Synthesis and Reactivity of Bis(alkoxyalkylidene)platinum(II) Complexes[§]

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The reaction of hexachloroplatinic acid with bis(trimethylsilyl)acetylene in various alcohols (EtOH, *i*-PrOH, *n*-BuOH, BnOH) led to the formation of the platina-β-diketone $[Pt_2(\mu\text{-Cl})_2\{(COMe)_2H\}_2]$ (**1a**). Unexpectedly, in absolute MeOH the reaction of hexachloroplatinic acid with trimethylsilyl-substituted alkynes yielded the *cis*-dichlorobis(methoxyalkylidene)platinum(II) complexes $[PtCl_2\{C(OMe)R'\}_2]$ (R = Me (**2a**), Et (**2b**), Hex (**2c**)). These complexes reacted in wet solvents, yielding the corresponding platina-β-diketones. Hexabromoplatinic acid was found to react with bis(trimethylsilyl)acetylene in different alcohols, resulting in the formation of the *cis*-dibromobis(alkoxyethylidene)platinum(II) complexes $[PtBr_2\{C(OR)Me\}_2]$ (R = Me (**3a**), Et (**3b**), *i*-Pr (**3c**), *n*-Bu (**3d**)). In contrast to this, analogous reactions with hexaiodoplatinic acid afforded the *trans*-diiodobis(alkoxyethylidene)platinum(II) complexes $[PtI_2\{C(OR)Me\}_2]$ (R = Me (**4a**), Et (**4b**), *i*-Pr (**4c**), *n*-Bu (**4d**), (*S*)-2-Bu (**4e**)). It was observed that complex **4a** isomerizes in CH_2Cl_2 to *cis*-diiodobis(methoxyethylidene)platinum(II), $[PtI_2\{C(OMe)Me\}_2]$ (**5**). All complexes were characterized by microanalyses and IR and ^1H and ^{13}C NMR spectroscopy. Complexes **2a**,**b** were also characterized by single-crystal X-ray diffraction analysis. Additionally, quantum-chemical calculations on the DFT level of theory dealing with the stability of *cis*-/*trans*-dihalobis(alkoxyalkyliden)platinum(II) complexes and rotational barriers were performed.

1. Introduction

Reactions of hexachloroplatinic acid with *n*-butyl alcohol and trimethylsilyl-substituted alkynes lead to the formation of the platina-β-diketones **1** (Scheme 1). Platina-β-diketones may be described as hydroxycarbene complexes stabilized by strong intramolecular hydrogen bonds to acyl ligands (A in Scheme 1).[1]

In contrast to Lukehart's metalla-β-diketones $[L_xM\{(COR)_2H\}]$ (L = CO, cp; M = Mo, Re, Fe, ...; R = alkyl, aryl) platina-β-diketones (**1**) are electronically unsaturated 16-ve complexes (ve = valence electrons) with a kinetically labile ligand sphere.[2] This gives rise to the completely different reactivity of **1** compared to that of Lukehart's electronically saturated and coordinatively inert metalla-β-diketones. For example, Lukehart's metalla-β-diketones react with amines, yielding metalla-β-ketoimines, while platina-β-diketones form platina-β-diketonates of platina-β-diketones.[3,4]

Although to date the reactivity of platina-β-diketones **1** has been extensively studied, relatively little experimental investigation has been undertaken regarding the route to their formation. On the basis of isolation of an analogue of Zeise's acid from the reaction of hexachloroplatinic acid with *n*-butyl alcohol and computational results, a mechanism was proposed in 2001[5] with the following key steps (Scheme 1): alkyne complex formation with cleavage of the ≡C−Si bond (C), vinylidene complex formation (D), hydroxycarbene complex formation (E) and its deprotonation yielding an acyl complex (F). The last two complexes are the building blocks of the platina-β-diketone **1**.

The formation of an intermediate Zeise's acid type complex (Scheme 1) is in accordance with the reactivity of hexachloroplatinic acid in alcohols and was established by isolation of $(PPN)[PtCl_3(\eta^2\text{-}H_2C{=}CHEt)]$ (PPN = $Ph_3PNPPh_3^+$) after the addition of (PPN)Cl to a reaction mixture of $H_2PtCl_6\cdot 6H_2O$ in *n*-butyl alcohol (2 h, 80 °C; B in Scheme 1).[6] Apart from our two-step procedure, which involves reacting $H_2PtCl_6\cdot 6H_2O$ with *n*-butyl alcohol followed by the addition of $Me_3SiC{\equiv}CSiMe_3$ (and other silylated alkynes), resulting in the formation of platina-β-diketones, a one-pot-synthesis leading to the formation of *cis*-dichlorobis(isopropoxyethylidene)platinum(II) by reaction of $H_2PtCl_6\cdot 6\ H_2O$ with $Me_3SiC{\equiv}CH$ in isopropyl alcohol was reported in 1979.[7]

With this background in mind, herein we report the reaction of hexachloroplatinic acid with silylated alkynes in various alcohols, including alcohols that cannot be dehydrated to olefins. Furthermore, we describe the reaction of hexabromoplatinic acid and hexaiodoplatinic acid with bis(trimethylsilyl)acetylene in different alcohols.

[§] This paper is dedicated to Prof. Rudolf Taube on the occasion of his 75th birthday.

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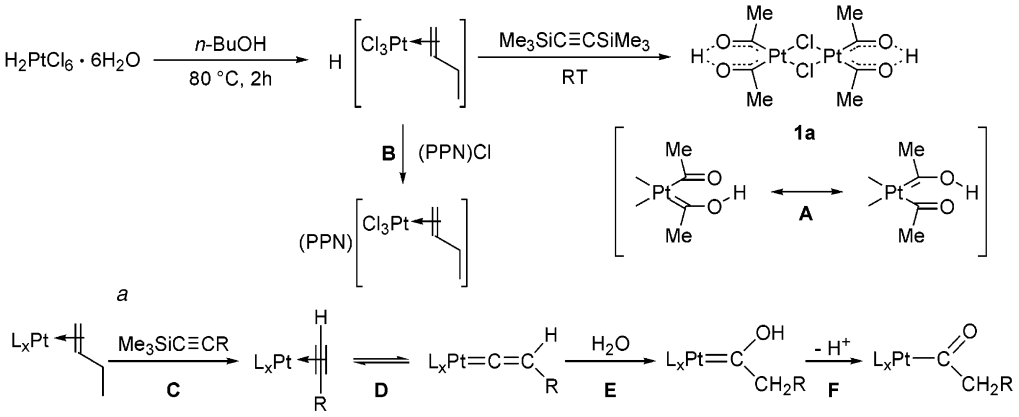
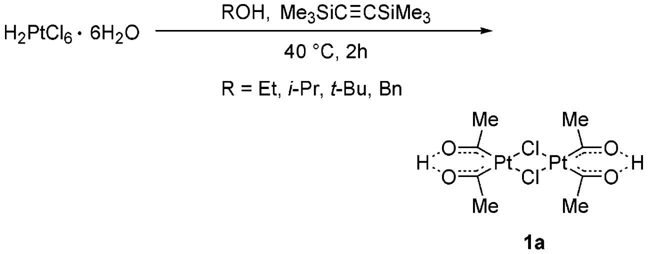
10.1021/om060725x CCC: \$33.50

Scheme 1



[a] Charges were omitted.

Scheme 2



2. Results and Discussion

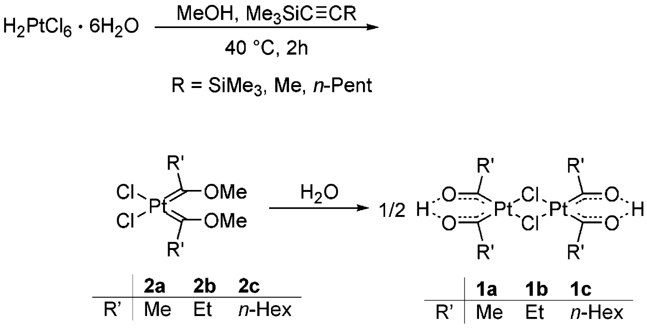
2.1. Platina-β-diketones and *cis*-Dichlorobis(alkylidene)platinum Complexes. 2.1.1. Syntheses and Reactivity. The reaction of hexachloroplatinic acid with bis(trimethylsilyl)acetylene in *n*-butyl alcohol under the published conditions led to the formation of the platina-β-diketone **1a** (Scheme 1).[1] Changing this procedure to a one-pot reaction, in different alcohols (EtOH, *i*-PrOH, *t*-BuOH, BnOH) with bis(trimethylsilyl)acetylene at slightly elevated temperatures, also led to the formation of platina-β-diketone **1a** in yields between 60 and 80% (Scheme 2).

Because benzyl alcohol (BnOH) cannot be dehydrated to an olefin, complexes of the Zeise's acid type must therefore not be necessary intermediates in the formation of platina-β-diketones.

In the reactions according to Scheme 2 it has been generally observed that the addition of a small percentage of water results in a decrease in the yield of the platina-β-diketone **1a**. On the other hand, performing the reaction in methanol containing about 5% water leads to the formation of **1a** in about 45% yield. In contrast to this, hexachloroplatinic acid was found to react with bis(trimethylsilyl)acetylene (40 °C, 2 h) in dried methanol, yielding *cis*-dichlorobis(methoxyethylidene)platinum (**2a**) (Scheme 3). Other trimethylsilyl-substituted alkynes $Me_3SiC{\equiv}CR$ (R = Me, *n*-Pent) reacted analogously, forming the bis(methoxyalkylidene) complexes **2b**,**c** (Scheme 3).

The bis(methoxyalkylidene) complexes **2a**−**c** were isolated as colorless crystals (**2a**) and powders (**2b**,**c**), respectively, in good yields (50−75%). They proved to be moisture sensitive: in nondried solvents (chloroform, diethyl ether, nitromethane) the alkylidene complexes reacted quantitatively, yielding the corresponding literature-known platina-β-diketones **1a**−**c** (Scheme 3). The identity of platina-β-diketones **1a**−**c** was established by comparison of NMR (^{1}H) data with those reported in the literature.[8]

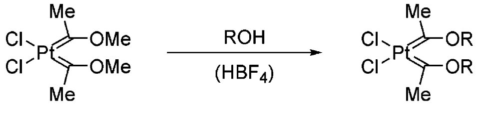
Scheme 3



	2a	2b	2c
R'	Me	Et	n-Hex

	1a	1b	1c
R'	Me	Et	n-Hex

Scheme 4



2a

2d R = *i*-Pr
2e R = *n*-Bu

To check the reactivity of bis(alkylidene)platinum(II) complexes, **2a** was suspended in dried isopropyl alcohol. Over a period of 7 days no reaction took place. Adding a small amount of HBF_4 in diethyl ether led to a nucleophilic substitution of the OMe group by the O-*i*-Pr group, yielding $[PtCl_2\{C(O\text{-}i\text{-}Pr)Me\}_2]$ (**2d**). The analogous reaction in *n*-butyl alcohol resulted in the formation of $[PtCl_2\{C(O\text{-}n\text{-}Bu)Me\}_2]$ (**2e**) (Scheme 4). It is worth mentioning that a nonaqueous acid must be used in this reaction if the formation of platina-β-diketone (**1a**) is to be avoided.

The bis(alkylidene) platinum complexes **2a**−**e** were characterized by microanalysis and IR and NMR (^{1}H, ^{13}C) spectroscopy. Furthermore, the molecular structures of the complexes **2a** and **2b** were obtained.

2.1.2. Structures. Suitable crystals for X-ray diffraction analyses have been obtained directly from the reaction mixture (**2a**) and from chloroform solutions (**2b**), respectively. The asymmetric unit of complex **2a** contains two symmetry-independent molecules with very similar geometries: one of them is shown in Figure 1. Selected bond lengths and angles are given in Table 1. Complex **2b** exhibits crystallographically imposed C_2 symmetry. The molecular structure of **2b** is shown in Figure 2. Selected bond lengths and angles are given in Table 2.

In both complexes **2a** and **2b** the platinum atom has a square-planar coordination and the complexes are in a cis configuration.

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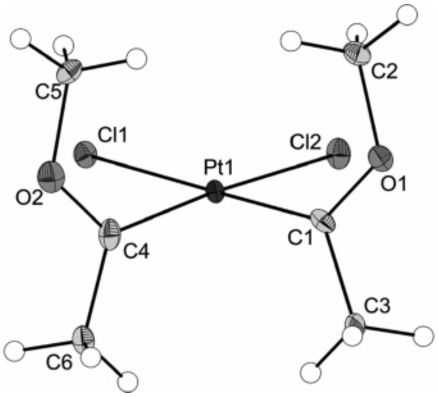

Figure 1. Structure of one of the two symmetry-independent molecules of *cis*-$[PtCl_2\{C(OMe)Me\}_2]$ (**2a**) (displacement ellipsoids at 30% probability).

Table 1. Selected Bond Lengths (in Å) and Angles (in deg) for *cis*-$[PtCl_2\{C(OMe)Me\}_2]$ (2a)[a]

Pt−C1	1.932(7)/1.965(7)	Pt1−Cl2	2.377(2)/2.376(2)
Pt1−C4	1.956(7)/1.944(7)	C1−O1	1.282(8)/1.253(9)
Pt1−Cl1	2.374(2)/2.377(2)	C4−O2	1.278(9)/1.259(9)
Cl1−Pt1−Cl2	91.50(6)/90.52(6)	C4−Pt1−Cl1	86.00(2)/88.2(2)
Cl2−Pt1−C1	87.5(2)/87.4(2)	O1−C1−C3	110.3(6)/113.6(6)
C1−Pt1−C4	95.1(3)/93.7(3)	O2−C4−C6	111.8(6)/110.5(6)

[a] The values for the two symmetry-independent molecules are separated by a slant.

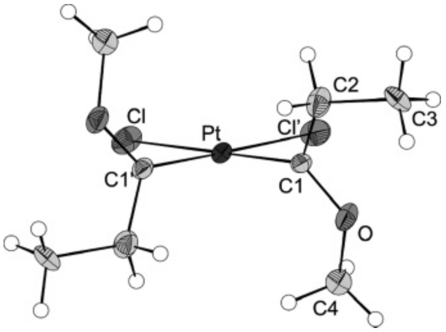

Figure 2. Molecular structure of *cis*-$[PtCl_2\{C(OMe)Et\}_2]$ (**2b**) (displacement ellipsoids at 30% probability).

Table 2. Selected Bond Lengths (in Å) and Angles (in deg) for *cis*-$[PtCl_2\{C(OMe)Et\}_2]$ (2b)

Pt−C1	1.941(3)	C1−O	1.272(3)
Pt−Cl	2.373(1)		
Cl−Pt−C1′	87.62(9)	C1−Pt−Cl	178.46(9)
C1′−Pt−C1	93.9(1)	O−C1−C2	111.4(2)

As expected, the backbones of the alkylidene ligands (═C(OC)C) are essentially planar (torsion angles: C2−O1−C1−C3 = −175.0(6)/−176.4(6)°, C5−O2−C4−C6 = 175.5(6)/174.0(6)°, **2a**; C4−O−C1−C2 = 179.4(2)°, **2b**). The alkylidene ligands lie nearly perpendicular to the coordination plane. The angles of a plane defined by the backbones of the alkylidene ligands and a coordination plane defined by the two chloro ligands and the two carbene carbon atoms are 70.8(6)−78.7(6)° (**2a**) and 73.82(9)° (**2b**). Remarkably, in **2a** the alkoxy substituents of the carbene carbon atom are on the same side of the coordination plane ("cisoid"), whereas those of **2b** are on opposite sides ("transoid"). The Pt−C bond lengths (1.932(7)−1.965(7) Å, **2a**; 1.941(3) Å, **2b**) are within the range reported for other platinum(II) alkoxyalkylidene complexes (median 1.949 Å, lower/upper quartile 1.875/2.003 Å, number of observations $n = 15$).[9] The C_{carb}−O bond lengths (1.253(9)−1.282(8) Å, **2a**; 1.272(3) Å, **2b**) are between a C−O single bond (median in ethers 1.42 Å) and a C═O double bond (median in ketones 1.21 Å).[10] Thus, these values provide clear evidence of the partial π character of the C−O bond in **2a**,**b**.

2.1.3. Spectroscopic Investigations. The constitution of the bis(alkylidene)platinum complexes *cis*-$[PtCl_2\{C(OR)R'\}_2]$ (**2a**−**e**) was derived from the respective NMR spectroscopic measurements. Selected data are given in Table 3.

The signals of the carbene carbon atoms are strongly low-field shifted (271.1−277.9 ppm). The magnitudes of the $^1J_{Pt,C}$ coupling constants (1274−1278 Hz) are in the range reported for other alkylidene complexes having a chloro ligand trans to an alkylidene ligand.[11] Whereas the ═CC*H* protons resonate in the narrow range between 2.72 and 2.99 ppm, the carbon atoms ═C*C*H resonate increasingly further downfield with increasing alkyl chain length R′ (R′ = Me, 43.9 ppm; R′ = Et, 50.8; R′ = *n*-Hex, 57.2 ppm). For the ═COC*H* protons an increasing low field shift of the order R = Me (5.09−5.16 ppm) < *n*-Bu (5.58 ppm) < *i*-Pr (6.89 ppm) is observed and is consistent with the case for other reported alkoxyalkylidene platinum(II) complexes.[12]

2.2. *cis*-Dibromobis(alkylidene)platinum Complexes. To investigate whether reactions analogous to those described for the hexachloroplatinic acid could be used to access bromo-bridged platina-β-diketones and/or dibromobis(alkylidene) complexes, $H_2PtBr_6{\cdot}6H_2O$ was heated in *n*-butyl alcohol at 80 °C for 2 h and bis(trimethylsilyl)acetylene was then added at room temperature. In contrast to the results using hexachloroplatinic acid (Scheme 1), dibromobis(butoxyethylidene)platinum (**3d**) could be isolated as a white powder in moderate yields (50%) (Scheme 5).

The same product could be isolated in the one-pot reaction of hexabromoplatinic acid and bis(trimethylsilyl)acetylene in *n*-butyl alcohol at 40 °C. This reaction carried out in other alcohols ROH (R = Me, Et, *i*-Pr) led to the formation of analogous dibromobis(alkoxyethylidene) complexes (**3a**−**c**) as white powders in yields between 50 and 65% (Scheme 5). The identities of the complexes **3a**−**d** have been unambiguously determined by microanalysis and IR and NMR (^{1}H, ^{13}C) spectroscopy. Remarkably, the NMR spectra of complexes **3a**−**d** are very similar to those of the analogous dichlorobis(alkoxyethylidene)platinum complexes (see the Experimental Section).

In contrast to the dichlorobis(alkylidene) platinum complexes **2a**−**c**, complexes **3a**−**d** did not react in nondried solvents to yield the corresponding bromo-bridged platina-β-diketones. Instead, decomposition resulting in the formation of platinum occurred within 1 week.

2.3. Diiodobis(alkylidene)platinum complexes. 2.3.1. Syntheses and Reactivity. To investigate the reactivity of hexaiodoplatinic acid toward bis(trimethylsilyl)acetylene, K_2PtI_6 was treated with HBF_4 in an alcohol ROH (R = Me, Et, *i*-Pr, *n*-Bu, (*S*)-2-BuOH) to form an alcoholic solution of H_2PtI_6. Following the addition of bis(trimethylsilyl)acetylene at slightly elevated temperatures (40 °C) the solution changes color from dark red to yellow within approximately 2 h. The solvent was removed, and the residue was extracted with hexane. The hexane extract

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[9] Cambridge Structural Database (CSD), Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, England.

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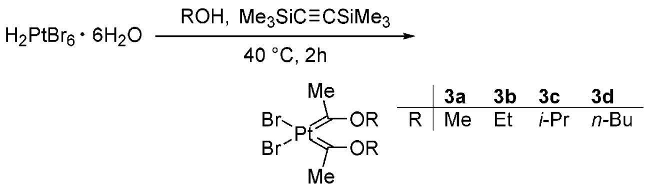
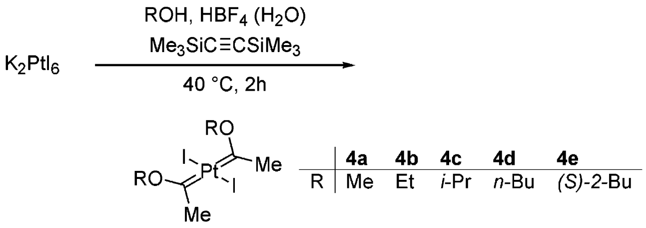
Table 3. Selected NMR Spectroscopic Parameters (δ in ppm, J in Hz) of *cis*-[$PtCl_2\{C(OR)R'\}_2$] (2a−e)

R/R′	=CC*H* $\delta(^1H)$ ($^3J_{Pt,H}$)	=C*C*H $\delta(^{13}C)$ ($^2J_{Pt,C}$)	=COC*H* $\delta(^1H)$ ($^4J_{Pt,H}$)	=CO*C*H $\delta(^{13}C)$ ($^3J_{Pt,C}$)	Pt=*C* $\delta(^{13}C)$ ($^1J_{Pt,C}$)
Me/Me (**2a**)	2.81 (20.4)	43.9 (151)	5.09 (8.6)	72.6 (94)	277.3 (1277)
Me/Et (**2b**)	2.99	50.8 (147)	5.16	71.8 (94)	277.9 (1278)
Me/Hex (**2c**)	2.95	57.2 (131)	5.15 (8.2)	71.6 (92)	277.9 (1274)
i-Pr/Me (**2d**)	2.72 (19.9)	44.1 (153)	6.89	85.5 (90.2)	271.1
n-Bu/Me (**2e**)	2.74	43.9 (131)	5.58	86.6 (81)	272.9

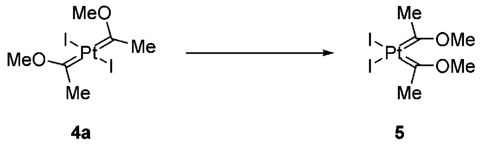
Scheme 5



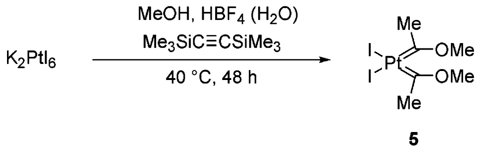
Scheme 6



Scheme 7



Scheme 8



was evaporated, yielding *trans*-[$PtI_2\{C(OR)Me\}_2$] (**4a**−**e**) as yellow powders (Scheme 6).

The isolated compounds (yields: 40−80%) are quite air and moisture stable. They were characterized by microanalysis and IR and NMR (^1H, ^{13}C) spectroscopy.

Dissolving *trans*-[$PtI_2\{C(OMe)Me\}_2$] (**4a**) in CH_2Cl_2 led to a complete isomerization, yielding *cis*-[$PtI_2\{C(OMe)Me\}_2$] (**5**) within 7 days (Scheme 7).

Complex **5** could also be synthesized directly just by increasing the reaction time in the described syntheses of *trans*-[$PtI_2\{C(OMe)Me\}_2$] from 2 h up to 2 days (Scheme 8).

After the solvents were removed, the resulting residue was extracted with CH_2Cl_2. In contrast to the trans isomer this complex was not soluble in hexane. Complex **5** is stable in air for more than 2 days and was characterized by microanalysis and ^1H and ^{13}C NMR spectroscopy.

2.3.2. Spectroscopic Investigations. The constitutions of complexes **4a**−**e** and **5** were confirmed by NMR spectroscopic investigations. Selected data are given in Table 4. The ^1H and ^{13}C NMR spectra of *cis*-[$PtI_2\{C(OMe)Me\}_2$] (**5**) are very similar to those of the dibromo (**3a**) and the dichloro (**2a**) analogues. This points clearly to the cis configuration of complex **5**.

Unlike the spectra of complex **5**, the spectra of complexes **4a**−**e** show pairs of signals in an approximately 1:1 ratio for each hydrogen and carbon atom. This can be explained by a hindered rotation of the alkylidene ligand around the Pt=C bond, resulting in two rotamers. In one rotamer both alkoxy groups of the alkylidene ligands are on the same side of the coordination plane (cisoid), whereas in the other rotamer they are on opposite sides (transoid). Each rotamer gives rise to a complete set of signals, hence the presence of two signals for each atom.

As shown for **4a** and in accordance with this explanation, temperature-dependent ^1H NMR spectra exhibit a broadening of the signals at slightly elevated temperatures (30 °C) followed by coincidence of all signals at approximately 35 °C (see Figure 3). Calculation of the rotational barrier on the basis of these ^1H NMR spectra gave a value of approximately 16 kcal/mol.[13]

As expected, the signals of the carbene carbon atoms of the *trans*-diiodobis(alkylidene) complexes **4** have stronger low-field shifts (307.0−315.6 ppm) than those of complex **5** (268.3 ppm), arising from the difference in trans influence, as described in the literature.[14] The value of the $^1J_{Pt,C}$ coupling constant gives a further indication of the constitution of complexes **4** and **5**. The higher trans influence of the alkylidene ligand compared to the iodo ligand results in a decrease in the $^1J_{Pt,C}$ coupling constant from about 1210 Hz (**5**) to approximately 740 Hz (**4**). All other signals are in a range typical for alkylidene complexes, as discussed above.

2.4. Computational Results. To gain further insight into stabilities and reactivities of the square-planar dihalobis(alkoxyalkylidene)platinum(II) complexes *cis*-/*trans*-[$PtX_2\{C(OMe)Me\}_2$] ($\mathbf{7_c}$, $\mathbf{7_t}$, X = Cl; $\mathbf{8_c}$, $\mathbf{8_t}$, X = Br; $\mathbf{9_c}$, $\mathbf{9_t}$, X = I) quantum-chemical calculations on the DFT level of theory were performed. In all of these complexes the alkylidene ligands were found to lie about perpendicular to the complex planes. This gives rise to the formation of rotational isomers having the methoxy substituents on the same side of the complex plane or on different sides: namely, a “cisoid” and “transoid” configuration[23] of alkylidene substituents, respectively. The molecular structures of two representative chloro complexes are shown in Figure 4. Energy values are compiled in Table 5. Energies given are corrected for the zero-point vibrational energies (ZPE). As shown by the comparison with the noncorrected values (see the Supporting Information), the ZPE corrections proved not to have a significant influence on the conclusions drawn below.

In the gas phase no significant differences in the energies between the transoid and the respective cisoid complexes were found. On the other hand, in the order Cl → Br → I the stabilities of the trans complexes relative to the cis complexes is increased. Thus, for X = Cl the trans complexes are slightly less stable than the cis complexes, whereas for X = I the trans complexes are stabilized by about 5 kcal/mol more than the cis complexes. To model the influence of the methanol solvent, calculations using Tomasi’s PCM model were performed.[15] Although the

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Table 4. Selected NMR Spectroscopic Parameters of *trans*-$[PtI_2\{C(OR')Me\}_2]$ (4a−e) and *cis*-$[PtI_2\{C(OR')Me\}_2]$ (5a)

R′	$=CCH$ $\delta(^1H)$ ($^3J_{Pt,H}$)	$=CCH$ $\delta(^{13}C)$ ($^2J_{Pt,C}$)	$=COCH$ $\delta(^1H)$ ($^4J_{Pt,H}$)	$=COCH$ $\delta(^{13}C)$ ($^3J_{Pt,C}$)	$Pt=C$ $\delta(^{13}C)$ ($^1J_{Pt,C}$)
Me (**4a**)	2.95/3.03	43.6/43.9	4.80/4.92	80.6/81.5	315.1/315.6 (742/745)
Et (**4b**)	2.90/3.00	42.5/42.9	5.28/5.47	84.7/85.6	312.0/312.4
i-Pr (**4c**)	2.84/2.95	42.5/43.0	6.35/6.69	90.3/91.3	307.0/307.4
n-Bu (**4d**)	2.90/3.00	42.9/43.3 (71/71)	5.21/5.39	84.7/85.6	312.0/312.6
(S)-2-Bu (**4e**)	2.83/2.96	42.7/43.1 (73/73)	6.18/6.47	94.7/95.6 (37/37)	308.2/308.5 (732/733)
Me (**5**)	2.96	43.6	4.93	71.9 (96)	268.3 (1210)

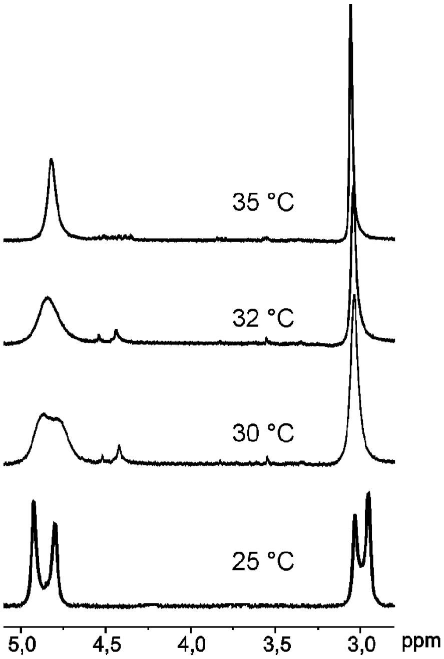

Figure 3. Temperature-dependent NMR spectra of *trans*-$[PtI_2\{C(OMe)Me\}_2]$ (**4a**) in C_6D_6 (200 MHz).

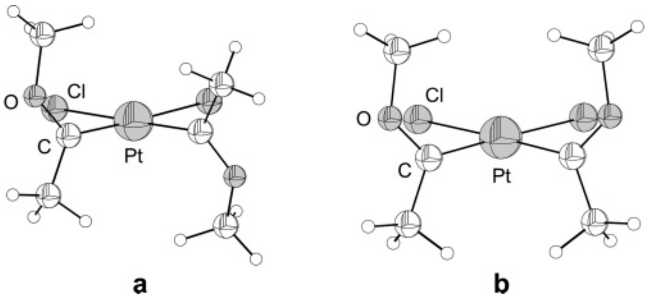

Figure 4. Molecular structures (calculated) of *cis*-$[PtCl_2\{C(OMe)Me\}_2]$: (a) transoid configuration $\mathbf{7_{ct}}$; (b) cisoid configuration $\mathbf{7_{cc}}$.

figures obtained in this way must not be overestimated, the trend is clear: In all cases the cis complexes are more strongly solvated than the requisite trans complexes. Thus, in methanol the trans complexes proved to be less stable than the cis complexes, even for X = I. This is in full accord with the experimental findings, where in the case of $[PtI_2\{C(OMe)Me\}_2]$ the trans isomer (**4a**) is the kinetic product and the cis isomer (**5**) is the thermodynamic product, as also found in other $[PtCl_2L_2]$ complexes.[16]

Rotation of an alkylidene ligand about the M═C bond results in an isomerization between the transoid and the corresponding cisoid complex. The rotational barriers are given in Table 5. Selected structures of the transition states are shown in Figure 5.

The most striking structural feature is the relative positioning of the two alkylidene ligands: one of them lies nearly in the complex plane, and the other remains approximately perpendicular to the complex plane. For *cis*-$[PtX_2\{C(OMe)Me\}_2]$ complexes two transition states each of approximately the same activation energies were found. In one of them, the OMe substituent of the in-plane alkylidene ligand is directed toward the out-of-plane alkylidene ligand (Figure 5a), whereas in the other one the Me group of the in-plane alkylidene ligand is directed toward the out-of-plane alkylidene ligand (Figure 5b). In the gas phase there are no meaningful differences in the rotational barriers (transoid−cisoid) between the cis and the trans complexes. In the order Cl → Br → I the rotational barriers for transoid/cisoid isomerizations are increased in the gas phase.

So far—in accordance with the experimental findings—we have discussed only complexes whose alkylidene ligands are *E* isomers with respect to the C═OMe bonds. Taking the *cis*-$[PtCl_2\{C(OMe)Me\}_2]$ ($\mathbf{7_{ct}}/\mathbf{7_{cc}}$) complexes as representatives, the requisite complexes having (*Z*)-C(OMe)Me ligands have been additionally calculated. The energies are given in Table 6. Selected structures are given in Figure 6.

In contrast to the (*E*)-C(OMe)Me ligands positioned approximately perpendicular to the complex plane, the (*Z*)-C(OMe)Me ligands tend to lie in the complex plane. For the complex with one (*E*)- and one (*Z*)-C(OMe)Me ligand three equilibrium structures of similar energies could be located. Their structures are also similar; only smaller differences in the position of the in-plane alkylidene ligand, (*Z*)-C(OMe)Me, with respect to the complex plane were observed. For the complex with two (*Z*)-C(OMe)Me ligands two equilibrium structures were found having similar energies and structures. It is likely that due to steric reasons and a preference to minimize electrostatic repulsion between the two oxygen atoms, the alkylidene ligands exhibit greater deviations from the in-plane position.

In the gas phase the complexes with two (*E*)-alkylidene ligands are more stable by about 5 kcal/mol than the complexes with one (*E*)- and one (*Z*)-alkylidene ligand and by about 11 kcal/mol than the complexes with two (*Z*)-alkylidene ligands. Obviously due to a much better solvation of (*Z*)- over (*E*)-alkylidene ligands, in methanol solution all complexes proved to have essentially the same energy. Nevertheless, isomerization of an (*E*)- into a (*Z*)-alkylidene ligand by rotation around the C═OMe bond was found to be energetically unfavored both in the gas phase and in methanol solution. The activation barrier for the transformation of c*is*-$[PtCl_2\{C(OMe)Me\}_2]$ ($\mathbf{7_{ct}}$, *E*,*E* isomer, transoid) into c*is*-$[PtCl_2\{C(OMe)Me\}_2]$ ($\mathbf{10_{EZ1}}$, *E*,*Z* isomer) was calculated to be about 16 kcal/mol.

2.5. Conclusion. There are two ways to form platina-*β*-diketones (Scheme 9), namely (A) the consecutive reaction of hexachloroplatinic acid with *n*-butyl alcohol at 80 °C followed by the addition of trimethylsilyl-substituted alkynes and—as presented in this work—(B) the one-pot reaction of hexachloroplatinic acid with alcohols in the presence of bis(trimethyl-

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[16] Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278.

Table 5. ZPE-Corrected Energies (in kcal/mol) of the Complexes *cis*-/*trans*-[PtX_2{C(OMe)Me}$_2$] (X = Cl, Br, I)

				ΔE		rotational barrier (transoid to cisoid)	
	isomer	X	alkylidene confign	gas phase	in MeOH[b]	gas phase	in MeOH[b]
7_{ct}	cis	Cl	transoid	0	0	8.94/9.21	8.61/6.82
7_{cc}	cis	Cl	cisoid	+0.33	+0.56		
7_{tt}	trans	Cl	transoid	+1.76	+11.20	7.38	6.98
7_{tc}	trans	Cl	cisoid	+1.62	+10.93		
8_{ct}	cis	Br	transoid	0	0	11.13/11.29	4.44/8.26
8_{cc}	cis	Br	cisoid	0.39	−2.68		
8_{tt}	trans	Br	transoid	−0.99	+5.21	10.11	9.40
8_{cc}	trans	Br	cisoid	−0.51	+6.57		
9_{ct}	cis	I	transoid	0	0	14.22/14.75	12.30/13.21
9_{cc}	cis	I	cisoid	+0.79	+1.12		
9_{tt}	trans	I	transoid	−5.21	+1.85	14.66	13.32
9_{tc}	trans	I	cisoid	−4.67	+2.57		

[a] Energies are relative to the *cis*-[PtX_2{C(OMe)Me}$_2$] complexes with the two alkylidene substituents in a transoid configuration. The alkylidene ligands lie about perpendicular to the complex planes. Configurations with the two methoxy substituents on the same side of the complex plane are denoted as "cisoid" and those on different sides as "transoid". [b] The solvent influence (methanol) was considered by using the PCM model.

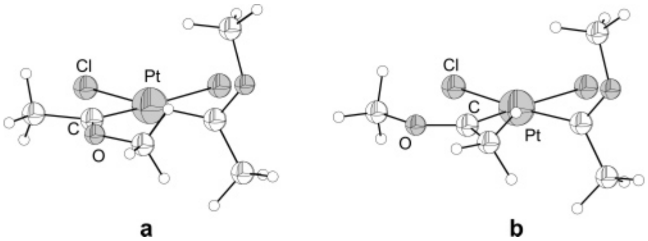

Figure 5. Molecular transition state structures (calculated) of *cis*-[$PtCl_2${C(OMe)Me}$_2$] for transoid/cisoid isomerization (for an explanation, see the text).

Table 6. ZPE-Corrected Energies (in kcal/mol) of the Complexes *cis*-[$PtCl_2${C(OMe)Me}$_2$] having Stereosiomeric (*E*/*Z*) Alkylidene Ligands[a]

		ΔE	
	isomer	gas phase	in MeOH[b]
7_{ct}	*E*,*E* (transoid)	0	0
7_{cc}	*E*,*E* (cisoid)	+0.33	+0.56
10_{EZ1}	*E*,*Z*	+5.17	−0.31
10_{EZ2}	*E*,*Z*	+5.12	+0.10
10_{EZ3}	*E*,*Z*	+4.99	+0.36
11_{EZ2}	*Z*,*Z*	+11.56	+0.52
	rotational barrier (*E*,*E*,transoid *to E*,*Z*)	16.89/17.11	16.06/16.17

[a] Energies are relative to *cis*-[$PtCl_2${C(OMe)Me}$_2$] (*E*,*E* isomer, transoid). [b] The solvent influence (methanol) was considered by using the PCM model.

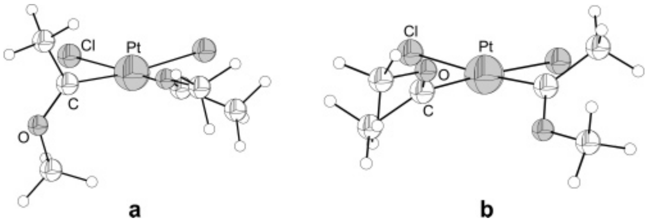

Figure 6. Molecular structures (calculated) of *cis*-[$PtCl_2${C(OMe)-Me}$_2$]: (a) *E*,*Z* isomer **10_{EZ1}**; (b) *Z*,*Z* isomer **11_{ZZ2}**.

silyl)acetylene. On this basis the following conclusions concerning the formation of platina-β-diketones can be drawn.

(a) Experimentally it was shown that the reaction of hexachloroplatinic acid with *n*-butyl alcohol at 80 °C resulted in the formation of H[$PtCl_3$(η^2-CH=CHEt)] (**6**), which was isolated and characterized from the reaction mixture as a PPN salt.[6] The formation of the parent ethylene complex in the analogous reaction with ethanol was first performed by Zeise in 1827, and in 1967 Hartley prepared other analogues using the corresponding alcohols.[17] Thus, the formation of the Zeise type complex **6** in the reaction mixture has been proved unequivocally.

(b) The Zeise type complex **6** may be an intermediate in the formation of platina-β-diketones; however, it is not an essential intermediate, since such complexes cannot be formed in the one-pot synthesis of platina-β-diketones using methanol or benzyl alcohol.

(c) Experimentally it has been shown that the reaction of hexachloroplatinic acid in methanol with bis(trimethylsilyl)-acetylene resulted in the formation of a bis(methoxyethylidene)-platinum(II) complex (**2a**) that was found to react with water, yielding the platina-β-diketone **1a**. Therefore, complex **2a** has been unambiguously identified as an intermediate in the platina-β-diketone formation under these reaction conditions.

We assume that—depending on the reaction conditions—there are several routes possible for the first reaction step, the reduction of the starting platinum(IV) compound to a platinum-(II) complex, which proceeds to react with bis(trimethylsilyl)-acetylene (or with another silylated alkyne), yielding platina-β-diketones **1**. Investigations are underway to determine which types of platinum(II) complexes may be used as starting compounds for the formation of platina-β-diketones.

The one-pot reaction of hexachloroplatinic acid with trimethylsilyl-substituted alkynes in methanol proved to be a versatile method to synthesize the bis(methoxyalkylidene)-platinum(II) complexes *cis*-[$PtCl_2${C(OMe)R′}$_2$] (**2a**−**c**). These complexes can be easily converted by reaction with alcohols into bis(alkoxyalkylidene)platinum(II) complexes, as shown for complex **2a**, which yielded *cis*-[$PtCl_2${C(OR)Me}] (**2d**,**e**). Analogous reactions starting from hexabromo- and hexaiodoplatinic acids lead to the formation of *cis*-[PtX_2{C(OR)Me}$_2$] (X = Br, **3a**−**d**; X = I, **5**) and *trans*-[PtI_2{C(OR)Me}$_2$] (**4a**−**e**). Relatively few complexes of these types have been previously reported.

Interestingly, only the bis(alkylidene)dichloroplatinum(II) complexes *cis*-[$PtCl_2${C(OR)R′}$_2$] (**2a**−**e**) were found to react with water quantitatively, yielding the platina-β-diketone **1a**. In contrast, the bromo and iodo analogues were found to decompose slowly under the same reaction conditions. As early as 1979 Voronkov reported the reaction of $H_2[PtCl_6]\cdot 6H_2O$ with (trimethylsilyl)acetylene in isopropyl alcohol, yielding the bis-(alkylidene) complex *cis*-[$PtCl_2${C(O-*i*-Pr)Me}$_2$] (**2d**), which

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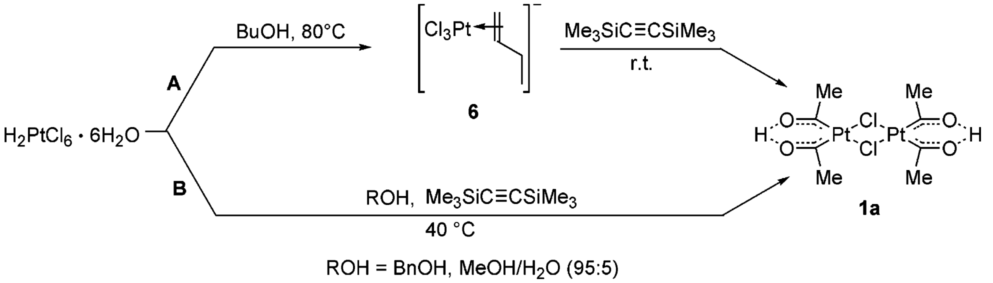
(17) (a) Hartley, F. R.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, *2*, 330. (b) Hartley, F. R. *Inorg. Chem. Acta* **1971**, *5*, 197.

Scheme 9



was characterized by single-crystal X-ray diffraction and was found to decompose.[7] Although we failed to synthesize complex **2d** by the procedure described in ref 7, we succeeded in synthesizing **2d** according to our route, via the reaction of *cis*-[PtCl$_2${C(OMe)Me}$_2$] (**2a**) with isopropyl alcohol. Furthermore, we found that **2d** reacts with water, yielding the platina-β-diketone **1a,** an electronically unsaturated and kinetically labile complex with a unique reactivity.

3. Experimental Section

3.1. General Comments. All reactions were performed under an argon atmosphere using the standard Schlenk techniques. Solvents were dried (Et$_2$O and THF over Na/benzophenone, CHCl$_3$ and CH$_2$Cl$_2$ over CaH$_2$, MeOH over NaBH$_4$/Fepc) and distilled prior to use if not otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 2000 (200 and 400 MHz) and Varian Unity 500 spectrometers. Assignment of NMR signals were partially revealed by COSY experiments (^{1}H, ^{13}C). IR spectra were recorded on a Galaxy Mattson 5000 FT-IR spectrometer using KBr pellets. Microanalyses were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (Elementaranalysensysteme) elemental analyzers.

3.2. Synthesis of [Pt$_2$(μ-Cl)$_2${(COMe)$_2$H}$_2$] (1a) in a One-Pot Reaction. A solution of hexachloroplatinic acid (500 mg, 0.96 mmol) and bis(trimethylsilyl)acetylene (6.0 mmol) in nondried ROH (R = Et, *i*-Pr, *t*-Bu, Bn) was warmed to 40 °C for approximately 2 h. After the solution changed in color from red to yellow the volume of the reaction mixture was reduced to about one-third. The yellow precipitate that formed was filtered, washed with Et$_2$O (2 mL) and *n*-pentane (2 mL), and dried under vacuum. The identity of the product was confirmed by comparison with literature ^{1}H NMR data.[8]

Yield: 250 mg (80%, R = Et); 215 mg (70%, R = *i*-Pr); 210 mg (70%, R = *t*-Bu); 180 mg (60%, R = Bn).

3.3. Synthesis of *cis*-[PtCl$_2${C(OMe)R′}$_2$] (2a−c). A solution of hexachloroplatinic acid (500 mg, 0.96 mmol) and the trimethylsilyl-substituted alkyne RC≡CSiMe$_3$ (6.0 mmol, R = SiMe$_3$, Me, *n*-Pent) in methanol (3 mL) was warmed to 40 °C for approximately 2 h. After the solution changed in color from red to yellow, the volume of the reaction mixture was reduced to about one-third. The white precipitate that formed was filtered, washed with *n*-pentane (2 × 2 mL), and dried under vacuum.

2a (R′ = Me). Yield: 270 mg (75%). Anal. Calcd for C$_6$H$_{12}$Cl$_2$O$_2$Pt (382.0): C, 18.86; H, 3.17; Cl, 18.55. Found: C, 18.59; H, 3.10; Cl, 18.80. IR (KBr): 2951 (w), 2885 (w), 1493 (s), 1321 (s), 1204 (m), 1132 (m), 1023 (m), 984 (m), 900 (m), 574 (w) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 2.81 (s + d, ^3J(Pt,H) = 20.4 Hz, 6 H, CC*H*$_3$), 5.09 (s + d, ^4J(Pt,H) = 8.6 Hz, 6 H, OC*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 43.9 (s + d, ^2J(Pt,C) = 151 Hz, C*C*H$_3$), 72.6 (s + d, ^3J(Pt,C) = 94 Hz, O*C*H$_3$), 277.3 (s + d, ^1J(Pt,C) = 1277 Hz, Pt=*C*).

2b (R′ = Et). Yield: 255 mg (65%). Anal. Calcd for C$_8$H$_{16}$Cl$_2$O$_2$Pt (410.2): C, 23.42; H, 3.93; Cl, 17.20. Found: C, 23.18; H, 4.25; Cl, 16.80. IR: 2984 (m), 2939 (m), 2852 (w), 1474 (s), 1328 (s), 1181 (m), 1100 (m), 1059 (m), 951 (m), 776 (m), 639 (w), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.18 (t, 6 H, CH$_2$C*H*$_3$), 2.99 (q, 4 H, C*H*$_2$CH$_3$), 5.16 (s, 6 H, OC*H*$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 9.4 (s, CH$_2$*C*H$_3$), 50.8 (s + d, ^2J(Pt,C) = 147 Hz, *C*H$_2$CH$_3$), 71.8 (s + d, ^3J(Pt,C) = 94 Hz, O*C*H$_3$) 277.9 (s + d, ^1J(Pt,C) = 1278 Hz, Pt=*C*).

2c (R′ = *n*-Hex). Yield: 250 mg (50%). Anal. Calcd for C$_{16}$H$_{32}$Cl$_2$O$_2$Pt (522.4): C, 36.79; H, 6.17; Cl, 13.57. Found: C, 36.30; H, 6.52; Cl, 13.71. IR: 2959 (s), 2928 (m), 2855 (s), 1536 (m), 1481 (s), 1325 (m), 1197 (m), 1123 (w), 1070 (m), 936 (w), 784 (w), 723 (w), 627 (w), 566 (w) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89 (t, 6 H, CH$_2$C*H*$_3$), 1.30 (m, 12 H, C*H*$_2$), 1.74 (m, 4 H, C*H*$_2$), 2.95 (t, 4 H, CC*H*$_2$), 5.15 (s + d, ^4J(Pt,H) = 8.2 Hz, 6 H, OC*H*$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.2 (s, CH$_2$*C*H$_3$), 22.6 (s, *C*H$_2$CH$_3$), 25.0 (s, *C*H$_2$), 29.0 (s, *C*H$_2$), 31.5 (s, *C*H$_2$), 57.2 (s + d, ^2J(Pt,C) = 131 Hz, C*C*H$_2$), 71.6 (s + d, ^3J(Pt,C) = 92 Hz, O*C*H$_3$), 277.9 (s + d, ^1J(Pt,C) = 1274 Hz, Pt=*C*).

3.3. Synthesis of [Pt$_2$(μ-Cl)$_2${(COR)$_2$H}$_2$] (1a−c). A suspension of *cis*-[PtCl$_2${C(OMe)R′}$_2$] (**2a**−**c**; 0.1 mmol) in nondried CH$_3$NO$_2$ (5 mL) was stirred for 24 h. The volume of the reaction mixture was reduced to about one-third. The yellow precipitate that formed was filtered, washed with Et$_2$O (2 mL) and *n*-pentane (2 mL), and dried under vacuum. The identity of the product was confirmed by comparison with literature ^{1}H NMR data.[8]

Yield: **1a** (R = Me), 30 mg (95%); **1b** (R = Et), 31 mg (90%); **1c** (R = *n*-Hex), 40 mg (85%).

3.5. Synthesis of *cis*-[PtCl$_2${C(OR)Me}$_2$] (2d,e). To a suspension of *cis*-[PtCl$_2${C(OMe)Me}$_2$] (**2a**; 150 mg, 0.39 mmol) in ROH (10 mL, R = *i*-Pr, *n*-Bu) was added a solution of HBF$_4$ in diethyl ether (0.05 mmol, 54%). After the mixture was stirred for 24 h, the volume was reduced to one-third. The solid was filtered, washed with *n*-pentane (2 × 2 mL), and dried under vacuum.

2d (R = *i*-Pr). Yield: 75 mg (45%). Anal. Calcd for C$_{10}$H$_{20}$Cl$_2$O$_2$Pt (438.3): C, 27.41; H, 4.60; Cl, 16.18. Found: C, 27.01; H, 4.34, Cl, 16.45. IR: 2959 (s), 2928 (m), 2855 (s), 1536 (m), 1481 (s), 1325 (m), 1197 (m), 1123 (w), 1070 (m), 936 (w), 784 (w), 723 (w), 627 (w), 566 (w) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.63 (d, 12H, CHC*H*$_3$), 2.72 (s + d, ^3J(Pt,H) = 19.9 Hz, 6H, CC*H*$_3$), 6.89 (m, 2H, OC*H*). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 21.8 (s, CH*C*H$_3$), 44.1 (s + d, ^2J(Pt,C) = 153 Hz, C*C*H$_3$), 85.5 (s + d, ^3J(Pt,C) = 90.2 Hz, O*C*H), 271.1 (s, Pt=*C*).

2e (R = *n*-Bu). Yield: 80 mg (45%). Anal. Calcd for C$_{12}$H$_{24}$Cl$_2$O$_2$Pt (466.3): C, 30.91; H, 5.19. Found: C, 31.13; H, 5.35. IR: 2961 (s), 2936 (m), 2861 (m), 1550 (w), 1460 (m), 1402 (m), 1333 (m), 1185 (w), 1163 (m), 1059 (w), 1026 (w), 979 (m), 910 (m), 820 (w), 602 (w), 564 (w) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (t, 6 H, CH$_2$C*H*$_3$), 1.49 (m, 4 H, C*H*$_2$CH$_3$), 1.99 (m, 4 H, C*H*$_2$), 2.74 (s, 6 H, CC*H*$_3$), 5.58 (s, 4 H, OC*H*$_2$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 13.6 (s, CH$_2$*C*H$_3$), 18.9 (s, *C*H$_2$CH$_3$), 30.4 (s, *C*H$_2$), 43.9 (s + d, ^2J(Pt,C) = 131 Hz, C*C*H$_3$), 86.6 (s + d, ^3J(Pt,C) = 81 Hz, O*C*H$_2$), 272.9 (s, Pt=*C*).

Due to incomplete combustion of complexes bearing bromo or iodo ligands, the microanalytical carbon values proved to be slightly lower than the calculated values. The purity and the identity of these complexes were proved by NMR spectroscopic investigations.

Table 7. Crystallographic and Data Collection Parameters for Compounds 2a,b

	2a	**2b**
empirical formula	$C_6H_{12}Cl_2O_2Pt$	$C_8H_{16}Cl_2O_2Pt$
M_r	382.14	410.19
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a/Å	11.448(3)	15.810(4)
b/Å	12.132(3)	7.331(2)
c/Å	14.356(3)	10.694(3)
β/deg	92.27(3)	98.64(3)
V/Å^3	1992.3(8)	1225.4(5)
Z	8	4
D_{calcd}/g cm^{-3}	2.548	2.223
μ(Mo Kα)/mm^{-1}	14.575	11.857
θ range/deg	3.29−30.00	2.61−24.99
no. of rflns collected	24 842	3737
no. of rflns obsd [$I > 2\sigma(I)$]	5008	1037
no. of indep rflns	5818	1075
no. of data/restraints/params	5818/0/199	1075/0/61
goodness of fit on F^2	1.075	1.354
R1, wR2 ($I > 2\sigma(I)$)	0.0494, 0.1324	0.0287/0.0889
R1, wR2 (all data)	0.0575, 0.1381	0.0306/0.0937
largest diff peak and hole/e Å^{-3}	4.388/−4.599	1.615/−2.401

3.6. Synthesis of *cis*-[$PtBr_2\{C(OR)Me\}_2$] (3a−d). A solution of hexabromoplatinic acid (300 mg, 0.38 mmol) and bis(trimethylsilyl)acetylene (0.7 mL, 3.0 mmol) in ROH (2 mL, R═Me, Et, *i*-Pr, *n*-Bu) was warmed to 40 °C for approximately 2 h. The color of the solution changed from red to yellow and a white precipitate was formed. The volume of the solution was reduced to 1/3. The precipitate was filtered, washed with *n*-pentane (2 × 2 mL) and dried in vacuum.

3a (R = Me). Yield: 120 mg (65%). Anal. Calcd for $C_6H_{12}Br_2O_2Pt$ (471.0): C, 15.30; H, 2.57; Br, 33.93. Found: C, 15.12; H, 2.75; Br, 33.25. IR: 2959 (s), 2928 (m), 2855 (s), 1536 (m), 1481 (s), 1325 (m), 1197 (m), 1123 (w), 1070 (m), 936 (w), 784 (w), 723 (w), 627 (w), 566 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.85 (s + d, ^3J(Pt,H) = 20.8 Hz, 6H, CCH_3), 5.04 (6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.6 (s + d, ^2J(Pt,C) = 152 Hz, CCH_3), 71.6 (s + d, ^3J(Pt,C) = 96 Hz, OCH_3), 277.5 (s, Pt═*C*).

3b (R = Et). Yield: 110 mg (60%). Anal. Calcd for $C_8H_{16}Br_2O_2Pt$ (499.1): C, 19.25; H, 3.23. Found: C, 18.56; H, 3.29. IR: 2984 (m), 2939 (m), 2852 (w), 1474 (s), 1328 (s), 1181 (m), 1100 (m), 1059 (m), 951 (m), 776 (m), 639 (w), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (t, 6 H, CH_2CH_3), 2.99 (s, 6 H, CCH_3), 5.66 (q, 4 H, OCH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0 (s, CH_2CH_3), 43.5 (s + d, ^2J(Pt,C) = 156 Hz, CCH_3), 82.7 (s + d, ^3J(Pt,C) = 94 Hz, OCH_2), 273.8 (s + d, ^1J(Pt,H) = 1256 Hz, Pt═*C*).

3c (R = *i*-Pr). Yield: 100 mg (50%). Anal. Calcd for $C_{10}H_{20}Br_2O_2Pt$ (527.2): C, 22.78; H, 3.82; Br, 30.32. Found: C, 21.68; H, 3.77, Br, 30.60. IR: 2959 (s), 2928 (m), 2855 (s), 1536 (m), 1481 (s), 1325 (m), 1197 (m), 1123 (w), 1070 (m), 936 (w), 784 (w), 723 (w), 627 (w), 566 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.64 (d, 12H, $CHCH_3$), 2.79 (s + d, ^3J(Pt,H) = 20.3 Hz, 6H, CCH_3), 6.91 (m, 2H, $COCH$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 21.8 (s, $CHCH_3$), 43.9 (s + d, ^2J(Pt,C) = 154 Hz, CCH_3), 93.5 (s + d, ^3J(Pt,C) = 89.4 Hz, OCH), 270.4 (s, Pt═*C*).

3d (R = *n*-Bu). Yield: 105 mg (45%). Anal. Calcd for $C_{12}H_{24}Br_2O_2Pt$ (555.2): C, 25.96; H, 4.36; Br, 28.78. Found: C, 25.29; H, 4.57; Br, 29.11. IR: 2984 (m), 2939 (m), 2852 (w), 1474 (s), 1328 (s), 1181 (m), 1100 (m), 1059 (m), 951 (m), 776 (m), 639 (w), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.99 (t, 6H, CH_2CH_3), 1.51 (m, 4H, CH_2CH_3), 1.99 (m, 4H, OCH_2CH_2), 2.80 (s + d, ^3J(Pt,H) = 18.7 Hz, 6H, CCH_3), 5.51 (s, 4H, $COCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 (s, CH_2CH_3), 19.0 (s, CH_2CH_3), 30.2 (s, CH_2CH_2), 43.5 (s + d, ^2J(Pt,C) = 154 Hz, CCH_3), 86.5 (s + d, ^3J(Pt,C) = 91 Hz, OCH_2), 274.3 (s + d, ^1J(Pt,H) = 1261 Hz, Pt═*C*).

3.7. Synthesis of *trans*-[$PtI_2\{C(OR)Me\}_2$] (4a−e). A suspension of potassium hexaiodoplatinate (500 mg, 0.48 mmol), HBF_4 in water (1 mL, 40%), and bis(trimethylsilyl)acetylene (0.7 mL, 3.0 mmol) in ROH (3 mL, R = Me, Et, *i*-Pr, *n*-Bu, (*S*)-2-Bu) was warmed to 40 °C for approximately 2 h. The color of the solution changed from red to yellow. The solvents were removed under vacuum, and the resulting residue was extracted with pentane (5 × 5 mL). The solvent was evaporated from the extract, and the residue was recrystallized from the corresponding alcohol, giving the product as colorless crystals. The crystals were filtered and dried under vacuum.

4a (R = Me). Yield: 195 mg (75%). Anal. Calcd for $C_6H_{12}I_2O_2Pt$ (565.0): C, 12.75; H, 2.41. Found: C, 12.20; H, 2.81. IR: 2984 (m), 2939 (m), 2852 (w), 1474 (s), 1328 (s), 1181 (m), 1100 (m), 1059 (m), 951 (m), 776 (m), 639 (w), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (s, 6H, CCH_3), 3.03 (s, 6H, CCH_3), 4.80 (s, 6H, $COCH_3$), 4.92 (s, 6H, $COCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): 43.6 (s, CCH_3), 43.9 (s, CCH_3), 80.6 (s, OCH_3), 81.5 (s, OCH_3), 315.1 (s + d, ^1J(Pt,C) = 742 Hz, Pt═*C*), 315.6 (s + d, ^1J(Pt,C) = 745 Hz, Pt═*C*).

4b (R = Et). Yield: 220 mg (80%). Anal. Calcd for $C_8H_{16}I_2O_2Pt$ (593.1): C, 16.20; H, 2.72. Found: C, 15.95; H, 2.59. IR: 2974 (m), 2941 (m), 2853 (w), 1479 (s), 1333 (s), 1182 (m), 1105 (m), 1059 (m), 951 (m), 776 (m), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65 (m, 6H, CH_2CH_3), 2.90 (s, 6H, CCH_3), 3.00 (s, 6H, CCH_3), 5.28 (m, 4H, $COCH_2$), 5.47 (m, 4H, $COCH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.9 (s, CH_2CH_3), 42.5 (s, CCH_3), 42.9 (s, CCH_3), 84.7 (s, OCH_2), 85.6 (s, OCH_2), 312.0 (s, Pt═*C*), 312.4 (s, Pt═*C*).

4c (R = *i*-Pr). Yield: 195 mg (65%). Anal. Calcd for $C_{10}H_{20}I_2O_2Pt$ (621.2): C, 19.34; H, 3.25. Found: C, 18.95; H, 3.38. IR: 2989 (m), 2951 (m), 1484 (s), 1323 (s), 1189 (m), 1102 (m), 1055 (m), 891 (m), 649 (w), 443 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (m, 12H, $CHCH_3$), 2.84 (s, 6H, CCH_3), 2.95 (s, 6H, CCH_3), 6.35 (m, 2H, $COCH$), 6.69 (m, 2H, $COCH$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.3 (s, $CHCH_3$), 42.5 (s, CCH_3), 43.0 (s, CCH_3), 90.3 (s, OCH), 91.3 (s, OCH), 307.0 (s, Pt═*C*), 307.4 (s, Pt═*C*).

4d (R = *n*-Bu). Yield: 135 mg (45%). Anal. Calcd for $C_{12}H_{24}I_2O_2Pt$ (649.2): C, 22.20; H, 3.73. Found: C, 22.42; H, 4.06. IR: 2984 (m), 2939 (m), 2852 (w), 1474 (s), 1328 (s), 1181 (m), 1100 (m), 1059 (m), 951 (m), 776 (m), 639 (w), 446 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (m, 6H, CH_2CH_3), 1.52 (m, 4H, CH_2CH_3), 2.00 (m, 4H, OCH_2CH_2), 2.90 (6H, s, CCH_3), 3.00 (6H, s, CCH_3), 5.21 (4H, s, $COCH_2$), 5.39 (4H, s, $COCH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1 (s, CH_2CH_3), 19.3 (s, CH_2CH_3), 30.7 (s, $CH_2CH_2CH_3$), 42.9 (s + d, ^2J(Pt,C) = 71 Hz, CCH_3), 43.3 (s + d, ^2J(Pt,C) = 71 Hz, CCH_3), 84.7 (s, OCH_2), 85.6 (s, OCH_2), 312.0 (s, Pt═*C*), 312.6 (s, Pt═*C*).

4e (R = (*S*)-2-Bu). Yield: 125 mg (45%). Anal. Calcd for $C_{12}H_{24}I_2O_2Pt$ (649.2): C, 22.20; H, 3.72. Found: C, 21.32; H, 4.02. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.99 (t, 6H, CH_2CH_3), 1.17 (t, 6H, CH_2CH_3), 1.55 (d, 6H, $CHCH_3$), 1.59 (d, 6H, $CHCH_3$), 1.8 − 2.2 (m, 4H, CH_2CH_3), 2.83 (s, 6H, CCH_3), 2.96 (s, 6H, CCH_3), 6.18 (m, 2H, OCH), 6.47 (m, 2H, OCH). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 9.5 (s, CH_2CH_3), 9.6 (s, CH_2CH_3), 18.3 (s, $CHCH_3$), 18.4 (s, $CHCH_3$), 28.4 (s, CH_2CH_3), 28.4 (s, CH_2CH_3), 42.7 (s + d, ^2J(Pt,C) = 73.0 Hz, CCH_3), 43.1 (s + d, ^2J(Pt,C) = 73.0 Hz, CCH_3), 94.7 (s + d, ^3J(Pt,C) = 37 Hz, OCH), 95.6 (s + d, ^3J(Pt,C) = 37 Hz, OCH), 308.2 (s + d, ^1J(Pt,C) = 732 Hz, Pt═*C*), 308.5 (s + d, ^1J(Pt,C) = 733 Hz, Pt═*C*).

3.8. Synthesis of *cis*-[$PtI_2\{C(OMe)Me\}_2$] (5). 3.8.1. Isomerization of 4a. A solution of *trans*-[$PtI_2\{C(OMe)Me\}_2$] (**4a**; 100 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was stirred for 7 days. The solvent was removed, and the resulting orange residue was suspended in *n*-hexane (5 mL), filtered, and dried in vacuo. Yield: 75 mg (75%).

3.8.2. Direct Synthesis. A suspension of potassium hexaiodoplatinate (500 mg, 0.48 mmol), HBF_4 in water (1 mL, 40%), and bis(trimethylsilyl)acetylene (0.7 mL, 3.0 mmol) in ROH (R = Me, Et; 3 mL) was warmed to 40 °C for approximately 7 days. The solvents were removed under vacuum, and the resulting residue was extracted with CH_2Cl_2 (2 × 5 mL). The extract was evaporated, and the residue was recrystallized from the corresponding alcohol, giving the product as colorless crystals. The crystals were filtered and dried under vacuum. Yield: 170 mg (60%).

Anal. Calcd for $C_6H_{12}I_2O_2Pt$ (565.1): C, 12.75; H, 2.41. Found: C, 13.55; H, 2.81. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.96 (s, 6H, CCH_3), 4.93 (6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.6 (s + d, ^2J(Pt,C) = 152 Hz, CCH_3), 71.6 (s + d, ^3J(Pt,C) = 96 Hz, OCH_3), 268.3 (s + d, ^1J(Pt,C) = 1210 Hz, Pt=*C*).

3.9. X-ray Crystallography. Single crystals suitable for X-ray diffraction measurements were obtained from the mother liquor (**2a**) and by recrystallization from chloroform/pentane (1:1) (**2b**). Intensity data were collected on a KUMA KM4 CCD with Mo Kα radiation (λ = 0.7103 Å, graphite monochromator) at 100(2) K (**2a**) and on a STADI IPDS with Mo Kα radiation (λ = 0.7103 Å, graphite monochromator) at 223(2) K (**2b**). Absorption corrections were applied numerically (T_{min}/T_{max} = 0.0263/0.1398, **2a**; T_{min}/T_{max} = 0.1345/0.3922, **2b**).

Both structures were solved by direct methods with SHELX-86 and refined using full-matrix least-squares routines against F^2 with SHELX-97.[18,19] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic displacement parameters (**2a**). In **2b** carbon atom C4 and the hydrogen atoms were refined with isotropic displacement parameters, whereas all other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were found in the difference Fourier map and refined according to the "riding model".

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-621994 (**2a**) and. CCDC-621995 (**2b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44(0)1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

Crystallographic data and data collection parameters for **2a**,**b** are given in Table 7.

3.10. Quantum-Chemical Calculations. All DFT calculations were carried out by the Gaussian98 program package[20] using the hybrid functional B3LYP.[21] The valence shell of platinum has been approximated by a split valence basis set; for its core orbitals an effective core potential in combination with consideration of relativistic effects has been used.[22] For iodine the SDD basis set as implemented in the Gaussian98 program with an additional d function has been used. For all other atoms the basis 6-31G* was employed. All systems have been fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures and transition states, respectively, by the analysis of the force constants of normal vibrations.

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Supporting Information Available: CIF files giving X-ray crystallographic data and tables of Cartesian coordinates of atom positions calculated for structures **7**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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