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A New Example of Etherification Reaction on a Platinum Complex. Crystal and Molecular Structure of *trans*-Chloro(1-ethinoxycyclohexylethynyl)bis(triphenylphosphine)platinum(II)

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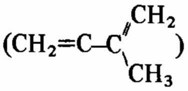
During our investigations on the synthesis of complexes of platinum with acetylenes, we found that the reaction between *cis*-$(Ph_3P)_2PtCl_2$ and hydrazine hydrate in the presence of isopropenylacetylene gives the platinum–isoprene complex *trans*-$(Ph_3P)_2PtCl$-  $(CH_2{=}C{-}C(\overset{\textstyle CH_2}{/\!/})(\underset{\textstyle CH_3}{\backslash}))$ (A) [1]. Its formation occurs by insertion of the isopropenylacetylene molecule into the Pt–H bond of *trans*-$(Ph_3P)_2PtHCl$, which in turn results as a hydrazine reduction product of *cis*-$(Ph_3P)_2PtCl_2$ [2].

Compound A was also obtained directly from *trans*-$(Ph_3P)_2PtHCl$ and isopropenylacetylene and the same insertion reaction occurs with phenylacetylene [1].

As an extension of these studies, we have examined the reaction between *trans*-$(Ph_3P)_2PtHCl$ and acetylenic alcohols. In this preliminary note we discuss the behaviour of 1-ethylcyclohexan-1-ol. The choice of this acetylenic alcohol was suggested by the fact that J. H. Nelson *et al.* [3] obtained from $(Ph_3P)_4Pt$ and 1-ethynylcycloexan-1-ol the dihydride $(Ph_3P)_2PtH_2(C{\equiv}C{-}R)_2$ ($R = C_6H_{10}OH$), which is the unique platinum bis-hydride-bis-acetylide complex known at present.

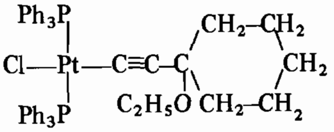
Thus, under our reaction conditions, the analogous $(Ph_3P)_2PtH_2Cl(C{\equiv}C{-}R)$ could alternatively be expected, should the insertion reaction into the Pt–H bond not occur.

The reaction follows however, a different path. When *trans*-$(Ph_3P)_2PtHCl$ and 1-ethynylcyclohexan-1-ol are warmed in benzene, after addition of ethanol, on standing overnight, a crystalline product (B) separates*. Its IR spectrum exhibits a band at about 2100 cm^{-1}, suggesting the presence of triple bonds in the molecule and weak bands in the region 1550–1600 cm^{-1}, thus excluding a simple insertion reaction.

The low frequency IR spectrum shows a band at 320 cm^{-1} characteristic of a Pt–Cl bond. However no bands are present in the region of OH stretching vibrations, as we observed previously in the IR spectra of the complexes obtained from α-hydroxyacetylenic alcohols and *cis*-$(Ph_3P)_2PtCl_2$. In fact in the course of the reactions complexes of alkenylalkynes were obtained; dehydration reactions take place and the tertiary alcoholic groups are converted into alkenyl groups [4].

The NMR spectrum of the reaction product B does not exhibit resonances indicating the presence of olefinic protons. Furthermore no metal hydride resonances have been evidentiated in the high field 10–40 τ region of the NMR spectrum. This result excluded that the product B was a mono or a dihydride platinum complex.

An X-ray crystal structure analysis was carried out to clarify the nature of the product. This showed the complex to be



(B)

where the ethyl ether of 1-ethynylcyclohexan-1-ol is present, σ-bonded to platinum. As can be seen from Fig. 1 the complex is monomeric with two triphenylphosphine molecules coordinated *trans* to platinum. The fourth coordination site is occupied by a chlorine

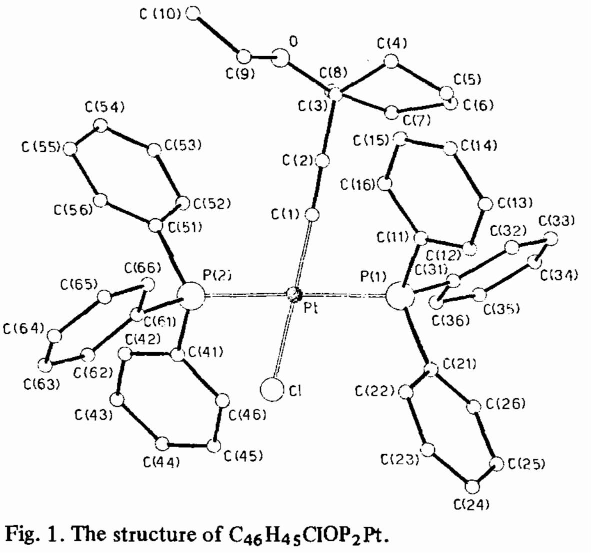


Fig. 1. The structure of $C_{46}H_{45}ClOP_2Pt$.

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*The same product is obtained using only ethanol as reaction medium, as for isopropenylacetylene and phenylacetylene [1].

TABLE I. Atomic Coordinates.

	x/a(σ)	y/b(σ)	z/c(σ)
Pt	0.2218(1)	0.2982(1)	0.2800(1)
P(1)	0.2279(3)	0.3029(2)	0.4778(3)
P(2)	0.2049(3)	0.2968(2)	0.0805(3)
Cl	0.3157(5)	0.3994(2)	0.2986(3)
O	0.1557(39)	0.0440(16)	0.1708(25)
C(1)	0.1493(17)	0.2135(7)	0.2653(13)
C(2)	0.1229(20)	0.1563(9)	0.2608(15)
C(3)	0.0954(23)	0.0856(10)	0.2590(18)
C(4)	0.1436(45)	0.0509(20)	0.3720(34)
C(5)	0.0657(53)	0.0874(22)	0.4508(36)
C(6)	−0.1164(59)	0.1004(23)	0.3885(41)
C(7)	−0.1802(54)	0.1102(24)	0.2577(43)
C(8)	−0.0728(48)	0.0838(19)	0.1847(33)
C(9)	0.3255(52)	0.0391(22)	0.1698(36)
C(10)	0.3620(73)	−0.0094(34)	0.0792(52)
C(11)	0.3833(15)	0.2390(6)	0.5641(11)
C(12)	0.4454(18)	0.2510(8)	0.6797(13)
C(13)	0.5616(20)	0.2012(9)	0.7445(15)
C(14)	0.6118(23)	0.1406(10)	0.6872(17)
C(15)	0.5479(22)	0.1295(9)	0.5679(16)
C(16)	0.4365(19)	0.1781(8)	0.5048(14)
C(21)	0.2528(16)	0.3836(7)	0.5620(12)
C(22)	0.3938(18)	0.4053(8)	0.5773(14)
C(23)	0.4162(24)	0.4672(10)	0.6400(18)
C(24)	0.2950(28)	0.5098(12)	0.6820(20)
C(25)	0.1527(28)	0.4879(12)	0.6653(20)
C(26)	0.1316(21)	0.4260(9)	0.6017(15)
C(31)	0.0464(15)	0.2905(6)	0.5005(11)
C(32)	0.0447(17)	0.2559(7)	0.5983(12)
C(33)	−0.0967(21)	0.2492(9)	0.6112(15)
C(34)	−0.2335(20)	0.2754(9)	0.5339(15)
C(35)	−0.2322(22)	0.3094(9)	0.4409(16)
C(36)	−0.0898(19)	0.3148(8)	0.4201(14)
C(41)	0.0446(14)	0.3622(6)	0.0059(10)
C(42)	−0.0095(18)	0.3605(8)	−0.1138(13)
C(43)	−0.1351(20)	0.4106(9)	−0.1675(15)
C(44)	−0.2058(19)	0.4611(8)	−0.1000(14)
C(45)	−0.1512(18)	0.4641(8)	0.0186(13)
C(46)	−0.0250(17)	0.4143(7)	0.0735(12)
C(51)	0.1734(16)	0.2204(7)	−0.0149(12)
C(52)	0.0373(17)	0.1981(8)	−0.0232(13)
C(53)	0.0034(22)	0.1417(9)	−0.1022(16)
C(54)	0.1015(26)	0.1121(11)	−0.1706(19)
C(55)	0.2418(23)	0.1345(10)	−0.1657(16)
C(56)	0.2725(19)	0.1899(8)	−0.0848(14)
C(61)	0.3805(14)	0.3130(6)	0.0538(10)
C(62)	0.3755(17)	0.3561(7)	−0.0309(13)
C(63)	0.5141(21)	0.3640(9)	−0.0534(15)
C(64)	0.6558(22)	0.3305(9)	0.0132(16)
C(65)	0.6589(23)	0.2898(10)	0.0979(17)
C(66)	0.5213(19)	0.2791(8)	0.1216(14)

atom. The Ligands are arranged around the metal in a nearly square planar configuration.

The geometry in the coordination plane can be compared with that observed in other Pt(II) complexes with the same *trans*-configuration [8]. The Pt–Cl and Pt–C distances fall in the range of values found in chloro-platinum(II) complexes where σ-donor ligands *trans* to chlorine exert a moderate *trans* influence [9]. The cyclohexyl ring is in a twisted-chair conformation flattened at C(7) with the Pt–C–C system in axial position. The geometry of the triphenylphosphine groups shows no unusual features.

The structural analysis evidentiates the influence of the substituent R of the acetylene molecule H–C≡C–R on the reactivity of monosubstituted acetylenes and the property of bis(triphenylphosphine)platinum chlorinated complexes to lead to the formation of alkenylalkynes [4] or to the formation of ethers as in this case. When μ-complexes $(Ph_3P)_2Pt(H–C≡C–R)$

TABLE II. Some Bond Lengths (Å) and Angles (deg).

Pt–Cl = 2.345(5)
Pt–C(1) = 1.935(15)
Pt–P(1) = 2.307(4)
Pt–P(2) = 2.310(4)

C(1)–C(2) = 1.22(2)
C(2)–C(3) = 1.49(3)
C(3)–C(4) = 1.49(4)
C(3)–C(8) = 1.55(5)
C(4)–C(5) = 1.37(6)
C(5)–C(6) = 1.60(7)
C(6)–C(7) = 1.51(7)
C(7)–C(8) = 1.45(6)
C(3)–O = 1.41(4)
C(9)–O = 1.53(6)

Cl–Pt–P(1) = 92.9(1)
Cl–Pt–P(2) = 86.8(1)
P(1)–Pt–C(1) = 87.1(5)
P(2)–Pt–C(1) = 93.3(5)
Cl–Pt–C(1) = 178.7(5)
P(1)–Pt–P(2) = 177.4(1)
Pt–C(1)–C(2) = 172(1)
C(1)–C(2)–C(3) = 178(2)
C(2)–C(3)–C(4) = 118(2)
C(2)–C(3)–C(8) = 109(2)
C(2)–C(3)–O = 110(2)
C(4)–C(3)–O = 111(2)
C(8)–C(3)–O = 90(2)
C(8)–C(3)–C(4) = 115(3)
C(3)–C(4)–C(5) = 110(3)
C(4)–C(5)–C(6) = 108(4)
C(5)–C(6)–C(7) = 123(4)

C(6)–C(7)–C(8) = 116(4)
C(7)–C(8)–C(3) = 109(3)
C(3)–O–C(9) = 119(3)
O–C(9)–C(10) = 109(4)

(H–C≡C–R = α-hydroxyacetylene) are treated with the corresponding α-hydroxyacetylenes, bis(triphenylphosphine)platinum-bis-acetylides are obtained [4, 5] and no dehydration reactions occur.

This peculiar property of chlorinated platinum complexes is the object of further investigation.

Experimental

Reagents and Apparatus

1-ethynylcyclohexan-1-ol (Fluka), benzene and absolute ethanol (C. Erba) were used without further purification.

trans-$(Ph_3P)_2PtHCl$ was prepared by the literature method [6].

Spectra were recorded on a Perkin Elmer mod. 521 (IR) and Bruker WH-90 (NMR) instruments.

Preparation

0.5 g of *trans*-$(Ph_3P)_2PtHCl$ were dissolved in 10 ml of benzene and 1 g of 1-ethynylcyclohexan-1-ol was added. The mixture was refluxed about 30 minutes and then 20 ml of absolute ethanol were added. On standing about 24 hours a white crystalline product separated, which was recrystallized from benzene–ethanol. Yield 51%. M.p. (uncorr.) 194–196 °C. *Anal.* Calculated for $C_{46}H_{45}ClOP_2Pt$, C% 60.93; H% 5.00; found: C% 61.04; H% 4.86.

Crystal Data

$C_{46}H_{45}ClOP_2Pt$, M = 906.4, triclinic, space group $P\bar{1}$ (from structural analysis), a = 9.104(1), b = 20.107(2), c = 11.775(1) Å, α = 96.43(1), β = 105.58(1), γ = 77.03(1)°, V = 2020 Å^3, Z = 2, D_x = 1.489 g cm^{-3}, μ(Mo-Kα) = 38.3 cm^{-1}.

Data were collected on a Siemens on-line single crystal diffractometer using Mo-Kα radiation; 7092 independent reflections ($5 \leqslant 2\theta \leqslant 50°$) were measured from a crystal of dimensions 0.05 × 0.24 × 0.40 mm. The coordinates of Pt, Cl and P atoms were located from a three-dimensional Patterson distribution. One Fourier map revealed the positions of all the remaining non-hydrogen atoms. Refinement was by full-matrix least-squares [7] assuming anisotropic thermal vibrations for Pt, Cl and P, and isotropic ones for the other atoms. The final R value is 7.9% for 5355 independent data ($I > 2\sigma(I)$) not corrected for absorption.

The structure is shown in Figure 1; final atomic fractional coordinates are quoted in Table I, some pertinent bond distances and angles are listed in Table II.

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