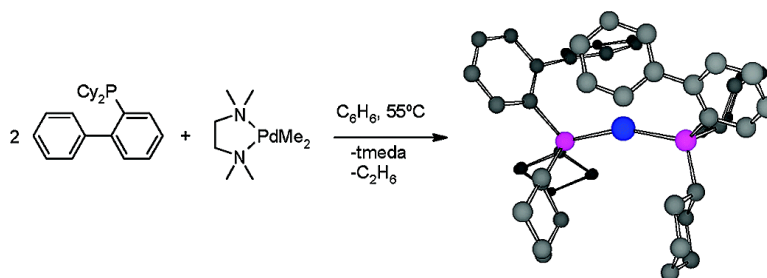


A Dicoordinate Palladium(0) Complex with an Unusual Intramolecular π -Arene Coordination

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A Dicoordinate Palladium(0) Complex with an Unusual Intramolecular η^1 -Arene Coordination

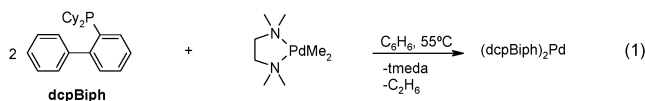
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Low-coordinate, low-valent complexes of palladium are extremely important catalytic intermediates in a variety of organic synthetic transformations.¹ Recent reports have illustrated the utility of bulky monophosphines such as 2-(dicyclohexylphosphino)biphenyl (dcpBiph) to accelerate palladium-mediated activation of the carbon–chlorine bond of chloroarenes under relatively mild conditions.² It has been proposed that either the highly reactive $14e^-$ fragment, $(R_3P)_2Pd$, or the $12e^-$ fragment, $(R_3P)Pd$, may be the key intermediate for the C–Cl oxidative addition with the chloroarene.^{3,4} Despite interest in these low-coordinate complexes, the structure and bonding of these species have not been extensively studied. We now report the synthesis and unusual structure of $(dcpBiph)_2Pd$ (**1**), some of its conformational behavior in solution, and reactions with halobenzenes.

The reaction of phosphines with $(tmeda)PdMe_2$ ⁵ often give bisphosphine dimethylpalladium complexes. For bulky phosphines, these readily reductively eliminate ethane to yield $P_2Pd(0)$ which may be trapped with cycloalkenes⁶ or allowed to dimerize.⁷ Similarly, heating a mixture of 2 equiv of dcpBiph and $(tmeda)PdMe_2$ in benzene led directly to the bright yellow and slightly air-sensitive $(dcpBiph)_2Pd$ in 82% yield (eq 1).⁸



An X-ray crystal structure of **1** was obtained. The ORTEP drawing in Figure 1 reveals a highly congested coordination sphere in which the biphenyl substituents shield nearly one hemisphere about the palladium atom and the cyclohexyl groups shield the rest.⁹ An obvious difference between this structure and those of the few other reported structures of $(R_3P)_2M$ ($M = Pd, Pt$) is the unusually

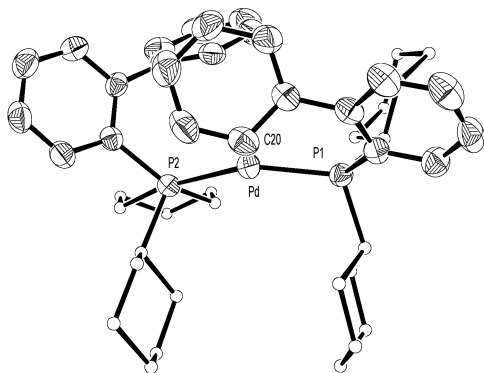
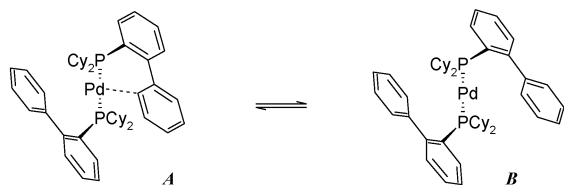


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are at the 30% probability level. For clarity, hydrogen atoms are omitted, and the cyclohexyl carbons are represented by spheres of arbitrary radius. Selected bond lengths (Å) and angles (deg): Pd–P1, 2.2744(11); Pd–P2, 2.2778(11); P1–Pd–P1, 154.82(4).

large deviation of the P1–Pd–P2 angle of $154.82(4)^\circ$ from linearity.¹⁰ Close inspection of the interatomic distances within the coordination sphere reveals an unusually close contact between only one biphenyl carbon atom, C20, and the palladium atom (C20–Pd = $2.676(5)$ Å). This intramolecular η^1 -coordination of an arene to palladium(0) is unprecedented and evidently partially satisfies the electron deficiency at palladium, a stabilizing interaction that is accommodated by the bent P1–Pd–P2 framework.¹¹ It should be noted that the coordinating arene ring is planar and that there is no significant bond alternation among the C–C bonds of the ring. Thus, the palladium atom appears to interact solely with the π cloud of the interacting arene, leaving the nominal sp^2 hybridization at C20 undisturbed.¹² By contrast, a more classical π -alkene interaction is evidenced by the recently reported biaryl complexes (*o*-phenanthryl)PCy₂Pd(dba)¹³ and [BINAP(O)]₂Pd¹⁴ where a rare intramolecular η^2 -arene coordination to Pd(0) exists. A CP-MAS ³¹P NMR spectrum of solid **1** shows a broad AB pattern indicative of the two inequivalent phosphorus environments.

The room-temperature ¹H and ¹³C{¹H} NMR spectra of **1** in solution show sharp resonances which are consistent with an “average” symmetric structure in which the two biphenyl groups are indistinguishable. The room-temperature ³¹P{¹H} NMR spectrum shows one broadened resonance at 31 ppm. This indicates that the π -coordinated and free biphenylphosphine substituents are rapidly exchanging on the NMR time scale. The origin of the exchange is not due to the interchange of free and bound ligands since an equimolar mixture of dcpBiph and **1** gave rise to two distinct ³¹P signals, ascribable to complex **1** and the free ligand, that remain unchanged up to 70 °C.

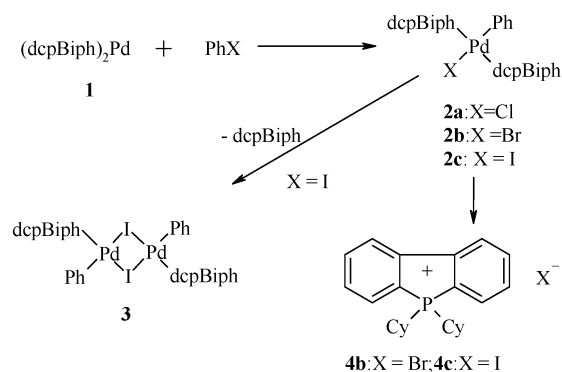
The variable temperature ³¹P{¹H} NMR spectrum of **1** in toluene-*d*₈ was examined. As the temperature is lowered, the ³¹P{¹H} NMR spectrum of pure **1** shows broadening of the ³¹P resonance followed by ultimate reacoalescence into two distinct features at –90 °C: a sharp AB pattern with $\delta_A = 58$ ppm, $\delta_B = 15$ ppm, $^2J(P-P) = 156$ Hz and a slightly broadened singlet at 13.5 ppm. The AB pattern is very similar to that found in the solid state, and is therefore assigned to a conformer of **1** that possesses both π -coordinated and free biphenylphosphine substituents (**A**). The larger remaining resonance at 13.5 ppm corresponds to the majority species in solution (75%) at –90 °C. The ³¹P chemical shift of this symmetrical species is virtually identical to δ_B of conformer **A** and is attributed to a species for which none of the arene substituents are interacting with the palladium atom. The NMR spectra of solutions containing **1** are insensitive to total concentration of **1** both at –90 °C and at room temperature, thereby precluding monomer–dimer or higher oligomerization equilibria. We therefore ascribe the majority low-temperature species to a conformer (or set of conformers) of **1** that possesses two noncoordinating biphenyl groups (**B**).¹⁵



Full line shape analysis¹⁶ of the variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra gave $\Delta H = 2.04(5)$ kcal mol⁻¹ and $\Delta S = -2.09(9)$ cal mol⁻¹ K⁻¹ for the equilibrium shown above. These small differences in energy are consistent with a conformer equilibrium. The thermodynamic parameters also reveal that conformer **A**, while the minority species at very low temperatures as indicated, becomes the predominant species near room temperature. The activation parameters for $\text{A} \rightarrow \text{B}$ of $\Delta H^\ddagger = 7.5(5)$ kcal mol⁻¹ and $\Delta S^\ddagger = -5(1)$ cal mol⁻¹ K⁻¹ reflect a fairly congested transition state for the conformer interconversion.

Since **1** may be relevant to catalytic chemistry involving C–X activation, the reaction of **1** with halobenzenes was investigated. The reaction of **1** with excess PhX (X = Cl, Br, I) in benzene at room temperature resulted in the expected formation of the *trans*-phenyl palladium halide complexes **2a–2c** (Scheme 1). The reaction times follow the expected order of PhI (minutes) < PhBr (1 day) < PhCl (several days). The phenyl palladium iodide (**2c**) is unstable, however, and quickly gives rise to the bridging diiodide (**3**) and free dcpBiph ligand. Complex **3** likely arises from ligand dissociation and dimerization of the resulting tricoordinate palladium intermediate. Most interesting is the formation of the phosphonium salts **4b,c** as minor products (~5% yields).¹⁷ These products probably arise from the metalation of an ortho carbon of the distal biphenyl ring of the phosphine ligand, followed by reductive elimination a P–C bond from the palladium. This implies that a palladium–arene interaction, similar to that observed in **1**, may exist for the Pd(II) complexes (**2b,c**). In the case of **2b,c**, the interaction has additional chemical significance in respect to arene metalation.

Scheme 1



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Supporting Information Available: Crystallographic data for **1** (CIF and PDF) and experimental procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Hegedus, L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley and Sons: New York, 1994; pp 383–459. (b) Hermann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds. A Comprehensive Handbook in Two Volumes*; Cornils, B., Hermann, W. A., Eds.; VCH Publishers: New York, 1996; Vol. 2, pp 712–732. (c) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1.
- (a) Ehrentraut, A.; Zapf, A.; Matthias, B. *Adv. Synth. Catal.* **2002**, *344*, 209. (b) Harris, M. C.; Huang, X.; Buchwald, S. L. *Org. Lett.* **2002**, *17*, 2885. (c) Lautens, M.; Mancuso, J. *Synlett* **2002**, 3, 394. (d) Ali, M. H.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 2560. (e) Huang, X.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3417. (f) Jonkers, T. H. M.; Maes, B. U. W.; Lemiere, G. L. F.; Dommissie, R. *Tetrahedron* **2001**, *57*, 7027. (g) Zapf, A.; Beller, Mathias *Chem.–Eur. J.* **2001**, *7*, 2908. (h) Andreu, M. G.; Zapf, A.; Beller, M. *Chem. Commun.* **2000**, 2475. (i) Baudoin, O.; Guenard, D.; Gueritte, F. *J. Org. Chem.* **2000**, *65*, 9268. (j) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360. (k) Old, D. W.; Harris, M. C.; Buchwald, S. L. *Org. Lett.* **2000**, *2*, 1403. (l) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *4*, 1158. (m) Zhang, X.-X.; Buchwald, X. L. *J. Org. Chem.* **2000**, *65*, 8027. (n) Mowery, M. E.; DeShong, P. *Org. Lett.* **1999**, *1*, 2137. (o) Wolf, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3415. (p) Wolf, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413. (q) Wolf, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.
- (R₃P)₂Pd: (a) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665. (b) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742. (c) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816. (d) Ben-David, Y.; Gozin, M.; Portnoy, M.; Milstein, D. *J. Mol. Catal.* **1992**, *73*, 173. (e) Fryzuk, M. D.; Clentsmith, G. K. B.; Rettig, S. J. *Organometallics* **1996**, *15*, 2083.
- (R₃P)Pd: (a) Galardon, E.; Ramdeehul, S.; Brown, J. M.; Cowley, A.; Hii, K. K.; Jutand, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1761. (b) Hartwig, J. P.; Roy, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 1232.
- de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G.; *Organometallics* **1989**, *8*, 2907.
- (a) Krause, J.; Cestarcic, G.; Haack, K.-J.; Seevogel, K.; Storm, W.; Pörschke, K.-R. *J. Am. Chem. Soc.* **1999**, *121*, 9807. (b) Andreu, M. G.; Zapf, A.; Beller, M. *Chem. Commun.* **2000**, 2475.
- Reid, S. M.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2001**, *17*, 4081–4082.
- Experimental:** A solid mixture of dcpBiph (900 mg, 2.568 mmol) and (tmeda)PdMe₂ (324 mg, 1.284 mmol) was dissolved in 17 mL of benzene and stirred at 55 °C (tmeda = *N,N,N',N'*-tetramethylethylenediamine). Within 5 min the color changed to yellow. After 16 h, $^{31}\text{P}\{^1\text{H}\}$ NMR indicated the full consumption of dcpBiph. Volatiles were removed in vacuo to leave a foamy yellow solid that was then dissolved in 20 mL of Et₂O. The product began to crystallize at 20 °C; the mixture was chilled to 0 °C after which the mother liquor was removed from yellow crystals that were washed quickly with 2 × 10 mL of cold pentane and dried in vacuo for 16 h; yield 855 mg (82%); ^1H NMR (C₆D₆) δ 1.22 (m, 6), 1.48–1.93 (m, 14), 1.99 (m, 2), 7.03 (m, 1), 7.14–7.25 (m, 5), 7.51 (m, 2), 7.94 (m, 1); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆) δ 26.80, 27.51 (t), 27.60 (t), 30.51 (t), 31.60 (t), 37.80 (t), 126.08, 126.12, 126.29, 126.66 (t), 128.45, 131.74 (t), 134.10 (t), 135.63 (br), 142.59 (t), 148.71 (t); $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆) δ 30.81 (br). Anal. Calcd for C₄₈H₆₂P₂Pd: C, 71.41; H, 7.74. Found: C, 71.17; H, 8.19.
- The conformation of the phosphine substituents, viewed down the P–P axis, result in a torsion angle of only 37.8° between the biphenyl substituents. This conformation may be in part stabilized by a weak C–H– π interaction between the distal rings of the two biphenyl groups. Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: New York, 2001.
- Typically, PdP₂ complexes adopt a linear or nearly linear coordination geometry. (a) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. (b) Tanaka, M. *Acta Crystallogr., Sec. C* **1992**, *4*, 739. (c) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.
- (a) Falvello, L. R.; Fornies, J.; Navarro, R.; Sicilia, B.; Tomás, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 891. (b) Falvello, L. R.; Fornies, J.; Navarro, R.; Sicilia, B.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3143.
- η^1 -arene complexes may be classified as π or σ . In the case of **1**, it is best designated as a η^1 - π complex. Hubig, S. N.; Lideman, S. V.; Kochi, S. K. *Coord. Chem. Rev.* **2000**, *200–202*, 831–873.
- Yin, Y. J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1163.
- Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 585.
- The relative broadness of the resonance at 13.5 ppm may result from an ensemble of closely related conformers, all of which possess two biphenyl groups with noncoordinating arenes. A specific arene interaction of conformer B with toluene-*d*₈ solvent is unlikely since the VT ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** in THF-*d*₆ are virtually identical.
- Full line shape analysis was performed with the gNMR 4.1 software package (Budzelaar, P. H. M. Cherwell Scientific Limited, 1999). Eyring plots of the rate constants afforded the activation parameters. A van't Hoff plot of the equilibrium constants afforded the thermodynamic parameters.
- X-ray crystal structures of **2b**, **3**, **4b**, and **4c** have been obtained. Details will be presented in a full paper.

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