Coordination Chemistry of Perhalogenated Cyclopentadienes and Alkynes. 17.[1] Reaction of Dichloroethyne with Platinum(0) Phosphine Complexes: Formation of a π-Complex, Isomerization to β-Chloroethynyl Complexes, and Syntheses of Diplatinioethyne Derivatives. Molecular Structures of (Ph₃P)₂Pt(η²-ClC≡CCl) and Cl(Ph₃P)₂Pt—C≡C—Pt(PPh₃)₂Cl[†]

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Dichloroethyne ClC≡CCl reacts with Pt(PPh₃)₂(C₂H₄) or Pt(PPh₃)₄ to give the π-complex Pt(PPh₃)₂(η²-ClC≡CCl) (1), which can be isomerized by prolonged refluxing in toluene to *trans*-(Ph₃P)₂ClPt—C≡CCl (2). 2 easily undergoes exchange reactions with alkylphosphines and with halide anions to yield *trans*-(R₃P)₂ClPt—C≡CCl (R = Et (3), Bu (4)) and *trans*-(Ph₃P)₂-(X)Pt—C≡CCl (X = F (5a), Br (5b), I (5c)), respectively. The alkylphosphine complexes 3 and 4 can also be obtained by reaction of Pt(PR₃)₄ (R = Et, ⁿBu) with ClC≡CCl or from 1 and the corresponding phosphine. When Pt(PPh₃)₂(C₂H₄) is added to a solution of 3, a dinuclear complex 6 is formed, in which the C≡C—Cl group acts as a σ,π-bridging ligand. Upon standing, oxidative addition of the remaining C—Cl bond occurs and the μ-ethynediyl complex *trans*-Cl(R₃P)₂Pt—C≡C—Pt(PPh₃)₂Cl-*cis* (R = Et (7a)) can be obtained. The corresponding μ-ethynediyl complex 7b (R = Ph) is formed directly from 2 and Pt(PPh₃)₂(C₂H₄). 7b isomerizes upon heating in toluene to the symmetrical all-trans isomer 8. The molecular structures of 1 and 8 were determined by X-ray diffraction (1: C₃₈H₃₀Cl₂P₂Pt·CH₂Cl₂, a = 10.311(3) Å, b = 10.392(4) Å, c = 33.675(16) Å, β = 90.17(3)°, monoclinic, P2₁/n, Z = 4. 8: C₇₄H₆₀Cl₂P₄Pt₂, a = 12.938(2) Å, b = 19.964(3) Å, c = 24.844(3) Å, β = 96.14(1)°, monoclinic, C2/c, Z = 4).

Introduction

Although the dihaloethynes are among the most reactive alkynes,[2] their coordination chemistry has been scarcely explored.[3] However, the few examinations that have been published show quite a "normal" coordination behavior, i.e. formation of π-complexes including dicobaltiotetrahedranes,[4,5] or cyclization reactions with or without incorporation of carbonyl ligands.[6,7] Only sometimes do they make use of their C–X functionality, i.e. oxidative addition of one C–X bond,[8,9] nucleophilic substitution of one or two halide ions,[10] isomerization to a dihalovinylidene ligand,[11] or oxidation of the metal by the positive halogen substituent.[12] During the course of our investigations on the coordination behavior of unsaturated halocarbons, we felt a more systematic examination of the coordination chemistry of this class of compounds, particularly of the most reactive of them, dichloroethyne, might be helpful to make use of their synthetic potential. Several years ago, we reported in a preliminary communication[9a] about the reaction of ClC≡CCl with Pt(PPh₃)₂(C₂H₄). Here we present a full account of this work and some related reactions.

Results and Discussion

In our preliminary communication, we reported that addition of a toluene solution of Pt(PPh₃)₂(C₂H₄) to a large excess of an ethereal solution of ClC≡CCl yielded the product *cis*-[Pt(PPh₃)₂(Cl)(C≡CCl)] (2a) by oxidative addition of one C—Cl bond to the Pt(PPh₃)₂ moiety. Just by dissolving in CH₂Cl₂, 2a isomerized to *trans*-[Pt(PPh₃)₂-(Cl)(C≡CCl)], 2, the crystal structure of which could be determined.[9a] We wondered if the reaction proceeded—as with monohaloalkynes[13]—via a π-complex of dichloroethyne.

Indeed, just by changing the reaction conditions (addition of an equimolar amount of the alkyne solution to the solution of Pt(PPh₃)₂(C₂H₄)), the π-complex Pt(PPh₃)₂-(ClC≡CCl) (1) could be obtained in high yield as the only

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Chart 1
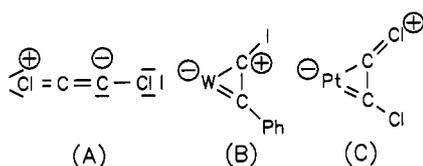
isolable product (besides traces of Pt(PPh₃)₂Cl₂). Using Pt(PPh₃)₄ as a starting material, 1 can be isolated in even higher yields, and no other products (besides free PPh₃) are formed. This is quite interesting, since with Pd(PPh₃)₄ we observed preformation of an ethynyl—phosphonium salt which finally yielded a phosphonium acetylide complex.[9b].

In sharp contrast to the explosiveness and instability of the free alkyne,[2] 1 decomposes in the solid state only at 220 °C and can be refluxed in CH₂Cl₂ or in benzene for several hours without decomposition.

IR Spectrum. Alkyne π-complexes of the Pt(PPh₃)₂ fragment usually display a more or less intense ν(C≡C) band between 1600 and 1800 cm⁻¹.[14,15] In the IR spectrum of 1, however, there is only one characteristic absorption besides those belonging to the PPh₃ ligands, a medium intensity band at ca. 840 cm⁻¹. This band might be due to the ν(C—Cl) vibration of the coordinated alkyne. (In free gaseous dichloroethyne this band is observed at ca. 990 cm⁻¹,[16] in the W(IV) dichloroethyne complexes described by Dehnicke et al. bands between 810 and 850 cm⁻¹ were attributed to the C—Cl vibration, but in the corresponding diiodoethyne complex several bands between 830 and 990 cm⁻¹ were interpreted as W—C vibrations.[5] Thus, as Pt is slightly heavier than W, Pt—C vibrations might also occur between 800 and 900 cm⁻¹.) Three intense bands at ca. 540, 520, and 510 cm⁻¹ are indicative of a mutual cis arrangement of two PPh₃ ligands.[17] The lack of any ν(C≡C) band needs explanation. The generally lower intensity of these bands in free monohaloalkynes has been reported,[18] but this effect seems usually to disappear on complexation.[5b,13b] Low intensities of the ν(C≡C) bands in complexes PtL₂(π-alkyne) are usually observed with donor-substituted alkynes.[15] A partial positive charge on the chlorine atoms (see A in Chart 1), as was already postulated from some reactions of the free alkyne,[2] supports this aspect of chlorine acting as a donor substituent. A strong contribution of a carbene-like bonding, according to formula B in Chart 1, was recently postulated for [WCl₄(Ph—C≡C—I)(THF)], where also no ν(C≡C) vibration could be found in the IR spectrum.[19] Consequently, the structure of 1 might be similar to formula C in Chart 1.

NMR Spectra. The ³¹P NMR chemical shift usually observed with complexes Pt(PPh₃)₂(η²-alkyne) ranges from 21 to 31 ppm (relative to external H₃PO₄), with the more electronegatively substituted alkynes at the high-field side.[20] Although there seems to be no general trend in the

Table 1. Relevant ³¹P, ¹³C, and ¹⁹⁵Pt NMR Data[i]

compd	δ(³¹P)	¹J_{PtP}	²J_{PP}	δ(¹³C_α)	δ(¹³C_β)	¹J_{PtC}	²J_{PtC}	δ(¹⁹⁵Pt)
1	22.2	3292		108.7	108.7[a]	405		-602
2	21.7	2616						
2a	19.3 (d)	2361	17.5					
	13.4 (d)	3740						
3	15.0	2361		59.3*	66.3*[b]	1501	500	-632*
4	8.2	2347		60.0*	65.8*[c]	1505	499	-642*
4a	9.1 (d)	2530	437					
	22.1 (d)	2388						
5a	19.6 (d)	2765[d]						
5b	20.7	2581						
5c	18.0	2539						
6	9.1	2713						
	29.9 (d)	3208[e]	31					
	32.6 (d)	3559[f]						
7a	24.3 (d)	2312	16[g]					
	15.2	2474						
	10.9 (d)	3954						
7b	21.5 (s)	2816						
	20.4 (d)	2151	16[h]					
	10.6 (d)	4018						
8	20.5	2837						
9	6.2	2514						
10	5.8 (s)	2460						
	0.2 (d)	2324	23					
	-5.2 (t)	2288						

[a] N = |J_{C-P} + J_{C-P}| = 152 Hz. [b] ²J_{PC} = 15 Hz. ³J_{PC} = 3 Hz. [c] ²J_{PC} = 15 Hz. [d] ²J_{FP} = 18 Hz. [e] ⁴J_{PtP} = 81 Hz. [f] ³J_{PtP} = 118 Hz. [g] ⁴J_{PtP} = 64 Hz. [h] ⁴J_{PtP} = 69 Hz. [i] All spectra recorded in CH₂Cl₂ solution, except where marked by * (in C₆D₆). Chemical shifts in ppm, coupling constants in Hz.

magnitudes of the ¹J(Pt—P) coupling constants, it was noted that "acetylenes having electron-withdrawing substituents give larger Pt—P coupling constants".[20] Thus, the coupling constant observed in 1 (see Table 1), being the lowest one described so far for Pt(0) alkyne complexes, indicates—like the IR results—a donor property of the halogen, while the ³¹P chemical shift is more typical for an acceptor. It should be noted, however, that the signals for the phosphorus trans to the CX group in Pt-(PPh₃)₂(Me₃Si—C≡C—X) (X = Cl, Br) show also rather low Pt—P coupling constants (3359 Hz/3384 Hz).[21]

In the ¹³C NMR spectrum, the alkyne carbon atoms form the X part of an AA'X system (at 67.9 MHz). The chemical shift (108.7 ppm) is observed at a relatively high field when compared with other compounds of the type Pt(PR₃)₂(R'C≡CR''), and the coupling constant ¹J(¹⁹⁵Pt—¹³C) of 405 Hz is one of the largest observed in π-alkyne complexes of Pt(0).[22] This indicates a high s electron density in the platinum—carbon bond and thus is consistent with a carbene-like structure (*vide supra*) (which also was postulated for the R—C≡C—SiMe₃ complexes from the ¹³C NMR parameters[22]). The chemical shift must be interpreted as a (dynamic) superposition of the two different carbon atoms in the "frozen" structure (C), as only half of the time each carbon atom is expected to have the *carbene*-like bonding to platinum; e.g. 109 ppm might be the averaged signal of a weakly bonded ≡C—Cl group, expected at δ = 60–70 ppm (*vide infra*) and a carbene-like Pt=C—Cl group, expected at δ = 150–160 ppm.[22]

The observed ¹⁹⁵Pt resonance is at the lowest field reported for PtL₂(π-alkyne) complexes (usual range from

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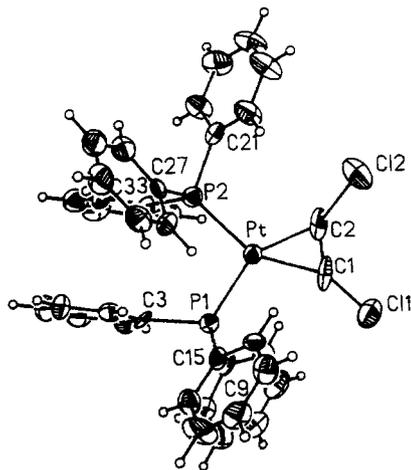
Figure 1. Molecular structure of 1 at −100 °C. Thermal ellipsoids shown at the 50% probability level.

Table 2. Details of the Crystal Structure Determinations

	1	8
formula	$C_{39}H_{32}Cl_4P_2Pt$	$C_{74}H_{60}Cl_2P_4Pt_2$
space group	$P2_1/n$	$C2/c$
cryst syst	monoclinic	monoclinic
a, Å	10.311(3)	12.9375(16)
b, Å	10.392(4)	19.964(3)
c, Å	33.675(16)	24.844(3)
β, deg	90.17(3)	96.14(1)
V, Å^3	3608(2)	6380(1)
Z	4	4
cryst dim, mm	0.38 × 0.25 × 0.10	0.25 × 0.25 × 0.10
cryst color	white	yellow
D(calc), g/cm^3	1.656	1.597
μ(Mo K$_\alpha$), cm^{-1}	43.42	46.51
temp, °C	−100	18
no. of rflns collcd	6699	6057
no. of ind rflns	4715	5559
R(merg), %	3.55	0.94
no. of indpt rflns obsd, $F_o \geq 4\sigma(F_o)$	3526	4328
2θ range, deg	4–45	5–50
data collcd	$+h,\pm k,\pm l$	$+h,+k,\pm l$
abs corr	ψ scan	ψ scan
transm	0.110/0.158	0.030/0.050
R/R_w(%) $(w^{-1} = \sigma^2(F_o) + 0.0000(F_o)^2)$	4.44/3.61	3.1/2.55
$\Delta_{max}(\rho)$, e Å^{-3}	0.83	0.84

−4480 to −4741 ppm relative to Na_2PtCl_6[20,23]), the closest value being that of the dicyanoacetylene complex.

Crystal Structure Determination. Since all these spectroscopic results seemed to us a little bit contradictory to each other, we thought an X-ray crystallographic examination might be helpful to understand the bonding in **1**. The result is shown in Figure 1. Details of the structure determination are summarized in Table 2, atomic coordinates are in Table 3, and selected bond lengths and angles are given in Table 5.

The geometry around platinum is planar, the interplanar angle between the PtP_2 plane and the PtC_2 plane being only 3°. The platinum—phosphorus distances are identical within experimental error and absolutely "normal" when compared to other structures of the type $Pt(PPh_3)_2$-(π-alkyne).[24] However, quite unusual is the significant

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Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of $Pt(PPh_3)_2(\pi$-$C_2Cl_2)$

	x	y	z	U(eq)^a
Pt	1107(1)	1872(1)	1369(1)	30(1)
C(1)	−32(10)	3478(10)	1305(3)	51(5)
C(2)	−609(9)	2545(10)	1534(4)	52(5)
Cl(1)	−312(3)	4945(3)	1144(1)	68(1)
Cl(2)	−2074(3)	2408(4)	1776(1)	77(1)
P(1)	3022(3)	2276(3)	1055(1)	32(1)
C(3)	4200(9)	961(9)	985(3)	31(4)
C(4)	5091(9)	649(10)	1286(3)	39(4)
C(5)	5898(10)	−381(11)	1240(4)	58(6)
C(6)	5831(12)	−1137(12)	894(4)	64(6)
C(7)	4977(11)	−800(11)	596(4)	53(5)
C(8)	4170(10)	215(10)	633(3)	43(4)
C(9)	2839(10)	2916(8)	548(3)	29(4)
C(10)	3907(10)	3229(11)	311(3)	47(4)
C(11)	3741(12)	3724(11)	−63(4)	58(5)
C(12)	2527(13)	3952(11)	−211(4)	58(5)
C(13)	1463(12)	3688(10)	26(4)	57(5)
C(14)	1630(10)	3176(11)	397(4)	46(4)
C(15)	3939(9)	3520(9)	1324(3)	32(4)
C(16)	5216(10)	3841(10)	1225(3)	42(4)
C(17)	5821(11)	4848(12)	1441(4)	69(6)
C(18)	5218(11)	5456(11)	1743(4)	49(5)
C(19)	3965(11)	5126(11)	1846(3)	48(5)
C(20)	3340(9)	4152(9)	1637(3)	31(4)
P(2)	1490(3)	−158(3)	1604(1)	32(1)
C(21)	47(9)	−894(9)	1830(3)	32(4)
C(22)	−533(10)	−298(11)	2139(3)	56(5)
C(23)	−1611(10)	−822(12)	2329(4)	63(5)
C(24)	−2146(10)	−1928(13)	2189(3)	60(5)
C(25)	−1566(11)	−2547(12)	1877(4)	61(5)
C(26)	−471(10)	−2052(11)	1695(3)	49(5)
C(27)	2656(8)	−265(10)	2011(3)	25(4)
C(28)	3355(9)	825(10)	2116(3)	37(4)
C(29)	4262(10)	761(11)	2431(3)	46(5)
C(30)	4491(10)	−372(12)	2619(3)	49(5)
C(31)	3768(10)	−1457(11)	2522(3)	46(5)
C(32)	2861(9)	−1400(11)	2222(3)	40(4)
C(33)	1948(10)	−1294(10)	1225(3)	35(4)
C(34)	1212(10)	−1276(10)	875(3)	44(4)
C(35)	1407(11)	−2200(11)	582(3)	52(5)
C(36)	2330(11)	−3146(12)	637(4)	55(5)
C(37)	3061(11)	−3157(12)	973(4)	55(5)
C(38)	2867(10)	−2261(9)	1267(3)	36(4)
Cl(4)	8419(3)	13(4)	279(1)	93(2)
Cl(3)	7768(4)	2708(4)	446(1)	95(2)
C(39)	8079(15)	1209(13)	617(4)	124(9)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

difference in the platinum—carbon distances (more than 6σ), and, corresponding to it, a large difference in the carbon—chlorine bond lengths. One C—Cl bond has about the same length as the one reported for the free alkyne (1.644(11) Å vs 1.64 Å[25]), while the other is more like the C—Cl bond lengths found in $Pt(PPh_3)_2(Cl_2C=CCl_2)$ (1.725(11) Å vs 1.75 Å (averaged)[26]), but still shorter than the 1.78(2) Å found in $PPh_4[WCl_5(C_2Cl_2)]\cdot0.5CCl_4$.[5b] The central C—C triple bond is at 1.375(16) Å drastically lengthened when compared to the free alkyne (1.195 Å by electron diffraction[25]) or to the value of 1.28(3) Å found in the W(IV) complex.[5b] Only in $Pt(PPh_3)_2$-(NC—C≡C—CN) does the C—C bond at "ca. 1.40 Å" (reported as a *preliminary* result 23 years ago(!)[27]) seem to be longer than the one found in **1**. Comparisons with structural features of other Pt(0) complexes of symmetrical

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Table 4. Fractional Coordinates (×10⁴) and Equivalent Thermal Factors (Å² × 10³) of 8

	x	y	z	U(eq)ᵃ
Pt(1)	4313(1)	845(1)	1491(1)	42(1)
C(1)	4830(4)	877(3)	2261(2)	43(2)
Cl(1)	3738(1)	816(1)	543(1)	65(1)
P(1)	3238(1)	−35(1)	1653(1)	46(1)
C(11)	1493(5)	513(4)	1052(3)	78(3)
C(12)	489(5)	487(4)	799(3)	90(3)
C(13)	−24(5)	−104(4)	726(3)	82(3)
C(14)	465(5)	−684(4)	908(3)	71(3)
C(15)	1466(4)	−671(3)	1162(2)	56(2)
C(16)	1980(4)	−60(3)	1240(2)	48(2)
C(21)	3916(5)	−1385(3)	1824(3)	70(3)
C(22)	4443(6)	−1951(3)	1674(3)	89(3)
C(23)	4891(5)	−1974(4)	1196(3)	81(3)
C(24)	4824(6)	−1422(4)	866(3)	79(3)
C(25)	4323(5)	−849(3)	1017(2)	66(2)
C(26)	3874(4)	−817(3)	1498(2)	49(2)
C(31)	1795(4)	31(3)	2419(2)	67(2)
C(32)	1475(5)	−15(4)	2933(3)	82(3)
C(33)	2156(6)	−216(4)	3354(3)	85(3)
C(34)	3160(5)	−368(3)	3277(3)	72(3)
C(35)	3496(4)	−323(3)	2767(2)	59(2)
C(36)	2804(4)	−126(3)	2327(2)	49(2)
P(2)	5404(1)	1699(1)	1296(1)	46(1)
C(41)	7197(5)	1937(3)	801(3)	69(3)
C(42)	7955(5)	1790(4)	469(3)	88(3)
C(43)	7935(6)	1199(5)	202(3)	95(4)
C(44)	7184(6)	727(4)	267(3)	82(3)
C(45)	6419(4)	876(3)	603(2)	65(2)
C(46)	6412(4)	1479(3)	870(2)	52(2)
C(51)	3769(5)	2586(3)	1136(3)	73(3)
C(52)	3102(5)	3028(3)	848(3)	82(3)
C(53)	3256(6)	3202(3)	329(3)	82(3)
C(54)	4084(6)	2950(3)	102(3)	73(3)
C(55)	4765(5)	2523(3)	391(2)	58(2)
C(56)	4629(4)	2334(3)	919(2)	48(2)
C(61)	6948(5)	1755(3)	2144(2)	68(2)
C(62)	7598(6)	2045(5)	2555(3)	90(3)
C(63)	7446(7)	2701(5)	2687(3)	96(4)
C(64)	6656(6)	3068(4)	2421(3)	86(3)
C(65)	6007(5)	2775(3)	1999(3)	67(3)
C(66)	6157(5)	2123(3)	1855(2)	54(2)

ᵃ $U(eq) = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in 1 and 8

	Pt–C$_\alpha$	Pt–P	C$_\alpha$–C$_\beta$	C–Cl	C$_\alpha$–C$_\beta$–Cl
1	2.051(11)	2.282(3)	1.375(16)	1.644(11)	139.7(9)
	1.983(10)	2.287(3)		1.725(11)	134.8(9)
8	1.958(4)	2.303(1)	1.221(9)		
		2.298(1)			
2	1.933(12)	2.327(4)	1.154(19)	1.690(15)	176.9(12)
		2.324(4)			
Tᵃ	1.973(30)	2.280(11)	1.179(48)		
	1.980(38)	2.307(12)			

ᵃ T represents I(Me₃P)₂Pt—C≡C—Pt(PMe₃)₂I;[42b] data for **2** from ref 9a.

alkynes (except for those of hexafluorobutyne) are quite difficult, because it is still today true what Payne stated some 20 years ago: "One notable aspect ... is the fairly high standard deviations associated with the parameters determined in most of metal–acetylene complexes studied".[24c] Besides that, the bond lengths found here are consistent with the above-mentioned *carbene* type structure, as was derived from the IR spectrum and the carbon—platinum coupling constant.

Formation of Alkynyl Complexes. If the structural features just described are real and there is no artifact, then formally one carbon atom (of course, there is no special preference for one particular C atom) is stronger bonded to platinum than the other, and the chlorine atom attached

Scheme 1

Scheme 2
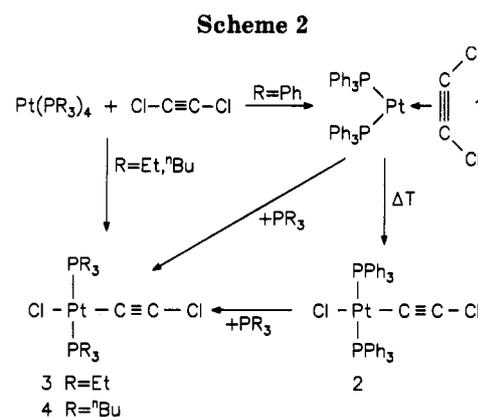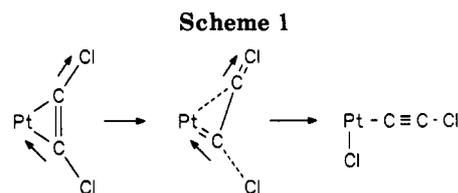
to it is much weaker bonded than in free ClC≡CCl. Theoretically, one could continue this "movement" away from the symmetrical situation, and at the end there would be a scission of the C—Cl bond and of one Pt—C bond: a *cis*-chloro-β-chloroethynyl complex is formed (see Scheme 1), a reaction usually called "oxidative addition".

As mentioned in the Introduction, such a reaction is the only one described for the interaction of di*iodo*ethyne with Pt(PPh₃)₄.[8] For monohaloalkynes the η²-complexes could be isolated and then isomerized to halo–alkynyl compounds Pt(PR₃)₂(X)(C≡CR).[13] Oxidative addition of terminal alkynes to give hydrido–alkynyl complexes and vinylidene complexes is quite common,[14,28] but also some unusual photoinduced C—C breakage reactions to give σ-alkynyl complexes have been reported for Pt(PPh₃)₂-(η²-RC≡CR) (R = Ph,[29] CN,[30] COOMe[31]).

When toluene solutions of **1** are heated to 120 °C for several hours, the π-complex isomerizes to the *trans*-chloro–chloroethynyl complex **2** described by us earlier (see Scheme 2).[9a] Only traces of the cis isomer **2a** can be detected by ³¹P NMR spectroscopy in these solutions, depending on the duration of the reflux process. It is obvious that the trans isomer must be thermodynamically more stable, and this fact prevents the isolation of the cis isomer in the high temperature reaction (see also Scheme 3).

When **1** or **2** was treated with the alkylphosphines PEt₃ or PⁿBu₃, a ³¹P NMR spectroscopic examination of the reaction mixture indicated liberation of PPh₃ with concomitant formation of new platinum *trans*-bis(phosphine) complexes, as can be derived from the ³¹P–¹⁹⁵Pt coupling constants.[32] The same compounds (³¹P NMR), although contaminated with other platinum phosphine complexes,

(28) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987. (c) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132.

(29) Anderson, G. K. A.; Lumetta, G. J.; Siria, J. W. *J. Organomet. Chem.* **1992**, *434*, 253.

(30) Baddley, W: H.; Panattoni, C.; Bandoli, G.; Clemente, D. A.; Belluco, U. *J. Am. Chem. Soc.* **1971**, *93*, 5590.

(31) Kubota, M.; Sly, W. G.; Santarsiero, B. D.; Clifton, M. S.; Kuo, L. *Organometallics* **1987**, *6*, 1257.

(32) (a) Sebald, A.; Wrackmeyer, B.; Beck, W. *Z. Naturforsch. B* **1983**, *38*, 45. (b) Al-Najjar, I. M. *Inorg. Chim. Acta* **1987**, *128*, 93.

Scheme 3
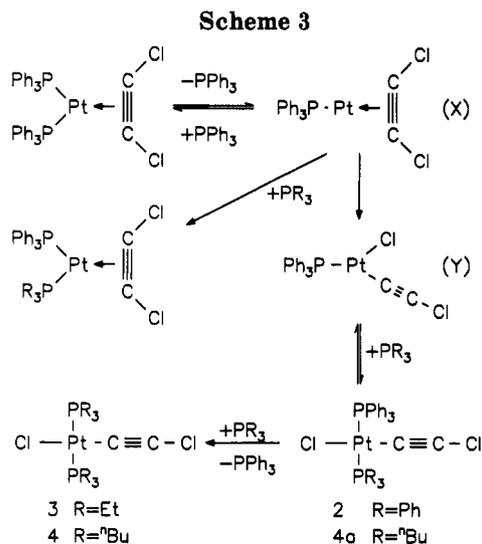
were formed when the complexes $Pt(PR_3)_4$ (R = Et,^{n}Bu) were treated with dichloroethyne. (In the case of PBu$_3$, a compound containing a *trans*-Pt(PPh$_3$)(P^{n}Bu$_3$) moiety could be detected by ^{31}P NMR spectroscopy, when only 1 equiv of PBu$_3$ was carefully added to the solution of **2**.)

IR and NMR Spectra. The IR spectra of **2** and **2a** show no bands between 2300 and 1600 cm^{-1}, while the two alkylphosphine complexes show very weak absorptions at ≈2110 cm^{-1} (visible only after several scans in a FT-IR spectrometer). The relatively strong band at 840 cm^{-1} observed in **1** is in all cases absent. **2** and **2a** only differ in the 550–500-cm^{-1} region, indicative of the relative cis or trans orientation of the phosphine ligands, and between 350 and 250 cm^{-1}, typical for ν(Pt—Cl) and ν(Pt—P) vibrations.[17,33] Characteristic for cis complexes are the medium to strong bands at 541, 301, and 296 cm^{-1} found in **2a**, while the occurrence of only one weak band at 316 ± 2 cm^{-1} in **2** and the two alkylphosphine compounds is consistent with a trans geometry. The solution stability of **2a** and the low solubility of **2** prevented their characterization by ^{13}C NMR spectroscopy. This was, however, possible for both alkylphosphine compounds (see Table 1). The two acetylene carbons could be identified, with significantly different coupling constants to ^{31}P and [195]Pt nuclei, thus indicating that they were not bonded in a symmetrical fashion. We therefore believe that these reaction products are the *trans*-chloro-β-chloroethynyl complexes (R$_3$P)(R′$_3$P)(Cl)Pt(C≡CCl) (R = R′ = Et (**3**), ^{n}Bu (**4**); R = Ph, R′ = ^{n}Bu (**4a**)), as is shown in Scheme 2. The coupling constants [13]C—[195]Pt in **3** are slightly larger than those observed with similar monoalkynyl complexes of Pt(II), e.g. in *trans*-[(Et$_3$P)$_2$(Cl)Pt(C≡CMe)], [1]J(C—Pt) = 1384.2 Hz, [2]J(C—Pt) = 400.6 Hz).[34] The ^{13}C chemical shifts of both carbon atoms are observed at a relatively high field, which is particularly unusual for the β-carbon atoms.[34] This finding, however, parallels the high field absorption of the acetylene carbon atoms in **1** (*vide supra*), and thus, such a chemical shift might be typical for ≡C—Cl groups. The [195]Pt chemical shifts are comparable to the shift observed in the above-mentioned propynyl complex,[34] the small relative low-field shift for **3** and **4** being not significant enough for further discussion.

The mechanism of the oxidative addition reaction merits some discussion. Obviously, with more basic phosphines this reaction takes place at much lower temperatures than with PPh$_3$. Since free ClC≡CCl is a gas at room temperature, a dissociation of the alkyne upon refluxing the toluene solution, followed by oxidative addition to the PtP$_2$ fragment, can be excluded. We therefore believe that in the absence of any other phosphine, dissociation of one PPh$_3$ ligand to form a two-coordinate intermediate (X) is the rate determining step. This intermediate (X) might then undergo fast intramolecular oxidative addition of the coordinated alkyne to give a three-coordinate Pt-(II) intermediate (Y), which then recombines with PPh$_3$ to give **2**, perhaps without preformation of **2a**. If another phosphine is added, it might either undergo addition to X, forming an unsymmetrical π-alkyne complex, or addition to Y to give an unsymmetrical alkynyl complex. Since we could observe complex **4a** (*vide supra*), the latter mechanism might be the right one, at least for PBu$_3$. A complex like **4a** might then lose another molecule of PPh$_3$, which is then substituted by the alkylphosphine and the final product **3** or **4** is formed (Scheme 3). (The formation of **2a** reported in our preliminary communication must operate on a different mechanism, since it was observed in a low temperature reaction.)

Since one of our initial goals was to make use of the high reactivity of dihaloalkynes without the disadvantages of handling volatile toxic and explosive substances all the time, we wanted to examine the chemical reactivities of our chloroalkyne complexes. Although σ-alkynyl complexes of platinum have been known for quite a while, there seem to be hardly any systematic studies on their chemical reactivities.[35,36] Basically, it seemed to us that there are five possible centers of reactivity: (1) the platinum–phosphorus bonds; (2) the platinum–chlorine bond; (3) the platinum–carbon bond; (4) the carbon–carbon triple bond; (5) the carbon–chlorine bond. Phosphine exchange reactions have been reported for several complexes of the metals of the platinum triad,[37] but to the best of our knowledge no such reactions have been reported for σ-alkynyl complexes; thus the above-mentioned syntheses of **3** and **4** starting from **2** are the first reports on such substitutions. In the case where the mixed phosphine complex **4a** could be detected, the final product consisted always of a mixture of **2** and **4** plus PPh$_3$, indicating that the reaction of **4a** with PBu$_3$ proceeded even faster than the reaction of **2**, thus leaving half of the starting material unreacted. However, the possibility of a disproportionation reaction of **4a** into **4** and **2** upon attempted isolation cannot be ruled out.

Halide exchange reactions are well-known in platinum-(II) chemistry,[35b,37a,38] although there seem to be no fluoro derivatives of alkynyl complexes in the literature. Again, we tried these reactions with **2**, and all three halide derivatives Pt(PPh$_3$)$_2$(X)(C≡CCl) (X = F (**5a**), Br (**5b**), I (**5c**)) could be obtained with AgF, KBr, or KI in clean and high-yield reactions (Scheme 4). The coupling con-

(33) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Ed.; Wiley-Interscience: New York, 1970; p 214.

(34) Sebald, A.; Stader, C.; Wrackmeyer, B.; Bensch, W. *J. Organomet. Chem.* **1986**, *311*, 233.

(35) (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 6, pp 547, 570. (b) *Ibid.*, p 530. (c) *Ibid.*, p 537.
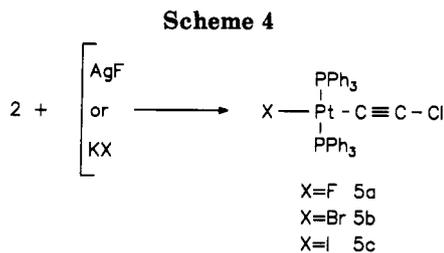
(36) (a) Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. *Inorg. Chem.* **1977**, *16*, 677. (b) Bell, R. A.; Chisholm, M. H. *Ibid.* 687. (c) Bell, R. A.; Chisholm, M. H. *Ibid.* 698.

(37) (a) Rahn, J. A.; Holt, M. S.; Nelson, J. H. *Polyhedron* **1989**, *8*, 897. (b) Chaloner, P. A.; Broadwood-Strong, G. T. L. *J. Organomet. Chem.* **1989**, *362*, C21.

(38) Cairns, M. A.; Dixon, K. R.; McFarland, J. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1259.

Scheme 4

$$2 + \begin{bmatrix} AgF \\ \text{or} \\ KX \end{bmatrix} \longrightarrow X-\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}-C\equiv C-Cl$$
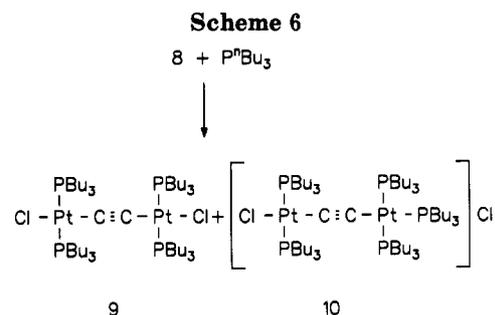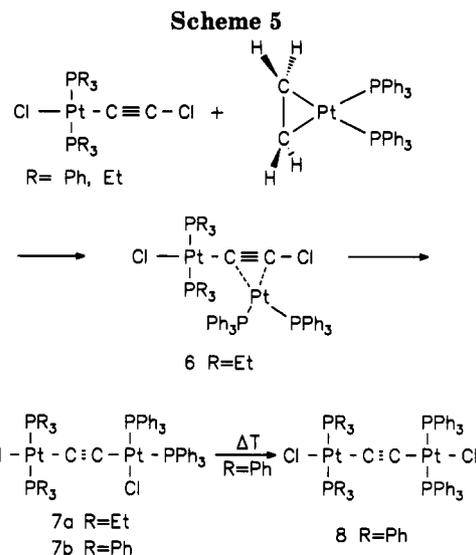
X=F **5a**
X=Br **5b**
X=I **5c**

stants $^1J(\text{PtP})$ decrease in the order X = F > Cl > Br > I, while the order of the chemical shifts $\delta(^{31}P)$ shows an irregularity for X = F, i.e. $\delta(^{31}P)$ for X = Cl > Br > F > I.

The use of other anionic nucleophiles so far gives no unambiguous results, with complex reaction mixtures or decomposition products as the only isolated substances. With butyllithium,[39] substitution of both chloride and chloroethynyl ligands occurs, and only bis(butyl)bis-(phosphine)platinum can be detected by ^{31}P NMR spectroscopy.[40]

Dinuclear Complexes. The chloroethynyl complexes 2–5 can be regarded as metallo-substituted chloroalkynes, and might still act as π-ligands via their triple bond or undergo another oxidative addition reaction with the remaining carbon—chlorine bond. When WCl_6, which is known[5] to form a π-complex with dihaloalkynes, is added to a solution of 2, scission of the Pt—C bond occurs and the only isolable platinum containing product is $Pt(PPh_3)_2$-Cl_2. $Pd(PPh_3)_4$, which gives a phosphonium acetylide complex with $ClC\equiv CCl$, does not react at all at room temperature with 2, and when heated to reflux, only Pd-$(PPh_3)_2Cl_2$ can be isolated. Also Vaska's complex, IrCl-$(CO)(PPh_3)_2$, which reacts rapidly with dichloroethyne[41] can be recovered unchanged from the room temperature reaction with 2.

When, however, a solution of $Pt(PPh_3)_2(C_2H_4)$ is added to a solution of 3, ^{31}P NMR spectroscopic examination of the reaction mixture shows the formation of a 60:40 mixture of two platinum phosphine complexes, both of which seem to be quite unsymmetrical. Slowly on standing, or faster on careful warming, the original minor product is enriched until it is the only compound in solution (no precipitates are formed). We therefore believe that one compound 6 is formed first at low temperature and gradually isomerizes to the other compound 7a. From the ^{31}P NMR spectra (see Table 1), we believe that 6 must be formulated as $(Cl)(PEt_3)_2Pt(\mu-\eta^1,\eta^2-C\equiv CCl)Pt(PPh_3)_2$. The $C\equiv C$—Cl group acts as a σ,π-bridging ligand between the two PtP_2 fragments, since chemical shift and coupling constants of the PPh$_3$ part of the spectrum are typical for a PtP$_2$ fragment π-coordinated to an alkyne like in 1, while the PEt$_3$ part corresponds more to an alkynyl complex like in 3. The isomerized product 7a must have a *trans* geometry in the PEt$_3$ part of the molecule, while there must be a *cis* arrangement of the $Pt(PPh_3)_2$ moiety, as in *trans*-$(Cl)(PEt_3)_2Pt$—$C\equiv C$—$Pt(PPh_3)_2(Cl)$-*cis*. We therefore believe that these compounds have the structures depicted in Scheme 5.

(39) For other reactions of alkynyl complexes of Pt with BuLi, see: Sebald, A.; Wrackmeyer, B.; Theocharis, C. R.; Jones, W. *J. Chem. Soc., Dalton Trans.* **1984**, 747.

(40) No literature data were available; however, independent synthesis of this compound (according to: Whitesides, G. M.; Gausch, J. F.; Stedrousky, E. H. *J. Am. Chem. Soc.* **1972**, *94*, 5258) proved its identity by ^{31}P NMR.

(41) Sünkel, K. Unpublished observation.

Scheme 5

$$Cl-\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Pt}}-C\equiv C-Cl \;+\; \overset{H\;\;H}{\underset{H\;\;H}{\underset{\displaystyle \|}{C}}}\overset{\displaystyle \|}{\underset{\displaystyle C}{}}Pt\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{}}$$

R= Ph, Et

$$\longrightarrow Cl-\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Pt}}-C\equiv C-Cl \longrightarrow$$
$$\underset{Ph_3P\;\;\;\;PPh_3}{Pt}$$

6 R=Et

$$Cl-\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Pt}}-C\vdots C-\overset{\displaystyle PPh_3}{\underset{\displaystyle Cl}{Pt}}-PPh_3 \xrightarrow[R=Ph]{\Delta T} Cl-\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Pt}}-C\vdots C-\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}-Cl$$

7a R=Et
7b R=Ph

8 R=Ph

Scheme 6

8 + P^{n}Bu$_3$

$$\downarrow$$

$$Cl-\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}-C\vdots C-\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}-Cl + \left[Cl-\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}-C\vdots C-\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}-PBu_3\right]Cl$$

9   **10**

When 2 is treated with $Pt(PPh_3)_2(C_2H_4)$, only one product can be isolated, and from the similarity of the ^{31}P NMR parameters, a μ-ethynediyl structure *trans*-(Cl)-$(PPh_3)_2Pt$—$C\equiv C$—$Pt(PPh_3)_2(Cl)$-*cis* (7b) can be derived. Remarkable is the fact that the four bond coupling constant $^4J(\text{PtP})$ can be observed only for the phosphorus atom trans to the alkynyl group in both compounds 7 (Table 1); i.e. obviously a linear arrangement P—Pt—C—C—Pt′ is necessary. In 6, however, both PPh$_3$ groups show $^1J(\text{P—Pt})$ as well as $^3J(\text{P—Pt})$ or $^4J(\text{P—Pt})$ coupling.

When a toluene solution of 7b is heated to reflux for several hours, complete isomerization to the symmetrical *trans,trans*-(Cl)(PPh$_3$)$_2$Pt—$C\equiv C$—Pt(PPh$_3$)$_2$(Cl) (8) occurs. A crystal structure determination of this compound proved this interpretation of the spectral data (*vide infra*).

Like its mononuclear precursor, 8 undergoes a phosphine exchange reaction when treated with excessive PBu$_3$ in an NMR tube. ^{31}P NMR spectra show the formation of *trans,trans*-(Cl)(PBu$_3$)$_2$Pt—$C\equiv C$—Pt(PBu$_3$)$_2$(Cl) (9) together with the ionic compound [(Cl)(PBu$_3$)$_2$-Pt—$C\equiv C$—Pt(PBu$_3$)$_3$]$^+$Cl$^-$ (10) (Scheme 6).

Compound 9 has been prepared recently together with other symmetrical Pd and Pt alkylphosphine μ-ethynediyl complexes by Takahashi et al. by another route.[42] However, no arylphosphine derivatives nor any unsymmetrical cis–trans isomers like 7b or 8 could be obtained by this alternate procedure.[43] In light of the great interest these μ-ethynediyl compounds have found during the last 5

(42) (a) Ogawa, H.; Joh, T.; Takahashi, S.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1220. (b) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257. (c) Onitsuka, K.; Joh, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1179.
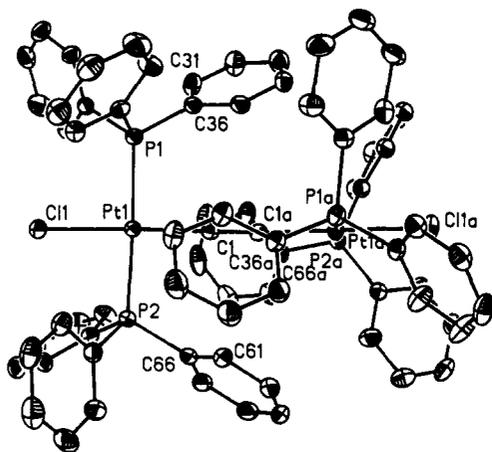
(43) Takahashi, S. Private communication.

Figure 2. Molecular structure of **8**. Thermal ellipsoids shown at the 20% probability level.
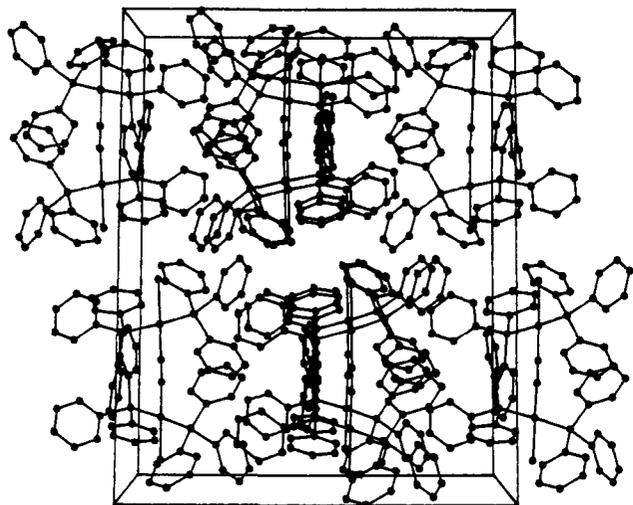

Figure 3. Unit cell of **8**, viewed down the *a*-axis.

years,[44] our reaction pathway might be superior where special phosphines are wanted that do not allow preparation of the starting materials Pt(PR₃)₂Cl₂ and Pt(PR₃)₂-(C≡CH)X needed for the Takahashi procedure.

Further investigations on the viability of unsymmetrical μ-ethynediyl complexes by oxidative addition of the C–Cl bond of **2** or its derivatives are in progress at the moment and will be published elsewhere.

Molecular Structure of 8

A view of one molecule of **8** is given in Figure 2, while Figure 3 shows the unit cell, viewed down the *a*-axis. The middle of the central C—C bond lies on a 2-fold symmetry axis, thus half of the molecule is symmetry-generated from the other. As a consequence of this, the two coordination planes around the platinum atoms include an angle of approximately 82°. In the structure of I(Me₃P)₂Pt—C≡C—Pt(PMe₃)₂I, reported by Takahashi et al. several years ago,[42] this angle is 90°. As a consequence of the greater steric bulk of PPh₃ ligands compared with PMe₃, four phenyl rings are oriented around the central C—C unit, which is not possible with the methyl groups. One could suspect that the phenyl groups protect the central C—C bond from any possible reactants, although, as the

view of the unit cell shows, there is still some empty space left. The molecule has a diameter of approximately 12.5 Å and a length of 10–11 Å, thus being far away from a rod shape and excluding (most likely) some sort of orientational effects in solution needed for special physical properties like formation of liquid crystals, etc., as has been discussed in connection with many other μ-ethynediyl complexes. The geometry around the Pt atoms deviates only slightly from square planar, mainly as a consequence of the different bond lengths Pt—P, Pt—Cl, and Pt—C. These values (Table 5) are quite similar to the distances observed in **2**[9a] and in other platinum acetylide complexes.[36c] Takahashi's compound shows longer Pt—C bonds, but since his data have much higher esds, this should not be further discussed. The carbon–carbon "triple" bond is significantly longer than in the chloroethynyl complex **2**, and also in Takahashi's compound—if the high standard deviations there are neglected- but is very normal when compared with other μ-ethynediyl complexes.[44b] Details of the structure determination are summarized in Table 2, atomic coordinates are in Table 4, and selected bond lengths and angles are listed in Table 5.

Experimental Section

General Procedures and Starting Materials. All manipulations were carried out under a dry, oxygen-free nitrogen or argon atmosphere, using standard Schlenk tube techniques. Solvents were purified, degassed, and dried by standard procedures. **Caution:** Free dichloroethyne is an explosive, neurotoxic, and carcinogenic substance! All operations must therefore be performed in a well ventilated hood. Nevertheless, it can be handled safely in an ethereal solution, in which it was prepared and distilled as the 1:1 adduct ClC≡CCl·Et₂O, with an approximate concentration of 3.5 mol/L.[45] Residues can be destroyed by adding an ethanolic solution of iodine, which transforms the alkyne to ClI₂C—CI₂Cl. Pt(PPh₃)₂(C₂H₄)[46a] and Pt(PR₃)₄[46b] were prepared according to literature procedures.

Physical Measurements. IR spectra were recorded as Nujol mulls on a Perkin-Elmer Model 881 or a Nicolet 520 FT-IR spectrometer. NMR spectra were recorded on a JEOL GSX 270 FT-NMR spectrometer. ¹³C NMR data were referenced to the solvent signal (C₆D₆ 128.00 ppm, CDCl₃ 77.00 ppm, CD₂Cl₂ 53.90 ppm). ³¹P signals were referred to external 85% H₃PO₄ as 0.00 ppm, with the negative sign to the high field. For ¹⁹⁵Pt NMR spectra an external reference of K₂Pt(CN)₆ as 0.00 ppm was used (for comparison with other data: δ(K₂Pt(CN)₆) = –3866 ppm relative to Na₂PtCl₆ = +667 ppm relative to the 21.4-MHz signal[23]). Elemental analyses were performed by the microanalytical laboratory of the institute for inorganic chemistry at the university of Munich.

Crystal Structure Determinations. The X-ray structure determinations were performed on a Syntex R3 (**1**) and a Nicolet R3m/V (**8**) diffractometer, using Mo Kα radiation with a graphite monochromator in the ω–2θ scan type. Several crystals of **1** were grown from saturated dichloromethane solutions. First, attempts were made by mounting a crystal by epoxy glue on a glass fiber, but the following crystal structure determinations showed a slow decay of the crystal, most likely due to solvent loss. Consequently, another crystal was mounted in a glass capillary, placed on the diffactometer, and slowly cooled in a stream of cold nitrogen to –100 °C. The unit cell was determined from 21 reflections (16° < 2θ < 30°). The data collection was performed with a variable scan speed (3.97–10.19°/min in ω) and a total scan width of 0.8° (in ω). Two check reflections were measured at an interval of

(44) For recent reviews, see: (a) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673. (b) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.

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(46) (a) Nagel, U. *Chem. Ber.* **1982**, *115*, 1998. (b) R = Ph, Et: Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 122. Ugo, R.; Cariati, F.; LaMonica, G. *Ibid.* 123. R = ⁿBu: Franks, B.; Hartley, F. R. *Inorg. Chim. Acta* **1981**, *47*, 235.

every 98 reflections, and showed no significant decay of the crystal. A ψ scan was performed using eight reflections with $\chi \approx 90°$, using the approximation of an ellipsoid for the crystal shape. The structure was solved and refined using the Siemens SHELXTL PLUS (VMS) program package (release 4.11/V). The strange asymmetry in the PtC_2Cl_2 unit was examined for librational effects, using the routine "LIBR" of the XP program part of this package. However, the corrected bond lengths still showed a significant asymmetry (Pt–C1 2.021, Pt–C2 1.951, C1–C2 1.423, C1–Cl1 1.661, C2–Cl2 1.739, Pt–P1 2.313, Pt–P2 2.311 Å), so the uncorrected values were used in the tables and in the discussion. Crystals of 8 were grown from THF solution, and one platelet was mounted in a glass capillary. The unit cell was determined from 15 reflections ($15° < 2\theta < 30°$). Data collection was performed with variable scan speed ($2.49–15.0°/\min$ in ω) and a scan width of $1.20°$ (in ω). One check reflection was measured every 50 reflections, where no decay of the crystal could be observed. Then the unit cell was redetermined using 18 reflections with $30° < 2\theta < 40°$. A ψ scan was performed using seven reflections with $\chi \approx 90°$, and the crystal shape was approximated as an ellipsoid. Structure solution and refinement were performed with the SHELXTL PLUS (VMS) program package (release 4.11/V). Further details are collected in Table 2.

Synthesis of $Pt(PPh_3)_2(\eta^2\text{-}ClC\equiv CCl)$ (1). (1) A suspension of $Pt(PPh_3)_4$ (6.310 g, 5.07 mmol) in toluene (60 mL) is treated with standard $ClC\equiv CCl$ solution (1.5 mL, approximately 5.25 mmol). After stirring for 20 min, another 0.4 mL of $ClC\equiv CCl$ solution is added dropwise, until sudden dissolution occurs and a new off-white precipitate forms. The white solid is isolated by filtration after another 35 min, and the solution is kept in the freezer (–30 °C) overnight. Another crop of a microcrystalline powder is isolated from this solution and combined with the first precipitate. The solids are washed three times with hexane (30 mL each) and then extracted twice with toluene (30 mL each). The toluene extracts are evaporated to dryness *in vacuo*, and the crude product is recrystallized from CH_2Cl_2 (dissolving in hot CH_2Cl_2, followed by filtration and slowly cooling to –30 °C). 1: colorless crystals; yield 3.66 g, 89%; mp 218–221 °C dec. IR (Nujol): ν 3045 (w), 1583 (vw), 1568 (vw), 1491 (vw), 1477 (s), 1436 (vs), 1434 (vs), 1325 (vw), 1307 (w), 1179 (w), 1154 (w), 1091 (vs), 1066 (w), 1023 (w), 996 (m), 918 (vw), 842 (s), 751 (m), 741 (vs), 700 (sh), 691 (vs), 617 (vw), 539 (vs), 520 (vs), 509 (vs), 492 (m), 460 (sh), 449 (w), 441 (w), 420 (w), 312 (w), 303 (sh) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.20–7.29 (m, C_6H_5), 7.30–7.41 (m, C_6H_5), 5.61 (CH_2Cl_2) ppm. ^{13}C NMR (CD_2Cl_2): $\delta(C_6H_5)$ 133.5–134.5 (m), 129.9 (s), 128.1 ("d") ppm. Anal. Calcd for $C_{38}H_{30}Cl_2P_2Pt \cdot 0.5CH_2Cl_2$: C, 54.0; H, 3.65. Found: C, 54.18; H, 3.86.

(2) A toluene solution of $Pt(PPh_3)_2(C_2H_4)$ (2.03 g, 2.72 mmol, in 50 mL) is treated with standard $ClC\equiv CCl$ solution (0.74 mL, approximately 2.6 mmol) under continuous stirring at room temperature. The color changes soon to orange or brown, before an off-white precipitate begins to form. After 16 h, hexane (50 mL) is added, and the suspension is kept at –30 °C overnight. The precipitate is then isolated by filtration, washed with hexane, and dried *in vacuo*. Yield: 1.67 g, 75%.

Synthesis of $trans\text{-}(Ph_3P)_2(Cl)Pt\text{—}C\equiv C\text{—}Cl$, 2. A suspension of 1 (1.75 g, 2.15 mmol) in toluene (25 mL) is boiled to reflux for 16 h. After cooling to room temperature, pentane is added (20 mL) and the white solid formed is isolated by filtration. After washing with pentane (5 mL), the product is dried *in vacuo*. 2: white crystals; yield 1.60 g, 91%. IR (Nujol): ν 3046 (w), 1585 (vw), 1571 (vw), 1480 (s), 1435 (vs), 1328 (vw), 1309 (vw), 1185 (w), 1155 (vw), 1100 (sh), 1095 (vs), 1068 (vw), 1025 (w), 997 (w), 754 (s), 742 (s), 703 (vs), 691 (vs), 617 (vw), 549 (m), 520 (vs, br), 498 (s), 464 (w), 456 (w), 431 (w), 426 (w), 395 (vw), 318 (w), 314 (sh), 294 (w) cm^{-1}. ^1H NMR (acetone-d_6): $\delta(C_6H_5)$ 7.38–7.52 (m), 7.65–7.75 (m) ppm. Anal. Calcd for $C_{38}H_{30}Cl_2P_2Pt$: C, 56.0; H, 3.71. Found: C, 55.62; H, 4.15.

Synthesis of $cis\text{-}(Ph_3P)_2(Cl)Pt\text{—}C\equiv C\text{—}Cl$, 2a. A solution of $Pt(PPh_3)_2(C_2H_4)$ (370 mg, 0.49 mmol) in toluene (10 mL) is

added to a large excess of ethereal standard $ClC\equiv CCl$ solution (5.0 mL, approximately 17.5 mmol) at –78 °C. After a few minutes a white precipitate begins to form, which is isolated by filtration, washed with cold toluene and dried *in vacuo*. Yield: 400 mg, <100% (contains variable amounts of toluene). IR (Nujol): ν 3072 (w), 3048 (w), 1582 (vw), 1568 (vw), 1490 (w), 1479 (m), 1437 (vs), 1432 (s), 1305 (vw), 1180 (w), 1151 (w), 1094 (vs), 1066 (vw), 1021 (w), 995 (w), 751 (m), 740 (s), 699 (sh), 693 (sh), 688 (vs), 613 (vw), 541 (s), 522 (s), 511 (s), 496 (s), 458 (w), 419 (w), 301 (m), 296 (m) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta(C_6H_5)$ 7.05–7.20 (m), 7.25–7.40 (m) ppm.

Synthesis of $trans\text{-}(Et_3P)_2(Cl)Pt\text{—}C\equiv C\text{—}Cl$, 3. (1) A suspension of 2 (85 mg, 0.1 mmol) in toluene (2 mL) is treated with several drops of PEt_3. Immediate dissolution of the complex occurs, and after 5 min, the solvent is removed *in vacuo* and the residue is redissolved in CH_2Cl_2 (1.0 mL). The progress of the reaction is followed by ^{31}P NMR spectroscopy, but no further changes can be observed, i.e. the reaction has come to an end after 5 min.

(2) $Pt(PEt_3)_4$ (850 mg, 1.27 mmol) is dissolved in hexane (20 mL) at –60 °C. With continuous stirring, standard $ClC\equiv CCl$ solution (0.4 mL, approximately 1.75 mmol) is added to the orange solution. After a short period of time, a white precipitate forms and the orange color disappears. After 2 h, stirring is stopped and the supernatant liquid is decanted off and discarded. The white residue is washed with cold hexane (5 mL) and dried at –30 °C *in vacuo*. Yield: 420 mg ($\approx 63\%$). ^{31}P NMR spectroscopic examination of this raw product shows two major signals of platinum containing species, $\delta(^{31}P)$ 15.6 ppm (in C_6D_6, $^1J(Pt\text{—}P)$ = 2378 Hz; 3) and $\delta(^{31}P)$ 15.2 ppm ($^1J(PtP)$ = 2543 Hz) in a ratio of 3:2, together with PEt_3O, $\delta(^{31}P)$ 48.0 ppm. Therefore, the crude product is recrystallized from hexane, by dissolving in the minimum amount of solvent at room temperature, and cooling to –78 °C. 3: white needles, with a strong odor of PEt_3; yield 200–350 mg, depending on the amount of hexane used, and the time for crystallization. The ^{31}P NMR spectrum shows only the signals due to 3. IR (KBr): ν 2969 (vs), 2932 (m), 2913 (m), 2875 (m), 2114 (vw), 1454 (m), 1415 (m), 1378 (w), 1308 (w), 1253 (m), 1239 (w), 1090 (m), 1037 (s), 1005 (w), 919 (w), 764 (s), 693 (vs), 636 (w), 532 (vw), 419 (w), 384 (vw), 330 (vw), 314 (w) cm^{-1}. ^1H NMR (C_6D_6): $\delta(PCH_2CH_3)$ 0.96 (m) (3H), 1.79 (m) (2H) ppm. ^{13}C NMR (C_6D_6): $\delta(PCH_2CH_3)$ 8.0 ("t", $^3J(PtC)$ = 22 Hz), 14.9 ("qn", $^1J(PC)$ = $^3J(P'C)$ 17 Hz, $^2J(PtC)$ 33 Hz) ppm.

(3) A solution of 1 (285 mg, 0.350 mmol) in toluene (5 mL) is treated with PEt_3 (0.110 mL, 0.700 mmol) and stirred for 2.5 h at room temperature. The solvent is removed *in vacuo*. Repeated recrystallization from pentane (5–6 mL, –30 °C) yields 3, still cocrystallized with PPh_3.

Synthesis of $trans\text{-}(Bu_3P)_2(Cl)Pt\text{—}C\equiv C\text{—}Cl$, 4. (1) A solution of PBu_3 (0.07 mL, 0.264 mmol) in toluene (5.0 mL) is carefully added to a solution of 2 (215 mg, 0.264 mmol) in CH_2Cl_2 (15 mL) during 15 min. After another 30 min of stirring, the solvent is removed *in vacuo*, and the residue is redissolved in CH_2Cl_2. ^{31}P NMR spectroscopic examination shows two products, 4 and 4a. After addition of another equivalent of PBu_3, only the NMR signals due to 4 can be observed (besides free PPh_3).

(2) A yellow solution of $Pt(PBu_3)_4$ (500 mg, 0.50 mmol) in a 4:1 mixture of hexane and toluene (25 mL) is treated at –30 °C with standard $ClC\equiv CCl$ solution (0.6 mL, ≈ 2.1 mmol). An immediate discoloration of the solution can be observed, and after 20 min a flocculent cream-colored precipitate forms. After another 2 h, the solvent is evaporated at –20 °C, and the residue is washed at –78 °C with pentane (5 mL) and dried *in vacuo*. ^{31}P NMR spectroscopic examination of this crude reaction product shows 4 as the main platinum containing product (90%) besides $Pt(PBu_3)_2Cl_2$ (10%) and varying amounts of PBu_3O.

(3) A solution of 1 (140 mg, 0.172 mmol) in toluene (4 mL) is treated with PBu_3 (0.088 mL, 0.344 mmol). After stirring for 2 h at room temperature, the solvent is evaporated *in vacuo*. The colorless oil is dissolved in pentane (3 mL) and left overnight at –30 °C. The white precipitate formed is PPh_3 and is discarded. The filtered solution is evaporated *in vacuo* again, and the oil

obtained is dissolved in methanol (3 mL) and kept for 3 days at -30 °C. White microcrystals of 4 form. Yield: 81 mg, 68%. IR (KBr): ν 2960 (vs), 2923 (vs), 2872 (s), 2850 (s), 2110 (vw), 1465 (s), 1417 (w), 1378 (w), 1305 (w), 1228 (vw), 1205 (m), 1120 (w), 1091 (vs), 1051 (w), 1002 (w), 968 (vw), 907 (s), 839 (w), 803 (m) 779 (m), 742 (s), 724 (s), 698 (s), 542 (m), 450 (w), 409 (vw), 394 (w), 316 (m), 302 (m, sh) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ(PCH$_2$-CH$_2$-CH$_2$-CH$_3$) 1.94 (m, 2H), 1.57 (m, 2H), 1.38 ("q", 2H), 0.89 ("t", 3H) ppm. ^{13}C NMR (C$_6$D$_6$): δ(PCH$_2$-CH$_2$-CH$_2$-CH$_3$) 26.5 ("t", "J(CP)" = 10 Hz), 24.6 ("t", "J(CP)" 6 Hz), 22.7 ("t", "J(CP)" 17 Hz), 13.9 (s) ppm (virtual triplets due to A parts of an AXX' spin system). Anal. Calcd for C$_{26}$H$_{54}$Cl$_2$P$_2$Pt: C, 44.95; H, 7.84. Found: C, 45.08; H, 7.67.

Synthesis of *trans*-(Ph$_3$P)$_2$(F)Pt—C≡C—Cl, 5a. A solution of 2 (44 mg, 0.054 mmol) in CH$_2$Cl$_2$ (5 mL) is treated with an excess of AgF and stirred for 3 h at room temperature. Filtration from AgCl and evaporation of the solvent *in vacuo* yields 5a as a colorless powder. Yield: 34 mg, 80%. IR (KBr): ν 3081 (w), 3055 (m), 2967 (w), 2923 (m), 2118 (vw), 1587 (w), 1572 (w), 1482 (s), 1436 (vs), 1331 (vw), 1311 (w), 1286 (w), 1100 (vs), 1072 (w), 1028 (w), 999 (w), 849 (w), 744 (s), 725 (m), 710 (s), 691 (vs), 618 (w), 545 (m), 525 (vs), 515 (s), 503 (s), 458 (m), 443 (sh), 426 (w), 401 (vw), 373 (vw) cm^{-1}. ^{1}H NMR (CH$_2$Cl$_2$, 60 MHz): δ(C$_6$H$_5$) 7.35-7.80 (m) ppm. Anal. Calcd for C$_{38}$H$_{30}$ClFP$_2$Pt: C, 57.19; H, 3.79. Found: C, 56.23; H, 4.08.

Synthesis of *trans*-(Ph$_3$P)$_2$(Br)Pt—C≡C—Cl, 5b. A solution of 2 (45 mg, 0.055 mmol) in acetone (5 mL) is treated with an excess of KBr and stirred for 3 d at room temperature. After removal of the solvent *in vacuo* the residue is extracted with CH$_2$Cl$_2$ (1 mL). 5b crystallizes from this extract at -30 °C: colorless needles; yield 41 mg, 87%. Anal. Calcd for C$_{38}$H$_{30}$BrClP$_2$Pt: C, 53.1; H, 3.52. Found: C, 52.80; H, 3.92.

Synthesis of *trans*-(Ph$_3$P)$_2$(I)Pt—C≡C—Cl, 5c. A solution of 2 (55 mg, 0.067 mmol) in a 1:1 mixture of acetone and CH$_2$Cl$_2$ (8 mL) is stirred together with an excess of KI for 24 h. The solvent is stripped off *in vacuo*, and the residue is extracted with CH$_2$Cl$_2$ (1.5 mL). After filtration, the extract is concentrated *in vacuo* to about one-third and then cooled to -30 °C. 5c: colorless needles; yield 60 mg, 98%. IR (Nujol): ν 3040 (vw), 1480 (m), 1436 (vs), 1310 (vw), 1184 (vw), 1160 (vw), 1099 (s), 1071 (w), 1000 (vw), 840 (vw), 694 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 60 MHz): δ(C$_6$H$_5$) 7.15-7.65 (m) ppm. Anal. Calcd for C$_{38}$H$_{30}$ClIP$_2$Pt: C, 50.4; H, 3.34. Found: C, 50.09; H, 3.44.

Synthesis of (Ph$_3$P)$_2$Pt(μ-η^2,η^1-Cl—C≡C)Pt(PEt$_3$)$_2$Cl (6) and *cis*-(Ph$_3$P)$_2$(Cl)Pt—C≡C—Pt(PEt$_3$)$_2$(Cl)-*trans*, 7a. A solution of 1 (140 mg, 0.172 mmol) in toluene (5 mL) is treated with PEt$_3$ (0.054 mL, 0.344 mmol) and stirred for 2 h. Upon addition of Pt(PPh$_3$)$_2$(C$_2$H$_4$) (129 mg, 0.172 mmol) an immediate color change from white to yellow is observed. Stirring is continued for 18 h, then the solvents are stripped off *in vacuo* and the oily residue is washed several times with pentane and Et$_2$O. Finally, a yellow powder can be obtained. Yield: 193 mg (90%). IR (Nujol): ν 1480 (m), 1439 (s), 1405 (w), 1312 (w), 1191 (s), 1165 (w), 1121 (s), 1097 (m), 1035 (m), 998 (w), 802 (w), 760 (sh), 752 (m), 696 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.95 (m, CH$_3$), 1.83 (m, CH$_2$), 6.98 (m, C$_6$H$_5$), 7.41 (m, C$_6$H$_5$), 7.58 (m, C$_6$H$_5$) ppm. When this powder is dissolved in a CD$_2$Cl$_2$/C$_6$D$_6$ mixture at room

temperature and brought to the NMR spectrometer immediately, integration of the ^{31}P NMR signals shows a 60:40 proportion of 6 and 7a; after longer periods, the intensity of the signals due to 6 decreases, and when the NMR tube is heated for a short time with hot water (50 °C), only 7a can be detected. Since the elemental analyses of 6 and 7a are essentially the same, we cannot say how pure the original sample is. The product recovered from such a warmed NMR solution gives a satisfactory elemental analysis. IR (Nujol): ν 1481 (s), 1435 (s), 1409 (w), 1301 (w), 1190 (s), 1160 (w), 1118 (s), 1097 (m), 1035 (m), 989 (w), 753 (s), 696 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.99 (m, CH$_3$), 1.90 (m, CH$_2$), 6.84 (m, C$_6$H$_5$), 7.50-7.90 (m, C$_6$H$_5$) ppm. Anal. Calcd for C$_{50}$H$_{60}$Cl$_2$P$_4$Pt$_2$: C, 48.20; H, 4.85. Found: C, 48.46; H, 4.58.

Synthesis of *trans*-(Ph$_3$P)$_2$(Cl)Pt—C≡C—Pt(PPh$_3$)$_2$(Cl)-*cis*, 7b. A suspension of 2 (218 mg, 0.268 mmol) in toluene (10 mL) is treated with Pt(PPh$_3$)$_2$(C$_2$H$_4$) (200 mg, 0.268 mmol) and tetrahydrofuran (40 mL). After 4 days of stirring, the solvent is evaporated *in vacuo* and the residue is washed with toluene (10 mL) and pentane (15 mL). Recrystallization from CH$_2$Cl$_2$ yields 7b as a colorless powder (371 mg, 90%). IR (Nujol): ν 1482 (s), 1435 (s), 1187 (w), 1158 (w), 1097 (s), 1078 (w), 959 (w), 743 (s), 692 (s), 545 (m), 522 (s), 501 (sh), 302 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ(C$_6$H$_5$) 6.89 (m), 7.10-7.50 (m), 7.70 (m) ppm. Anal. Calcd for C$_{74}$H$_{60}$Cl$_2$P$_4$Pt$_2$: C, 57.9; H, 3.94. Found: C, 57.35; H, 4.40.

Synthesis of *trans,trans*-(Ph$_3$P)$_2$(Cl)Pt—C≡C—Pt(PPh$_3$)$_2$-(Cl), 8. A suspension of 7b (50 mg, 0.033 mmol) in toluene (6 mL) is refluxed for 4 h. Then the solvent is evaporated *in vacuo*, and the residue is washed with pentane (5 mL) and dried. 8: white powder; yield 47 mg, 94%. IR (KBr): ν 3046 (w), 1581 (vw), 1567 (vw), 1478 (m), 1431 (vs), 1325 (vw), 1306 (vw), 1179 (w), 1151 (vw), 1092 (s), 1063 (vw), 1021 (w), 992 (w), 738 (s), 701 (s), 686 (vs), 612 (vw), 535 (m), 515 (vs), 510 (sh) 493 (m), 449 (w), 287 (vw) cm^{-1}. ^{1}H NMR (CDCl$_3$, 60 MHz): δ(C$_6$H$_5$) 6.95 (m), 7.10-7.75 (m) ppm. Recrystallization from CH$_2$Cl$_2$. Anal. Calcd for C$_{74}$H$_{60}$Cl$_2$P$_4$Pt$_2$·0.5CH$_2$Cl$_2$: C, 56.7; H, 3.90. Found: C, 56.70; H, 3.93.

Reaction of 8 with PBu$_3$. A solution of 8 (40 mg, 0.03 mmol) in CH$_2$Cl$_2$ (2 mL) is stirred for 4 d at room temperature with an excess of PBu$_3$. The progress of the reaction is followed by ^{31}P NMR spectroscopy. After 4 days, formation of 10 is complete. 10 cannot be obtained in a pure form due to contamination with PPh$_3$ and PBu$_3$. Consequently, ^{1}H NMR spectra are overlapped by strong signals of these free ligands.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and H atom positional parameters for 1 and 8 (8 pages). Ordering information is given on any current masthead page.