Table I. Properties of Atoms and Critical Points in Formamide Structures

				$\nabla^2\rho$							
	ΔE, kcal/mol	r_{CN}, au	r_{CO}, au	h1, au × 10^3	h2, au × 10^3	ncc, au × 10^3	θ,[a] deg	d(h1–ncc),[b] au	ϕ,[c] deg	q(C),[d] electrons	τ,[e] deg
1	0.0	2.548	2.255	130	130	−214	0.0	2.3	14	1.978	94.1
2	3.1	2.588	2.247	152	116	−270	6.0	2.4	30	1.936	106.6
3	7.6	2.616	2.242	153	114	−285	7.4	2.5	46	1.902	110.3
4	18.7	2.686	2.228	128	128	−332	0.0	3.0	109	1.777	110.8

[a] The angle the carbonyl H makes with the OCN plane. [b] The distance between h1 and ncc. [c] The torsion angle between h1 and ncc along the C–N bond. [d] The net charge on the carbonyl carbon. [e] The nitrogen pyramidalization angle, ncc–N–H.

The SCF calculations were done at the HF/6-31G**//HF/6-31G** level.[9] We optimized the planar equilibrium structure, **1**, the structure corresponding to the transition state for internal rotation,[2] which maximizes the pyramidalization of the nitrogen, **4**, and two distorted geometries with fixed O–C–N–H torsional angles of 40° and 60°, **2** and **3**, respectively (Figure 1).

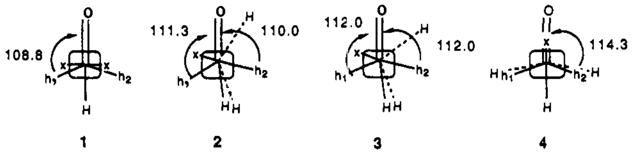

Figure 1. Newman projections of the four rotamers of formamide. Here h1 and h2 represent the more and less reactive holes in the VSCC of carbon, respectively, and x represents the ncc on nitrogen. The dashed lines to H represent the N–H bonds.

The Laplacian quantitatively determines the extent of pyramidalization of N during C–N bond rotation. The charge concentrations of the Laplacian ($\nabla^2\rho < 0$) are the physical analogues of Lewis electron pairs.[3,10] Thus the VSCC of the pyramidalized N in **4** exhibits three bonded and one nonbonded charge concentrations, approximately tetrahedrally directed. In **1** the nonbonded charge concentration (ncc, Table I) on N is necessarily present as two equivalent maxima, above and below the plane. The VSCCs of N in **2** and **3** already exhibit the tetrahedral structure found in **4**.

Rotation about the C–N bond also results in slight pyramidalization of the carbon. This enlarges the hole (i.e., increases the value of $\nabla^2\rho$ at the critical point), h1, occupying the tetrahedral position in the VSCC of the carbonyl carbon. *This is the origin of enhanced susceptibility in distorted amides, the greater depletion of charge at the hole in the carbon's VSCC.* This prediction of increased susceptibility to nucleophilic attack is made quantitative by the values of $\nabla^2\rho$. The holes in the VSCC of structures **2** and **3** display different reactivities. The one syn to the amide hydrogens and interior to the pyramid, h2, is less positive and hence less reactive than are the corresponding critical points in the planar amide while the enlarged hole on the opposing face, h1, is more positive and more reactive. The distance between h1 and ncc and their associated torsion angle ϕ across the C–N bond increase with increased rotation about the C–N bond.

The relative location of a critical point predicts the angle of nucleophilic attack.[3-6] The critical points denoting the holes of the carbonyl carbon are found ~0.53 Å from its nucleus (Figure 1). In the planar amide each forms an angle of 109° with the C–O bond, increasing to a maximum of 112° in **3**, in agreement with experiment.[8] The net charges on the carbonyl carbon atoms are determined by spatial integration of the charge density over the atomic basins (Table I). The pyramidalization of N changes its hybridization from sp^2 to sp^3, resulting in the transfer of electronic charge from N to C, decreasing somewhat the large net positive charge on C. The distortion found in **2** is predicted to significantly increase the reactivity of the carbonyl carbon in spite of a slight decrease in its net charge. This demonstrates that the dominant factor in determining relative reactivity is not the magnitude of an atomic charge but rather the extent of charge concentration or charge depletion, as determined by the Laplacian of the density.[3-7]

Our predictions of increased propensity for reaction are the result of the response of the VSCC to the geometric distortion about the carbonyl carbon. This reorganization of charge will occur in solution as well as in the gas phase. The field generated by solvent molecules might make a small perturbation to the VSCC, but previous experience with electric fields has shown that the greatest perturbations are made to the outer, diffuse distribution.[11a] The VSCC, a tightly bound region of charge, is much less likely to be affected by external fields. This will be considered in detail in a future publication.[11b]

The barrier to amidic rotation and its associated bond lengthening results from the transfer of charge from N to C, induced by the accompanying pyramidalization of N, which decreases the electron–nuclear attractive energy more than it decreases the repulsive energies.[12] Bennet et al.[1] explain the enhanced reactivity of the distorted amides by arguing that since N is pyramidalized in the transition state, the more distorted amide is closer in energy to the transition state. The present results show that this investment in energy also pyramidalizes the carbon, increasing the extent of its charge depletion, thereby increasing its susceptibility to nucleophilic attack.

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Facile Aryl–Aryl Exchange between the Palladium Center and Phosphine Ligands in Palladium(II) Complexes

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It is known that $PdL_2(Ar)X$ **1** (L = phosphine, Ar = aryl) is involved as an important intermediate in a vast number of palladium-mediated organic syntheses such as carbonylation of aromatic halides,[1] arylation of olefins,[2] and coupling of aryl halides

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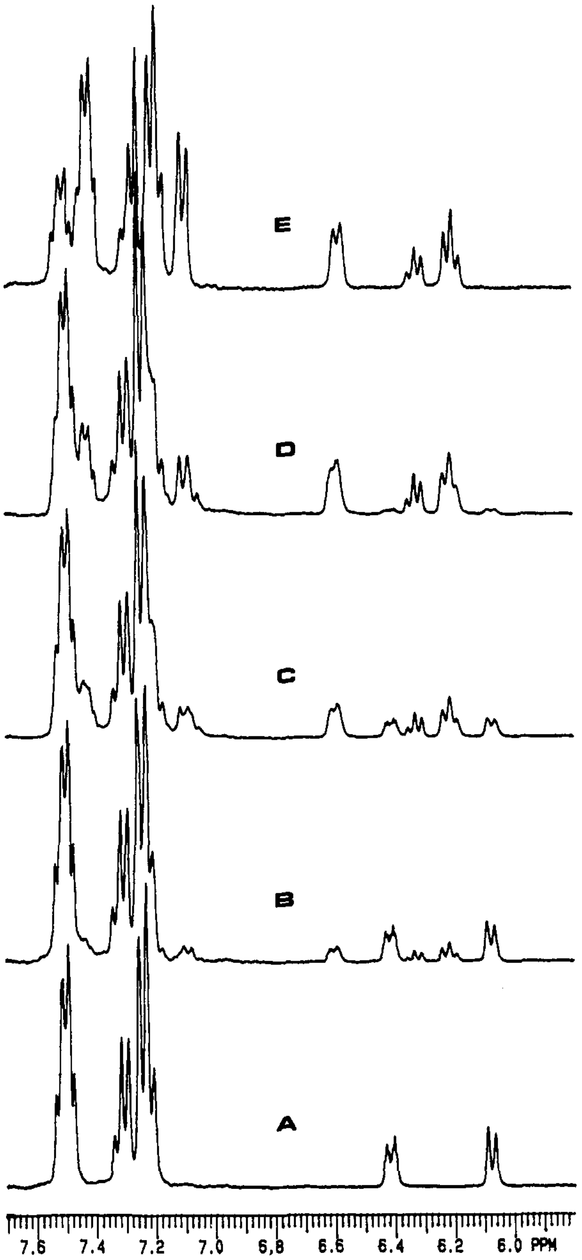

Figure 1. The ^{1}H NMR spectra of *trans*-$Pd(PPh_3)_2(C_6H_4\text{-}p\text{-}CH_3)I$ (**1a**) in the aromatic region ($CDCl_3$): (A) at 23 °C; (B) as the solution was heated at 60 °C for 60 min, (C) 90 min, and (D) 180 min. (E) The ^{1}H NMR spectrum of *trans*-$Pd[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]_2(Ph)I$ at 23 °C. For spectra (B–D), **1a** dissolved in THF (0.030 M) was heated at 60 °C for a specified period. A small portion of the solution was withdrawn and the solvent removed by vacuum. The residue was then dissolved in $CDCl_3$ for NMR measurement.

with organometallic reagents[3] and with terminal acetylenes.[4] In spite of the extensive involvement of **1** in catalytic reactions, its properties have not been fully explored. In this paper, we report an interesting exchange reaction of **1** between the aryl groups bound to the coordinated phosphine and that bound to the palladium center.

When $Pd(PPh_3)_2(C_6H_4\text{-}p\text{-}CH_3)I$ (**1a**) prepared from the oxidative addition of *p*-iodotoluene to $Pd(PPh_3)_4$[5] was heated at 50–60 °C in THF or chloroform, a regiospecific exchange between the aryl on the palladium center and the phenyls on the phosphine took place. This intriguing reaction was readily monitored by ^{1}H NMR spectroscopy. The proton resonances at 6.42 (d, H_o), 6.08 (d, H_m) (see Figure 1A), and 1.91 (s, CH_3) ppm are due to the tolyl group of **1a**. As the solution of **1a** was heated, these peaks decreased in intensity and new resonances at 6.59 (d), 6.33 (t), and 6.21 (t) ppm grew in (Figure 1B,C). These new resonances were assigned as the proton chemical shifts of a phenyl group bound to the palladium center on the basis of their appearance at the same frequencies as those of the palladium-bound phenyl group in *trans*-$Pd[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]_2(Ph)I$ (**3a**) (Figure 1E) and $Pd(PPh_3)_2(Ph)I$ (**4a**). It is noteworthy that both of these two complexes have essentially the same chemical shifts for the phenyl ligand, although their phosphine ligands are different. Two other signals at 7.42 (dd) and 7.10 (d) in spectra B and C of Figure 1 and a signal at 2.34 (s) ppm also increased in intensity as heating proceeded. These resonances come at the same frequencies as those of the ortho protons of the two phenyl groups and the meta and methyl protons of the tolyl group, respectively, on the coordinated $PPh_2(C_6H_4\text{-}p\text{-}CH_3)$ in **3a** (Figure 1E). This observation strongly supports the formation of $PPh_2(C_6H_4\text{-}p\text{-}CH_3)$ in the exchange reaction. After the solution was heated for 3 h, no further change of the relative intensity of these signals was observed, indicating that an equilibrium for the reaction was established. The degree of migration, i.e., the ratio of P-tolyl to Pd-tolyl at equilibrium, was obtained by measurement of the peak intensities in Figure 1D and is 90/10 at 60 °C. In a similar manner, $Pd(PPh_3)_2(C_6H_4\text{-}p\text{-}OCH_3)I$ (**1b**) also undergoes aryl–aryl exchange, with a degree of migration of 96/4 at the same temperature.

It appears, on the basis of the foregoing results, that the aryl exchange product of **1a** should be *trans*-$Pd(PPh_3)[PPh_2(C_6H_4\text{-}p\text{-}CH_3)](Ph)I$ (**2a**). However, owing to the lability of phosphines coordinated to Pd(II),[6] rapid intermolecular phosphine scrambling of **2a** is expected, leading to the formation of **3a** and **4a** in addition to **2a** (eq 1). The presence of **2a**, **3a**, and **4a** gains strong support

$$\begin{aligned} &Pd(PPh_3)_2(C_6H_4\text{-}p\text{-}CH_3)I \rightleftharpoons \\ &\quad Pd(PPh_3)[PPh_2(C_6H_4\text{-}p\text{-}CH_3)](Ph)I\ (\mathbf{2a}) + \\ &\quad Pd[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]_2(Ph)I\ (\mathbf{3a}) + Pd(PPh_3)_2(Ph)I\ (\mathbf{4a}) \end{aligned} \tag{1}$$

from the mass spectrum of the product mixture of **1a**.[7] Although no parent peak was observed, the fragments $Pd(PPh_3)[PPh_2(C_6H_4\text{-}p\text{-}CH_3)](Ph)$, $Pd[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]_2(Ph)$, and $Pd(PPh_3)_2(Ph)$ at m/e = 721, 735, and 707, respectively, with medium intensities were clearly seen. It should be noted that, under the same conditions for mass spectral measurement, **1a** gave only the fragment $Pd(PPh_3)_2(C_6H_4\text{-}p\text{-}CH_3)$ at m/e = 721. The absence of the other two peaks at m/e = 707 and 735 indicates that no aryl exchange occurs during the process of mass measurement. Similarly, in the mass spectrum of the exchange products of **1b**,[8] the corresponding fragments of **2b**, **3b**, and **4b** were observed.

One of the interesting questions in the present studies is whether $Pd(PPh_3)_2(Ph)I$ also undergoes aryl–aryl exchange. To answer

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[7] The ionization mode used for measuring the mass spectrum is FAB. Important peaks in the spectrum of the exchange products of **1a** are as follows: (m/e) 735 ($M^+ - I$ of **3a**), 721 ($M^+ - I$ of **2a**), 707 ($M^+ - I$ of **4a**), 658 ($Pd[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]_2^+$), 644 ($Pd(PPh_3)[PPh_2(C_6H_4\text{-}p\text{-}CH_3)]^+$), 630 ($Pd(PPh_3)_2^+$), 367 ($PPh_2(C_6H_4\text{-}p\text{-}CH_3)_2^+$), 353 ($PPh_3(C_6H_4\text{-}p\text{-}CH_3)^+$), 339 ($PPh_4^+$), 291 ($HPPh[C_6H_4\text{-}p\text{-}CH_3]_2^+$), 277 ($HPPh_2[C_6H_4\text{-}p\text{-}CH_3]^+$), 263 ($HPPh_3^+$).

[8] Important peaks in the mass spectrum of the exchange products of **1b** are as follows: (m/e) 767 ($M^+ - I$ of **3b**), 737 ($M^+ - I$ of **2b**), 707 ($M^+ - I$ of **4b**), 690 ($Pd[PPh_2(C_6H_4\text{-}p\text{-}OCH_3)]_2^+$), 660 ($Pd[PPh_2(C_6H_4\text{-}p\text{-}OCH_3)]^+$), 630 ($Pd(PPh_3)_2^+$), 399 ($PPh_2(C_6H_4\text{-}p\text{-}OCH_3)_2^+$), 369 ($PPh_3(C_6H_4\text{-}p\text{-}OCH_3)^+$), 339 ($PPh_4^+$), 323 ($HPPh[C_6H_4\text{-}p\text{-}OCH_3]_2^+$]), 293 ($HPPh_2[C_6H_4\text{-}p\text{-}OCH_3]^+$]), 263 ($HPPh_3^+$).

the question, deuterated phosphine complex Pd[P(C_6D_5)$_3$]$_2$(Ph)I was prepared.[5] Heating the compound in THF at 50 °C led to exchange between the phenyl and the deuterated phenyls with a degree of migration of 6.3:1.[9] This value was obtained from measuring the relative intensity in the ^{1}H NMR spectrum[10] of the exchange mixture and is consistent with the expected value of 6:1 calculated on the basis of a random distribution of all the phenyl groups.

There are indications that the exchange products such as **3a** and Pd[PPh$_2$(C_6H_4-*p*-OCH$_3$)]$_2$(Ph)I (**3b**) further undergo exchanges to yield complexes containing coordinated PPh(C_6H_4-*p*-CH$_3$)$_2$ and PPh(C_6H_4-*p*-OCH$_3$)$_2$, respectively. In the ^{1}H NMR spectrum of the exchange products of **1a**, a small doublet at 7.07 ppm (overlapped with the doublet at 7.10 ppm)[11] and a singlet at 2.32 ppm are likely due to the meta and methyl protons of the tolyl group in the coordinated PPh(C_6H_4-*p*-CH$_3$)$_2$ on the basis of the observation that the corresponding chemical shifts of Pd[PPh(C_6H_4-*p*-CH$_3$)$_2$]$_2$(Ph)I also appear at the same frequencies. Similar results were also observed in the exchange products of **1b**. Further proof for the presence of PPh(C_6H_4-*p*-OCH$_3$)$_2$ was obtained by the addition of dppe (1.1 equiv) to the exchange products of **1b** followed by separation on silica gel. Three phosphines, PPh$_3$, PPh$_2$(C_6H_4-*p*-OCH$_3$), and PPh(C_6H_4-*p*-OCH$_3$)$_2$, in a 9:7:1 ratio were isolated.[12]

The exchange reaction is sensitive to air and free phosphine. In the presence of air, an unknown decomposition is dominant and only a complete degassing of the solution prior to heating can stop the side reaction. While the presence of 0.1 equiv of Pd(PPh$_3$)$_4$ did not influence the exchange rate, the addition of 1 equiv of PPh$_3$ to the solution of **1** led to a nearly total inhibition of the aryl exchange. Thus, it is reasonable to assume that the dissociation of a phosphine from **1** to give a three-coordinate intermediate is a necessary step for the exchange reaction. Oxidative addition of a P–Ar bond to the metal center in the same intermediate to yield a transient Pd(IV) species, followed by migration of the aryl group originally bound to the palladium to the phosphorus, would complete the exchange reaction.

Although aryl–aryl exchange had not been observed previously, one-way aryl migration from coordinated phosphine to the metal center was implicated in several cobalt-,[13] nickel-,[14] and palladium-mediated[15] reactions. Examples on the closely related oxidative addition of triarylphosphine to low-valent transition-metal complexes were also known.[16] In addition, ortho metalation[17] and the related ortho hydrogen exchange of coordinated triarylphosphine were extensively investigated.[18]

In conclusion, we have demonstrated a facile two-way aryl migration between the metal center and coordinated phosphine in Pd(II) complexes. The generality and detailed mechanism of the exchange in palladium as well as in nickel and platinum systems is currently under investigation. The effect of this reaction on the catalytic reaction is which **1** is involved as catalyst intermediate is also being explored, and the results will be reported shortly.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

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[9] The ^{31}P{^{1}H} NMR spectrum of the heated solution showed that only a new signal at 22.8 ppm in addition to the original resonance at 22.7 ppm was observed. The new signal was assigned as the signal of coordinated P(C_6D_5)$_2$(C_6H_5) from the aryl–aryl exchange of Pd[P(C_6D_5)$_3$]$_2$(Ph)I. For comparison, the ^{31}P resonance of the coordinated PPh$_3$ in Pd(PPh$_3$)$_2$(Ph)I appears at 23.3 ppm. These results indicate that the exchange is a clean reaction.

[10] The resonances of the phenyl bound to palladium appear at 6.59 (d), 6.33 (t), and 6.21 (t) ppm, while the corresponding values of the phenyl bound to phosphorus come at 7.51 (dd), 7.32 (t), and 7.26 (t) ppm.

[11] Both doublets were well separated in acetone-d_6.

[12] To the exchange product mixture (0.23 g, 0.27 mmol) of **1b** was added dppe (0.12 g, 0.30 mmol). The resulting solution was separated on TLC using ethyl acetate/hexane (1/30) as the eluent to give 70.7 mg (0.27 mmol) of PPh$_3$, 61.0 mg (0.21 mmol) of PPh$_2$(C_6H_4-*p*-OCH$_3$), and 9.4 mg (0.03 mmol) of PPh(C_6H_4-*p*-OCH$_3$)$_2$. The total yield of these monodentate phosphines was 94%. All these species were characterized by NMR and mass spectroscopy.

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Palladium-Catalyzed Coupling of Alkenyl Iodonium Salts with Olefins: A Mild and Stereoselective Heck-Type Reaction Using Hypervalent Iodine

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Hypervalent iodine reagents have been used for carbon–carbon coupling.[1] We now report a palladium-catalyzed variation of this process with phenyl(alkenyl)iodonium salts and various alkenes as exemplified in eq 1. Both Kitamura, Stang et al.,[2] and Ochiai[3] have demonstrated Pd-catalyzed carbonylation of phenyl(alkynyl)- and phenyl(alkenyl)iodonium systems. However extension to olefination is novel and of considerable synthetic potential.[4]

The present coupling reaction (eq 1, Table I) shares in common with the obviously related Heck reaction[5] high yields and transstereoselectivity. A key distinguishing advantage of the hypervalent iodine reaction is that it proceeds at room temperature. Thus polymerization of activated olefins at temperatures in excess of 100 °C as practiced in the Heck reaction is obviated, and this is exemplified by the success with acrolein as an olefinic component[5] (entry 6). Styrene (entries 5 and 9) is noteworthy in that,

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