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# A novel platinum methylene complex

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## Abstract

The dichlorobridged diplatinum organyls **4** and **5** undergo the expected chlorine–iodine exchange when treated with lithium iodide in diiodomethylene. Surprisingly, a second type of product, the triple-bridged (one methylene group plus two iodo units between the two Pt atoms) diplatinum complexes **7** and **8**, respectively, are also formed in these unusual reactions. The formation of these latter two interesting, novel compounds takes place via a change of configuration of their two ligand sections from *anti* of their precursors (**4** and **5**, respectively) to *syn* present in **7** and **8**; the mechanism of this process, however, is not yet clear. The molecular structures of **7** and **8** are based on an X-ray crystal analysis of **7** and on their comparable characteristic NMR data.

*Keywords:* *Anti*/*syn*-transformation; Cycloplatination; Halogen exchange; Liquid crystal discussion; Overcrowded platinum organyls; Oxidative addition; Platinum complexes of different oxidation states; Platinum methylene complexes; X-ray structure analysis

## 1. Introduction

The chemistry of cyclometallated complexes has attracted much attention due to their applications in organic synthesis. Whereas cyclometallated organopalladium compounds have been studied extensively, there are fewer studies of platinum(II) complexes with *ortho*-metallated nitrogen donor ligands exhibiting liquid-crystalline properties [1]. In particular, *ortho*-metallated platinum(IV) complexes with nitrogen donor ligands were unknown until recently and current knowledge is restricted to a few compounds synthesized by oxidative addition of halogens or halocarbons to platinum(II) precursors [2].

Since the discovery of the first example of metal complexes with *methylene bridged* two metal atoms by Herrmann et al. [3], such metal organyls have become of special interest because of their affinity to methylene groups on metal surfaces in heterogeneous reactions [4,5].

Here, we report not only the synthesis and characterization of two new planar diplatinum organyls (**4** and **6**), but also the preparation of novel type μ-methylene bridged bis-metal complexes (**7** and **8**) formed by intermolecular oxidative addition reactions of diiodomethane onto cyclometallated diplatinum(II) complexes.

## 2. Results and discussion

The double-(chloro-)bridged platinum organyls **4** and **5** [6] containing two platinum atoms forming a *flat* molecular core region were obtained by similar methods of *ortho*-metallation of diaryl imines — here **1** and **2** — as applied [6–8] for the syntheses of other equally shaped dipalladium and diplatinum organyls with liquid-crystalline properties (Scheme 1).

The exchange of the chloro-bridges in the diplatinum organyl **4** with lithium iodide in dichloromethane–acetone yielded not only the planar double-(iodo-)bridged diplatinum(II) complex **6** but, surprisingly, also the triple-bridged (methylene plus two iodo-bridges between the two Pt atoms) diplatinum(IV) organyl **7** (Scheme 1). Furthermore, this interesting and novel

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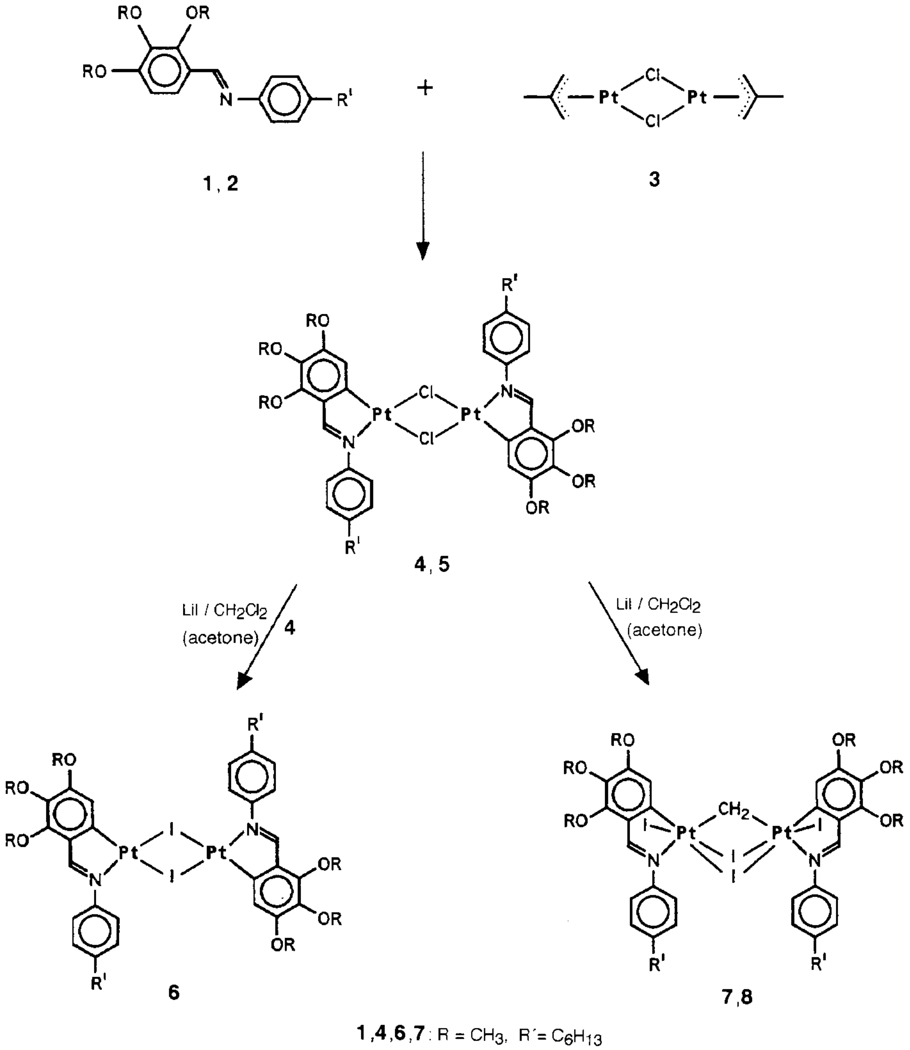
bis-octahedral diplatinum methylene complex **7** could be isolated exclusively under the same conditions but using longer reaction times.

Alternatively, **7** can also be obtained from the reaction of **4** with diiodomethane but in lower yields, see Section 3.

Another example of this kind of triple-bridged platinum complex is the diplatinum organyl **8** (Scheme 1), now having eight longer alkoxy chains. This homologue was obtained analogously from the liquid-crystalline diplatinum organyl **5** (Cr *91.7°C* {$N_D$ *54.4°C*} Iso [6]; Cr = crystalline, $N_D$ = nematic discotic, Iso = isotropic liquid) and lithium iodide excess in dichloromethane–acetone. Numerous repetitions of this transformation reaction yielded **8** as the only product.

Oxidative addition of alkyl halides or halogens on Pt(II) compounds can proceed via several mechanisms [2]. Depending on the metal substrate, the alkyl halide, or the halogen, and the reaction conditions both $S_{N2}$ and free-radical reactions (chain- and nonchain-types) have been found. However, the $S_{N2}$ process is dominant in reactions of alkyl halides or halogens and square-planar $d^8$ complexes with ligands that do not block the coordination sites above and below the coordination plane [2,9,10]. These studies cited indicate that the oxidative addition reactions of the related chloro-bridged diplatinum(II) complexes forming the Pt(IV) species **7** and **8** may proceed in an $S_{N2}$ manner about which details are yet unknown.

All the compounds described here were fully characterized by $^1$H-, $^{13}$C-, and also (in part) by $^{195}$Pt-NMR spectroscopy as well as by elemental analysis. The $^1$H- and $^{13}$C-NMR data for the diplatinum organyls **4** and **6** are similar to those of the analogous *anti*-configurated, proved by X-ray analysis [6], square-planar platinum organyl **5**. The $\delta(^{195}\text{Pt})$ value of −3130.3 ppm for the chloro-bridged platinum organyl **4** is well within the range expected for organoplatinum(II) compounds [6b,8] with *ortho*-metallated nitrogen donor ligands.



**1**,**4**,**6**,**7**: R = $CH_3$, R′ = $C_6H_{13}$

**2**,**5** [6], **8**: R = R′ = $C_6H_{13}$

Scheme 1.

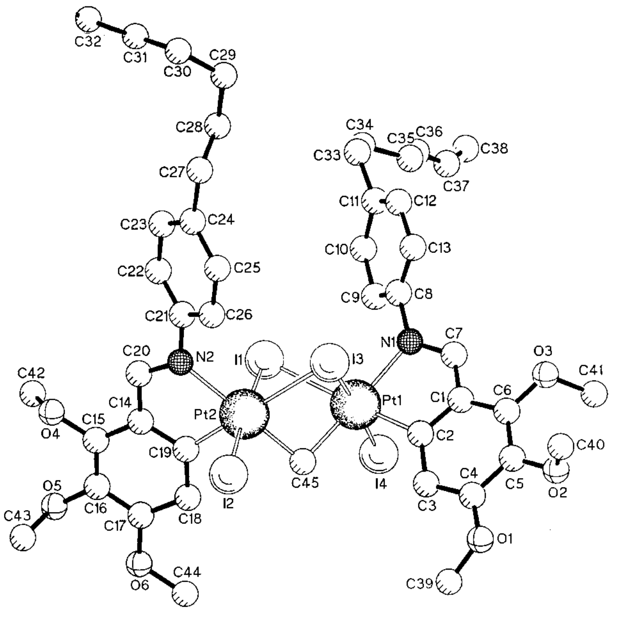


Fig. 1. The crystal structure of **7**.

Table 1
Crystal and data collection parameters for **7** [a]

| | |
|---|---|
| Formula | $C_{45}H_{58}I_4N_2O_6Pt_2$ |
| Formula weight | 1620.74 |
| Crystal size (mm) | $0.05 \times 0.2 \times 0.5$ |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| $Z$ | 2 |
| $a$ (Å) | 10.543(7) |
| $b$ (Å) | 16.132(8) |
| $c$ (Å) | 17.156(29) |
| $\alpha$ (°) | 100.54(10) |
| $\beta$ (°) | 95.89(11) |
| $\gamma$ (°) | 101.31(5) |
| $V$ (Å$^3$) | 2783.8 |
| $d_c$ (g cm$^{-3}$) | 1.93 |
| Radiation $\lambda$ (Å) | Mo–K$_\alpha$, 0.71069 |
| $\mu$ (cm$^{-1}$) | 73.1 |
| $2\theta_{max}$ (°) | 40.0 |
| $hkl$ range | $0 \leq h \leq 7$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$ |
| Scan type | $\omega$-scan |
| Scan speed (deg min$^{-1}$) | Min 1.0, max 29.3 |
| No. of data measured | 4933 |
| No. of unique data | 3194<br>$I > 2\sigma(I)$ |
| $R$ | 0.053 |
| $R_w$ | 0.055 |
| $w$ | $1/[\sigma^2(F) + 0.001951F^2]$ |
| Res. electron density (e Å$^{-3}$) | $-0.96/1.89$ |
| Absorption correction | Empirical, min/max corrections 0.710/1.459 |

[a] Estimated standard deviations are given in parentheses.

The data given in the literature for the chemical shift of $CH_2$-bridges (3.43–8.03 ppm) [4,5] in related materials differ considerably depending on the type of metal atom as well as the nature of the ligands. The $^1$H-NMR spectra for **7** and **8** display a single absorption at 6.55 and 6.52 ppm, respectively, for the $CH_2$-bridges. The interpretation of the $^{13}$C-NMR signals of the μ-$CH_2$ groups of the triple-bridged, bis-octahedral complexes **7** and **8** was possible on the basis of a 2D C–H COSY spectrum. The $^{13}$C-NMR spectra of **7** and **8** showed a triplet at 9.88 and at 9.80 ppm, respectively, for the $CH_2$-bridges.

Furthermore, for the bis-octahedral compounds **7** and **8** the resonance frequency of the iminic protons ($\delta$ 8.36 and 8.33 ppm, respectively) was shifted to a lower field relative to the bis-square-planar platinum(II) compounds **4**, **5** [6] and **6**, cf. Section 3. The aforementioned selected NMR data undoubtedly prove that **7** and **8** are of identical basic molecular structure.

Suitable crystals of **7** as a model compound for an X-ray analysis, due to its short substituents compared with those of the homologue **8**, were grown by slowly evaporating its methanol–acetone solution. The molecular structure of **7** including the atom labelling based on that X-ray study is illustrated in Fig. 1.

The new organyl **7** crystallizes in the triclinic space group $P\bar{1}$. The crystal data, data collection and refinement details are summarized in Table 1. Table 2 gives the atomic coordinates and Table 3 a compilation of selected bond lengths and angles.

All atoms occupy general positions in the unit cell. The two platinum atoms are each octahedrally coordinated by a terminal iodine atom, two bridging iodine atoms, and a methylene group (C45) as well as by a nitrogen atom and a ring carbon (C19) of the trimethoxyphenyl ring. The (nonbonding) distance Pt1···Pt2 is 3.137(6) Å. The iodine bridges are unsymmetric with mean distances of 2.82(1) and 2.67(1) Å, most probably due to the *trans*-effects of the ligand carbon versus the iodine atoms. The methylene bridge is symmetric with a mean Pt–C distance of 2.08 Å. The smallest intermolecular distance Pt···Pt is 8.74(2) Å.

To the best of our knowledge, no dinuclear platinum(IV) compounds with methylene or related bridges are known up until to now. However, there exists a limited number of platinum(II) compounds of this type, but, with the coordination number four, e.g.

1. $[Pt_2(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$ (dppm = $Ph_2PCH_2PPh_2$) with distances between Pt–C 2.13(3) and Pt···Pt 3.12(2) Å [11],
2. $[Pt_2(\mu\text{-}CH_2)(\mu\text{-}Ph_2PC_2H_4PPh_2)_2]$ with a Pt–C distance of 2.08 Å [12],
3. $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ with distances between Pt–C 2.02(3) and Pt···Pt 2.95(2) Å [13],
4. $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3I]$ with the following three distances: Pt–C 2.10(9), Pt···Pt 2.72 (1) [14] and Pt–I 2.69(1) Å.

A comparison of these excerpted measures shows that the Pt–C distance of 2.02(3) Å in the third com-

Table 2
Atom positions and $U_{eq}$ values for **7** [a]

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [b] (Å$^2$) |
|---|---|---|---|---|
| Pt1 | 0.00964(12) | 0.14016(7) | 0.24473(7) | 0.0373(5) |
| Pt2 | 0.15141(12) | 0.33419(7) | 0.31135(7) | 0.0388(5) |
| I1 | 0.23563(21) | 0.22968(12) | 0.19765(12) | 0.0500(8) |
| I2 | 0.04860(23) | 0.43236(13) | 0.41369(12) | 0.0595(9) |
| I3 | 0.13227(21) | 0.19761(12) | 0.39491(11) | 0.0506(8) |
| I4 | −0.12474(23) | 0.09400(13) | 0.10058(12) | 0.0605(9) |
| O1 | −0.4478(22) | 0.0882(13) | 0.3736(12) | 0.0648(58) |
| O2 | −0.4157(22) | −0.0631(15) | 0.3997(14) | 0.0767(60) |
| O3 | −0.2038(22) | −0.1298(14) | 0.3492(15) | 0.0799(61) |
| O4 | 0.4384(22) | 0.5950(13) | 0.2250(12) | 0.0679(58) |
| O5 | 0.2418(22) | 0.6208(13) | 0.1161(12) | 0.0719(58) |
| O6 | 0.0000(23) | 0.5264(15) | 0.0979(13) | 0.0799(60) |
| N1 | 0.0621(24) | 0.0142(13) | 0.2397(11) | 0.0448(56) |
| N2 | 0.3522(20) | 0.4098(14) | 0.3598(12) | 0.0371(56) |
| C1 | −0.1325(32) | −0.0025(18) | 0.3000(18) | 0.0564(64) |
| C2 | −0.1446(29) | 0.0784(16) | 0.2895(14) | 0.0443(61) |
| C3 | −0.2555(28) | 0.1107(17) | 0.3101(16) | 0.0433(62) |
| C4 | −0.3468(30) | 0.0615(17) | 0.3470(14) | 0.0403(61) |
| C5 | −0.3283(28) | −0.0179(19) | 0.3642(15) | 0.0407(61) |
| C6 | −0.2233(31) | −0.0505(20) | 0.3386(18) | 0.0573(65) |
| C7 | −0.0302(32) | −0.0317(18) | 0.2743(15) | 0.0523(64) |
| C8 | 0.1792(34) | −0.0103(16) | 0.2141(17) | 0.0544(62) |
| C9 | 0.2073(31) | 0.0035(18) | 0.1399(18) | 0.0563(65) |
| C10 | 0.3213(35) | −0.0201(18) | 0.1156(19) | 0.0649(65) |
| C11 | 0.4026(30) | −0.0538(17) | 0.1654(18) | 0.0486(65) |
| C12 | 0.3643(29) | −0.0660(16) | 0.2340(16) | 0.0421(64) |
| C13 | 0.2511(30) | −0.0487(17) | 0.2589(17) | 0.0476(64) |
| C14 | 0.2890(29) | 0.4770(16) | 0.2546(15) | 0.0396(61) |
| C15 | 0.3153(30) | 0.5426(18) | 0.2095(18) | 0.0549(65) |
| C16 | 0.2195(32) | 0.5568(17) | 0.1608(18) | 0.0518(64) |
| C17 | 0.0967(34) | 0.5084(20) | 0.1533(16) | 0.0561(64) |
| C18 | 0.0647(31) | 0.4382(18) | 0.1921(15) | 0.0525(64) |
| C19 | 0.1651(26) | 0.4260(15) | 0.2477(15) | 0.0321(59) |
| C20 | 0.3893(33) | 0.4662(16) | 0.3163(17) | 0.0605(64) |
| C21 | 0.4470(30) | 0.3924(16) | 0.4158(14) | 0.0364(61) |
| C22 | 0.5720(29) | 0.3938(15) | 0.4025(17) | 0.0385(64) |
| C23 | 0.6618(30) | 0.3751(17) | 0.4600(20) | 0.0557(66) |
| C24 | 0.6215(29) | 0.3490(17) | 0.5281(17) | 0.0484(65) |
| C25 | 0.4888(31) | 0.3481(18) | 0.5414(18) | 0.0552(65) |
| C26 | 0.4027(29) | 0.3694(17) | 0.4831(16) | 0.0479(65) |
| C27 | 0.7145(34) | 0.3246(21) | 0.5937(20) | 0.0744(81) |
| C28 | 0.7802(37) | 0.2548(23) | 0.5544(22) | 0.0887(89) |
| C29 | 0.8738(32) | 0.2325(20) | 0.6230(19) | 0.0699(79) |
| C30 | 0.9917(36) | 0.2996(23) | 0.6714(22) | 0.0886(89) |
| C31 | 1.0857(40) | 0.3381(26) | 0.6239(25) | 0.1076(97) |
| C32 | 1.1859(39) | 0.4161(24) | 0.6815(24) | 0.1069(96) |
| C33 | 0.5269(34) | −0.0686(21) | 0.1416(20) | 0.0719(80) |
| C34 | 0.5339(54) | −0.1073(35) | 0.0572(33) | 0.172(12) |
| C35 | 0.4394(39) | −0.1827(25) | 0.0166(24) | 0.0992(93) |
| C36 | 0.4427(72) | −0.2228(52) | −0.0644(48) | 0.283(13) |
| C37 | 0.3764(68) | −0.2809(49) | −0.1284(47) | 0.256(13) |
| C38 | 0.3803(57) | −0.3393(38) | −0.1900(36) | 0.199(12) |
| C39 | −0.4898(34) | 0.1530(21) | 0.3390(21) | 0.0803(85) |
| C40 | −0.3753(41) | −0.0625(26) | 0.4738(25) | 0.1119(98) |
| C41 | −0.3131(39) | −0.2021(25) | 0.3073(24) | 0.1039(95) |
| C42 | 0.5058(39) | 0.5876(25) | 0.1524(24) | 0.1059(95) |
| C43 | 0.2243(44) | 0.7013(28) | 0.1521(27) | 0.128(10) |
| C44 | −0.1299(38) | 0.4728(24) | 0.0805(23) | 0.0965(92) |
| C45 | −0.0323(27) | 0.2621(16) | 0.2572(15) | 0.0417(59) |

[a] Estimated standard deviations are given in parentheses.
[b] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

pound quoted here and the Pt–I distance of 2.69(1) Å in the fourth compound are in good agreement with those reported here for **7**: 2.08(3) Å and its shorter one of the two Pt–I distances of 2.67(1) and 2.82(1) Å, respectively.

Since the work presented in this paper originated from our interest in novel materials and the relationship between their molecular structures and thermomesomorphic properties, we want to comment on the following observations with regard to the five platinum organyls **4**–**8**.

Whereas the flat **5** shows liquid-crystalline behaviour, the four complexes **4** and **6**–**8** do not for different reasons:

1. **4** and **6**, although disc-like and flat, both carry too short substituents,
2. **7** and **8** mainly due to their bulkiness and the fact that they are bent too much, impressingly, as Fig. 1 and a ball-and-stick model demonstrate.

Surprisingly, in contrast to its precursor **4** the 'dimeric' product **7**, model compound of our X-ray study, adopts now *syn*-configuration! The interesting *anti*–*syn*-transformation process involved here can not yet be rationalized by us.

In each half of this molecule the platinum atom, the anellated heterobicyclic part of the ligand, the bridging carbon C45, and one of the bridging iodine atoms (I-1 for Pt-1, I-3 for Pt-2) lie in a plane; the terminal iodine and the remaining bridging iodine atom are stretching perpendicularly out of this plane. The two planes about the platinum atoms form an angle of approximately 65°, but the axes through the two heterobicyclic ligand sections lie nearly perpendicular to each other. The two substituted phenyl rings bound to the nitrogen atoms are nearly coplanar to each other and tilted relative to their flat N-bicyclic carriers by about 60°.

In summary, both **7** and **8** are repeatedly folded and indeed very bulky, depicting a kind of spacious knot, i.e. suffering from a heavily overcrowded molecular situation, due to which it is not possible for thermomesomorphism to be exhibited — not even when this material (**8**) carries eight middle long chains: two hexyl and six hexyloxy groups.

## 3. Experimental

The $^1$H- and $^{13}$C-NMR spectra were recorded with a Bruker WH 400 or AM 270 spectrometer, respectively, in $CDCl_3$ solutions; only structurally relevant data are reported in the following. The $^{195}$Pt-NMR spectra were run on a Bruker ARX 400 spectrometer (86.02 MHz) in $CDCl_3$ solutions using a separate reference sample (0.5 g $Na_2PtCl_6$ in 2 ml $D_2O$). The MS spectrum was recorded with a VARIAN MAT 711 spectrometer. The melting points and enthalpies were obtained using dif-

Table 3
Selected bond distances (Å) and angles (°) for **7** [a]

| | | | |
|---|---|---|---|
| Pt1–I1 | 2.808(6) | I1–Pt1–I3 | 86.4(1) |
| Pt1–I3 | 2.673(5) | I1–Pt1–I4 | 95.2(1) |
| Pt1–I4 | 2.622(5) | I1–Pt1–N1 | 99.0(7) |
| Pt1–N1 | 2.20(2) | I1–Pt1–C2 | 174.6(7) |
| Pt1–C2 | 2.03(3) | I1–Pt1–C45 | 80.5(8) |
| Pt1–C45 | 2.08(3) | I3–Pt1–I4 | 174.6(1) |
| Pt2–I1 | 2.679(5) | I3–Pt1–N1 | 91.4(5) |
| Pt2–I2 | 2.610(5) | I3–Pt1–C2 | 88.2(7) |
| Pt2–I3 | 2.827(5) | I3–Pt1–C45 | 84.7(7) |
| Pt2–N2 | 2.22(2) | I4–Pt1–N1 | 93.4(5) |
| Pt2–C19 | 1.99(3) | I4–Pt1–C2 | 90.2(7) |
| Pt2–C45 | 2.08(3) | I4–Pt1–C45 | 90.5(7) |
| | | N1–Pt1–C2 | 80.6(10) |
| | | N1–Pt1–C45 | 176.1(9) |
| | | C2–Pt1–C45 | 99.6(11) |
| | | I1–Pt2–I2 | 174.7(1) |
| | | I1–Pt2–I3 | 85.9(1) |
| | | I1–Pt2–N2 | 92.6(6) |
| | | I1–Pt2–C19 | 91.4(8) |
| | | I1–Pt2–C45 | 83.7(8) |
| | | I2–Pt2–I3 | 95.2(1) |
| | | I2–Pt2–N2 | 92.2(6) |
| | | I2–Pt2–C19 | 87.4(8) |
| | | I2–Pt2–C45 | 91.4(8) |
| | | I3–Pt2–N2 | 101.4(6) |
| | | I3–Pt2–C19 | 177.2(8) |
| | | I3–Pt2–C45 | 80.9(7) |
| | | N2–Pt2–C19 | 79.6(9) |
| | | N2–Pt2–C45 | 175.6(9) |
| | | C19–Pt2–C45 | 98.0(11) |
| | | Pt1–I1–Pt2 | 69.7(1) |
| | | Pt1–I3–Pt2 | 69.5(1) |

[a] Estimated standard deviations are given in parentheses.

ferential scanning calorimetry (Mettler TA 3000/DSC-30 S with TA 72.5 software).

Single-crystal X-ray diffraction analysis: the determination of the lattice parameters and the data collection were performed with a diffractometer Syntex P21 at room temperature (r.t.). As only small, weakly diffracting crystals could be obtained, the 2θ-limit for the data collection was set to 40°. Lorentz and polarisation corrections as well as an empirical absorption correction (DIFABS [15]) were applied. The structure was solved with the Patterson method using SHELXS-86 [16] and completed by successive Fourier difference maps using SHELX-76 [17]. The alkyl side chains proved to be disordered and these atoms were included with isotropic thermal parameters, as were the methyl group C atoms, which were treated as rigid groups. The remaining non-hydrogen atoms were included with anisotropic thermal parameters. Geometry calculations and plots were obtained using PLATON and PLUTON [18]. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallograhy [19] or as supplied by SHELX. All the hydrogen positions were introduced in the last step of the refinement process in calculated positions.

### *3.1. Preparation of the compounds **1**, **2**, **4–8***

#### *3.1.1. Synthesis of the imine ligands **1** and **2***

The imine **1** was prepared in the usual way by *p*-toluenesulfonic acid (40 mg) catalyzed condensation of 10 mmol (1.96 g) 2,3,4-tri(methoxy)benzaldehyde with 12 mmol (2.13 g) 4-hexylaniline — both commercially available — in 50 ml toluene and purified by column chromatography on alkaline aluminium oxide (eluent petroleum ether (b.p. 30–70°C)–ethyl acetate 10:1).

The analogous preparation and spectroscopic data for imine **2** is given in Ref. [6].

4-Hexylbenzene[2,3,4-tri(methoxy)benzal]imine (**1**): yield 3.3 g (93%), yellow oil. $^1$H-NMR: $\delta = 8.74$ (s; HC=N), 7.89, 7.20, 7.14, 6.78 (4d, $J \approx 8$ Hz each; 1, 2, 2 and 1 arom. Hs, respectively), 3.96, 3.93, 3.90 (3s; 3 $OCH_3$ groups), 2.62 (t, $J \approx 7.5$ Hz; α-$CH_2$ group). — $^{13}$C-NMR: $\delta = 156.32$, 154.50, 150.25, 141.74, 140.45, 123.03 (6s; 6 arom. Cs), 155.15 (d; HC=N), 128.97, 122.49, 120.83, 107.75 (4d; 2, 1, 2 and 1 arom. CH, respectively), 61.96, 60.87, 56.02 (3q; 3 $OCH_3$ groups), 35.43 (t; α-$CH_2$ group). — $C_{22}H_{29}NO_3$; MS: $m/z = 355.2147$ [$M^+$], Calc. 355.2147.

#### *3.1.2. Synthesis of the chloro-bridged dinuclear platinum compounds **4** and **5***

A solution of 2.05 mmol (0.73 g) of the imine **1** in 10 ml of dry methanol was added under Ar to a suspension of 1 mmol (0.57 g) of di-μ-chloro-bis(η$^3$-2-methylallylplatinum) [20] (**3**) in 25 ml of dry methanol. After stirring the reaction mixture at r.t. for 20 days a yellow precipitate was filtered off. Crystallization from methanol–acetone yielded the platinum organyl **4** as yellow crystals.

The analogues preparation and spectroscopic data for compound **5** is given in Ref. [6].

Based on the $^1$H-NMR data for **4** we assume this platinum organyl to be a mixture of two isomers, at least in solutions, as reported in a previous paper for the hexyloxy-substituted diplatinum analogue **5** [6]. This is probably due to the different orientations of the two ligands i.e. parallel or antiparallel to each other, in the molecule.

Di-μ-chlorobis[3,4,5-tris(methoxy)-2-{[(4-hexylphenyl)imino]methyl}phenyl-C,N]diplatinum(II) (**4**): yield 0.55 g (47%), m.p. 223.5°C (57.3 kJ mol$^{-1}$) (at ≈232.2°C decomposition). $^1$H-NMR: $\delta = 8.18$, 8.16 [2s, ratio 1 (*anti*):0.2 (*syn*); HC=N], 7.30, 7.19 as well as ≈7.19, ≈7.08 (2 × 2d, $J \approx 8$ Hz each; arom. Hs of disubstituted rings), 6.67, 6.48 [2s, ratio 0.2 (*syn*):1 (*anti*); arom. Hs of the platinated rings], 3.95, 3.82, 3.76 (3s; 3 types of $OCH_3$), 2.63 (t, $J \approx 7.5$ Hz; α-$CH_2$ groups). — $^{13}$C-NMR: $\delta = 172.44$ (d; 2HC=N), 157.34, 153.13, 146.53, 142.72, 137.21, 135.33, 130.80 (7s; 14 arom. Cs), 128.55, 123.51, 109.36 (3d; 4, 4, and 2 arom.

CH, respectively), 61.75, 60.73, 55.96 (3q; 6 $OCH_3$ groups), 35.56 (t; 2 α-$CH_2$ groups). — $^{195}$Pt-NMR: $\delta = -3130.3$ (s). — Anal. Calc. for $C_{44}H_{56}Cl_2N_2O_6Pt_2$ (1170.0): C, 45.17; H, 4.82; N, 2.39. Found C, 45.12; H, 4.64; N, 2.49%.

### 3.1.3. *Synthesis of the iodo-bridged dinuclear platinum compounds* ***6****,* ***7****, and* ***8***

To a solution of 0.1 mmol (0.12 g) of the chloro-bridged platinum organyl **4** in 30 ml dichloromethane and 15 ml acetone an excess of lithium iodide (8 mmol, 1.07 g), under Ar was added. This reaction mixture was stirred at r.t. for 7 days. After filtration and evaporation of the solvents under reduced pressure the crude product was purified by repeated crystallization from an acetone–methanol mixture.

The first crystallization step of the crude product yielded the planar iodo-bridged diplatinum(II) compound **6**.

The platinum organyl **6** is also a mixture of two isomers, at least in solution, as mentioned above for compound **4**.

Di-μ-iodobis[3,4,5-tris(methoxy)-2-{[(4-hexylphenyl)-imino]methyl}phenyl-C,N]diplatinum(II) (**6**): yield 0.03 g (22%), orange crystals, m.p. 158.4°C (decomposition). $^1$H-NMR: $\delta = 8.21$, 8.19 [2s, ratio 1 (*anti*):0.2 (*syn*); HC=N], 7.27, 7.20 as well as 7.16, 7.09 (2 × 2 d, $J \approx 8$ Hz each; arom. Hs of the disubstituted rings), 6.75, 6.57 [2s, ratio 0.2 (*syn*):1 (*anti*); arom. Hs of the platinated rings], 3.93, 3.82, 3.76 (3s; 3 types of $OCH_3$), 2.64 (t, $J \approx 7.5$ Hz; α-$CH_2$ groups). — $^{13}$C-NMR: $\delta = 172.52$ (d; 2 HC=N), 157.24, 152.89, 146.70, 142.56, 136.63, 134.96, 131.12 (7 s; 14 arom. Cs), 128.48, 123.59, 110.20 (3d; 4, 4, and 2 arom. CH, respectively), 74.52, 73.46, 68.55 (3 q; 6 $OCH_3$ groups), 35.60 (t; 2 α-$CH_2$ groups). — Anal. Calc. for $C_{44}H_{56}I_2N_2O_6Pt_2$ (1352.9): C, 39.06; H, 4.17; N, 2.07. Found C, 39.44; H, 4.27; N, 2.13%.

Surprisingly, the second and slower crystallization step of the crude product yielded the methylene-bridged diplatinum(IV) compound **7**.

Di-μ-iododiiodo-μ-methylenebis[3,4,5-tris(methoxy)-2-{[(4-hexylphenyl)imino]methyl}phenyl-C,N]diplatinum(IV) (**7**): yield 0.05 g (31%), orange crystals, m.p. 127.4°C (decomposition). $^1$H-NMR: $\delta = 8.36$ (s; 2HC=N), 7.35, 7.19 (2 d, $J \approx 8$ Hz each; arom. Hs of the disubstituted rings), 6.86 (s; arom. Hs of the platinated rings), 6.55 (s; μ-$CH_2$), 4.05, 4.02, 3.85 (3s; 6 $OCH_3$ groups), 2.63 (t, $J \approx 7.5$ Hz; 2 α-$CH_2$ groups). — $^{13}$C-NMR: $\delta = 166.61$ (d; 2HC=N), 157.46, 153.86, 146.14, 142.39, 138.54, 129.43, 128.98 (7s; 14 arom. Cs), 128.65, 123.57, 110.56 (3 d; 4, 4, and 2 arom. CH, respectively), 61.90, 61.31, 56.53 (3q; 6 $OCH_3$ groups), 35.46 (t; 2 α-$CH_2$ groups), 9.88 (t; μ-$CH_2$). — Anal. Calc. for $C_{45}H_{58}I_4N_2O_6Pt_2$ (1620.7): C, 33.34; H, 3.60; N, 1.72. Found C, 33.57; H, 3.41; N, 1.72%.

It should be mentioned here that extending the reaction time beyond 7 days lead exclusively to the methylene-bridged platinum complex **7**.

Alternatively, compound **7** can also be obtained from the reaction of 0.1 mmol (0.12 g) of compound **4** either with 10 ml diiodomethane or with lithium iodide (0.67 g) in 10 ml diiodomethane by stirring the reaction mixture at r.t. for 15 days, however, with poorer yields (25 and 22%, respectively).

Compound **8** was prepared by a procedure analogous to that for compound **7**. Starting from 0.1 mmol (0.16 g) of the chloro-bridged diplatinum organyl **5** [6], compound **8** appeared in the form of orange crystals, which were purified by crystallization from acetone–methanol.

Di-μ-iododiiodo-μ-methylenebis[3,4,5-tris(hexyloxy)-2-{[(4-hexylphenyl)imino]methyl}phenyl-C,N]diplatinum(IV) (**8**): yield 0.12 g (60%), orange crystals, m.p. 117.5°C (42.8 kJ mol$^{-1}$). $^1$H-NMR: $\delta = 8.33$ (s; 2HC=N), 7.34, 7.19 (2d, $J \approx 8$ Hz each; arom. Hs of the disubstituted rings), 6.82 (s; arom. Hs of the platinated rings), 6.52 (s; μ-$CH_2$), 4.29–4.10, 3.99–3.89 (2m; 6 $OCH_2$ groups), 2.63 (t, $J \approx 7.5$ Hz; 2 α-$CH_2$ groups). — $^{13}$C-NMR: $\delta = 166.72$ (d; 2HC=N), 157.34, 153.55, 146.30, 142.23, 138.14, 129.35, 128.95 (7s; 14 arom. Cs), 128.63, 123.61, 111.44 (3 d; 4, 4, and 2 arom. CH, respectively), 74.73, 74.00, 69.13 (3t; 6 $OCH_2$ groups), 35.49 (t; 2 α-$CH_2$ groups), 9.80 (t; μ-$CH_2$). — Anal. Calc. for $C_{75}H_{118}I_4N_2O_6Pt_2$ (2041.5): C, 44.12; H, 5.83; N, 1.37. Found C, 43.54; H, 5.99; N, 1.33%.

## 4. Supplementary material

Crystallographic data have been deposited at the Cambridge Data Center and may be obtained without charge on quoting the depository number CCDC 120198 from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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## References

[1] (a) A.-M. Giroud-Godquin, P.M. Maitlis, Angew. Chem. 103 (1991) 370; Angew. Chem. Int. Ed. Engl. 30 (1991) 375. (b) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215. (c) D.W. Bruce, in: D.W. Bruce, D. O'Hare, (Eds.), Inorganic Materials, Wiley, Chichester, 1992, Ch. 8. (d) S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861. (e) J.L. Serrano (Ed.), Metallomesogens, Synthesis, Properties, and Applications, VCH, Weinheim, 1996.

[2] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[3] W.A. Herrmann, B. Reiter, H. Biersack, J. Organomet. Chem. 97 (1975) 245.

[4] Review: W.A. Herrmann, Adv. Organomet. Chem. 20 (1982) 159.

[5] Review: J.E. Hahn, Progr. Inorg. Chem. 31 (1984) 205.

[6] (a) K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, Chem. Ber. 127 (1994) 1543. (b) B. Bilgin, Ph.D. Dissertation, Faculty 5/Chemistry, Technische Universität Berlin, Germany, 1996.

[7] (a) K. Praefcke, D. Singer, B. Gündoğan, Mol. Cryst. Liq. Cryst. 223 (1992) 181. (b) B. Gündoğan, K. Praefcke, Chem. Ber. 126 (1993) 1253. (c) K. Praefcke, D. Singer, B. Gündoğan, K. Gutbier, M. Langner, Ber. Bunsenges. Phys. Chem. 98 (1994) 118. (d) N. Usol'tseva, K. Praefcke, D. Singer, B. Gündoğan, Liq. Cryst. 16 (1994) 601.

[8] K. Praefcke, B. Bilgin, N. Usol'tseva, B. Heinrich, D. Guillon, J. Mater. Chem. 5 (1995) 2257.

[9] (a) M.F. Lappert, P.W. Lednor, Adv. Organomet. Chem. 14 (1976) 345. (b) J.P. Collman, L.S. Hegedus, in: A. Kelly (Ed.), Principles and Application of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1980, Ch. 4.

[10] (a) G. Ferguson, M. Parvez, P.K. Monaghan, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1983) 267. (b) R.J. Puddephatt, J.D. Scott, Organometallics 4 (1985) 1221. (c) G. Ferguson, P.K. Monaghan, M. Parvez, R.J. Puddephatt, Organometallics 4 (1985) 1669.

[11] K.A. Azam, A.A. Frew, B.R. Lloyd, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, Organometallics 4 (1985) 1400.

[12] D.P. Arnold, M.A. Bennett, G.M. McLaughlin, G.B. Robertson, J. Chem. Soc. Chem. Commun. (1983) 34.

[13] G.P. Elliot, J.A.K. Howard, T. Mise, I. Moore, C.M. Nunn, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1986) 2091.

[14] E. Baralt, E.A. Boudreaux, J.N. Demas, P.G. Lenhert, C.M. Lukehart, A.T. McPhail, D.R. McPhail, J.B. Myers, L. Sacksteeder, W.R. True, Organometallics 8 (1989) 2417.

[15] N. Walker, D. Stuart, DIFABS, Acta Crystallogr. Sect. A 39 (1983) 158.

[16] G.M. Sheldrick, SHELXS-86, Program for crystal structure solution, University of Göttingen, Germany, 1986.

[17] G.M. Sheldrick, SHELXS-76, Program for crystal structure determination, University of Cambridge, UK, 1976.

[18] A.L. Spek, The Euclid Package, in: D. Sayre (Ed.), Computational Crystallography, Clarendon Press, Oxford, 1982, p. 528.

[19] International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.

[20] D.J. Mabbott, B.E. Mann, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 294.