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Dinuclear Olefin and Alkyne Complexes of Platinum(II)

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Bis(olefin) complexes of Zeise's dimer type – [{$PtCl_2$(*cis*-MeHC=CHMe)}$_2$] (**2**) or [{$PtCl_2$(*c*-Hex)}$_2$] (**3**, *c*-Hex = cyclohexene) – were prepared by treatment of $K_2[PtCl_4]$ in the presence of $SnCl_2$ or K[$PtCl_3$(*cis*-MeHC=CHMe)] with the corresponding olefin. Zeise's dimer, [{$PtCl_2(H_2C=CH_2)$}$_2$] (**1**), was found to react in chloroform or dichloromethane with the internal alkynes RC≡C*t*Bu (R = Me, *t*Bu), provided that the cleaved-off ethene was removed, to yield bis(alkyne) complexes of Zeise's dimer type [{$PtCl_2$(RC≡C*t*Bu)}$_2$] (R = Me, **11**; *t*Bu, **12**). Without removal of the ethene, mononuclear mixed ethene/alkyne complexes *cis*-[$PtCl_2(H_2C=CH_2)$(RC≡C*t*Bu)] (R = Me, **8**; *t*Bu, **9**) and *cis*-[$PtCl_2(H_2C=CH_2)_2$] (**10**) were formed. Analogous reactions with alkynes RC≡CR′ bearing sterically less demanding substituents (R, R′ = Me, Et, *n*Pr, Ph) led to (cyclobutadiene)platinum(II) complexes [$PtCl_2(C_4R_2R'_2)$] (R/R′ = Me/Me **4**; Et/Et **5**; Me/*n*Pr **6**) and [$PtCl_2(C_4Me_2Ph_2)$] (**7**). Furthermore, use of acetone (instead of $CHCl_3/CH_2Cl_2$) as solvent in the reactions between **1** and sterically undemanding substituted alkynes resulted in bridge cleavage of Zeise's dimer (**1**) and in aldol addition and condensation reactions, thereby confirming why Chatt et al. in his analogous classical experiments (1961) observed only decomposition. Complexes **2**–**7** and **11**/**12** were isolated in pure states and fully characterized by elemental analysis, NMR spectroscopy, and X-ray diffraction measurements (**2**, **11**, **12**). For the dinuclear bis(olefin) (**1**–**3**) and bis(alkyne) complexes (**11**, **12**) solvent-dependent equilibria between the *transoid* and *cisoid* isomers were observed, and these could even be ascertained crystallographically for complex [{$PtCl_2$(*t*BuC≡C*t*Bu)}$_2$] (**12**), which crystallized both as the *transoid* isomer **12a** and as the *cisoid* isomer **12b**·$CHCl_3$. Furthermore, consistent with DFT calculations, NMR measurements provided evidence of fast rotation and of hindered rotation of olefin and alkyne ligands, respectively, resulting in conformational isomers in **8** and **11**.

Introduction

The synthesis of the first organotransition metal compound, Zeise's salt K[$PtCl_3(H_2C=CH_2)$]·H_2O, in 1825 is a milestone both in coordination chemistry and in organometallic chemistry.[1] Shortly after (1830/1831), Zeise considered that he had obtained the compound known today as Zeise's dimer [{$PtCl_2(H_2C=CH_2)$}$_2$].[2] It was prepared in a pure state and recognized as a dinuclear chlorido-bridged complex by Anderson in 1934.[3] Substitution of the ethene ligand in Zeise's dimer by other olefins resulted in the formation of analogous dinuclear olefin complexes [{$PtCl_2$(RHC=CHR′)}$_2$] (R, R′ = alkyl, aryl).[4,5] The equilibria and kinetics relating to the bridge cleavage in [{$PtCl_2$(cot)}$_2$] (cot = cyclooctene) with neutral nucleophiles L (such as MeOH, MeCN, cot) and anionic nucleophiles X (such as Br, I, N_3, SCN) with formation of neutral and anionic mononuclear complexes of the type [$PtCl_2$(cot)L] and [$PtCl_2$X(cot)]$^-$, respectively, were investigated in detail by multinuclear NMR and UV/Vis spectroscopy.[4,6] In general, the thermodynamic balances of these reactions were found to be significantly dependent on the approaching ligands: anionic ligands led to complete conversions, whereas σ-donating neutral ligands such as MeCN and MeOH and π ligands such as cot were found to result in equilibrium reactions.[4,6]

Alkyne complexes of platinum(II) are less common than those of platinum(0). When starting from $M^I_2[PtX_4]$ (M^I = K, Na, [PPh_4]; X = Cl, Br) or K[$PtCl_3(H_2C=CH_2)$]·H_2O, by halide or ethene displacement, respectively, alkyne complexes $M^I[PtX_3(RC≡CR')]$ (M^I = K, Na, [PPh_4]; X = Cl, Br) of the Zeise's salt type were thus only accessible with alkyne ligands bearing sterically demanding or oxygen-functionalized substituents [such as *t*Bu, $C(OH)R_2$] or with phenyl-substituted alkynes.[7–9] On the other hand, when starting from the crown ether adducts [K(18C6)][$PtCl_3$L] (L = but-2-ene, but-2-yne) or [K(18C6)]$_2$[Pt_2Cl_6], complexes of the [K(18C6)][$PtCl_3$(RC≡CR′)] type (R, R′ = H, alkyl, aryl) were obtained with a wide scope of alkynes, terminal alkynes among them.[10,11]

Alkyne complexes [{$PtCl_2$(RC≡C*t*Bu)}$_2$] (R = Et, *i*Pr, *t*Bu, CMe_2R') of the Zeise's dimer type were synthesized either from $Na_2[PtCl_4]$ or directly from Zeise's dimer, but only with alkynes bearing sterically demanding substituents.[7] From the historical point of view, it is of interest

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to clarify why analogous reactions with alkynes RC≡CR′ bearing sterically less demanding substituents R/R′ [such as H, Me, Et, *n*Pr, *i*Pr, *n*Bu, Ph, $C(OH)Me_2$, $CMe_2OC(O)Ph$] resulted only in decomposition.[7,8] Furthermore, (cyclobutadiene)platinum(II) complexes are accessible through reactions between internal alkynes and $H_2[PtCl_6]\cdot 6H_2O$[12] or $[PtCl_2L_2]$ (L = CO, MeCN).[13]

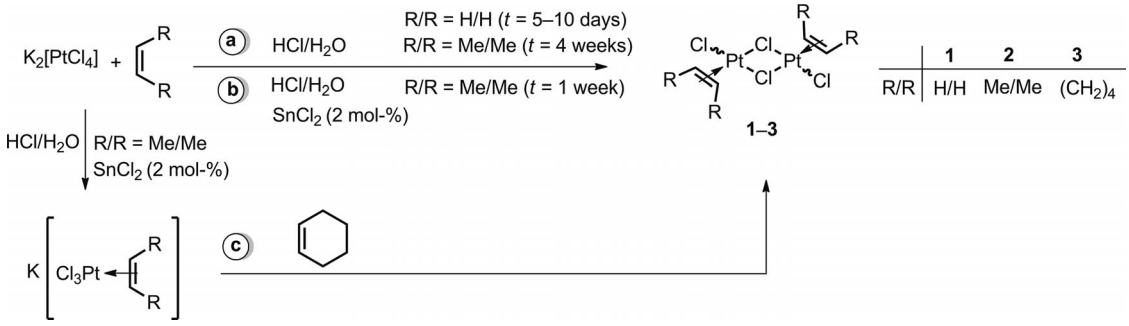
Here we present corresponding investigations into reactions of $[\{PtCl_2(RHC{=}CHR)\}_2]$ (R = H, Me) with alkynes RC≡CR′ (R, R′ = Me, Et, *n*Pr, Ph, *t*Bu) resulting in alkyne complexes of Zeise's dimer type and in mononuclear mixed (olefin)(alkyne)- and (cyclobutadiene)platinum(II) complexes. The influence of the alkyne substituents R/R′ on the courses of these reactions is the subject of this study, which permits, with the aid of DFT calculations, conclusions about the relative stabilities of olefin and alkyne complexes.

Results and Discussion

Synthesis and Spectroscopic Characterization of Dinuclear Olefin Complexes

The synthesis of the dinuclear ethene complex $[\{PtCl_2(H_2C{=}CH_2)\}_2]$ (Zeise's dimer) from $K_2[PtCl_4]$ and ethene is described in the literature (Scheme 1a).[14] Here, however, we observed that the analogous reaction with *cis*-but-2-ene was very slow and required a reaction time of several weeks. The formation of Zeise's salt from $K_2[PtCl_4]$ with ethene was reported to be catalyzed by $SnCl_2$ in HCl_{aq},[15] so it was felt that reactions with higher olefins yielding complexes of the Zeise's dimer type might be catalyzed by $SnCl_2$ as well. The synthesis of the neutral dinuclear bis(olefin) complex $[\{PtCl_2(MeHC{=}CHMe)\}_2]$ (**2**) by this approach was found to be significantly accelerated by addition of catalytic amounts of $SnCl_2$ (Scheme 1b). On the other hand, the synthesis of the complex $[\{PtCl_2(c\text{-Hex})\}_2]$ (**3**) could be performed by substitution of *cis*-but-2-ene in $K[PtCl_3(MeHC{=}CHMe)]$ by the less volatile cyclohexene (Scheme 1c).

Complexes **2** and **3** were isolated in good (75%) and moderate yields (60%), respectively, and characterized unambiguously by microanalysis and NMR spectroscopy, as well as by X-ray diffraction measurement in the case of **2**. Selected NMR spectroscopic parameters for complexes **2** and **3** are given in Table 1. Additionally, the parameters of the corresponding ethene complex **1** (Zeise's dimer) are presented for comparison. Closer inspection of the ^{13}C and ^{195}Pt NMR spectra of the dinuclear complexes **1**–**3** shows two sets of signals with very similar chemical shifts for the olefinic C atoms (except for **1**) and Pt atoms, indicating the presence of two configurational isomers (*transoid*/*cisoid*) in



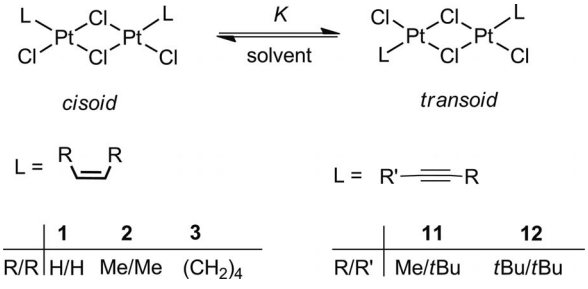
Scheme 1.

Table 1. Selected ^1H, ^{13}C, and ^{195}Pt NMR spectroscopic data (δ in ppm, J in Hz) for (olefin)- and (olefin)(alkyne)platinum(II) complexes.

Olefin	$\delta(=CH)$	$\Delta\delta$[a]	$^2J_{Pt,H}$	$\delta(=CH)$	$\Delta\delta$[a]	$^1J_{Pt,C}$	$\delta(^{195}Pt)$
Neutral dinuclear olefin complexes $[\{PtCl_2(olefin)\}_2]$							
1 (ethene)	4.82	–0.46	74	72.1	–51.2	199	–2490[c]
(2.2:1)[d,f]							–2495[b]
2 (*cis*-but-2-ene)	5.55	0.10	71	86.9[b]	–37.3	190	–2426[b]
(3.0:1)[d,f]				87.4[c]	–36.8	182	–2405[c]
3 (cyclohexene)	5.96	0.30	81	91.5[b]	–35.8	196	–2298[b]
(12.6:1)[d,f]				90.9[c]	–36.4	[e]	–2374[c]
Anionic olefin complexes $M^I[PtCl_3(olefin)]$ (M^I = K, [K(18C6)])							
cis-But-2-ene	5.13	–0.32	76	84.2	–40.0	183	
cis-But-2-ene[g]	5.17	–0.28	75	82.8	–41.4	182	
Ethene[g]	4.46	–0.82	64	68.0	–55.3	192	
Neutral olefin complexes $[PtCl_2(olefin)(RC{\equiv}CtBu)]$ (R = Me, **8**; *t*Bu, **9**), $[PtCl_2(olefin)_2]$ (**10**)							
8 (ethene)	4.56	–0.77	60	80.2	–43.1	141	–3145
9 (ethene)	4.55	–0.78	55	80.4	–42.9	138	–3143
10 (ethene)	4.70	–0.57	56	84.3	–39.0	131	–3642

[a] $\Delta\delta = \delta_{complex} - \delta_{noncoord.\,ligand}$. [b] Major isomer. [c] Minor isomer. [d] Ratio of isomers in parentheses. [e] Not found for reasons of intensity. [f] Measured in CD_2Cl_2. [g] Values taken from ref.[16,17]

solution in each case (Scheme 2). The chemically induced shifts (CISs: $\Delta\delta = \delta_{complex} - \delta_{noncoord.\,ligand}$) of the olefinic carbon atoms of the dinuclear olefin complexes **1**–**3** (–35.8 to –51.2 ppm) and the $^1J_{Pt,C}$ coupling constants (182–199 Hz) are of the same order of magnitude as those found in complexes of the Zeise's salt type $M^I[PtCl_3(R_2C{=}CR'_2)]$ {M^I = K, [K(18C6)], (PPh_4), [N(nBu)$_4$]; R, R′ = H, alkyl, aryl} [$\Delta\delta(=CH)$ = –40 to –55 ppm; $^1J_{Pt,C}$ = 180–195 Hz].[4,16,6,17] On the other hand, significantly smaller coupling constants ($^1J_{Pt,C}$ = 131–152 Hz) are observed in neutral mononuclear *cis*-configured complexes of the $[PtCl_2L_2]$ type (L = ethene, 1,5-cod), indicating weaker Pt–C interaction in these complexes.[18,19] Furthermore, the ^{195}Pt chemical shifts of complexes **1**–**3** were found to be in the range from –2298 to –2495 ppm.



Scheme 2.

Molecular Structure of [{PtCl$_2$(*cis*-MeHC=CHMe)}$_2$] (2)

Crystals of the dinuclear olefin complex **2** suitable for X-ray diffraction analysis were obtained from $CHCl_3/Et_2O$ solutions. In crystals of **2**, discrete dinuclear molecules without unusual intermolecular interactions were found. The molecular structure, depicted in Figure 1, shows crystallographically imposed inversion symmetry. Selected structural parameters are given in Table 2. The central $Pt_2(\mu\text{-}Cl)_2$ unit is precisely planar. The platinum atoms are square-planar coordinated to a good approximation, as shown by the angles between *trans*-disposed ligands $Cl_{term.}$–Pt–μ-Cl [174.5(1)°] and Cg–Pt–μ-Cl [179.70(8)°] (Cg = center of gravity of the two olefinic C atoms). The olefin ligand is oriented almost perpendicularly to the $PtCl_3$ coordination plane as measured by the interplanar angle $\Phi(PtCl_3/PtC_2)$ = 88.1(6)°. Furthermore, comparison of the C1=C2 double bond in **2** [1.40(2) Å] with that in noncoordinated *cis*-but-2-ene [1.346(3) Å[20]] shows a coordination-induced bond lengthening of 0.054 Å, as would be anticipated for (olefin)-platinum(II) complexes. The terminal Pt–Cl2 bond [2.278(3) Å] is significantly shorter than the two bridging Pt–Cl1/Pt–Cl1′ bonds [2.378(3)/2.338(3) Å]. Furthermore, the Pt–Cl bond *trans* to the olefin was found to be longer than that *trans* to the terminal chlorido ligand [2.378(3) vs. 2.338(3) Å]. All of these structural features are in the range of those of Zeise's dimer complexes [{$PtCl_2L$}$_2$] with various olefin ligands L (cyclopentene, cycloheptene, cyclooctene, ethene;[4,5,21,22] cf. S2 in the Supporting Information).

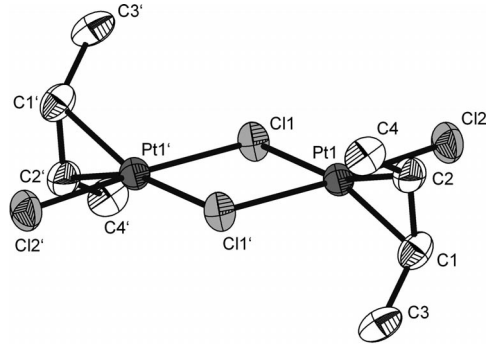


Figure 1. Structure of [{$PtCl_2$(*cis*-MeHC=CHMe)}$_2$] (**2**). Displacement ellipsoids are drawn at 50% probability. H atoms have been omitted for clarity.

Synthesis and Spectroscopic Characterization of Alkyne Complexes of the Zeise's Dimer Type and of Cyclobutadiene Complexes

Reactions between the dinuclear ethene complex [{$PtCl_2(H_2C{=}CH_2)$}$_2$] (**1**) and stoichiometric amounts of alkynes RC≡CtBu (R = Me, tBu) with removal of the cleaved-off ethene in CH_2Cl_2 or $CHCl_3$ as solvent resulted in the formation of dinuclear alkyne complexes [{$PtCl_2$(RC≡CtBu)}$_2$] (R = Me, **11**; tBu, **12**; Scheme 3a), which were isolated as deep red powders in good yields (90, 95%). When alkynes RC≡CR′ with sterically less demanding substituents (R/R′ = Me/Me, Et/Et, Me/nPr) were

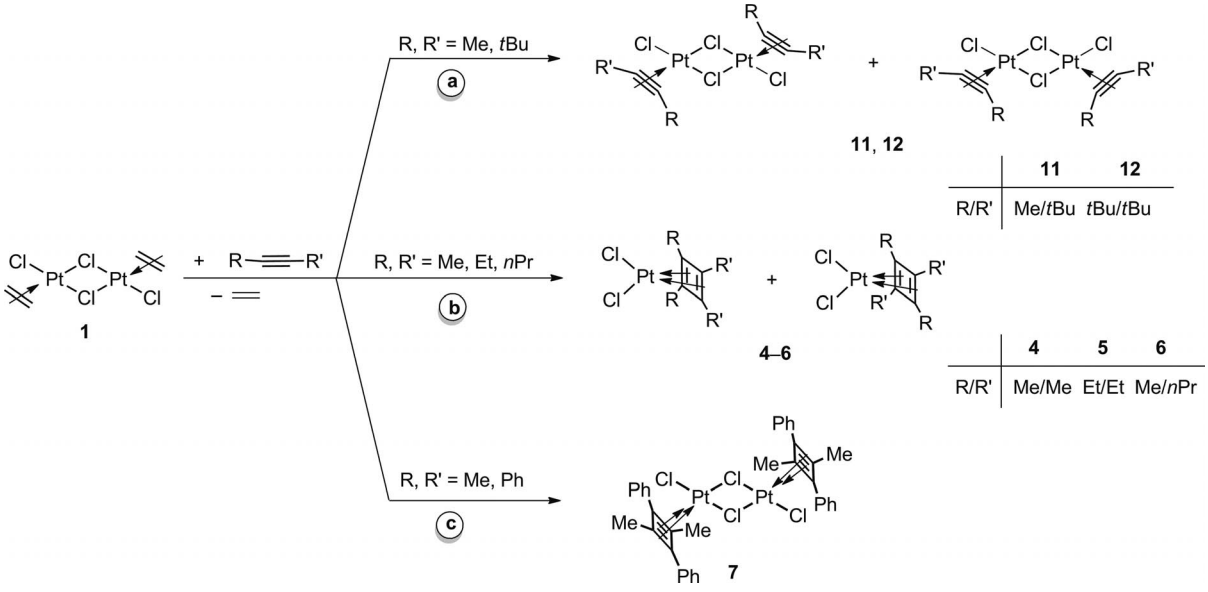
Table 2. Selected bond lengths [Å] and angles [°] in crystals of [{$PtCl_2$(MeHC=CHMe)}$_2$] (**2**) and calculated values for the same complex **2a**′.

	2	**2a**′		**2**	**2a**′
C1–C2	1.40(2) (1.346(3))[a]	1.410 (1.334)[a]	Cl2–Pt–Cl1′	174.5(1)	173.94
Pt–C1	2.18(2)	2.175	Cl2–Pt–Cl1	91.0(1)	90.91
Pt–C2	2.16(2)	2.175	Cl1–Pt–Cl1′	83.6(1)	83.03
Pt–Cl2	2.278(3)	2.305	Pt–Cl1–Pt′	96.4(1)	96.97
Pt–Cl1′	2.338(3)[b]	2.405	Cl2–Pt–Cg[b]	88.81(9)	89.07
Pt–Cl1	2.378(3)[b]	2.429	Cg–Pt–Cl1[b]	179.70(8)	179.98
			$\Phi(PtCl_3/PtC_2)$[c]	88.1(6)	90.0

[a] For comparison, values (measured by electron diffraction[20] and obtained by DFT calculation, respectively) for non-coordinated *cis*-but-2-ene in parentheses. [b] Cg: Center of gravity of the two olefinic C atoms (C1–C2). [c] $\Phi(PtCl_3/PtC_2)$: angle between the planes defined by Pt,Cl1,Cl1′,Cl2 and Pt,C1,C2.

used, [2+2] cycloadditions were observed with formation of neutral mononuclear cyclobutadiene complexes [$PtCl_2$-($C_4R_2R'_2$)] (**4**–**6**, Scheme 3b), which were isolated as yellow microcrystals in 73–81% yields. The corresponding reaction with MeC≡CPh also led to a cyclobutadiene complex: compound **7** (Scheme 3c), which proved to be, most likely, dinuclear. Notably, in the case of complex **6**, bearing an unsymmetrically Me-/*n*Pr-substituted cyclobutadiene ligand, the two regioisomeric cyclobutadienes (1,2-dimethyl-3,4-dipropyl, *cis*; 1,3-dimethyl-2,4-dipropyl, *trans*), were formed in a 1:1 ratio, so the cycloaddition did not proceed regioselectively. On the other hand, the coupling of MeC≡CPh to yield complex **7** proceeded regioselectively: both the cyclobutadiene ligands and their substituents of the same kind are believed to be in a mutual *trans* position.

All complexes were characterized unambiguously by microanalysis and NMR spectroscopy, and in the cases of **11** and **12** also by X-ray diffraction measurements. Selected NMR spectroscopic parameters of the complexes are given in Table 3. The CISs ($\Delta\delta = \delta_{complex} - \delta_{noncoord.\,ligand}$) of the alkyne carbon atoms of the dinuclear alkyne complexes **11** and **12** (–3.7 to –8.6 ppm) and the $^1J_{Pt,C}$ coupling constants (190–231 Hz) are of the same order of magnitude as those found in complexes of the Zeise's salt type with alkyne ligands [K(18C6)][$PtCl_3$(RC≡CR′)] (R, R′ = H, alkyl, aryl; $\Delta\delta$ = –5.6 to –17.8 ppm, $^1J_{Pt,C}$ = 173–236 Hz).[10,11] Moreover, all of these values differ from those found in neutral homoleptic mononuclear bis(alkyne)platinum(0) complexes of the type [Pt(RC≡CR′)$_2$] (R, R′ = Me, *t*Bu, Ph; $\Delta\delta$ = 35.2–41.6 ppm, $^1J_{Pt,C}$ = 266–311 Hz).[23]



Scheme 3.

Table 3. Selected ^{13}C and ^{195}Pt NMR spectroscopic data (δ in ppm, J in Hz) for (cyclobutadiene)- and (alkyne)platinum(II) complexes.

R/R′	δ(*C*R)/δ(*C*R′)	$\Delta\delta$[a]	$^1J_{Pt,C}$	$\delta(^{195}Pt)$
Cyclobutadiene complexes [$PtCl_2(C_4R_2R'_2)$]				
4 (Me/Me)	104.1	29.5	145	–3168
5 (Et/Et)	106.3	25.3	150	–3265
6 (Me/*n*Pr)	99.2/103.3	23.7/23.5	[e]/159	–3180
(1:1)[d]	102.8/106.9	27.8/27.7	148/158	–3186
7 (Me/Ph)	101.5/110.0	21.7/10.0	150/156	–1672
16 (Me/*t*Bu)	107.8/98.7	33.2/11.2	153/132	[e]
Mononuclear alkyne complexes [$PtCl_2(H_2C{=}CH_2)$(RC≡CR′)]				
8 (Me/*t*Bu)	74.9/84.8	1.2/–3.2	115/156	–3145
9 (*t*Bu/*t*Bu)	85.9	–1.6	151	–3143
Dinuclear alkyne complexes [{$PtCl_2$(RC≡CR′)}$_2$]				
11 (Me/*t*Bu)	70.0/80.0[b]	–3.7/–8.0	190/224	–1960[b]
(5.5:1:1.2)[d]	69.7/79.5[c]	–4.0/–8.5	[e]/228	–1955
	69.4/79.4[c]	–4.3/–8.6	[e]	–1971[c]
12 (*t*Bu/*t*Bu)	80.7[b]	–6.4	221	–1968[b]
(2.7:1)[d]	80.6[c]	–6.5	231	–2005[c]

[a] $\Delta\delta = \delta_{complex} - \delta_{noncoord.\,alkyne}$. [b] Major isomer. [c] Minor isomer. [d] Ratio of isomers in parentheses. [e] Not found for reasons of intensity.

In cyclobutadiene complexes of the type [$PtCl_2$-($C_4R_2R'_2$)] (**4**–**7**; R, R′ = Me, Et, *n*Pr, Ph), significantly smaller coupling constants ($^1J_{Pt,C}$ = 145–159 Hz) and downfield shifts between δ = 10.0 and 29.5 ppm relative to the non-coordinated alkynes are observed for the C ring atoms. Apart from the ^{13}C NMR spectroscopic data already discussed, the ^{195}Pt NMR shifts offer a straightforward method to distinguish between the different kinds of complexes: for the dinuclear bis(alkyne) complexes ^{195}Pt NMR shifts between δ = –1955 and –2005 ppm (**11**, **12**) are found, whereas the cyclobutadiene complexes (**4**–**6**) exhibit shifts from δ = –3168 to –3265 ppm. The significant difference from these values in the ^{195}Pt NMR shift of complex **7** (δ = –1672 ppm) indicates a dinuclear structure (Scheme 3c).

Molecular Structures of [{$PtCl_2$(RC≡C*t*Bu)}$_2$] (R = Me, **11**; *t*Bu, **12**)

Crystals of the dinuclear bis(alkyne) complexes **11** and **12** suitable for X-ray diffraction analysis were obtained from $CHCl_3$/Et_2O/*n*-pentane solutions. Complex **12** was found to crystallize as two configurational isomers, with the two alkyne ligands either in a mutual *transoid* (**12a**) configuration or in a *cisoid* configuration (**12b**·$CHCl_3$). In all crystals, discrete dinuclear complexes were found without unusual intermolecular interactions. In the crystals of **12a**, two symmetry-independent molecules of very similar structure were found. The molecular structures are depicted in Figures 2, 3, and 4; selected structural parameters are given in the figure captions.

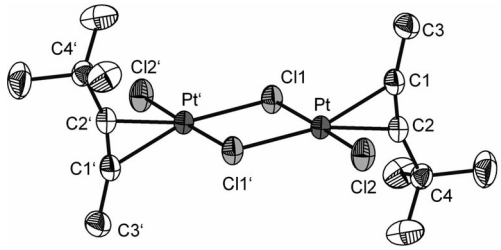


Figure 2. Molecular structure of [{$PtCl_2$(MeC≡C*t*Bu)}$_2$] (**11**). Displacement ellipsoids are drawn at 50% probability. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Pt–C1 2.147(5), Pt–C2 2.143(5), Pt–Cl1 2.341(1), Pt–Cl1′ 2.354(1), Pt–Cl2 2.267(1), C1–C2 1.254(7); C2–C1–C3 163.0(5), C1–C2–C4 159.8(5), Cl1–Pt–Cl2 176.67(4), Cl1–Pt–Cl1′ 84.92(4), Cl1′–Pt–Cl2 91.88(4); Φ($PtCl_3$/PtC_2)[a] 87.5(2). [a] Angle between the planes defined by Pt,Cl1,Cl1′,Cl2 and Pt,C1,C2.

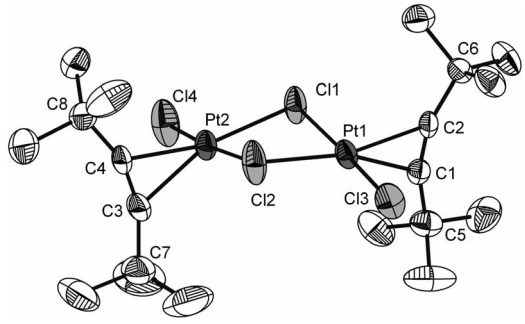


Figure 3. One of the two symmetry-independent molecules of [{$PtCl_2$(*t*BuC≡C*t*Bu)}$_2$] (*transoid* configuration) in crystals of **12a**. Displacement ellipsoids are drawn at 50% probability. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °; the values for the two symmetry-independent molecules are separated by slashes): Pt1–C1 2.142(4)/2.130(4), Pt1–C2 2.126(4)/2.140(4), Pt2–C3 2.135(5)/2.132(4), Pt2–C4 2.135(4)/2.133(4), Pt1–Cl3 2.262(1)/2.263(1), Pt1–Cl1 2.347(1)/2.349(1), Pt1–Cl2 2.351(1)/2.346(1), Pt2–Cl1 2.349(1)/2.353(1), Pt2–Cl2 2.337(1)/2.330(1), Pt2–Cl4 2.263(1)/2.267(1), C1–C2 1.244(6)/1.238(6), C3–C4 1.229(7)/1.226(6); C1–C2–C6 159.3(4)/161.4(4), C2–C1–C5 161.1(5)/159.2(5), C3–C4–C8 159.2(5)/160.7(5), C4–C3–C7 159.9(5)/160.5(5), Cl1–Pt1–Cl3 176.04(4)/175.67(4), Cl4–Pt2–Cl2 175.11(5)/176.08(5), Cl1–Pt1–Cl2 84.57(4)/84.53(4), Cl1–Pt2–Cl2 84.84(4)/84.80(4), Cl3–Pt1–Cl2 91.58(5)/91.20(5), Cl4–Pt2–Cl1 90.41(4)/91.51(4); Φ($Pt1Cl_3$/$Pt1C_2$)[a] 89.7(3)/89.8(2), Φ($Pt2Cl_3$/$Pt2C_2$)[b] 89.5(3)/89.0(2). [a] Angle between the planes defined by Pt1, Cl1, Cl2, Cl3 and Pt, C1, C2. [b] Angle between the planes defined by Pt2, Cl1, Cl2, Cl4 and Pt2, C3, C4.

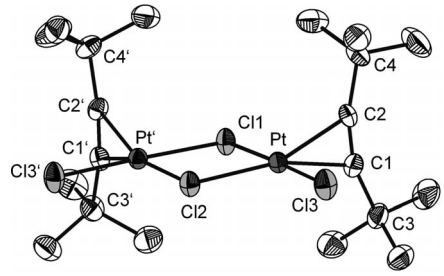


Figure 4. Molecular structure of [{$PtCl_2$(*t*BuC≡C*t*Bu)}$_2$] (**12b**, *cisoid* configuration) in crystals of **12b**·$CHCl_3$. Displacement ellipsoids are drawn at 50% probability. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Pt–C1 2.135(4), Pt–C2 2.144(4), Pt–Cl1 2.3394(9), Pt–Cl2 2.3779(8), Pt–Cl3 2.272(1), C1–C2 1.258(5); C2–C1–C3 159.8(4), C1–C2–C4 160.8(4), Cl1–Pt–Cl3 177.55(4), Cl1–Pt–Cl2 84.93(3) Cl2–Pt–Cl3 92.72(3); Φ($PtCl_3$/PtC_2)[a] 89.7(2). [a] Angle between the planes defined by Pt, Cl1, Cl2, Cl3 and Pt, C1, C2.

Molecules of complex **11** and of the *cisoid* complex **12b** exhibit crystallographically imposed inversion and mirror symmetry, respectively. In each of these two complexes, the central $Pt_2(\mu\text{-}Cl)_2$ unit is precisely (**11**) or nearly planar [Pt–Cl1···Cl2–Pt′ 177.00(5)°, **12b**]. In complex **12a** the central four-membered ring is more folded [Pt1–Cl1···Cl2–Pt2 152.51(5)/153.35(6)°].[1] The platinum atoms are square-planar coordinated to a good approximation, as shown by the angles between the *trans*-disposed ligands $Cl_{term.}$–Pt–μ-Cl and Cg–Pt–μ-Cl (Cg = center of gravity of the two alkyne C atoms), which were found to be between 175.05(3) and 177.88(3)°.

The alkyne ligands are orientated almost perpendicular to the $PtCl_3$ coordination planes, as measured by the interplanar angles Φ($PtCl_3$/PtC_2) = 87.5(2) to 89.8(2)°. The terminal Pt–$Cl_{term.}$ bonds [2.262(1) to 2.272(1) Å] are significantly shorter than the bridging Pt–μ-Cl bonds [2.330(1) to 2.3779(9) Å] (cf. S3 in the Supporting Information).

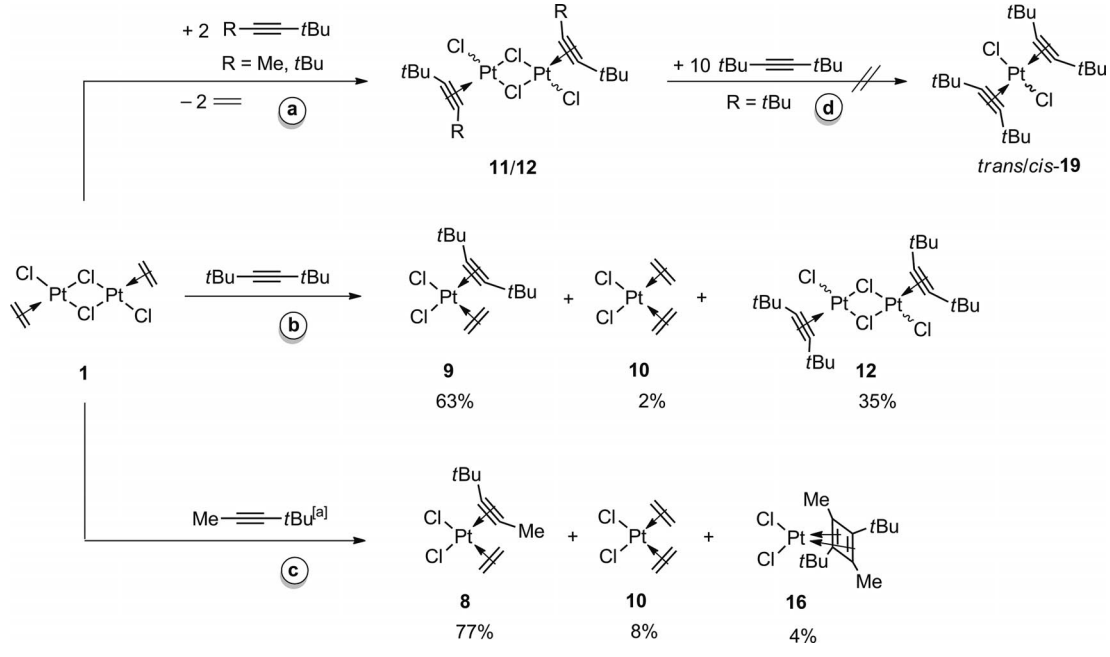
Furthermore, in the *cisoid*-configured complex **12b**, the Pt–μ-Cl bond *trans* to the alkyne ligand is significantly longer than the corresponding bond *trans* to the chlorido ligand [2.3779(9) vs. 2.3394(9) Å].

In the complexes **11** and **12a/b**, the Pt–C bonds [2.126(4) to 2.147(5) Å] were found to be of lengths comparable to those in complexes of the type $M^{I}[PtCl_3(RC{\equiv}CR')]$ {M^{I} = K, [K(18C6)], (PPh_4); R, R′ = alkyl, phenyl}.[9] Furthermore, bond lengthening of the C≡C bonds in complexes **12a** and **12b** relative to non-coordinated bis(*tert*-butyl)-acetylene can be observed [1.226(6) to 1.258(5) vs. 1.202(1) Å[24]]. This finding and the "bending back" of the substituents R/R′, as measured by the angle α [α = 180 – γ(C≡C–C); 17.0(5) to 20.8(4)°], reflect a degree of back-donation as would be anticipated for Pt^{II} complexes. Analogous values [C≡C 1.22(1) to 1.24(2) Å; α = 16(1)° to 21(1)°] were found in neutral mononuclear alkyne complexes $[PtCl_2(RC{\equiv}CR)L]$ (R = CMe_2OH, *t*Bu; L = $NMeH_2$, toluidine) and in alkyne complexes $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (R/R′ = Me, *t*Bu) of the Zeise's salt type[10,11,25,26] (cf. S3 in the Supporting Information).

Reactivity of Zeise's Dimer Toward Sterically Demanding Alkynes

As already described, reactions between $[\{PtCl_2(H_2C{=}CH_2)\}_2]$ (**1**) and stoichiometric amounts of alkynes RC≡C*t*Bu (R = Me, *t*Bu) resulted in the formation of $[\{PtCl_2(RC{\equiv}Ct\text{Bu})\}_2]$ (R = Me, **11**; *t*Bu, **12**, Scheme 4, path a). When these reactions were monitored by ^{1}H NMR spectroscopy in sealed NMR tubes (i.e., without removal of cleaved-off ethene), within 7 d the formation of mononuclear complexes of the type $[PtCl_2(H_2C{=}CH_2)(RC{\equiv}Ct\text{Bu})]$ (R = Me, **8**; *t*Bu, **9**) as main products, according to Scheme 4, paths b/c, was observed. As side products, apart from small amounts of $[PtCl_2(H_2C{=}CH_2)_2]$ (**10**), the dinuclear complex $[\{PtCl_2(t\text{BuC}{\equiv}Ct\text{Bu})\}_2]$ (**12**, Scheme 4, path b) was formed in the case of *t*BuC≡C*t*Bu, whereas in that of MeC≡C*t*Bu traces of the cyclobutadiene complex $[PtCl_2(C_4Me_2t\text{Bu}_2)]$ (**16**, path c) were observed. Notably, the coupling of the alkynes proceeded regioselectively, yielding only the *trans* isomer of complex **16**. Furthermore, it was shown with complex **12** as an example that the use of a tenfold excess of bis(*tert*-butyl)acetylene does not lead to bridge cleavage in complex **12** to yield the bis(*tert*-butyl)-acetylene complexes *trans*-**19** and/or *cis*-**19** (Scheme 4, path d).

Selected ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopic parameters of the complexes formed in these reactions are given in Tables 1 and 3. The identity of $[PtCl_2(H_2C{=}CH_2)_2]$ (**10**) was confirmed by comparison with data given in ref.[19] The cyclobutadiene complex **16** showed chemical shifts and coupling constants typical of mononuclear cyclobutadiene complexes of the same type (**4**–**6**). Although the isolation of the mixed olefin/alkyne complexes $[PtCl_2(H_2C{=}CH_2)(RC{\equiv}Ct\text{Bu})]$ (R = Me, **8**; *t*Bu, **9**) failed, their identities could be determined unambiguously by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR signal of the methyl group in **8** (δ_H = 2.26 ppm; Figure 5) shows a $^3J_{Pt,H}$ coupling constant of 31 Hz, typical for Pt^{II} complexes bearing methyl-substituted alkyne ligands (≡CCH_3: δ_H = 2.10–2.44 ppm; $^3J_{Pt,H}$ = 30–33 Hz).[10,11] Selective irradiation at the resonance frequency of the methyl protons was found to result in small intensity enhancements of the two signals at δ = 4.50 and 1.40 ppm (see NOE difference spectrum in Figure 5). This indicates a distance of less than 5 Å between the irradiated protons and the protons of the ethene ligand, thus demonstrating a mononuclear complex.[27] At ambient



Scheme 4. [a] Additionally, the reaction mixture contained 11% of the starting complex **1**.

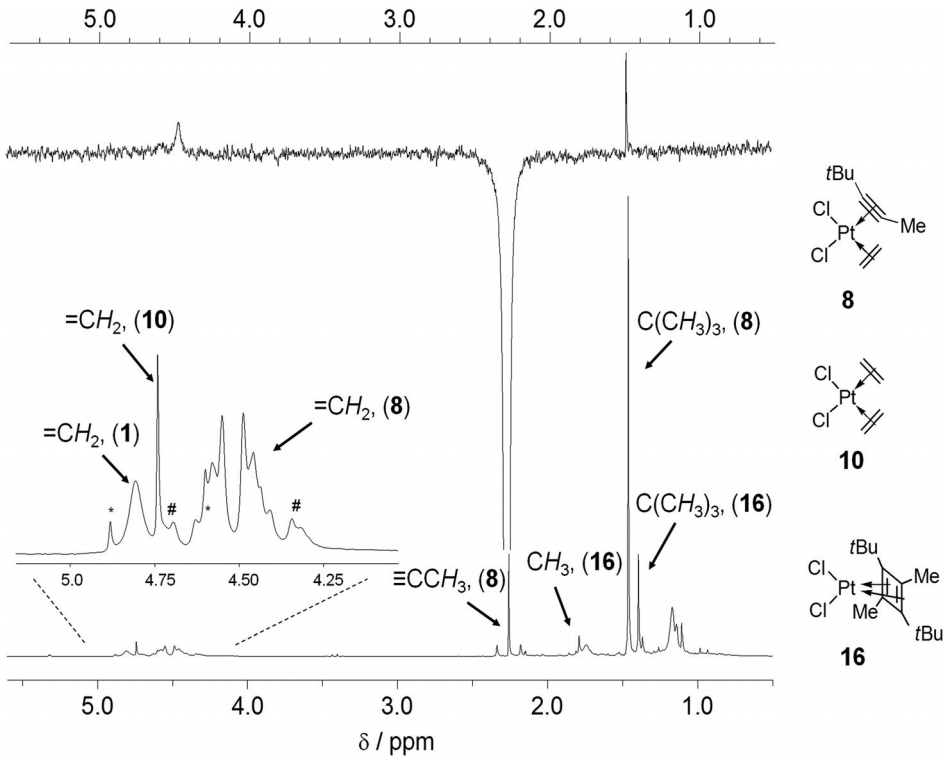


Figure 5. ^{1}H NMR spectrum (300 K, 200 MHz in CD_2Cl_2) of the reaction mixture of [{$PtCl_2(H_2C{=}CH_2)$}$_2$] (**1**) with MeC≡C*t*Bu (bottom) and NOE difference spectrum (top). In the expanded spectrum, platinum satellites are assigned with crosses and stars for the complexes [$PtCl_2(H_2C{=}CH_2)$(*t*BuC≡C*t*Bu)] (**8**) and [$PtCl_2(H_2C{=}CH_2)_2$] (**10**), respectively.

temperature, in complex **8** a highly complex ethene signal (=CH_2: δ = 4.56 ppm) was found, simulation of which resulted in an AA′BB′ spin system (see S1 in the Supporting Information). At –80 °C the spin system was found to change to an ABCD system with four chemically nonequivalent protons (Figure 6). These findings give confirmation both of the *cis* configuration of complex **8** and of a fast rotation of the ethene ligand at ambient temperature. The temperature dependence of the rotation of the olefin, as well as the alkyne ligand, is discussed in the following section.

The CISs ($\Delta\delta = \delta_{complex} - \delta_{noncoord.\,ligand}$) of the ethene carbon atoms of the mononuclear complexes [$PtCl_2$-($H_2C{=}CH_2$)(RC≡C*t*Bu)] (R = Me, **8**; *t*Bu, **9**) [$\Delta\delta$(=*C*H) = –43.1/–42.9 ppm, **8**/**9**] are in the same range as those found in complexes of the Zeise's dimer type [{$PtCl_2$(RHC=CHR)}$_2$] (R = H, alkyl) and of the Zeise's salt type M^I[$PtCl_3(R_2C{=}CR'_2)$] {M^I = K, [K(18C6)], (PPh_4), [N(*n*Bu)$_4$]; R, R′ = H, alkyl, aryl} [$\Delta\delta$(=*C*H) = –40 to –55 ppm].[4,16,6,17] The $^1J_{Pt,C}$ coupling constants of ethene in the ethene/alkyne complexes [$PtCl_2(H_2C{=}CH_2)$-(RC≡C*t*Bu)] (R = Me, **8**; *t*Bu, **9**; $^1J_{Pt,C}$ = 141/138 Hz) are of the same order of magnitude as those of neutral mononuclear bis(olefin) complexes [$PtCl_2L_2$] (2 L = ethene, 1,5-COD; $^1J_{Pt,C}$ = 131/152 Hz).[18,19] On the other hand, significantly larger coupling constants are found in Zeise's complexes [{$PtCl_2$(RHC=CHR′)}$_2$] (R, R′ = H, alkyl; $^1J_{Pt,C}$ = 182–199 Hz) and M^I[$PtCl_3(R_2C{=}CR'_2)$] {M^I = K, [K(18C6)], (PPh_4), [N(*n*Bu)$_4$]; R, R′ = H, alkyl, aryl; $^1J_{Pt,C}$ = 180–195 Hz}.[4,16,6,17] The same trend can be observed for the $^1J_{Pt,C}$ coupling constants of the alkyne ligands (Table 3): values between 115 and 156 Hz are found for [$PtCl_2(H_2C{=}CH_2)$(RC≡C*t*Bu)] (R = Me, **8**; *t*Bu, **9**), and these are significantly smaller than those in the neutral dinuclear complexes [{$PtCl_2$(RC≡C*t*Bu)}$_2$] (R = Me, *t*Bu; $^1J_{Pt,C}$ = 190–231 Hz) and anionic mononuclear complexes [K(18C6)][$PtCl_3$(RC≡CR′)] (R, R′ = H, alkyl, aryl; $^1J_{Pt,C}$ = 173–236 Hz).[10,11]

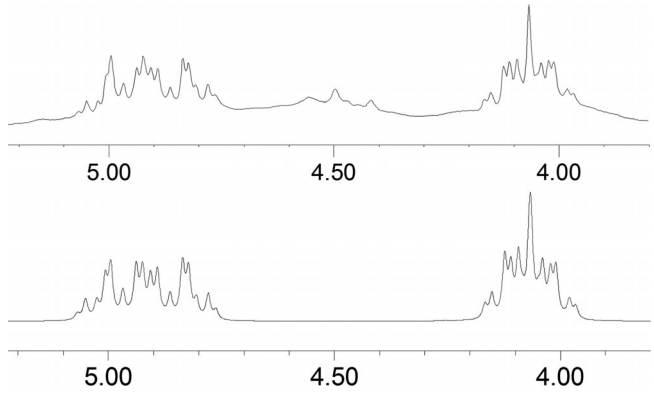


Figure 6. Experimentally measured (193 K, 200 MHz in CD_2Cl_2; top) and simulated (bottom) ^{1}H NMR spectrum of the ethene protons of [$PtCl_2(H_2C{=}CH_2)$(*t*BuC≡C*t*Bu)] (**8**). Coupling constants ($J_{H,H}$) from higher-order multiplets (given in S1 in the Supporting Information) were obtained by use of the PERCH NMR software package.[37]

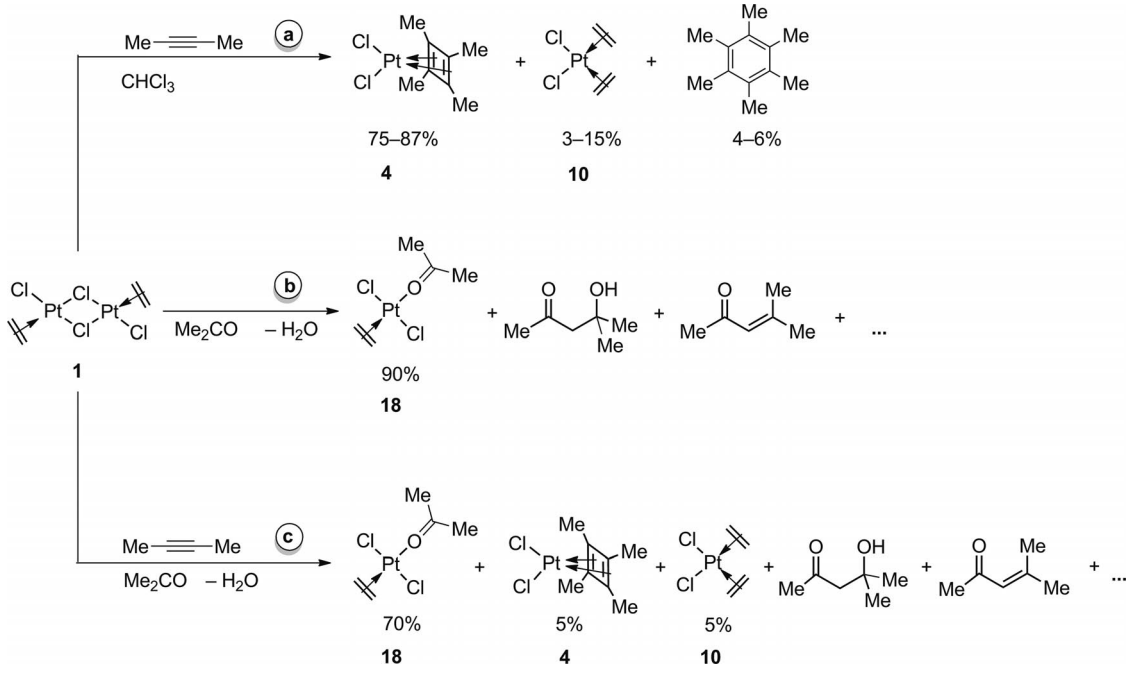
Reactivity of Zeise's Dimer Toward Sterically Less Demanding Alkynes

As described above, reactions between [{$PtCl_2$-(H_2C=CH_2)}$_2$] (**1**) and stoichiometric amounts of alkynes RC≡CR′ bearing sterically less demanding substituents (R, R′ = Me, Et, *n*Pr, Ph) in chloroform or dichloromethane resulted – if the cleaved-off ethene was removed from the reaction mixtures – in the formation (Scheme 3, paths b/c) of cyclobutadiene complexes [$PtCl_2$($C_4R_2R'_2$)] (**4**–**6**) and [{$PtCl_2$($C_4R_2R'_2$)}$_2$] (**7**). As a representative example, the reaction between **1** and but-2-yne was carried out in a sealed NMR tube (i.e., without the removal of the cleaved-off ethene). Apart from the formation of the cyclobutadiene complex **4** as main product, smaller amounts of the bis(ethene) complex **10** were produced. Furthermore, on a small scale, a cyclotrimerization yielding hexamethylbenzene took place (Scheme 5, path a). In contrast with these reactions (solvent: $CHCl_3$, CH_2Cl_2), in the classical work of Chatt et al.,[7,8] decomposition was observed on addition of stoichiometric amounts of internal or terminal alkynes bearing only sterically less demanding substituents to Zeise's dimer in acetone as solvent. In order to clarify the reason for this observation, corresponding NMR experiments were performed. Dissolution of Zeise's dimer in acetone resulted immediately in a change of color from orange to yellow. ^{195}Pt NMR spectroscopic data indicated the formation of the mononuclear complex *trans*-[$PtCl_2$(Me_2CO)(H_2C=CH_2)] (**18**) and of one unidentified complex. Furthermore, the solvent acetone underwent both aldol addition and condensation reactions (Scheme 5, path b). After several days, the formation of higher acetone condensation products containing Me–(MeC=CH)$_n$–C(O)Me (n = 5–7) units was observed.[28]

Addition of but-2-yne to a freshly prepared solution of Zeise's dimer in acetone resulted immediately in a change in color from yellow to red. ^{13}C and ^{195}Pt NMR spectroscopic data indicated the formation of the mononuclear complex *trans*-[$PtCl_2$(Me_2CO)(H_2C=CH_2)] (**18**, Scheme 5, path c) and after several days the formation of the cyclobutadiene complex [$PtCl_2$(C_4Me_4)] (**4**) and [$PtCl_2$-(H_2C=CH_2)$_2$] (**10**), analogously to the reaction performed in chloroform. The decomposition of the solvent, especially the formation of higher condensation products of acetone (see above), led – after removal of all volatile components in vacuo – to black oils, as also described by Chatt et al.[7,8]

Configurational and Conformational Isomers of Alkyne and Olefin Complexes of the Zeise's Dimer Type

To obtain insight into the structures of the dinuclear (olefin)- and (alkyne)platinum(II) complexes, in particular into the stabilities of the configurational and conformational isomers, quantum-chemical calculations at the DFT level of theory were performed. The structures and relative energies of these isomers, together with selected structural parameters, are given in Figures 7 and 8 and in Tables 2 and 4. In all these complexes, inspection of the Gibbs free energies of the different isomers shows that, in general, the *transoid* isomer was found to be only slightly more stable (maximum 1.6 kcal mol^{-1}) than the corresponding *cisoid* isomer. This difference is even less pronounced when solvent effects are considered (Table 6, below).



Scheme 5.

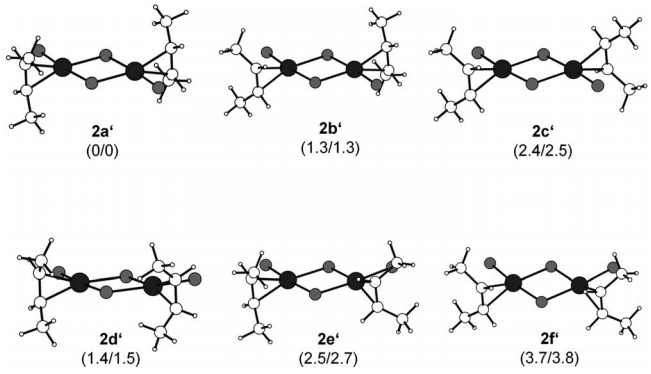


Figure 7. Calculated structures of [{$PtCl_2$(*cis*-MeHC=CHMe)}$_2$] (**2a′**–**2f′**) along with the standard Gibbs free energies (kcal mol^{-1}) in parentheses relative to the most stable isomer **2a′**. Values for the gas phase and in $CHCl_3$ as solvent are separated by slashes. DFT calculations: B3LYP/6-311G(d,p) for main-group atoms; for details, see Experimental Section.

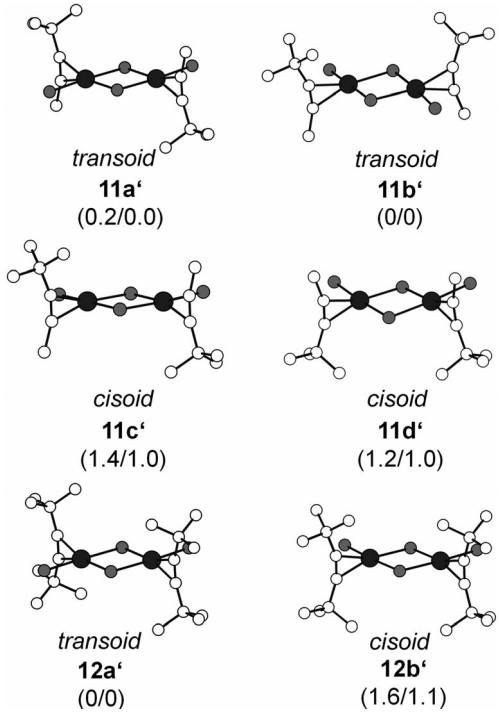


Figure 8. Calculated configurational (R = Me: **11a′**/**11c′**, **11b′**/**11d′**; R = *t*Bu: **12a′**/**12b′**) and conformational (R = Me: **11a′**/**11b′**, **11c′**/**11d′**) isomers of [{$PtCl_2$(RC≡C*t*Bu)}$_2$] along with the Gibbs free energies (kcal mol^{-1}) in parentheses relative to the most stable isomers (**11b′**, **12a′**). Values for the gas phase and in $CHCl_3$ as solvent are separated by slashes. H atoms have been omitted for clarity. DFT calculations: B3LYP/6-311G(d,p) for main-group atoms; for details, see Experimental Section.

The rates of rotation around the platinum–olefin/alkyne bonds were calculated (Table 5) for the dinuclear complexes [{$PtCl_2$(*cis*-MeHC=CHMe)}$_2$] (**2a′**) and [{$PtCl_2$-(MeC≡C*t*Bu)}$_2$] (**11a′**) and for the mixed mononuclear complex *cis*-[$PtCl_2$(H_2C=CH_2)(MeC≡C*t*Bu)] (**8′**). Under standard conditions, the activation barriers ($\Delta G^{\ddagger}$) for the rotation of the olefin ligands (13.4/12.1 kcal mol^{-1}, **2a′**/**8′**) proved to be significantly lower than those of the *tert*-butyl-substituted alkyne ligands (20.6/23.9 kcal mol^{-1}, **11a′**/**8′**), which seems to be mainly for steric reasons. These values fit well with the activation barriers found experimentally for rotations of olefin ligands in platinum(II) complexes (10.0–15.0 kcal mol^{-1}).[29] As far as is known, and in good agreement with this work, in olefin and alkyne complexes with the same structure, higher barriers (by 3–6 kcal mol^{-1}) were found for rotations of alkynes.[30] One exception was observed in the five-coordinate platinum complexes [PtI_2-(Me_2phen)L] (L = MeC≡CH, MeHC=CH_2; Me_2phen = 2,9-dimethyl-1,10-phenanthroline), in which the alkyne ligand was found to be associated with a lower barrier (by about 3 kcal mol^{-1}) than the olefin ligand, which might be interpreted in terms of a dissociative/associative process instead of an intramolecular rotation.[31]

Furthermore, the DFT calculations are in good agreement with the experimental findings relating to the fast and (with respect to the NMR timescale) the frozen rotations of the ethene ligand in complex **8** at room temperature and at –80 °C, respectively. In addition, in accordance with the NMR spectroscopic investigations of complex **8** and **11**, the calculations give confirmation that the alkyne ligands both

Table 4. Calculated structural parameters of selected isomers of complexes [{$PtCl_2$(MeC≡C*t*Bu)}$_2$] (**11a′**/**11c′**) and [{$PtCl_2$(*t*BuC≡C*t*Bu)}$_2$] (**12a′**/**12b′**).

	11a′[a] (*transoid*)[b]	**11c′** (*cisoid*)[b]	**12a′**[a] (*transoid*)	**12b′**[a] (*cisoid*)
Pt–C[c]	2.156/2.135	2.158/2.138	2.150	2.153
Pt–$Cl_{term.}$	2.300	2.296	2.301	2.296
Pt–μ-$Cl_{trans\ C\equiv C}$[d]	2.409	2.402	2.412	2.404
Pt–μ-$Cl_{trans\ Cl}$[d]	2.412	2.421	2.412	2.423
C≡C[e]	1.247 (1.204)	1.247 (1.204)	1.250 (1.206)	1.250 (1.206)
C≡C–C[c]	159.3/161.9	159.3/161.9	159.5	159.4
Cg–Pt–$Cl_{term.}$	91.0	90.8	91.8	91.6
Cg–Pt–μ-$Cl_{trans\ C\equiv C}$[d]	176.9	177.2	176.7	177.0
Cg–Pt–μ-$Cl_{trans\ Cl}$[d]	92.5	92.8	92.5	92.9

[a] Corresponding values obtained experimentally by X-ray diffraction measurements in the captions of Figures 2, 3, and 4. [b] Head-to-tail arrangement of the two alkyne ligands. [c] Values for the *tert*-butyl- and methyl-substituted carbon atoms separated by slashes. [d] M–$Cl_{trans\ C\equiv C}$/μ-$Cl_{trans\ Cl}$: μ-chlorido ligand *trans* to the alkyne and to the terminal chlorido ligand, respectively. Cg = center of gravity of the two alkyne C atoms. [e] Values for the corresponding non-coordinated alkynes in parentheses.

Table 5. Calculated standard Gibbs free energies of activation (kcal mol^{-1}) and corresponding first-order rate constants (s^{-1}) for the rotation of π ligands in complexes of the Zeise's dimer type [{$PtCl_2$(MeHC=CHMe)}$_2$] (**2**) and [{$PtCl_2$(MeC≡C*t*Bu)}$_2$] (**11**), and in the mononuclear complex [$PtCl_2$(H_2C=CH_2)(MeC≡C*t*Bu)] (**8**).

	Olefin	$\Delta G^{\ddagger}$	k		Alkyne	$\Delta G^{\ddagger}$	k
2a′	*cis*-but-2-ene	13.4	9.1×10^{2}	**11′a**	MeC≡C*t*Bu	20.6	4.7×10^{-3}
8′	ethene	12.1	8.2×10^{3}	**8′**	MeC≡C*t*Bu	23.9	1.8×10^{-5}
8′[a]	ethene	11.8	1.7×10^{-1}	**8′**[a]	MeC≡C*t*Bu[a]	22.9	4.5×10^{-14}

[a] T = 193 K.

in the mononuclear complex **8** and in the dinuclear complexes **11/12** do not rotate even at room temperature.

In summary, these findings give further support for the complexity of the NMR spectra of the dinuclear olefin complex **2** and of the alkyne complexes **11** and **12** being due to the presence of configurational/conformational isomers.

On the Equilibria Between *cisoid* and *transoid* Isomers

The ^{13}C and ^{195}Pt NMR spectra of the dinuclear olefin complexes **1**–**3** each showed two sets of signals for the olefinic ^{13}C atoms (except in the case of **1**) and ^{195}Pt atoms. These findings can be explained in terms of the presence in each case (in solution) of two configurational isomers: namely a *transoid* and a *cisoid* configuration (Scheme 2). The major isomers were assigned as the *transoid* complexes, on the basis of single-crystal and powder diffraction measurements (**2**, S5 in the Supporting Information) and the thermodynamic stabilities predicted by DFT calculations. The relative intensities of the two signal sets were found to depend on the solvent. From these values, equilibrium constants for the isomerization were obtained (K_{NMR} = 1.5–12.6), corresponding to standard Gibbs free energies from –0.2 to –1.5 kcal mol^{-1} (Table 6 and Table 1). In general, more polar solvents give rise to smaller energy differences between the two isomers, which can be understood in terms of the different dipole moments of the isomers.

Table 6. Solvent dependence of the equilibrium constants for the *cisoid*/*transoid* interconversion as shown in Scheme 2 derived from ^{13}C and ^{195}Pt NMR spectra (K_{NMR}), together with the corresponding standard Gibbs free energies (kcal mol^{-1}) obtained from K_{NMR} (ΔG_{NMR}) and DFT calculations (ΔG_{DFT}). Relative dielelctric constants $\varepsilon/\varepsilon_0$ given are taken from ref.[47]

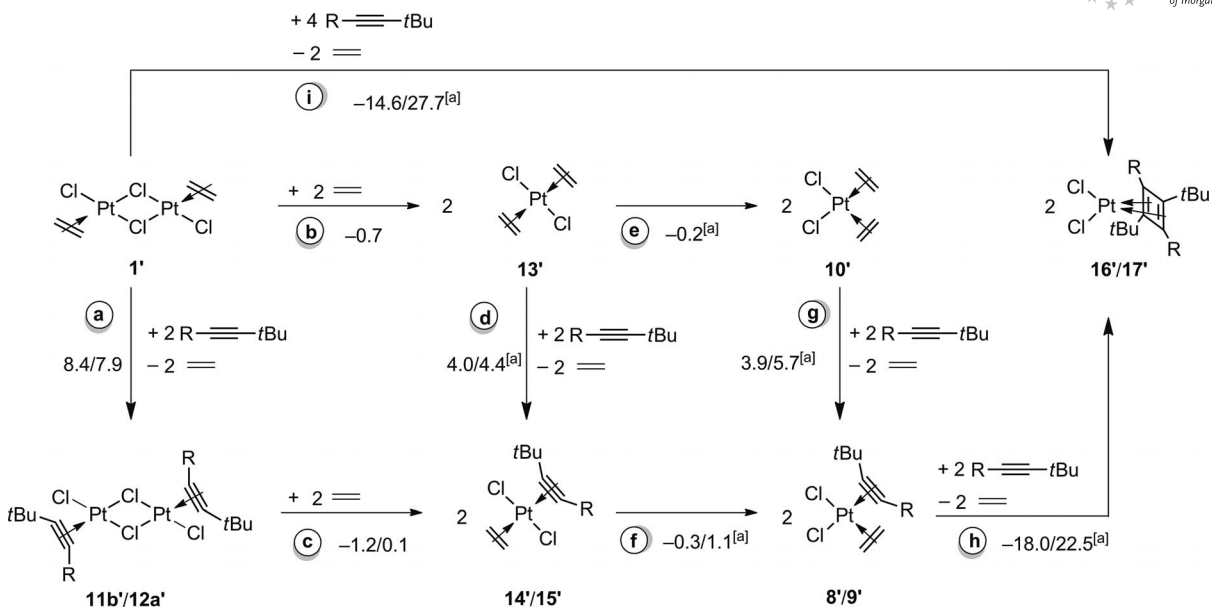
Solvent	CH_3NO_2	CH_2Cl_2	$CHCl_3$	CCl_4	Et_2O	C_6H_6	Gas phase
$\varepsilon/\varepsilon_0$	38.6	8.9	4.8	2.2	4.3	2.3	
[{$PtCl_2$(H_2C=CH_2)}$_2$] (**1**)							
K_{NMR}		2.2	1.7			6.8	
ΔG_{NMR}		–0.5	–0.3			–1.1	
ΔG_{DFT}	–0.5	–0.7	–0.8	–1.0		–1.0	–1.1
[{$PtCl_2$(*cis*-MeHC=CHMe)}$_2$] (**2**)							
K_{NMR}	1.5	3.0	4.7	7.5			
ΔG_{NMR}	–0.2	–0.7	–0.9	–1.2			
ΔG_{DFT}	–0.8	–0.9	–1.5	–1.4		–1.5	–1.4
[{$PtCl_2$(*t*BuC≡C*t*Bu)}$_2$] (**12**)							
K_{NMR}		2.7	2.5		2.2	5.1	
ΔG_{NMR}		–0.6	–0.5		–0.4	–1.0	
ΔG_{DFT}		–0.2	–1.1		–0.4	–0.6	–1.6

In the ^{1}H, ^{13}C, and ^{195}Pt NMR spectra of the dinuclear alkyne complex **12**, with the coordinated symmetrically substituted *t*BuC≡C*t*Bu alkyne, two sets of signals were observed, whereas in the analogous complex **11**, with the coordinated unsymmetrically substituted MeC≡C*t*Bu alkyne, three sets of signals were found. These findings for the two complexes (**11** and **12**) can be explained in terms of the presence of two configurational isomers (*cisoid*/*transoid*), and for complex **11**, additionally, by the presence of conformational isomers as shown in Figure 8. As in the cases of the olefin complexes, in the NMR spectra the major isomers of the dinuclear alkyne complexes were assigned as the *transoid* complexes, on the basis of X-ray diffraction measurements (**11** and **12**; see S6/S7 in the Supporting Information) and DFT calculations. It remains unclear whether the signal of the *transoid* or of the *cisoid* isomer is split into **11a′**/**11b′** and **11c′**/**11d′**, respectively.

Ligand Substitution and Bridge Cleavage Reactions of Complexes of the Zeise's Dimer Type

In the literature, only relatively few examples of mononuclear complexes bearing two monodentately bound olefin ligands have been reported. One of the first examples was the reaction between Zeise's dimer [{$PtCl_2$(H_2C=CH_2)}$_2$] and ethene to yield a yellow, unstable complex, postulated to be *trans*-[$PtCl_2$(H_2C=CH_2)$_2$],[14] which has also been assumed to exist as a short-lived intermediate in the ethene exchange reaction of [$PtCl_3$(H_2C=CH_2)]$^-$.[32] Furthermore, for cleavage reactions between dinuclear chlorido-bridged complexes [($PtCl_2$L)$_2$] (L = ethene, styrene, cot) and nucleophiles (L = ethene, styrene, cot) to yield *trans*-[$PtCl_2L_2$] (L = styrene, cot, ethene) chemical equilibria [K = 0.0235 ± 0.0003 (styrene), 2.05 ± 0.06 (cot), and 6.8 ± 0.6 M^{-1} (ethene)] corresponding to ΔG values between 2.2 and –1.1 kcal mol^{-1} were observed.[19,4,33]

To address the stabilities of various mono- and dinuclear olefin and alkyne complexes in this study, further DFT calculations were performed. For this purpose, the thermodynamic balances of ligand substitution and bridge cleavage reactions as shown in Scheme 6 were calculated with consideration of solvent effects ($CHCl_3$); the values for the gas phase are given in the Supporting Information (S8). The substitution of ethene in Zeise's dimer by *tert*-butyl-substituted alkynes RC≡C*t*Bu (R = Me, *t*Bu) resulting in the formation of [{$PtCl_2$(RC≡C*t*Bu)}$_2$] (R = Me, **11b′**; *t*Bu, **12a′**; Scheme 6, reaction path a) was found to be endergonic (ΔG_{solv} = 8.4/7.9 kcal mol^{-1} for R = Me/*t*Bu), pointing to a



Scheme 6. Figures given are standard Gibbs free energies [kcal mol^{-1}] with consideration of $CHCl_3$ as solvent (ΔG_{solv}). The values for R = Me and R = *t*Bu are separated by slashes. [a] ΔG_{solv} refers to the formation of 1 mol complex.

stronger binding of ethene to platinum than of the alkyne. It can thus be understood that in the synthesis of complexes **11** and **12** the removal of ethene through evaporation is crucial for significant conversion.

The bridge cleavage in complexes [{$PtCl_2(H_2C{=}CH_2)$}$_2$] (**1′**) and [{$PtCl_2(RC{\equiv}CtBu)$}$_2$] (R = Me, **11b′**; *t*Bu, **12a′**) with formation of [$PtCl_2(H_2C{=}CH_2)_2$] (**13′**) and *trans*-[$PtCl_2(H_2C{=}CH_2)(RC{\equiv}CtBu)$] (R = Me, **14′**; *t*Bu, **15′**), respectively, was found to be nearly thermoneutral (ΔG_{solv} = –1.2 to 0.1 kcal mol^{-1}; reaction paths b/c), indicating the presence of chemical equilibria in these reactions. Notably, for the bridge cleavage reaction path b of Zeise's dimer by ethene a Gibbs free energy of –0.7 kcal mol^{-1} was calculated, which fits well with the experimentally measured value (–1.1 kcal mol^{-1}) obtained by Elding et al.,[19] demonstrating the appropriateness of the quantum-chemical model used.

The isomerization of the mononuclear *trans*-configured complexes [$PtCl_2(H_2C{=}CH_2)(RC{\equiv}CtBu)$] (R = Me, **14′**; *t*Bu, **15′**) and [$PtCl_2(H_2C{=}CH_2)_2$] (**13′**) into the analogous *cis* complexes **8′**–**10′** was found to be almost thermoneutral (ΔG_{solv} = –0.3 to 1.1 kcal mol^{-1}; reaction paths e/f). The substitution of one ethene ligand in the mononuclear complexes *cis*/*trans*-[$PtCl_2(H_2C{=}CH_2)_2$] (**10′**/**13′**) by an alkyne to yield *cis*/*trans*-[$PtCl_2(H_2C{=}CH_2)(RC{\equiv}CtBu)$] (R = Me, **8′**/**14′**; *t*Bu, **9′**/**15′**) was found to be only moderately endergonic (ΔG_{solv} = 3.9–5.7 kcal mol^{-1}; reaction paths g/d).

Furthermore, the [2+2] cycloaddition of MeC≡C*t*Bu as in the reaction paths h and i (Scheme 6) to yield the cyclobutadiene complexes [$PtCl_2(C_4R_2tBu_2)$] (R = Me, **16′**; *t*Bu, **17′**) could proceed via precursor complexes [$PtCl_2(RC{\equiv}CtBu)_2$] (R = Me, **20′**; *t*Bu, **19′**; see the Supporting Information). The formation of complex **16′** (R = Me) is strongly exergonic (ΔG_{solv} = –18.0 kcal mol^{-1}). In contrast, the analogous reactions with a sterically more demanding alkyne (*t*BuC≡C*t*Bu) to yield [$PtCl_2(C_4tBu_4)$] (**17′**) proved to be endergonic (ΔG_{solv} = 22.5 kcal mol^{-1}). Although the formation of **16′** was calculated to be strongly exergonic, only small amounts of this complex were observed spectroscopically, whereas the formation of **17′** was not observed, even in traces.

Conclusions

This work presents a straightforward method for the preparation of mono- and dinuclear (alkyne)platinum(II) complexes by ligand substitution and bridge cleavage reactions. The following conclusions can be drawn:

(1) Zeise's dimer was found to react smoothly with alkynes bearing *tert*-butyl substituents RC≡C*t*Bu (R = Me, *t*Bu) to yield complexes [{$PtCl_2(RC{\equiv}CtBu)$}$_2$] if ethene was removed from the reaction mixture, but to yield *cis*-[$PtCl_2(H_2C{=}CH_2)(RC{\equiv}CtBu)$] without removal of ethene. Although the complexes *cis*-[$PtCl_2(H_2C{=}CH_2)(RC{\equiv}CtBu)$] (R = Me, *t*Bu) were not isolated as solids, they could be unambiguously characterized in solution by NMR spectroscopy. Consistent with the NMR spectroscopic investigations, DFT calculations indicate unhindered rotation of the ethene ligand around the Pt–C bond at room temperature, whereas the analogous rotation of the alkyne ligand is frozen under these conditions.

(2) Olefin complexes of the Zeise's dimer type [{$PtCl_2(RHC{=}CHR)$}$_2$] (R = H, Me, *c*-Hex) and analogous alkyne complexes [{$PtCl_2(RC{\equiv}CtBu)$}$_2$] (R = Me, *t*Bu) exist in solvent-dependent equilibria between the *transoid* and *cisoid* isomers (cf. Scheme 2). This configurational isomerism is described for the first time in this work and could even be structurally established (Figures 3 and 4). In accordance with the experiments, DFT calculations gave con-

firmation of the equilibria between the *transoid* and *cisoid* isomers.

(3) Zeise's dimer reacts with alkynes RC≡CR′ bearing sterically less demanding substituents (R, R′ = Me, Et, *n*Pr, Ph) with formation of (cyclobutadiene)platinum(II) complexes $[PtCl_2(C_4R_2R'_2)]$. Notably, these [2+2] cycloadditions proceed under very mild reaction conditions (room temp.), whereas the formation of (cyclobutadiene)platinum(II) complexes by starting from $H_2[PtCl_6]\cdot 6H_2O$[34] or from $[PtCl_2L_2]$ (L = CO, MeCN)[35] requires harsher reaction conditions. Furthermore, with regard to the experimental findings, it can be deduced from DFT calculations that the formation of the complexes $[PtCl_2(C_4tBu_4)]$ and $[PtCl_2(C_4Me_2tBu_2)]$ is thermodynamically and kinetically, respectively, hampered.

(4) From the historical point of view, it is of interest to clarify why Chatt et al.,[7,8] on the one hand, succeeded in the synthesis of $[\{PtCl_2(RC{\equiv}CtBu)\}_2]$ by treatment of Zeise's dimer or $Na_2[PtCl_4]$ with sterically demanding substituted alkynes RC≡C*t*Bu, whereas – on the other hand – analogous reactions with alkynes RC≡CR′ bearing sterically less demanding substituents (such as R, R′ = H, Me, Et, *n*Pr, *i*Pr, *n*Bu, ...) resulted in decomposition. Apart from the much more sophisticated spectroscopic and preparative methods available today, the following reasons can be named:

(a) Chatt's experiments were performed in acetone (Gutmann's donor number *DN* = 17.0), which might act concurrently as a donor for the olefins and alkynes; this is not the case in dichloromethane (*DN* = 1)[36] or chloroform (*DN* = 4)[36] used in this study.

(b) In these reactions acetone is not inert, but undergoes aldol coupling and condensation reactions, giving rise to the formation of, among others, at least oligomeric products containing Me–$(MeC{=}CH)_n$–C(O)Me (*n* = 5–7) units.

To sum up, for reactions between Zeise's dimer and alkynes, which have been known for 50 years, both the experimental and the theoretical investigations presented here give insight for the first time into how subtly the courses of these reactions depend on the substitution patterns of the alkynes and on the solvent, thus opening a way to targeted syntheses of (cyclobutadiene)- and (alkyne)platinum(II) complexes starting from Zeise's dimer.

Experimental Section

General Procedures: All reactions were performed under Ar with use of standard Schlenk techniques. Solvents were dried (Et_2O, *n*-pentane, and benzene with Na benzophenone; $CHCl_3$, $CDCl_3$, and CH_2Cl_2 with CaH_2; acetone with molecular sieves, 3 Å) and distilled prior to use. NMR spectra were recorded with Varian Gemini 200, VXR 400, and Unity 500 NMR spectrometers. ^1H and ^{13}C chemical shifts are relative to solvent signals. ^{195}Pt NMR spectra were calibrated with external $H_2[PtCl_6]$ (δ_{Pt} = 0.0 ppm). Coupling constants ($J_{H,H}$) from higher-order multiplets ("m") were obtained by use of the PERCH NMR software package.[37] Microanalyses were performed by the University of Halle microanalytical laboratory with a CHNS-932 (LECO) elemental analyzer. Bis(*tert*-butyl)-acetylene was synthesized according to published methods[38] and $K[PtCl_3(MeHC{=}CHMe)]$ as described in ref.[15] but with use of *cis*-but-2-ene instead of ethene. All other chemicals were commercially available.

Synthesis of $[\{PtCl_2(RHC{=}CHR)\}_2]$ (R/R = H/H, 1; R/R = Me/Me, 2): An aqueous HCl solution (1.1 M, 25 mL) of $K_2[PtCl_4]$ (2.10 g, 5.06 mmol) and $SnCl_2$ (22.8 mg, 0.10 mmol) was purged with the requisite olefin at –30 °C, stirred for 1–2 h, and allowed to warm to room temperature. The purging was repeated three or four times over 6–7 d until an orange-colored solution had formed and the precipitation of a yellow solid was observed. The solvent was removed by evaporation, and the yellow solid residue was dried with $MgCl_2$ in vacuo. The resulting residue was extracted with a mixture of EtOH (30 mL) and HCl (12 M, 4 mL), the non-dissolved KCl was filtered off, and the filtrate was concentrated to dryness. The resulting residue was extracted with dry chloroform (50 mL), and after filtration of some yellowish solid $K[PtCl_3(RHC{=}CHR)]$/KCl the solution was taken to dryness under vacuum. The residue was dissolved in CH_2Cl_2 (40 mL). The solution was reduced to half of its volume, and the same volume of diethyl ether was added, resulting in precipitation of the complex. This was filtered off, washed with diethyl ether (2 × 2 mL), and dried in vacuo.

Compound 1 (R/R = H/H): Yield: 1.11 g, 68%. ^1H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 4.82 (s, d, $^2J_{Pt,H}$ = 74 Hz, 8 H, =CH_2) ppm. ^{13}C NMR (50.29 MHz, 300 K, CD_2Cl_2): δ = 72.1 (s, d, $^1J_{Pt,C}$ = 199 Hz, =*C*H_2) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –2490 (s), –2495 (s) ppm. $C_4H_8Cl_4Pt_2$ (588.08): calcd. C 8.17, H 1.37; found C 8.08, H 1.40.

Compound 2 (R/R = Me/Me): Yield: 1.22 g, 75%. ^1H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.55 (m, dm, $^3J_{Pt,H}$ = 38 Hz, 12 H, CH_3), 5.55 (m, dm, $^2J_{Pt,H}$ = 71 Hz, 2 H, =C*H*) ppm. ^{13}C NMR (50.29 MHz, 300 K, CD_2Cl_2): δ = 15.5 (s, d, $^2J_{Pt,C}$ = 24 Hz, *C*H_3), 86.9 (s, d, $^1J_{Pt,C}$ = 190 Hz, =*C*HMe), 87.4 (s, d, $^1J_{Pt,C}$ = 182 Hz, =*C*HMe) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –2426 (s), –2405 (s) ppm. $C_8H_{16}Cl_4Pt_2$ (644.19): calcd. C 14.91, H 2.50; found C 15.00, H 2.62.

Synthesis of $[\{PtCl_2(c\text{-}Hex)_2\}]$ (3): Cyclohexene (2.05 g, 25.2 mmol) was added to a solution of $K[PtCl_3(MeHC{=}CHMe)]$ (500 mg, 1.26 mmol) in EtOH (15 mL)/HCl (12 M, 2 mL). After the mixture had been stirred at room temperature for 24 h, the solvent was removed in vacuo. The resulting residue was extracted with dry chloroform (50 mL), and the non-dissolved KCl was filtered off. The filtrate was then concentrated to dryness, and the residue was redissolved in CH_2Cl_2 (40 mL). The solution was reduced to half of its volume, and the same volume of diethyl ether was added, resulting in precipitation of **3**, which was filtered off, washed with diethyl ether (2 × 2 mL), and dried in vacuo. Yield: 263 mg, 60%. ^1H NMR (200 MHz, 300 K, $CDCl_3$): δ = 1.41–1.50 (m, 4 H, =CHCH_2CH*H*), 1.62–1.72 (m, 4 H, =CHCH_2CH*H*), 1.98–2.07 (m, 4 H, =CHCH*H*), 2.22–2.32 (m, 4 H, =CHC*H*H), 5.96 (m, dm, $^2J_{Pt,H}$ = 81 Hz, 4 H, =C*H*) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 20.9 (s, *C*H_2), 27.2 (s, =CH*C*H_2), 90.9 (s, =*C*HCH_2), 91.5 (s, d, $^1J_{Pt,C}$ = 196 Hz, =*C*HCH_2) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –2298 (s), –2374 (s) ppm. $C_{12}H_{20}Cl_4Pt_2$ (696.26): calcd. C 20.7, H 2.89; found C 19.90, H 2.93.

Synthesis of $[PtCl_2(C_4R_2R'_2)]$ (R/R′ = Me/Me, 4; R/R′ = Et/Et, 5; R/R′ = Me/*n*Pr, 6) and $[\{PtCl_2(C_4Me_2Ph_2)_2\}]$ (7): The requisite alkyne (0.51 mmol) was added at room temperature to a suspension of $[\{PtCl_2(H_2C{=}CH_2)\}_2]$ (**1**, 50 mg, 0.085 mmol) in $CHCl_3$ (5 mL). After the orange-colored solution had been stirred at room temperature for 5 d, its volume was reduced to about 2 mL. Layering with diethyl ether (2 mL) resulted in precipitation of the complex,

which was filtered off, washed with diethyl ether (2 × 2 mL), and dried in vacuo.

R/R′ = Me/Me (4): Yield 52 mg, 81%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.61 (s, d, $^3J_{Pt,H}$ = 18.7 Hz, 12 H, CH_3) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 8.8 (s, d, $^2J_{Pt,C}$ = 15 Hz, *C*H$_3$), 104.1 (s, d, $^1J_{Pt,C}$ = 145 Hz, C_4) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –3168 (s) ppm. $C_8H_{12}Cl_2Pt$ (374.17): calcd. C 25.68, H 3.23, Cl 18.95; found C 25.56, H 3.52, Cl 19.02.

R/R′ = Et/Et (5): Yield 56 mg, 76%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.28 (t, $^3J_{H,H}$ = 7.47 Hz, 12 H, CH_2CH_3), 2.01 (q, $^3J_{H,H}$ = 7.47 Hz, 8 H, CH_2CH_3) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 10.9 (s, d, $^3J_{Pt,C}$ = 14.9 Hz, CH_2CH_3), 18.1 (s, d, $^2J_{Pt,C}$ = 12.6 Hz, CH_2CH_3), 106.3 (s, d, $^1J_{Pt,C}$ = 150 Hz, C_4) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –3265 (s) ppm. $C_{12}H_{20}Cl_2Pt$ (430.27): calcd. C 33.49, H 4.68, Cl 16.48; found C 33.00, H 4.84, Cl 16.43.

R/R′ = Me/*n*Pr (6): Yield 51 mg, 73%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 0.98 (t, $^3J_{H,H}$ = 7.32 Hz, 6 H, CH_2CH_3), 0.99 (t, $^3J_{H,H}$ = 7.32 Hz, 6 H, CH_2CH_3), 1.62 (s, 6 H, CH_3), 1.63 (s, 6 H, CH_3), 1.66 (m, 8 H, CH_2CH_3), 1.90 (m, 8 H, CH_2CH_2) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 9.26 (s, d, $^3J_{Pt,C}$ = 12.8 Hz, *C*H$_3$), 9.38 (s, d, $^3J_{Pt,C}$ = 14.4 Hz, *C*H$_3$), 14.41 (s, *C*H$_3$), 14.49 (s, *C*H$_3$), 19.48 (s, d, $^3J_{Pt,C}$ = 16.0 Hz, *C*H$_2$), 19.78 (s, d, $^3J_{Pt,C}$ = 15.3 Hz, *C*H$_2$), 25.86 (s, d, $^2J_{Pt,C}$ = 11.6 Hz, *C*H$_2$), 26.18 (s, d, $^2J_{Pt,C}$ = 11.6 Hz, *C*H$_2$), 99.2 (s, C_4), 102.8 (s, d, $^1J_{Pt,C}$ = 148 Hz, C_4), 103.3 (s, d, $^1J_{Pt,C}$ = 159 Hz, C_4), 106.9 (s, d, $^1J_{Pt,C}$ = 158 Hz, C_4) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –3180 (s), –3186 (s) ppm. $C_{12}H_{20}Cl_2Pt$ (430.27): calcd. C 33.49, H 4.68, Cl 16.48; found C 33.13, H 4.89, Cl 16.45.

R/R′ = Me/Ph (7): Yield 51 mg, 60%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.90 (s, d, $^3J_{Pt,H}$ = 20 Hz, 12 H, CH_3), 7.30–7.49 (m, 12 H, *m*-H/*p*-H), 7.53–7.77 (m, 8 H, *o*-*H*) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 3.1 (s, d, $^2J_{Pt,C}$ = 16 Hz, *C*H$_3$), 101.5 (s, d, $^1J_{Pt,C}$ = 150 Hz, C_4), 110.0 (s, d, $^1J_{Pt,C}$ = 156 Hz, C_4), 131.9 (s, d, $^2J_{Pt,C}$ = 21 Hz, *i*-*C*), 135.9 (s, *m*-*C*), 136.8 (s, d, $^3J_{Pt,C}$ = 21 Hz, *o*-*C*), 138.7 (s, *p*-*C*) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –1672 (s) ppm.

Reaction between [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (1) and RC≡C*t*Bu (R = Me, *t*Bu): A solution of the requisite alkyne (0.36 mmol) in CD_2Cl_2 (0.7 mL) was added at –80 °C to [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (**1**, 97 mg, 0.165 mmol) and benzene (5 μL) as standard in an NMR tube. The NMR tube was then sealed by melting and allowed to warm to room temperature. The courses of the reactions were monitored for up to several months by means of ^{1}H and ^{13}C NMR spectroscopic measurements showing the formation of [PtCl$_2$(H$_2$C=CH$_2$)-(RC≡C*t*Bu)] (R = Me, **8**; *t*Bu, **9**) as the main products and of [PtCl$_2$(H$_2$C=CH$_2$)$_2$] (**10**) as well as [{PtCl$_2$(*t*BuC≡C*t*Bu)}$_2$] (**12**) and [PtCl$_2$(C_4Me$_2$*t*Bu$_2$)] (**16**), respectively, as sideproducts.

Reaction with MeC≡C*t*Bu: ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.39 [s, C(CH_3)$_3$, 18 H, **16**], 1.47 [s, 9 H, C(CH_3)$_3$, **8**], 1.77 (s, d, $^3J_{Pt,H}$ = 21 Hz, 6 H, CH_3, **16**), 2.26 (s, d, $^3J_{Pt,H}$ = 31 Hz, 3 H, CH_3, **8**), 4.47–4.56 (m, dm, $^2J_{Pt,H}$ = 60 Hz, 4 H, =CH_2, **8**), 4.70 (s, d, $^2J_{Pt,H}$ = 56 Hz, 8 H, =CH_2, **10**) ppm. ^{13}C NMR (50.3 MHz, 300 K, $CDCl_3$): δ = 8.5 (s, d, $^3J_{Pt,C}$ = 24 Hz, ≡C*C*H$_3$, **8**), 11.0 (s, *C*H$_3$, **16**), 28.2 [s C(*C*H$_3$)$_3$, **16**], 30.6 [s, d, $^2J_{Pt,C}$ = 28 Hz, *C*(CH$_3$)$_3$, **8**], 31.1 [s, d, $^3J_{Pt,C}$ = 17 Hz, C(*C*H$_3$)$_3$, **8**], 74.9 (s, d, $^1J_{Pt,C}$ = 115 Hz, ≡*C*, **8**), 80.2 (s, d, $^1J_{Pt,C}$ = 141 Hz, =*C*H$_2$, **8**), 84.3 (s, d, $^1J_{Pt,C}$ = 131 Hz, =*C*H$_2$, **10**), 84.8 (s, d, $^1J_{Pt,C}$ = 156 Hz, ≡*C*), 98.7 (s, d, $^1J_{Pt,C}$ = 132 Hz, =*C*t*Bu, **16**), 107.8 (s, d, $^1J_{Pt,C}$ = 153 Hz, =*C*Me, **16**) ppm. ^{195}Pt NMR (86.0 MHz, 300 K, CD_2Cl_2): δ = –3145 (s, **8**), –3642 (s, **10**) ppm.

Reaction with *t*BuC≡C*t*Bu: ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.48 [s, 36 H, C(CH_3)$_3$, **12**], 1.51 [s, 36 H, C(CH_3)$_3$, **12**], 1.47 [s, 9 H, C(CH_3)$_3$, **9**], 4.55 (s, d, $^2J_{Pt,H}$ = 55 Hz, 4 H, =CH_2, **9**), 4.70 (s, d, $^2J_{Pt,H}$ = 56 Hz, 8 H, =CH_2, **10**) ppm. ^{13}C NMR (50.3 MHz, 300 K, $CDCl_3$): δ = 27.9 [s, *C*(CH$_3$)$_3$], 30.4 [s, C(*C*H$_3$)$_3$, **12**], 31.4 [s, C(*C*H$_3$)$_3$, **12**], 31.7 [s, C(*C*H$_3$)$_3$, **9**], 80.4 (s, d, $^1J_{Pt,C}$ = 138 Hz, =*C*H$_2$, **9**), 80.7 (s, d, $^1J_{Pt,C}$ = 221 Hz, ≡*C*, **12**), 80.6 (s, d, $^1J_{Pt,C}$ = 231 Hz, ≡*C*, **12**), 84.3 (s, **10**, =*C*H$_2$), 85.9 (s, d, $^1J_{Pt,C}$ = 151 Hz, ≡*C*, **9**) ppm. ^{195}Pt NMR (86.0 MHz, 300 K, CD_2Cl_2): δ = –1958 (s, **12**), –1995 (s, **12**), –3143 (s, **9**) ppm.

Synthesis of [{PtCl$_2$(RC≡C*t*Bu)}$_2$] (R = Me, 11; R = *t*Bu, 12): The requisite alkyne (0.76 mmol) was added at room temperature to a suspension of [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (**1**, 186 mg, 0.316 mmol) in $CHCl_3$ (3 mL), resulting in a deep red solution. After having been stirred at room temperature for 24 h, the solution was reduced to 1 mL and layered with diethyl ether (1 mL)/*n*-pentane (2–3 mL), resulting in precipitation of the requisite complex, which was filtered off, washed with small amounts of *n*-pentane, and dried in vacuo.

R/R′ = Me/*t*Bu (11): Yield 206 mg, 90%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.61 [s, 18 H, C(CH_3)$_3$], 2.26 (s, d, $^3J_{Pt,H}$ = 32 Hz, 6 H, CH_3) ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 7.9 (s, d, $^2J_{Pt,C}$ = 22 Hz, *C*H$_3$), 26.9 [s, *C*(CH$_3$)$_3$], 30.0 [s, C(*C*H$_3$)$_3$], 69.4 (s, ≡*C*), 69.7 (s, ≡*C*), 70.0 (s, d, $^1J_{Pt,C}$ = 190 Hz, ≡*C*), 79.4 (s, ≡*C*), 79.5 (s, d, $^1J_{Pt,C}$ = 228 Hz, ≡*C*), 79.7 (s, d, $^1J_{Pt,C}$ = 224 Hz, ≡*C*) ppm. ^{195}Pt NMR (107 MHz, 300 K, CD_2Cl_2): δ = –1971 (s), –1960 (s), –1955 (s) ppm. $C_{14}H_{24}Cl_4Pt_2$ (724.31): calcd. C 23.21, H 3.34; found C 23.63, H 3.58.

R/R′ = *t*Bu/*t*Bu (12): Yield 242 mg, 95%. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ = 1.48 [s, 36 H, C(CH_3)$_3$], 1.51 [s, 36 H, C(CH_3)$_3$] ppm. ^{13}C NMR (50.29 MHz, 300 K, $CDCl_3$): δ = 29.8 [s, *C*(CH$_3$)$_3$], 29.9 [s, d, $^2J_{Pt,C}$ = 21 Hz, *C*(CH$_3$)$_3$], 30.3 [s, d, $^3J_{Pt,C}$ = 21 Hz, C(*C*H$_3$)$_3$], 30.4 [s, C(*C*H$_3$)$_3$], 81.1 (s, d, $^1J_{Pt,C}$ = 230.8 Hz, ≡*C*), 81.2 (s, ≡*C*) ppm. ^{195}Pt NMR (107 MHz, 300 K, $CDCl_3$): δ = –1968 (s), –2005 (s) ppm. $C_{20}H_{36}Cl_4Pt_2$ (808.47): calcd. C 29.71, H 4.49; found C 29.76, H 4.81.

Reaction between [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (1) and But-2-yne in CDCl$_3$: [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (**1**, 18 mg, 0.03 mmol) was placed in an NMR tube and dissolved in $CDCl_3$ (0.7 mL), and but-2-yne (6 mg, 0.12 mmol) was added. The course of the reaction was monitored for up to several days by ^{1}H and ^{13}C NMR spectroscopic measurements and showed the formation of [PtCl$_2$(C_4Me$_4$)] (**4**) as main product, and hexamethylbenzene and [PtCl$_2$(H$_2$C=CH$_2$)$_2$] (**10**) as sideproducts. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ = 1.63 (s, d, $^3J_{Pt,H}$ = 20 Hz, 12 H, CH_3, **4**), 2.22 [s, 18 H, C_6(CH_3)$_6$], 4.70 (s, d, $^2J_{Pt,H}$ = 56.0 Hz, 8 H, **10**), 5.07 (br., =CH_2) ppm. ^{13}C NMR (50.3 MHz, 300 K, $CDCl_3$, after two weeks): δ = 8.9 (s, *C*H$_3$, **4**), 16.2 [s, C_6(*C*H$_3$)$_6$], 84.3 (s, =*C*H$_2$, **10**), 104.1 (s, C_4, **4**) ppm.

Reaction between [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (1) and Acetone: [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (**1**, 18 mg, 0.03 mmol) was placed in an NMR tube and dissolved in [D$_6$]acetone (0.7 mL). The course of the reaction was monitored for up to several days by ^{13}C and ^{195}Pt NMR spectroscopic measurements and showed the formation of [PtCl$_2$(Me$_2$CO)(H$_2$C=CH$_2$)] (**18**) as main product and of 4-hydroxy-4-methylpentan-2-one, 4-methylpent-3-en-2-one, and higher condensation products of acetone containing Me–(MeC=CH)$_n$–C(O)Me (n = 5–7) units, as side products, as well as an unidentified platinum complex. ^{13}C NMR [50.3 MHz, 300 K, (CD$_3$)$_2$CO]: δ = 20.6 (s, =C*C*H$_3$), 27.6 (s, =C*C*H$_3$), 29.3 [s, =C(*C*H$_3$)$_2$OH], 31.6 (s, H$_3$*C*CO), 31.8 (s, H$_3$*C*CO), 54.6 (s, *C*H$_2$), 69.3 (s, *C*Me$_2$OH), 89.0 (br., =*C*H$_2$, **18**), 124.8 (s, =*C*HCO), 154.3 (s, =*C*Me$_2$), 198.3 (s, =CH*C*O), 210.0 (s, CH$_2$*C*O) ppm. ^{195}Pt NMR [86 MHz, 300 K,

$(CD_3)_2CO$]: δ = –2245 (s), –2719 (s, **18**) ppm. The δ_{Pt} value of complex **18** is in the range (δ_{Pt}: –2696/–2892 ppm) of other *trans*-[$PtCl_2L$(COE)] (L = MeOH, MeCN) complexes,[4] thus showing the constitution of **18**.

Me–(MeC=CH)$_5$–C(O)Me: HRMS (ESI): calcd. for $[C_{18}H_2D_{25}O]^+$ 284.36256 $[M]^+$; found 284.36269.

Me–(MeC=CH)$_6$–C(O)Me: HRMS (ESI): calcd. for $[C_{21}D_{31}O]^+$ 330.43152 $[M]^+$; found 330.43131.

Me–(MeC=CH)$_7$–C(O)Me: HRMS (ESI): calcd. for $[C_{24}D_{35}O]^+$ 374.48793 $[M]^+$; found 374.48747.

Me–(MeC=CH)$_6$–C(OH)MeCH$_2$C(O)Me: HRMS (ESI): calcd. for $[C_{24}H_2D_{35}O_2]^+$ 392.49849 $[M]^+$; found 392.49779.

Me–(MeC=CH)$_7$–C(OH)MeCH$_2$C(O)Me: HRMS (ESI): calcd. for $[C_{27}H_2D_{39}O_2]^+$ 436.55490 $[M]^+$; found 436.55428.

Reaction between [{PtCl$_2$(H$_2$C=CH$_2$)}$_2$] (1) and But-2-yne in Acetone: [{$PtCl_2(H_2C=CH_2)$}$_2$] (**1**, 18 mg, 0.03 mmol) was placed in an NMR tube and dissolved in [D_6]acetone (0.7 mL), and but-2-yne (83 mg, 1.54 mmol) was added. The course of the reaction was monitored for up to several days by ^{13}C and ^{195}Pt NMR spectroscopic measurements and showed the formation of [$PtCl_2$(Me_2CO)($H_2C=CH_2$)] (**18**) as main product and of 4-hydroxy-4-methylpentan-2-one, 4-methylpent-3-en-2-one, higher condensation products of acetone, [$PtCl_2(C_4Me_4)$] (**4**), and [$PtCl_2(H_2C=CH_2)_2$] (**10**) as sideproducts, as well as an unidentified platinum complex. ^{13}C NMR [50.3 MHz, 300 K, $(CD_3)_2CO$]: δ = 8.8 (s, d, $^2J_{Pt,C}$ = 15 Hz, *C*H$_3$, **4**), 20.6 (s, =C*C*H$_3$), 27.6 (s, =C*C*H$_3$), 29.3 [s, =C(*C*H$_3$)$_2$OH], 31.6 (s, H$_3$*C*CO), 31.8 (s, H$_3$*C*CO), 54.6 (s, *C*H$_2$), 69.3 (s, *C*Me$_2$OH), 84.3 (s, d, $^1J_{Pt,C}$ = 131 Hz, =*C*H$_2$, **10**), 89.0 (br., =*C*H$_2$, **18**), 104.1 (s, d, $^1J_{Pt,C}$ = 145 Hz, *C*$_4$, **4**), 124.8 (s, =*C*HCO), 154.3 (s, =*C*Me$_2$), 198.3 (s, =CH*C*O), 210.0 (s, CH$_2$*C*O) ppm. ^{195}Pt NMR [86 MHz, 300 K, $(CD_3)_2CO$]: δ = –2244.9 (s), –2719 (s, **18**), –3648 (s, **10**), –3168 (s, **4**) ppm.

X-ray Structure Determinations: Crystals suitable for X-ray diffraction analyses were grown at room temperature from solutions of complexes **2**, **11a**, **12a**, and **12b** in $CHCl_3$ by slow addition of either diethyl ether (**2**) or diethyl ether/*n*-pentane (**11a**, **12a** and **12b**). Intensity data were collected with a STOE IPDS diffractometer at 203(2) K (**2**), 200(2) K (**11a**, **12a**), or 173(2) K (**12b**) with Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). Crystallographic data and data collection parameters are given in S4 in the Supporting Information. Absorption corrections were applied empirically with the PLATON program package[39] (0.02/0.09, **11a**), numerically (T_{min}/T_{max}0.12/0.69, **12a**) and by integration[40] (T_{min}/T_{max} 0.19/0.39, **2**; T_{min}/T_{max} 0.10/0.56, **12b**). The structures were solved by direct methods with SHELXS-97 and refined by full-matrix, least-squares routines against F^2 with SHELXL-97.[41] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic displacement parameters. Hydrogen atoms were added to their calculated positions and refined according to the riding model.

Computational Details: DFT calculations were carried out with the aid of the Gaussian 03 program package[42] and use of the B3LYP hybrid functional. The 6-311G(d,p) basis sets[43] as implemented in Gaussian 03 were employed for C, H, and Cl atoms, whereas the relativistic pseudopotential of the Ahlrichs group and related basis functions of TZVPP quality were employed for Pt atoms.[44] The appropriateness of the functional in combination with the basis sets and effective core potential used for reliable interpretation of structural and energetic aspects of related platinum complexes has been demonstrated.[45] All systems were fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium and transition-state structures, respectively, by analysis of the force constants of normal vibrations. Solvent effects were considered according to the polarized continuum model.[46]

Supporting Information (see footnote on the first page of this article): NMR spectroscopic data of **8** obtained by spectra simulation, comparison of structural parameters of Zeise's dimer type complexes, crystallographic data for **2**, **11**, **12a** and **12b,** powder diffraction data of **2**, **11** and **12**, a detailed route according to Scheme 6 including calculated values for the gas phase, and Cartesian coordinates and energies of the calculated molecules are presented.

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