Electron-Poor Pentafluorophenyl-Substituted PCP−Palladium Pincer Complexes

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Received January 4, 2005

Summary: A novel fluoroaryl-substituted PCP ligand has been synthesized and used to generate the corresponding Pd complexes. The bonding of the fluoroaryl phosphine has been investigated by X-ray crystallography, NMR spectroscopy, and a competition experiment, which indicate that the ligand is sterically comparable to its well-known phenyl analogue but clearly imparts significant electronic differences to the metal center.

Mono- and multidentate phosphine ligands are seemingly ubiquitous in coordination and organometallic chemistry and have been used to stabilize a wide variety of metal complexes and catalysts.[1] Prominent members of the chelating phosphine family are the monoanionic, potentially terdentate PCP pincer-type ligands[2] with the formula $[2,6\text{-}(R_2PCH_2)_2C_6H_3]^-$, where R = alkyl, aryl. One of the main advantages of ECE-type (E = N, P, S, O) pincers is the ease with which functionality may be incorporated to tune electronic and steric properties at the metal center.[3] Indeed, many variations to the basic PCP structure have been utilized to stabilize metal complexes or generate highly active catalysts.[2−4] Conspicuously absent from this list are PCP ligands incorporating electron-withdrawing functions directly bonded to the P centers, even though electron-poor phosphines, such as $P(C_6F_5)_3$ and $[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]$ (dfppe), are known to potentially enhance catalytic activity or alter selectivity over electron-rich analogues.[5] Some pincer ligands[6] have been synthesized that included perfluorinated alkyl chains for use in fluorous biphasic catalysis.[7] However, the electronic effect of the fluorous "ponytail" is often mitigated by inclusion of an insulating spacer group, such as R_2Si or R_2C. Herein, we report the synthesis of a PCP ligand with electron-withdrawing pentafluorophenyl groups directly incorporated at phosphorus. Cationic and neutral Pd complexes were synthesized, and the effect of the pentafluorophenyl phosphine group on the bonding and electronic character of the metal center was investigated.

Attempts to generate ligand **1** via reaction of $(C_6F_5)_2$-PLi salts with benzylic halides were not successful, as the naked $(C_6F_5)_2P^-$ anion is unstable, even at low temperatures.[8] Formation of $[\{1,3\text{-}(C_6F_5)_2P(H)CH_2\}_2Ar]$-$[Br]_2$ salts by reaction of $(C_6F_5)_2PH$ with α,α′-dibromo-*m*-xylene, species which can be deprotonated to give PCP pincers,[9] was also unproductive, due to the low *σ* basicity of the P centers. Alternately, the synthesis of ligand **1** was realized via reaction of $1,3\text{-}(ClMgCH_2)_2C_6H_4$ with 2 equiv of $BrP(C_6F_5)_2$ in diethyl ether (Scheme 1). The meta-substituted di-Grignard reagent was cleanly generated using the method of Lappert[10] with α,α′-dichloro-*m*-xylene. Ligand **1** was purified by column chromatography with no signs of oxidation and can be

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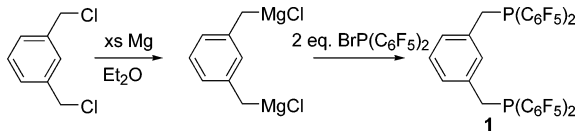
10.1021/om0500063 CCC: $30.25
Publication on Web 03/23/2005

Scheme 1. Synthesis of the Pentafluorophenyl-Substituted PCP Ligand 1



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stored for months in air in the solid state without formation of P═O products. Conversely, the phenyl analogue 1,3-$(Ph_2PCH_2)_2C_6H_4$ is readily oxidized by atmospheric oxygen. In a comparative reaction, C_6D_6 solutions of **1** and 1,3-$(Ph_2PCH_2)_2C_6H_4$ were heated to 55 °C in air and monitored periodically by ^1H and ^{31}P NMR spectroscopy. While no oxidation of **1** was observed over 1 day under these conditions, 1,3-$(Ph_2PCH_2)_2C_6H_4$ decomposed cleanly to its singly and doubly oxidized products with a half-life of approximately 5 h. However, prolonged (>1 month) exposure of solutions of **1** to air does result in the formation of a small amount of oxidized products (see below). In the ^1H NMR spectrum in CD_2Cl_2, the benzylic protons are found as a single doublet ($^2J_{H-P}$ = 4.2 Hz), indicating C_{2v} symmetry in the ligand. This is confirmed in the ^{19}F NMR spectrum, as all four of the C_6F_5 groups are equivalent, giving rise to signals for the ortho, para, and meta fluorines at δ −132.4, −152.6, and −163.2, respectively. The ^{31}P NMR spectrum exhibits a single quintet ($^3J_{P-F}$ = 23.0 Hz) at δ −44.2 with coupling due to the four ortho fluorines of the $P(C_6F_5)_2$ group. An X-ray crystal structure of ligand **1** was obtained, and a view with selected bond lengths and angles is given in Figure 1.[11] The two $P(C_6F_5)_2$ groups are oriented on opposite faces of the central aryl ring to minimize steric effects between the functions (P(1)−C(7)−C(20)−P(2) = 127.62(9)°). The lone pairs at phosphorus are stereochemically active, and each P atom is in a distorted-pyramidal environment with an average C−P−C angle of 101.3(1)°. The C_6F_5−P−C_6F_5 angles (e.g. C(8)−P(1)−C(14) = 98.37(8)°) are slightly compressed compared to those found in the C_6F_5−P−CH_2 group (C(7)−P(1)−C(8) = 100.11(9)°; C(7)−P(1)−C(14) = 105.15(9)°). In the crystal structure of **1**, a small amount of singly oxidized product was present (18% occupancy), which was refined with a disorder model. Crystals of **1** were obtained via slow evaporation of pentane solutions in air and, during the 1 month required for crystallization, approximately 15−20% of **1** was oxidized. In the crystal, only P(1) was partially oxidized and this species cocrystallizes with the reduced form. The presence of a P═O function was corroborated by a new signal at δ 14 in the ^{31}P NMR spectrum.

With the new ligand in hand, cationic Pd complex **2** was synthesized via electrophilic C−H activation using the synthon $[Pd(NCMe)_4][BF_4]_2$.[12] Species **2** was smoothly converted to the PdCl complex **3** by treatment with excess LiCl (Scheme 2). The ^1H, ^{19}F, and ^{31}P NMR data for both **2** and **3** support binding of the PCP ligand in a terdentate fashion. Indeed, the ^1H NMR spectra for **2** and **3** exhibit a single pseudo triplet for the benzylic protons, due to coupling with both phosphorus centers, a situation analogous to that observed for the phenyl PCP PdCl species **4**.[13] The ^{31}P NMR spectra contain only one resonance at δ 4.2 and 7.0 for **2** and **3**, respectively, which is downfield with respect to **1**. Also, only three signals for the ortho, meta, and para fluorines in the equivalent C_6F_5 rings are observed in the ^{19}F NMR spectra.

The difference in chemical shift between the meta and para fluorines ($\Delta_{\delta m,p}$) may be used as an indication of the electron density at the P centers. A similar technique has been employed to probe the coordination environment about $B(C_6F_5)_3$, related species, and their adducts.[14] In this case, there is a small but significant increase of $\Delta_{\delta m,p}$ for **2** and **3** (14.5 and 13.3 ppm, respectively) compared to **1** (10.6 ppm) upon complexation with the Pd center. This is indicative of net withdrawal of electron density from the P center by the Pd metal. Subtle effects are also noted in comparison of $\Delta_{\delta m,p}$ for **2** and **3**. The slightly larger value for cationic **2** indicates that the P centers are slightly more electron deficient than in **3** by virtue of the positive charge and presence of a less donating ligand (MeCN vs Cl^-) on the complexed Pd atom.

The terdentate binding mode of the PCP ligand in **2** and **3** was confirmed by X-ray crystallographic studies. Views of the molecular structures of **2** and **3** are shown in Figures 2 and 3, respectively, and selected bond lengths and angles are shown in Table 1. The Pd−P bond distances for **2** and **3** are slightly shorter than those in **4**,[13] a previously observed property for fluoroaryl vs protioaryl phosphine Pd complexes.[15] The Pd centers reside in a slightly distorted square planar environment with C(1)−Pd−Cl = 177.23(9)° and P(1)−Pd−P(2) = 160.76(3)° for **3**. In **2**, the P atoms are displaced out of the plane defined by the aryl ring, benzylic carbons, and Pd and N centers by 0.6905(10) and −0.6277(11) Å for P(1) and P(2), respectively. Corresponding distances are 0.7931(9) and −0.8004(8) Å in **3** and 0.695(2) and −0.795(2) Å in **4**. This twist minimizes steric repulsion between the two $P(C_6F_5)_2$ groups, and NMR experiments indicate that wagging of the pincer arms is fluxional in solution at all recorded temperatures. The average C−P−C angles for **2** and **3** are 106.8(2)° (range 103.82(16)−111.4(2)°) and 106.1(2)° (range 100.36(15)−109.95(16)°), respectively, and are only slightly larger than in **4** (105.8(2)°, range 102.7(6)−108.1(6)°). These data suggest that the fluoroaryl PCP ligand provides a steric environment comparable to that of the phenyl derivative in square-planar complexes or on coordination in an equatorial fashion.

(11) Abbreviated crystal structure parameters are as follows. **1**: $0.82(C_{32}H_8F_{20}P_2)\cdot0.18(C_{32}H_8F_{20}OP_2)$, $P2_1/c$ (No. 14), a = 6.0387(1) Å, b = 32.3369(5) Å, c = 15.9373(2) Å, β = 103.0616(6)°, V = 3031.60(8) Å^3, R1 = 0.0381, wR2 = 0.1046. S = 1.072. **2**: $[C_{34}H_{10}F_{20}NP_2Pd]BF_4$ + disordered solvent, $P2_1/c$ (No. 14), a = 10.1565(2) Å, b = 25.6619(5) Å, c = 16.1795(3) Å, β = 110.5437(8)°, V = 3948.77(13) Å^3. R1 = 0.0407, wR2 = 0.1001, S = 1.040. **3**: $C_{32}H_7ClF_{20}P_2Pd\cdot2.1C_7H_8$, $P2_1/c$ (No. 14), a = 15.4853(1) Å, b = 13.6515(1) Å, c = 26.0274(2) Å, β = 122.5592(3)°, V = 4637.39(6) Å^3, R1 = 0.0430, wR2 = 0.1381, S = 1.060. For further data see the Supporting Information.

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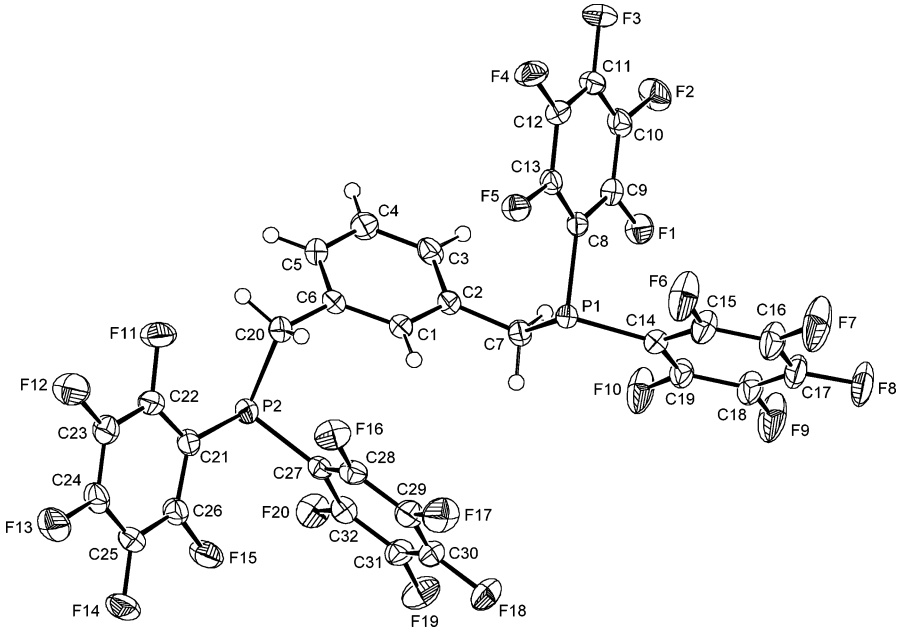
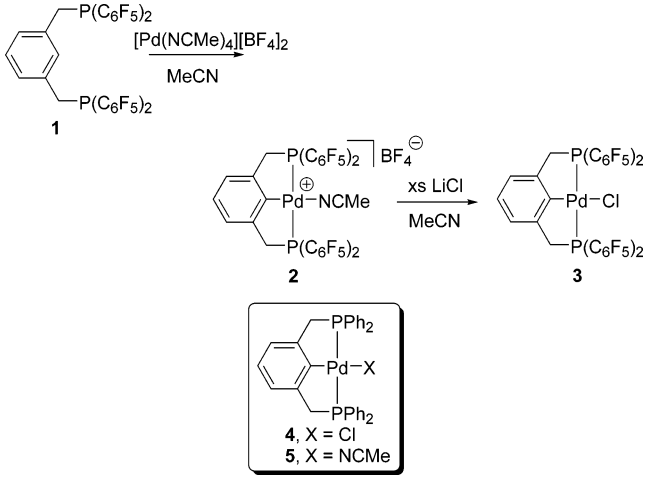


Figure 1. Structure of **1**. Ellipsoids are drawn at the 50% probability level. The oxygen atom at the partially oxidized P1 has been omitted in the drawing. Selected bond lengths (Å) and angles (deg): P(1)−C(7) = 1.846(2), P(1)−C(8) = 1.8401-(19), P(1)−C(14) = 1.8479(19), P(2)−C(20) = 1.857(2), P(2)−C(21) = 1.848(2), P(2)−C(27) = 1.8471(19); C(7)−P(1)−C(8) = 100.11(9), C(7)−P(1)−C(14) = 105.15(9), C(8)−P(1)−C(14) = 98.37(8), C(20)−P(2)−C(21) = 105.19(9), C(20)−P(2)−C(27) = 100.73(9), C(21)−P(2)−C(27) = 98.17(8), average C−P−C = 101.3(1).

Scheme 2. Synthesis of Fluoroaryl PCP−Pd Complexes 2 and 3 and Structures of Phenyl PCP−Pd Complexes 4 and 5



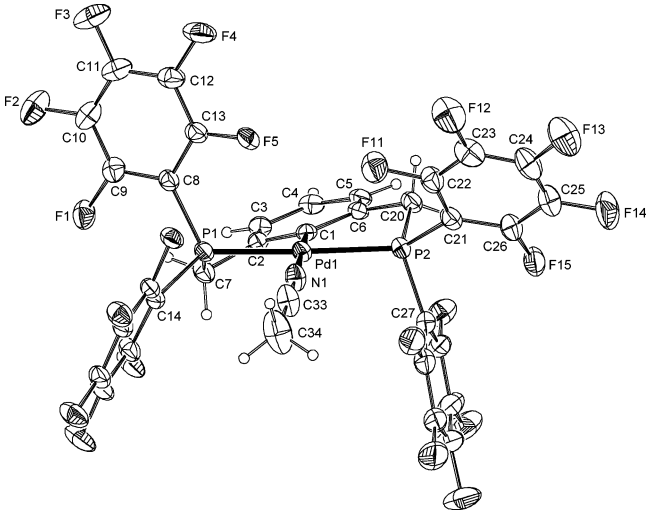


Figure 2. Structure of the cation of **2**. Ellipsoids are drawn at the 30% probability level. The disordered BF_4 anion and disordered CH_2Cl_2 solvent molecules are removed for clarity.

While ligation of **1** places the metal center in a steric environment similar to that in protioaryl systems, the electronic situation should be vastly different. For example, $LNi(CO)_3$ complexes, where L = PPh_3, $P(C_6F_5)_3$, have ν_{CO} values of 2069 and 2090 cm^{-1}, respectively, indicating that the $P(C_6F_5)_3$ ligand is a much poorer donor,[16] and, by corollary, the metal center is more electron deficient. Bonding between phosphines and transition metals is viewed as a synergistic combination of P to metal σ donation and metal to P π back-bonding.[17] As fluoroaryl phosphines are relatively poor σ donors but good π acceptors[16] in comparison to phenyl phosphines, *both* of these effects will place the metal center in a much more electron deficient state in the fluoroaryl system. The IR spectra of the MeCN adducts are uninformative in this regard; the ν_{CN} value of the stretching mode for **2** (2324 cm^{-1}) is essentially identical with that of **5** (2325 cm^{-1}).[18] However, comparison of the ^{31}P NMR spectra for the protio species **4** and **5** show the expected downfield shift upon substitution of Cl (δ 33.4)[13b] for MeCN (δ 43.2).[12] Similar analyses of **3** (δ 7.0) and **2** (δ 4.2) indicate that the same transformation results in a slightly upfield shift. As the σ-donating ability is much lower for the fluoroaryl ligand, it is less able to release electron density to compensate for the positive charge at the metal center and, thus, the ^{31}P chemical shift is less effected.

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(18) A value of 2316 cm^{-1} for ν_{CN} was obtained in CH_2Cl_2 solution.[12]

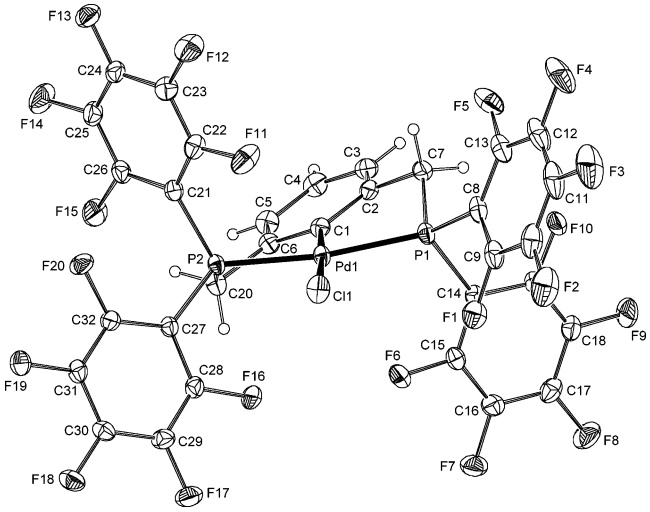


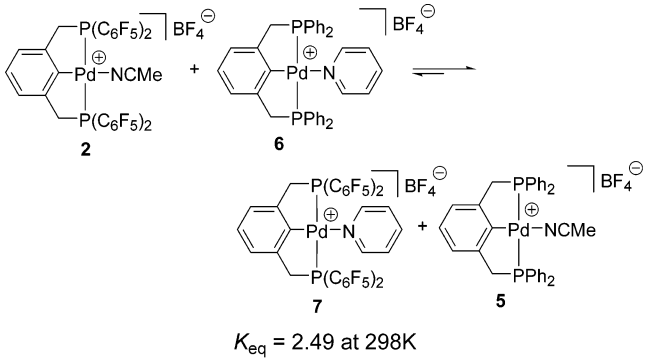
Figure 3. Structure of **3**. Ellipsoids are drawn at the 30% probability level. The toluene solvent molecules have been omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2−4

	2 (X = N)	3 (X = Cl)	**4** (X = Cl)[a]
C(1)−Pd	2.023(4)	2.028(3)	1.998(8)
P(1)−Pd	2.2838(10)	2.2725(8)	2.294(3)
P(2)−Pd	2.2719(10)	2.2678(8)	2.288(3)
[X]−Pd	2.081(4)	2.3619(8)	2.367(3)
P(1)−Pd−P(2)	161.55(4)	160.76(3)	162.0(1)
C(1)−Pd−[X]	175.81(14)	177.23(9)	178.7(3)
C−P−C	103.82(16)−111.4(2)	100.36(15)−109.95(16)	102.7(6)−108.1(6)

[a] Data obtained for equivalent parameters from ref 6a.

Scheme 3. Competition Experiment with Fluoroaryl and Phenyl PCP−Pd Complexes



To gain further insight into the electronic situation at the Pd center, a competition experiment was performed to determine the relative Lewis acid strength between phenyl and fluoroaryl PCP Pd complexes. Equimolar amounts of **2** and the pyridine adduct[19] of phenyl PCP−Pd (**6**) were dissolved in CD_2Cl_2, and rapid equilibration was observed. The ^{1}H NMR signals for the benzylic protons of the four species involved are baseline separated, and the ^{31}P NMR spectrum also exhibits four separate signals in approximately the same ratios. As shown in Scheme 3, the fluoroaryl PCP complex preferentially binds the stronger base, pyridine, to generate **7**. Integration of the benzylic protons allowed for evaluation of K_{eq}, and a value of 2.49 was obtained at 298 K in favor of **7**. Of note is the fact that the ^{1}H NMR signals of the benzylic protons for the individual species are pseudo triplets, indicating that the terdentate binding mode is intact for all complexes and the exchange is likely mediated by the presence of small amounts of free Lewis base. Variable-temperature ^{1}H NMR spectra were obtained over a 60 K range, and a van't Hoff plot was constructed (see the Supporting Information). The thermodynamic parameters obtained show that binding of pyridine in **7** is strongly preferred over that in **6**[20] on enthalpic terms ($\Delta H° = -7.4 \pm 0.2$ kJ mol^{-1}) but that the equilibrium is slightly disfavored entropically ($\Delta S° = -17.5 \pm 0.3$ J mol^{-1} K^{-1}). Due to the atomic radius of fluorine being slightly larger than that of hydrogen (van der Waals radii: H, 1.20 Å; F, 1.47 Å),[21] there may be steric interactions between the larger pyridine base and the fluoroaryl rings in **7** that are not present in **6**, resulting in lowered mobility of the fluoroaryl rings or pyridine. The negative value for $\Delta H°$ and the position of the equilibrium in favor of **7** clearly illustrates that the fluoroaryl PCP ligand conveys greater Lewis acidity to the metal center in these complexes by virtue of the poorer σ donating and greater π back-bonding ability of the phosphine arms.

In conclusion, we have presented an efficient synthetic approach to an electron-deficient fluoroaryl PCP ligand and the generation of a number of Pd complexes. In these Pd species, crystallographic studies show that the ligand provides a metal-centered geometrical environment similar to that of phenyl PCP in Pd complexes but spectroscopic investigations indicate that it imparts significant electronic differences. A competition experiment for pyridine convincingly demonstrates that the Pd center in the fluoroaryl ligand is significantly more Lewis acidic than its phenyl counterpart. Analysis of the van't Hoff plot indicate that the equilibrium is favored by preferential binding of pyridine to the fluoroaryl PCP Pd cation but slightly disfavored by entropic considerations. While not generally useful in fluorous biphasic catalysis, inclusion of pentafluorophenyl phosphine functions is known to enhance the solubility of metal complexes in supercritical CO_2,[22] opening the possibility for use of these metal complexes or other species incorporating ligand **1** in "green" catalysis. Research is underway to generate organometallic complexes in which the effect of the altered electronics induced by this ligand impacts reactivity and catalysis.

Acknowledgment. This work was supported in part by the Council for Chemical Sciences from the Dutch Organization of Scientific Research (CW-NWO) and Utrecht University. P.A.C. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for a postdoctoral fellowship.

Supporting Information Available: Full details of the synthesis of **1**, **2**, **3** and **6**, details of the competition experiment, equilibrium data, chart for van't Hoff analysis, and cif files with crystallographic data for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The pyridine adduct **6** was simply generated by treatment of **5** with a slight excess of pyridine in CH_2Cl_2; see the Supporting Information for more details.

(20) There will also be a difference in the strength of binding of the acetonitrile in the fluoroaryl and phenyl PCP Pd complexes, but this difference should be much smaller than for binding of pyridine.

(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(22) (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (b) For a specific example see: Fugita, S.; Yuzawa, K.; Bhanage, B. M.; Ikushima, Y.; Arai, M. *J. Mol. Catal. A* **2002**, 35.