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Reaction of the Carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ with Platinum(II) and -(0) Compounds: Platinum Induced Activation of C−H Bonds

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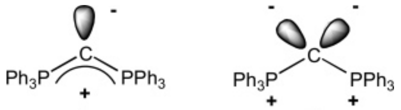
The complex $[(cod)PtI_2]$ (cod = 1,5-cyclooctadiene) reacts with 3 equiv of the hexaphenylcarbodiphosphorane $Ph_3P{=}C{=}PPh_3$ (**1**) in THF solution to give the novel Pt(II) complex $[(\eta^3\text{-}C_8H_{11})Pt(C_6H_4PPh_2CPPh_3)]$ (**2**) along with the salt $[HC(PPh_3)_2]I$. In addition to the coordination of the ylidic carbon atom at the Pt atom, **2** contains two further Pt−C σ bonds originating from H to Pt exchange in the ortho position of one phenyl group of the carbodiphosphorane ligand and in the former cod ligand. The resulting C_8H_{11} moiety is coordinated to the Pt atom in an η^3 manner via a double bond and a σ bond and contains a further uncoordinated double bond. From a 1:1 reaction mixture in toluene/CH_2Cl_2 the majority of the crystals consist of the salt $[HC(PPh_3)_2]I{\cdot}2CH_2Cl_2$ (**3**) with small amounts of platinum compounds as byproducts. The Pt(0) complex $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ does not react with **1** but decomposes at elevated temperatures to give the known dinuclear complex $[Pt_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$ (**4**). The complexes **2** and **4** and the salt **3** could be characterized by X-ray analyses and the usual spectroscopic methods.

Introduction

The double ylide hexaphenylcarbodiphosphorane, $Ph_3P{=}C{=}PPh_3$ (**1**), has been known for more than 40 years,[1] and the bent structure[2] with an approximate sp^2 carbon atom and a free pair of electrons predestines this compound to act as a Lewis base. **1** can also be seen as a zerovalent carbon atom which is stabilized by two neutral phosphine ligands, thus attaining eight electrons. Those compounds are of considerable interest as possible transfer reagents for a single unsubstituted carbon atom. Earlier reviews concerning the chemistry of ylides were collected by Schmidbaur[3] and Kaska,[4] and parts were referred to in a chapter of a monograph.[5]

In principle, **1** can act as a donor with one or two pairs of electrons, involving sp^2 (**1a**) or sp^3 (**1b**) hybridization of the carbon atom, as depicted in Chart 1. As electron pair acceptors, main-group or transition-metal Lewis acids may be operative. In main-group chemistry adducts of **1** (or **1a**) with the atoms or ions S, Se,[6] $[I^+]$,[7] or $[Cl^+]$, respectively, and the electron-deficient compounds $InMe_3$ and $AlBr_3$[8] were established by X-ray analyses.

Chart 1



1a **1b**

The only proven transition-metal carbonyl complexes in which **1** acts as a ligand are the nickel complexes $[(CO)_3NiC(PPh_3)_2]$ and $[(CO)_2NiC(PPh_3)_2]$.[9] Other transition-metal adducts are known with ReO_3^+ [10] and with copper compounds;[11] several Au complexes have also been published recently, including the first example of a complex with **1b** bridging an aurophilic Au···Au interaction.[12] The nucleophilic attack of **1** at a carbonyl carbon atom was reported with $[Fe(CO)_5]$[13] and $[Mn(CO)_5Br]$[14] to produce the metal-bonded heterocumulene ligand $C{=}C{=}PPh_3$ with $OPPh_3$ being split off. With the 16-electron heteroallene Lewis acids $E{=}C{=}E$ (E = S, O) adducts are formed with C−C bond formation[15] which could be characterized by X-ray analyses;[16] also

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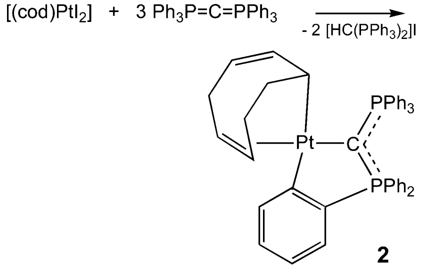
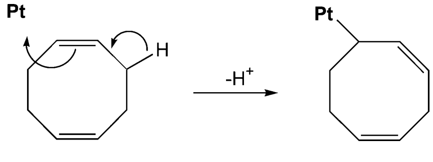
Scheme 1



Scheme 2



one example with E = NPh was described.[17] Furthermore, some complexes with platinum compounds have also been mentioned in which either **1** coordinates in an η^2 manner[18] or ortho metalation of phenyl groups of **1** was theorized with formation of Pt−C bonds.[19] In this contribution we describe the reaction of **1** with [(cod)-PtI_2] and the crystal structure of the resulting compound. Additionally, we have studied again the reaction of **1** with [$(PPh_3)_2Pt(CH_2{=}CH_2)$] in order to prove the existence of the η^2 coordination of **1** described earlier.[18]

Results and Discussion

We have studied the reaction of **1** with [(cod)PtI_2] under various conditions. If a 3:1 mixture of **1** and the platinum complex were allowed to react in THF for several hours, an orange solution along with a white precipitate was obtained. The precipitate was found to be the salt [$HC(PPh_3)_2$]I, which is only slightly soluble in THF. From the solution orange-yellow crystals of the carbodiphosphorane complex [$Pt(\eta^3\text{-}C_8H_{11})(C_6H_4PPh_2\text{-}CPPh_3)$] (**2**) could be isolated in high yield, as shown in Scheme 1. The new complex **2** exhibits an unusual bonding situation. In addition to the coordination of the double ylide at the metal atom via the ylidic carbon atom, a Pt−C σ bond to an ortho carbon atom of a phenyl group has formed and, surprisingly, a second Pt−C σ bond has been established to a carbon atom of the former cod ligand to give the fragment C_8H_{11}. The platinum-induced proton abstraction produces 2 mol of HI, which is trapped as the salt [$HC(PPh_3)_2$]I. The reaction of [(cod)$PtCl_2$] with **1** under the same conditions leads also to the formation of **2** with similar yields, and the HCl was trapped as the corresponding salt [$HC(PPh_3)_2$]Cl.

The cod deprotonation to produce the 2,5-cyclooctadienyl ligand takes place in the position α to one double bond followed by formation of a new uncoordinated double bond via a 1,2-shift, as depicted in Scheme 2. One of the former π-bonded carbon atoms of one double bond has changed into a carbon to platinum σ bond; for an allyl-like interaction with the platinum atom the related Pt−C and C−C distances are inconsistent, and also the electronic counting for a planar 16-electron Pt(II) complex does not need a further pair of electrons. Ortho metalation of phenyl groups of **1** was mentioned earlier with another Pt source,[19] but without confirmation by a crystal structure. C−H activation of the cod ligand coordinated at iridium was described, but the resulting complexes contain the cyclooctadienyl group in an η^3:η^2 coordination mode.[20]

The H^+ abstraction from different sources generates two types of phosphorus atoms. Thus, in the ^{31}P NMR spectrum two doublets are observed at 55.7 and 14.9 ppm with the expected ^{195}Pt satellites and $^2J(Pt,P)$ coupling constants of 55 and 51 Hz, respectively. The low-field signal presumably belongs to the phosphorus atom in the P−C−C−Pt−C ring. **2** dissolves readily in $CHCl_3$ and CH_2Cl_2, but solutions are not stable and decomposition occurs more quickly in $CHCl_3$ and more slowly in CH_2Cl_2. The ^1H NMR spectrum shows two sets of multiplets; one set between 4.0 and 4.9 ppm can be assigned to the olefinic protons, whereas the set between 1.2 and 2.7 ppm belongs to the aliphatic ones.

Attempts were also made to reject the cod ligand during the reaction. However, even in the presence of excess PPh_3 or MeCN only the complex **2** could be isolated from the THF solution and the former cod ligand remains strongly bonded as the C_8H_{11} fragment.

The IR spectrum of **2** exhibits two strong bands at 1098 and 1047 cm^{-1}, which can be assigned to the ν(PCP) vibration, and, relative to the related bands of **1**, a shift to lower frequencies has occurred. The majority of bands, however, belong to the vibrations of the PPh_3 group and were not assigned further.

Several runs of the reaction were carried out with other molar ratios of the components, including a 1:1 molar ratio. The oily material obtained in this case was dissolved in CH_2Cl_2. From this solution layered with *n*-pentane a few crystals could be isolated after several weeks. One sort of crystal was identified by X-ray analysis to be a platinum complex containing the Pt atom in the formal oxidation number IV with a pincer ligand derived from double deprotonation of **1**, but the complex could not be characterized sufficiently as yet. The majority of crystals were found to be the salt [$HC(PPh_3)_2$]I·$2CH_2Cl_2$ (**3**).

Among the possible coordination modes of **1**, the most interesting one, however, would be that of an η^2 coordination which mimics the well-established bond of CO_2 and CS_2 at transition metals. One example of such a complex has been published earlier, obtained from the reaction of **1** with the Pt(0) complex [$(PPh_3)_2Pt(CH_2{=}CH_2)$], in which the olefin was thought to be replaced by the P−C double bond to give the complex [$(PPh_3)_2Pt(\eta^2\text{-}\{Ph_3P{=}C{=}PPh_3\})$].[18] In contrast, we found that **1** does not react with the Pt(0) complex. If a mixture of both components was stirred for several hours at room temperature in toluene solution, no change of the ^{31}P NMR signals of the starting materials was observed, even after prolonged reaction times. The ^{31}P NMR data

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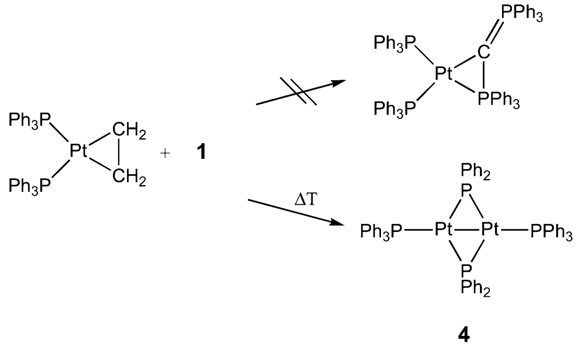
Scheme 3



(in THF) given in this paper as a proof of η^2 coordination were found to be identical with the chemical shifts and coupling constants of the hydrolysis product $Ph_2P(O)CHPPh_3$ (doublets at 24.6 and 20.9 ppm; J(P,P) = 19.1 Hz) and of $OPPh_3$ (23.2 ppm). However, if the reaction was carried out at elevated temperature, the solution turned red and we isolated a deep red crystalline compound, which was identified as the dinuclear compound $[Ph_3PPt(\mu\text{-}PPh_2)_2PtPPh_3]$ (**4**), and **1** was not consumed (Scheme 3). The complex **4** was prepared and characterized earlier and obtained upon refluxing $[Pt(PPh_3)_4]$ in benzene.[21] It is obvious that at elevated temperature loss of the olefin generates the carbene-like $[Pt(PPh_3)_2]$, which is also formed from $[Pt(PPh_3)_4]$, finally leading to the same thermal decomposition product without participation of **1**.

Crystal Structures

General Remarks. To get more detail on the properties of the compounds, the structures of the complexes **2** and **4** and the salt **3** have been determined by single-crystal X-ray diffraction studies. Suitable yellow crystals of **2** (with 1.5 molecules of THF) were obtained by layering a THF solution with n-pentane. **3** was grown from CH_2Cl_2 solutions. Crystals of the dinuclear complex **4** contain one disordered toluene molecule; the product reported earlier was described with one molecule of benzene. ORTEP views of the molecules **2** and **3** are depicted in Figures 1 and 2; the structure of the previously described platinum complex **4** is not depicted. Details of the structure determinations are collected in Table 1; selected bond lengths and angles are summarized in Tables 2−4.

Crystal Structure of 2. The central part of the molecule is the five-membered planar heterocycle containing the atoms Pt and P(2), the sp^2 carbon atom C(1) ($\Sigma = 360°$) of the carbodiphosphorane ligand, and two sp^2 phenyl carbon atoms. The planarity may be indicative of some electron delocalization within the ring. The ligand arrangement around the platinum atom is essentially planar and is composed of three carbon atoms and the center of the cod double bond, as shown in Figure 1. The platinum atom is in the formal oxidation state II. The Pt−C bond length to the ylide carbon atom is found at the lower limit of a single bond (2.07 Å),[21,22] and the bond to the ortho carbon atom of the phenyl group is appreciably longer (2.09 Å) than in related compounds containing a similar ortho carbon bond,[23] whereas the distances to the three C_8H_{11} carbon atoms are 0.05−0.06 Å longer (2.14 Å) with nearly identical Pt−C distances (σ and π). In the former η^4-cod ligand a deprotonation in the position α to one double bond occurred, followed by a 1,2-shift to give the η^3-C_8H_{11} ligand, and the new double bond established between C(44) and C(45) is not involved in the coordination, as shown by the short C−C bond length of 1.29 Å. Thus, an alternative allylic bond can be excluded and the Pt atom attains 16 electrons, which is typical for a square-planar coordination of Pt(II) compounds. The new C_8H_{11} (cyclooctadienyl) moiety is now coordinating at the Pt atom via a π bond and a σ bond, and according to the asymmetric connections this σ-bonded carbon atom is chiral. Thus, the unit cell contains a pair of enantiomers. The P−C bond distances to the ylidic carbon atom C(1) are slightly different (1.69 and 1.72 Å), and the shorter one belongs to that of the "free" (dangling) PPh_3 group. The P−C−P bond angle is 121.3°, a value which is among the lowest recorded for addition compounds of the type $E{-}C(PPh_3)_2$.[8] The large P−C−P bond angles of carbodiphosphorane adducts (125−136°) are probably due to a parallel arrangement of two phenyl rings found in all these compounds, which have their ipso C atoms within the ECP_2 plane. This arrangement is probably necessary for an optimal interaction of the occupied p orbital at C(1) with the $P{-}C_{ipso}$ σ^* orbitals derived from the other two $P{-}C_{phenyl}$ bonds out of the plane (or their mixtures with d orbitals); the repulsive interaction of these parallel phenyl groups may be responsible for the large P−C−P angles. In **2**, however, upon $Pt{-}C_{phenyl}$ bond formation this ortho-metalated phenyl ring is now located within the ECP_2 plane, the repulsive interaction is lost, and the P−C−P angle approaches 120° due to a normal sp^2 carbon atom.

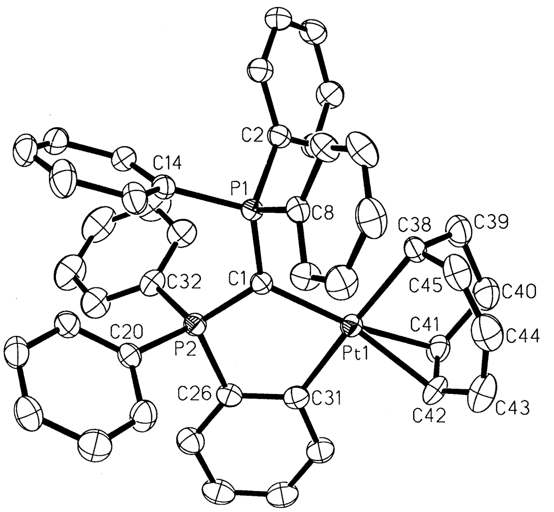


Figure 1. Projection view of $[(\eta^3\text{-}C_8H_{11})Pt(C_6H_4PPh_2CPPh_3)]$ (**2**) with the labeling scheme (40% ellipsoids). The hydrogen atoms and the disordered THF molecule have been omitted for clarity.

Crystal Structure of 3. The salt **3** crystallizes as an ion pair with two molecules of CH_2Cl_2, and this

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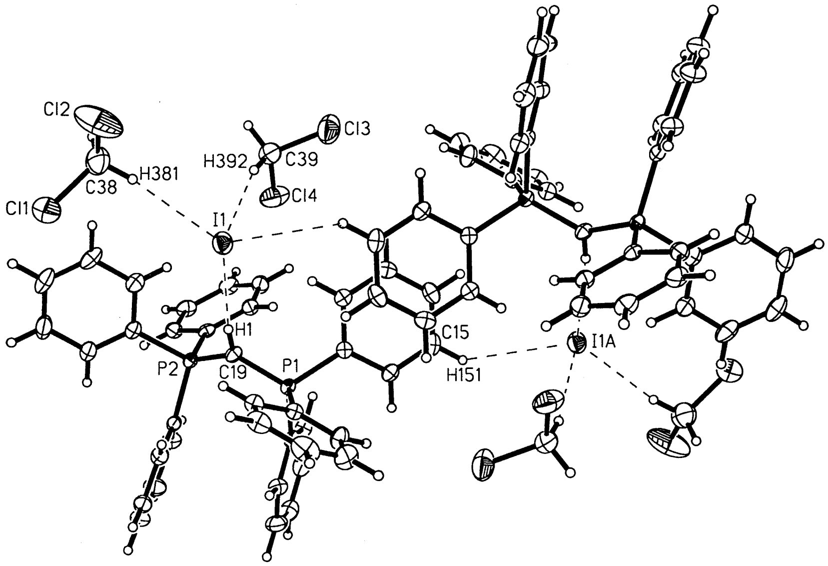

Figure 2. Projection view of the centrosymmetric dimer $[HC(PPh_3)_2]I·2CH_2Cl_2$ (**3**) with the labeling scheme (40% ellipsoids), indicating the weak H bridges.

Table 1. Summary of the X-ray Data for Complexes 2 and 4 and the Salt 3

	2	**3**	**4**
formula	$C_{51}H_{52}O_{1.5}P_2Pt$	$C_{39}H_{35}Cl_4IP_2$	$C_{67}H_{58}P_4Pt_2$
mol wt	946.00	1668.75	1377.27
a/Å	9.627(1)	11.182(1)	15.868(1)
b/Å	12.184(1)	13.486(1)	16.638(1)
c/Å	18.230(1)	14.818(1)	21.362(2)
α/deg	83.50(1)	102.85(1)	90
β/deg	87.75(1)	104.65(1)	97.24(1)
γ/deg	77.00(1)	112.14(1)	90
cryst size/mm	0.24 × 0.14 × 0.07	0.33 × 0.15 × 0.1	0.11 × 0.07 × 0.04
$V/Å^3$	2069.9(3)	1872.4(3)	5594.9(7)
Z	2	2	4
d_{calcd} (g/cm^3)	1.518	1.48	1.635
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
diffractometer	IPDS II (Stoe)	IPDS I (Stoe)	IPDS II (Stoe)
radiation	Mo Kα	Mo Kα	Mo Kα
temp (K)	193	193	193
μ (cm^{-1})	35.1	12.5	51.5
$2\theta_{max}$/deg	52.62	51.90	52.53
index ranges	$-11 \leq h \leq 11$ $-15 \leq k \leq 14$ $-22 \leq l \leq 22$	$-13 \leq h \leq 13$ $-16 \leq k \leq 16$ $-18 \leq l \leq 18$	$-19 \leq h \leq 19$ $-19 \leq k \leq 20$ $-26 \leq l \leq 26$
no. of rflns collected	24 971	18 466	80 189
no. of indep rflns (R_{int})	8298 (0.0366)	6783 (0.044)	11 255 (0.1402)
no. of obsd rflns with $F_o > 4\sigma(F_o)$	7310	5143	5912
no. of params	529	420	618
abs cor	numerical	numerical	numerical
structure soln	Patterson method, SHELXTL-Plus [27]	direct methods, SIR-92 [29]	direct methods, SHELXS-97 [28]
refinement against F^2	SHELXL-97 [30]	SHELXL-97 [30]	SHELXL-97 [30]
R_1	0.03	0.0321	0.041
wR_2 (all data)	0.074	0.0781	0.0759
max electron density left/(e/10^{-6} pm^3)	1.15	0.75	1.1

composition forms a centrosymmetric dimer connected by four very weak H···I bridges, as shown in Figure 2. The sequence P(1)−C(19)H(1)−P(2) is planar. Four nearer contacts exist from the iodine ion to H(1) (C−H····I = 4.066(4) Å), to a proton of both CH_2Cl_2 molecules (C−H····I = 3.787(5), 3.944(4) Å), and to a meta proton of a phenyl group (C−H····I = 3.892(4) Å). The latter pair of C−H····I interactions leads to the dimeric unit; all values given are C····I contacts. The other parameters of the cation are close to those reported earlier.[8]

Crystal Structure of 4. The crystallographic data of **4** do not differ markedly from those reported earlier.[21] However, in **4** the more precise low-temperature structure exhibits slightly shorter Pt−P and Pt−Pt bond lengths within the Pt_2P_2 ring system, and both terminal Pt−P distances are identical. The bridging phosphorus atoms are in an approximately tetrahedral environment with acute Pt−P−Pt angles of 69° and a less acute C−P−C angle of 103°. The different Pt−P−C angles in pairs indicate a slight twist of the carbon atoms out of the local mirror plane, which can be drawn through the

Table 2. Selected Bond Lengths and Angles in [Pt(η^3-C_8H_{11})($C_6H_4PPh_2CPPh_3$)] (2)

Distances (Å)			
Pt(1)−C(1)	2.072(3)	Pt(1)−C(31)	2.086(4)
Pt(1)−C(38)	2.139(4)	Pt(1)−C(41)	2.148(4)
Pt(1)−C(42)	2.143(4)	P(1)−C(1)	1.694(4)
P(1)−C(2)	1.830(4)	P(1)−C(8)	1.818(4)
P(1)−C(14)	1.823(4)	P(2)−C(1)	1.716(4)
P(2)−C(20)	1.825(4)	P(2)−C(26)	1.794(4)
P(2)−C(32)	1.827(4)	C(26)−C(27)	1.379(6)
C(26)−C(31)	1.408(6)	C(27)−C(28)	1.390(6)
C(28)−C(29)	1.371(7)	C(29)−C(30)	1.377(6)
C(30)−C(31)	1.413(6)	C(38)−C(39)	1.530(6)
C(38)−C(45)	1.478(7)	C(39)−C(40)	1.572(8)
C(40)−C(41)	1.522(7)	C(41)−C(42)	1.393(7)
C(42)−C(43)	1.490(7)	C(43)−C(44)	1.460(8)
C(44)−C(45)	1.288(8)		
Angles (deg)			
C(1)−Pt(1)−C(31)	86.0(1)	C(1)−Pt(1)−C(38)	97.5(1)
C(1)−Pt(1)−C(41)	163.5(2)	C(1)−Pt(1)−C(42)	158.6(2)
C(31)−Pt(1)−C(38)	175.9(1)	C(31)−Pt(1)−C(41)	95.2(2)
C(31)−Pt(1)−C(42)	90.9(2)	C(38)−Pt(1)−C(41)	80.8(2)
C(38)−Pt(1)−C(42)	86.7(2)	C(41)−Pt(1)−C(42)	37.9(2)
C(1)−P(1)−C(2)	114.8(2)	C(1)−P(1)−C(8)	111.9(2)
C(1)−P(1)−C(14)	116.2(2)	C(2)−P(1)−C(8)	107.5(2)
C(2)−P(1)−C(14)	102.1(2)	C(8)−P(1)−C(14)	103.3(2)
C(1)−P(2)−C(20)	117.4(2)	C(1)−P(2)−C(26)	104.8(2)
C(1)−P(2)−C(32)	116.4(2)	C(20)−P(2)−C(26)	105.2(2)
C(20)−P(2)−C(23)	105.3(2)	C(26)−P(2)−C(23)	106.6(2)
Pt(1)−C(1)−P(1)	124.1(2)	Pt(1)−C(1)−P(2)	114.6(2)
P(1)−C(1)−P(2)	121.3(2)	P(2)−C(26)−C(27)	121.1(3)
P(2)−C(26)−C(31)	114.1(3)	C(27)−C(26)−C(31)	124.8(4)
C(26)−C(27)−C(28)	119.0(4)	C(27)−C(28)−C(29)	118.8(4)
C(28)−C(29)−C(30)	121.2(4)	C(29)−C(30)−C(31)	123.0(4)
Pt(1)−C(31)−C(26)	120.1(3)	Pt(1)−C(31)−C(30)	126.8(3)
C(26)−C(31)−C(30)	113.1(3)	Pt(1)−C(38)−C(39)	106.1(3)
Pt(1)−C(38)−C(45)	112.3(3)	C(39)−C(38)−C(45)	110.5(3)
C(38)−C(39)−C(40)	110.1(4)	C(39)−C(40)−C(41)	111.3(4)
Pt(1)−C(41)−C(40)	112.2(4)	Pt(1)−C(41)−C(42)	70.9(2)
C(40)−C(41)−C(42)	119.3(4)	Pt(1)−C(42)−C(41)	71.3(2)
Pt(1)−C(42)−C(43)	119.4(3)	C(41)−C(42)−C(43)	127.3(4)
C(42)−C(43)−C(44)	120.1(5)	C(43)−C(44)−C(45)	128.2(5)
C(38)−C(45)−C(44)	129.3(5)		

Table 3. Selected Bond Lengths and Angles in [HC(PPh_3)$_2$]I·2CH_2Cl_2 (3)

Distances (Å)			
P(1)−C(1)	1.803(3)	P(1)−C(7)	1.813(3)
P(1)−C(13)	1.805(3)	P(1)−C(19)	1.699(3)
P(2)−C(19)	1.705(3)	P(2)−C(20)	1.806(3)
P(2)−C(26)	1.820(3)	P(2)−C(32)	1.810(3)
C(19)−H(1)	0.90(4)	C(19)······I(1)	4.066(4)
Angles (deg)			
C(1)−P(1)−C(7)	108.4(1)	C(1)−P(1)−C(7)	106.6(1)
C(1)−P(1)−C(19)	111.2(2)	C(1)−P(1)−C(13)	104.4(2)
C(7)−P(1)−C(19)	110.8(1)	C(13)−P(1)−C(19)	115.1(1)
C(19)−P(2)−C(20)	113.8(1)	C(19)−P(2)−C(26)	115.9(1)
C(19)−P(2)−C(32)	107.8(2)	C(20)−P(2)−C(26)	107.8(2)
C(20)−P(2)−C(32)	106.2(1)	C(26)−P(2)−C(32)	104.3(1)
P(1)−C(19)−P(2)	129.1(2)	P(1)−C(19)−H(1)	115(2)
P(2)−C(19)−H(1)	116(2)		

Table 4. Selected Bond Lengths and Angles in [Pt_2(PPh_3)$_2$(μ-PPh_2)$_2$] (4)

Distances (Å)			
Pt(1)−Pt(2)	2.5946(5)	Pt(1)−P(1)	2.288(2)
Pt(1)−P(2)	2.305(2)	Pt(1)−P(3)	2.230(2)
Pt(2)−P(1)	2.307(2)	Pt(2)−P(2)	2.302(2)
Pt(2)−P(4)	2.230(2)	P(1)−C(1)	1.823(9)
P(1)−C(7)	1.82(1)	P(2)−C(13)	1.823(9)
P(2)−C(19)	1.807(9)	P(3)−C(25)	1.805(9)
P(3)−C(31)	1.804(9)	P(3)−C(37)	1.832(9)
P(4)−C(43)	1.826(8)	P(4)−C(49)	1.843(7)
P(4)−C(55)	1.824(9)		
Angles (deg)			
Pt(2)−Pt(1)−P(1)	55.96(5)	Pt(2)−Pt(1)−P(2)	55.66(5)
Pt(2)−Pt(1)−P(3)	175.47(6)	P(1)−Pt(1)−P(2)	111.62(7)
P(1)−Pt(1)−P(3)	125.28	P(2)−Pt(1)−P(3)	122.93(7)
Pt(1)−Pt(2)−P(1)	55.27(5)	Pt(1)−Pt(2)−P(2)	55.78(5)
Pt(1)−Pt(2)−P(4)	177.48(6)	P(1)−Pt(2)−P(2)	111.04(7)
P(1)−Pt(2)−P(4)	126.16(7)	P(2)−Pt(2)−P(4)	122.77(7)
Pt(1)−P(1)−Pt(2)	68.77(6)	Pt(1)−P(1)−C(1)	117.8(3)
Pt(1)−P(1)−C(7)	122.7(3)	Pt(2)−P(1)−C(1)	123.6(3)
Pt(2)−P(1)−C(7)	119.7(3)	C(1)−P(1)−C(7)	102.9(4)
Pt(1)−P(2)−Pt(2)	68.56(6)	Pt(1)−P(2)−C(13)	117.9(3)
Pt(1)−P(2)−C(19)	123.4(3)	Pt(2)−P(2)−C(13)	123.7(3)
Pt(2)−P(2)−C(19)	118.0(3)	C(13)−P(2)−C(19)	103.5(4)

bridging phosphorus atoms, and the middle of the Pt−Pt bond.

Conclusion

From the reaction of **1** with [(cod)PtI_2] or [(cod)$PtCl_2$] at present we could only isolate and characterize the complex **2** sufficiently, and to our knowledge this is the first structural proof of a cod C−H activation with platinum. The unusual deprotonation of a phenyl ring and of the cod ligand during the reaction is as yet not understood. Hints from ^{31}P NMR data and the isolation and the crystallographic characterization of some crystals of complexes with symmetric tridentate ligands derived from **1** with participation of the solvent CH_2Cl_2 show that under special conditions also a double phenyl ring C−H activation with platinum can occur, and our efforts are now concentrated on the variation of the reaction conditions in such a way that those compounds can be reproduced and increased in yield for further characterization. The carbodiphosphorane **1** is a potential four-electron-donor ligand (**1b**), and if one pair of electrons is donating at a Lewis acid in adducts such as E←C(PPh_3)$_2$, an additional pair is possibly available for further reactions. Thus, exploring its chemistry is a challenge for preparative and theoretical chemists. The insertion of a metal atom into the ortho CH bond of **1** could as yet not be observed with other transition or main group metals or elements.[24] The role of platinum in the activation of C−H bonds[23,25] is very important for catalytic processes, and further studies on this subject are in progress.

Another question deals with the properties of the P−C "double bond" in **1**, concerning its ability to form an interesting η^2 coordination at a transition metal; however, as yet, we were not able to confirm such a bonding mode.

Experimental Section

General Considerations. All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. IR spectra (in Nujol) were run on a Nicolet 510 spectrometer. ^{13}C NMR and ^{1}H NMR spectra were recorded on a Bruker AC 300 instrument using $SiMe_4$ (δ 0.00 ppm) as the external standard. ^{31}P NMR spectra were run on a Bruker ARX 200 spectrometer and referenced to external

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H_3PO_4. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Marburg, Germany). [(cod)PtI_2] was prepared from $K_2[PtCl_4]$ and cod to give [(cod)$PtCl_2$], followed by halogen exchange with NaI according to a literature procedure,[26] and **1** was obtained by a modified procedure, as described earlier.[15] Commercially available $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ was used without further purification.

Preparation of $[(\eta^3\text{-}C_8H_{11})Pt(C_6H_4PPh_2CPPh_3)]$ (2). To a solution of 1.15 g (2.15 mmol) of **1** in about 30 mL of THF at room temperature was added 0.40 g (0.72 mmol) of $[I_2Pt(cod)]$, and the mixture was stirred magnetically for 2 h. A white precipitate had formed along with an intense orange-yellow solution. The precipitate was filtered and identified as the salt $[HC(PPh_3)_2]I$. From the clear solution **2** was precipitated with *n*-pentane as a pale yellow powder, which was filtered, washed with *n*-pentane, and dried under vacuum for 2 h. Yield: 0.60 g (90%). ^1H NMR ($CDCl_3$): 1.20, 1.67 (m's, 5 H), 2.60 (m's, 2 H), 4.0−4.9 (m's, 4 H), all C_8H_{11}; 6.7−to 7.5 (m's, Ph, C_6H_4). According to the low stability of **2** in $CDCl_3$ solution, the signals of the C_8H_{11} ligand in the ^{13}C NMR spectrum could not be assigned. ^{31}P NMR ($CDCl_3$): 55.7 (P(2), d, $^2J(P,P) = 59.8$; $^2J(P,Pt) = 54.7$ Hz), 14.9 (P(1), d, $^2J(P,P) = 59.8$; $^2J(P,Pt) = 50.9$ Hz). IR (Nujol mull): 1481 m, 1437 s, 1310 w, 1098 vs, 1074 vs, 1026 w, 999 w, 910 w, 810 vs, 743 s, 725 m, 710 s, 694 s, 529 m, 515 m, 498 s, 478 w, 403 m cm^{-1}. Anal. Calcd for $C_{45}H_{40}P_2Pt$: C, 64.51; H, 4.81. Found: C, 63.81; H, 4.84. Data for $[HC(PPh_3)_2]I$ are as follows. ^1H NMR (CD_2Cl_2): 1.78 (CH, t, $^2J(HP) = 5.26$ Hz), 7.46−7.56 (m, Ph). ^{31}P NMR (CH_2Cl_2): 20.03 (s). IR (Nujol mull): 1586 w, 1480 m, 1437 s, 1312 w, 1231 s, 1182 m, 1163 w, 1119 m, 1100 s, 1073 w, 1030 w, 1011 m, 990 s, 801 w, 754 m, 747 m, 712 s, 691 s, 671 w, 558 s, 548 s, 517 m, 505 m, 492 m, 482 m, 459 w cm^{-1}.

Reaction of 1 with [(cod)$PtCl_2$]. To a solution of 0.944 g (1.76 mmol) of **1** in about 20 mL of THF at room temperature was added 0.219 g (0.59 mmol) of [(cod)$PtCl_2$], and the mixture was worked up as described above. The ^{31}P NMR signals of the THF solution were identical with the signals of the complex **2**, and the precipitate was identified as the salt $[HC(PPh_3)_2]Cl$. From the THF solution **2** was precipitated with *n*-pentane as described above. Yield: 0.42 g (85%). Yield of $[HC(PPh_3)_2]Cl$: 0.62 g, 1.08 mmol (92%). ^{31}P NMR (CH_2Cl_2): 20.03 ppm.

Reaction of 1 with [(cod)PtI_2] in the Presence of Donor Ligands. The reaction described for the synthesis of **2** was also carried out in the presence of excess PPh_3 and acetonitrile, respectively. However, in all cases only the complex **2** could be identified by ^{31}P NMR spectroscopy and no hints of splitting off cod and a symmetric HI abstraction were detected.

Reaction of 1 with [(cod)PtI_2] (1:1 Molar Ratio). The above procedure was carried out with a 1:1 molar ratio of the starting materials in toluene. After the mixture was stirred for several days, the solvent was evaporated, the oily residue extracted with CH_2Cl_2, and the solution filtered. The clear yellow solution was layered with pentane. After some weeks, a few crystals were obtained along with an amorphous powder. Some pale yellow and orange-brown crystals were identified by X-ray analyses as platinum complexes, whereas the majority of crystals were found to be the salt $[HC(PPh_3)_2]I\cdot 2CH_2Cl_2$ (**3**).

Reaction of 1 with $[(PPh_3)_2Pt(CH_2{=}CH_2)]$. To a solution of 0.58 g (0.78 mmol) of $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ in about 30 mL of toluene was added an excess of **1** (1.11 g, 2.30 mmol), and the mixture was stirred for 24 h at room temperature. After this time the ^{31}P NMR spectrum of the solution showed only the signals of the starting materials. Then, the mixture was heated under reflux for 1 h, during which time the solution turned dark red. After the solution was cooled, red crystals separated (0.30 g; 60% yield), which were identified as the binuclear complex $[Pt_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$ (**4**) described earlier;[21] the ylide **1** was recovered unchanged.

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Supporting Information Available: Tables of atomic positions, equivalent isotropical thermal parameters, and anisotropic thermal displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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