Cyclotrimerization of phenylethynes to fulvene: reactivity of *cis*-dichloro(1,1′-bis(diphenylphosphino)ferrocene)palladium(II)

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Abstract

In the presence of triethylamine (NEt$_3$) and ethanol (EtOH), phenylethyne (or phenylacetylene, PhC≡CH) underwent cyclotrimerization: *cis*-dichloro(1,1′-bis(diphenylphosphino)ferrocene)palladium(II), [PdCl$_2$(dppf)] (**1**), reacted with phenylethyne to give [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**). Reaction of **2** with dimethyl acetylenedicarboxylate in dichloromethane gave [Pd(dppf)(CH$_3$O$_2$CC≡CCO$_2$CH$_3$)] (**3**) and a free 2,3,5-triphenylfulvene. Crystallographic data for **2·**H$_2$O: triclinic space group $P\bar{1}$, $a = 10.658(2)$, $b = 10.896(2)$, $c = 21.080(3)$ Å, $\alpha = 85.303(9)°$, $\beta = 76.556(9)°$, $\gamma = 80.447(10)°$, $Z = 2$, $R(wR_2) = 0.0487(0.1083)$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cyclotrimerization of phenylethyne; 2,3,5-Triphenylfulvene; Crystallographic data

1. Introduction

Cyclotrimerization of substituted alkynes in the presence of transition-metal complexes usually gives 1,3,5- or 1,2,4-trisubstituted benzene derivatives in high selectivity, which are sometimes difficult to prepare by other methods. Cobalt, rhodium, nickel, and palladium complexes have been employed for this reaction, and selectivity control to **A** or **B** is possible to some extent [1]. For example, phenylethyne (or phenylacetylene) can be converted to 1,2,4-triphenylbenzene by cyclotrimerization in the presence of [(CO)$_3$Ni(O^{i}Pr)$_3$]. On the contrary, it can be converted mainly to 1,3,5-triphenylbenzene in the presence of [(η^3-allyl)NiCl]$_2$ or NiBr$_2$(PBu$_3$)$_2$ [2].
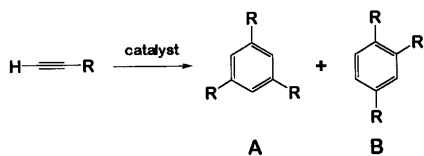

There have been only a few reports on the formal [2 + 2 + 1] cyclotrimerization of alkynes to give fulvene

products [3–7]. Two mechanisms have been proposed: a metallacyclopentadiene [3–6] route and a metallacyclohexadiene route [7]. For example, O'Conner and co-workers have recently reported the [2 + 2 + 1] alkyne cyclotrimerization to give fulvenes via a metallacyclopentadiene route, using chlorobis(phosphine) iriacyclopentadiene compounds [3]. Their proposed mechanism involves initial coordination of an alkyne to the Ir metal, rearrangement of the alkynyl ligand to a vinylidene ligand, and reductive cyclization to the fulvene products by the coupling of the vinylidene ligand and the metallacyclopentadiene ring. On the other hand, Moran and co-workers reported the trmerization of 3,3,-dimethylbut-1-yne, proposing that the reaction proceeds via a metallacyclobutene intermediate that reacts with the alkyne by insertion, followed by reductive elimination from the metallacyclohexadiene to give the final product (Scheme 1) [7].

Very recently, we reported the preparation and structure of *trans*-bis(phenylethynyl)bis(triethylphosphine)palladium(II), *trans*-Pd(C≡CPh)$_2$(PEt$_3$)$_2$, which was prepared from *cis*-PdCl$_2$(PEt$_3$)$_2$ and phenylethyne (HC≡CPh) in the presence of triethylamine (NEt$_3$) [8]. In order to prepare a *cis*-bis(phenylethynyl)palladium derivative, we treated phenylethyne with *cis*-dichloro-(1,1′ - bis(diphenylphosphino)ferrocene)palladium(II),

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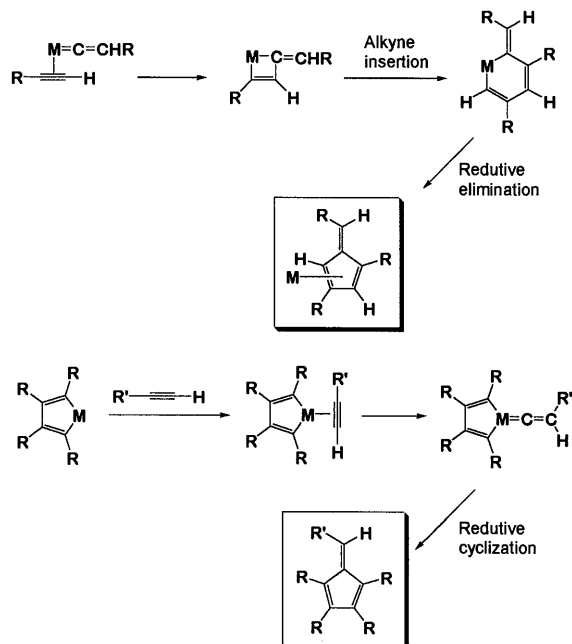
Scheme 1.

[PdCl$_2$(dppf)] (**1**), in the presence of triethylamine and ethanol, in which case the dppf ligand is a sterically bulky and chelating ligand. However, an unexpected product [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**) was obtained from this reaction. We report here the preparation, structure, and some properties of **2**.

2. Experimental

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use. Glassware was either flame- or oven-dried. Hydrocarbon solvents were stirred over concentrated H$_2$SO$_4$ for about 48 h, neutralized with K$_2$CO$_3$, stirred over sodium metal, and distilled by vacuum transfer. Diethyl ether (Et$_2$O) was distilled over sodium metal and dichloromethane (CH$_2$Cl$_2$) over CaH$_2$. NMR solvent (CDCl$_3$) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. PdCl$_2$, phenylethyne (or phenylacetylene, PhC≡CH), and dimethyl acetylenedicarboxylate (CH$_3$O$_2$CC≡CCO$_2$CH$_3$) were purchased from Fluka company. Triethylamine (NEt$_3$) and ethanol (EtOH) were distilled and stored under argon. *cis*-PdCl$_2$(dppf) (**1**) was prepared by the literature method [9].

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to

tetramethylsilane. ^{31}P{^{1}H}-NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to 85% H$_3$PO$_4$. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses and mass spectrometry were performed by the Korea Basic Science Center.

2.1. Preparation of [Pd(dppf)(2,3,5-triphenylfulvene)] (2)

At room temperature (r.t.), NEt$_3$ (0.11 ml, 0.84 mmol) was added to a mixed solvent of EtOH (5 ml) and CH$_2$Cl$_2$ (7 ml) containing **1** (0.15 g, 0.205 mmol) and PhC≡CH (0.21 ml, 2.05 mmol). The mixture was stirred for 10 h. The resulting solution was concentrated under vacuum to about 7 ml to give a yellow powder. The resulting precipitates were filtered, washed with Et$_2$O (3 × 10 ml) and MeOH (1 × 10 ml), and then dried under vacuum to give a yellow solid of [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**) (0.058 g, 0.060 mmol, 29%). This product conveniently recrystallized from dichloromethane–hexane.

^{1}H-NMR (CDCl$_3$): δ 7.494–6.856 (35H, *Ph*), 6.409 (1H, d, C*H* in fluvene, $J = 3$ Hz), 4.353–3.896 (8H, m, *Cp*), 2.999 (1H, m, diastereotopic, Pd–C*H*$_2$), 2.934 (1H, m, diastereotopic, Pd–C*H*$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 140.251–122.488 (*Ph*, fulvene C_1–C_5), 93.367–71.174 (*Cp*), 50.057 (fulvene C_6). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 21.744 (1P, s), 18.155 (1P, s). Anal. Calc. for C$_{58}$H$_{46}$P$_2$FePd ($M_r = 967.21$): C, 72.03; H, 4.79. Found: C, 72.42; H, 4.61%. M.p. (decomp.): 165–167°C. IR (KBr): 3051, 1595, 1479, 1465, 1435, 1365, 1163, 1093, 1029, 744, 696, 633 cm^{-1}.

2.2. Preparation of [Pd(dppf)(CH$_3$O$_2$CC≡CCO$_2$CH$_3$)] (3) and isolation of 2,3,5-triphenylfulvene

To a yellow compound **2** (0.073 g, 0.075 mmol) in CH$_2$Cl$_2$ (15 ml) was added dimethyl acetylenedicarboxylate, CH$_3$O$_2$CC≡CCO$_2$CH$_3$ (0.019 ml, 0.16 mmol). After 30 min, the reaction flask was wrapped with an aluminum foil, and the mixture was stirred at r.t. for 24 h. The color of the solution turned from yellow to red. Volatile materials were removed under vacuum, and the resulting red residue was washed with pentane (5 ml). The remaining solid was dried under vacuum to give a yellow powder of [Pd(dppf)(CH$_3$O$_2$CC≡CCO$_2$CH$_3$)] (**3**) (0.044 g, 0.055 mmol, 73%).

^{1}H-NMR (CDCl$_3$): δ 7.635–7.184 (20H, m, *Ph*), 4.271 (4H, d, CpH_γ, $J = 2$ Hz), 4.154 (4H, d, CpH_β, $J = 2$ Hz), 3.367 (6H, s, C*H*$_3$O$_2$CC≡CCO$_2$C*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 165.844 (CH$_3$O$_2$C*C*≡*C*CO$_2$-CH$_3$) 136.946–128.017 (*Ph*), 115.697 (CH$_3$O$_2$C*C*≡

Table 1
X-ray data collection and structure refinement for **2**·H_2O

Formula	$C_{58}H_{48}OP_2FePd$
Formula weight	985.15
Temperature (K)	297(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.658(2)
b (Å)	10.896(2)
c (Å)	21.080(3)
α (°)	85.303(9)
β (°)	76.556(9)
γ (°)	80.447(10)
V (Å^3)	2345.5(6)
Z	2
D_{calc} (g cm^{-3})	1.395
μ (mm^{-1})	0.801
T_{min}	0.6874
T_{max}	0.7262
$F(000)$	1012
No. of reflections measured	9122
No. of reflections unique	8642
No. of reflections with $I > 2\theta(I)$	6291
No. of parameters refined	591
2θ Range (°)	3.5–51.0
Scan type	ω
Scan speed	Variable
GoF (goodness-of-fit on F^2)	1.035
Max., min. in $\Delta\rho$ (e Å^{-3})	1.052, −0.382
R	0.0487
$^a wR_2$	0.1083

^{a} $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

CCO_2CH_3), 80.614 (Cp C_{ipso}), 75.481 (Cp C_α), 72.325 (Cp C_β), 52.343 ($CH_3O_2CC\equiv CCO_2CH_3$). $^{31}P\{^1H\}$-NMR (CDCl$_3$): δ 26.418 (s). Anal. Calc. for $C_{40}H_{34}O_4P_2FePd$ ($M_r = 802.92$): C, 59.84; H, 4.26. Found: C, 59.76; H, 4.63%. M.p. (decomp.): 160–162°C. IR (KBr): 2948, 1850 (C≡C), 1688 (C=O), 1433, 1225 (C–O), 1172 (C–O), 1094, 1030, 749, 698, 488 cm^{-1}.

When the pentane extract was stored at −25°C for 1 day, red crystalline solids were formed. The precipitates were filtered off and washed with cold pentane to give red solids of 2,3,5-triphenylfulvene (0.01 g, 0.033 mmol, 44%).

^1H-NMR (CDCl$_3$): δ 7.500–7.207 (15H, *Ph*), 6.910 (1H, d, C*H* in fluvene, $J = 1$ Hz), 6.121 (1H, d, diastereotopic, C*H*$_2$, $J = 0.5$ Hz), 5.939 (1H, d, diastereotopic, C*H*$_2$, $J = 0.5$ Hz). $^{13}C\{^1H\}$-NMR (CDCl$_3$): δ 153.210 (C_1), 141.621–125.117 (*Ph*, fulvene C_2–C_6). Anal. Calc. for $C_{24}H_{18}$ ($M_r = 306.41$): C, 94.08; H, 5.92. Found: C, 93.87 H, 6.09%. M.p.: 138–140°C. MS (EI): 306 (M$^+$, 100), 229 (M$^+$–Ph, 25), 152 (M−2Ph, 17), 77 (Ph, 9). IR (KBr): 3062, 1655, 1600, 1565, 1485, 1441, 1409, 1373, 1064, 1028, 933, 858, 762, 698 cm^{-1}.

2.3. X-ray structure determination

All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 34 reflections in the range $15.0 < 2\theta < 25.0°$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with psi-scan data. All calculations were carried out with use of the Siemens SHELXTL programs [10].

A yellow crystal of **2**·H_2O, shaped as a block of approximate dimensions $0.32 \times 0.24 \times 0.10$ mm^3, was used for crystal and intensity data collection. The unit cell parameters suggested a triclinic lattice, and successful structural convergence was obtained in the centrosymmetric space group $P\bar{1}$. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2 values, and all non-hydrogen atoms were refined anisotropically. The cocrystallized H_2O exhibited a structural disorder. The best fit for the oxygen was obtained by considering the O atom to be distributed over two positions with the site occupation factors of 0.59:0.41. The hydrogen atoms (H351, H352, and H39) on the fulvene ring were located and refined with isotropic temperature factors. The hydrogen atoms of the cocrystallized water molecule were not located. The other hydrogen atoms were generated in idealized positions and refined in a riding model. The selected bond distances and bond angles are shown in Table 2.

3. Results and discussion

3.1. Preparation

In the presence of triethylamine, [PdCl$_2$(dppf)] (**1**) reacts with excess (ten equivalents) phenylethyne (PhC≡CH) to give a fulvene complex [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**) (Eq. 1). In this reaction, triethylamine acts as a base to remove HCl liberating from the reaction mixture. When the amount of PhC≡CH is reduced down to two equivalents, the reaction does not go to completion, and at least six equivalents of PhC≡CH is required to complete the reaction. However, using more than ten equivalents of PhC≡CH does not improve the yield. Compound **2** must be washed with methanol in order to remove [NEt$_3$H]Cl from the reaction mixture in the workup process. Compound **2** appears to be air- and moisture-stable both in solution and in the solid state.

$$(1)$$
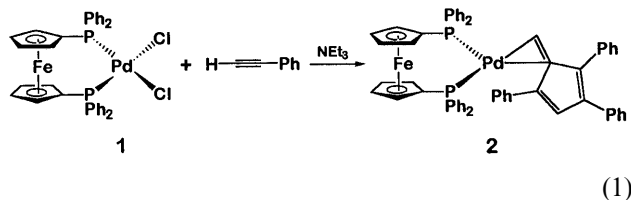
In the preparation of **2**, a mixed solvent of EtOH and CH_2Cl_2 is used. In the absence of EtOH, the reaction does not proceed at all. In addition, the reaction with methanol (MeOH) in place of EtOH also proceeds well, but the following workup gives a lower yield. We have carried out this reaction in *N,N*-dimethylformamide ($HCONMe_2$, DMF), a polar solvent with no ionizable hydrogen atoms, to check the possibility that the alcohol in this reaction acts as a proton donor. The reaction with DMF in place of EtOH does not occur at all. These experimental results suggest that EtOH maybe acts as a proton donor and is preferable to MeOH in terms of workup although both have almost the same acid strength (pK_a = 16.00 for EtOH; pK_a = 15.54 for MeOH). However, we cannot rule out the possibility that EtOH acts as a reducing agent and consequently reduces the Pd metal.

The presence of bidentate coligands in metal complexes allows the isolation *cis*-dialkynyl Pd complexes [11,12]. However, in our reaction, the expected *cis*-di-alkynyl complex *cis*-[Pd(C≡CPh)$_2$(dppf)] is not obtained, but the reaction proceeds to give the unexpected product [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**). The palladium metal appears to have been formally reduced form $+2$ (in **1**) to 0 (in **2**) during the reaction, but its actual oxidation state is not clear (see below). Compound **2** has a 2,3,5-triphenylfulvene ligand, which has probably been formed by the cyclotrimerization of

phenylethynes. Unfortunately, we cannot give a clear-cut explanation about the mechanism for the formation of the fulvene ligand in this reaction. The known mechanisms involving a metallacyclohexadiene or metallacyclopentadiene intermediate do not seem to be appropriate for our case, because they cannot clearly explain the relative orientation of the three phenyl groups on the fulvene ring. In other words, the cy-clotrimerization of alkynes generally gives, except one example, the fulvenes with a substituent at the exocyclic double bond, as shown in Scheme 1. Very recently, Yamamoto and co-workers have reported the cy-clotrimerization of aliphatic akynes (1-pentyne, 1-hexyne, 1-octyne, 1-dodecyne, and 3-cyclopentyl-propyne), in which the catalyst is a mixture of [(η^3-al-lyl)PdCl]$_2$ (5 mol%) and dppf (10 mol%), to give the fulvenes with no substituent at the exocyclic double bond (Eq. 2) [13]. They observed that, under their reaction conditions, phenylethyne undergoes the reaction to give several unidentified products and the compound 2,3,5-triphenylfulvene can be detected by GC.


$$(2)$$
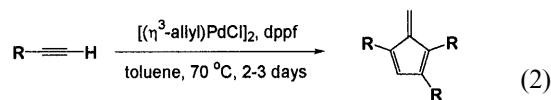
When this reaction is carried out in neat NEt_3, which is expected to act as a base as well as a solvent to promote deprotonation, the product gives a mixture of the starting material (**1**), the compound **2**, and a new product. No matter how hard we have tried to completely remove NEt_3, it has always remained in the product mixture. Moreover, the separation of the mixture has not been successful, and therefore we have given up further reactions.

Table 2
Selected bond distances (Å) and bond angles (°) for **2·H₂O**

Pd1–C35	2.113(4)	Pd1–C36	2.218(4)	Pd1–P1	2.308(1)
Pd1–P2	2.334(1)	C35–C36	1.425(6)	C36–C40	1.461(6)
C36–C37	1.469(6)	C37–C38	1.390(6)	C38–C39	1.439(7)
C39–C40	1.372(6)	C35–H351	0.93(5)	C35–H352	1.00(5)
C39–H39	0.94(5)	Fe1–Ct(1)[a]	1.645	Fe1–Ct(2) [a]	1.647
C35–Pd1–C36	38.3(2)	C35–Pd1–P1	99.9(1)		
C36–Pd1–P1	138.1(1)	C35–Pd1–P2	156.1(1)		
C36–Pd1–P2	117.9(1)	P1–Pd1–P2	103.62(4)		
C1–P1–Pd1	121.5(1)	C6–P2–Pd1	113.2(1)		
C36–C35–Pd1	74.8(2)	C36–C35–H351	117(3)		
Pd1–C35–H351	113(3)	C36–C35–H352	120(3)		
Pd1–C35–H352	106(2)	H351–C35–H352	117(4)		
C35–C36–C40	126.2(4)	C35–C36–C37	125.8(4)		
C40–C36–C37	106.7(4)	C35–C36–Pd1	66.9(2)		
C40–C36–Pd1	104.3(3)	C37–C36–Pd1	114.1(3)		
C38–C37–C36	107.2(4)	C37–C38–C39	108.6(4)		
C40–C39–C38	109.9(4)	C40–C39–H39	130(3)		
C38–C39–H39	120(3)	C39–C40–C36	107.5(4)		
Ct(1)–Fe1–Ct(2)	178.37				

[a] Ct(1) and Ct(2) refer to the computed centroids of the ring carbons C1–C5 and C6–C10, respectively.
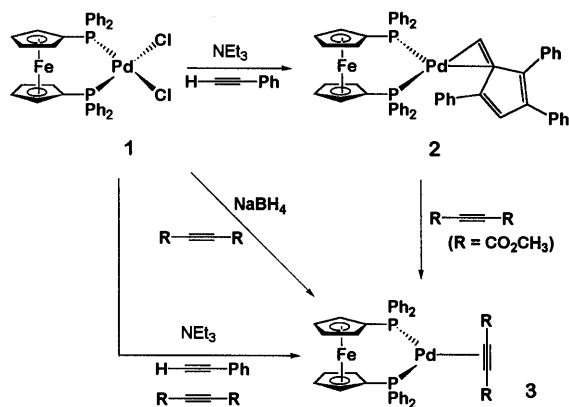
Scheme 2.

In compound **2**, the exocyclic double bond of the fulvene ligand appears to be a neutral CH_2 group bonded to Pd in the η^2-type. In ^{1}H-NMR spectra of **2**, the vinyl protons of the exocyclic double bond exhibit two multiplets at δ 2.999 and 2.934 ppm, which indicates that these protons are diastereotopic and the resonance structure **II** is a major contributor in which the five-membered ring has an aromatic character. In the free fulvene, which has been isolated from the substitution reaction of **2** and dimethyl acetylenedicarboxylate ($CH_3O_2CC\equiv CCO_2CH_3$), the corresponding protons appear as two doublets at δ 6.121 and 5.939 ppm with the coupling constant $J = 0.5$ Hz. The high-field shift of the exocyclic CH_2 protons on bonding to the Pd metal is consistent with a well-known fact that the chemical shifts of protons alpha to a metal are often considerably shifted to high field of those in the parent (or free) ligand [14]. We speculate the hybridzation of the terminal carbon of the exocyclic double bond (C6) to be intermediate between sp^2 and sp^3, and therefore the oxidation state of Pd might be intermediate between 0 and $+2$. The C-6 atom appears at an extremely high field of δ 50.057 ppm in the ^{13}C{^{1}H}-NMR spectra, which might further support the structure of **II** as a major contributor. ^{1}H-NMR spectra of **2** exhibit four peaks assigned to the Cp protons, indicating a low symmetry of **2**. In ^{31}P{^{1}H}-NMR spectra of **2**, two broad singlets appear at δ 21.744 and 18.155 ppm, indicating that two phosphorus nuclei of the dppf ligand are inequivalent.
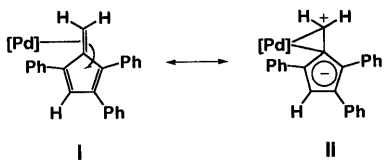
[Pd(dppf)($CH_3O_2CC\equiv CCO_2CH_3$)] (**3**) has been prepared by the reaction of compound **2** with dimethyl acetylenedicarboxylate (2.2 equivalents) in CH_2Cl_2 (Eq. 3). Compound **3** has been characterized by ^{1}H-NMR,

^{31}P{^{1}H}-NMR, ^{13}C{^{1}H}-NMR, and IR. The yellow compound **3** is stable both in solution and in the solid state. The NMR spectra of **3** became so simple compared with those of **2**, probably due to the enhanced symmetry. For example, ^{1}H-NMR spectra of **3** exhibit two sharp doublets at δ 4.154 and 4.271 ppm with the coupling constant $J = 2$ Hz for the Cp protons, and its ^{31}P{^{1}H}-NMR spectra exhibit only one singlet at δ 26.468 ppm to indicate the two phosphorus nuclei of the dppf ligand to be equivalent. In the IR spectra of **3**, the band at 1850 cm^{-1} can be assigned to the C≡C stretching and that at 1688 cm^{-1} to the C=O stretching.
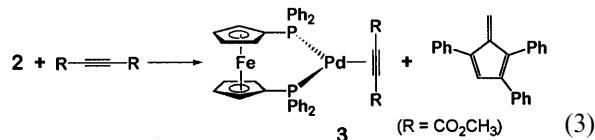
The 2,3,5–triphenylfulvene, which has been liberated from the reaction of **2** with dimethyl acetylenedicarboxylate, can be isolated from the pentane extract when the reaction mixture is washed with pentane in preparing **3**. The free fulvene has been characterized by spectroscopy (^{1}H-NMR, ^{13}C{^{1}H}-NMR, and IR), high-resolution mass spectrometry, and elemental analysis. ^{1}H-NMR spectra of the fulvene exhibit two doublets at δ 5.939 and 6.121 ppm for the vinyl protons of the exocyclic double bond, and one doublet at δ 6.910 ppm for the proton on the fulvene ring. Very recently, Bazan and co-workers have reported that transition-metal complexes containing cyclopentadienyl-based ligands can be obtained from fulvene and a suitable homoleptic complex of the type ML_4 (M = Zr or Hf; L = CH_2Ph or NMe_2) [15]. In their study, (η^6-fulvene)-metal species has been proposed as an intermediate, which undergoes intramolecular nucleophilc substitution to give the desired product.

3.2. Property

When **1** is treated with propargyl chloride ($HC\equiv CCH_2Cl$) in the presence of NEt_3, no sign of reaction can be observed. In the presence of phenylethyne and triethylamine, **3** can be directly obtained by treating **1** with excess dimethylacetylene dicarboxylate (Scheme 2). However, the free fulvene cannot be isolated in this reaction. In addition, in the presence of sodium borohydride, **1** reacts with dimethylacetylene dicarboxylate to also give **3**.

Compound **2** has been treated with excess triethylphosphine (PEt_3) to check whether substitution reaction for the fulvene or dppf ligand occurs, but no sign of reaction has been observed. Compound **2** has also been treated with iodomethane (MeI) to check whether oxdative addition occurs, but the reaction has not occurred, either. Moreover, **2** does not react with

unsaturated organic compounds such as a tetrasubstituted alkene (2,3-dimethyl-2-butene), ethylene ($H_2C=CH_2$), and carbon monoxide ($C\equiv O$).

3.3. Structure

The structure of **2** with the atomic numbering scheme is shown in Fig. 1, in which the cocrystallized H_2O molecule is omitted for clarity. Compound **2** has one bidentate dppf ligand and one η^2-fulvene ligand. The coordination sphere of the Pd metal can be described as a distorted square plane. The equatorial plane, which is defined by C35, C36, P1, and P2, is relatively planar with an average atomic displacement of 0.0083 Å. The Pd metal lies below the equatorial plane by 0.077(7) Å. The Pd–P1 and Pd–P2 bond distances of 2.308(1) and 2.334(1) Å in compound **2** are longer than the Pd–P bond distances of 2.283(1) and 2.301(1) Å found for the parent compound **1** [9]. The P–Pd–P angle in **2** also becomes larger from 99.07° in **1** to 103.62(4)°.

The two Cp rings are not perfectly parallel but twisted from each other with a dihedral angle of 1.8(2)°. The torsion angle of P1···C1···C6···P2 is 30.4(2)°, indicating that the two Cp rings adopt a gauche (or staggered) conformation. For comparison, the ideal torsion angle for the gauche conformation is 36°. The Fe1–Ct (Ct: a centroid of the Cp ring) distances are 1.645 and 1.647 Å, and the angle of the Ct(1)–Fe–Ct(2) (Ct(1): C1–C5; Ct(2): C6–C10) is 178.37°. The bite angle of P1···Fe1···P2 is 64.32(3)°, and the distance of P1···P2 is 3.648(2) Å. The above bonding parameters within a ferrocene moiety are consistent with those found in

square planar palladium complexes in which the dppf fragment acts as a ligand [16]. The distance of Pd1···Fe1 is 4.242(1) Å, which clearly rules out direct bonding interaction between the two metals.

The bond distances of Pd–C35 (2.113(4) Å) and Pd–C36 (2.218(4) Å) are fairly typical of Pd–η^2-alkene ($H_2C=CR_2$; 2.187–2.107 Å) [17]. The C35–C36 bond distance of 1.425(6) Å is somewhat shorter than that of $C(sp^3)$–$C(sp^3)$ (1.54 Å) but longer than that of $C(sp^2)$–$C(sp^2)$ (1.33 Å). This distance, therefore, indicates that C35–C36 bond has a partial double bond character. However, the sums of bond angles around C35 {354°: C36–C35–H351 (117(3)°); C36–C35–H352 (120(3)°); H351–C35–H352 (117(4)°)} and C36 {358.7°: C35–C36–C40 (126.2(4)°); C35–C36–C37 (125.8(4)°); C37–C36–C40 (106.7(4)°)} are very close to 360°, suggesting that both carbon atoms are sp^2-hybridized. The ideal value for the sum of the corresponding three bond angles around the sp^3-hybridized carbon is 328.5° (109.5° × 3). The fulvene ring plane, defined by C35–C40, is relatively planar with an average atomic displacement of 0.048 Å. The dihedral angle between the equatorial plane and the fulvene ring is 83.6(2)°.

In summary, we have observed the cyclotrimerization of phenylethynes to fulvene from the reaction of *cis*-[PdCl$_2$(dppf)] (**1**) with excess PhC≡CH in the presence of NEt$_3$ and EtOH. We have isolated and characterized the free fulvene. The Pd–fulvene complex, [Pd(dppf)(2,3,5-triphenylfulvene)] (**2**), undergoes substitution with dimethyl acetylenedicarboxylate (CH$_3$O$_2$CC≡CCO$_2$CH$_3$) to give a corresponding Pd–alkyne π-complex.
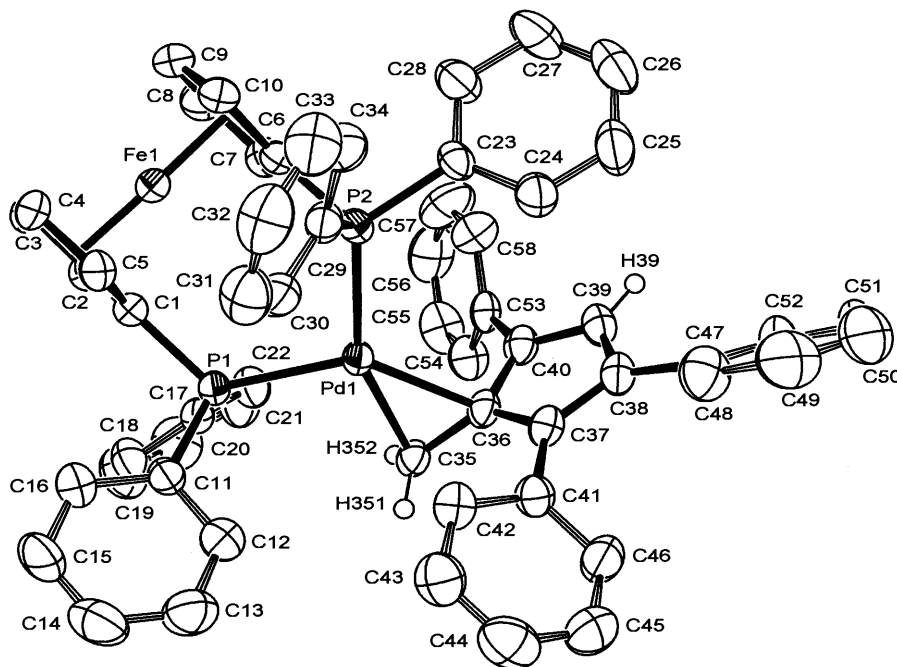

Fig. 1. ORTEP drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144172 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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