_{12}H_{25}Cl_2NO_4Pt_2}$ (708.40): calcd. C 20.35, H 3.56, Cl 10.01, N 1.98; found C 20.13, H 3.49, Cl 10.20, N 1.85.

[*B* = *(iPr)*$_2$*NH*] (**3b**): Yellow crystals. − M.p. (dec) 95−97°C. − Yield: 190 mg (82%). − IR: $\tilde{\nu}$ = 1556 cm^{-1} (sh, CO), 1534 (s, CO), 275 (w, PtCl), 250 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 1.45 (d, 12 H, $\mathrm{NCHC}H_3$), 2.3−2.5 (m, 12 H, $\mathrm{COC}H_3$), 3.38 (sept, 2 H, $\mathrm{NC}H\mathrm{CH_3}$), 8.33 [s(br), 2 H, $\mathrm{N}H_2$], resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (248 K, CDCl$_3$): δ = 1.44 (d, 12 H, $\mathrm{NCHC}H_3$), 2.31 (s, 4.2 H, $\mathrm{COC}H_3$), 2.36 (s, 1.8 H, $\mathrm{COC}H_3$), 2.48 (s, 1.8 H, $\mathrm{COC}H_3$), 2.51 (s, 4.2 H, $\mathrm{COC}H_3$), 3.38 (sept, 2 H, $\mathrm{NC}H\mathrm{CH_3}$), 8.24 (s, 2 H, $\mathrm{N}H_2$), 20.02 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$]. − $\mathrm{C_{14}H_{29}Cl_2NO_4Pt_2}$ (736.45): calcd. C 22.83, H 3.97, Cl 9.63, N 1.90; found C 22.47, H 3.83, Cl 10.36, N 1.99.

(*B* = *NEt*$_3$) (**3c**): Yellow microcrystals. − M.p. (dec) 90−92°C. − Yield: 139 mg (60%). − IR: $\tilde{\nu}$ = 1553 cm^{-1} (sh, CO), 1530 (s, CO), 280 (w, PtCl), 257 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 1.37 (t, 9 H, $\mathrm{NCH_2C}H_3$), 2.3−2.5 (m, 12 H, $\mathrm{COC}H_3$), 3.21 (dq, 6 H, $\mathrm{NC}H_2\mathrm{CH_3}$, $^3J_\mathrm{NH,H}$ = 5.1 Hz), 9.08 [s(br), 1 H, $\mathrm{N}H$], resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (248 K, CDCl$_3$): δ = 1.34 (t, 9 H, $\mathrm{NCH_2C}H_3$), 2.31 (s, 4.4 H, $\mathrm{COC}H_3$), 2.35 (s, 1.6 H, $\mathrm{COC}H_3$), 2.42 (s, 1.6 H, $\mathrm{COC}H_3$), 2.51 (s, 4.4 H, $\mathrm{COC}H_3$), 3.19 (dq, 6 H, $\mathrm{NC}H_2\mathrm{CH_3}$, $^3J_\mathrm{NH,H}$ = 5.3 Hz), 8.71 (s, 1 H, $\mathrm{N}H$), 20.06 (s, 1 H, $\mathrm{O}H\mathrm{O}$). − $\mathrm{C_{14}H_{29}Cl_2NO_4Pt_2}$ (736.45): calcd. C 22.83, H 3.97, Cl 9.63, N 1.90; found C 22.56, H 3.86, Cl 10.04, N 1.94.

(*B* = *PhNHMe*) (**3d**): Orange rubberlike solid. − Yield: 131 mg (56%). − IR: $\tilde{\nu}$ = 1556 cm^{-1} (sh, CO), 1531 (s, CO), 274 (w, PtCl), 249 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 2.2−2.6 (m, 12 H, $\mathrm{COC}H_3$), 3.01 (s, 3 H, $\mathrm{NC}H_3$), 7.1−7.4 (m, 5 H, $\mathrm{C}H$), 11.61 [s(br), 2 H, $\mathrm{N}H_2$], resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (248 K, CDCl$_3$): δ = 2.2−2.5 (m, 12 H, $\mathrm{COC}H_3$), 3.09 (s, 3 H, $\mathrm{NC}H_3$), 7.42 (m, 3 H, *m,p*-$\mathrm{C}H$), 7.60 (m, 2 H, *o*-$\mathrm{C}H$), 10.55 (s, 2 H, $\mathrm{N}H_2$), 20.03 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$]. − $\mathrm{C_{15}H_{23}Cl_2NO_4Pt_2}$ (742.41): calcd. C 24.27, H 3.12, Cl 9.55, N 1.89; found C 24.88, H 3.43, Cl 10.36, N 2.05.

(*B* = *PhNMe*$_2$) (**3e**): Orange rubberlike solid. Yield: 148 mg (62%). − IR: $\tilde{\nu}$ = 1554 cm^{-1} (sh, CO), 1530 (s, CO), 274 (w, PtCl), 251 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 2.3−2.6 (m, 12 H, $\mathrm{COC}H_3$), 3.12 (d, 6 H, $\mathrm{NC}H_3$, $^3J_\mathrm{NH,H}$ = 1.2 Hz), 7.37 (m, 5 H, $\mathrm{C}H$), ca 10.8 [s(br), 1 H, $\mathrm{N}H$], resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (248 K, CDCl$_3$): δ = 2.21 (s, 4.6 H, $\mathrm{COC}H_3$), 2.39 (s, 1.4 H, $\mathrm{COC}H_3$), 2.44 (s, 1.4 H, $\mathrm{COC}H_3$), 2.52 (s, 4.6 H, $\mathrm{COC}H_3$), 3.25 (s, 6 H, $\mathrm{NC}H_3$), 7.36 (t, 1 H, *p*-$\mathrm{C}H$), 7.47 (m, 2 H, *m*-$\mathrm{C}H$), 7.57 (d, 2 H, *o*-$\mathrm{C}H$), 11.8 (s, 1 H, $\mathrm{N}H$), 20.03 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$]. − $\mathrm{C_{16}H_{25}Cl_2NO_4Pt_2}$ (756.44): calcd. C 25.41, H 3.33, Cl 9.37, N 1.85; found C 25.13, H 3.67, Cl 10.25, N 1.94.

[*B* = $C_{10}H_6(NMe_2)_2$] (**3f**): Yellow microcrystals. − M.p. (dec) 108−110°C. − Yield: 182 mg (68%). − IR: $\tilde{\nu}$ = 1552 cm^{-1} (sh, CO), 1529 (s, CO), 271 (w, PtCl), 248 (w, PtCl). − ^{1}H NMR (293 K, CDCl$_3$): δ = 2.3−2.5 [s(br), 12 H, $\mathrm{COC}H_3$], 3.27 (d, 12 H, $\mathrm{NC}H_3$, $^3J_\mathrm{H,H}$ = 2.8 Hz), [7.69 (t, 2 H, $^3J_\mathrm{H,H}$ = 7.7 Hz), 7.80 (dd, 2 H, $^3J_\mathrm{H,H}$ = 7.7 Hz, $^4J_\mathrm{H,H}$ = 1.1 Hz), 7.99 (dd, 2 H, $^3J_\mathrm{H,H}$ = 8.4 Hz, $^4J_\mathrm{H,H}$ = 0.7 Hz)], 18.85 (s, 1 H, $\mathrm{N}H\mathrm{N}$), resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (233 K, CD$_2$Cl$_2$): δ = 2.27 (s, 4.4 H, $\mathrm{COC}H_3$), 2.35 (s, 1.6 H, $\mathrm{COC}H_3$), 2.45 (s, 1.6 H, $\mathrm{COC}H_3$), 2.48 (s, 4.4 H, $\mathrm{COC}H_3$), 3.21 (d, 12 H, $\mathrm{NC}H_3$, $^3J_\mathrm{H,H}$ = 2.8 Hz), [7.69 (t, 2 H, $^3J_\mathrm{H,H}$ = 7.8 Hz), 7.80 (dd, 2 H, $^3J_\mathrm{H,H}$ = 7.5 Hz, $^4J_\mathrm{H,H}$ = 0.8 Hz), 7.97 (dd, 2 H, $^3J_\mathrm{H,H}$ = 8.4 Hz, $^4J_\mathrm{H,H}$ = 0.7 Hz)], 19.15 (s, 1 H, $\mathrm{N}H\mathrm{N}$), 20.1 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$], Resonances of the aromatic H atoms are given in brackets. − $\mathrm{C_{22}H_{32}Cl_2N_2O_4Pt_2}$ (849.56): calcd. C 31.10, H 3.80, Cl 8.35, N 3.30; found C 30.47, H 3.97, Cl 9.16, N 3.10.

Synthesis of $[NMe_4]_2[\{Cl_2Pt(\mu\text{-}COMe)_2Pt[(COMe)_2H]\}_2]$ ($\mathbf{3g}\cdot\mathrm{CH_2Cl_2}$): A 2.2 M solution of [NMe$_4$]OH in methanol (142 μl, 0.32 mmol) was added to a stirred suspension of $[\mathrm{Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2}]$ (**1**) (200 mg, 0.32 mmol) in dichloromethane (3 ml) at ambient temp., immediately producing an orange solution. On standing overnight (−40°C), orange crystals precipitated from solution, which were filtered off at −78°C, washed with diethyl ether, and dried briefly in vacuo. − M.p. (dec) 79−81°C. − Yield: 142 mg (60%). − IR: $\tilde{\nu}$ = 1553 cm^{-1} (sh, CO), 1524 (s, CO), 271 (w, PtCl), 256 (w, PtCl). − ^{1}H NMR (293 K, CD$_2$Cl$_2$): δ = 2.2−2.5 [s(br), 12 H, $\mathrm{COC}H_3$], 3.39 (s, 12 H, $\mathrm{NC}H_3$), resonance for $\mathrm{O}H\mathrm{O}$ not observed. − ^{1}H NMR (248 K, CD$_2$Cl$_2$): δ = 2.28 (s, 4.0 H, $\mathrm{COC}H_3$), 2.36 (s, 2.0 H, $\mathrm{COC}H_3$), 2.41 (s, 2.0 H, $\mathrm{COC}H_3$), 2.44 (s, 4.0 H, $\mathrm{COC}H_3$), 3.33 (s, 12 H, $\mathrm{NC}H_3$), ca 20.0 [s(br), 1 H, $\mathrm{O}H\mathrm{O}$]. − $\mathrm{C_{24}H_{50}Cl_4N_2O_8Pt_4\cdot CH_2Cl_2}$ (1501.72): calcd. C 19.99, H 3.49, Cl 14.16, N 1.86; found C 20.00, H 3.63, Cl 14.51, N 1.96. HMQC (248 K, CD$_2$Cl$_2$): δ(^{1}H/^{13}C) = 2.28/37.6 (CH_3), 2.36/41.4 (CH_3), 2.41/40.6 (CH_3), 2.44/42.6 (CH_3), 3.33/53.8 ($\mathrm{N}CH_3$). − HMBC (248 K, CD$_2$Cl$_2$): δ(^{1}H/^{13}C) = 2.28/233.2 ($\mathrm{C}H_3$, $C\mathrm{O}$), 2.36/242.1 ($\mathrm{C}H_3$, $C\mathrm{O}$), 2.41/237.6 ($\mathrm{C}H_3$, $C\mathrm{O}$), 2.44/248.8 ($\mathrm{C}H_3$, $C\mathrm{O}$).

Crystal Structure Determination of Complexes $\mathbf{3a}\cdot 0.5\ \mathrm{CH_2Cl_2}$ *and* $\mathbf{3g}\cdot 2\ \mathrm{CH_2Cl_2}$: Crystals were taken directly from the solution and selected under perfluoro ether. A suitable crystal was quickly mounted on a glass fiber. Intensity data were collected on a Stoe IPDS diffractometer with Mo-K_α radiation (0.71073 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 1. Absorption corrections were carried out numerically. The structures were solved by direct methods using *SHELXS*-86[13] and refined with full matrix least squares routines against F^2 using

Table 1. Crystal data and details on the structure determination of complexes **3a**$\cdot$0.5 CH_2Cl_2 and **3g**$\cdot$2 CH_2Cl_2

compound	**3a**$\cdot$0.5 CH_2Cl_2	**3g**$\cdot$2 CH_2Cl_2
Empirical formula	$C_{24.5}H_{51}Cl_5N_2O_8Pt_4$	$C_{26}H_{54}Cl_8N_2O_8Pt_4$
Formula weight	1459.28	1586.67
Crystal system	monoclinic	monoclinic
Space group	*C*2/c (no. 15)	$P2_1$/a (no. 14)
a [Å]	34.648(7)	14.932(2)
b [Å]	10.540(2)	9.372(1)
c [Å]	13.557(3)	18.023(5)
β [°]	57.42(2)	112.34(2)
Z	4	2
V [$Å^3$]	4172(2)	2332.8(7)
$D_{calcd.}$ [g cm^{-3}]	2.323	2.259
F (000)	2692	1472
μ(MoK_α) [cm^{-1}]	13.730	12.453
Crystal size	0.2 × 0.2 × 0.1	0.24 × 0.13 × 0.04
Temperature [K]	298(2)	223(2)
θ (min., max.) [°]	2.05, 24.00	2.44, 24.07
Recip. latt. segment *h*	$-42 \rightarrow 41$	$-16 \rightarrow 17$
k	$-13 \rightarrow 12$	$-10 \rightarrow 10$
l	$-16 \rightarrow 16$	$-20 \rightarrow 20$
Measured reflections	11890	15148
Independent refl. [$R_{int.}$]	3274 [0.1354]	3631 [0.1029]
$T_{min.}/T_{max.}$	0.09/0.22	0.04/0.49
Observed reflections	2209	3187
Parameters	186	248
*R*1, *wR*2 [$I>2\sigma(I)$]	0.0430/0.0857	0.0328/0.0815
*R*1, *wR*2 (all data)	0.0737/0.0944	0.0389/0.0842
S	0.917	1.053
Min. and max. resd. electron dens. [e/$Å^3$]	−2.427 and 1.256	−1.443 and 2.615

SHELXL-93[13]. All non-H atoms were refined with anisotropic displacement parameters. As a result of disorder in **3a**$\cdot$0.5 CH_2Cl_2 the two outer C atoms of the butyl group in the cation $[n\mathrm{BuNH_3}]^+$ were refined isotropically. The H atoms were added to the model in their calculated positions and refined isotropically, except for the bridging H-atom in **3g**$\cdot$2 CH_2Cl_2, which was found in the difference Fourier map.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101858 (**3a**$\cdot$0.5 CH_2Cl_2) and no. CCDC-101859 (**3g**$\cdot$2 CH_2Cl_2), respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK [Fax: (internat.) + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] D. Steinborn, M. Gerisch, K. Merzweiler, K. Schenzel, K. Pelz, H. Bögel, J. Magull, *Organometallics* **1996**, *15*, 2454−2457.

[2] Reviews: [2a] C. M. Lukehart, *Acc. Chem. Res.* **1981**, *14*, 109−116. − [2b] C. M. Lukehart, *Adv. Organomet. Chem.* **1986**, *25*, 45−71.

[3] [3a] C. M. Lukehart, J. V. Zeile, *J. Am. Chem. Soc.* **1978**, *100*, 2774−2778. − [3b] C. M. Lukehart, J. V. Zeile, *Inorg. Chem.* **1978**, *17*, 2369−2374. − [3c] K. P. Darst, C. M. Lukehart, *Inorg. Chim. Acta* **1980**, *41*, 239−243. − [3d] C. M. Lukehart, M. Raja, *Inorg. Chem.* **1982**, *21*, 1278−1280. − [3e] D. Afzal, C. M. Lukehart, *Inorg. Chem.* **1983**, *22*, 3954−3956.

[4] [4a] C. M. Lukehart, G. P. Torrence, *Inorg. Chem.* **1979**, *18*, 3150−3155. − [4b] C. M. Jensen, Y. J. Chen, H. D. Kaesz, *J. Am. Chem. Soc.* **1984**, *106*, 4046−4047. − [4c] P. G. Lenhert, C. M. Lukehart, P. O. Sotiropoulos, K. Srinivasan, *Inorg. Chem.* **1984**, *23*, 1807−1810. − [4d] D. Xu, H. D. Kaesz, S. I. Khan, *Inorg. Chem.* **1991**, *30*, 1341−1344. − [4e] E. Lippmann, C. Robl, H. Berke, H. D. Kaesz, W. Beck, *Chem. Ber.* **1993**, *126*, 933−940.

[5] D. Steinborn, M. Gerisch, F. W. Heinemann, C. Bruhn, *J. Chem. Soc., Chem. Commun.* **1997**, 843−844.

[6] K. A. Hoffmann, G. Bugge, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 312−314.

[7] Reviews: [7a] J. K. Barton, S. J. Lippard, *Ann. N. Y. Acad. Sci.* **1978**, *313*, 686−700. − [7b] S. J. Lippard, *Science* **1982**, *218*, 1075−1082.

[8] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597−636.

[9] [9a] L. S. Hollis, S. J. Lippard, *J. Am. Chem. Soc.* **1981**, *103*, 1230−1232. − [9b] L. S. Hollis, S. J. Lippard, *Inorg. Chem.* **1983**, *22*, 2600−2604. − [9c] J. P. Laurent, P. Lepage, F. Dahan, *J. Am. Chem. Soc.* **1982**, *104*, 7335−7336. − [9d] G. Bernadinelli, P. Castan, R. Soules, *Inorg. Chim. Acta* **1986**, *120*, 205−207. − [9e] L. S. Hollis, S. J. Lippard, *J. Am. Chem. Soc.* **1983**, *105*, 3494−3503. − [9f] K. Matsumoto, H. Miyamae, H. Moriyama, *Inorg. Chem.* **1989**, *28*, 2959−2964.

[10] [10a] W. B. Connick, R. E. Marsh, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1997**, *36*, 913−922. − [10b] J. M. Williams, *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 235−268.

[11] In ref.[5] the angles between the normals to the planes are given [**2a**: 95.7(6)°, **2b**: 103.6(4)°], which are the supplemental angles to α.

[12] [12a] J. K. Barton, H. N. Rabinowitz, D. J. Szalda, S. J. Lippard, *J. Am. Chem. Soc.* **1977**, *99*, 2827−2829. − [12b] J. K. Barton, S. A. Best, S. J. Lippard, R. A. Walton, *J. Am. Chem. Soc.* **1978**, *100*, 3785−3788. − [12c] J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszczak, S. J. Lippard, *J. Am. Chem. Soc.* **1979**, *101*, 1434−1441. − [12d] J. K. Barton, C. Caravana, S. J. Lippard, *J. Am. Chem. Soc.* **1979**, *101*, 7269−7277. − [12e] T. V. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts, S. J. Lippard, *Inorg. Chem.* **1987**, *26*, 1261−1270. − [12f] K. Matsumoto, K. Sakai, K. Nishio, Y. Tokisue, R. Ito, T. Nishide, Y. Shichi, *J. Am. Chem. Soc.* **1992**, *114*, 8110−8118.

[13] G. M. Sheldrick, *SHELXS-86*, *SHELXL-93*, *Programs for Crystal Structure Determination*; University of Göttingen, Göttingen, **1986**, **1993**.

[14] M. N. Burnett, C. K. Johnson, *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, **1996**.

[98199]