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Cumulenes as ligands

IV *. Rhodium and platinum complexes of tetraphenylhexapentaene. X-ray crystal structure of bis(triphenylphosphine)chloro(tetraphenylhexapentaene)rhodium

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Abstract

The interaction of tetraphenylhexapentaene with chlorotris(triphenylphosphine) rhodium produces a red complex in which rhodium is bound to the second C=C bond of the cumulene. In contrast, reaction of the same cumulene with $(PPh_3)_2Pt^0$ generated by reducing $(PPh_3)_2PtCl_2$ with hydrazine in ethanol results in the formation of a yellow symmetrical complex as the kinetic product. This complex isomerizes to a red unsymmetrical complex. An X-ray crystal structure of bis(triphenylphosphine)chloro(tetraphenylhexapentaene)rhodium is reported.

Introduction

Cumulenes as ligands have received considerable attention in organometallic chemistry [1]. The smallest cumulene, allenes, have been shown to form π-complexes with a variety of metals [2]. Considerably less is known about transition metal complexes of the higher cumulenes. Tetraphenylbutatriene and related butatrienes have been reported to react with chlorotris(triphenylphosphine)rhodium and ethylenebis(triphenylphosphine)platinum to give complexes **1** and **2**, respectively [1,3]. Interestingly rhodium is bound to the central π-bond of the cumulene in **1** and platinum, on the other hand, is bound to the terminal π-bond of the cumulene in **2**. In the case of complex **3** where there is a three-membered ring in the cumulene ligand, the platinum is bound to the cumulene in an η^2-fashion and the three-membered ring is retained. To our knowledge complexes **4** and **5** are the only known examples for hexapentaenes [4]. In this paper we wish to report the rhodium and

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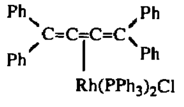
* For Part III see ref. 1.



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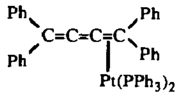

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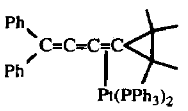

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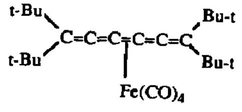

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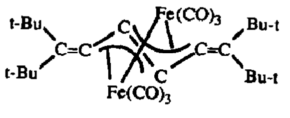

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platinum complexes of tetraphenylhexapentaene and the crystal structure of the rhodium complex. This provides the first such analysis of hexapentaene complexes.

Results and discussion

Reaction with chlorotris(triphenylphosphine)rhodium

The reaction of tetraphenylhexapentaene [5,6] with chlorotris(triphenylphosphine)rhodium [7] in refluxing benzene followed by chromatography on silica gel gives air stable, red, needle shaped crystals. The ^{31}P NMR spectrum shows only one ^{103}Rh coupled ^{31}P doublet centered at 30.4 ppm (^{1}J(Rh–P) = 123.2 Hz), indicating

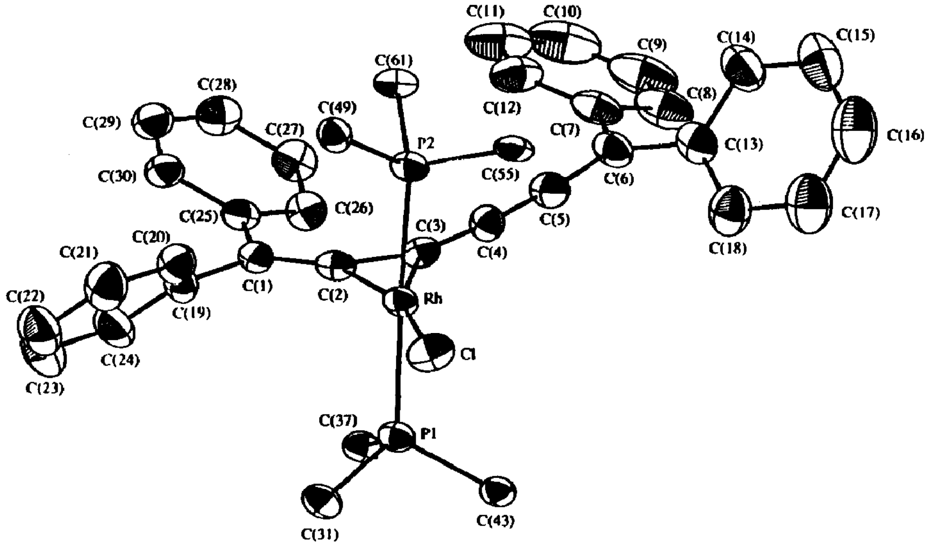


Fig. 1. ORTEP drawing of **7**.

the magnetic equivalence of the two triphenylphosphine ligands. It has been shown [1] that in square planar cumulene rhodium complexes, the cumulenes are bound perpendicularly to the least-square plane defined by rhodium and the other three ligands. There are five π-bonds in the hexapentaene cumulene chain; therefore, three possible products with structures **6**, **7**, and **8** could be formed by the perpendicular binding of the cumulene to the $Rh-(PPh_3)_2-Cl$ plane through the three different π-bonds. The two triphenylphosphine ligands are magnetically equivalent in each case; therefore, the ^{31}P NMR spectrum cannot distinguish between these three different structures.

The ^1H NMR spectrum shows complex aromatic resonances between 7.55 to 6.96 ppm. The important feature of the ^1H NMR spectrum is the presence of two sets of doublet of doublets, one centered at 8.02 ppm ($J = 7.5$, 1.7 Hz) and the other at 6.99 ppm ($J = 8.1$, 1.5 Hz). By integration each set represents two protons; this is typical of the H-2 (H-6) protons in a phenyl group which are split by the H-3 (H-5) protons and one H-4 proton into a doublet of doublets. Each phenyl group has two such magnetically equivalent protons (H-2 and H-6). Therefore, the presence of two sets of doublet of doublets, each corresponding to two protons, uniquely corre-

Table 1

Summary of crystallographic data for **7**

molecular formular	$C_{66}H_{50}ClP_2Rh \cdot C_8H_{10}$
molecular weight	1149.61
crystal system	triclinic
space group	$P\bar{1}$
cell dimensions	
$a = 11.429(3)$, $b = 19.438(7)$, $c = 14.601(4)$ Å	
$\alpha = 105.59(2)$, $\beta = 110.40(2)$, $\gamma = 86.51(3)°$	
volume, Å^3	2926.5
Z	2
d(calcd), g/cm^3	1.31
T°, C	15.0
crystal dimensions, mm	0.30 × 0.30 × 0.22
diffractometer	Syntex $P\bar{1}$
radiations, Å	0.71073
data collection method	$\theta - 2\theta$
scan speed, deg/min	variable, 3.0–8.0
reflections measured	6737, h (0, 11), k (−19, 19), l (−14, 14)
scan range	$k - 1.0$ to $k + 1.0$
2θ limit, °	3.0–42.0
total bkdg. time/scane time	0.5
no. of reflections between std.	98
total unique data	5927
observed data, $I > 3\sigma(I)$	5054
absorption coeff, (μ), cm^{-1}	4.28
no. of variables	667
R (averaging)	0.013, 0.015
max. shift/error	0.02
R (F)	5.47
R_w (F)	6.32
goodness of fit	3.32
max. diff. Fourier peak	0.721 e/Å^3

Table 2

Selected bond distances (Å) for **7** [a]

Rh–Cl	2.364(1)	P(1)–C(43)	1.824(5)	C(2)–C(3)	1.366(7)
Rh–P(1)	2.346(1)	P(2)–C(49)	1.835(5)	C(3)–C(4)	1.310(7)
Rh–P(2)	2.360(1)	P(2)–C(55)	1.819(5)	C(4)–C(5)	1.244(7)
Rh–C(2)	2.025(5)	P(2)–C(61)	1.839(5)	C(5)–C(6)	1.333(7)
Rh–C(3)	2.035(4)	C(1)–C(2)	1.336(6)	C(6)–C(7)	1.502(7)
P(1)–C(31)	1.822(5)	C(1)–C(19)	1.491(6)	C(6)–C(13)	1.471(7)
P(1)–C(37)	1.837(5)	C(1)–C(25)	1.489(6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

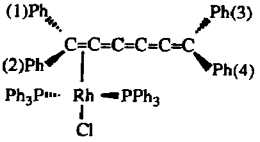
sponds to two magnetically nonequivalent phenyl groups that must not have other equivalent phenyls. That is to say, the four phenyl substituents of the cumulene itself must be magnetically nonequivalent. In structure **6** Ph(1) and Ph(2) are equivalent although different from the two equivalent Ph(3) and Ph(4). In contrast all the phenyl groups of the cumulene in **8** are equivalent. Therefore the product must have structure **7**, the only isomer with four nonequivalent phenyls in the cumulene portion. Likewise the ^{13}C NMR spectrum shows four distinct resonances at 140.70, 140.06, 138.75, and 138.06 ppm corresponding to the four *ipso* carbons of the cumulene phenyls. The low field signal at 161.63 ppm is assigned to either C(4) or C(5) in the cumulene chain. Two resonances are observed in the high field region, one at 117.18 ppm as a singlet [C(2) or C(3)] and the other at 115.52 ppm as a doublet of triplets [^{1}J(Rh–C) = 15.1 Hz, ^{2}J(P–C) = 4Hz, C(3) or C(2)]. These assignments are based on the observation [8] that olefin carbons are highly shielded upon π-bonding to metals. It is not clear to us, however, why only one carbon [C(2) or C(3)] couples to rhodium and the two magnetically equivalent triphenylphosphine ligands. The remaining signals from the aromatic carbons are too complex and impossible to assign. A definitive structure assignment for **7** was established by

Table 3

Selected bond angles (°) for **7** [a]

Cl–Rh–P(1)	89.46(4)	Rh–P(2)–C(49)	118.8(2)
Cl–Rh–P(2)	88.74(4)	Rh–P(2)–C(55)	110.4(1)
Cl–Rh–C(2)	161.5(1)	Rh–P(2)–C(61)	114.6(1)
Cl–Rh–C(3)	159.1(1)	C(49)–P(2)–C(55)	104.0(2)
P(1)–Rh–P(2)	177.58(5)	C(49)–P(2)–C(61)	102.4(2)
P(1)–Rh–C(2)	88.7(1)	C(55)–P(2)–C(61)	105.3(2)
P(1)–Rh–C(3)	93.5(1)	C(2)–C(1)–C(19)	120.6(4)
P(2)–Rh–C(2)	93.6(1)	C(2)–C(1)–C(25)	120.4(4)
P(2)–Rh–C(3)	87.6(1)	C(19)–C(1)–C(25)	118.9(4)
C(2)–Rh–C(3)	39.3(2)	C(1)–C(2)–C(3)	147.4(4)
Rh–P(1)–C(31)	113.2(2)	C(2)–C(3)–C(4)	153.8(5)
Rh–P(1)–C(37)	115.0(1)	C(3)–C(4)–C(5)	175.2(5)
Rh–P(1)–C(43)	115.8(2)	C(4)–C(5)–C(6)	175.5(5)
C(31)–P(1)–C(37)	103.3(2)	C(5)–C(6)–C(7)	118.5(5)
C(31)–P(1)–C(43)	105.3(2)	C(5)–C(6)–C(13)	120.8(5)
C(37)–P(1)–C(43)	102.8(2)	C(7)–C(6)–C(13)	120.7(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



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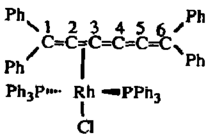

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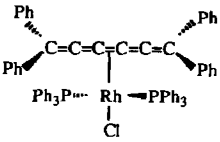

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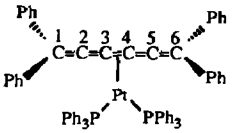

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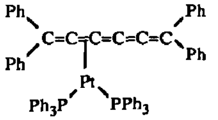

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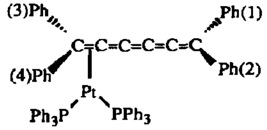

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X-ray crystallography. A summary of the crystallographic data and selected bond distances and bond angles are listed in Tables 1–3. The ORTEP drawing of 7 (Fig. 1) clearly shows that the rhodium is bound to the second π-bond of the cumulene. The coordination around rhodium can be described as square planar. The dihedral angle between the least-square planes of the cumulene and the P_2RhCl plane is 98.05°. The two triphenylphosphine ligands are diagonal, the angle of P(1)–Rh–P(2) being 177.6°. The distances of Rh–C(2) and Rh–C(3) are 2.025 and 2.035 Å, respectively and comparable to those in the reported butatriene rhodium complex where the Rh–C distances [1] are 2.008 and 2.043 Å, respectively. The coordination of rhodium to tetraphenylhexapentaene is therefore more symmetrical than to the lower homolog of the reported butatriene [1]. The two triphenylphosphine ligands are almost equally separated from rhodium, the distances of Rh–P(1) and Rh–P(2) being 2.346 and 2.360 Å, respectively. There is considerable bending of the cumulene ligand upon coordination from the normal linear arrangement of the free cumulene, the C(1)–C(2)–C(3) and C(2)–C(3)–C(4) angles being 147.4 and 153.8°, respectively. The bending of the rest of the cumulene is relatively small, the C(3)–C(4)–C(5) and C(4)–C(5)–C(6) angles being 175.2 and 175.5°, respectively. The Rh–Cl bond approximately equally divides the P(1)–Rh–P(2) and C(2)–Rh–C(3) angles, the Cl–Rh–P(1), Cl–Rh–P(2), Cl–Rh–C(2) and Cl–Rh–C(3) angles being 89.46, 88.74, 161.5, and 159.1°, respectively.

Reactions with platinum

The reaction of tetraphenylhexapentaene with $(PPh_3)_2Pt^0$ generated by reducing $(PPh_3)_2PtCl_2$ [9] with hydrazine in ethanol leads to the isolation of a yellow powder. Once again three different planar structures 9, 10, and 11 are possible [3] for a Pt-adduct based upon coordination with the different π-bonds of the cumulene. The ^{31}P NMR spectrum showed a single resonance at 28.3 ppm with ^{195}Pt satellites (^1J(Pt–P) = 3475 Hz), indicating that the two triphenylphosphine ligands are magnetically equivalent. This clearly establishes the structure of the product as **9** which, among **9**, **10**, and **11**, is the only one with two equivalent triphenylphosphine ligands. In the ^{13}C NMR spectrum C3(C4) is shifted up field to 109.73 ppm as an unresolved multiplet. C(2) is shifted down field to 187.16 ppm and C(1) resonates at 139.06 ppm. Compared to the free tetraphenylhexapentaene in which C(1) resonates at 124.71 ppm, C(2) at 149.42 ppm, and C(3) at 127.33 ppm [10], hence, C(1) and C(2) in **9** are shifted down field by approximately 14 and 38 ppm, respectively. In contrast, as expected, C(3) is shifted up field by 18 ppm.

Interestingly the yellow complex **9** gradually changes to red in either the solid state or solution (benzene or chloroform). The change is obvious in the ^{31}P NMR spectrum. Two more doublets with ^{195}Pt satellites appear and the original singlet decreases in intensity. This clearly indicates that the initially formed symmetrical complex **9** has isomerized to an unsymmetrical isomer, **10** or **11** in which the two triphenylphosphine ligands are no longer equivalent. The two ^{31}P atoms couple to each other to give two doublets and to ^{195}Pt to give the usual satellites. In one experiment **9** was stirred in benzene for two days at room temperature and the conversion was still incomplete as monitored by ^{31}P NMR. Attempts to separate these two complexes by recrystallization in different solvents failed. They may however, be separated by HPLC. Unfortunately, to get reasonable separation only small amounts of sample can be injected each time and the process is extremely time consuming. As a result, only a very small sample of the red complex was obtained, moreover its ability to form solvates made it very difficult to purify the compound. Hence, we could only obtain ^{1}H and ^{31}P NMR spectra.

The ^{31}P NMR spectrum shows two doublets with ^{195}Pt satellites (Fig. 2) (31.4 ppm, ^1J(Pt–P) = 3077 Hz; 28.3 ppm, ^1J(Pt–P) = 3399 Hz, ^2J(P–P) = 32 Hz) and hence cannot distinguish between two different unsymmetrical structures **10** and **11**. The ^{1}H NMR spectrum shows complex aromatic resonances between 7.37 to 6.61 ppm. Also present are distinct doublet of doublets at 7.62 ppm (J = 7.3, 1.9 Hz) and a triplet at 6.43 ppm (J = 7.6 Hz). Each of these resonances corresponds to two protons by integrations. The doublet of doublets must be the H-2 (H-6) protons of a cumulene phenyl group and the triplet must be either the H-3 (H-5) or the H-4 protons of a cumulene phenyl. The fact that each of these signals represents only two protons clearly indicates that the four cumulene phenyl groups must be magnetically nonequivalent. Based upon these data the new complex is assigned as

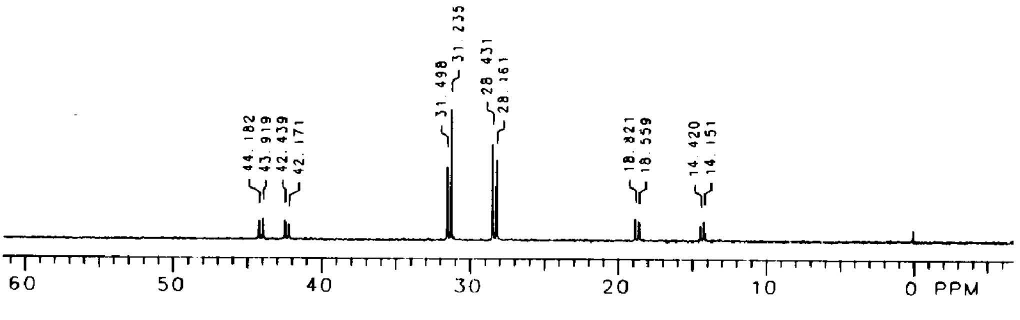

Fig. 2. ^{31}P NMR spectrum of **10**.

10 as the most likely structure since it is the only isomer in which all the four cumulene phenyls are nonequivalent. Isomer **11** is ruled out simply by the presence of two sets of equivalent phenyls [Ph(1) and Ph(2); Ph(3) and Ph(4)]. The triplet at 6.43 ppm represents two protons and they must be from a single phenyl group, therefore, those two protons must be H-3 and H-5. We believe that the H-2(H-6) protons at 7.62 ppm and the H-3 (H-5) protons at 6.43 ppm are from two different phenyls because there is no reason why they are separated so much in the ^{1}H NMR spectrum if they are from the same phenyl group.

In conclusion, we have shown that upon reaction with chlorotris(triphenylphosphine)rhodium, tetraphenylhexapentaene gives a π-complex **7** in which rhodium is bound to the second C=C bond of the cumulene. In comparison, reaction of the same cumulene with $(PPh_3)_2Pt^0$ generated by reducing $(PPh_3)_2PtCl_2$ with hydrazine gives the yellow symmetrical complex **9** as the kinetic product. It undergoes isomerization in either the solid state or solution to the unsymmetrical isomer, tentatively assigned as **10**.

Experimental

General

Tetraphenylhexapentaene [5,6], chlorotris(triphenylphosphine)rhodium [7], and bis(triphenylphosphine)platinum dichloride [9] were prepared using literature procedures. All reactions were carried out under an atmosphere of dry argon, but they were worked up in air. All solvents were either reagent grade or purified according to standard procedures. Melting points were recorded on a Mel-Temp capillary apparatus and were not corrected. Infrared spectra were recorded on a Perkin Elmer 298 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer. Tetramethylsilane was used as internal reference for ^{1}H NMR and 85% H_3PO_4 was used as external reference for the ^{31}P NMR spectra. ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.00 ppm. The fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical 750-E instrument using chloroform and 3-nitrobenzyl alcohol as the matrix. HPLC separation was performed on a Varian 5000 liquid chromatograph.

Chloro(tetraphenylhexapentaene)bis(triphenylphosphine)rhodium (7). Chlorotris (triphenylphosphine)rhodium (185 mg, 0.200 mmol) and tetraphenylhexapentaene (76 mg, 0.20 mmol) were heated in benzene (25 mL) at reflux for 21 h. Benzene was then removed and the residue obtained was chromatographed on a silica gel column (2 × 15 cm). Hexanes were used first to elute the most mobile unreacted cumulene and chloroform was then used to elute the second (major) band. The chloroform solution was concentrated and red crystals were obtained upon the slow addition of hexanes. The product was filtered off to yield 180 mg of **7** after drying in air (86%). X-ray quality crystals were grown from hot xylenes. One xylene molecule was trapped in the unit cell. M.p. 201–202°C (dec); IR (KBr pellet, cm^{-1}) 3050, 1590, 1480, 1430, 1090, 1025, 765, 745, 690; ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, $J = 7.5$, 1.7 Hz, 2H), 7.55–7.46 (m, 16H), 7.40–7.20 (m, 15H), 7.16–7.07 (m, 12H), 7.06–6.96 (m, 3H), 6.69 (dd, $J = 8.1$, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 161.63 (C(4) or C(5)), 140.70 (*ipso*), 140.06 (*ipso*), 138.75 (*ipso*), 138.06 (*ipso*), 134.71 (t, $J = 5.9$ Hz), 130.77, 130.47, 130.21, 129.80, 129.17, 128.50, 128.25, 128.07, 127.91, 127.77, 127.71, 127.65, 127.36, 127.13, 126.76, 125.81, 117.18 (C(2) or C(3)), 115.52 (C(3) or C(2), dt, ${}^1J$(Rh–C) = 15.1 Hz, ${}^2J$(P–C) = 4 Hz); ^{31}P NMR ($CDCl_3$) δ 30.4 (d, ${}^1J$(Rh–P) = 123.2 Hz); MS, *m/z* (%) 1042 (12, *M*), 780 (12, *M* – PPh_3), 745 (41, *M* – PPh_3 – Cl), 662 (64, *M* – cumulene), 627 (74, $Rh(PPh_3)_2$), 287 (100), 286 (100).

Bis(triphenylphosphine)(tetraphenylhexapentaene)platinum (9 and 10). To a suspension of $(PPh_3)_2PtCl_2$ (60 mg, 0.076 mmol) in degassed ethanol (4 mL) was added hydrazine monohydrate (0.1 mL). The mixture was stirred at room temperature until the suspension disappeared to give a clear yellow solution. To this solution was added a suspension of tetraphenylhexapentaene (29 mg, 0.076 mmol) in the same solvent (4 mL) through a pipet. The mixture was heated to reflux and kept there for 4 min. After cooling to room temperature the yellow precipitate was filtered off and washed with water (3 × 2 mL), then cold (0 °C) ethanol (3 × 2 mL) and finally ethyl ether (2 × 2 mL). After drying under vacuum 61 mg of product **9** was obtained as a yellow powder (73%). M.p. 136–140 (dec); IR (KBr pellet, cm^{-1}) 3050, 1920 (cumulene), 1595, 1490, 1430, 1090, 1025, 770, 740, 690; ^{1}H NMR ($CDCl_3$) δ 7.32–7.20 (m, 12H), 7.20–7.02 (m, 26H), 7.00–6.89 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 187.16 (C(2)), 139.06 (C(1)), 133.87 (t, J = 6.5 Hz), 129.54, 128.48, 127.86, 127.69, 125.48, 109.73 (unresolved mult., C(3)); ^{31}P NMR ($CDCl_3$) δ 28.3 (s with ^{195}Pt satellites, ${}^1J$(Pt–P) = 3457 Hz); MS, *m/z* (%) 1099 (0.5, *M*), 719 (27, *M* – cumulene), 307 (100), 289 (93), 279 (68). **9** was heated in xylenes at 90 °C for 15 h to give a red solution. Complex **10** was isolated via HPLC using 9:1 hexane: ethylacetate. ^{1}H NMR ($CDCl_3$) δ 7.62 (dd, J = 7.3, 1.9 Hz, 2H), 7.37–7.22 (m, 16H), 7.21–7.10 (m, 12H), 7.06–6.89 (m, 13H). 6.75–6.61 (m, 5H), 6.43 (t, J = 7.6 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ 31.4 (d, with ^{195}Pt satellites, ${}^1J$(Pt–P) = 3077 Hz, ${}^2J$(P–P) = 32 Hz), 28.3 (d with ^{195}Pt satellites, ${}^1J$(Pt–P) = 3399 Hz, ${}^2J$(P–P) = 32 Hz).

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