

Synthesis and characterization of platinum(II) complexes with terminal alkynes analogous to Zeise's salt - structure of $[K(18\text{-crown-6})][PtCl_3(PhC\equiv CD)] \cdot CH_2Cl_2$

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Received 4 June 1997

Abstract

The reaction of $[K(18\text{-cr-6})][PtCl_3(MeC\equiv CMe)]^+$ (**1a**) with 1-alkynes $RC\equiv CH$ ($R = n\text{-Pr}, n\text{-Bu}, t\text{-Bu}, Ph$) and $PhC\equiv CD$ in methylene chloride at low temperatures results in the formation of $[K(18\text{-cr-6})][PtCl_3(RC\equiv CH)]$ (**2a–d**) and $[K(18\text{-cr-6})][PtCl_3(PhC\equiv CD)]$ (**2e**), respectively. The complexes were characterized by microanalysis as well as by NMR, Raman and IR spectroscopy. The stretching frequencies $\nu(C-H(D))$ and $\nu(C\equiv C)$ are lowered by $141\text{--}151\text{ cm}^{-1}$ and $159\text{--}200\text{ cm}^{-1}$, respectively, due to the coordination of the alkyne to the $PtCl_3$ unit. The molecular structure of **2e**· CH_2Cl_2 (triclinic, $P\bar{1}$, $a = 10.155(2)$, $b = 11.368(3)$, $c = 14.047(2)$ Å, $\alpha = 86.28(2)^\circ$, $\beta = 70.42(1)^\circ$, $\gamma = 77.64(2)^\circ$, $Z = 2$) reveals an angle between the $PtCl_3$ and $Pt(C\equiv C)$ planes of $82.5(5)^\circ$ and an out-of-plane bending of the phenyl group of $15.2(9)^\circ$. The phenyl group is twisted by $33.9(7)^\circ$ from the $Pt(C\equiv C)$ plane. There are tight contacts between the cation $[K(18\text{-cr-6})]^+$ and the anion $[PtCl_3(PhC\equiv CD)]^-$ via the *trans*-chlorine and one of the *cis*-chlorines ($d(K1-C13) = 3.331(3)$ Å, $d(K1-C12) = 3.220(3)$ Å). © 1997 Elsevier Science S.A.

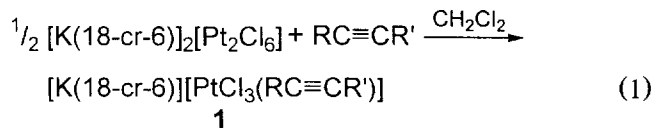
Keywords: Platinum; Alkyne complexes; Crown ether complexes; X-ray diffraction

1. Introduction

The synthesis of Zeise's salt, $K[PtCl_3(H_2C=CH_2)] \cdot H_2O$, and the elucidation of the mode of olefin bonding to platinum are landmarks in organometallic chemistry [1,2]. Alkyne complexes of Zeise's salt type, $K[PtCl_3(RC\equiv CR')]$, were prepared by Chatt et al. [3,4] but only with internal alkynes with bulky *tert*-butyl substituents. Furthermore, Zeise's salt type complexes with oxygen functionalized alkynes such as $Me_2(OH)CC\equiv CC(OH)Me_2$ [5–7] and with diphenyl acetylene [8] were described.

We found that $[K(18\text{-cr-6})]_2[Pt_2Cl_6]$ reacts smoothly in methylene chloride with a wide variety of internal alkynes according to Eq. (1) to give the crown ether adducts of Zeise's salt type alkyne complexes $[K(18\text{-cr-6})][PtCl_3(RC\equiv CR')]$ (**1**) [9]. Owing to platinum cat-

alyzed oligo- and polymerization reactions, attempts failed to synthesize complexes **1** with terminal alkynes (1-pentyne, acetylene) in this way. However, the 1-pentyne complex could be prepared via a ligand substitution reaction from the reaction of the 2-butyne complex (**1a**, $R = R' = Me$) with 1-pentyne.



To date, there have been no further reports on platinum(II) complexes with terminal alkynes without electron-withdrawing substituents. Five-coordinate platinum(II) complexes with alkynes having electron-withdrawing substituents of the types $[PtMe\{HB(pz)_3\}(RC\equiv CH)]$ ($pz = \text{pyrazolyl}$; $R = CO_2Me, C(O)Me, CF_3$), $[Pt(X)Me(N-N)(MeO_2CC\equiv CH)]$ ($N-N = \text{bidentate nitrogen ligand}$) and dinuclear complexes with

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¹ Abbreviation: 18-cr-6 = 18-crown-6.

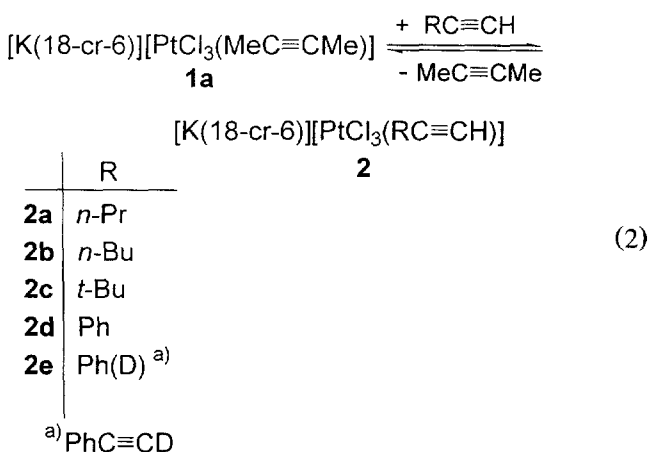
bridging terminal alkynes of the type $[\text{Pt}_2\text{Cl}_2\text{Me}_2(\text{N}-\text{N})(\mu\text{-RC}\equiv\text{CH})]$ ($\text{R} = \text{CO}_2\text{Me}$, Ph) are known [10,11].

Here we report the synthesis and characterization of 1-alkyne complexes of Zeise's salt type and the X-ray structure of the phenylacetylene complex.

2. Results and discussion

2.1. Syntheses

The 2-butyne complex $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{MeC}\equiv\text{CMe})]$ (**1a**) reacts with 1-alkynes in a ligand substitution reaction to give the 1-alkyne complexes $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{RC}\equiv\text{CH})]$ (**2**) with liberation of 2-butyne (Eq. (2)).



Methylene chloride was used as solvent and the reaction temperature was -20°C . At temperatures higher than -15°C the reaction mixtures turn to dark color owing to platinum catalyzed oligomerization reactions of the terminal alkynes. As long as the 1-alkynes used in the reactions (Eq. (2)) are less volatile than 2-butyne, a complete conversion of **1a** into the 1-alkyne complexes **2** could be achieved by repeated addition excess of 1-alkyne to complex **1a** followed by evaporation of all volatile products in vacuo.

The 1-alkyne complexes **2** were isolated as yellow powdered substances that are moderately air-sensitive. The phenylacetylene complexes **2d** and **2e** crystallize as solvates with methylene chloride. Solutions of complexes **2** decompose within few minutes at room temperature. In the solid state, they are stable for several hours at room temperature. Heating (ca. 5°K/min) of complexes **2** leads to decomposition between 85 and 95°C .

2.2. NMR and vibrational spectra

All complexes **2** were characterized by microanalysis as well as NMR, IR and Raman spectroscopically. Selected NMR data are compiled in Table 1. The chemical shifts of terminal protons (^1H) are between 2.9 and 3.9 ppm. Thus, the coordination of alkynes to platinum(II) in complexes **2** gives rise to downfield shifts of these protons by about 0.8 – 1.0 ppm. In marked contrast to it, the terminal protons in platinum(0) alkyne complexes are shifted downfield typically by about 3.9 – 4.8 ppm [12,13]. Thus, the chemical shifts are in the range of olefinic protons (6.2 – 6.8 ppm) indicating a much stronger π back-donation in platinum(0) than in platinum(II) alkyne complexes. In five-coordinate platinum(II) alkyne complexes the downfield shift of the methine proton amounts to 1.5 – 1.9 ppm [10,11]. The ^{13}C NMR resonances of the acetylenic carbons $\equiv\text{CR}$ and $\equiv\text{CH(D)}$ in complexes **2** are upfield shifted by 4.0 – 8.1 and 10.9 – 13.3 ppm, respectively. Contrary to that, very strong (ca. 40 ppm) [14] and slight (ca. 3 ppm) [11] downfield shifts were observed in platinum(0) and five-coordinate platinum(II) alkyne complexes, respectively.

Selected IR and Raman data of complexes **2** are listed in Table 2. Compared with the non-coordinated alkynes, the stretching frequencies $\nu(\text{C}\equiv\text{C})$ and $\nu(\equiv\text{C}-\text{H})$ are lowered by about 180 – 200 cm^{-1} (8 – 10%) and 140 – 180 cm^{-1} (4 – 5%), respectively. The lowering of the $\text{C}\equiv\text{C}$ frequencies is in full agreement with those in the analogous complexes **1** with internal alkynes [9]. As in the alkyne complexes of Zeise's salt type, the relative lowering of the $\nu(\text{C}=\text{C})$ in the olefin

Table 1
Selected ^1H and ^{13}C NMR data for $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{RC}\equiv\text{CH})]$ (**2**)

R	$\delta(\equiv\text{CH})$ [ppm]	$\Delta\delta^a$ [ppm]	$^2J(\text{Pt,H})$ [Hz]	$^4J(\text{H,H})$ [Hz]	$\Delta^4J(\text{H,H})^b$ [Hz]	$\delta(\equiv\text{CH})$ [ppm]	$\Delta\delta^a$ [ppm]	$\delta(\equiv\text{CR})$ [ppm]	$\Delta\delta^a$ [ppm]
2a <i>n</i> -Pr	2.91	1.01	70	2.1	−0.5	56.6	−11.5	80.4	−4.0
2b <i>n</i> -Bu	2.91	0.98	68	2.2	−0.4	58.3	−9.6	80.1	−4.4
2c <i>t</i> -Bu	2.87	0.91	70			56.2	−10.9	87.9	−4.4
2d Ph	3.86	0.77	66			63.8	−13.3	75.6	−8.0
2e Ph(D) ^c						64.0	−13.1	75.5	−8.1

^a $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free alkyne}}$

^b $\Delta J = J_{\text{complex}} - J_{\text{free alkyne}}$

^cPhC≡CD as ligand.

Table 2
Selected IR and Raman data for $[K(18\text{-cr-6})][PtCl_3(RC\equiv CH)]$ (**2**)

	R	$\nu(C\equiv C)$ [cm ⁻¹]	$\Delta \nu(C\equiv C)^a$ [cm ⁻¹]	$\Delta \nu/\nu_{\text{free alkyne}}$ [%]	$\nu(\equiv C-H)$ [cm ⁻¹]	$\Delta \nu(\equiv C-H)^a$ [cm ⁻¹]	$\Delta \nu/\nu_{\text{free alkyne}}$ [%]
2a	<i>n</i> -Pr	1937	-181	-8.5	3142	-177	-5.3
2b	<i>n</i> -Bu	1938	-206	-9.6	3169	-144	-4.3
2c	<i>t</i> -Bu	1905	-202	-9.6	3171	-141	-4.3
2d	Ph	1908	-202	-9.6	3149	-142	-4.3
2e	Ph(D) ^b	1828	-159	-8.0	2433 ^c	-151 ^c	-5.8

^a $\Delta \nu = \nu_{\text{complex}} - \nu_{\text{free alkyne}}$.

^bPhC≡CD as ligand.

^c $\nu(\equiv C-D)$.

complexes $K[PtCl_3(\text{olefin})]$ amounts to about 10%, too [15]. As expected, the $\nu(C\equiv C)$ in platinum(0) alkyne complexes is about at 1680–1800 cm⁻¹ corresponding to a lowering by 410–510 cm⁻¹ (20–23%) [12–14,16,17]. In the five-coordinate platinum(II) complexes with the electron-withdrawing alkynes the relative lowering is also much higher (15–19%) [10,11] than in **2**, pointing to a greater extent of π back-donation from platinum orbitals into π^* antibonding orbitals of the alkynes.

A quantitative analysis of the degree of π back-donation on the basis of $\nu(C\equiv C)$ failed due to a strong mixing between the $\nu(C\equiv C)$ and the $\nu(\equiv C-H)$ as can be seen by comparison of the phenylacetylene complex **2d** with the deuterated complex **2e** (Table 2). In the same way, a strong mixing of $\delta(CH_2)$ with $\nu(C\equiv C)$ in Zeise's salt prevents to calculate the degree of π back-donation from vibrational spectra [15]. But there is no doubt, that the π back-donation in the platinum(II)

alkyne complexes **2** is only of minor importance. Thus, calculations of $[PtCl_3(RC\equiv CR)]^-$ (R = Me, Et) show that there is a σ donation from alkyne to platinum of 0.33 (R = Me) and 0.35 (R = Et) electrons and a π back-donation of -0.07 (R = Me) and -0.05 (R = Et) electrons only [9].

2.3. Structure of $[K(18\text{-cr-6})][PtCl_3(PhC\equiv CD)] \cdot CH_2Cl_2$ (**2e** · CH_2Cl_2)

Suitable crystals for X-ray structure determination were obtained by slow condensation of diethyl ether into a solution of **2e** in methylene chloride at -25 °C. The molecular structure is shown in Fig. 1. Selected bond lengths and angles are listed in Table 3. The complex crystallizes in discrete molecules as methylene chloride solvate.

The length of the C–C triple bond in **2e** is 1.23(1) Å. Thus, a significant elongation caused by the coordina-

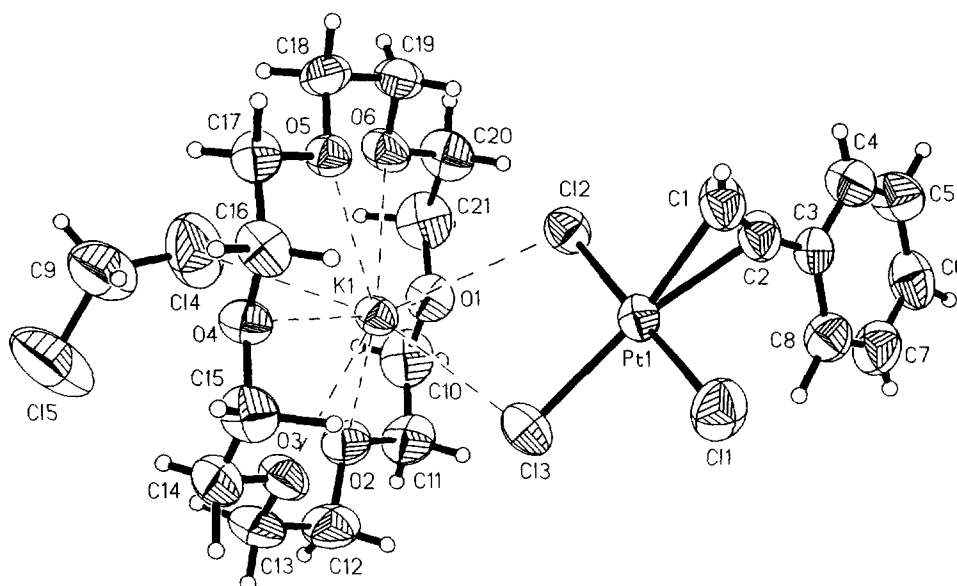


Fig. 1. Molecular structure of $[K(18\text{-cr-6})][PtCl_3(PhC\equiv CD)] \cdot CH_2Cl_2$ (**2e** · CH_2Cl_2), 50% thermal ellipsoids.

Table 3

Selected interatomic distances (Å) and angles (°) for compound **2e** · CH₂Cl₂

Pt(1)–C(1)	2.11(1)	K(1)–Cl(2)	3.331(3)
Pt(1)–C(2)	2.155(8)	K(1)–Cl(3)	3.220(3)
Pt(1)–Cl(1)	2.295(2)	K(1)–Cl(4)	3.389(4)
Pt(1)–Cl(2)	2.307(2)	C(1)–C(2)	1.23(1)
Pt(1)–Cl(3)	2.317(2)	C(2)–C(3)	1.44(1)
K(1)–O(1) ... K(1)–O(6)	2.829(5) ... 2.901(6)		
C(1)–Pt(1)–Cl(1)	87.8(3)	Cl(1)–Pt(1)–Cl(2)	178.65(8)
C(1)–Pt(1)–Cl(2)	90.8(3)	Cl(1)–Pt(1)–Cl(3)	91.43(9)
C(1)–Pt(1)–Cl(3)	165.8(3)	Cl(2)–Pt(1)–Cl(3)	89.86(8)
C(2)–Pt(1)–Cl(1)	92.3(3)	C(2)–C(1)–Pt(1)	75.3(6)
C(2)–Pt(1)–Cl(2)	86.6(2)	C(1)–C(2)–C(3)	164.8(9)
C(2)–Pt(1)–Cl(3)	160.5(2)		

tion of PhC≡CD to platinum(II) (PhC≡CH: $d(\text{C}\equiv\text{C}) = 1.208(1)$ Å [18]) cannot be proved. The angle between the planes PtCl₃ and Pt(C≡C) amounts to 82.5(5)°. A similar value was found in the 3-hexyne complex **1b** (R = R' = Et) (81°) and in Zeise's salt itself (84.1°) whereas both planes are perpendicular in the 2-butyne complex **1a** [9,19].

The out-of-plane bending of the phenyl group (defined by the angle $180^\circ - \angle \text{C1} - \text{C2} - \text{C3}$) is 15.2(9)°, being in the range (12–21°) of other platinum(II) alkyne complexes [9,20–22] and much smaller than in platinum(0) alkyne complexes (38–41°) [23–25]. The bent away of the terminal D atom (H1) will not be discussed because it could be located relatively imprecisely only.

The phenyl ring of phenylacetylene is twisted by 33.9(7)° from the Pt(C≡C) plane. This fact and the bending of the phenyl group (15.2(9)°) clearly show that a conjugation between π orbitals of the C–C triple bond and the phenyl substituent does not play any role. The twist angles (Ph vs. M(C≡C)) in phenylacetylene complexes exhibit a wide range of variation: Angles of 8.3° in [K(18-cr-6)][WF₅(PhC≡CH)] · MeCN [26] and of 10.3° in [PPh₄][WCl₅(PhC≡CH)] [27] allow π conjugation between the triple bond and the phenyl ring, whereas angles of 24.1° in [W(S₂CNMe₂)₂(ma)(PhC≡CH)] (ma = maleic anhydride) [28] or 38° in [Cu(PhC≡CH)(phen)] [29] do not.

The cation [K(18-cr-6)]⁺ has close contacts both to the *trans* (Cl3) and to one of the *cis* (Cl2) chlorine atoms ($d(\text{K1} - \text{Cl3}) = 3.331(3)$ Å, $d(\text{K1} - \text{Cl2}) = 3.220(3)$ Å) of the PtCl₃ moiety. The distance of potassium to the mean plane of the crown ether defined by its six oxygen atoms is 0.639(2) Å. The angle between the mean plane of the crown ether and the PtCl₃ plane is 110.3°. All these values are very similar to those in the 3-hexyne complex [K(18-cr-6)][PtCl₃(EtC≡CEt)] (**1b**) ($d(\text{K} - \text{cr}) = 0.771(2)$ Å; $\angle \text{PtCl}_3/\text{cr} = 105.5^\circ$). Different from **2e**, the contact of K⁺ to Cl_{*trans*} (3.126(5) Å) is more tight than those to Cl_{*cis*} (3.356(6) Å) in **1b** [9]. In

2e there is a solvent molecule (methylene chloride) coordinated to potassium via one of its chlorine atoms ($d(\text{K1} - \text{Cl4}) = 3.389(4)$ Å).

The experimental structure of **2e** corresponds well with the calculated structure of the anion [PtCl₃(PhC≡CH)][−], see Table 4. The bond lengths $d(\text{C}\equiv\text{C})$ and $d(\text{C}=\text{C})$ agree within the 3 σ criterion. As experimentally found, the phenylacetylene ligand in the calculated structure is not perpendicular to the PtCl₃ plane (calc.: 86.9°; obs.: 82.5°). Furthermore, the calculations reflect — in principle — correctly the out-of-plane bending of the phenyl group (calc.: 11.6°; obs.: 15.2°) and the twist between the phenyl group and the Pt(C≡C) moiety (calc.: 35.4°; obs.: 33.9°).

The investigations demonstrate that complexes of Zeise's salt type with terminal alkynes as ligands are relatively stable and can be properly prepared provided that platinum catalyzed oligomerization reaction of terminal alkynes are suppressed. The molecular structure of [K(18-cr-6)][PtCl₃(PhC≡CD)] · CH₂Cl₂ is the first example for a platinum(II) complex with a terminal alkyne ligand.

Table 4

Results of ab initio MO calculations (distances in Å, angles in °) of [PtCl₃(PhC≡CH)][−] in comparison with experimental data of **2e** · CH₂Cl₂

	2e · CH ₂ Cl ₂ (exp. data)	[PtCl ₃ (PhC≡CH)] [−] (calc. data) ^a
C≡C	1.23(1)	1.223 (1.172)
C=C	1.44(1)	1.474 (1.460)
$\angle \text{C}\equiv\text{C}-\text{C}$	164.8(9)	168.4 (180)
Pt–C(H)≡	2.11(1)	2.250
Pt–C(Ph)≡	2.155(8)	2.266
Pt–Cl _{<i>cis</i>}	2.307(2)/2.295(2)	2.333/2.338
Pt–Cl _{<i>trans</i>}	2.317(2)	2.315
Cl ₃ Pt/PtC≡C	82.5(5)	86.9
Pt(C≡C)/Ph	33.9(7)	35.4

^a The calculated values for PhC≡CH are given in parentheses.

3. Experimental section

All preparations were carried out under argon using standard Schlenk techniques. The solvents were dried and distilled prior to use. NMR spectra were obtained on Jeol JNM-FX200 and Varian Gemini 300 spectrometers. Chemical shifts are relative to CH_2Cl_2 (δ 5.32 ppm) and CD_2Cl_2 (δ 53.8 ppm) as internal references. IR and Raman spectra were recorded on a Bruker IFS66 FT-IR spectrometer (with Raman unit) using CsI pellets. $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{MeC}\equiv\text{CMe})]$ (**1a**) was synthesized according to literature procedure [9].

3.1. Synthesis of $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{RC}\equiv\text{CH})]$ (**2a–e**)

In a typical synthesis, $[\text{K}(18\text{-cr-6})][\text{PtCl}_3(\text{MeC}\equiv\text{CMe})]$ (**1a**) (200 mg, 0.30 mmol) was placed into a Schlenk tube and dissolved in a solution of the 1-alkyne in methylene chloride (5 ml, 1.5 M) at -20°C . The reaction solution was stirred for 30 min at this temperature followed by the removal of the solvent under reduced pressure. Another five times the residue was dissolved at -20°C in the solution of the 1-alkyne in methylene chloride (5 ml, 1.5 M). Finally, the residue was dissolved in the CH_2Cl_2 /1-alkyne solution (2 ml) and diethyl ether (5 ml) was added. The precipitate was filtered off, washed with diethyl ether and dried briefly in vacuo (degree of conversion: 100%, yield: > 50%).

2a: see [9].

2b: Anal. Found: C, 31.44; H, 4.96; Cl, 15.62. $\text{C}_{18}\text{H}_{34}\text{Cl}_3\text{KO}_6\text{Pt}$ (687.01). Calc.: C, 31.47; H, 4.99; Cl, 15.48. Fp. (dec.): $85\text{--}88^\circ\text{C}$. Infrared: $\nu(\text{C}\equiv\text{H}) = 3169\text{ cm}^{-1}$ (m), $\nu(\text{C}\text{--}\text{O}) = 1109\text{ cm}^{-1}$ (s), $\nu(\text{Pt}\text{--}\text{Cl}) = 334$ (sh), 325 (m), 313 (sh) cm^{-1} . Raman: $\nu(\text{C}\equiv\text{C}) = 1938\text{ cm}^{-1}$ (m), $\nu(\text{Pt}\text{--}\text{Cl}) = 335$ (s), 313 (m) cm^{-1} . ^1H NMR (CD_2Cl_2 , 200 MHz, 233 K): $\delta(\text{CH}_3) = 0.85$ (t), $(\text{Me}\text{--}\text{CH}_2) = 1.37$ (sext), $(\text{Et}\text{--}\text{CH}_2) = 1.74$ (quin), $(\text{C}\equiv\text{C}\text{--}\text{H}_2) = 2.46$ (dt, $^4J(\text{H},\text{H}) = 2.2$ Hz), $(\text{C}\equiv\text{H}) = 2.91$ (t, $^4J(\text{H},\text{H}) = 2.2$ Hz, $^2J(\text{Pt},\text{H}) = 68$ Hz), $(\text{O}\text{--}\text{CH}_2) = 3.57$ (s). ^{13}C NMR (CD_2Cl_2 , 50 MHz, 233 K): $\delta(\text{CH}_3) = 13.4$, $(\text{Me}\text{--}\text{CH}_2) = 18.0$, $(\text{Et}\text{--}\text{CH}_2) = 21.9$, $(\text{C}\equiv\text{C}\text{--}\text{H}_2) = 32.5$, $(\text{C}\equiv\text{C}\text{--}\text{H}) = 58.3$, $(\text{O}\text{--}\text{CH}_2) = 70.0$, $(\text{C}\equiv\text{H}) = 80.1$.

2c: Anal. Found: C, 31.32; H, 4.91; Cl, 15.99. $\text{C}_{18}\text{H}_{34}\text{Cl}_3\text{KO}_6\text{Pt}$ (687.01). Calc.: C, 31.47; H, 4.99; Cl, 15.48. Fp. (dec.): $91\text{--}95^\circ\text{C}$. Infrared: $\nu(\text{C}\equiv\text{H}) = 3171\text{ cm}^{-1}$ (m), $\nu(\text{C}\text{--}\text{O}) = 1106\text{ cm}^{-1}$ (s), $\nu(\text{Pt}\text{--}\text{Cl}) = 330$ (sh), 325 (m), 310 (sh) cm^{-1} . Raman: $\nu(\text{C}\equiv\text{C}) = 1905\text{ cm}^{-1}$ (m), $\nu(\text{Pt}\text{--}\text{Cl}) = 331$ (s), 312 (m) cm^{-1} . ^1H NMR (CD_2Cl_2 , 200 MHz, 233 K): $\delta(\text{CH}_3) = 1.51$ (s), $(\text{C}\equiv\text{H}) = 2.87$ (s, $^2J(\text{Pt},\text{H}) = 70$ Hz), $(\text{O}\text{--}\text{CH}_2) = 3.59$ (s). ^{13}C NMR (CD_2Cl_2 , 50 MHz, 233 K): $\delta(\text{CH}_3) = 29.0$, $(\text{CMe}_3) = 30.3$, $(\text{C}\equiv\text{C}\text{--}\text{H}) = 56.2$, $(\text{O}\text{--}\text{CH}_2) = 70.1$, $(\text{C}\equiv\text{H}) = 87.9$.

2d: Anal. Found: C, 31.71; H, 4.56; Cl, 22.25. $\text{C}_{21}\text{H}_{32}\text{Cl}_5\text{KO}_6\text{Pt}$ (791.93). Calc.: C, 31.85; H, 4.07;

Cl, 22.38. Fp. (dec.): $85\text{--}88^\circ\text{C}$. Infrared: $\nu(\text{C}\equiv\text{H}) = 3149\text{ cm}^{-1}$ (m), $\nu(\text{C}\text{--}\text{O}) = 1108\text{ cm}^{-1}$ (s), $\nu(\text{Pt}\text{--}\text{Cl}) = 331$ (m), 310 (w) cm^{-1} . Raman: $\nu(\text{C}\equiv\text{C}) = 1908\text{ cm}^{-1}$ (m), $\nu(\text{Pt}\text{--}\text{Cl}) = 334$ (s), 311 (m) cm^{-1} . ^1H NMR (CD_2Cl_2 , 200 MHz, 233 K): $\delta(\text{O}\text{--}\text{CH}_2) = 3.55$ (s), $(\text{C}\equiv\text{H}) = 3.86$ (s, $^2J(\text{Pt},\text{H}) = 66$ Hz), $(m, p\text{--}\text{CH}) = 7.40$ (m), $(o\text{--}\text{CH}) = 8.05$ (m). ^{13}C NMR (CD_2Cl_2 , 50 MHz, 233 K): $\delta(\text{C}\equiv\text{H}) = 63.8$, $(\text{O}\text{--}\text{CH}_2) = 69.5$, $(\text{C}\equiv\text{C}\text{--}\text{H}) = 75.6$, $(i\text{--}\text{C}) = 120.4$, $(m\text{--}\text{C}) = 128.6$, $(p\text{--}\text{C}) = 129.7$, $(o\text{--}\text{C}) = 132.1$.

2e: Anal. Found: C, 31.91; H, 4.46; Cl, 22.43. $\text{C}_{21}\text{H}_{31}\text{Cl}_5\text{DKO}_6\text{Pt}$ (792.93). Calc.: C, 31.81; H, 4.19; Cl, 22.36. Fp. (dec.): $87\text{--}90^\circ\text{C}$. Infrared: $\nu(\text{C}\equiv\text{D}) = 2433\text{ cm}^{-1}$ (m), $\nu(\text{C}\text{--}\text{O}) = 1108\text{ cm}^{-1}$ (s), $\nu(\text{Pt}\text{--}\text{Cl}) = 331$ (m), 312 (w) cm^{-1} . Raman: $\nu(\text{C}\equiv\text{C}) = 1828\text{ cm}^{-1}$ (m), $\nu(\text{Pt}\text{--}\text{Cl}) = 334$ (m), 312 (w) cm^{-1} . ^1H NMR (CD_2Cl_2 , 200 MHz, 233 K): $\delta(\text{O}\text{--}\text{CH}_2) = 3.55$ (s), $(m, p\text{--}\text{CH}) = 7.40$ (m), $(o\text{--}\text{CH}) = 8.05$ (m). ^{13}C NMR (CD_2Cl_2 , 125 MHz, 203 K): $\delta(\text{C}\equiv\text{D}) = 64.0$ (t, $^1J(\text{C},\text{D}) = 37$ Hz), $(\text{O}\text{--}\text{CH}_2) = 70.0$, $(\text{C}\equiv\text{C}\text{--}\text{D}) = 75.5$, $(i\text{--}\text{C}) = 120.3$, $(m\text{--}\text{C}) = 128.4$, $(p\text{--}\text{C}) = 129.6$, $(o\text{--}\text{C}) = 131.1$.

3.2. X-ray structure determination

A STOE-IPDS diffractometer was used. Intensities were collected with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). All non-hydrogen atoms were refined anisotropically. The H atoms have been

Table 5
Crystal data and structure refinement for **2e**· CH_2Cl_2

Formula	$\text{C}_{21}\text{H}_{31}\text{Cl}_5\text{DKO}_6\text{Pt}$
Mol. wt.	792.93
Temperature	220(2) K
Radiation	Mo $K\alpha$
Crystal size	$0.3 \times 0.2 \times 0.1\text{ mm}^3$
Crystal system	triclinic
Space group	$\text{P}\bar{1}$ (No. 2)
Z	2
a, b, c	10.155(2), 11.368(3), 14.047(2) Å
α, β, γ	86.28(2), 70.42(1), 77.64(2)°
V	1492.4(5) Å ³
D_{calc}	1.762 g cm ^{−3}
$\mu(\text{Mo } K\alpha)$	5.32 mm ^{−1}
F(000)	776
θ Range for data collection	1.83–24.12°
Total data	13121
Total unique data	4458
Observed data ($F > 4\sigma(F)$)	3939
R_{int}	0.0987
wR_2	0.0994
R1	0.0418
GooF	1.048
Parameters	426
Residual density max./min.	1.198/−1.722 e Å ^{−3}

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $2\mathbf{e} \cdot \text{CH}_2\text{Cl}_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Pt(1)	5873(1)	–1421(1)	6377(1)	40(1)
K(1)	6646(2)	1714(2)	7684(1)	42(1)
Cl(1)	7212(3)	–3197(2)	5585(2)	70(1)
Cl(2)	4492(2)	367(2)	7150(2)	50(1)
Cl(3)	7693(2)	–1158(2)	6938(2)	56(1)
Cl(4)	6647(4)	4570(3)	8242(4)	124(2)
Cl(5)	9417(5)	4844(4)	8083(5)	163(2)
O(1)	4445(7)	2060(5)	9596(4)	57(2)
O(2)	7301(7)	1453(5)	9519(5)	60(2)
O(3)	9536(6)	1083(5)	7684(5)	58(2)
O(4)	8945(6)	2271(5)	6020(4)	49(1)
O(5)	6121(6)	3079(5)	6044(4)	44(1)
O(6)	3977(6)	3418(5)	7940(5)	55(1)
C(1)	4491(12)	–1442(9)	5548(8)	57(2)
C(2)	3913(10)	–1864(7)	6376(7)	52(2)
C(3)	2927(9)	–2312(7)	7243(6)	47(2)
C(4)	1478(11)	–2004(9)	7438(9)	65(3)
C(5)	559(10)	–2417(9)	8239(8)	67(3)
C(6)	1046(12)	–3219(10)	8921(8)	70(3)
C(7)	2508(14)	–3540(10)	8735(9)	74(3)
C(8)	3447(10)	–3100(8)	7917(7)	56(2)
C(9)	8225(14)	4938(12)	7445(12)	104(4)
C(10)	4871(14)	2006(12)	10461(7)	74(3)
C(11)	6180(14)	1077(11)	10325(8)	70(3)
C(12)	8665(14)	737(11)	9437(9)	74(3)
C(13)	9779(12)	1221(11)	8607(9)	70(3)
C(14)	10635(10)	1388(10)	6824(9)	65(2)
C(15)	10160(10)	1343(10)	5947(8)	64(3)
C(16)	8565(10)	2383(9)	5120(6)	53(2)
C(17)	7299(10)	3402(8)	5265(6)	51(2)
C(18)	4866(10)	4003(8)	6225(7)	55(2)
C(19)	3655(10)	3598(10)	7018(8)	56(2)
C(20)	2867(10)	3048(11)	8739(8)	66(3)
C(21)	3241(12)	2995(12)	9679(8)	76(3)

found in the difference Fourier map and could be refined isotropically except the H atoms of the solvent molecule which were placed in calculated positions. The structure was solved by direct methods using the program SHELXS-86 [30]. The structure refinement was carried out by full-matrix least-squares procedures on F^2 (SHELXL-93 [31]). Crystal data and details of the data collection and refinement for $2\mathbf{e}$ are summarized in Table 5. The final atomic coordinates are listed in Table 6.

3.3. Quantum chemical calculations

Optimization of the structure $[\text{PtCl}_3(\text{PhC}\equiv\text{CH})]^-$ was carried out with the program TURBOMOLE [32] by using an effective core potential and DZ basis functions for Pt [33] and STO-3G basis functions for all other atoms on an IBM RS/6000-580 work station (ca. 10 h CPU-time). Such an unbalanced basis set may not be

able to compare energies but is useful for getting optimized structures.

4. Supplementary material

Tables of hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, all bond distances and bond angles are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, citing the deposition No. CSD-407056, the authors and the reference.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the companies Merck (Darmstadt) and Degussa (Hanau) for gifts of chemicals as well as Dr. Karla Schenzel for IR and Raman spectroscopic investigations.

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