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Inorganica Chimica Acta 360 (2007) 286–292
Inorganica Chimica Acta
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Retardation of β-hydrogen elimination in PNP Pincer complexes of Pd

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Received 20 June 2006; accepted 13 July 2006
Available online 4 August 2006

Inorganic Chemistry – The Next Generation.

Abstract

A series of new alkyl and alkoxide (^{F}PNP)Pd complexes have been synthesized. The alkyls and alkoxides containing β-hydrogens display remarkable thermal stability. Thermal decomposition of (^{F}PNP)PdOEt is very slow in pure C_6D_6 but is accelerated by the addition of EtOH co-solvent. It is proposed that the β-hydrogen elimination from (^{F}PNP)Pd–OCH_2R occurs via dissociation of the alkoxide anion.

Keywords: Palladium; Elimination; Pincer; Alkyl complexes; Alkoxide complexes

1. Introduction

β-Hydrogen elimination (BHE) in metal alkyl and alkoxide compounds is one of the fundamental organometallic reactions [1]. BHE converts metal alkyls to metal hydrides with the evolution of corresponding olefins and metal alkoxides to metal hydrides and the evolution of corresponding aldehydes or ketones. BHE in alkyl compounds is common across the periodic table. Early metal alkoxides are usually resistant to BHE because of the high M–O bond strengths. Late metal alkoxides, on the other hand, typically readily undergo BHE [2,3].

The classical mechanism of BHE requires the presence of an empty coordination site *cis* to the alkyl or alkoxide [1–3]. The absence of such a *cis*-site may stabilize the β-H-containing alkyl or alkoxide kinetically. In the last few years, our group has been engaged in the exploration of the rigid pincer-type PNP ligands [4–6]. We have devoted special attention to the chemistry of square-planar complexes of Pd [4] One of the key features of this PNP ligand is the tight, unremitting tridentate coordination that is enforced by the rigidity of the backbone. In this work, we report that BHE is retarded in the (PNP)Pd–R and (PNP)Pd–OR compounds (R = alkyl, RO = alkoxide) in non-polar solvents. However, (PNP)Pd–OR compounds are shown to be able to undergo BHE in the more polar media apparently by a non-classical mechanism.

2. Results and discussion

2.1. Syntheses of (^{F}PNP)Pd-alkyl compounds and their thermal stability

We have previously reported the synthesis of **1**–**3** (Scheme 1) and analogous Pd complexes with minor PNP ligand variations [4,5c]. (^{F}PNP)PdOTf (**6**) was prepared via the reaction of MeOTf with **5**, in full analogy with previously reported synthesis of **3** (as well as its Ni and Pt analogues [5c]). Compounds **3** and **6** are of similar distinctive purple color and possess similar solubility. In this work, we elected to work with the ^{F}PNP ligand primarily because of the convenience of ^{19}F NMR as an analytical tool. All of the compounds in this study display C_{2v} symmetry in solution on the NMR time scale. We have previously structurally characterized several PNP Pd complexes, all of which possess an approximately square-planar geometry about Pd [4].

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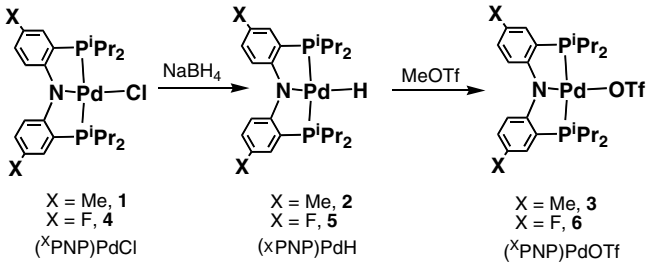
doi:10.1016/j.ica.2006.07.067



Scheme 1.

The preparation of (^{F}PNP)PdR compounds (**7**–**11**) can be accomplished by the action of an alkylating agent (alkyllithium, alkylzinc, or alkylmagnesium reagents) on either **4** or **6** (Scheme 2). We have previously described the preparation of **7** in this fashion [4a]. The alkylating agent may be used in excess with no detriment to the yield of product. Compounds **8**–**11** were fully characterized by solution NMR methods and **8** was also characterized by elemental analysis.

All of compounds **7**–**11** displayed outstanding thermal stability. Remarkably, thermolysis of C_6D_6 solutions of **7**–**11** at 100 °C for 20 h did not result in any change observable by NMR. Compounds **8** and **9** are arguably the most thermally stable β-hydrogen-containing Pd alkyls known [7]. Recently, Liang et al. described β-hydrogen-containing Ni alkyls supported by closely related PNP ligands [8]. Liang's compounds displayed high thermal stability as well. However, the stability of some of these Ni alkyls is at least of the thermodynamic origin as the corresponding hydrides reacted irreversibly with alkenes by insertion (the reverse of β-hydrogen elimination). In contrast, **5** did not react with ethylene (1 atm) in C_6D_6, even after 18 h at 90 °C. Thus, in the (PNP)Pd case, it remains unclear whether the insertion product (Pd-alkyl) or the BHE products (XXX + olefin) are thermodynamically favorable.

Our attempts to prepare **12** and **13** were unsuccessful. ^{i}PrMgCl and ^{t}BuMgCl did not react with **4**. The action of ^{i}PrMgCl on **6** produced only **4** and **5**. Similarly, the reaction of ^{t}BuMgCl or ^{t}BuLi with **6** produced mostly **5**. Compound **12** or **13** was not observed at all in these experiments.

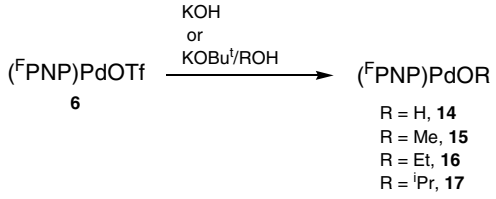
At first glance, β-hydride elimination from a secondary or tertiary Pd alkyl might be the most "obvious" path to the observed **5** in these reactions. However, to us this seems unlikely, given the outstanding thermal stability of **8** and **9** (vide supra). While differences between primary and secondary alkyls are to be expected, it would be very hard to reconcile the essentially infinite lifetime of **8/9** at elevated temperature with the rapid BHE of **12/13** at ambient temperature, should they have been formed. Literature examples of square-planar Pd–CHMe$_2$ compounds that are observable at ambient conditions do exist [9].

It is possible that the production of **5** in the reactions of **6** with ^{i}PrMgCl and ^{t}BuMgCl results from a direct hydride transfer (that is, without the formation of a Pd–C bond). An alternative possibility is that an initial one-electron reduction of **5** by the bulky Grignard or ^{t}BuLi with subsequent transfer of H atom to Pd. The sluggishness of the transfer of a secondary alkyl group to Pd is also evidenced by the fact that we were able to use the commercial (Aldrich) dibutylmagnesium solution that contains a 1:1 mixture of *n*-Bu and *sec*-Bu groups to selectively prepare **9** from **6**.

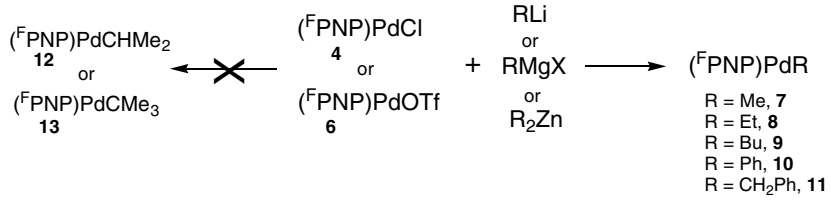
2.2. Syntheses of (^{F}PNP)Pd-alkoxide compounds and their thermal stability

The alkoxide derivatives **15**–**17** were conveniently synthesized from the corresponding potassium alkoxides and **6** (Scheme 3). The potassium alkoxides were prepared in situ via dissolution of KOBu^t in MeOH, EtOH, or ^{i}PrOH, respectively. We have also prepared the hydroxo complex **14** via the reaction of **6** with KOH (Scheme 3). Compound **14** was sometimes observed as an impurity in the syntheses of **15**–**17** if the corresponding alcohol were not rigorously water-free. An analogous terminal hydroxo (PCP)PdOH complex is known [10]. Similarly to the latter, the OH proton of **14** resonates in the upfield region of the ^{1}H NMR spectrum (δ −2.15 ppm, *t*, $J_{HP} = 2$ Hz).

Compounds **14**–**17** are isolable materials that are stable in solution at ambient temperature. While we were successful in isolating a small analytically pure batch of **16**, it was typically contaminated by small amounts (<3%) of **5** and/or **20**. Compounds **14**–**17** also display high stability at



Scheme 3.

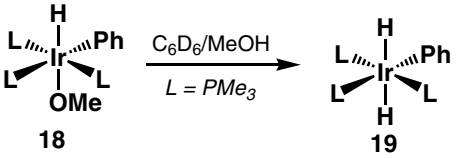


Scheme 2.

elevated temperatures. The stability of the hydroxo complex **14** is perhaps unexceptional, but the high stability of the β-hydrogen containing alkoxides **15**–**17** is striking. Thermolysis of **17** in C_6D_6 (1 h, 75 °C) did not result in any NMR-observable change. Thermolysis of **16** in C_6D_6 at 75 °C for 20 h resulted in the decomposition of only 2% of **16** and the thermolysis of **15** in C_6D_6 (1 h, 80 °C) resulted in the decomposition of only 8% of **15**.

Blum and Milstein described a related case where BHE from an Ir-methoxide **18** proceeded in the absence of *cis*-empty site (Scheme 4) and found that the rate of BHE depended on the concentration of MeOH present [11]. We selected **16** for further study, desiring to probe the influence of the solvent on BHE. We performed a series of experiments in which **16** was thermolyzed at 75 °C and at 100 °C in mixtures with different C_6D_6/EtOH ratios (Tables 1 and 2). It is apparent from the data that increasing ethanol concentration enhances the rate of the disappearance of **16**. Blum and Milstein determined that the BHE from **18** displayed an apparent kinetic order of 2.7 in methanol [11]. In this report, we only strive to show the qualitative trend. Drastically changing benzene/ethanol ratios in our case not only simply vary the ethanol concentration but also substantially change the polarity of the medium. It is not immediately clear to us how this can be quantitatively accounted for in a kinetic study.

The major product of the thermal decomposition of **16** is **5**; however, **20** was also consistently observed as a minor by-product (Scheme 5). We have not been able to isolate this compound in a pure state and its identification is based on the solution NMR data. We propose that the enolate complex **20** is formed by the reaction of free acetaldehyde (the by-product of the BHE from **16**) with **16**. The aldehydic proton in **20** resonates as a triplet ($J_{HH} = 5$ Hz) at δ 9.82 ppm and the hydrogens of the Pd-bound methylene group give rise to apparent quartet (doublet of triplets, $J_{HH} \approx J_{PH} \approx 5$ Hz) at d 2.81 ppm. Tsutsui and co-workers reported **21** (Scheme 5) in which the Pt–CH_2CHO fragment gave rise to two resonances at δ 9.3 and 3.3 ppm with a 5.5 Hz J_{HH} coupling [12].



Scheme 4.

Table 1
Data for the thermolyses of (PNP)PdOEt (**16**) in C_6D_6/EtOH mixtures of varying composition at 75 °C

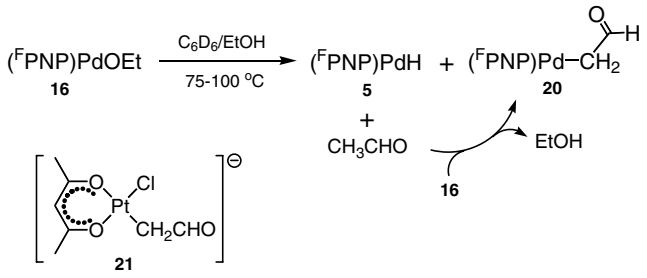
Fraction EtOH, v/v	0%	10%	25%	50%	75%	90%	100%
At mixing							
16	100	100	100	100	100	100	100
5	2	2	2	2	2	2	2
20	1	1	1	1	1	1	1
After 20 h							
16	98	97	94	90	85	80	71
5	4	5	7	9	13	16	22
20	3	2	2	4	7	8	10

Relative concentrations of compounds **16**, **5**, and **20** (vs. ^{19}F NMR standard) are given.

Table 2
Data for the thermolyses of (PNP)PdOEt (**16**) in C_6D_6/EtOH mixtures of varying composition at 100 °C

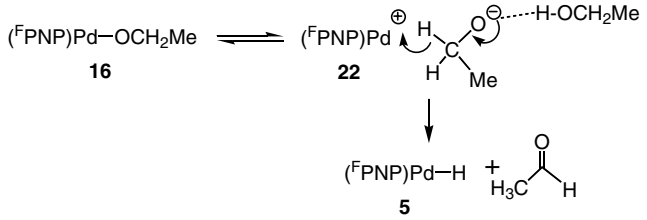
Fraction EtOH, v/v	10%	25%	50%	75%	90%
At mixing					
16	100	100	100	100	100
5	3	3	3	3	3
20	1	1	1	1	1
After 1 h					
16	99	99	98	95	93
5	4	4	6	8	9
20	1	1	2	2	2
After 20 h					
16	90	88	83	69	59
5	9	11	16	26	32
20	4	5	7	10	14

Relative concentrations of compounds **16**, **5**, and **20** (vs. ^{19}F NMR standard) are given.



Scheme 5.

The high thermal stability of alkoxides **15**–**17** is remarkable, considering that BHE in late metal alkoxides is commonplace [2]. The fact that **16** does undergo BHE in ethanol indicates that the process is thermodynamically favorable and the lack of BHE in non-polar solvents must be ascribed to kinetic reasons. Based on the observed solvent dependence, we propose a mechanism for BHE similar to that outlined by Blum and Milstein for **18** [11] (Scheme 6). Heterolytic dissociation of the alkoxide anion would



Scheme 6.

produce a (PNP)Pd cation **22**, which may be stabilized by the solvent (alcohol). The alkoxide may then attack the metal with its hydrocarbyl end and in effect function as a hydride transfer agent. The accelerating effect of the alcohol solvent is seen as both owing to the increase of the general polarity and the more direct stabilization of the alkoxide via hydrogen bonding.

Square-planar complexes such as **15**–**17** possess a high-lying empty orbital that in some cases is available for bonding. Thus it is possible to envision that the BHE in **15**–**17** proceeds in a more conventional fashion, intramolecularly, through a five-coordinate transition state. However, such a mechanism, while burdensome to rule out completely, is difficult to reconcile with the observed dependence of the rate on the medium of the reaction (Table 1).

2.3. Summary

In summary, we demonstrate that the PNP system can give rise to remarkably robust Pd alkyls and alkoxides despite the presence of β-hydrogens in these moieties. The square-planar alkoxides apparently undergo BHE via a non-classical mechanism that involves alkoxide dissociation.

3. Experimental

3.1. General considerations

Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, C_6D_6, THF, and isooctane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. Hexamethyldisiloxane was refluxed over and then distilled from NaK alloy. Ethanol and fluorobenzene were dried with and then distilled from CaH_2. Methanol and isopropanol were degassed by the freeze–pump–thaw technique. (^{F}PNP)PdCl (**4**) [4b], (^{F}PNP)PdH (**5**) [4a], and (^{F}PNP)-PdMe (**7**) [4a] were prepared according to be published procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^{19}F NMR, 375.912 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally using 1.0M CF_3CO_2H in $CDCl_3$ at −78.5 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ).

3.2. Preparation of (^{F}PNP)PdOTf (6)

One hundred and seventy six milligrams (0.323 mmol) of (^{F}PNP)PdH (**5**) was added to a 50 mL Schlenk flask and then dissolved in 25 mL of toluene. To the flask, 73.0 μL (0.646 mmol) of MeOTf was added and the solution stirred overnight. The solution was then filtered through Celite. The volatiles were removed from the filtrate under vacuum. The residue was dissolved in a minimum amount of toluene, pentane was carefully layered on the top, and then the flask was placed in a freezer at −35 °C. The reaction yielded 185.0 mg (83%) of a purple crystalline solid of (^{F}PNP)PdOTf (**6**). ^{1}H NMR (C_6D_6): δ 7.11 (m, 2 H, Ar–*H*), 6.63 (m, 2H, Ar–*H*), 6.51 (m, 2H, Ar–*H*), 2.22 (m, 4H, C*H*), 1.25 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$), 0.88 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.8 (m, *C*–N), 113.2 (d, $J_{C-F} = 24$ Hz), 118.5 (d, $J_{C-F} = 22$ Hz), 117.5 (m), 100.2 (s), 25.3 (t, 12 Hz, P*C*HMe$_2$), 18.6 (PCH*Me*$_2$), 17.8 (s, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 52.8. ^{19}F NMR (C_6D_6): δ −79.4 (s, 3F), −128.8 (s, 2F).

3.3. Preparation of (^{F}PNP)PdCH$_2$CH$_3$ (8)

Two hundred milligrams (0.288 mmol) of (^{F}PNP)PdOTf (**6**) was added to a 50 mL Schlenk and flask then dissolved in 10 mL of ethyl ether. To the flask, 461.9 μL (0.374 mmol) of 10 wt% Et_2Zn in hexane was added and the solution stirred for 10 min. The solution was then filtered through a pad of silica gel. The volatiles were removed from the filtrate under vacuum and the residue was redissolved in ether. The solution was then filtered through a pad of Celite, the volatiles were removed from the filtrate under vacuum then the residue dissolved in a minimum amount of ether, layered with pentane and placed in a freezer at −35 °C. The flask was covered with aluminum foil to prevent exposure to light. The reaction yielded 68 mg (41%) of an orange crystalline solid of (^{F}PNP)PdEt (**8**). ^{1}H NMR (C_6D_6): δ 7.47 (m, 2H, Ar–*H*), 6.78 (m, 2H, Ar–*H*), 6.73 (td, 2H, $J_{HP} = 8$ Hz, $J_{HF} = 3$ Hz, Ar–*H*), 1.99 (m, 4H, C*H*), 1.78 (m, 2H, C*H*$_2$CH$_3$), 1.47 (tt, 3H, $J_{HP} = 2$ Hz, $J_{HH} = 8$ Hz, CH$_2$C*H*$_3$), 1.13 (app. quartet (dvt), 12H, $J = 9$ Hz, PCH*Me*$_2$), 0.93 (app. quartet (dvt), 12H, $J = 8$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.8 (s, *C*–N), 154.2 (dt, $J_{CF} = 235$ Hz, $J_{CP} = 4$ Hz, *C*–F), 121.8 (m, *C*–P), 118.6 (d, $J_{C-F} = 21$ Hz), 118.5 (d, $J_{C-F} = 23$ Hz), 115.4 (app. q (dvt), $J = 7$ Hz), 24.9 (t, $J_{CP} = 11$ Hz, P*C*HMe$_2$), 19.1 (t, $J_{CP} = 2$ Hz, PCH*Me*$_2$), 18.9 (s, CH$_2$*C*H$_3$), 18.1 (s, PCH*Me*$_2$), −6.13 (t, $J = 4$ Hz, *C*H$_2$CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 37.1. ^{19}F NMR (C_6D_6): δ −133.3 (m). Elem. *Anal.* Calc. for $C_{26}H_{39}NP_2F_2Pd$: C, 54.64; H, 6.83. Found: C, 54.28; H, 7.12%.

3.4. Preparation of (^{F}PNP)PdCH$_2$CH$_2$CH$_2$CH$_3$ (9)

Two hundred and forty three milligrams (0.351 mmol) of (^{F}PNP)PdOTf (**6**) was added to a 50 mL Schlenk flask and dissolved in 10 mL of ethyl ether. To this solution, 790 μL (0.794 mmol) of 1.0 M Bu_2Mg (1:1 *n*-Bu:*s*-Bu) in heptane was added and the solution stirred for 10 min. The flask was covered with aluminum foil to prevent exposure

to light. The solution was then filtered through a pad of silica gel. The volatiles were removed from the filtrate under vacuum and the residue was redissolved in ether. The solution was then filtered through a pad of Celite, the volatiles were removed from the filtrate under vacuum and then the residue was dissolved in a minimum of pentane and placed in a freezer at −35 °C. The reaction yielded 110 mg (51%) of a yellow-brown crystalline solid of (^{F}PNP)Pd(*n*-Bu) (**9**). ^{1}H NMR (C_6D_6): δ 7.47 (m, 2H, Ar–*H*), 6.78 (m, 2H, Ar–*H*), 6.73 (td, 2H, $J_{HP} = 8$ Hz, $J_{HF} = 3$ Hz, Ar–*H*), 2.00 (m, 4H, C*H*), 1.75 (br m, 4H, α and β-H of $(CH_2)_3CH_3$), 1.54 (m, 2H, γ-H of $(CH_2)_3CH_3$), 1.11 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$), 1.09 (t, 3H, $J = 7$ Hz, $(CH_2)_3CH_3$), 0.92 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.8 (t, 10 Hz, *C*–N), 154.2 (dt, $J_{CF} = 235$ Hz, $J_{CP} = 4$ Hz, *C*–F), 121.8 (td, $J_{CF} = 5$ Hz, $J_{CP} = 17$ Hz, *C*–P), 118.5 (d, $J_{C–F} = 22$ Hz), 118.6 (d, $J_{C–F} = 21$ Hz),115.4 (app. q (dvt), $J = 7$ Hz), 36.6 (s, CH_2), 28.5 (s, CH_2), 24.9 (t, 11 Hz, P*C*HMe$_2$), 19.1 (t, 3 Hz, PCH*Me*$_2$), 18.1 (s, PCH*Me*$_2$), 14.6 (s, CH_3), 1.5 (t, $J = 5$ Hz, α-CH_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 37.3. ^{19}F NMR (C_6D_6): δ −133.4 (m).

3.5. Preparation of (^{F}PNP)PdPh (**10**)

Five hundred milligrams (0.865 mmol) of (^{F}PNP)PdCl (**4**) was dissolved in 5 mL of toluene. 648 μL (1.29 mmol) of a 2.0 M PhLi solution in diethyl ether was added and the solution stirred for an hour. The solution was then filtered through a pad of silica gel and the volatiles removed under vacuum. The residue was dissolved in ether and then placed in a freezer at −35 °C. 189 mg (35% yield) of (^{F}PNP)PdC_6H_5 (**10**) was collected as a yellow crystalline solid. ^{1}H NMR (C_6D_6): δ 7.53 (m, 4H, overlapping Ar–*H* of PNP and *o*-*H* of phenyl group), 7.15 (t, 2H, *m*-*H* of phenyl overlapping with residual C_6D_5H and toluene signals), 7.00 (t, 1H, *p*-*H* of benzyl overlapping with residual toluene signal), 6.75 (m, 4H, Ar–*H* of PNP), 1.91 (m, 4H, C*H*), 0.86 (overlapping app. quartets (dvt), 24H PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.2 (t, $J = 11$ Hz, *C*–N), 154.4 (d, $J = 236$ Hz, *C*–F), 148.1 (m, *ipso*-*C*), 138.9 (s, *o*-*C*), 127.7 (s, *m*-*C*), 123.0 (s, *p*-*C*), 121.5 (m, *C*–P), 118.9 (d, $J_{C–F} = 21$ Hz), 118.7 (d, $J_{C–F} = 22$ Hz), 115.4 (app. q (dvt), $J = 6$ Hz), 23.8 (t, $J = 11$ Hz, P–*C*HMe$_2$), 18.4 (t, $J = 3$ Hz, PCH*Me*$_2$), 17.42 (s, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 39.2. ^{19}F NMR (C_6D_6): δ −132.8.

3.6. Preparation of (^{F}PNP)PdCH_2Ph (**11**)

Two hundred milligrams (0.288 mmol) of (^{F}PNP)PdOTf (**6**) was added to a 50 mL Schlenk flask and then dissolved in 10 mL of ethyl ether. To the flask, 317 μL (0.317 mmol) of a 1 M benzyl magnesium chloride in ether was added and the solution stirred for 10 min. The volatiles were removed under vacuum from the filtrate. The residue was dissolved in ether and filtered through a pad of silica gel. The volatiles were removed under vacuum from the filtrate and the residue redissolved in ether. The solution was then filtered through a pad of Celite, the volatiles were removed under vacuum and then the residue was dissolved in a minimum amount of pentane, layered with hexamethyldisiloxane and placed in a freezer at −35 °C. The flask was covered with aluminum foil to prevent exposure to light. The reaction yielded 108.5 mg (59%) of (^{F}PNP)Pd$CH_2C_6H_5$ (**11**) as an orange crystalline solid. ^{1}H NMR (C_6D_6): δ 7.45 (m, 4H, overlapping Ar–*H* of PNP and *o*-*H* of benzyl group), 7.12 (t, 2H, $J = 7$ Hz, *m*-*H* of benzyl), 6.95 (t, 1H, $J = 8$ Hz *p*-*H* of benzyl), 6.80 (m, 2H, Ar–*H* of PNP), 6.71 (td, 2H, $J_{HP} = 8$ Hz, $J_{HF} = 3$ Hz, Ar–*H* of PNP), 3.04 (t, 2H, $J = 6$ Hz, CH_2–Ar–H), 1.81 (m, 4H, C*H*), 1.01 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$), 0.91 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.8 (t, $J = 11$ Hz, *C*–N),154.3 (d, $J = 239$ Hz, *C*–F), 152.0 (s, *ipso*-*C*), 130.4 (s, *o*-*C*), 128.3 (s, *m*-*C*), 123.6 (s, *p*-*C*), 122.1 (m, *C*–P), 118.5 (d, $J_{C–F} = 23$ Hz), 118.4 (d, $J_{C–F} = 21$ Hz), 115.7 (app. q (dvt), $J = 7$ Hz), 24.8 (t, $J = 11$ Hz, P–*C*HMe$_2$), 19.2 (t, $J = 2$ Hz, PCH*Me*$_2$), 18.2 (s, PCH*Me*$_2$), 7.3 (t, $J = 4$ Hz, CH_2Ph). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.1. ^{19}F NMR (C_6D_6): δ −132.8.

3.7. Preparation of (^{F}PNP)PdOH (**14**)

One hundred milligrams (0.144 mmol) of (^{F}PNP)PdOTf (**6**) was added to a 25 mL Schlenk flask and then dissolved in 10 mL of THF. To the flask 8.8 mg (0.158 mmol) of KOH and three drops of distilled and degassed water were added. The solution was stirred for 2 h. The volatiles were removed under vacuum. The residue was dissolved in ether then filtered through a pad of Celite, the volatiles were removed under vacuum from the filtrate and then the residue was dissolved in a minimum amount of ether and placed in a freezer at −35 °C. The reaction yielded 83 mg (94%) of (^{F}PNP)PdOH (**14**) as a red orange crystalline solid. ^{1}H NMR (C_6D_6): δ 7.32 (m, 2H, Ar–*H*), 6.70 (m, 2H, Ar–*H*), 6.65 (td, 2H, $J_{HP} = 8$ Hz, $J_{HF} = 3$ Hz, Ar–*H*), 1.95 (m, 4H, C*H*), 1.28 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$), 1.00 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$), −2.15 (t, 1H, $J = 2$ Hz, –O*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ160.7 (t, $J = 11$ Hz, *C*–N),155.5 (d, $J = 237$ Hz, *C*–F), 121.1 (td, $J_{CP} = 17$ Hz, $J_{CF} = 5$ Hz, *C*–P), 118.6 (d, $J = 23$ Hz), 118.5 (d, $J = 21$ Hz),116.3 (app. q (dvt) $J = 7$ Hz), 24.8 (t, $J = 11$ Hz, P*C*HMe$_2$), 18.8 (t, $J = 3$ Hz, PCH*Me*$_2$), 18.2 (s, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.4. ^{19}F NMR (C_6D_6): δ −131.6 (m). Elem. *Anal.* Calc. for $C_{24}H_{35}ONP_2F_2Pd$: C, 51.48; H, 6.30. Found: C, 51.48; H, 6.33%.

3.8. Preparation of (^{F}PNP)PdOMe (**15**)

9.63 μL (0.23 mmol) of degassed MeOH and 26.7 mg (0.23 mmol) of KOBu^{t} were combined in THF and allowed to stir for 5 min. To that 150 mg (0.22 mmol) of (^{F}PNP)PdOTf (**6**) was added and the solution stirred for

10 min. The volatiles were removed under vacuum. The residue was dissolved in pentane and then filtered through a pad of Celite. The volatiles were removed under vacuum and the residue was redissolved in a minimum amount of pentane and placed in a freezer at −35 °C. The reaction yielded 50 mg (40%) of (^{F}PNP)PdOMe (**15**) as an orange powder. ^{1}H NMR (C_6D_6): δ 7.31 (m, 2H, Ar–*H*), 6.72 (m, 2H, Ar–*H*), 6.23 (app. td, 2H, $J_{HP} = 9$ Hz, $J_{HF} = 3$ Hz, Ar–*H*), 3.91 (s, 3H, OCH_3), 2.03 (m, 4H, C*H*), 1.32 (app. quartet (dvt), 12H, $J = 8$ Hz, PCH*Me*$_2$), 1.01 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.9 (t, $J = 11$ Hz, *C*–N), 154.7 (d, $J_{CF} = 238$ Hz, *C*–F), 120.8 (t), 118.8 (s), 118.5 (s), 116.4 (s), 62.2 (s, –O*C*H$_3$), 24.8 (t, $J = 11$ Hz, PCH*Me*$_2$), 18.5 (s,CH*Me*$_2$), 18.0 (s, *C*HMe$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.6. ^{19}F NMR (C_6D_6): δ −131.5.

3.9. Preparation of (^{F}PNP)PdOEt (**16**)

75.5 μL (1.3 mmol) of distilled EtOH and 132.5 mg (1.18 mmol) of KOBu^{t} were combined in THF and allowed to stir for 5 min. To that 500 mg (0.72 mmol) of (^{F}PNP)PdOTf (**6**) was added and the solution stirred for 1 h. The solution was filtered through a pad of Celite and the volatiles were then removed under vacuum from the filtrate. The residue was then redissolved in toluene and filtered again through a pad of Celite. One microliter of *iso*-octane was added and the volatiles were removed under vacuum. The reaction yielded 372 mg (88%) of (^{F}PNP)PdOEt (**16**) as an orange powder. ^{1}H NMR (C_6D_6): δ 7.30 (m, 2H, Ar–*H*), 6.72 (m, 2H, Ar–*H*), 6.62 (app. td, 2H, Ar–*H*), 3.97 (q, 2H, O–*C*H$_2$CH3), 2.02 (m, 4H, C*H*), 1.44 (t, 3H, $J = 8$ Hz, O–CH$_2$CH_3) 1.30 (app. quartet (dvt), 12H, $J = 8$ Hz, PCH*Me*$_2$), 1.00 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 160.8 (*C*–N), 154.7 (d, $J_{CF} = 237$ Hz, *C*–F), 120.8 (m, *C*–P), 118.7 (s), 118.5 (s), 116.4 (app. q (dvt), $J = 6$ Hz), 68.1 (s, –O*C*H$_2$CH$_3$), 24.9 (t, $J = 11$ Hz, PCH*Me*$_2$), 22.4 (s, –OCH$_2$*C*H$_3$), 18.5 (t, $J = 3$ Hz, CH*Me*$_2$), 17.9 (s, *C*HMe$_2$); ^{31}P{^{1}H} NMR (C_6D_6): δ 38.7; ^{19}F NMR (C_6D_6): δ −131.6.

3.10. Preparation of (^{F}PNP)PdO^{i}Pr (**17**)

36.4 μL (0.51 mmol) of degassed *i*-PrOH and 56.6 mg (0.51 mmol) of KOBu^{t} were combined in THF and allowed to stir for 5 min. To that 350 mg (0.51 mmol) of (^{F}PNP)PdOTf (**6**) was added and the solution stirred for 10 min. The volatiles were removed under vacuum. The residue was dissolved in pentane and then filtered through a pad of Celite. The volatiles were removed under vacuum from the filtrate and the residue was dissolved in a minimum amount of pentane and placed in a freezer at −35 °C. The reaction yielded 115.8 mg (38%) of (^{F}PNP)PdOPr^{i} (**17**) as an orange crystalline solid. ^{1}H NMR (C_6D_6): δ 7.29 (m, 2H, Ar–*H*), 6.74 (m, 2H, Ar–*H*), 6.62 (app. td, 2H, $J_{HP} = 9$ Hz, $J_{HF} = 3$ Hz, Ar–*H*), 3.86 (m, 1H, OC*H*Me$_2$), 2.04 (m, 4H, C*H*), 1.49 (d, 6H, OCH*Me*$_2$), 1.30 (app. quartet (dvt), 12H, $J = 8$ Hz, PCH*Me*$_2$), 1.01 (app. quartet (dvt), 12H, $J = 7$ Hz, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.8 (t, $J = 11$ Hz, *C*–N), 154.8 (d, $J_{CP} = 237$ Hz, *C*–F), 120.9 (td, $J_{C-P} = 18$ Hz, $J_{C-F} = 4$ Hz, *C*–P), 118.4 (d, $J_{C-F} = 21$ Hz), 118.6 (d, $J_{C-F} = 23$ Hz), 116.6 (app. q (dvt), $J = 6$ Hz), 74.0 (s, –O*C*HMe$_2$), 31.1 (s, –OCH*Me*$_2$), 25.1 (t, $J = 11$ Hz, PCH*Me*$_2$), 18.6 (s, CH*Me*$_2$), 17.9 (s, *C*HMe$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.6. ^{19}F NMR (C_6D_6): δ −131.5. Elem. *Anal.* Calc. for $C_{27}H_{41}ONP_2F_2Pd$: C, 53.91; H, 6.82. Found: C, 53.90; H, 6.98%.

3.11. General procedure for the thermolysis of (PNP)Pd-alkyl complexes

Twenty milligrams of each (PNP)Pd-alkyl (**7**–**11**) was dissolved in C_6D_6 (0.5 mL, J. Young tube). The samples were then heated in an oil bath at 100 °C for 20 h. Subsequent NMR analysis showed no change in composition of solutions.

3.12. Thermolysis of (PNP)PdOH (**14**)

Twenty milligrams of (PNP)PdOH (**14**) was dissolved in C_6D_6 (0.5 mL, J. Young tube). The sample was then heated in an oil bath at 75 °C for 2.5 h. Subsequent NMR analysis showed no change in composition of the solution.

3.13. Thermolysis of (PNP)PdOMe (**15**)

Seventeen milligrams of (PNP)PdOMe (**15**) was dissolved in C_6D_6 (0.5 mL, J. Young tube). The sample was then heated in an oil bath at 80 °C for 1 h. An 8% decrease in the concentration of **15** was observed by ^{19}F NMR.

3.14. Thermolysis of (PNP)PdOPr^{i} (**17**)

Ten milligrams (0.017 mmol) of (PNP)PdOPr^{i} (**17**) was dissolved in 0.5 mL of C_6D_6. One drop of α,α,α-trifluorotoluene was added to the sample as an internal integration standard for ^{19}F NMR. The sample was then heated in an oil bath at 75 °C for 1 h. No change in the concentration of **17** was noted by ^{19}F NMR.

3.15. General procedure for the thermolysis of (PNP)PdOEt (**16**) in the C_6D_6/EtOH mixtures

Samples of (PNP)PdOEt (**17**) (18–23 mg, 0.031–0.039 mmol) were dissolved in 0.5 mL of a solvent mixture. Solutions made contained 0%, 10%, 25%, 50%, 75%, 90% and 100% ethanol by volume in C_6D_6. Five microliters (0.051 mmol) of fluorobenzene was added to each sample as an internal integration standard for ^{19}F NMR. These samples were then heated in an oil bath and analyzed by ^{19}F and ^{31}P NMR at indicated times. Following the thermolysis, (PNP)PdOEt (**16**), (PNP)PdH (**5**) and

(PNP)Pd–CH_2CHO (**20**) were observed. Selected NMR data for **20** follow. ^1H NMR (C_6D_6): δ 9.82 (t, 1H, $J = 5$ Hz, C(O)*H*), 2.81 (app. q (dt), 2H, $J_{H\text{-}P} = 6$ Hz, $J = 5$ Hz, CH_2C(O)H); $^1H\{^{31}P\}$ NMR (C_6D_6): δ 9.82 (t, 1H, $J = 5$ Hz, C(O)*H*), 2.81 (d, 2H, $J = 5$ Hz, CH_2C(O)H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.7; ^{19}F NMR (C_6D_6): δ −131.8.

Acknowledgements

We are grateful to NSF (CHE-0517798), Brandeis University, the Donors of the American Chemical Society Petroleum Research Fund, Research Corporation, and the Sloan Foundation for support of this research.

Appendix A. Supporting information available

Graphical depictions of ^1H NMR spectra of selected compounds. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.07.067.

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