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On the Equilibrium between Alkyne and Olefin Platinum(II) Complexes of Zeise's Salt Type: Syntheses and Characterization of $[K(18C6)][PtCl_3(RC{\equiv}CR')]$

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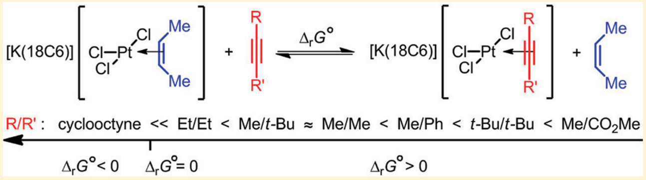
Supporting Information



ABSTRACT: Zeise's type alkyne complexes $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (R/R′ = Me/Me, **3**; Et/Et, **4**; Me/*t*-Bu, **5**; *t*-Bu/*t*-Bu, **6**; Me/Ph, **7**; Me/CO_2Me, **8**; $RC{\equiv}CR'$ = COC, **9**; COC = cyclooctyne; 18C6 = 18-crown-6) were obtained from the *cis*-but-2-ene complex $[K(18C6][PtCl_3($*cis*-but-2-ene$)]$ (**2**) and the requisite alkyne via a ligand substitution reaction. ^{1}H NMR spectroscopically determined equilibrium constants showed that the formation of all these alkyne complexes is endergonic, except that of the cyclooctyne complex **9**, which is strongly exergonic. The identities of the complexes were proved by microanalysis and NMR spectroscopy (^{1}H, ^{13}C). X-ray diffraction analyses of complexes **5**−**7** exhibited slightly elongated $C{\equiv}C$ triple bonds (1.23(1)−1.24(1) Å) and a back bending of the substituents on the alkyne between 16(1)° and 21(1)°. In contrast, a longer $C{\equiv}C$ bond (1.27(1) Å) was found for the cyclooctyne complex **9**, whereas the $C-C{\equiv}C$ angles in this complex (26.8(7)°/26.0(7)°) are the same as in the noncoordinated cyclooctyne (26(2)°). Quantum chemical calculations on the DFT level of theory of the complex anions $[PtCl_3(RC{\equiv}CR')]^-$ (**3a′**−**9a′**) showed analogous structural features for the coordinated alkynes. Furthermore, energy decomposition analysis exhibited that the extraordinarily high stability of the cyclooctyne complex **9a′** can be understood in terms of a very low preparation energy of the cyclooctyne (due to the "prebended" structure of the noncoordinated COC) and a relatively high (instantaneous) interaction energy. NBO analyses made clear that the π back-donation in complexes bearing alkynes with electron-withdrawing substituents (Ph, CO_2Me) and in the COC complex is significantly greater than that in complexes bearing alkynes with alkyl substituents (Me, Et, *t*-Bu).

1. INTRODUCTION

Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$, the first organo transition metallic compound, was synthesized in 1825 by W. C. Zeise.[1] However, the exact nature of this compound was the subject of long discussions,[2] which finally ended with the development of the corresponding bonding model by M. J. S. Dewar, J. Chatt, and L. A. Duncanson in 1951/1953[3] and the determination of the molecular structure by X-ray and neutron diffraction analysis in 1954 and 1975, respectively.[4] Although numerous olefin complexes of Zeise's salt type $M^I[PtCl_3(R_2C{=}CR_2)]$ (M^I = alkaline metal; R = H, alkyl, aryl) have been synthesized, alkyne complexes of Zeise's salt type, $M^I[PtCl_3(RC{\equiv}CR')]$,[5,6] could be obtained only to a limited extent. These complexes were mainly obtained for alkyne ligands with sterically demanding *tert*-butyl substituents or oxygen-functionalized substituents such as $-C(OH)R_2$ (R = alkyl, aryl) as well as phenyl substituents. Typically, they were synthesized by (i) halide displacement reactions starting from $M^I_2[PtX_4]$ (X = Cl, Br) or (ii) ethylene displacement reactions starting from $M^I[PtCl_3(C_2H_4)]$.

In our group it was found that the chloro-bridged dinuclear platinum(II) complex $[K(18C6)]_2[Pt_2Cl_6]$ (18C6 = crown ether 18-crown-6) reacts readily not only with olefins but also with alkynes in methylene chloride at room temperature to yield complexes $[K(18C6)][PtCl_3(RHC{=}CHR')]$[7] (Scheme 1a) and $[K(18C6)][PtCl_3(RC{\equiv}CR')]$[8] (Scheme 1b), respectively. The synthesis of the alkyne complexes was found to be restricted to internal alkynes, whereas analogous reactions with terminal alkynes failed due to fast oligo- and polymerization reactions. However, the synthesis of such complexes with terminal alkyne ligands, $[K(18C6][PtCl_3(RC{\equiv}CH)]$,[8] succeeded via ligand substitution of a volatile alkyne ($MeC{\equiv}CMe$) by a terminal alkyne (Scheme 1c).

Here, we present a straightforward method for the preparation of alkyne platinum(II) complexes of the type $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ via ligand substitution (olefin/alkyne) starting from the easily accessible *cis*-but-2-ene complex $[K(18C6)][PtCl_3($*cis*-$MeHC{=}CHMe)]$ (**2**). The influence of the alkyne substituents R/R′ on the equilibria of the ligand substitution reactions and, thus, on the course of these reactions is the subject of this study, which permits, with the use of DFT calculations, statements about the relative stability of olefin and alkyne complexes.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Spectroscopic Characterization of $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (3−9).

$[K(18C6)][PtCl_3($*cis*-$MeHC{=}CHMe)]$ (**2**), a Zeise's salt type complex, was

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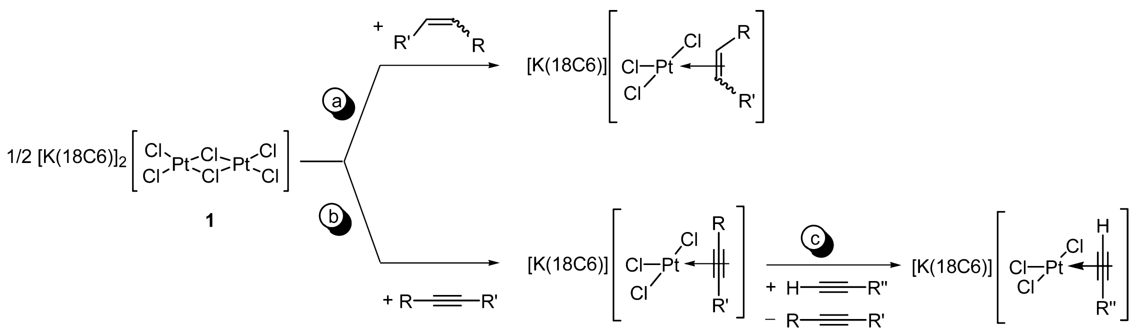
Scheme 1



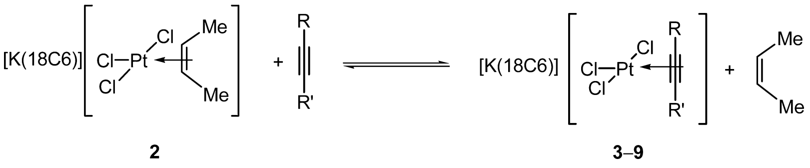
found to react with different internal alkynes in methylene chloride or chloroform as solvent within several minutes, yielding the corresponding alkyne complexes $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (**3**−**9**) with liberation of *cis*-but-2-ene (Scheme 2). As revealed by NMR experiments in sealed NMR tubes, alkyne complexes **3**−**8** are in equilibrium with the starting olefin complex **2** (see Section 2.4, Table 5). Thus, a complete degree of conversion toward the alkyne complexes could be achieved only by the addition of an excess of the alkynes supported by evaporation of the volatile olefin in vacuo. Complexes **3**−**9** were isolated as yellow or orange-yellow, slightly air-sensitive microcrystalline substances in 54−96% yields. NMR spectra of complexes **3** and **4** proved to be identical with those prepared according to route b in Scheme 1.[8] The identities of the new complexes **5**−**9** were confirmed by microanalysis, ^1H and ^{13}C NMR spectroscopic measurements, and single-crystal X-ray diffraction analyses (**5**−**7**, **9**).

Selected ^1H and ^{13}C NMR spectroscopic parameters of the alkyne complexes **3**−**9** are presented in Table 1. The coordination induced shifts (CIS; $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{noncoord.ligand}}$)[9] of the acetylenic carbon atoms ($\equiv$CR/$\equiv$CR′) are between −5.6 and −17.8 ppm. The $^1J_{Pt,C}$ coupling constants in complexes with η^2-RC≡CR′ ligands (R, R′ = primary alkyl, aryl) were found to be in the range between 173 and 188 Hz, whereas in complexes with *tert*-butyl-substituted alkyne ligands and in the cyclooctyne (COC) complex values between 216 and 236 Hz were observed. These values differ from those found in Pt(0) complexes of the type $[Pt(RC{\equiv}CR')_2]$ (R/R′ = Me, *t*-Bu, Ph; CIS: 35.2−41.6 ppm; $^1J_{Pt,C}$ = 266−311 Hz).[10] In complexes of the type $[Pt(Cl)Me(Me_2phen)(RC{\equiv}CR)]$[11] (R = CF_3, CO_2Me) coupling constants of $^1J_{Pt,C}$ = 476−497 Hz are observed. Within the framework of the valence bond theory the magnitude of these coupling constants points to a substantial contribution of a platina(IV)-cyclopropene resonance (canonical) structure.

Due to $^nJ_{H,H}$ couplings and signal overlapping, in the ^1H NMR spectra only spectral parameters of methyl-substituted alkynes are indicative. The coordination-induced shifts of the methyl protons were found to be between 0.35 and 0.43 ppm, and the $^3J_{Pt,H}$ coupling constants are in a narrow range of 31−33 Hz. Both parameters are comparable to analogous data of alkyne platinum complexes of the type $[PtX_2(Me_2phen)(MeC{\equiv}CR)]$ (R = H, Me, Ph; X = Br, I; CIS: 0.37−0.45 ppm; $^3J_{Pt,H}$ = 30−39 Hz) described in the literature.[12]

2.2. Molecular Structures of Alkyne Platinum(II) Complexes. Crystals suitable for X-ray diffraction analyses were obtained from the alkyne complexes **5**−**7** and **9**. In all crystals contact ion pairs were found without unusual intermolecular interactions between them. The molecular structures of these complexes are depicted in Figure 1, and selected structural parameters are given in Table 2. The geometry around the Pt(II) center is square planar, in very good approximation (Cl2−Pt−Cl3, Cl1−Pt−Cg(C1/C2)[13] 178.07(5)−179.2(1)°). The alkyne ligands are orientated almost perpendicularly to the coordination plane (Pt,Cl1,Cl2,Cl3) as measured by the interplanar angle Φ (Pt,Cl1,Cl2,Cl3/Pt,C1,C2: 84.1(6)−89.6(4)°, Scheme 3). Within the 3σ criterion the two Pt−C distances in the alkyne complexes are of the same length (Pt−C 2.10(1)−2.141(9) Å). Furthermore, the C1≡C2 triple bonds in the alkyne complexes **5**−**7** (1.23(1)−1.24(1) Å) are only slightly elongated, compared to those in noncoordinated alkynes RC≡CR′ (R, R′ = alkyl, aryl; median: 1.191 Å, lower/upper quartile: 1.185/1.199 Å, number of observations n = 85).[14,15] A similar situation was found in the cyclooctyne complex **9**, where the C≡C bond of both the noncoordinated and coordinated COC are slightly longer (1.23 Å versus 1.27(1) Å) than the respective values in acyclic alkynes. The coordination-induced back bending of the alkyne substituents R/R′ (measured by the angle α, Scheme 3) was found to be between 16(1)° and 21(1)° for complexes **5**−**7**, whereas significantly higher angles (26.8(7)°/26.0(7)°) were observed for the COC complex **9**, although it has to be taken into consideration that, as a consequence of ring formation, the C−C≡C angles in the

Scheme 2



	3	4	5	6	7	8	9
R/R'	Me/Me	Et/Et	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	Me/CO_2Me	COC

Table 1. Selected ^{1}H and ^{13}C NMR Spectroscopic Data of $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (3–9) (δ in ppm, J in Hz)[a]

	3	4	5	6	7	8	9
R/R′	Me/Me	Et/Et	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	Me/CO_2Me	COC
$\delta(\equiv CCH_3)$	2.11		2.15		2.44	2.35	
$\Delta\delta$	0.39		0.41		0.43	0.35	
$^3J_{Pt,H}$	33		32		31	33	
$\delta(\equiv C)$	67.3	72.6	68.1/77.7	78.8	68.2/76.6	–[b]	76.6
$\Delta\delta$	−7.3	−8.4	−5.6/−10.3	−8.3	−11.5/−9.6		−17.8
$^1J_{Pt,C}$	173	188	176/223	216	172/180		236
$^2J_{Pt,C}$	27	20	27/17	14	27/28		11
$^3J_{Pt,C}$		27	19	20	20		42

[a] Values for complexes **3** and **4**, taken from ref 8, are given for comparison. [b] In concentrated solutions of **8** a decomposition within 12 h was observed at rt.

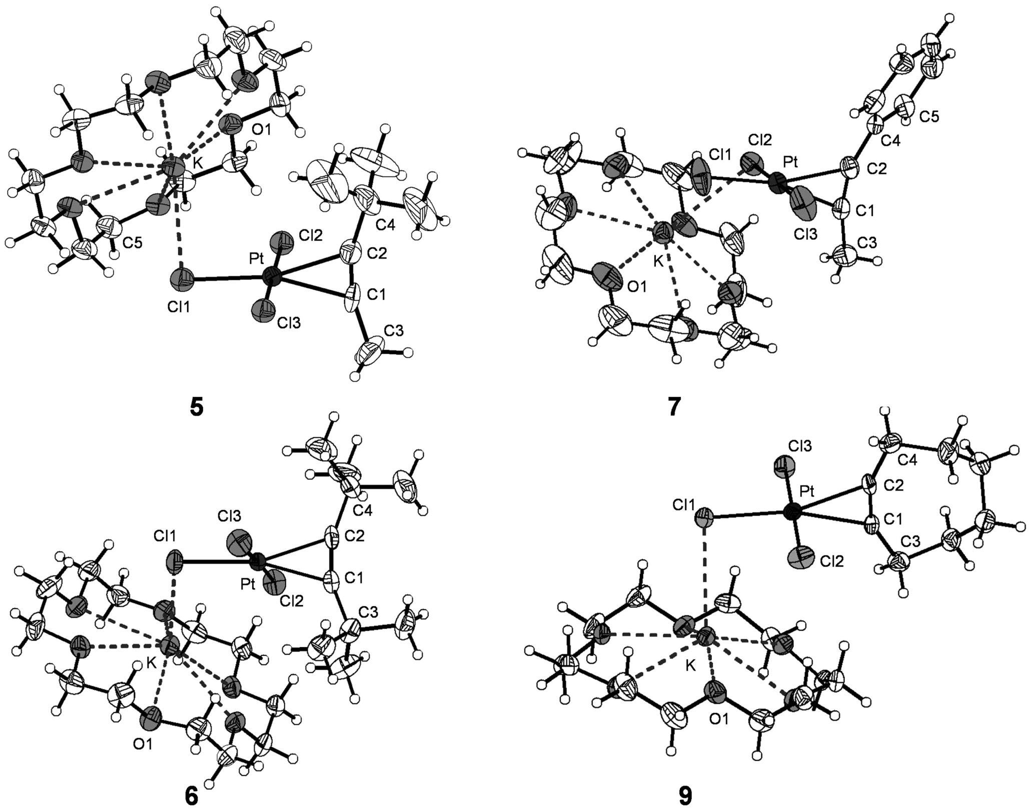


Figure 1. Structures of $[K(18C6)][PtCl_3(RC{\equiv}CR')]$ (R/R′ = Me/*t*-Bu, **5**; *t*-Bu/*t*-Bu, **6**; Me/Ph, **7**; RC≡CR′ = COC, **9**). Displacement ellipsoids are drawn at 30% probability.

noncoordinated cyclooctyne are already severely bent (α = 26(2)°).[14] The structural parameters of complexes **5**–**7** were found to be similar to other alkyne platinum(II) complexes $M^I[PtCl_3(RC{\equiv}CR)]$[5,8] ($M^I$ = K, [K(18C6)]), $[PtCl_2(RC{\equiv}CR')(amin)]$[16] (R/R′ = H, Me, Et, *t*-Bu, Ph, CMe_2OH, CEt_2OH), and $[PtI_2(Me_2phen)(PhC{\equiv}CPh)]$[12] described in the literature (C≡C 1.18(3)–1.27(4) Å, Pt–C 2.01(2)–2.18(1) Å, α = 15(1)–27(2)°). Furthermore, the significantly higher back bending found in complex **9** (α = 26.8(7)°/26.0(7)°) is comparable to that in other COC complexes $[\{Cu(X)(COC)\}_2]$ and $[Cu(X)(COC)\ _2]$[17] (X = Cl, Br, I; median: 25.4°, lower/upper quartile: 24.8/26.4°, number of observations n = 9), but significantly lower than in the alkyne platinum(0) complex $[Pt(COC)(PPh_3)_2]$ (α = 35(1)°/34.5(9)°).[18]

In complexes **5**–**7** all Pt–Cl bond lengths are between 2.286(4) and 2.316(5) Å; significant differences in the length between the Pt–Cl bond *trans* to the alkyne and *trans* to Cl were not found. In contrast, the Pt–Cl1 bond in **9** *trans* to the cyclooctyne ligand proved to be significantly longer than those *trans* to the chloro ligand (Pt–Cl1 2.329(2) Å vs Pt–Cl2/Cl3 2.292(2)/2.296(2) Å), thus indicating a relatively high *trans* influence of the COC ligand.

In all structures relatively short distances between the cation $[K(18C6)]^+$ and one of the chloro ligands of the anion indicate cation–anion interactions. The shortest K···Cl contacts (Cl1: **5**, **6**, **9**; Cl2: **7**) were determined to be 3.071(3)–3.191(5) Å (Table 2). These values are in the range of the K···Cl distance in solid $\{KCl\}_s$ (CN(K) = 6; 3.146 Å) but slightly longer than that in gaseous mono- and dinuclear $\{(KCl)_n\}_g$ (CN(K) = 1, n = 1, 2.667 Å; CN(K) = 2, n = 2, 2.950 Å).[19] For a discussion of the conformation of the crown ethers see the Supporting Information (S2).

Table 2. Selected Interatomic Distances (in Å) and Angles (in deg) in Complexes $[K(18C6)][PtCl_3(RC\equiv CR')]$ (5−7, 9)

	5	6	7	9
R/R′	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	COC
Pt−C1	2.10(1)	2.141(9)	2.12(1)	2.132(6)
Pt−C2	2.13(1)	2.130(9)	2.125(8)	2.125(7)
Pt−Cl1	2.316(5)	2.310(3)	2.296(3)	2.329(2)
Pt−Cl2	2.301(3)	2.309(3)	2.286(4)	2.292(2)
Pt−Cl3	2.314(3)	2.299(3)	2.286(3)	2.296(2)
C1−C2	1.24(1)	1.24(1)	1.23(1)	1.27(1)
K···Cl1	3.191(5)	3.071(3)	3.265(4)	3.114(3)
K···Cl2	3.410(6)	3.345(4)	3.176(4)	3.541(3)
K···O	2.796(8)−2.98(1)	2.791(7)−2.967(8)	2.813(8)−2.933(8)	2.781(5)−2.971(6)
K···(O1,... ,O6)[a]	0.780(3)	0.709(2)	0.743(2)	0.774(1)
Cl1−Pt−Cl3	90.9(1)	89.1(1)	89.5(1)	90.67(8)
Cl2−Pt−Cl3	179.2(1)	178.2(1)	179.0(1)	178.87(8)
Cl1−Pt−Cl2	89.7(1)	89.7(1)	90.7(1)	89.53(8)
Cl1−Pt−Cg[b]	178.7(1)	178.62(8)	178.64(8)	178.07(5)
α(C2−C1−C3)[c]	16(1)	21(1)	16(1)	26.8(7)
α(C1−C2−C4)[c]	18(1)	20(1)	20(1)	26.0(7)
Φ[d]	88.3(6)	89.6(4)	84.1(6)	86.7(3)

[a] Distance between the K atom and the mean plane of the crown ether defined by its six O atoms. [b] Cg: Center of gravity between the two acetylenic C atoms (C1/C2). [c] Measure of the back bending α; see Scheme 3. [d] Φ: Angle between the Pt,Cl1,Cl2,Cl3 and the Pt,C1,C2 planes.

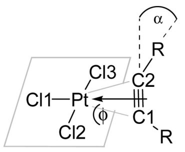
2.3. Quantum Chemical Calculations of Alkyne Platinum(II) Complexes. In order to gain deeper insight into the nature of the bond of the alkynes $RC\equiv CR'$ to platinum and the influence of the substituents R/R′ in complexes **3**−**9**, DFT calculations of the corresponding anions $[PtCl_3(RC\equiv CR')]^-$ (**3a′**−**9a′**)[20] have been performed, using high-quality functional and basis sets. The structures of these complex anions as well as selected structural parameters are given in Figure 2 and Table 3. In general, a good agreement between the calculated values (representing structures of anions in the gas phase) and the corresponding values in crystals of $[K(18C6)][PtCl_3(RC\equiv CR')]$ complexes was found.

The Pt−C bond lengths of all complexes $[PtCl_3(RC\equiv CR')]^-$ (**3a′**−**9a′**) were found in a narrow range (2.136−2.150 Å) except for the complexes with alkyne ligands $MeC\equiv CPh$ and $MeC\equiv CCO_2Me$ bearing electron-withdrawing substituents (**7a′**, 2.119/2.136 Å; **8a′**, 2.103/2.110 Å) as well as with the cyclooctyne ligand (**9a′**; 2.118/2.118 Å). The coordination-induced bond lengthening of the $C\equiv C$ bonds amounts to 0.039−0.050 Å, and the back bending (measured by the angle α) of alkyl/phenyl substituents R/R′ in the alkyne complexes **5a′**−**7a′** to 18.0−22.2°, whereas the back bending of the strongly electron-withdrawing CO_2Me substituent in **8a′** was found to be 27.9°. In the cyclooctyne complex **9a′** α values of 27.5°/27.5° were found, which proved to be similar to those in noncoordinated cyclooctyne (27.0°/25.3°).

Energy decomposition analysis (EDA) allows to investigate the metal−ligand bond strength. According to the EDA, the energy for the [M]−L bond formation ([M] + L → [M]−L, $-E_{diss}$) can formally be split up into the contribution of two processes: (i) The preparation energy, which is required to promote the two isolated fragments [M] and L from their equilibrium structures to the structures that they acquire in the complex ($[M] + L \rightarrow [M]^* + L^*$, E_{prep}); and (ii) the interaction energy, which is the instantaneous interaction energy of the two "prepared" fragments ($[M]^* + L^* \rightarrow [M]{-}L$, E_{int}). Thus, the equation $-E_{diss} = E_{int} + E_{prep}$ holds. For a brief explanation of these fundamental steps, see ref 21. The results of the energy decomposition analysis of the platinum−alkyne bonds on the complexes **3a′**−**9a′** are shown in Scheme 4 and Table 4.

A comparison of the values of the dissociation energy E_{diss} of complexes **3a′**−**9a′** demonstrates the order R/R′ = *t*-Bu/*t*-Bu, **6a′** < Me/*t*-Bu, **5a′** ≈ Me/Ph, **7a′** < Me/Me, **3a′** ≈ Et/Et, **4a′** < Me/CO_2Me, **8a′** ≪ COC, **9a′**. Thus, similar values (25.0−26.6 kcal/mol) were found for complexes **3a′**−**7a′**, bearing acyclic alkyl- and aryl-substituted alkyne ligands, whereas a slightly larger value was calculated for **8a′** (28.3 kcal/mol) and an exceptionally high value for the COC complex **9a′** (38.0 kcal/mol). Evaluation of the different energetic contributions shows that the preparation energies of the $PtCl_3^-$ fragment from the equilibrium structure (Cl2−Pt−Cl3 166.3°, Scheme 4) into the "prepared" T-shaped structure (Cl2−Pt−Cl3 177.4−179.7°, Scheme 4) requires less energy (ΔE_{prep} = 3.3−3.7 kcal/mol) than the promotion of the alkyne fragments (ΔE_{prep} = 7.8−11.0 kcal/mol). An exception was found in the case of the cyclooctyne ligand, where a significantly lower preparation energy (ΔE_{prep}(COC) = 3.3 kcal/mol) is required. Interestingly, *t*-Bu substituents as well as electron-withdrawing CO_2Me and Ph substituents in **5a′**−**8a′** give rise to both an increase of the preparation energy of the alkyne fragment by about 1.7−3.2 kcal/mol and an increase in the interaction energy by about 1.5−4.9 kcal/mol, compared to **3a′** and **4a′**, having coordinated alkynes with sterically less bulky methyl and ethyl substituents. By far the highest dissociation energy was found in the cyclooctyne complex **9a′**. It exhibits the highest interaction energy of all investigated complexes as well as a significantly lower preparation energy of the alkyne fragment, which can be attributed to the already bent structure of cyclooctyne in the noncoordinated state.

Scheme 3



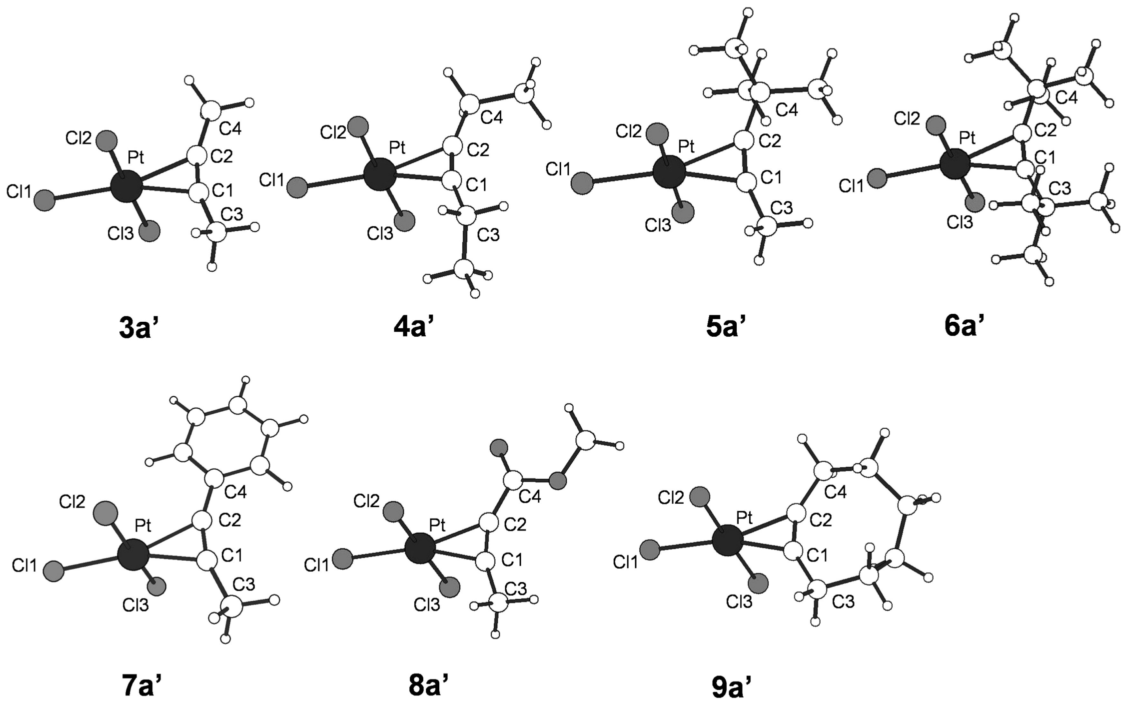


Figure 2. Calculated structures of the complex anions $[PtCl_3(RC{\equiv}CR')]^-$ (R/R′ = Me/Me, **3a′**; Et/Et, **4a′**; Me/*t*-Bu, **5a′**; *t*-Bu/*t*-Bu, **6a′**; Me/COOMe, **8a′**; and RC≡CR′ = COC, **9a′**).

Table 3. Calculated Structural Parameters of $[PtCl_3(RC{\equiv}CR')]^-$ (3a′–9a′) (interatomic distances in Å, angles in deg)

	3a′	4a′	5a′	6a′	7a′	8a′	9a′
R/R′	Me/Me	Et/Et	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	Me/CO_2Me	COC
Pt–C1	2.143	2.141	2.136	2.147	2.119	2.103	2.118
Pt–C2	2.143	2.141	2.150	2.147	2.136	2.110	2.118
Pt–Cl1	2.348	2.347	2.349	2.349	2.343	2.341	2.352
Pt–Cl2	2.365	2.365	2.365	2.366	2.362	2.363	2.365
Pt–Cl3	2.365	2.365	2.365	2.366	2.362	2.363	2.365
C1–C2[a]	1.243	1.244	1.245	1.248	1.251	1.254	1.246
	(1.203)	(1.205)	(1.204)	(1.206)	(1.206)	(1.204)	(1.205)
α(C2–C1–C3)	18.0	18.2	18.2	21.5	18.9	20.7	27.5
α(C1–C2–C4)	18.0	18.2	21.9	21.5	22.2	27.9	27.5
Cl1–Pt–Cl3	91.0	91.0	90.6	90.1	90.7	90.7	90.8
Cl2–Pt–Cl3	178.0	178.0	177.4	179.7	178.2	178.0	178.4
Cl1–Pt–Cl2	91.0	91.0	90.6	90.1	90.7	90.7	90.8

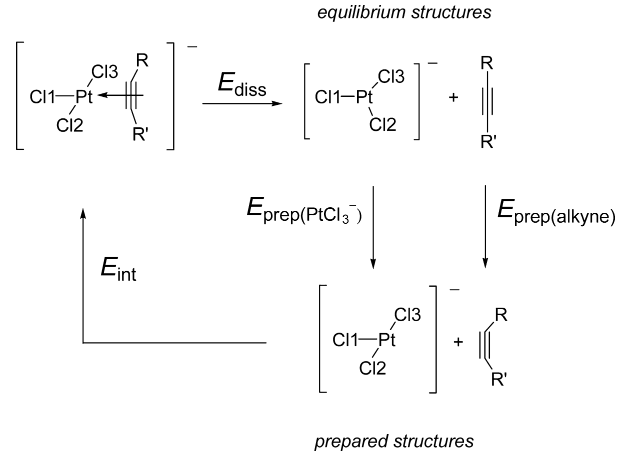
[a] The values for the corresponding noncoordinated alkynes are given in parentheses.

As expected, NBO analyses show a depopulation of the bonding π orbitals and a population of the antibonding π^* orbitals of the alkyne ligands in the complex anions **3a′**–**9a′** compared to the noncoordinated alkynes (Table 4). A remarkable difference can be seen between complexes bearing alkynes with alkyl substituents (R/R′ = Me/Me, **3a′**; Et/Et, **4a′**; Me/*t*-Bu, **5a′**; *t*-Bu/*t*-Bu, **6a′**) and those with electron-withdrawing substituents and the COC ligand (R/R′ = Me/Ph, **7a′**; Me/CO_2Me, **8a′**; COC, **9a′**). In the latter ones a significantly higher population of the antibonding π^* orbitals (P_{π^*}: 0.297–0.307, **3a′**–**6a′** versus 0.322–0.377, **7a′**–**9a′**) can be observed, indicating a larger back-donation. This is also reflected by the total charge of the alkyne ligands, q_{alkyne}, which was found to be slightly positive for **3a′**–**6a′** (0.001 to 0.024 e) and slightly negative for **7a′**–**9a′** (−0.021 to −0.071 e).

2.4. On Ligand (Olefin/Alkyne) Substitution Reactions in Zeise's Salt Type Complexes.

The equilibrium positions of the substitution reactions (according to Scheme 5) were determined NMR spectroscopically in sealed NMR tubes in chloroform at 27 °C. These equilibrium constants give insight into the relative stability of olefin and alkyne complexes of Zeise's type. Values of K_{NMR} between 0.0055 (**8a**) and 0.47 (**4a**) were observed for the formation of alkyne complexes $[PtCl_3(RC{\equiv}CR')]^-$ (R/R′ = Me/Me, Et/Et, Me/*t*-Bu, *t*-Bu/*t*-Bu, Me/Ph, Me/CO_2Me; Table 5) from $[PtCl_3(cis\text{-}MeHC{=}CHMe)]^-$ (**2a**). In contrast, the reaction of the but-2-ene complex **2a** with cyclooctyne resulted in a complete degree of conversion (K_{NMR} estimated to be >500). Thus, the Gibbs free energies, $\Delta_rG°$, for the ligand substitution reactions (but-2-ene versus alkyne) according to Scheme 2 were found to be slightly positive, except for cyclooctyne, which was found to be strongly negative (Table 5). Furthermore, the standard Gibbs free energies of the investigated alkyne complexes (**3a′**–**9a′**), the olefin complex $[PtCl_3(cis\text{-}MeHC{=}CHMe)]^-$ (**2a′**), the

Scheme 4

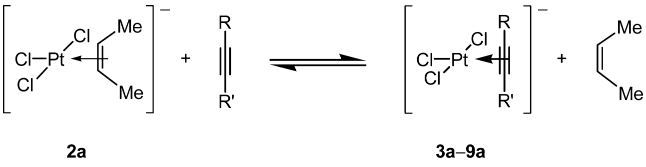


noncoordinated alkynes, and *cis*-but-2-ene were calculated at the DFT level of theory. On the basis of these calculations (Section 2.3) the standard Gibbs free energies for the substitution equilibria between $[PtCl_3(cis\text{-}MeHC{=}CHMe)]^-$ (**2a′**) and $[PtCl_3(RC{\equiv}CR')]^-$ (**3a′–9a′**) (Scheme 5) were determined both in the gas phase and with consideration of solvent effects ($CHCl_3$), modeled according to Tomasi's polarized continuum model (Table 5).[22] The solvent influence on the free energy of the substitution reactions was found to be of minor importance for most alkyne complexes, except for the complex $[PtCl_3(MeC{\equiv}CCO_2Me)]^-$ (**8a′**), bearing a polar substituent on the alkyne ligand. Considering a margin of error of the DFT method in the range 1−2 kcal/mol, the calculated values were found to be in good agreement with the experimentally determined values. This demonstrates the capability of the employed DFT model to represent properly the alkyne bonding in Zeise's type complexes.

2.5. On Dissociation Constants of Zeise's Salt Type Complexes.

To get insight into the dissociation of Zeise's salt type complexes in solution, conductivity measurements of the *cis*-but-2-ene and the 5,5-dimethylpent-2-yne complex [K(18C6)][$PtCl_3(cis\text{-}MeHC{=}CHMe)$] (**2**) and [K(18-C-6)][$PtCl_3(MeC{\equiv}Ct\text{-}Bu)$] (**5**), respectively, were performed in chloroform, the same solvent that was used for the ligand substitution reactions. At room temperature the plot of molar conductivity, Λ_M, as a function of the square root of the concentration $\sqrt{c}$ gave proof that [K(18C6)][$PtCl_3(cis\text{-}MeHC{=}CHMe)$] (**2**) and [K(18C6)][$PtCl_3(MeC{\equiv}Ct\text{-}Bu)$] (**5**) are weak electrolytes (Figure 3a).

Scheme 5



R/R'	3a	4a	5a	6a	7a	8a	9a
	Me/Me	Et/Et	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	Me/CO_2Me	COC

From the graph of $1/\Lambda_M$ against the specific conductivity $\kappa = c\cdot\Lambda_M$ in the concentration range 1×10^{-4} to 3×10^{-3} mol/L (Figure 3b) the molar conductivity at infinite dilution, Λ_0, was determined by extrapolation against $\kappa \rightarrow 0$. From the obtained values of Λ_0 the dissociation constants K_d of the two complexes were estimated to be about 2×10^{-6} mol/L (**2**) and 6×10^{-5} mol/L (**5**), respectively. Both values correspond to a degree of dissociation α in the range of ≈2% for (**2**) and ≈14% for (**5**) in diluted chloroform solutions ($c = 3 \times 10^{-2}$ mol/L) used in the NMR experiments. Thus, conductivity measurements show a significant dissociation of the ion pairs in diluted $CHCl_3$ solutions, indicating the absence of strongly directed cation−anion interactions. Therefore, it can be assumed that the cation influence on the (olefin/alkyne) substitution reactions is of minor importance.

2.6. Conclusion.

We have described a straightforward synthesis for a series of alkyne platinum(II) complexes via ligand substitution (olefin versus alkyne) according to Scheme 2. Furthermore, the equilibria of these reactions were studied both by NMR spectroscopic measurements and by quantum chemical calculations at the DFT level of theory. The following conclusions can be drawn:

Table 4. Bond Characteristics of Alkynes in the Complex Anions $[PtCl_3(RC{\equiv}CR')]^-$ (3a′–9a′): Results of the Energy Decomposition Analysis (EDA) (ΔE_{diss} = bond dissociation energy, ΔE_{int} = instantaneous interaction energy, ΔE_{prep} = preparation energy; all energies in kcal/mol) and NBO Analysis (P_π/P_{π^*} = population of the π/π^* orbitals of the alkyne complexes/noncoordinated alkynes; q_{alkyne} = ligand charge; values in electrons)

	3a′	4a′	5a′	6a′	7a′	8a′	9a′
R/R′	Me/Me	Et/Et	Me/*t*-Bu	*t*-Bu/*t*-Bu	Me/Ph	Me/CO_2Me	COC
ΔE_{diss}[a]	26.5	26.6	26.0	25.0	26.0	28.3	38.0
ΔE_{int}[a]	−37.9	−37.7	−39.2	−39.4	−39.8	−42.6	−44.8
ΔE_{prep}[b]	11.4	11.1	13.2	14.5	13.8	14.3	6.9
$\Delta E_{prep(alkyne)}$	8.1	7.8	9.5	10.8	10.3	11.0	3.3
$\Delta E_{prep(PtCl_3^-)}$	3.3	3.3	3.7	3.7	3.5	3.3	3.6
NBO analysis							
alkyne complexes							
P_π	1.642	1.648	1.642	1.645	1.642	1.631	1.625
P_{π^*}	0.301	0.297	0.301	0.307	0.322	0.377	0.365
q_{alkyne}	0.024	0.012	0.011	0.001	−0.021	−0.071	−0.036
noncoordinated alkynes							
P_π	1.962	1.962	1.963	1.963	1.917	1.905	1.955
P_{π^*}	0.063	0.055	0.054	0.046	0.092	0.061	0.060

[a] With consideration of the BSSE, obtained by counterpoise calculations (BSSE = 1.71−2.56 kcal/mol). [b] $\Delta E_{prep} = \Delta E_{prep(alkyne)} + \Delta E_{prep(PtCl_3^-)}$.

Table 5. Standard Gibbs Free Energies, $\Delta_rG°$ (in kcal/mol), and Equilibrium Constants, K_{NMR}, of the Ligand Substitution Reaction According to Scheme 5, Obtained from NMR Spectroscopic Measurements and Quantum Chemical Calculations, Respectively

	R/R′	K_{NMR}	$\Delta_rG°_{NMR}$	$\Delta_rG°_{gp}$[a]	$\Delta_rG°_{CHCl_3}$[b]
3a	Me/Me	0.25	0.8	1.5	1.1
4a	Et/Et	0.47	0.5	0.8	0.6
5a	Me/*t*-Bu	0.26	0.8	1.8	1.9
6a	*t*-Bu/*t*-Bu	0.020	2.3	2.3	3.0
7a	Me/Ph	0.061	1.7	2.0	4.1
8a	Me/CO_2Me	0.0055	3.1	−0.3	3.4
9a	COC	>500[c]	<−3.7[c]	−10.9	−9.8

[a] Calculated Gibbs free energies under gas phase conditions. [b] Calculated Gibbs free energies considering solvent effects ($CHCl_3$). [c] The absence of any signal of noncoordinated COC in the ^{1}H NMR spectrum indicates a degree of formation toward **9a** greater than 0.96.

(1) Structural investigations of alkyne Pt(II) complexes of Zeise's type and DFT calculations of the corresponding anions exhibited that the coordination-induced lenghtening of the alkyne C≡C bond and the back bending of its substituents are much smaller than in alkyne Pt(0) complexes. This can be attributed to a, in general, smaller capability for π back-donation in Pt(II) compared to Pt(0) complexes.

(2) NMR spectroscopic investigations and DFT calculations ascertained that the substitution of *cis*-but-2-ene in Zeise's type complexes (Schemes 2 and 5) by alkynes bearing alkyl, aryl, and methoxycarbonyl substituents is endergonic. Thus, the platinum−alkyne bond has to be regarded as slightly less stable than the platinum−olefin bond. An exceptional case was found for the cyclooctyne (COC) ligand. Here, the analogous substitution reaction was found to be distinctly exergonic, demonstrating an unusually strong platinum−alkyne bond.

(3) An energy decomposition analysis gave further insights into the alkyne bonding and clarified that the exceptionally higher dissociation energy by 10−14 kcal/mol of the COC ligand can be attributed both to a reduced preparation energy, ΔE_{prep}(alkyne), due to the already "prebended" alkyne and an increased interaction energy, ΔE_{int}, in the COC complex in about equal amounts. NBO analyses made clear that the COC complex and the complexes bearing alkynes with electron-withdrawing substituents (Ph, CO_2Me) exhibit significantly more back-donation than the complexes bearing alkynes with alkyl substituents (Me, Et, *t*-Bu).

Thus, both the presented experimental and theoretical investigations give insight how subtly the stability of alkyne−platinum(II) complexes depends on the substitution pattern of the alkyne and the ring strain in cyclic alkynes. Furthermore, due to the applicability of the synthesis method for a wide range of alkynes, the diversity of alkyne−platinum(II) complexes could be significantly expanded.

3. EXPERIMENTAL SECTION

3.1. General Procedures. All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Solvents were dried (Et_2O and *n*-pentane over Na benzophenone; $CHCl_3$, $CDCl_3$, CH_2Cl_2, and CD_2Cl_2 over CaH_2; acetone over molecular sieve 3 Å) and distilled prior to use. ^{1}H, ^{13}C, and ^{195}Pt NMR spectra were recorded on Varian Gemini 200, VXR 400, and Unity 500 NMR spectrometers. Chemical shifts are relative to $CHCl_3$ (δ = 7.24) and $CDCl_3$ (δ = 77.0 ppm) as internal references. ^{195}Pt NMR spectra were calibrated with external H_2PtCl_6 (δ_{Pt} 0.0 ppm). Microanalyses were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (Elementar Analysensysteme) elemental analyzers. The starting compounds cyclooctyne (COC), 2,2,5,5-tetramethylhex-3-yne, $[K(18C6)]_2[Pt_2Cl_6]$ (**1**), and $[K(18C6)][PtCl_3(cis\text{-MeHC=CHMe})]$ (**2**) were synthesized according to published methods.[7,23,24] All other chemicals were commercially available.

*Synthesis of [K(18C6)][PtCl$_3$(RC≡CR′)] (R/R′ = Me/Me, **3**; Et/Et, **4**; Me/t-Bu, **5**; Me/Ph, **7**).* To a solution of **2** (126 mg, 0.190 mmol) in CH_2Cl_2 (4 mL) was added the corresponding alkyne (1.14 mmol), and the solution was stirred for 24 h at room temperature, whereby from time to time the liberated volatile olefin was removed by short evaporation of some solvent in vacuo. Then the intense yellow-colored solution was concentrated by evaporation in vacuo to 1−2 mL, and diethyl ether (2 mL) was added. The precipitate was filtered off, washed with Et_2O (2·1 mL), and dried briefly in vacuo. The crude product was purified by dissolving in CH_2Cl_2/acetone and layering with Et_2O.

R/R′ = Me/Me (**3**): Yield 67 mg, 54%. Anal. Calcd for $C_{16}H_{30}Cl_3KO_6Pt$ (658.94): C, 29.16; H, 4.59; Cl, 16.14. Found: C, 28.89; H, 4.86; Cl, 16.07. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ 2.11 (s+d, $^3J_{Pt,H}$ = 33 Hz, 3H, CH_3), 3.66 (s, 24H, OCH_2). ^{13}C NMR (101 MHz, 300 K, CD_2Cl_2): δ 7.7 (s+d, $^2J_{Pt,C}$ = 27 Hz, CH_3), 67.3 (s+d, $^1J_{Pt,C}$ = 173 Hz, ≡CCH_3), 70.0 (s, OCH_2).

R/R′ = Et/Et (**4**): Yield 91 mg, 70%. Anal. Calcd for $C_{18}H_{34}Cl_3KO_6Pt$ (686.99): C, 31.47; H, 4.99; Cl, 15.48. Found: C, 32.02; H, 5.56; Cl, 16.07. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ 1.34 (t, $^3J_{H,H}$ = 7.5 Hz, 6H, CH_3), 2.48 (q, $^3J_{H,H}$ = 7.5 Hz, 4H, CH_2), 3.65

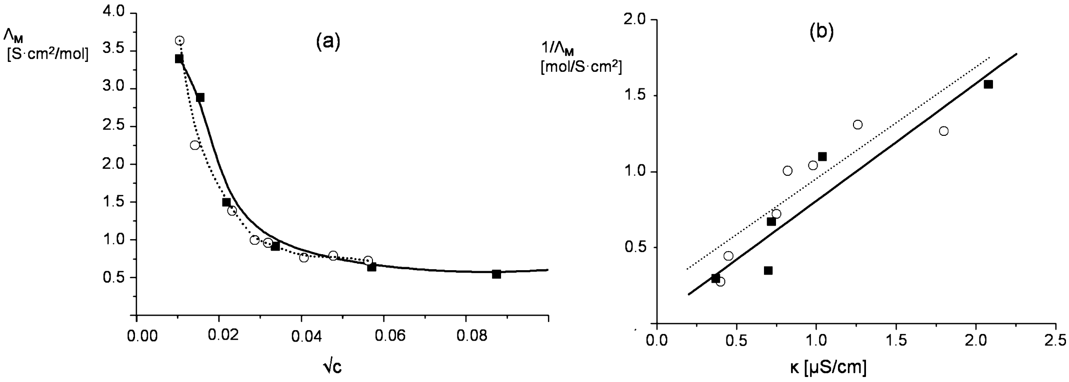


Figure 3. Plot of molar conductivity, Λ_M, as a function of the square root of concentration $\sqrt{c}$ (a) and plot of reciprocal molar conductivity $1/\Lambda_M$ against specific conductivity κ (b) for solutions of **2** (■) and **5** (○) in $CHCl_3$.

(s, 24H, OCH_2). ^{13}C NMR (101 MHz, 300 K, CD_2Cl_2): δ 12.7 (s+d, $^3J_{Pt,C}$ = 27 Hz, CH_3), 15.6 (s+d, $^2J_{Pt,C}$ = 20 Hz, CH_2), 70.4 (s, OCH_2), 72.6 (s+d, $^1J_{Pt,C}$ = 188 Hz, $\equiv CCH_2$).

R/R′ = Me/*t*-Bu (**5**): Yield 120 mg, 90%. Anal. Calcd for $C_{19}H_{36}Cl_3KO_6Pt$ (701.02): C, 32.55; H, 5.18; Cl, 15.17. Found: C, 32.62; H, 5.56; Cl, 15.31. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ 1.42 (s, 9H, $C(CH_3)_3$), 2.15 (s+d, $^3J_{Pt,H}$ = 32 Hz, 3H, $\equiv CCH_3$), 3.63 (s, 24H, OCH_2). ^{13}C NMR (101 MHz, 300 K, CD_2Cl_2): δ 7.7 (s+d, $^2J_{Pt,C}$ = 27 Hz, $\equiv CCH_3$), 29.1 (s+d, $^2J_{Pt,C}$ = 17 Hz, $C(CH_3)_3$), 30.4 (s+d, $^3J_{Pt,C}$ = 19 Hz, $C(CH_3)_3$), 68.1 (s+d, $^1J_{Pt,C}$ = 176 Hz, $\equiv CCH_3$), 70.0 (s, OCH_2), 77.7 (s+d, $^1J_{Pt,C}$ = 223 Hz, $\equiv C(CH_3)_3$).

R/R′ = Me/Ph (**7**): Yield 115 mg, 84%. Anal. Calcd for $C_{21}H_{32}Cl_3KO_6Pt$ (721.01): C, 34.98; H, 4.47; Cl, 14.75. Found: C, 34.80; H, 4.66; Cl, 15.01. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ 2.44 (s+d, $^3J_{Pt,H}$ = 31 Hz, 3H, CH_3), 3.63 (s, 24H, OCH_2), 7.33−7.38 (m, 3H, *p*-H/*m*-H), 7.96−8.01 (m, 2H, *o*-H). ^{13}C NMR (50 MHz, 300 K, CD_2Cl_2): δ 8.8 (s+d, $^2J_{Pt,C}$ = 27 Hz, $\equiv CCH_3$), 68.2 (s+d, $^1J_{Pt,C}$ = 172 Hz, $\equiv CCH_3$), 70.4 (s, OCH_2), 76.6 (s+d, $^1J_{Pt,C}$ = 180 Hz, $\equiv CPh$), 123.4 (s+d, $^2J_{Pt,C}$ = 28 Hz, $CC\equiv CCH_3$), 128.6 (s+d, $^2J_{Pt,C}$ = 20 Hz, *m*-C), 131.4 (s, o-C), 131.7 (s, p-C).

*Synthesis of [K(18C6)][PtCl$_3$(t-BuC≡Ct-Bu)] (**6**).* To a solution of **2** (200 mg, 0.303 mmol) in $CHCl_3$ (3 mL) was added 2,2,5,5-tetramethylhex-3-yne (167 mg, 1.21 mmol), resulting in an intense yellow-colored solution. After stirring the solution for 24 h at room temperature the solvent and the volatile olefin were removed by evaporating the solution to dryness in vacuo. Then the residue was redissolved in $CHCl_3$ (3 mL), a new batch of 2,2,5,5-tetramethylhex-3-yne (167 mg, 1.21 mmol) was added, and the resulting solution was treated as mentioned above. After eight repetitions of this procedure a nearly complete degree of conversion (>96%) was observed by NMR spectroscopy. Finally, the residue was washed with Et_2O (2·1 mL) and purified by dissolving in CH_2Cl_2/acetone and layering with Et_2O. Yield: 180 mg, 80%. Anal. Calcd for $C_{22}H_{42}Cl_3KO_6Pt$ (743.10): C, 35.56; H, 5.70. Found: C, 35.58; H, 5.71. ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): δ 1.44 (s, 18H, $C(CH_3)_3$), 3.64 (s, 24H, OCH_2). ^{13}C NMR (101 MHz, 300 K, CD_2Cl_2): δ 28.8 (s+d, $^2J_{Pt,C}$ = 14 Hz, $C(CH_3)_3$), 30.7 (s+d, $^3J_{Pt,C}$ = 20 Hz, $C(CH_3)_3$), 70.5 (s, OCH_2), 78.8 (s+d, $^1J_{Pt,C}$ = 216 Hz, ≡*C*t-Bu).

*Synthesis of [K(18C6)][PtCl$_3$(MeC≡CCO$_2$Me)] (**8**).* At −30 °C to a solution of **2** (190 mg, 0.287 mmol) in $CHCl_3$ (3 mL) was added methyl but-2-ynoate (1.41 g, 14.4 mmol), resulting in an intense yellow-colored solution. After stirring the solution for 1 h at −30 °C the solvent and the volatile olefin were removed by evaporating the solution to the dryness in vacuo at this temperature and stirring for another 3 h applying a vacuum (0.1 bar, −30 °C). Finally the product was precipitated by layering with Et_2O/*n*-pentane (3 mL) and washed with *n*-pentane (2 × 3 mL). This product had to be recrystallized from $CHCl_3$ (2 mL) by layering with Et_2O/*n*-pentane (3 mL) and washing with *n*-pentane (2 × 3 mL). Yield: 121 mg, 60%. Anal. Calcd for $C_{17}H_{30}Cl_3KO_8Pt$ (702.95): C, 29.05; H, 4.30. Found: C, 28.90; H, 4.46. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ 2.28 (s+d, $^3J_{Pt,H}$ = 33 Hz, 3H, $\equiv CCH_3$), 3.62 (s, 24H, OCH_2), 3.83 (s, 3H, OCH_3).

*Synthesis of [K(18C6)][PtCl$_3$(COC)] (**9**).* To a solution of **2** (260 mg, 0.393 mmol) in CH_2Cl_2 (4 mL) was added cyclooctyne (63.8 mg, 0.590 mmol). After stirring the solution for 30 min at room temperature the intense yellow-colored solution was filtered, concentated in vacuo to 1 mL, and layered with *n*-pentane (2 mL). The precipitate was filtered off, dried briefly in vacuo, and purified by dissolving in CH_2Cl_2/acetone and layering with Et_2O/*n*-pentane. Yield: 269 mg, 96%. Anal. Calcd for $C_{20}H_{36}Cl_3KO_6Pt$ (713.03): C, 33.69; H, 5.09. Found: C, 33.69; H, 5.08. ^{1}H NMR (200 MHz, 300 K, CD_2Cl_2): δ 1.65 (m, $\equiv CCH_2CH_2CH_2$, 4H), 1.66 (m, $\equiv CCH_2CH_2$, 4H), 2.57 (m, $\equiv CCH_2CH_2$, 4H), 3.65 (s, OCH_2, 24H). ^{13}C NMR (50 MHz, 300 K, CD_2Cl_2): δ 22.4 (s+d, $^2J_{Pt,C}$ = 11 Hz, $\equiv CCH_2CH_2$), 28.9 (s, $\equiv CCH_2CH_2CH_2$), 30.2 (s+d, $^3J_{Pt,C}$ = 42 Hz, $\equiv CCH_2CH_2$,), 70.4 (s, OCH_2), 76.6 (s+d, $^1J_{Pt,C}$ = 236 Hz, $\equiv CCH_2$). ^{195}Pt NMR (107 MHz, 300 K, CD_2Cl_2): δ −2078.7 (s).

*Reaction of [K(18C6)][PtCl$_3$(MeHC=CHMe)] (**2**) with Alkynes.* In a typical experiment complex **2** (15 mg, 0.023 mmol) was placed into an NMR tube, and a solution of the requisite alkyne RC≡CR′ in $CDCl_3$ (0.7 mL) was added at −80 °C. Then the NMR tube was closed by melting and warmed to room temperature. ^{1}H NMR spectroscopic measurements revealed that in all cases the equilibrium composition was reached within 10 min. The positions of the equilibria were calculated from signals of nonsuperimposed protons; see Supporting Information. The equilibrium constants given in Table 5 were obtained from at least two independent experiments using different stoichiometric ratios (Table S3).

X-ray Structure Determinations. Crystals suitable for X-ray diffraction analyses were grown at room temperature from solutions of complexes in CH_2Cl_2/acetone by slow addition of diethyl ether (**5**−**7**) and diethyl ether/*n*-pentane (**9**), respectively. Intensity data were collected on a STOE IPDS diffractometer at 200(2) K (**9**) and a STOE STADI IV diffractometer at 293(1) K (**5**−**7**), with Mo Kα radiation (λ = 0.71073 Å, graphite monochromator). Crystallographic data and data collection parameters are given in Table S1. Absorption corrections were applied using Ψ-scans for **5** (T_{min}/T_{max} 0.16/0.26), **6** (T_{min}/T_{max} 0.21/0.42), and **7** (T_{min}/T_{max} 0.21/0.42) and numerically for **9** (T_{min}/T_{max} 0.28/0.88). The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against F^2 with SHELXL-97.[25] 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 by the Gaussian03 program package[26] using the hybrid functional B3LYP. The 6-311G(d,p)[27] basis sets as implemented in Gaussian03 were employed for C, H, O, and Cl atoms, while the relativistic pseudopotential of the Ahlrichs group and related basis functions of TZVPP quality[28] were employed for Pt atoms. 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.[29] All systems were fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. Solvent effects were considered according to the polarized continuum model.[22] Basis set superposition errors (BSSE) were calculated according to the counterpoise method as implemented in Gaussian03.[30] The atom coordinates as well as energies of all calculated equilibrium structures are given in the Supporting Information (S4). Energy decomposition analyses were performed on the basis of the optimized structures of the complexes and fragments, as given in the literature.[21] The NBO analyses were performed with the NBO module as implemented in Gaussian03.[31]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for **5**−**7**, **9** (CCDC 838514−839517), crystallographic and structure refinement data for **5**−**7**, **9** (S1), description of crown ether conformations in **5**−**7**, **9** (S2), details of equilibrium constants of substitution reactions (S3), as well as energies and atom coordinates of all calculated equilibrium structures (S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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