*Organometallics* **1998,** *17,* 5427−5430

# *Notes*

## Single-Crystal X-ray and Solution $^{13}$C NMR Study of Fluoro(*p*-nitrophenyl)bis(triphenylphosphine)palladium(II). Are There Effects of Through-Conjugation?[†]

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*Summary: The Pd−F and Pd−C bond distances in the X-ray structure of trans-fluoro(p-nitrophenyl)bis(triphenylphosphine)palladium(II),* ***1****, are shorter by ca. 0.036 and 0.013 Å, respectively, than those in the analogous σ-phenyl complex,* ***2****. This structural feature along with the $^{13}$C NMR spectral characteristics of* ***1*** *and its iodo counterpart indicates a contribution from the quinoid-type canonical form* ***A*** *to the structure of* ***1****. However, the geometry of the p-nitrophenyl ligand in* ***1*** *does not exhibit effects of through-conjugation, suggesting that the resonance effect of trans-[$(Ph_3P)_2Pd(F)$] is weaker than those of $NH_2$ and MeO.*

### Introduction

In continuation of the recent studies of fluoro complexes of palladium,[1−4] we report here a highly precise X-ray structure of *trans*-fluoro(*p*-nitrophenyl)bis(triphenylphosphine)palladium(II), **1**. There were two reasons for studying this compound. First, we wanted to compare the structure of **1** with that of the only other structurally characterized molecular palladium fluoride, [$(Ph_3P)_2Pd(Ph)F$], **2**.[1] More importantly, due to the exceptionally high $\pi$-basicity of the fluoro ligand, complex **1** seemed to be ideally suited for studying $\pi$-interactions between the metal and $\sigma$-aryl ligand in complexes of the type [$(R_3P)_2Pd(Ar)X$]. Such compounds are known to mediate various Pd-catalyzed reactions of haloarenes, involving the formation and cleavage of Pd−Ar bonds.[5] Because of that there has been considerable interest in the detailed nature of palladium aryls. Substantial effort has been put toward studying, mostly by NMR techniques, $\pi$-bonding interactions between the metal and Ar in [$(R_3P)_2Pd(Ar)X$] and their platinum analogues.[6−11] Nevertheless, much controversy still remains about the ability of the Pd and Pt atoms to interact strongly with the $\pi$-system of the aryl ligand. Structural methods have proven useful in recognizing intense through-conjugation effects in aromatics.[12] However, no X-ray studies have been reported on arylpalladium complexes that might exhibit structural effects of $\pi$-conjugation within the Ar−Pd moiety.

### Results and Discussion

Complex **1** was synthesized as described previously,[3] except toluene was used as the solvent instead of benzene (See the Experimental Section). Single crystals of **1**·$C_6H_6$ were grown by slowly adding hexanes to a concentrated solution of **1** in benzene. The structure of the complex is shown in Figure 1, and a summary of the crystallographic data is presented in Table 1. As anticipated, **1** is square-planar, with the deviation of Pd1, P1, P2, F1, and C1 from the metal coordination mean plane being only 0.099, −0.107, −0.108, 0.061, and 0.054 Å, respectively. The Pd−F bond distance in **1** is remarkably shorter (by ca. 0.036 Å) and the Pd−C bond length in this complex is marginally shorter (by ca. 0.013 Å) than in [$(Ph_3P)_2Pd(Ph)F$], **2** (Table 2). However, all other geometrical parameters found for **1** are very similar to those of **2**.[1,4] It is worth noting the short F−C contacts (3.162(4)−3.272(4) Å), both intramolecular

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[†] Contribution No. 7789.

[1] Fraser, S. L.; Antipin, M. Yu.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769.

[2] Grushin, V. V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 994.

[3] Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774.

[4] Flemming, J. P.; Pilon M. C.; Borbulevitch O. Ya.; Antipin M. Yu.; Grushin, V. V. *Inorg. Chim. Acta* **1998**, *280*, 87.

[5] For recent reviews of various Pd-catalyzed reactions of haloarenes, such as the Stille coupling, Heck, Sonogashira, Suzuki, various carbonylation and $S_NAr$-type reactions, see: (a) Beletskaya, I. P.; Cheprakov, A. V. In *Organic Synthesis in Water*; Grieco, P., Ed.; Blackie Academic & Professional: London, 1998. (b) Grushin, V. V.; Alper, H. In *Topics in Organometallic Chemistry. Activation of Inert Bonds*; Murai, S., Ed.; Springer, in press. (c) Percec, V.; Hill, H. H. *ACS Symp. Ser.* **1996**, *624*, 2. (d) Tsuji, J. *Palladium Reagents and Catalysis: Innovations in Organic Synthesis*; Wiley: Chichester, 1995. (e) Miyaura N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (f) Cabri, W.; Caudiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (g) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2589. (h) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proc. Int.* **1995**, *27*, 129. (i) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. (j) de Meijere, A.; Meyer, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (k) Kalinin, V. N. *Synthesis* **1992**, 413.

[6] Parshall, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 704.

[7] Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710.

[8] Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360.

[9] Clark, H. C.; Ward, J. E. H. *J. Am. Chem. Soc.* **1974**, *96*, 1741.

[10] Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111.

[11] Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J. *Organometallics* **1997**, *16*, 1897.

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10.1021/om980529t CCC: $15.00
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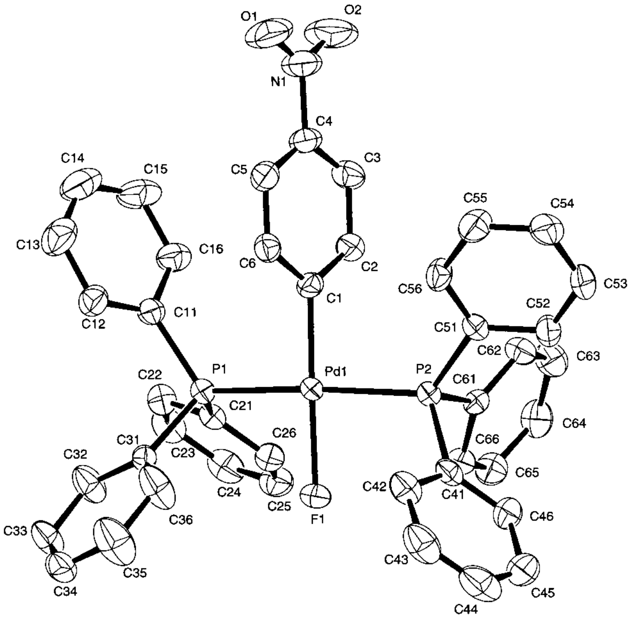
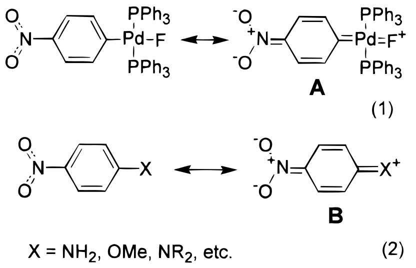


**Figure 1.** ORTEP drawing for **1**, showing the atom-labeling scheme.

(C26, C36, C42, and C66) and intermolecular (C25a and C34b). These contacts likely emerge from F···H−C interactions,[13] which alleviate strong $d_\pi - p_\pi$ Pd−F filled/filled repulsions[14] and may be one of the reasons for the $PPh_3$ ligands to adopt the eclipsed conformation observed in the structures of **1** and **2**.[1,4]

A contribution from the quinoid canonical form **A** (eq 1) would readily account for the short Pd−F and Pd−C bond distances in **1**.[15] The high $\pi$-basicity of the F ligand is expected to enhance the metal-to-aryl $\pi$-donation due to $d_\pi - p_\pi$ Pd−F filled/filled repulsions.[14] However, the geometry of the *p*-nitrophenyl ligand does not provide support for a strong contribution from **A** to the structure of **1**.



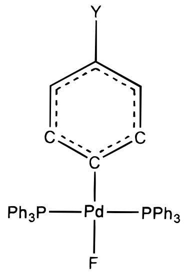
(1)

X = $NH_2$, OMe, $NR_2$, etc. (2)

**Table 1. Selected Crystallographic Data for 1 (1:1 Benzene Solvate)**

| | |
|---|---|
| empirical formula | $C_{48}H_{40}FNO_2P_2Pd$ |
| fw | 850.20 |
| crystal size, mm | 0.36 × 0.40 × 0.44 |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| temp, K | 223 |
| *a*, Å | 10.206(2) |
| *b*, Å | 14.103(2) |
| *c*, Å | 14.406(2) |
| α, deg | 101.27(1) |
| *β*, deg | 95.08(1) |
| *γ*, deg | 97.26(1) |
| volume, Å$^3$ | 2003.5 |
| *Z* | 2 |
| calcd density, g·cm$^{-3}$ | 1.409 |
| $\mu$(Mo), cm$^{-1}$ | 5.78 |
| diffractometer | Enraf-Nonius CAD4 |
| 2$\theta$ range, deg | 2.9−52.0 |
| scan type | $\omega$ |
| abs corr | no |
| no. of reflns collected | 8195 |
| no. of unique reflns used in refinement ($I > 3\sigma(I)$) | 5569 |
| params refined | 496 |
| data-to-param ratio | 11.23 |
| $R_1$, % | 3.6 |
| $R_w$, % | 3.2 |
| goodness of fit | 1.06 |

**Table 2. Important Geometry Parameters for 1 and 2**



| parameter | **1** (Y = $NO_2$) | **2** (Y = H)[1,4] |
|---|---|---|
| | Interatomic Distances, Å | |
| Pd−F | 2.049(2) | 2.085(3) |
| Pd−C | 1.985(3) | 1.998(5) |
| Pd−P | 2.316(1) | 2.315(1) |
| Pd−P | 2.316(1) | 2.318(1) |
| | Bond Angles, deg | |
| C−Pd−F | 177.6(1) | 179.0(2) |
| P−Pd−P | 169.04(7) | 174.24(5) |
| P−Pd−F | 89.52(6) | 89.90(9) |
| P−Pd−F | 86.39(6) | 86.57(9) |
| P−Pd−C | 90.47(9) | 91.1(1) |
| P−Pd−C | 93.19(9) | 92.5(1) |
| C−C−C | 118.0(3) | 117.0(5) |
| | Interplanar Angle, $\sigma$-Ar/Pd Coordination Plane, deg | |
| | 70.6 | 71.5 |

Structural parameters of the *p*-nitrophenyl ring in **1** are given in Table 3, which also contains, for comparison, analogous data reported for precise X-ray structures of nitrobenzene,[16] *p*-nitrobenzoic acid,[17] *p*-nitroaniline,[18] *p*-nitroanisol,[19] *trans*-iodo(*p*-nitrophenyl)bis(triethylphosphine)platinum(II),[20] and **2**.[1] Of the six sets of structural data for the nitro compounds (Table 3), only two manifest through-conjugation effects consistent with a substantial contribution of the canonical form **B**, an organic counterpart to **A** (eqs 1 and 2). The mole-

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[13] The general importance of CH···X interactions (X = O, halogen) is emphasized in a number of articles, for example: Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891. A recent example of M−X···HC (ligand) interactions is provided by: Cavaglioni, A.; Cini, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1149 (M = Rh, X = Cl, HC (ligand) = triphenylstibine). Examples of the "inverse" pattern of interactions, M−CH···X (ligand), are discussed by: Marshall, W.; Simpson, R. D.; Thorn, D. L. Unpublished work (M = Pt, X = O).

[14] Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

[15] A similar quinoid structure, although without halogen-to-metal $\pi$-donation, has been recently used to rationalize the $^{13}C$ NMR data for *trans*-$[(Et_3P)_2Pd(Br)(4\text{-}NO_2C_6H_4)]$.[11]

[16] Boese, R.; Blaser, D.; Nussbaumer, M.; Krygowski, T. M. *Struct. Chem.* **1992**, *3*, 363.

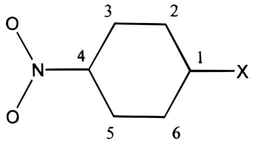
[17] Colapietro, M.; Domenicano, A. *Acta Crystallogr. B* **1977**, *33*, 2240.

[18] Colapietro, M.; Domenicano, A.; Marciante, C.; Portalone, G. *Z. Naturforsch. B* **1982**, *37*, 1309; *Acta Crystallogr. A* **1981**, *37*, C199.

[19] Talberg, H. J. *Acta Chem. Scand. A* **1978**, *32*, 373.

[20] Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1988**, *144*, 79.

**Table 3. Structural Parameters of *p*-Nitrosubstituted Benzene Derivatives**



| parameter | H<br>ref 16 | COOH<br>ref 17 | $NH_2$<br>ref 18 | $OCH_3$[a]<br>ref 19 | $(Et_3P)_2PtI$[b]<br>ref 20 | $(Ph_3P)_2PdF$<br>this work (**1**) | $(Ph_3P)_2PdF$ (no $NO_2$)<br>refs 1,4 (**2**) |
|---|---|---|---|---|---|---|---|
| | | | | Bond Distances, Å | | | |
| C1−C2 | 1.388(1) | 1.392(2) | 1.406(3) | 1.392 | 1.398 | 1.386(4) | 1.406(8) |
| C2−C3 | 1.385(1) | 1.389(2) | 1.366(3) | 1.355 | 1.396 | 1.386(4) | 1.391(8) |
| C3−C4 | 1.387(1) | 1.383(2) | 1.393(3) | 1.400 | 1.374 | 1.385(5) | 1.386(10) |
| C4−C5 | 1.387(1) | 1.382(2) | 1.391(3) | 1.373 | 1.355 | 1.379(5) | 1.370(9) |
| C5−C6 | 1.386(1) | 1.389(2) | 1.368(3) | 1.367 | 1.414 | 1.372(4) | 1.389(8) |
| C1−C6 | 1.389(1) | 1.394(2) | 1.407(3) | 1.410 | 1.387 | 1.400(4) | 1.400(8) |
| C−N | 1.467(1) | 1.475(2) | 1.434[b] | 1.450 | 1.467 | 1.464(4) | |
| N−O | 1.228(1) | 1.223(2) | 1.237[b] | 1.235 | 1.206 | 1.223(4) | |
| N−O | 1.225(1) | 1.221(2) | 1.227[b] | 1.229 | 1.203 | 1.218(4) | |
| | | | | Bond Angles, deg | | | |
| C2−C1−C6 | 120.5(1) | 120.7(1) | 118.4(2) | 119.3 | 118.9 | 118.0(3) | 117.0(5) |
| C3−C4−C5 | 122.7(1) | 123.3(1) | 120.2(2) | 121.7 | 122.6 | 122.0(3) | 120.9(6) |
| O−N−O | 123.2(1) | 124.3(1) | 121.6[b] | 121.8 | 123.3 | 122.9(3) | |
| | | | | Dihedral Angle, $NO_2$/C1−C6, deg | | | |
| | 1.7 | 13.7 | 1.9 | 7.3 | 0 | 7.8 | |

[a] esd: 0.003−0.006 Å; 0.4−0.5°. [b] No esd reported.

cules of *p*-nitroaniline[18] and *p*-nitroanisol[19] exhibit, in the solid state, the following features characteristic of through-conjugation.[21]

(I) Both the C2−C3 and C5−C6 bonds are noticeably shorter than in nitrobenzene.

(II) The C−N bond lengths are 0.015−0.03 Å shorter than in $PhNO_2$.

(III) The average of the two N−O bond distances is greater than in $PhNO_2$ by ca. 0.01 Å.

(IV) The internal angles C3−C4−C5 and O−N−O angles are 1.2−2.7° more acute than in nitrobenzene.

If considered separately, these structural effects might seem subtle. However, their combination constitutes firm evidence for the interaction between the $\pi$-basic and $\pi$-acidic substituents through the benzene ring.[12] The geometry of the *p*-nitrophenyl ligand in **1** does not reveal *any* of the above structural features. As seen from Table 3, the C−C bond distances within the benzene ring and even more responsive parameters, the C−N bond length and O−N−O and C3−C4−C5 bond angles, do not unambiguously indicate a contribution from the quinoid form. It should be stressed that the structural data for **1** demonstrate only the lack of $\pi$-interactions *comparable in strength* with those previously observed for *p*-nitroaniline,[18] *p*-nitroanisol,[19] and *N,N*-diethyl-*p*-nitroaniline.[21] Inferring the *complete* absence of cross-conjugation within the Ar−Pd framework would be inappropriate.

The above geometrical features of **A**/**B** are well-pronounced for the structures of *p*-nitroaniline and *p*-nitroanisol, molecules containing strong $\pi$-donating amino ($\sigma_R = -0.48$) and methoxy ($\sigma_R = -0.43$) groups.[22−24] The $\pi$-basicity of $[(Et_3P)_2PdX]$ and $[(Et_3P)_2PtX]$ (X = Cl, Br, I) ($\sigma_R = -0.27$ and $-0.26$, respectively)[8] is insufficient to give rise to observable cross-conjugation effects, as exemplified by the structure of $[(Et_3P)_2Pt(I)(p\text{-}C_6H_4NO_2)]$[20] (see Table 3). Electronic effects of $[(Ph_3P)_2Pd(X)]$ are likely to be close to those of the $[(Et_3P)_2Pd(X)]$.[8]

The nature of X is known[8] to affect $\sigma_I$ rather than $\sigma_R$ parameters of $[(R_3P)_2PdX]$, where X = Cl, Br, and I. However, one might expect both $\sigma$-constants to be significantly lower for X = F,[4] owing to more intense $d_\pi-p_\pi$ filled/filled repulsions[14] between the metal and F. The $^{13}C$ NMR chemical shift of the Pd-substituted carbon in **1** (167.6 ppm) was found to be almost 10 ppm *upfield* from the value (177.1 ppm) measured for its iodo analogue, $[(Ph_3P)_2Pd(I)(4\text{-}NO_2C_6H_4)]$, **3**.[25] This difference does indicate[10] an *increase* in electron-donating properties of the metal center in $[(Ph_3P)_2Pd(X)]$ when going from the iodo to fluoro complex. Firm structural evidence[12] for $[(Ph_3P)_2PdF]$ being a strong electron donor is provided by the considerably decreased C2−C1−C6 internal angles of the benzene ring in **1** (118.0°) and **2** (117.0°). It is conceivable that both inductive and resonance effects are the reason for the shortened Pd−F and Pd−C bond distances in **1**, as compared to those in **2**.[1,4] As a strong resonance and also inductive ($\sigma_I = +0.64$)[22] electron acceptor, the nitro group possibly provides a relief to filled/filled repulsions within the C−Pd−F fragment, yet without introducing structurally significant contributions of quinoid resonance structure **A**.

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[21] A considerable contribution of the quinoid form has also been found in the less accurate structure of *N,N*-diethyl-*p*-nitroaniline. See: Maurin, J.; Krygowski, T. M. *J. Mol. Struct.* **1988**, *172*, 413.

[22] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

[23] A large dihedral angle $NO_2$/C(1)−C(6) certainly points to the lack of $\pi$-interactions.[12,17,18] Nonetheless, the benzene ring and nitro group being coplanar cannot provide unambiguous proof for through-conjugation, unless complemented by the geometrical distortions described in the text above. For instance, this angle is 1.7° in nitrobenzene,[16] where cross-conjugation is impossible by definition, and 7.3° in *p*-nitroanisol,[19] in which the substituents experience considerable $\pi$-interactions through the ring.

[24] (a) It has been shown[24b] that in $p\text{-}AC_6H_4B$ (A = $\pi$-acceptor; B = $\pi$-donor) deformations of the benzene ring geometry are determined by the $\pi$-basicity of substituent B, rather than $\pi$-acidity of A. (b) Krygowski, T. M. *J. Chem. Res. (S)* **1987**, 120.

[25] A similar trend has also been observed[4] for a series of analogous $\sigma$-phenyl complexes $[(Ph_3P)_2Pd(Ph)(X)]$ (X = F, Cl, Br, and I).

## Experimental Section

**Synthesis of 1.**[3] A mixture of $[(Ph_3P)_2Pd(I)(4\text{-}NO_2C_6H_4)]$[26] (300 mg; 0.34 mmol), AgF (57 mg; 0.45 mmol), 4-iodonitrobenzene (8 mg; 0.03 mmol), and toluene (15 mL) was sonicated under nitrogen at 18−25 °C for 4.5 h. The reaction was monitored by $^{31}P$ NMR. After complete conversion was achieved the reaction mixture was worked up in air. The suspension was filtered through Celite to give a clear, pale-yellow filtrate, which was reduced in volume to ca. 3−5 mL. The residual solution was treated with hexanes (9 mL; portionwise), and the mixture was kept at room temperature for 2 h. The white crystalline solid was separated, washed with hexanes (3 × 5 mL), and dried under vacuum. The yield was 255 mg (97%). $^{31}P$ NMR ($CD_2Cl_2$, 20 °C): $\delta$ 19.3 (d, $J_{F-P} = 12.3$ Hz). $^{13}C$ NMR ($CD_2Cl_2$, 20 °C):[27] $\delta$ 120.7 (s, 3-$C_6H_4Pd$), 128.5 (virtual t, $J = 10.5$ Hz, 3-$C_6H_5P$), 130.9 (s, 4-$C_6H_5P$), 131.1 (virtual t, $J = 45.2$ Hz, 1-$C_6H_5P$), 135.0 (virtual t, $J = 12.7$ Hz, 2-$C_6H_5P$), 137.2 (t, $J_{C-P} = 4.4$ Hz, 2-$C_6H_4Pd$), 144.1 (s, 4-$C_6H_4Pd$), 167.6 (dt, $J_{C-F} = 51.7$ Hz, $J_{C-P} = 6.1$ Hz, 1-$C_6H_4$-Pd).

**X-ray Diffraction Study of 1·$C_6H_6$.** The structure of **1·$C_6H_6$** was determined using a CAD4 diffractometer and the teXsan structure solution package.[28] Crystal and data parameters for the structure determinations may be found in Table 1. The final refinement was done using the Z-refinement package[29] and converged at $R_1 = 3.6\%$ and $R_w = 3.2\%$, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w$ proportional to $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV, including anomalous terms for Pd and P.

**Supporting Information Available:** ORTEP drawings of **1** and **1·$C_6H_6$**, tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and selected intermolecular distances (9 pages). Ordering information is given on any current masthead page.

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[26] $^{13}C$ NMR ($CD_2Cl_2$, 20 °C): $\delta$ 121.3 (s, 3-$C_6H_4Pd$), 128.5 (virtual t, $J = 10.5$ Hz, 3-$C_6H_5P$), 130.8 (s, 4-$C_6H_5P$), 132.0 (virtual t, $J = 47.8$ Hz, 1-$C_6H_5P$), 135.4 (virtual t, $J = 12.7$ Hz, 2-$C_6H_5P$), 136.4 (t, $J_{C-P} = 5.2$ Hz, 2-$C_6H_4Pd$), 144.4 (s, 4-$C_6H_4Pd$), 177.1 (t, $J_{C-P} = 3.5$ Hz, 1-$C_6H_4$-Pd).

[27] The $^{13}C$ NMR spectrum was measured under rigorously anhydrous conditions to avoid exchange processes caused by water-induced Pd−F ionization.[3]

[28] *Crystal Structure Analysis Package*; Molecular Structure Corporation, 1985&1992.

[29] Calabrese, J. C. *Crystal Structure Analysis Package,* E. I. DuPont de Nemours & Co., 1994.