(Diphenylphosphino)alkyl-Functionalized Nucleophilic Carbene Complexes of Palladium

Nikolaos Tsoureas,[†] Andreas A. Danopoulos,*[,†] Arran A. D. Tulloch,[‡] and Mark E. Light[†]

Department of Chemistry, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ, and Johnson Matthey Catalysts, Belasis Avenue, Billingham, Cleveland, U.K. TS23 1LB

Received July 22, 2003

The (diphenylphosphino)alkyl-functionalized nucleophilic heterocyclic carbene (NHC) complexes of palladium $LPdX_2$ (L = (3-R^1)[1-$Ph_2P(CH_2)_2$]-imidazol-2-ylidene; R^1 = 2,6-$Pr^i_2C_6H_3$, 2,4,6-$Me_3C_6H_2$; X = CH_3 (**3a**,**b**), X = Br (**4a**,**b**)) have been synthesized by the reaction of the in situ generated functionalized NHC ligand $\mathbf{L^a}$ or $\mathbf{L^b}$ with Pd(tmed)$(CH_3)_2$ and Pd(COD)Br_2, respectively, and structurally characterized. Interaction of **3a** with H(Et_2O)-{B[3,5-$(CF_3)_2C_6H_2]_4$} and pyridine or with $(CF_3)_2$CHOH and pyridine in CH_2Cl_2 gave the monocationic complexes $[(L^a)Pd(CH_3)(pyridine)]^+(A)^-$ (A^- = {B[(3,5-$CF_3)_2C_6H_2)]_4$}$^-$, $(CF_3)_2CHO^-$); acetonitrile and benzonitrile analogues can be prepared in an analogous way. Reaction of **4a** with $AgBF_4$ in MeCN gave the dicationic complexes $[(L^a)Pd(MeCN)_2](BF_4)_2$. Complexes **3** show moderate catalytic activity for the coupling of acrylates with aryl bromides but not chlorides. The cationic species generated in situ from **3a** and H(Et_2O){B[(3,5-$CF_3)_2C_6H_2)]_4$} in CH_2Cl_2 under CO/ethylene acts as a copolymerization catalyst under mild conditions.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

Introduction

There is a continuing effort to improve our mechanistic understanding of the organometallic transformations and catalytic reactions involving NHC complexes.[1] The reductive elimination of methylimidazolium salts from $[Pd(tmim)CH_3(L)_2]^+$ (tmim = tetramethylmethylimidazol-2-ylidene, L = phosphine, phosphite) and the microscopic reverse, oxidative addition, have been observed in simple systems and studied by theoretical methods;[2] methyl migration to the NHC carbon has also been observed in a Pd complex with a preorganized "pincer" NHC ligand and studied theoretically.[3] The extent of these reactions is critically dependent on the nature of the coligating functionalities, the presence and size of chelating rings, and other structural variables. Consequently, the design of successful carbene catalysts should be based on ligands promoting productive catalytic steps while inhibiting decomposition or deactivation. The use of bulky groups on imidazole and imidazolin-2-ylidene is becoming a common feature of most catalytically active complexes. In addition, incorporation of the carbene functionality into ligand systems containing other "classical" donor groups facilitates electronic tuning of the metal coordination sphere.[4]

We have recently reported the synthesis of several thermally stable N-functionalized NHCs with various substituted pyridines, ethers, and arylphosphines.[5] Furthermore, a range of complexes with platinum-group metals, mainly Pd, Ru, Ir, and Rh, have been also prepared by the interaction of the isolated or in situ generated functionalized NHCs or their silver adducts with transition-metal precursors.[6] Herein, we wish to report the synthesis, structural characterization, and selected reactions of 3-aryl-1-(β-(diphenylphosphino)ethyl)imidazol-2-ylidene (aryl = 2,6-Pr^i_2-C_6H_3, $\mathbf{L^a}$; aryl = 2,4,6-trimethylphenyl, $\mathbf{L^b}$) complexes of palladium. The compounds described in the paper are summarized in Scheme 1.

Results and Discussion

Ligand Synthesis. The ligand synthetic strategy is shown in Scheme 2.

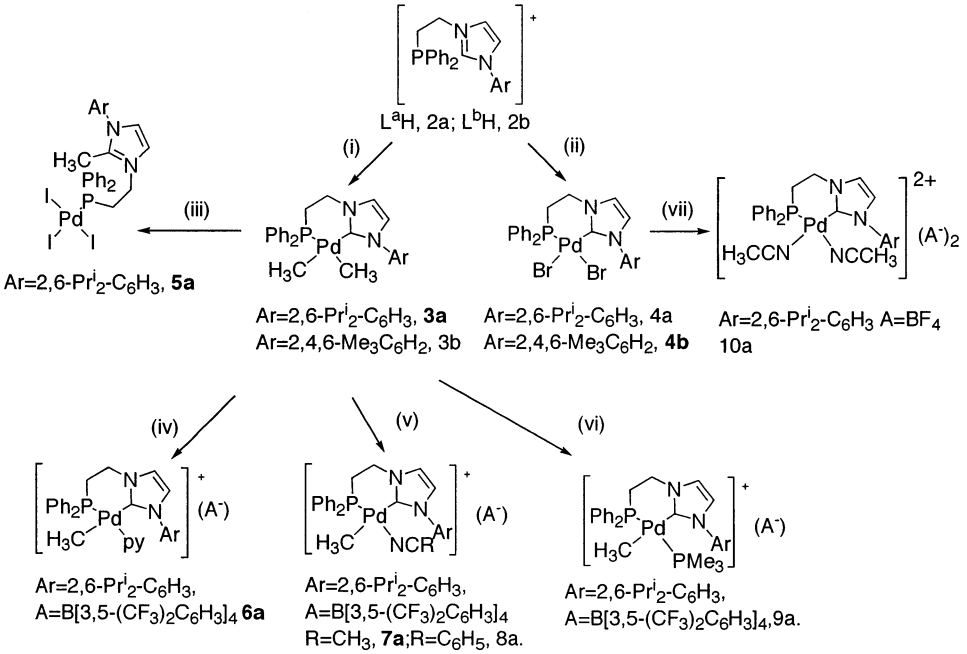
It is based on the quaternization of 1-arylimidazoles with (ω-bromoalkyl)diphenylphosphine oxide followed by reduction with $SiHCl_3$. A similar procedure was used for the synthesis of the 1-(β-(diphenylphosphino)ethyl)-3-methylimidazolium salt.[4] However, under the previously reported conditions both reaction steps failed with the bulky, less nucleophilic 1-arylimidazoles. When the

* To whom correspondence should be addressed. E-mail: ad1@soton.ac.uk.
[†] University of Southampton.
[‡] Johnson Matthey Catalysts.

(1) For recent reviews of the area see: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Bourisou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
(2) (a) McGuinness, S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029. (b) McGuiness, S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317. (c) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2163.
(3) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756.
(4) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 1627.
(5) Danopoulos, A. A.; Gelbrich, T.; Hursthouse, M. B.; Winston, S. *Chem. Commun.* **2002**, 482.
(6) (a) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Hursthouse, M. B.; Eastham, G. *Dalton Trans.* **2003**, 699 and references therein. (b) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Hursthouse, M. B.; Eastham, G. *Dalton Trans.* **2003**, 1009. (c) Lappert, M. F. *J. Organomet. Chem.* **1993**, *451*, 389. (d) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340. (e) Fürstner, A.; Krause, H.; Ackermann, L.; Lehmann, C. W. *Chem. Commun.* **2001**, 2240.

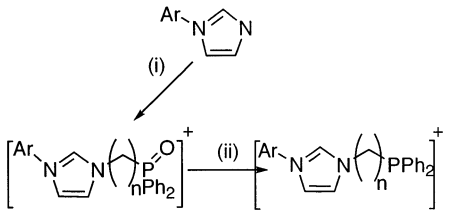
10.1021/om034061s CCC: $25.00 © 2003 American Chemical Society
Publication on Web 10/14/2003

Scheme 1. Palladium Complexes and Chemical Transformations Described in This Paper[a]



[a] Compound given in boldface type have been structurally characterized. Reagents and conditions: (i) 1.1 equiv of $KN(SiMe_3)_2$, THF, −78 °C and then 1 equiv of tmedPd$(CH_3)_2$; (ii) 1.1 equiv of $KN(SiMe_3)_2$, THF, −78 °C and then 1 equiv of (1,5-COD)PdCl_2; (iii) CH_3I excess in THF; (iv) 1 equiv of $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ at −78 to −30 °C and then 1 equiv of Py; (v) 1 equiv of $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ at −78 to −30 °C and then 1 equiv of CH_3CN or PhCN; (vi) 1 equiv of $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ at −78 to −30 °C and then 1 equiv of PMe_3; (vii) 2 equiv of $AgBF_4$ in CH_3CN.

Scheme 2. Synthesis of the Ligand Precursor Imidazolium Salts[a]



[a] Reagents and conditions: (i) $Ph_2P(=O)(CH_2)_nBr$, 150−160 °C, 4−5 days; (ii) $SiHCl_3$ in chlorobenzene, 120 °C (n = 2, 3).

quaternization reactions were carried out at 150−160 °C (most conveniently in the melt in the absence of solvent), they gave good yields. Furthermore, the yield of the subsequent reduction was also dramatically improved when using $SiHCl_3$ in refluxing chlorobenzene as a reducing agent. The synthesis of the 1-(*β*-(diphenylphosphino)ethyl)-3-mesitylimidazolium salt (L^{b}H)Br from 1-(*β*-bromoethyl)-3-mesitylimidazolium and PPh_2H in DMSO in the presence of KOBu^t has recently been communicated, although the reported yields were poor.[7] All imidazolium phosphines were isolated as white, air-sensitive powders and characterized by spectroscopic and analytical methods. The microanalysis data support the presence of mixed chloride/bromide salts; the chloride ion originates from the hydrolytic workup of the excess $SiHCl_3$ during the reduction step. Mixed halide imidazolium salts and palladium NHC complexes have been observed before.[6a]

Synthesis of the Palladium Complexes. Neutral Species. The best method for the introduction of the new functionalized NHC ligands onto the palladium center is by trapping of the in situ generated L with a suitable metal precursor. The generation of carbenes by deprotonation of the imidazolium precursors with $KN(SiMe_3)_2$ in THF is complete within a few minutes at −78 °C. Reaction of L with Pd(tmed)$(CH_3)_2$ or Pd(1,5-COD)Br_2 gave good yields of complexes **3** and **4**. The isolation and characterization of the free **L^a** has already been communicated,[5] and details on its reactivity together with other N-functionalized NHCs will be reported in a forthcoming paper. The air-stable, colorless **3a**,**b** are soluble in THF and CH_2Cl_2, although the two solutions in the latter develop a dark coloration on standing at room temperature for 2−3 h. Complexes **4a**,**b** are yellow and soluble in THF and CH_2Cl_2 but insoluble in $CHCl_3$. They were characterized by spectroscopic and analytical methods.

The observed ^{1}H NMR spectra of the new complexes are consistent with nonsymmetric structures. The doublets at δ −0.4 to −0.6 in the spectra of **3** are attributable to inequivalent Pd−CH_3 groups. They are almost isochronous with the methyls of Pd(tmed)$(CH_3)_2$[8] but more shielded relative to the methyls of *cis*-Pd$(P)_2(CH_3)_2$ (P = tertiary phosphine)[9] and the recently reported *cis*-Pd$(CH_3)_2$[(carbene-$CH_2)_2$].[10] The ethylene bridge protons appear as two sets of multiplets. In **3a** the *o*-isopropyl methyls are diastereotopic and appear as two doublets. Characteristic signals for the carbene carbons are

(7) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511.

(8) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

(9) Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.

(10) Douthwaite, R. E.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T. *J. Chem. Soc., Dalton Trans.* **2002**, 1386.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

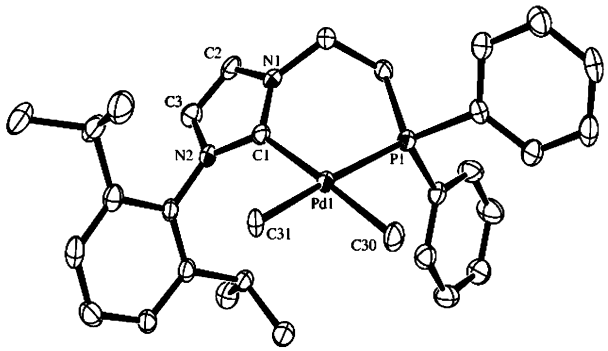


Figure 1. ORTEP representation of the structure of **3a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−N(1) = 1.357(6), C(1)−N(2) = 1.389(6), C(1)−Pd(1) = 2.088(5), P(1)−Pd(1) = 2.2994(13), C(30)−Pd(1) = 2.098(5), C(31)−Pd(1) = 2.111(5); N(1)−C(1)−Pd(1) = 124.4(4), N(2)−C(1)−Pd(1) = 131.6(4), C(1)−Pd(1)−P(1) = 91.06(14), C(30)−Pd(1)−P(1) = 89.23(15), C(31)−Pd(1)−P(1) = 172.31(14), C(1)−Pd(1)−C(31) = 95.84(18), C(1)−Pd(1)−C(30) = 177.0(2), C(30)−Pd(1)−C(31) = 84.05(19).

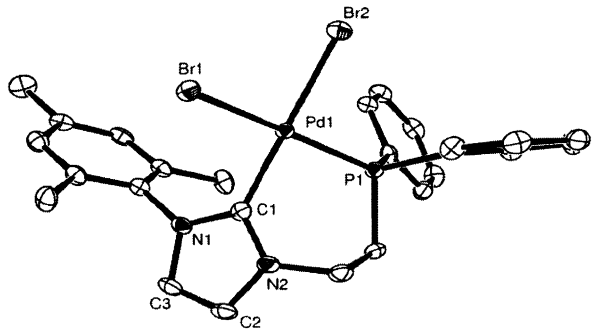


Figure 2. ORTEP representation of the structure of **4b** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−Pd(1) = 1.996(3), P(1)−Pd(1) = 2.2461(7), Pd(1)−Br(1) = 2.4989(3), Pd(1)−Br(2) = 2.4708(3), C(1)−N(1) = 1.349(3), C(1)−N(2) = 1.349(3); N(1)−C(1)−Pd(1) = 129.9(9), N(2)−C(1)−Pd(1) = 124.8(2), C(1)−Pd(1)−Br(2) = 176.63(7), C(1)−Pd(1)−P(1) = 89.24(8), C(1)−Pd(1)−Br(1) = 90.37(7), P(1)−Pd(1)−Br(1) = 168.96(2), P(1)−Pd(1)−Br(2) = 89.32(2), Br(2)−Pd(1)−Br(1) = 91.622(11).

observed as singlets in the range δ 185−187 for **3** and δ 160−165 for **4**.

X-ray-quality crystals of **3a** were obtained by layering a THF solution with ether. The structure of **3a** as determined by single-crystal X-ray diffraction is shown in Figure 1. The geometry around the palladium is square planar, and the ligand acts as a chelate occupying two cis positions. The two Pd−CH_3 bond lengths, 2.098(5) and 2.111(5) Å, are equal within the esds. The Pd−C(carbene) bond length at 2.088(5) Å is comparable to that recently reported, where the NHC is trans to an alkyl group.[10] The six-membered chelate ring is puckered, and the ligand bite angle is 91.06(14)°.

It is interesting to note that, due to the fact that the NHC ligands are better σ-donors than trialkylphosphines, they should be exerting a higher trans influence, which is not evidenced by the structural data of **3a**. However, the reactivity reported below shows that the two cis methyls are kinetically different.

X-ray-quality crystals of **4b** have been obtained by slow diffusion of ether in CH_2Cl_2 solution of the complex. The structure of the molecule, as determined by single-crystal X-ray diffraction, is shown in Figure 2. The geometry around the metal is square planar, with the ligand occupying two cis sites. The Pd−Br bond trans to the P atom is longer than that trans to the NHC by ca. 0.03 Å. This observation is in contrast to that expected on the basis of the relative trans influence of the phosphine and NHC ligands and is not understood at present. The Pd−carbene bond length is the same as that observed in **3a** within the observed esds. Finally, the Pd−P bond length in **3a** is longer in **4b**, as expected.

The existence of two types of Pd−C bonds (i.e. Pd−CH_3 and Pd−carbene) in **3a**, arranged in a way that one Pd−CH_3 bond is flanked by one Pd−CH_3 bond and one Pd−carbene bond, provides an opportunity to test the preferred decomposition pathway of the complexes by reductive elimination of either ethane or methylimidazolium. Complexes **3** are stable at room temperature in the solid state or in solution. Heating a d_8-THF solution of **3a** to 60 °C results in the formation of palladium colloids and a colorless solid. The NMR spectrum shows only the existence of **3a** in solution, while formation of ethane or methane was not observed. Removal of the volatiles, extraction in dichloromethane, and filtration through Celite resulted in a beige-yellow solution. The ES+ mass spectrum of this solution in acetonitrile showed the presence of 2-methyl-[3-(2,6-diisopropylphenyl)-1-(β-((diphenylphosphino)oxy)ethyl)]-imidazolium as well as the cationic $[(L^a)PdMe]^+$ and $[(L^a)PdMe{+}MeCN]^+$ in a 1:1 ratio.

Attempts were also made to explore the reactivity of **3a** with CH_3I. It is established that Pd(L−L)$(CH_3)_2$ (L−L = tmed, bipy, phen) react with CH_3I to form Pd(IV) complexes. Some of them have been characterized structurally.[8,11] The Pd(IV) methyls can reductively eliminate ethane and form new Pd(II) complexes. Reaction of **3a** with excess CH_3I in CH_2Cl_2 at room temperature gave after crystallization from dichloromethane/ether the product **5a**. Its identity was unequivocally established by single-crystal X-ray diffraction and is shown in Figure 3. The molecule comprises a square-planar Pd center coordinated by one imidazolium-functionalized phosphine, two iodides, and one chloride. The bond lengths and angles are not unusual. We believe that the source of chloride is chlorinated solvent. A plausible mechanism for the formation of **5a** is given in Scheme 3. It involves successive Pd(II)−Pd(IV) oxidative addition of CH_3I and reductive elimination of CH_3CH_3 leading to L^aPdI_2. The last oxidative addition is followed by reductive elimination of methylimidazolium cation, leading to the observed species. Reductive elimination of methylimidazolium after the first oxidative addition step is also plausible, leading to iodo dimethyl species, which can undergo further oxidative addition steps to the observed product. An alternative pathway involving Pd(II)−Pd(0) cycles is less likely, on the basis of the high thermal stability of **3a** at room temperature. Attempts to monitor the reaction by VT NMR spectroscopy (^1H and $^{31}P\{^1H\}$) showed that the formation of methylimidazolium (singlet at 2.4 ppm) occurs at room tempera-

(11) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

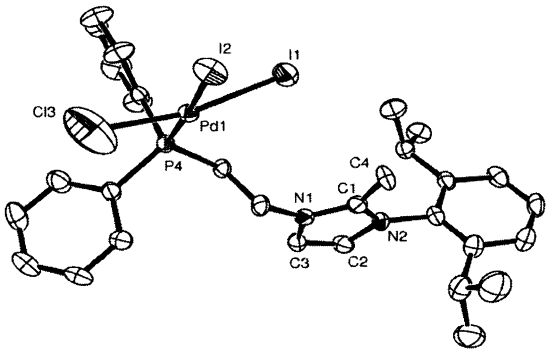
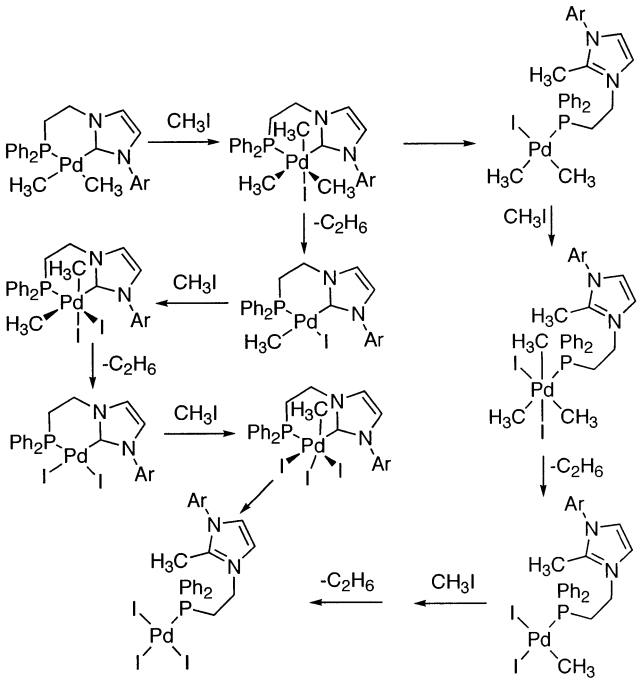


Figure 3. ORTEP representation of the structure of the cation in **5a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pd(1)−I(1) = 2.6613(7), Pd(1)−P(4) = 2.2483(18), Pd(1)−I(2) = 2.6674-(7), C(1)−C(4) = 1.470(10), C(1)−C(4) = 1.470(10), Pd(1)−I(3) = 2.360(5), C(1)−N(1) = 1.353(9), C(2)−C(3) = 1.335-(10), C(1)−N(2) = 1.335(9); I(3)−Pd(1)−I(1) = 168.10(14), I(1)−Pd(1)−I(2) = 92.25(2), I(3)−Pd(1)−I(2) = 86.37(11), P(4)−Pd(1)−I(1) = 90.98(5), P(4)−Pd(1)−I(3) = 90.07(12).

Scheme 3. Proposed Mechanism for the Formation of 5a



ture overnight and is accompanied by disappearance of the two Pd − Me doublets and the formation of ethane. However, a complex reaction mixture prevented the full identification of all products from the reaction.

Cationic Species. Square-planar cationic complexes of palladium and nickel stabilized by bidentate chelating ligands have received much attention, due to their involvement in catalytic C−C bond-forming reactions.[10,12] The most studied ligands include diphosphines and diimines, although in recently published reports cationic complexes with chelating dicarbenes[10] have been observed spectroscopically and in some cases structurally characterized.[13] Furthermore, mixed donor nonsymmetric chelating neutral or anionic ligands with N−O, P−P′, P−N, and P−O donor atoms have also been studied.[14] We thought that the mixed donor chelates $\mathbf{L^a}$ and $\mathbf{L^b}$ synthesized in this paper could give rise to the first cations incorporating chelates with nonsymmetric NHC and "classical" donors and provide useful insight into the mechanism of their formation and possible catalytic activity.

Recent reports[2a] provide experimental and theoretical evidence that cationic *cis*-$[L_2Pd(NHC)(CH_3)]^+$ complexes undergo facile concerted reductive elimination, resulting in the formation of alkylimidazolium salts. However, chelating ligands (i.e. L_2 = dppp) suppress this transformation.[2a] The results presented below amplify the fact that Pd(II) cationic complexes with NHC donors as part of a chelate ring are resistant to reductive elimination of alkylimidazolium salts and show that cation formation occurs with unexpected regiospecificity.

The interaction of **3a** with 1 equiv of $(CF_3)_2CHOH$ in CH_2Cl_2 or CH_2Cl_2/ether at −78 °C and warming to −20 °C results in the formation of Pd black and unidentified decomposition products. However, addition to the above reaction mixture of 1 equiv of pyridine at −30 °C, warming to room temperature, and workup gave a white, air-stable solid. The ^{1}H NMR spectrum of this solid shows the presence of one methyl attached to the Pd (doublet at δ −0.3), in addition to pyridine and resonances assignable to the $\mathbf{L^a}$ and the anion $[(CF_3)_2CHO^-]$. The appearance of one single Pd−CH_3 peak and one signal in the ^{31}P NMR spectrum implies the presence of one isomer in solution. An identical spectrum was obtained by replacing $(CF_3)_2CHOH$ with $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_3)]_4\}$, in which case **6a** was isolated and crystallized by slow evaporation of the ether solution. Its structure in the solid state was determined by a single-crystal X-ray diffraction study. A diagram of the molecule is shown in Figure 4.

The geometry around the Pd center in the cation is square planar; its coordination sphere comprises the ligand $\mathbf{L^a}$, one methyl group, and one pyridine ligand. The methyl group is trans to the NHC functionality. The Pd−carbene and Pd−CH_3 bond lengths and ligand bite angle compare with the corresponding values observed in **3a**.

Monitoring the reaction of **3a** with $(CF_3)_2CHOH$ by ^{1}H NMR spectroscopy provides evidence that the only one isomer is formed under kinetic control and, and this is the isomer characterized crystallographically. The reason for the selective abstraction of the palladium methyl group trans to the phosphorus, in the absence of any apparent trans influence as established by the crystal structure of **3a**, could lie in the different steric demands of the two electronically dissimilar parts of $\mathbf{L^a}$. The steric bulk imposed by the phosphine end could hinder the coordination of a donor ligand, thus making the attack to the methyl trans to it more kinetically favored.

Complex **6a** is stable in the solid state and in solution. On prolonged standing at room temperature, it develops a yellow coloration, even though the compound is unchanged spectroscopically. Its stability could possibly

(12) For a recent review on late-transition-metal cationic complexes as alkene polymerization catalysts see: Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(13) Gardiner, M. A.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239.

(14) For recent work in this area see: Liu, W.; Malinowski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836 and references therein.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

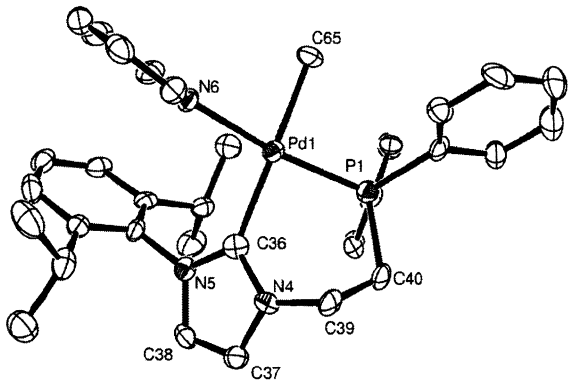


Figure 4. ORTEP representation of the structure of the cation in **6a** showing 50% probability ellipsoids. The asymmetric unit consists of two cations and two anions and two molecules of ether. The BAr^f_4 anion, the ether molecules, and the H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(36)−Pd(1) = 2.092(6), C(36)−N(4) = 1.356(6), C(65)−Pd(1) = 2.099(6), N(6)−Pd(1) = 2.128(5), C(36)−N(5) = 1.375(6), P(1)−Pd(1) = 2.2221(18); N(5)−C(36)−Pd(1) = 129.0(4), N(6)−Pd(1)−P(1) = 171.75(13), C(36)−Pd(1)−P(1) = 89.86(17), C(36)−Pd(1)−C(65) = 173.9(2), C(65)−Pd(1)−P(1) = 89.12(17), N(4)−C(36)−Pd(1) = 125.7(4), C(65)−Pd(1)−N(6) = 84.13(17).

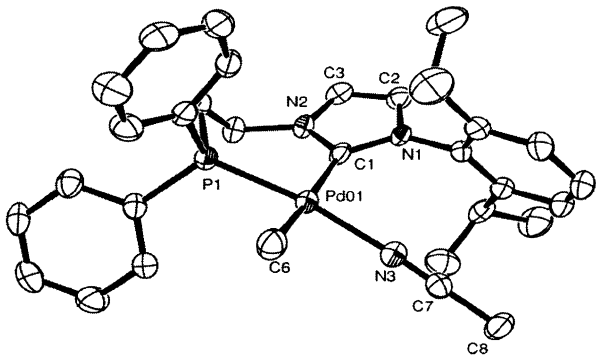


Figure 5. ORTEP representation of the structure of the cation in **7a** showing 50% probability ellipsoids. The BAr^f_4 anion and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−Pd(01) = 2.090(4), C(6)−Pd(01) = 2.070(4), N(3)−Pd(01) = 2.091(3), P(1)−Pd(01) = 2.2043(9), C(1)−N(1) = 1.369(4), C(1)−N(2) = 1.358(4), C(7)−N(3) = 1.139(5), C(7)−C(8) = 1.464(5); C(1)−Pd(01)−C(6) = 85.68(14), C(1)−Pd(01)−P(1) = 93.56(9), P(1)−Pd(01)−N(3) = 169.48(9), N(3)−C(7)−C(8) = 179.4(4), P(1)−Pd(01)−C(6) = 84.32(11), N(2)−C(1)−N(1) = 103.1(3).

arise from the trans arrangement of the methyl and the NHC groups, rendering methyl migration to the NHC carbon or reductive elimination of methylimidazolium salts unfavorable. Thermal decomposition of **6a** occurs at 90 °C to colloidal Pd and intractable mixtures of organic products (by ^{1}H NMR).

Complexes **7a**, **8a**, and **9a** were prepared in a way analogous to **6a** using acetonitrile, benzonitrile, and trimethylphosphine instead of pyridine, respectively. All three complexes are colorless, air-stable solids. The ^{1}H NMR spectra show that in these cations as well, the methyl groups are located trans to the NHC. There is no evidence of the presence of any other isomers in solution. This was further established by a single-crystal X-ray diffraction study of **7a**. A diagram of the molecule is shown in Figure 5. Here, too, the Pd center in the cation is square planar with chelating $\mathbf{L^a}$, one methyl group trans to the NHC end, and one acetonitrile ligand trans to the phosphine. The Pd−carbene and Pd−CH_3 bond lengths and ligand bite angle compare with those observed in **6a**. Complex **7a** is stable in d_3-acetonitrile up to 65 °C; the only process that can be detected involves exchange of coordinated and free acetonitrile.

Dications are also accessible by the reaction of **4** with $AgBF_4$ in MeCN. Due to their air and light sensitivity and reduced thermal stability complex **9a** was characterized by multinuclear NMR spectroscopy, which supports the structure proposed in Scheme 1. Attempts to crystallize this complex were unsuccessful.

Catalytic Studies. Heck Coupling Reactions. It has been claimed that the imidazolium salts $\mathbf{L^bH}$ in the presence of $Pd(dba)_2$ and $KOBu^t$ or Cs_2CO_3 are highly active catalysts for the Heck coupling of arylbromides with acrylates.[7] Our studies using **3a**,**b** and **4b** as catalysts are given in Table 1. All data given in Table 1 are the average of at least two runs. From the information given, it is clear that **3a**,**b** show good activity, albeit not as high as previously claimed for catalysts formed in situ. In addition, after the completion of the reaction the formation of Pd colloids was evident in the reaction mixture. Attempts to reproduce the activity reported in the literature under identical conditions met also with limited success in our hands.

Copolymerization of Ethylene and CO. A dichloromethane solution of complex **3a** when pressurized at 5 bar with a mixture of CO and ethylene (1:1) at room temperature, in the presence of Brookhart's acid, yielded the desired copolymer over a period of 2 h.

Conclusions

The high-yield synthesis of chelate (diphenylphosphino)ethyl carbene complexes of palladium(II) established

Table 1. Representative Catalytic Data for the Heck Coupling of Aryl Halides with Methyl Acrylate in the Presence of the Palladium Complexes Reported in This Paper

aryl halide	base	solvent	time (h)	temp (°C)	catalyst loading (M)	yield (%)	TON
p-C(O)MePhBr	NEt_3	NMP	6	120	2×10^{-4} (**3a**)	92	184
PhBr	Cs_2CO_3	DMAC	6	120	2.5×10^{-4} (**3a**)	60	122
p-C(O)MePhBr	NEt_3	NMP	6	120	2.5×10^{-4} (**3b**)	66	134
p-C(O)MePhBr	Cs_2CO_3	NMP	6	120	2.5×10^{-4} (**3b**)	54	110
PhBr[a]	NEt_3	NMP	12	140	5×10^{-5} (**3b**)	19	1920
PhBr	NEt_3	NMP	6	120	2.5×10^{-4} (**3b**)	22	44
PhBr[c]	NEt_3	NMP	12	140	5×10^{-5} (**3b**)	22	2242
PhBr[b]	NEt_3	NMP	6	120	2.5×10^{-4} (**3b**)	14	28

[a] Alkene is *n*-butyl acrylate; 2 mL of [2.2.1]-1,5-norbonadiene was added. [b] In the presence of 1.1 equiv of $N_2H_4 \cdot H_2O$. [c] Alkene is *n*-butyl acrylate.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

a new family of well-defined, electronically nonsymmetric, square-planar complexes. The thermally stable dimethyl analogues served as useful starting materials for the synthesis of cationic species by their reaction with Lewis acids containing noncoordinating anions. In all studied cases only one cationic isomer in which the methyl is trans to the carbene is spectroscopically observed and isolated. The reasons for this selectivity are not well understood.

Furthermore, the neutral dimethyl complexes showed moderate catalytic activity in the Heck coupling of aryl halides with acrylates. This activity is lower than that previously reported for systems generated in situ from $Pd(dba)_2$ and the (diphenylphosphino)ethyl imidazolium salts in the presence of Cs_2CO_3. The synthesis of well-defined chelate (diphenylphosphino)ethyl carbene Pd(0) complexes, which is under way, may provide an explanation for the reduced catalytic activity observed with the Pd(II) complexes.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

Experimental Section

General Methods. Elemental analyses were carried out by the University College, London, microanalytical laboratory. All manipulations were performed under nitrogen in a Braun glovebox or using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior to use. The light petroleum used throughout had a boiling point of 40−60 °C.

The starting materials 1-(2,6-diisopropylphenyl)imidazole, 1-(2,4,6-trimethylphenyl)imidazole,[15] Ph_2POEt,[16] $Ph_2P(O)(CH_2)_2Br$,[16] $Pd(tmed)Me_2$,[8] and $Pd(COD)Br_2$[17] were prepared according to literature procedures. $Ph_2P(O)(CH_2)_3Br$ was prepared from Ph_2POEt and 1,3-$C_3H_6Br_2$ by a method analogous to that for $Ph_2P(O)(CH_2)_2Br$ and was recrystallized from benzene/petroleum. NMR data were recorded on Bruker AMX-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^1H), respectively. The spectra were referenced internally using the signal from the residual protio solvent (^1H) or the signals of the solvent (^{13}C). $^{31}P\{^1H\}$ spectra were recorded on a Bruker AC-300 spectrometer at 121.44 MHz and referenced externally relative to 85% H_3PO_4 in D_2O. ^{19}F spectra were recorded on a Bruker AC-300 instrument at 282.36 MHz and were referenced externally relative to C_6F_6. The phosphine oxide−imidazolium salts are hygroscopic, while the ligand precursors **2a**−**c** are mixtures of the bromide and chloride salts.

3-(2,6-Diisopropylphenyl)-1-(*β*-((diphenylphosphino)-oxy)ethyl)imidazolium Bromide (1a). A 9.7 g (31.5 mmol) portion of $Ph_2P(O)(CH_2)_2Br$ and 7.2 g (31.6 mmol) of (2,6-diisopropylphenyl)imidazole were placed in a glass ampule, which was then sealed under vacuum and immersed in an oil bath heated at 150−160 °C for 1 week. After the ampule was opened, the brown solid was dissolved in dichloromethane and the volatiles were removed under reduced pressure to yield a beige solid, which was washed with ether (2 × 50 mL). It was then redissolved in the minimum amount of dichloromethane and reprecipitated by addition of ether, giving the product as a white powder. Yield: 15.2 g (90%). NMR ($CDCl_3$): ^1H, δ 0.9 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.1 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.1 (septet, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 3.4 (2H, m, $Ph_2P(O)CH_2CH_2$−imidazole), 5.1 (m, 2H, $Ph_2P(O)CH_2CH_2$−imidazole), 6.9 (s, 1H, imidazole backbone), 7.1−7.2 (m, 3H, aromatics and the other imidazole backbone), 7.4−7.7 (m, 8.5H, aromatics), 7.8−8.0 (m, 4.5H, aromatics), 8.7 (s, 1H, aromatic), 10.3 (s, 1H, NC(*H*)N proton); $^{13}C\{^1H\}$, δ 24.41 (s, $CH(CH_3)_2$), 24.47 (s, $CH(CH_3)_2$), 28.7 (s, $Ph_2P(O)CH_2CH_2$−imidazole), 44.6 (s, $Ph_2P(O)CH_2CH_2$−imidazole), 123.9 (s, imidazole backbone), 124.8 (s, aromatic), 125 (s, imidazole backbone), 129.2 (d, J_{PC} = 12.08 Hz, aromatic), 130.2 (s, aromatic), 130.9 (d, J_{PC} = 9.81 Hz), 132 (s, aromatic), 132.1 (s, aromatic), 132.5 (s, aromatic), 138.4 (s, ipso at imidazole moiety), 145.4 (s, N*C*N); $^{31}P\{^1H\}$, δ 33.4 ppm (s, $Ph_2P(O)(CH_2)_2$−imidazole). Anal. Found: C, 61.93; H, 6.14; N, 5.12. Calcd for $C_{29}H_{34}BrN_2OP\cdot H_2O$: C, 62.70; H, 6.63; N, 5.04.

3-Mesityl-1-(*β*-((diphenylphosphino)oxy)ethyl)imidazolium Bromide (1b). This was prepared by a method analogous to **1a** from 10 g (32.5 mmol) of $Ph_2P(O)(CH_2)_2Br$ and 6.1 g (32.6 mmol) of mesitylimidazole. Yield: 13.4 g, 83%. NMR ($CDCl_3$): ^1H, δ 1.8 (s, 6H, *o*-methyls of mesityl), 2.7 (s, 3H, *p*-methyl of mesityl), 3.4 (m, 2H, $Ph_2P(O)CH_2CH_2$−imidazole), 4.8 (m, 2H, $Ph_2P(O)CH_2CH_2$−imidazole), 6.6 (s, 1H, imidazole backbone), 6.9 (s, 1H, imidazole backbone), 7.2−7.5 (m, 5H, aromatics), 7.7−7.9 (m, 4H, aromatics), 8.4 (s, 1H, aromatic), 10.1 (s, 1H, NCN proton); $^{13}C\{^1H\}$, δ 17.8 (s, *o*-methyls of mesityl), 21.2 (s, *p*-methyl of mesityl), 44.5 (s, $Ph_2P(O)CH_2CH_2$−imidazole), 122.8 (s, imidazole backbone), 124.8 (s, imidazole backbone), 129.1 (d, J_{PC} = 12.83 Hz, aromatic), 129.8 (s, aromatic), 131 (d, J_{PC} = 18.12 Hz, aromatic), 131.4 (s, aromatic), 132.2 (s, aromatic), 134.7 (s, aromatic), 138.3 (s, ipso to the imidazole moiety), 141.3 (s, N*C*N); $^{31}P\{^1H\}$, δ 31.0 (s, $Ph_2P(O)(CH_2)_2$-imidazole). Anal. Found: C, 62.90; H, 5.70; N, 5.64. Calcd for $C_{26}H_{28}BrN_2OP$: C, 63.04; H, 5.70; N, 5.64.

3-Mesityl-1-(*γ*-((diphenylphosphino)oxy)-*n*-propyl)imidazolium Bromide (1c). This was prepared by following a method analogous to that for **1a** from 4.34 g (13.5 mmol) of $Ph_2P(O)(CH_2)_3Br$ and 2.80 g (15 mmol) of mesitylimidazole. Yield: 6.09 g (89%). NMR ($CDCl_3$), ^1H, δ 1.9 (s, 6H, *o*-methyls of mesityl), 2,4 (s, 3H, *p*-methyl of mesityl), 2.3−2.5 (m, 2H, $Ph_2P(O)CH_2(CH_2)_2$−imidazole), 2.6−2.8 (m, 2H, $Ph_2P(O)CH_2CH_2CH_2$−imidazole), 5.0 (t, 2H, $Ph_2P(O)(CH_2)_2CH_2$−imidazole), 6.9 (s, 2H, aromatics of mesityl), 7.1 (s, 1H, imidazole backbone), 7.3 (s, 1H, imidazole backbone), 7.5 (br s, 5H, aromatics of phosphine oxide), 7.7−7.9 (m, 4H, aromatic), 8.2 (s, 1H, aromatic), 10.4 (s, 1H, NC(H)N proton); ^{13}C, δ 17.9 (s, *o*-methyls of mesityl), 21 (s, *p*-methyl of mesityl), 24.6 (d, $^1J_{PC}$ = 11.57 Hz, $Ph_2P(O)CH_2CH_2CH_2$−imidazole), 27.0 (s, $Ph_2PCH_2CH_2CH_2$−imidazole), 50.8 (s, $Ph_2PCH_2CH_2CH_2$−imidazole), 122.5 (s, imidazole backbone), 123.9 (s, imidazole backbone), 127.5 (d, J_{PC} = 6.63 Hz, aromatic), 128.3 (s, aromatic), 129.1 (s, aromatic), 131.3 (d, J_{PC} = 17.34 Hz, aromatic), 131.6 (s, aromatic), 132.9 (s, aromatic), 133.6 (s, aromatic), 138.8 (s, ipso to the imidazole moiety), 142.3 (s, N*C*N); $^{31}P\{^1H\}$, δ 33.8 (s, $Ph_2P(O)(CH_2)_3$−imidazole).

3-(2,6-Diisopropylphenyl)-1-(*β*-(diphenylphosphino)ethyl)imidazolium Bromide (2a; L^{a}H). The phosphine oxide **1a** (4.5 g, 8.4 mmol) was placed in a three-neck 1 L flask (Schlenk adapter, double-jacket condenser, and a pressure-equalizing funnel) and was dissolved in 110 mL of chlorobenzene by heating to the reflux temperature under a nitrogen atmosphere. The temperature was then maintained at 120 °C (oil bath), and excess trichlorosilane was added in small portions (14 mL, 100.7 mmol, 12-fold excess). After completion of the addition, the reaction mixture was heated at 120 °C for 3 h and then cooled to room temperature. After addition of 100 mL of CH_2Cl_2 the excess of trichlorosilane was quenched by careful dropwise addition of 300 mL of degassed 10% NaOH (aqueous) at 0 °C. The organic phase was separated, and the aqueous phase was washed with CH_2Cl_2 (3 × 50 mL). After the combined organic extracts were dried over $MgSO_4$, the volatiles were removed under reduced pressure and the resulting white solid was washed with ether (2 × 150 mL) and dried under vacuum overnight. The imidazolium salt was further dried azeotropically with toluene and was stored in the glovebox. Yield: 3.3 g (75%). NMR ($CDCl_3$): ^1H, δ 1.1 (d,

(15) (a) Johnson, A. L.; Del, W. U.S. Patent 3,637,731, 1972; *Chem. Abstr.* **1972**, *76*, 113215. (b) Arduengo, A. G., III. U.S. Patent 6,177,-575, 2001; *Chem. Abstr.* **2001**, *134*, 115958.

(16) Struck, R. F.; Sheally, Y. F. *J. Org. Chem.* **1965**, *30*, 414.

(17) Drew, D.; Doyle, J. R. *Inorg Synth.* **1972**, *13*, 53.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

6H, CH(CH_3)$_2$), 1.2 (d, 6H, CH(CH_3)$_2$), 2.4 (sept, 2H, CH(CH$_3$)$_2$), 2.9 (m, 2H, PPh$_2$CH_2CH$_2$−imidazole), 4.9 (m, 2H, PPh$_2$-CH$_2$CH_2−imidazole), 6.9 (s, 1H, imidazole backbone), 7.1−7.8 (m, 13H, aromatics), 8.0 (s, 1H, aromatic), 10.4 (s, 1H, NCN proton); ^{13}C{^{1}H}, δ 24.5 (s, CH(*C*H$_3$)$_2$), 28.8 (s, *C*H(CH$_3$)$_2$), 30.0 (d, $^1J_{P-C}$ = 12.98 Hz, PPh$_2$*C*H$_2$CH$_2$−imidazole), 48.2 (d, $^2J_{P-C}$ = 18.12 Hz, PPh$_2$CH$_2$*C*H$_2$−imidazole), 123.8 (s, imidazole backbone), 124.0 (s, imidazole backbone), 124.8 (s, aromatic), 129.05 (d, J_{P-C} = 6.78 Hz, aromatic), 130.3 (s, aromatic), 130.8 (s, aromatic), 132 (s, aromatic), 132.9 (d, J_{P-C} = 19.55 Hz, aromatic), 136.2 (d, J_{P-C} = 11.32 Hz, aromatic), 138.6 (s, ipso to imidazole moiety, aromatic), 145.5 (s, N*C*N); ^{31}P{^{1}H}, δ −22.4 (s, Ph$_2$*P*(CH$_2$)$_3$−imidazole). Anal. Found: C, 69.07; H, 6.63; N, 5.08. Calcd for $C_{58}H_{68}BrClN_4P_2$ (1:1 bromide/chloride salt): C, 69.77; H, 6.86; N, 5.61.

3-Mesityl-1-(β-(diphenylphosphino)ethyl)imidazolium Bromide, L^{b}H (2b). This was prepared by a method analogous to **2a** from 5 g (10.1 mmol) of the phosphine oxide and 18 mL of trichlorosilane. Yield: 3.6 g, 75%. NMR (CDCl$_3$): ^{1}H, δ 2.1 ppm (s, 6H, *o*-methyls of mesityl), 2.4 ppm (s, 3H, *p*-methyl of mesityl), 2.9 (m, 2H, Ph$_2$PCH_2CH$_2$−imidazole), 4.9 (m, 2H, Ph$_2$PCH$_2$CH_2−imidazole), 6.7 (s, 1H, imidazole backbone), 6.9 (s, 1H, imidazole backbone), 7.0 (aromatics of mesityl), 7.5 (5H, br, aromatics), 7.6 (br, 4H, aromatic), 7.9 (s, 1H, aromatic) 10.6 (s, 1H, NCN proton); ^{13}C{^{1}H}, δ 17.8 (s, *o*-methyls of mesityl), 21.2 (s *p*-methyl of mesityl), 29.8 (d, $^1J_{PC}$ = 15.99 Hz, Ph$_2$P*C*H$_2$CH$_2$−N), 48.15 (d, $^2J_{PC}$ = 21.89 Hz, Ph$_2$PCH$_2$*C*H$_2$−imidazole), 123 (s, imidazole backbone), 123.5 (s, imidazole backbone), 129 (d, J_{PC} = 6.80 Hz, aromatic), 129.15 (d, J_{PC} = 8.31 Hz, aromatic), 129.9 (s, aromatic), 130.8 (s, aromatic), 132.9 (d, J_{PC} = 18.87 Hz, aromatic), 134.4 (s, aromatic), 136.3 (d, J_{PC} = 11.32 Hz, aromatic), 138.5 (s, ipso to the imidazole), 141.3 (s, NCN); ^{31}P{^{1}H}, δ −22.4 (s, Ph$_2$*P*(CH$_2$)$_2$−imidazole). Anal. Found: C, 63.57; H, 5.69; N, 5.31. Calcd for $C_{52}H_{56}BrClN_4P_2$·CH_2Cl_2 (1:1 bromide/chloride salt): C, 63.70; H, 5.85; N, 5.61.

3-Mesityl-1-(γ-(diphenylphosphino)-*n*-propyl)imidazolium Bromide (2c). This compound was prepared by following a method analogous to that for **2a** from 4.5 g (8.8 mmol) of the oxide. Yield: 3.30 g (75%). NMR (CDCl$_3$): ^{1}H, δ 2.0 (s, 6H, *o*-methyls of mesityl), 2.1−2.3 (m, 4H, Ph$_2$P(O)CH$_2$(CH$_2$)$_2$−imidazole and Ph$_2$P(O)CH$_2$CH$_2$CH$_2$−imidazole), 2.4 (s, 3H, *p*-methyl of mesityl), 5 (t, 2H, Ph$_2$P(O)(CH$_2$)$_2$CH$_2$−imidazole), 6.9 (s br, 2H, aromatics of mesityl), 7.1 (s br, 2H, imidazole backbone), 7.4−7.7 (m, 10H, aromatics of phosphine), 10.9 (s, 1H, NCN proton); ^{13}C{^{1}H}, δ 17.8 (s, *o*-methyls of mesityl), 21.2 (s, *p*-methyls of mesityl), 24.4 (d, $^1J_{PC}$ = 10.56 Hz, Ph$_2$P*C*H$_2$-CH$_2$CH$_2$−imidazole), 27.1 (d, $^2J_{PC}$ = 18.09 Hz, Ph$_2$PCH$_2$*C*H$_2$-CH$_2$−imidazole), 50.6 (d, $^3J_{PC}$ = 19.06 Hz, Ph$_2$PCH$_2$CH$_2$*C*H$_2$−imidazole), 122.3 (s, imidazole backbone), 123.3 (s, imidazole backbone), 128.8 (d, J_{PC} = 6.78 Hz, aromatic), 129.1 (s, aromatic), 130 (s, aromatic), 130.8 (s, aromatic), 132.9 (d, J_{PC} = 19.22 Hz, aromatic), 134.3 (s, aromatic), 137.6 (d, J_{PC} = 12.44 Hz, aromatic), 139.1 (s, ipso to the imidazole moiety), 141.5 (s, N*C*N); ^{31}P{^{1}H}, δ −16.6 (s, Ph$_2$*P*(CH$_2$)$_3$−imidazole) Anal. Found: C, 68.66; H, 6.28; N, 6.39. Calcd for $C_{54}H_{60}BrClN_4P_2$ (1:1 bromide/chloride salt): C, 68.82; H, 6.42; N, 5.95.

Preparation of the Palladium Complexes. General Method. To a mixture of solid imidazolium salt (1 equiv) and KN(Si(CH$_3$)$_3$)$_2$ (1.1 equiv) was added precooled (−78 °C) THF with vigorous stirring. The solution of the free carbene generated in this way was added after 10 min via cannula to a solution of palladium precursor in THF at −78 °C. After the mixture was stirred at −78 °C for 10 min, it was allowed to reach room temperature and stirred for 2 h. Evaporation of the volatiles under reduced pressure, extraction of the solid residue into cold (0 °C) dichloromethane, filtration of the cold solution through Celite, concentration of the filtrates to 1−3 mL, and addition of ether precipitated the product as a white to beige solid, which was collected by filtration and dried under vacuum.

[L^a]PdMe$_2$ (3a). This was prepared according to the general method using 0.11 g (0.44 mmol) of Pd(tmed)Me$_2$, 0.23 g (0.46 mmol) of **L^{a}H**, and 0.10 g of KN(SiMe$_3$)$_2$ (0.50 mmol). Yield: 0.18 g (70%). X-ray-quality crystals were grown by layering a THF solution with Et$_2$O. NMR (CD$_2$Cl$_2$): ^{1}H, δ −0.6 (d, $^3J_{PH}$ = 7.15 Hz, 3H, PdMe), −0.4 (d, $^3J_{PH}$ = 8.24 Hz, 3H, PdMe), 1.0 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.1 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$), 2.3 (m, 2H, (PPh$_2$CH_2CH$_2$-ylidene)PdMe$_2$), 2.7 (sept. $^3J_{HH}$ = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 4.3 and 4.4 (each br dt, 1H, (PPh$_2$CH$_2$CH_2-ylidene)PdMe$_2$), 6.8 (d, 1H, ylidene backbone), 7.0 (d, 1H, ylidene backbone), 7.1 and 7.2 (each s, 1H, aromatics), 7.3−7.4 (m, 7H, aromatics), 7.6−7.7 (m, 4H, aromatics); ^{13}C{^{1}H} (C$_5$D$_5$N), δ 0.05 (d, $^2J_{PC}$ = 9.96 Hz, Pd*C*H$_3$), 2.4 (d, $^2J_{PC}$ = 9.34 Hz, Pd*C*H$_3$), 24.4 (s, CH(*C*H$_3$)$_2$), 26 (s, CH(*C*H$_3$)$_2$), 29.7 (s, *C*H(CH$_3$)$_2$), 30.3 (d, (PPh$_2$*C*H$_2$CH$_2$-ylidene)-PdMe$_2$, $^1J_{C-P}$ = 14.61 Hz), 49.35 (d, (PPh$_2$CH$_2$*C*H$_2$-ylidene)-PdMe$_2$, $^2J_{C-P}$ = 10.62 Hz), 121 (s, imidazole backbone), 125.2 (s, aromatic), 125.4 (s, aromatic), 129.69 (d, J_{PC} = 9.06 Hz, aromatic), 130.34 (d, J_{PC} = 7.04 Hz, aromatic), 130.8 (s, aromatic), 134.74 (s, aromatic), 134.83 (d, J_{PC} = 5.03 Hz, aromatic), 147.15 (ipso carbon of aryl), 187.77 (s, NCN). ^{31}P{^{1}H} (CD$_2$Cl$_2$), δ 12.45 (s, (*P*Ph$_2$CH$_2$CH$_2$-ylidene)PdMe$_2$). MS (ES+): *m*/*z* 561 [(P−C)PdMe]$^+$, 602 [M + MeCN]$^+$. Mp: 154−156 °C dec. Anal. Found: C, 64.50; H, 6.77; N, 4.81. Calcd for $C_{31}H_{39}N_2PPd$: C, 64.52; H, 6.81; N, 4.85.

[L^b]PdMe$_2$ (3b). This was prepared according to the general synthetic method from 0.10 g (0.44 mmol) of Pd(tmed)Me$_2$, 0.24 g (0.45 mmol) of **L^{b}H**, and 0.09 g (0.46 mmol) of KN(SiMe$_3$)$_2$. Yield: 0.16 g (75%). NMR (CD$_2$Cl$_2$): ^{1}H, δ −0.6 (d, $^3J_{P-H}$ = 7.68 Hz, 3H, PdCH_3), −0.5 (d, $^3J_{P-H}$ = 6.50 Hz, 3H, PdCH_3), 2.0 (s, 6H, 2,6-methyls of mesityl), 2.1 (s br, 2H, (PPh$_2$CH_2-CH$_2$-ylidene)PdMe$_2$), 2.3 (s, 3H, 4-methyl of mesityl), 4.4 and 4.5 (two sets of dt 1H each, (PPh$_2$CH$_2$CH_2-ylidene)PdMe$_2$), 6.7 (d, $^3J_{PH}$ = 7.68 Hz, 1H, ylidene backbone), 6.9 (s. br., 2H, aromatics of mesityl), 7.0 (d, $^3J_{PH}$ = 7.68 Hz, 1H, ylidene backbone), 7.4 (m, 5H, aromatics), 7.5−7.7 (m, 5H, aromatics); ^{13}C{^{1}H} (C$_5$D$_5$N), δ 0.04 (d, $^2J_{PC}$ = 9.87 Hz, Pd*C*H$_3$), 1.9 (d, $^2J_{PC}$ = 9.26 Hz, Pd*C*H$_3$), 18.1 (s, *o*-methyls of mesityl), 22.2 (s, *p*-methyl of mesityl), 31.1 (d, $^1J_{PC}$ = 14.22 Hz, (PPh$_2$*C*H$_2$CH$_2$-ylidene)PdMe$_2$), 49.2 (d, $^2J_{PC}$ = 10.31 Hz, (PPh$_2$CH$_2$*C*H$_2$-ylidene)PdMe$_2$), 120 (s, imidazole backbone), 120.5 (s, imidazole backbone), 122.5 (s, aromatic), 123.8 (d, J_{PC} = 8.05 Hz, aromatic), 124.2 (s, aromatic), 124.7 (s, aromatic), 126.20 (d, J_{PC} = 9.06 Hz, aromatic), 126.38 (d, J_{PC} = 5.03 Hz, aromatic), 128.6 (s, aromatic), 148.5 (s, ipso carbon of the aryl), 185.8 (s, NCN); ^{31}P{^{1}H}, δ 12.24 (s, (*P*Ph$_2$CH$_2$CH$_2$-ylidene)PdMe$_2$). MS (ES+): *m*/*z* 519 [L^{b}PdMe]$^+$ (M), 560 [M + MeCN]$^+$. Mp: 133−134 dec. Anal. Found: C, 57.33; H, 5.73; N, 4.49. Calcd for $C_{28}H_{34}N_2PPd$·CH_2Cl_2: C, 56.10; H, 5.84; N, 4.51.

[L^a]PdBr$_2$ (4a). This compound was prepared by following the general method from 0.10 g of Pd(COD)Br$_2$ (0.27 mmol), 0.14 g (0.28 mmol) of **L^{a}H**, and 0.06 g (0.30 mmol) of KN(SiMe$_3$)$_2$. Yield: 0.14 g (70%). NMR (CD$_2$Cl$_2$): ^{1}H, δ −0.4 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.3 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.9 (m, 2H, (PPh$_2$CH_2CH$_2$-ylidene)PdBr$_2$), 2.1 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 4.3 and 4.4 (each dt, 1H, (PPh$_2$CH$_2$CH_2-ylidene)PdBr$_2$), 6.9 (s, 1H, ylidene backbone), 7.4−7.7 (m, 11H, aromatics), 7.7−7.8 (m, 3H, aromatics); ^{13}C-{^{1}H}, δ 20.0 (s, CH(*C*H$_3$)$_2$), 23.5 CH(*C*H$_3$)$_2$), 26.2 (s, *C*H(CH$_3$)$_2$), 29.8 (s, (PPh$_2$*C*H$_2$CH$_2$-ylidene)PdBr$_2$), 48.0 (s, (PPh$_2$CH$_2$*C*H$_2$-ylidene)PdBr$_2$), 122.2 (s, ylidene backbone), 124.6 (s, ylidene backbone), 127.1 (s, aromatic), 129.35 (d, J_{PC} = 10.69 Hz, aromatic), 130.3 (s, aromatic), 131.5 (s, aromatic), 132.13 (d, J_{PC} = 2.92 Hz, aromatic), 134.38 (d, J_{PC} = 9.72 Hz, aromatic), 136.8 (s, aromatic), 146.1 (s, ipso carbon of the aryl group), 160.8 (NCN); ^{31}P{^{1}H}, δ 21 (s, (*P*Ph$_2$CH$_2$CH$_2$-ylidene)PdBr$_2$) Anal. Found: C, 50.88; H, 4.94; N, 3.55. Calcd for $C_{29}H_{34}Br_2N_2$-PPd·Et$_2$O: C, 50.69; H, 5.67; N, 3.58.

[L^b]PdBr$_2$ (4b). This was prepared by following the general method from 0.10 g (0.27 mmol) of Pd(COD)Br$_2$, 0.13 g (0.28 mmol) of **L^{b}H** and 0.06 g (0.30 mmol) of KN(SiMe$_3$)$_2$. Yield:

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s

0.12 g (69%). X-ray-quality crystals were grown in an NMR tube by slow diffusion of Et_2O into a CH_2Cl_2 solution. NMR (CD_2Cl_2): ^1H, δ 0.9 (s, 6H, *o*-methyls), 1.3 (s, 3H, *p*-methyl), 1.8 (m, 2H, ($PPh_2CH_2CH_2$-ylidene)$PdBr_2$), 4.3 and 4.4 (each dt, 1H, ($PPh_2CH_2CH_2$-ylidene)$PdBr_2$), 6.8 (d, 1H, imidazolylidene backbone), 7.1 (s br, 1H, imidazolylidine backbone), 7.2 (s, 2H, mesityl aromatic protons), 7.2−7.7 (m, 10H, aromatics); $^{13}C\{^1H\}$, δ 17.9 (s, *o*-methyls of mesityl), 21.8 (s, *p*-methyl of mesityl), 30.1 (s, ($PPh_2CH_2CH_2$-ylidene)$PdBr_2$), 48.0 (s, ($PPh_2CH_2CH_2$-ylidene)$PdBr_2$), 121.0 (s, ylidene backbone), 124.4 (s, ylidene backbone), 127 (s, aromatic), 128.85 (d, J_{PC} = 9.06 Hz, aromatic), 130.3 (s, aromatic), 132.3 (s, aromatic), 133.5 (s, aromatic), 134.15 (d, J_{PC} = 3.02 Hz, aromatic), 135.03 (d, J_{PC} = 12.08 Hz, aromatic), 138.2 (s, aromatic), 147.1 (s, ipso carbon of the aryl group attached to the ylidene backbone), 162.4 (NCN); $^{31}P\{^1H\}$, δ 19 (s, ($PPh_2CH_2CH_2$-ylidene)$PdBr_2$). Anal. Found: C, 44.24; H, 3.93; N, 3.85. Calcd for $C_{26}H_{28}Br_2N_2PPd\cdot CH_2Cl_2$: C, 43.20; H, 4.03; N, 3.73.

Reaction of 3a with CH_3I. Formation of 5a. To a precooled (0 °C) solution of 0.08 g (0.14 mmol) of compound **3a** dissolved in 15 mL of dichloromethane was added via a microliter syringe a 3-fold excess of MeI (26 μL, 0.42 mmol). The solution was brought to room temperature and was stirred overnight. A color change occurred within the first 30 min of stirring at room temperature, from pale yellow to deep orange. The solution was filtered through Celite, and the volatiles were removed under vacuum. Repeated recrystallizations from dichloromethane/ether at −35 °C gave orange crystals.

Preparation of the Salts 6a, 7a, 8a, and 9a. General Method. To a solution of **3a** in dichloromethane (20 mL) at −78 °C was added a solution of $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (1 equiv in 20 mL of dichloromethane). The mixture was warmed to −40 to −50 °C when 1 equiv of pyridine, nitrile, or trimethylphosphine was added. After the mixture was warmed to room temperature, the volatiles were removed under reduced pressure and the residue was washed three times with ca. 10 mL of petroleum ether and dried under vacuum.

Preparation of $[L^aPd(CH_3)(C_5H_5N)]\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (6a). This was prepared by following the above general method from **3a** (0.06 g, 0.1 mmol), $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_3)]_4\}$ (0.09 g, 0.1 mmol), and pyridine (8 μL, 0.1 mmol). Yield: 0.15 g, 96%. NMR (CD_2Cl_2): ^1H, δ −0.3 (d, $^3J_{PH}$ = 2.73 Hz, 3H, PdCH_3), 0.8 (d, 6H, CH(CH_3)$_2$), 1.0 (d, 6H, CH(CH_3)$_2$), 2.5 (m, 4H, CH(CH$_3$)$_2$ and [$Ph_2PCH_2CH_2$-ylidene]PdMe(py)$^+$), 4.3 and 4.4 (m, 1H each [$Ph_2PCH_2CH_2$-ylidene]PdMe(py)$^+$), 6.9 (s, 1H, imidazole backbone), 7.0−7.2 (m, 4H, aromatic), 7.3−7.4 (d, 2H, aromatic), 7.5−7.9 (m, 25H, aromatic); $^{13}C\{^1H\}$, δ 7.6 (s, PdCH_3), 23.3 (s, CH(*C*H$_3$)$_2$), 26.1 (s, CH(*C*H$_3$)$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 32.0 (s, [$Ph_2PCH_2CH_2$-ylidene]PdMe(py)$^+$), 47.9 (s, [$Ph_2PCH_2CH_2$-ylidene]PdMe(py)$^+$); $^{31}P\{^1H\}$, δ 34.8 (s, [$Ph_2PCH_2CH_2$-ylidene]PdMe(py)$^+$); ^{19}F, δ 100.2 (s, B[(3,5-CF_3)$_2$C$_6$H$_3$]$_4^-$). Anal. Found: C, 51.77; H, 3.77; N, 2.49. Calcd for $C_{67}H_{54}BF_{24}N_3PPd\cdot CH_2Cl_2$: C, 51.36; H, 3.55; N, 2.64.

Preparation of $[L^aPd(CH_3)(CH_3CN)]\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (7a). This was prepared by following the above general method from **3a** (0.06 g, 0.1 mmol), $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (0.09 g, 0.1 mmol), and CH_3CN (6 μL, 0.11 mmol). Yield: 0.110 g, 75%. NMR (CD_2Cl_2, 300 MHz): ^1H, δ −0.1 (d, $^3J_{PH}$ = 1.83 Hz, 3H, Pd*Me*), 1.1 (d, $^3J_{HH}$ = 6.37 Hz, 6H, CH(CH_3)$_2$), 1.2 (dd, $^3J_{HH}$ = 6.37 Hz, 6H, CH(CH_3)$_2$), 1.9 (s, 3H, *Me*CN), 2.6 (m, 4H, CH(CH$_3$)$_2$ and [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCMe)$^+$), 4.1 and 4.2 (m, 1H each, [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCMe)$^+$), 6.9 (s, 1H, ylidene backbone), 7.0 (s, 1H, ylidene backbone), 7.3 (d, 2H, aromatics), 7.4−7.6 (m, 8H, aromatic), 7.7−7.9 (m, 15H, aromatic). No $^{13}C\{^1H\}$ NMR data are available, due to sample decomposition during acquisition. Anal. Found: C, 49.76; H, 3.29; N, 4.26. Calcd for $C_{64}H_{52}BF_{24}N_3PPd\cdot CH_2Cl_2\cdot 2CH_3CN$: C, 50.71; H, 3.70; N, 4.29.

Preparation of $[L^aPd(CH_3)(C_6H_5CN)]\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (8a). This was prepared by following the above general method from **3a** (0.06 g, 0.1 mmol), $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (0.09 g, 0.1 mmol), and C_6H_5CN (10 μL, 0.1 mmol). Yield: 0.14 g, 88%. NMR (CD_2Cl_2): ^1H, δ 0.0 (d, $^3J_{PH}$ = 2.73 Hz, 3H, Pd*Me*), 1.1 (d, $^3J_{HH}$ = 7.29 Hz, 6H, CH(CH_3)$_2$), 1.3 (d, $^3J_{HH}$ = 6.38 Hz, 6H, CH(CH_3)$_2$), 2.7 (m, 4H, CH(CH$_3$)$_2$ and [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$), 4.1 and 4.2 (m, 1H each, [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$), 6.9 (s, 1H, ylidene backbone), 7.1 (s, 1H, ylidene backbone), 7.2 (s, 4H, aromatic), 7.3 (broad s, 3H, aromatic), 7.4 (d, 2H, aromatic), 7.5−7.6 (m, 9H, aromatic), 7.7−7.9 (m, 12H, aromatic); $^{31}P\{^1H\}$, δ 36.5 [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$); ^{19}F, δ 100.2 (s, B[(3,5-CF_3)$_2$C$_6$H$_3$]$_4^-$). $^{13}C\{^1H\}$, δ 4.9 (s, PdCH$_3$), 24.4 (s, CH(CH$_3$)$_2$), 25.2 (s, CH(CH$_3$)$_2$), 29.3 (s, CH(CH$_3$)$_2$), 31.6 (d, $^1J_{PC}$ = 34.41 Hz, [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$)), 47.3 (s, [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$), 117.5 (broad CF_3's of BAr_4^{F-}), 118.2 (s, PhCN), 121.8 (s, ylidene backbone), 122.8 (s, ylidene backbone), 124.0 (s, aromatic), 124.2 (s, aromatic), 124.8 (s, aromatic), 126.7 (s, aromatic), 129.4 (s, aromatic), 129.9 (broad doublet J = 11 Hz, aromatic of BAr_4^F), 131.5 (s, aromatic), 132.6 (s, aromatic), 133.2 (s, aromatic), 134.16 (d, J_{PC} = 11 Hz, aromatic), 135.5 (s, aromatic), 136.3 (s, aromatic), 146.8 (s, ipso aromatic to the ylidene moiety), 161.7 (s, aromatic), 162.2 (s, aromatic), 162.7 (s, aromatic), 163.2 (s, NCN carbon); $^{31}P\{^1H\}$, δ 36.5 ([$Ph_2PCH_2CH_2$-ylidene]PdMe(NCPh)$^+$), 36.3 (s, [$Ph_2PCH_2CH_2$-ylidene]PdMe(NCMe)$^+$); ^{19}F, δ 100.2 (s, B[(3,5-CF_3)$_2$C$_6$H$_3$]$_4^-$).

Preparation of $[L^aPd(CH_3)(PMe_3)]\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (9a). This was prepared by following the above general method from **3a** (0.058 mg, 0.1 mmol), $H(Et_2O)\{B[(3,5\text{-}CF_3)_2C_6H_2)]_4\}$ (0.094 mg, 0.1 mmol), and PMe_3 (8 μL, 0.11 mmol). Yield: 140 mg, 93.3%. NMR (CD_2Cl_2): ^1H, δ 0.0 (t, $^3J_{PH}$ = 7.29 Hz, 3H, PdCH$_3$), 0.9 (m, 15H, PMe_3 and CH(CH$_3$)$_2$), 1.2 (d, $^3J_{HH}$ = 7.29 Hz, 6H, CH(CH$_3$)$_2$), 2.4 (m, 2H, [$Ph_2PCH_2CH_2$-ylidene]PdMe(PMe_3)$^+$), 2.6 (sept, $^3J_{HH}$ = 6.38 Hz), 4.3 and 4.4 (m, 1H each [$Ph_2PCH_2CH_2$-ylidene]PdMe(PMe_3)$^+$), 7.0 (s, 1H, ylidene backbone), 7.15 (s, 1H, ylidene backbone), 7.2 (d, 2H, aromatic), 7.3−7.6 (m, 16H, aromatic), 7.7 (broad s., 7H, aromatic); $^{31}P\{^1H\}$, δ 4.6 (d, $^2J_{PP}$ = 32.81 Hz, [$Ph_2PCH_2CH_2$-ylidene]PdMe(PMe_3)$^+$), −15.8 (d, $^2J_{PP}$ = 32.81 Hz, [$Ph_2PCH_2CH_2$-ylidene]PdMe(*P*Me$_3$)$^+$); ^{19}F, δ 100.2 (s, B[(3,5-CF_3)$_2$C$_6$H$_3$]$_4^-$).

Preparation of 10a. To a cold solution of **4b** (60 mg, 0.085 mmol) in 20 mL of acetonitrile was added by cannela a solution of $AgBF_4$ (33 mg, 0.17 mmol in 5 mL of acetonitrile). Upon addition a gray precipitate was formed, which was filtered off through Celite while the mixture was kept at 0 °C. The resultant bright yellow solution was evaporated to dryness, and the yellow solid was characterized by NMR spectroscopy after dissolution in d_3-acetonitrile. NMR (CD_3CN): ^1H, δ 0.8 (d, 6H, CH(CH_3)$_2$), 0.9 (d, 6H, CH(CH_3)$_2$), 2.5 (2H, sept, CH(CH$_3$)$_2$), 2.8 (m, 2H, ($PPh_2CH_2CH_2$-ylidene)Pd(MeCN)$_2^{2+}$), 4.4 and 4.6 (each dt, 1H, ($PPh_2CH_2CH_2$-ylidene)Pd(MeCN)$_2^{2+}$), 7.1−8.0 (15H, aromatics and imidazole backbone); $^{31}P\{^1H\}$, δ 29.9 (s). The compound was unstable for further characterization.

Monitoring of the Reaction of 3a with $(CF_3)_2CHOH$ by NMR Spectroscopy. In the glovebox 20 mg of complex **3a** was dissolved in C_5D_5N. The solution was then cooled to −78 °C, and 3−4 drops of hexafluoro-2-propanol using a microsyringe were added. The solution was brought to room temperature, and the NMR spectra were acquired. ^1H NMR (C_6D_5N, 400 MHz): δ 0.0 (d, $^3J_{P-H}$ = 2.68 Hz, 3H, PdCH_3), 0.2 (CH_4), 0.9 (d, 6H, CH(CH_3)$_2$), 1.1 (d, 6H, CH(CH_3)$_2$), 2.6 (2H, sept, CH(CH$_3$)$_2$), 2.8 (m, 2H, ($Ph_2PCH_2CH_2$-ylidene)PdMe$^+$), 4.4 and 4.6 (each dt, 1H, ($Ph_2PCH_2CH_2$-ylidene)PdMe$^+$), 5.4 (sept, $(CF_3)_2CHO^-$), 7.0−7.8 (m, 10H, aromatic and imidazolylidene backbone), 7.9−8.1 (m, 5H, aromatic). ^{13}C NMR (C_6D_5N, 100.65 MHz): δ 7.98 and 8.03 (d, $^2J_{P-C}$ = 4.6 Hz, PdCH_3), 23.7 (s, CH(*C*H$_3$)$_2$), 26.4 (s, CH(*C*H$_3$)$_2$), 29.4 (s, *C*H(CH$_3$)$_2$), 31.53 and 31.87 (d, $^1J_{P-C}$ = 34.2 Hz ($PPh_2CH_2CH_2$-ylidene)PdMe$^+$), 47.7

Table 2. Crystallographic Data for Complexes 3a, 4b, 5a, 6a, and 7a

	3a	4b	5a	6a	7a
chem formula	$C_{31}H_{39}N_2PPd$	$C_{26}H_{27}Br_2N_2PPd$	$C_{31}H_{38}Cl_2I_3N_2PPd$	$C_{136}H_{105}B_2F_{48}N_6O_{0.50}P_2Pd_2$	$C_{64}H_{51}BF_{24}N_3PPd$
formula wt	577.01	664.69	999.64	3039.62	1466.26
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$I2/a$ of $C2/cc$	$P\bar{1}$	$P\bar{1}$
a/Å	12.7219(5)	9.3880(2)	18.5870(4c	14.258(5)	10.2531(2)
b/Å	15.2549(8)	10.4022(2)	14.5626(3))	17.042(5)	15.1598(5)
c/Å	15.3658(6)	13.8831(3)	27.2787(6	27.324(5)	22.1848(7)
α/deg	90	69.2150(10)	90	92.213(5)	74.158(2)
β/deg	110.421(3)	88.9380(10)	108.7830(10)	94.633(5)	80.735(2)
γ/deg	90	77.9220(10)	90	91.630(5)	73.122(2)
V/Å^3	2794.7(2)	1237.17(4)	6990.4(3)	6610(3)	3161.89(16)
Z	4	2	4	2	2
T/K	150(2)	150(2)	120(2)	153(2)	120(2)
μ/mm^{-1}	0.743	4.062	2.596	0.417	0.433
no. of data collected	28 963	10 490	34 885	60 460	56 165
no. of unique data	6290	5607	7990	18 875	14 437
R_{int}	0.1825	0.0188	0.0484	0.1037	0.1028
final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0674	0.0283	0.0576	0.0669	0.0561
final $R(F^2)$ for all data	0.1051	0.0347	0.0877	0.1194	0.1117

(s, ($PPh_2CH_2CH_2$-ylidene)$PdMe^+$), 71.7 (quintet, $^1J_{CF} = 31$ Hz, $(CF_3)_2CHO^-$), 123.5 (s, ylidene backbone), 123.8 (s, ylidene backbone), 124.8 (s, aromatic), 125.5 (s, aromatic), 130.22 and 130.32, 131.4 (s, aromatic), 131.7 (s, aromatic), 132.6 (s, aromatic), 134.53 and 134.65, 146.6 (s, ipso aromatic carbon attached to the ylidene backbone), 180.3 (N*C*N carbon); $^{31}P\{^1H\}$ NMR (C_6D_5N, 121.44): δ 35.26 (s, ($PPh_2CH_2CH_2$-ylidene)$PdMe^+$).

Heck Catalytic Studies. A 1 mmol portion of aryl halide, 1.4 equiv of alkene (methyl acrylate unless otherwise stated), 2 equiv of base (NEt_3 or dried Cs_2CO_3), and 0.3 equiv of diethylene glycol−dibutyl ether (internal standard) were placed in a 50 mL Rotaflo ampule using a microliter syringe. A 1 mL portion of *N*-methyl-2-pyrrolidinone or *N*,*N*′-dimethylacetamide was added to dissolve organics and 1 mL of solution of catalyst in the same solvent so that 0.5 or 0.01 mol % of catalyst/substrate was obtained. The ampule was then evacuated and placed in a preheated oil bath fitted with a thermostat. After the end of the catalytic run the ampule was cooled to room temperature and opened and the reaction mixture worked up by addition of water and dichloromethane, extraction, phase separation, drying and GC of the organic phases. GC yields (average of two runs) were calculated using diethylene glycol−dibutyl ether as an internal standard.

Copolymerization of CO and Ethylene. In a typical run 11 mg of complex **3a** was dissolved in 10 mL of dichloromethane, and the solution was transferred via cannula to a glass pressure reactor and cooled to −78 °C. To this solution was added 18 mg of Brookhart's acid dissolved in 10 mL of dichloromethane and cooled to −78 °C. After the addition was complete, the temperature was raised slowly to −30 °C and the apparatus was slowly pressurized with a 1:1 mixture of CO and ethylene up to about 20 psi. The slush bath was then removed, and the reaction mixture was pressurized to 5 bar. After 30 min the solution became cloudy. The reaction was quenched after 2 h with 30 mL of methanol. The precipitated polymer was filtered and dried under vacuum to yield 69 mg of poly(CO-*block*-ethylene). The polymer was dissolved in a 1:1 mixture of C_6D_6 and $(CF_3)_2CHOH$, and the NMR spectra were recorded. NMR (C_6D_6): δ 2.4 (s, poly(CO-*block*-(CH_2)$_2$), 3.2 (broad s, $(CF_3)_2CHOH$), 3.7 (sept, $(CF_3)_2CHOH$); $^{13}C\{^1H\}$, δ 35.9 (s, poly(CO-*block*-(CH_2)$_2$), 69.8 (sept. $^2J_{FH} = 33.70$ Hz, $(CF_3)_2$-*C*HOH), 122.5 (q, $^1J_{FH} = 281.80$ Hz, (CF_3)$_2$CHOH), 212.3 (s, poly(*C*O-*block*-(CH_2)$_2$). IR: 2906 cm^{-1} (CO stretching).

X-ray Crystallography. A summary of the crystal data and data collection and refinement details for compounds **3a**, **4b**, **5a**, **6a**, and **7a** are given in Table 2. All data sets were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode and an Oxford Cryosystems low-temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[18] The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[19] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model.

Acknowledgment. We thank Johnson Matthey Catalysts and the University of Southampton for financial support (to N.T.) and Prof. R. P. Tooze for initiating this collaborative research project and for helpful discussions.

Supporting Information Available: Full details of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034061S

(18) Hooft, R. COLLECT; Nonius BV, 1997−2000. Otwinowski, Z.; Minor, W. SCALEPACK, DENZO. *Methods Enzymol.* **1997**, *276*, 307.
(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 83.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 14, 2003 on http://pubs.acs.org | doi: 10.1021/om034061s