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Notes

Synthesis and Molecular Structure of $Pd_2(C_6F_5)_2[\mu\text{-}P(C_6F_5)CH_2CH_2P(C_6F_5)_2]_2$. A Rare Example of P−C Bond Cleavage in a Fluoroaryl Phosphine

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Summary: *Prolonged reflux of a THF solution of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) and 2 equiv of the fluoroaryl phosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ results in formation of the phosphido-phosphino-bridged dimer $Pd_2(C_6F_5)_2[\mu\text{-}P(C_6F_5)CH_2CH_2P(C_6F_5)_2]_2$, which is structurally characterized as the Et_2O adduct.*

Fluorinated phosphines are of interest as sterically tunable, π-acceptor ligands capable of supporting electron-poor metal centers.[2] One commercially available member of this class of ligands is the chelating fluoroaryl phosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, dfppe, which is reported to give enhanced hydroformylation[3] and olefin polymerization[4] catalytic activities compared to its more common, perprotio analogue, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. While dfppe was first synthesized some 20 years ago,[5] only a handful of coordination complexes containing it have been isolated.[6]

An important, salutary property of fluorinated phosphines is their considerable inertness within the coordination sphere of a metal center.[2] The exception to the rule is the *ortho* C−F bonds in fluoroaryl phosphines, which have been disrupted in M(dfppe) (M = Ru, Rh, Ir)[6e−j] and $Pt[PPh_2(C_6F_5)]$ systems.[7] However, while transition metals are known to activate the P−C bond in standard phenyl-containing mono- and chelating diphosphines,[8] the corresponding cleavage of the P−C(fluoroaryl) (P−Ar_f) bond is still a very rare occurrence. We know of only one literature report of a transition metal-mediated P−Ar_f bond cleavage, and that in a secondary phosphine.[9] We report herein the first example of a transition metal-mediated P−Ar_f cleavage in a tertiary phosphine, which leads to an uncommon Pd dimer with a chelating, bridging phosphino-phosphido ligand. The first Pd(dfppe) complexes were characterized only recently.[4]

Results and Discussion

The reaction of $Pd_2(dba)_3$ and 2 equiv of dfppe in thf-d_8 changes from a dark red and slightly heterogeneous mixture to a yellow solution with a small amount of black precipitate within 2 h. The $^{31}P\{^1H\}$ NMR spectrum of this solution contains three signals: two sharp peaks at −16.5 and −6.5 ppm and a broad multiplet at 13.4 ppm. One explanation for the spectrum is an equilibrium mixture of $Pd(dfppe)_2$, Pd(dfppe)(thf-d_8), and Pd(dfppe)(dba), respectively, as has been observed in related systems.[10] The upfield signal is unambiguously assigned to $Pd(dfppe)_2$, as this is the only resonance observed upon mixing $Pd_2(dba)_3$ and 4 equiv of dfppe.[11]

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[2] (a) White, S.; Bennett, B. L.; Roddick, D. M. *Organometallics* **1999**, *18*, 2536. (b) Houlis, J. F.; Roddick, D. M. *J. Am. Chem. Soc.* **1998**, *120*, 11020. (c) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972. (d) Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450. (e) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1989**, *28*, 1624.

[3] Chan, A. S. C.; Pai, C.-C.; Yang, T.-K.; Chen, S.-M. *J. Chem. Soc., Chem. Commun.* **1995**, 2031.

[4] Wursche, R.; Debaerdemaeker, T.; Klinga, M.; Rieger, B. *Eur. J. Inorg. Chem.* **2000**, 2063.

[5] Cook, R. L.; Morse, J. G. *Inorg. Chem.* **1982**, *21*, 4103.

[6] M = Cr, Mo, W: (a) Hersh, W. H.; Xu, P.; Wang, B.; Yom, J. W.; Simpson, C. K. *Inorg. Chem.* **1996**, *35*, 5453. (b) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1990**, *29*, 3627. (c) Reference 2e. (d) Cook, R. L.; Morse, J. G. *Inorg. Chem.* **1984**, *23*, 2332. M = Ru: (e) Bellabarba, R. M.; Saunders, G. C.; Scott, S. *Inorg. Chem. Commun.* **2002**, *5*, 15. M = Rh, Ir: (f) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Inorg. Chim. Acta* **2001**, *323*, 78. (g) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C. *J. Organomet. Chem.* **1999**, *582*, 163. (h) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Martin, S. M.; Russell, D. R.; Saunders, G. C. *J. Organomet. Chem.* **1998**, *555*, 67. (i) Fawcett, J.; Friedrichs, S.; Holloway, J. H.; Hope, E. G.; McKee, V.; Nieuwenhuyzen, M.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1998**, 1477. (j) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1996**, 3215. (k) Atherton, M. J.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Peck, L. A.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1995**, 4029. (l) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936. M = Pd, Pt: (m) Reference 4. (n) Bennett, B. L.; Hoerter, J. M.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2000**, *19*, 615. (o) Reference 2c.

[7] Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *Inorg. Chem.* **1990**, *29*, 2689.

[8] Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

[9] (a) Ang, H. G.; Kwik, W. L.; Leong, W. K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1990**, *396*, C43. (b) Ethylmagnesium bromide cleaves the P−C bond in $P(C_6F_5)_3$. Sicree, S. A.; Tamborski, C. *J. Fluor. Chem.* **1992**, *59*, 269.

[10] Amatore, C.; Broeker, G.; Jutland, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

[11] No changes were observed in the $^{31}P\{^1H\}$ spectrum of this reaction after 3 days at RT. Heating to 66 °C for 66 h gave mainly free dfppe plus unidentified products.

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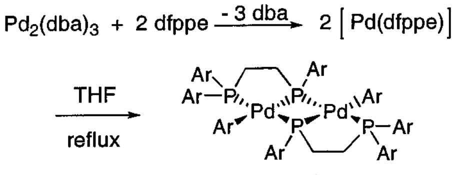
Scheme 1



1, Ar = C_6F_5

Upon warming the equimolar reaction to 65 °C, a new set of resonances in the $^{31}P\{^1H\}$ NMR spectrum grows in over 66 h. At 100 °C, the reaction proceeds faster, but free dfppe (as observed via $^{31}P\{^1H\}$ NMR spectroscopy) and an increased amount of the black precipitate result. The reaction also proceeds at room temperature; yet, in contrast to the nearly quantitative conversion observed at higher temperatures, only approximately 50% conversion is observed after 5 weeks, with no further change in the ^{31}P NMR spectrum after up to 15 weeks.

A scaled-up reaction in refluxing thf provides the isolation of air-stable, yellow microcrystals from Et_2O. The ^1H NMR spectrum of the product is characterized by four multiplets of equal intensity, in addition to signals for Et_2O. The ^{19}F NMR spectrum shows 11 resolvable signals. Of these, three multiplets between −123 and −128 ppm, each integrating to two F atoms, and the three multiplets between −144 and −149 ppm, each integrating to 1 F atom, can be respectively assigned to the *ortho*- and *para*-F of three inequivalent C_6F_5 groups derived from dfppe.[2c,6e−k] Additionally, the spectrum shows a broad singlet integrating to two F atoms at −112.32 ppm and an extra signal for 1 F atom in the *meta* region (−155 to −165 ppm). These two resonances are consistent with the *ortho*- and *para*-F atoms, respectively, of a Pd-bound C_6F_5 group.[12] The $^{31}P\{^1H\}$ NMR spectrum consists of two AA′XX′ six-line multiplets at 19.34 and −99.06 ppm and has been simulated to give coupling constants $^4J_{12} = -48.6$, $^2J_{13} = -7.9$, $^2J_{14} = 142.2$, and $^2J_{34} = 0$ Hz. No P−F coupling could be observed. The high-field signal is diagnostic for a phosphido group bridging two noninteracting metal centers.[13] A structure consistent with the interpreted spectroscopic data is shown in Scheme 1. Formally, each of two [Pd(dfppe)] moieties has oxidatively added one $P-Ar_f$ bond of the other, giving rise to a dimer with two chelating, bridging phosphino-phosphido ligands.

While the structure of this product can be deduced, the NMR spectroscopic data cannot resolve the actual stereochemistry of the compound arising from the two stereogenic phosphido P atoms. As it cannot be determined whether the Pd_2P_2 core is planar, giving rise to a meso compound, or bent, for which one or both of the two enantiomers are possible,[13c] an X-ray crystal structure of the compound was undertaken. Two ORTEP[14] views of the *R*,*R*-enantiomer of racemic **1**·Et_2O are shown in Figures 1 and 2; pertinent bonds and angles are also listed in Figure 1. Overall, the molecule possesses a butterfly structure, resulting from the bent Pd_2P_2 core. A vertical C_2 symmetry axis runs through the center of the Pd_2P_2 core and relates the two halves of the dimer. The symmetry element also passes asymmetrically through an Et_2O solvent molecule of crystallization, resulting in a disorder. Despite the distortions arising from the C_2-bridge in **1**·Et_2O (vida infra), this is one of the few structural examples of an edge-sharing square planar bimetallic complex with a strongly bent bisphosphido bimetallic core.[13d,15]

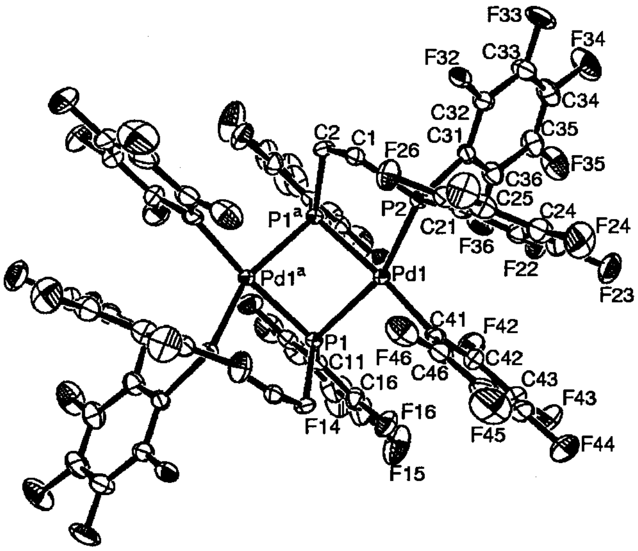


Figure 1. ORTEP drawing of the top view of *R*,*R*-**1**·Et_2O showing a partial atom-labeling scheme and thermal ellipsoids at the 30% probability level. Both the Et_2O solvent of crystallization and the H atoms are removed for clarity. Selected bond distances (Å): Pd(1)−P(1) 2.3204(8), Pd(1)−P(1a) 2.3211(8), Pd(1)−P(2) 2.2800(8), Pd(1)−C(41) 2.057(3). Selected bond angles (deg): P(1)−Pd(1)−P(1a) 81.34(3), P(1)−Pd(1)−P(2) 156.40(3), P(1a)−Pd(1)−P(2) 84.32(3), P(1)−Pd(1)−C(41) 94.8(1), P(1a)−Pd(1)−C(41) 172.9(1), P(2)−Pd(1)−C(41) 97.3(1), Pd(1)−P(1)−Pd(1a) 87.51(3).

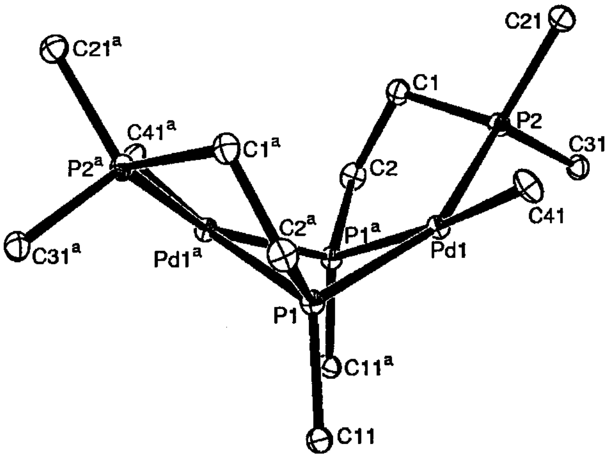


Figure 2. ORTEP drawing of *R*,*R*-**1**·Et_2O showing only the core atoms of the dimer with thermal ellipsoids at the 30% probability level.

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(12) (a) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Rosair, G. M.; Welch, A. J. *Inorg. Chem.* **1997**, *36*, 4426. (b) Forniés, J.; Fortuño, C.; Navarro, R.; Martínez, F.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 643. (c) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Navarro, R. *J. Chem. Soc., Dalton Trans.* **1989**, 169.

(13) (a) Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777. (b) Falvello, L. R.; Forniés, J.; Fortuño, C.; Martínez, F. *Inorg. Chem.* **1994**, *33*, 6242. (c) Glaser, R.; Kountz, D. J.; Waid, R. D.; Gallucci, J. C.; Meek, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 6324. (d) Meek, D. W.; Waid, R.; Tau, K. D.; Kirchner, R. M.; Morimoto, C. N. *Inorg. Chim. Acta* **1982**, *64*, L221.

(14) ORTEP-3 for Windows. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 1. Structural Data[a] for Comparative Bent $L_2M(\mu\text{-}XR_2)ML_2$ Complexes

entry	compound[b]	θ[c]	M−X−M	X−M−X	M−X	M−M	ref
1	$[Pt(\mu\text{-}PhP(CH_2)_3PPh_2)Me]_2$	145[d]	99	75	2.32	3.52	13d
2	$[(dppe)Rh(\mu\text{-}PPh_2)]_2$	133	95	75	2.36	3.47	15b
3	$[(dppe)_2Pd_2(\mu\text{-}PPE)]Cl_2$	126	95	68	2.34	3.47	15a
4	$[(dppe)_2Pd_2(\mu\text{-}MPE)]Cl_2$	118	90	69	2.34	3.30	15a
5	**1**·Et_2O	131.5	87.5	81.3	2.32	3.21	this work
6	$\{Pt[\mu\text{-}NHCH(C_2H_4SOMe)CO_2]\}_2$	136	89	82	2.04	2.86	20
7	$\{Pd[\mu\text{-}N(p\text{-tol})CH_2py]Cl\}_2$	141[d]	89	84	2.05	2.88	19a
8	$[Pt(\mu\text{-}NMeC_6H_4CH_2{=}CMe)Cl]_2$	144[d]	91	82	2.08	2.98	19b

[a] All angles in degrees, all distances in Å. [b] Abbreviations: dppe, $Ph_2PCH_2CH_2PPh_2$; PPE, $PhPCH_2CH_2PPh$; MPE, $MePCH_2CH_2PMe$. [c] Dihedral angle between the two X−M−X planes. [d] From ref 16a.

Table 2. Crystallographic and Refinement Parameters for 1·Et_2O

formula	$C_{56}H_{18}F_{40}OP_4Pd_2$	radiation	Mo Kα
wt	1803.4	λ (Å)	0.7107
syst	orthorhombic	T (K)	293(2)
space group	*Pbcn*	D_{calcd} (g/mL)	2.012
a	13.800(2) Å	μ (mm^{-1})	0.881
b	21.551(3) Å	$R(F_o)^a$	0.0394
c	20.021(2) Å	$R_w(F_o^2)^b$	0.0882
V	5954(1) Å^3	GOF	1.501
Z	4		

[a] Calculated on 5399 reflections with $I > 2\sigma(I)$. [b] Calculated on all 6806 reflections.

Recent theoretical studies[16] of the structural and conformational preferences of edge-sharing binuclear d^8 complexes of the form $L_2M(\mu\text{-}XR_2)ML_2$ concluded that both the M−X distance and X−M−X angle are virtually unaffected by the bending angle between the square planes, θ, while the M−X−M angle decreases with bending. Additionally, structures with five-membered chelate rings were found to be bent, while those with six-membered chelate rings were generally planar. Table 1 collects comparative structural data for **1**·Et_2O and related complexes with either a bent bisphosphido bimetallic core (entries 1−5) or a five-membered chelate ring incorporating the bridging and terminal ligands (entries 5−9). Perusal of these data reveals much less variation in the M_2X_2 bond angles for complexes incorporating the chelate ring irrespective of the size of θ or the M−X and M−M distances. The variance between the metrical parameters for the M_2P_2 complexes and theoretical predictions[16a] could be a consequence of the different constraints placed upon the phosphido P atoms in each of the bent bisphosphido bimetallic complexes.

The Pd atom possesses a severely distorted square planar geometry, with P(2) displaced 0.61 Å out of the plane defined by the remaining atoms Pd(1), P(1), P(1a), and C(41)[17] and a *trans* P(1)−Pd(1)−P(2) angle of 156.40(3)°. Distortions of similar proportions have recently been measured in Pd[18a] and Rh[18b] complexes, and aromatic π−π interactions have been held responsible for these distortions.[18b,c] Analogous interactions exist between the C(21)−C(26)/C(41)−C(46) rings and the C(11)−C(16)/C(11a)−C(16a) rings of **1**·Et_2O; the closest contact distance for the first pair of rings is 3.25 Å between C(22) and C(46), while the minimum separation for the latter pair is the 3.23 Å between C(12) and C(12a). Furthermore, two of the three other structural examples containing a five-membered chelate ring also suffer from similar deformations.[19] Only $\{Pt[\mu\text{-}NHCH(C_2H_4SOMe)CO_2]\}_2$, which also has a six-membered heterocyclic ring fused with the five-membered chelate ring, exhibits a planar geometry at the metal center.[20] The Pd(1)−Pd(1a) distance is 3.2100(5) Å, which indicates the absence of a Pd−Pd bond.[12a] The Pd−P bond distances in the Pd_2P_2 core are effectively equal at 2.32 Å, and these distances are 0.04 Å longer than the external Pd(1)−P(2) bond distance of 2.2800(8) Å. The different *trans* ligands account for the slightly shorter Pd−P distance (av 2.256 Å) in (dfppe)PdI_2.[4] The Pd(1)−C(41) distance of 2.057(3) Å is the same as reported[21] for *cis*-$Pt(C_6F_5)_2(PPh_3)_2$ and *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)]ClO_4$,[22] but shorter than the corresponding bond (av 2.086 Å) in $[PEtPh_3]_2[Pt_2(\mu\text{-}PPh_2)(C_6F_5)_4]$.[23]

Attempts to synthesize the analogous Ni dimer via related chemistry with $Ni(COD)_2$ as a starting material were unsuccessful. Prolonged heating (up to 6 days) at 65 °C of a stoichiometric 1:1 $Ni(COD)_2$/dfppe thf-d_8 solution gave free dfppe as the primary ^{31}P NMR signal, in addition to a number of unidentifiable signals and a black precipitate. An analogous reaction in toluene-d_8 at 100 °C gave only black decomposition products. Interestingly, Pt(dfppe) complexes also do not appear to undergo this P−C cleavage; refluxing Pt(dfppe)$(Ph)_2$ in toluene or DMSO gives exclusively Pt$(dfppe)_2$ after the reductive elimination of biphenyl.[2c]

In summary, we have observed the first example of transition metal-mediated P−Ar_f bond cleavage in a tertiary fluoroarylphosphine, a consequence of a formal oxidative addition to a presumed Pd(0) intermediate. The resulting dimer contains two bridging, chelated, fluoroaryl phosphino-phosphido ligands and is a rare example of a bent bisphosphido bimetallic complex. That other Pd(0) intermediates with bulky, chelating phosphines, such as $R_2PCH_2CH_2PR_2$ (R = ^{i}Pr, Cy), do not

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[15] (a) Mizuta, T.; Aoki, S.; Nakayama, K.; Miyoshi, K. *Inorg. Chem.* **1999**, *38*, 4361. (b) Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860.

[16] The dimers are defined as bent when the M_2X_2 dihedral angle is less than 160°. (a) Aullón, G.; Lledós, A.; Alvarez, S. *Inorg. Chem.* **2000**, *39*, 906. (b) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S.; Alemany, P. *Inorg. Chem.* **1998**, *37*, 804.

[17] The maximum displacement of the atoms defining the plane is 0.077 Å for Pd(1).

[18] (a) Drago, D.; Pregosin, P. S.; Tschoerner, M.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1999**, 2279. (b) Magistrato, A.; Merlin, M.; Pregosin, P. S.; Rothlisberger, U.; Albinati, A. *Organometallics* **2000**, *19*, 3591. (c) Magistrato, A.; Pregosin, P. S.; Albinati, A.; Rothlisberger, U. *Organometallics* **2001**, *20*, 4178.

[19] (a) Cuevas, J. V.; García-Herbosa, G.; Muñoz, A.; García-Granda, S.; Miguel, D. *Organometallics* **1997**, *16*, 2220. (b) Cooper, M. K.; Stevens, P. V.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1983**, 553.

[20] Freeman, W. A.; Nicholls, L. J.; Liu, C. F. *Inorg. Chem.* **1978**, *17*, 2989.

[21] Miki, K.; Kasai, N.; Kurosawa, H. *Acta Crystallogr., Cryst. Struct. Commun.* **1988**, *C44*, 1132.

[22] Usón, R.; Forniés, J.; Navarro, R.; Usón, M. A.; Garcia, M. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 345.

[23] Alonso, E.; Casas, J. M.; Cotton, F. A.; Feng, X.; Forniés, J.; Fortuño, C.; Tomas, M. *Inorg. Chem.* **1999**, *38*, 5034.

undergo a similar oxidative addition but instead are in equilibrium with the dinuclear complexes [(μ-$R_2PCH_2CH_2PR_2$)Pd]$_2$[24] is consistent with the observation that P$-$C(sp^3) bonds are more difficult to cleave than P$-$C(sp^2) bonds.[8] The singularity of this P$-$Ar$_f$ bond cleavage is somewhat surprising, however, considering that strong electron-withdrawing groups enhance the rate of P$-$C(Ar) oxidative addition to low-valent transition metals.[25]

Experimental Section

General Comments. All procedures were conducted using Schlenk techniques under argon unless otherwise noted. Where necessary, solvents were dried from Na/benzophenone (thf and toluene) or $LiAlH_4$ (pentane) and distilled prior to use. $Pd_2(dba)_3$ and dfppe (Strem Chemicals) were used as received. NMR spectra were referenced to the residual solvent peaks (^{1}H and ^{13}C{^{1}H} NMR), external $C_6H_5CF_3$ (^{19}F{^{1}H} NMR, referenced to -63.72 ppm), or external 85% H_3PO_4 (^{31}P{^{1}H} NMR). The software package gNMR (Cherwell Scientific, Inc.) was used for the NMR simulation. Elemental analysis was performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

$Pd_2(C_6F_5)_2[\mu$-$P(C_6F_5)CH_2CH_2P(C_6F_5)_2]_2 \cdot Et_2O$ (1·Et$_2$O). In a 100 mL Schlenk flask, $Pd_2(dba)_3$ (0.34 g, 0.37 mmol) and dfppe (0.57 g, 0.75 mmol) were dissolved in thf (40 mL) to give a dark red solution. A condenser was placed on the flask, and the solution was refluxed for 86 h. Upon reaching reflux, the solution became golden-brown, and at the end of the reflux the reaction was dark yellow with a small amount fine black precipitate. After cooling, the volatiles were removed, and the resulting olive green residue was washed with pentane (50 mL) and Et_2O (50 mL) to remove dba. The remaining reaction residue was extracted with toluene (25 mL), the extract was filtered through Celite, and the Celite was washed with additional toluene (20 mL). The combined yellow filtrate and wash were concentrated to ca. 10 mL, warmed to provide a clear solution, and then cooled to -40 °C. The resulting mass of yellow precipitate was filtered in air and washed with pentane (50 mL). Dissolution of the solid in Et_2O (75 mL), followed by slow evaporation of the yellow solution, provided 0.15 g of **1**·Et$_2$O as yellow microcrystals (0.080 mmol, 22% yield). X-ray quality crystals were obtained from slow evaporation from a concentrated thf-d_8 solution. Anal. Calcd for $C_{52}H_8F_{40}P_4Pd_2 \cdot 0.25C_4H_{10}O$:[26] C, 36.42; H, 0.61. Found: C, 36.41; H, 0.63. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.44 (q, 4 H, $J = 7.0$ H, OCH_2), 3.13 (dm, 2 H, $J = 60$ Hz, PCH), 2.69 (m, 2 H, PCH), 2.17 (dm, 2 H, $J = 57$ Hz, PCH), 1.83 (m, 2 H, PCH), 1.16 (t, 6 H, $J = 7.0$ Hz, OCCH_3). ^{19}F{^{1}H} NMR (282.2 MHz, thf-d_8): δ -112.32 (br s, 2 F, *o*-PdC$_6F_5$), -123.39 (d, $J_{FF} = 15$ Hz, 2 F), -125.45 (br s, 2 F), -127.67 (d, $J_{FF} = 20$ Hz, 2F, *o*-PC$_6F_5$), -144.30 (m, 1 F), -146.47 (app t, $J_{FF} = 20$ Hz, 1 F), -148.47 (app t, $J_{FF} = 20$ Hz, 1 F; *p*-PC$_6F_5$), -158.65 (overlapping signals, 3 F, *p*-PdC$_6F_5$, *m*-C$_6F_5$), -159.00 (m, 2 F), -160.06 (m, 2 F), -161.13 (m, 2 F, *m*-C$_6F_5$). ^{31}P{^{1}H} NMR (121.5 MHz, thf-d_8): δ 19.34 (m, PdP^{12}C$_3$), -99.06 (m, $^4J_{12} = -48.6$, $^2J_{13} = -7.9$, $^2J_{14} = 142.2$, $^2J_{34} = 0$ Hz, μ-P^{34}Pd$_2$).

Crystal Structure Determination. A yellow blocklike crystal was mounted on a glass fiber at room temperature. Pertinent data for the crystal and solution are collected in Table 2. Diffraction data were collected on a Siemens SMART CCD diffractometer with SMART[27a] software and were integrated using SAINT.[27b] A semiempirical absorption correction was made with SADABS,[27c] the structure was solved by direct methods in SHELXTL,[27d] and it was refined on F^2 (SHELXTL).[27d] The diethyl ether solvent molecule is disordered over two positions with occupancy 0.500. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions with U_{iso} values at 1.2 or 1.5U_{eq} of the carrier atom. Atomic scattering factors were taken from the International Table for X-ray Crystallography Vol C.

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Supporting Information Available: Tables of refined and calculated atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**·Et$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Reid, S. M.; Fink, M. J. *Organometallics* **2001**, *20*, 2959.

[25] Dubois, R. A.; Garrou, P. E. *Organometallics* **1986**, *5*, 466.

[26] Amount of residual Et$_2$O after exposure to full vacuum for 36 h as determined by ^{1}H NMR spectroscopy.

[27] (a) *SMART*, Version 5.054; Bruker AXS Inc.: Madison, WI, 1998. (b) *SAINT*, Version 6.01; Bruker AXS Inc.: Madison, WI, 1998. (c) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996. (d) Sheldrick, G. M. *SHELXTL*, Version 5.10; Bruker AXS Inc.: Madison, WI, 1998.