Hindered Rotation about the Palladium–Aryl Bonds in [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PR_3)] and Related Molecules: X-ray Crystal Structure of (η^5-Cyclopentadienyl)[2-(phenylazo)phenyl-C^1](tricyclohexylphosphine)palladium

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The compound [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)] has been isolated from the reaction of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)] with PCy_3. It crystallizes in space group *Pbca* with a = 11.958 (1) Å, b = 19.079 (2) Å, c = 28.247 (3) Å, V = 6444.5 (12) Å^3, and Z = 8. The structure was refined by using 3252 reflections to R = 0.029. There are no significant intermolecular interactions. The PPdC(aryl) bond angle is 92.4 (2)°, and the 2-(phenylazo)phenyl group is constrained nearly perpendicular to the plane defined by these three atoms. Calculations indicate a considerable barrier to rotation about the Pd–C(aryl) bond even with phosphines less bulky than PCy_3. The retention of this conformation in solution at low temperatures is revealed by ^1H and $^{13}C\{^1H\}$ NMR studies of the related complexes [Pd(Ar)(η^5-C_5H_5)(PR_2Ph)] (Ar = 2-(phenylazo)phenyl or 2-[(methylimino)methyl]phenyl; R = Me or Et), in which the phosphine methyl or ethyl groups are magnetically nonequivalent. The observations of four nonequivalent hydrogens and five nonequivalent carbons in the analogous C_5H_4Me and $C_5H_4SiMe_3$ complexes, typical of η^5-C_5H_4R rings attached to chiral metal centers, are also compatible with significant barriers to Pd–C(aryl) rotation and allow detection of this phenomenon in complexes of the more symmetrical phosphines PEt_3 and PCy_3. Raising the solution temperatures causes coalescence of the ^1H NMR signals due to the methyl or ethyl groups of the PMe_2Ph or PEt_2Ph complexes, and merging of the ^1H and ^{13}C resonances of the C_5H_4R rings, in keeping with the onset of rapid rotation about the Pd–aryl bonds in the PEt_3, PMe_2Ph, and PEt_2Ph complexes. The NMR spectra of the more crowded [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_4Me)(PCy_3)] retain their "static" pattern above room temperature to the onset of decomposition.

Introduction

The majority of η^5-cyclopentadienyl complexes of palladium are 18-electron species. Their reactions with nucleophiles, therefore, involve substitution of a previously coordinated ligand, as in the reactions of [Pd(η^5-C_5H_5)X(PR_3)] with tertiary phosphine[1] or with CO or C_2H_4 in the presence of $AgClO_4$.[2] Where a readily displaced ligand is not present, for example in [Pd(η^5-C_5R_5)(η^3-allyl)] (R = H, Me),[3] nucleophilic attack results in a change in bonding mode of one of the coordinated ligands, in this case a η^3–η^1 conversion of the allyl group.

We have shown recently[4] that [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)] reacts with PEt_3 or P-*n*-Bu_3 by initial displacement of the coordinated nitrogen, but this reaction is reversible and the liberated phosphine attacks [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PR_3)] to give *trans*-[Pd(C_6H_4-2-N=NPh)(η^1-C_5H_5)(PR_3)$_2$]. Thus the initial product could be studied in solution but could not be isolated.

We have found that the second step in the sequence does not proceed when more bulky phosphines are employed. In this paper we report the isolation and crystal structure of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)], as well as variable-temperature NMR studies of analogous cyclopentadienyl and substituted cyclopentadienyl complexes which reveal that rotation about the Pd-C(aryl) bond is hindered at low temperatures.

Results and Discussion

Treatment of a CD_2Cl_2 or toluene-d_8 solution of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)] with PCy_3, P-*i*-Bu_3, or P(CH_2Ph)$_3$ produces a complex of the form [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PR_3)] (R = Cy, *i*-Bu, or CH_2Ph), as previously observed with PEt_3 and P-*n*-Bu_3.[4] The compounds are identified by their characteristic NMR spectra (see Experimental Section). These sterically demanding phosphines[5] differ in their reactions from those of PEt_3 and P-*n*-Bu_3 in that they do not react further to give *trans*-[Pd(C_6H_4-2-N=NPh)(η^1-C_5H_5)(PR_3)$_2$], even when present in large excess.

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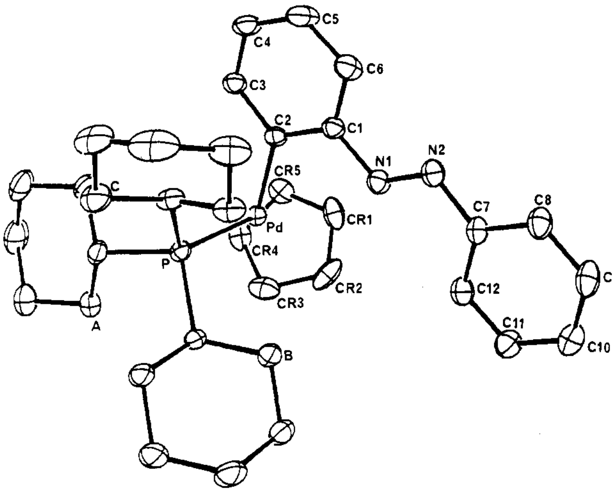

Figure 1. A perspective view of a molecule of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$. The carbon atoms of each cyclohexyl ring are numbered in order C(n1) to C(n6), starting with the atom attached to P; atom C(n2) is labeled with the ring identifier *n* = A, B, or C. Hydrogen atoms are omitted and 50% probability ellipsoids are shown.

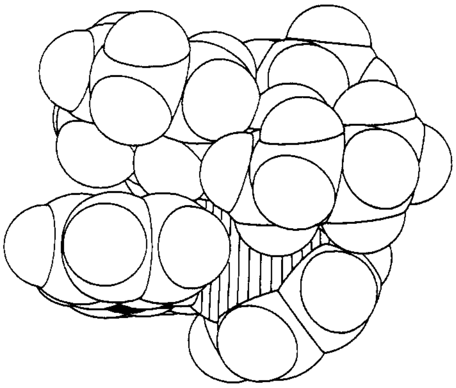

Figure 2. A space-filling model of the $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$ molecule viewed down the normal to the PdPC(2) plane. N atoms are in black, and the Pd atom is cross-hatched.

On a larger scale, when solid PCy_3 is added to a deep blue hexane solution of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)]$ the color changes to a dark blue-brown and, after solvent removal, $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$ is isolated as red crystals from petroleum ether by cooling to −30 °C. On redissolution, a deep blue solution is again produced by partial dissociation of PCy_3. Presumably it is the inability of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$ to react further with PCy_3 that allows its isolation.

Structural and Conformation Studies. X-ray analysis reveals that crystals of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$ are built up of well-separated molecules. The molecular structure is shown in Figures 1 and 2, and it is defined by the bond distances and angles presented in Table I.

The coordination of the Pd atom comprises the PCy_3 phosphine (Pd–P is 2.261 (2) Å), the 2-(phenylazo)phenyl ligand (Pd–C(2) is 1.993 (5) Å), and a η^5-C_5H_5 ring. The P–Pd–C(2) angle is 92.4 (2)°. The centroid of the η^5-C_5H_5 ring is nearly coplanar with the atoms Pd, P, and C(2), and the η^5-C_5H_5 and PdPC(2) planes are approximately normal to one another (dihedral angle = 99.4°). The metal coordination, which is conveniently described as square planar with the η^5-C_5H_5 ring occupying two mutually cis sites, is thus of a type well-established for Pd: similar $(\eta^5\text{-}C_5H_5)PdP(\sigma\text{-}C)$ units have been found in $[Pd(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(P\text{-}i\text{-}Pr_3)]$ and $[Pd(\eta^5\text{-}C_5H_5)(P\text{-}i\text{-}Pr_3)\{C_3H_4PdBr(P\text{-}i\text{-}Pr_3)\}]$.[6,7]

Table I. Selected Interatomic Distances and Angles in $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$

Bond Lengths (Å)			
Pd–P	2.261 (2)	Pd–C(2)	1.993 (5)
Pd–C(R)[a]	2.058	Pd–C(R1)	2.303 (6)
Pd–C(R2)	2.385 (6)	Pd–C(R3)	2.337 (5)
Pd–C(R4)	2.382 (5)	Pd–C(R5)	2.336 (5)
P–C(A1)	1.846 (5)	P–C(B1)	1.840 (5)
P–C(C1)	1.866 (5)	N(1)–N(2)	1.228 (6)
N(1)–C(1)	1.437 (6)	N(2)–C(7)	1.426 (6)
C(1)–C(2)	1.406 (6)	C(1)–C(6)	1.387 (7)
C(2)–C(3)	1.401 (7)	C(3)–C(4)	1.368 (7)
C(4)–C(5)	1.378 (8)	C(5)–C(6)	1.375 (8)
C(7)–C(8)	1.384 (7)	C(7)–C(12)	1.380 (7)
C(8)–C(9)	1.372 (8)	C(9)–C(10)	1.367 (8)
C(10)–C(11)	1.384 (8)	C(11)–C(12)	1.376 (7)
C(A1)–C(A2)	1.531 (7)	C(A1)–C(A6)	1.536 (7)
C(A2)–C(A3)	1.529 (8)	C(A3)–C(A4)	1.498 (9)
C(A4)–C(A5)	1.503 (10)	C(A5)–C(A6)	1.531 (8)
C(B1)–C(B2)	1.528 (6)	C(B1)–C(B6)	1.535 (6)
C(B2)–C(B3)	1.510 (7)	C(B3)–C(B4)	1.522 (7)
C(B4)–C(B5)	1.504 (8)	C(B5)–C(B6)	1.533 (7)
C(C1)–C(C2)	1.543 (7)	C(C1)–C(C6)	1.506 (7)
C(C2)–C(C3)	1.527 (8)	C(C3)–C(C4)	1.489 (11)
C(C4)–C(C5)	1.511 (10)	C(C5)–C(C6)	1.531 (7)
C(R1)–C(R2)	1.354 (9)	C(R1)–C(R5)	1.383 (9)
C(R2)–C(R3)	1.427 (9)	C(R3)–C(R4)	1.393 (9)
C(R4)–C(R5)	1.355 (7)		

Bond Angles (deg)			
P–Pd–C(2)	92.4 (2)	P–Pd–C(R)	133.6
C(2)–Pd–C(R)	133.9	Pd–P–C(A1)	110.7 (2)
Pd–P–C(B1)	110.5 (2)	Pd–P–C(C1)	115.9 (2)
C(A1)–P–C(B1)	103.9 (2)	C(A1)–P–C(C1)	105.5 (2)
C(B1)–P–C(C1)	109.6 (2)	N(2)–N(1)–C(1)	115.8 (4)
N(1)–N(2)–C(7)	115.0 (4)	N(1)–C(1)–C(2)	116.8 (4)
N(1)–C(1)–C(6)	120.9 (4)	C(2)–C(1)–C(6)	122.3 (5)
Pd–C(2)–C(1)	122.8 (4)	Pd–C(2)–C(3)	121.7 (4)
C(1)–C(2)–C(3)	115.5 (4)	C(2)–C(3)–C(4)	122.0 (5)
C(3)–C(4)–C(5)	121.2 (5)	C(4)–C(5)–C(6)	118.9 (5)
C(1)–C(6)–C(5)	119.9 (5)	N(2)–C(7)–C(8)	115.4 (4)
N(2)–C(7)–C(12)	124.5 (4)	C(8)–C(7)–C(12)	120.1 (5)
C(7)–C(8)–C(9)	119.7 (5)	C(8)–C(9)–C(10)	120.8 (5)
C(9)–C(10)–C(11)	119.3 (5)	C(10)–C(11)–C(12)	120.7 (5)
C(7)–C(12)–C(11)	119.3 (5)	P–C(A1)–C(A2)	114.3 (4)
P–C(A1)–C(A6)	109.5 (3)	C(A2)–C(A1)–C(A6)	110.2 (4)
C(A1)–C(A2)–C(A3)	111.1 (4)	C(A2)–C(A3)–C(A4)	111.8 (5)
C(A3)–C(A4)–C(A5)	111.8 (5)	C(A4)–C(A5)–C(A6)	111.7 (5)
C(A1)–C(A6)–C(A5)	112.1 (4)	P–C(B1)–C(B2)	114.5 (3)
P–C(B1)–C(B6)	116.0 (3)	C(B2)–C(B1)–C(B6)	110.7 (4)
C(B1)–C(B2)–C(B3)	111.1 (4)	C(B2)–C(B3)–C(B4)	111.6 (4)
C(B3)–C(B4)–C(B5)	111.2 (5)	C(B4)–C(B5)–C(B6)	112.0 (4)
C(B1)–C(B6)–C(B5)	110.2 (4)	P–C(C1)–C(C2)	118.5 (4)
P–C(C1)–C(C6)	113.7 (4)	C(C2)–C(C1)–C(C6)	110.2 (4)
C(C1)–C(C2)–C(C3)	109.1 (5)	C(C2)–C(C3)–C(C4)	113.4 (6)
C(C3)–C(C4)–C(C5)	111.3 (5)	C(C4)–C(C5)–C(C6)	111.2 (5)
C(C1)–C(C6)–C(C5)	111.5 (5)	C(R2)–C(R1)–C(R5)	110.4 (5)
C(R1)–C(R2)–C(R3)	105.9 (5)	C(R2)–C(R3)–C(R4)	107.0 (5)
C(R3)–C(R4)–C(R5)	108.6 (5)	C(R1)–C(R5)–C(R4)	107.7 (5)

[a] C(R) is the centroid of the cyclopentadienyl ring carbon atoms C(R1)–C(R5).

The $(\eta^5\text{-}C_5H_5)Pd$ unit displays approximate local C_s rather than C_{5v} symmetry: the approximate plane of symmetry contains Pd, C(R3), and the midpoint of the C(R1)–C(R5) bond and nearly coincides with the PdPC(2) plane. The PdC(R2) and PdC(R4) distances (2.385 (6) and 2.382 (5) Å) are longer than the other Pd–C (cyclopentadienyl) distances (2.303 (6)–2.337 (5) Å), mainly because of deviations of the C_5 ring from planarity: C(R2)

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Table II. Variable-Temperature ^1H NMR Data[a] for the Complexes $[Pd(C_6H_4\text{-}2\text{-}X)(\eta^5\text{-}C_5H_4R)L]$ in C_7D_8 Solution

				δ (J_{PH}, Hz)	
R	X	L	temp (°C)	C_5H_4R	L
CH_3	N=NPh	PEt_3	−70	5.63 (s), 5.70 (s), 5.83 (s), 5.95 (s), 1.94 (d, 3.1)	
			$+23^b$	5.58 (m), 5.68 (m), 1.86 (d, 3.3)	
H	N=NPh	PMe_2Ph	-60^c	5.81 (d)	0.92 (d, 11.3), 0.96 (d, 11.2)
			−10	5.77 (d)	1.01 (d, 10.2)
CH_3	N=NPh	PMe_2Ph	−80	5.64 (d, 1.9), 5.73 (d, 1.6), 5.84 (br), 5.88 (br), 1.86 (d, 3.4)	0.92 (d, 10.8), 0.96 (d, 10.7)
			0^d	5.59 (m), 5.67 (m), 1.79 (d, 3.4)	1.03 (d, 10.0)
H	N=NPh	PEt_2Ph	-70^e	5.88 (d, 1.2)	$\mathrm{pC}H_2$ at 1.02 (br), 1.24 (br); $\mathrm{PCH_2C}H_3$ at 0.55 (dt, 17.0, $^3J_{HH}$ = 7.5), 0.74 (dt, 18.3, $^3J_{HH}$ = 7.5)
			0	5.80 (d)	$\mathrm{PC}H_2$ at 1.31 (m); $\mathrm{PCH_2C}H_3$ at 0.67 (dt, 17.6, $^3J_{HH}$ = 7.4)
CH_3	N=NPh	PEt_2Ph	-50^f	5.69 (s), 5.71 (s), 5.81 (s), 5.85 (s), 1.83 (d, 3.7)	$\mathrm{PC}H_2$ at 1.05 (m), 1.31 (m); $\mathrm{PCH_2C}H_3$ at 0.60 (dt, 17.2, $^3J_{HH}$ = 7.9), 0.75 (dt, 18.1, $^3J_{HH}$ = 7.5)
			+30	5.60 (br), 5.68 (br), 1.80 (d)	$\mathrm{PC}H_2$ at 1.38 (m); $\mathrm{PCH_2C}H_3$ at 0.70 (dt)
CH_3	N=NPh	PCy_3	−70	5.72–5.86 (complex m), 1.83 (d, 3.2)	
			$+23^g$	5.68 (br), 1.79 (d, 3.3)	
$SiMe_3$	N=NPh	PMe_2Ph	-70^h	5.53 (s), 5.65 (m), 5.97 (m), 6.00 (s), 0.29 (s)	0.89 (d, 9.8), 0.92 (d, 9.9)
			0	5.64 (br), 5.89 (br), 0.23 (s)	1.04 (d, 10.2)
$SiMe_3$	N=NPh	PEt_2Ph	-50^i	5.75 (m), 5.80 (m), 5.92 (m), 6.16 (br), 0.29 (s)	$\mathrm{PC}H_2$ at 0.96 (m), 1.32 (m); $\mathrm{PCH_2C}H_3$ at 0.58 (dt, 16.8, $^3J_{HH}$ = 8.0), 0.72 (dt, 18.1, $^3J_{HH}$ = 7.5)
			+20	5.76 (m), 5.92 (v br), 0.21 (s)	$\mathrm{PC}H_2$ at 1.4 (m); $\mathrm{PCH_2C}H_3$ at 0.68 (dt, 16.9, $^3J_{HH}$ = 8.0)
H	$CH{=}NCH_3$	PMe_2Ph	-70^j	5.75 (d, 1.4)	0.80 (d, 10.0), 0.83 (d, 10.0)
			+20	5.68 (d)	0.96 (d, 9.9)
H	$CH{=}NCH_3$	PEt_2Ph	-70^k	5.77 (d, 1.2)	$\mathrm{PC}H_2$ at 1.15 (m); $\mathrm{PCH_2C}H_3$ at 0.58 (dt, 17.3, $^3J_{HH}$ = 7.6), 0.61 (dt, 17.3, $^3J_{HH}$ = 7.4)
			0	5.72 (d, 1.5)	$\mathrm{PC}H_2$ at 1.24 (m); $\mathrm{PCH_2C}H_3$ at 0.64 (dt, 17.5, $^3J_{HH}$ = 7.5)

[a] Recorded at 300 MHz and referenced to CHD_2 at 2.09 ppm. [b] δ(P) 32.6. [c] δ(P) 7.3 (−50 °C). [d] δ(P) 6.1 (−20 °C). [e] δ(P) 35.8 (−50 °C). [f] δ(P) 35.3. [g] δ(P) 51.5. [h] δ(P) 5.6 (−60 °C). [i] δ(P) 33.3. [j] $CH{=}$ at δ 8.99 (d, 1.2), $\mathrm{NC}H_3$ at δ 3.51 (d); δ(P) 6.8. [k] $CH{=}$ at δ 8.96 (d, 1.3), $\mathrm{NC}H_3$ at δ 3.51 (d, 1.5); δ(P) 34.1 (−50 °C).

and C(R4) are displaced by 0.037 (6) and 0.022 (5) Å from the mean ring plane away from the Pd atom, counterbalanced by the displacements of C(R1), C(R3), and C(R5) (respectively 0.017 (5), 0.035 (5), and 0.005 (5) Å) toward the Pd atom. The ring C–C bond lengths fall into two groups, C(R1)–C(R2) and C(R4)–C(R5) (1.354 (9) and 1.355 (7) Å) being somewhat shorter than the remainder (1.383 (9)–1.427 (9) Å). Electronic factors, arising from lack of axial symmetry at the metal, may be responsible for these distortions, as has been suggested for $[Pd(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(P\text{-}i\text{-}Pr_3)]$.[6]

The C_6H_4-2-N=NPh ligand has the expected trans stereochemistry about the N=N bond [C(1)–N(1)–N(2)–C(7) = 177.4 (6)°] and is coplanar to within ±0.12 Å. The ligand plane is roughly normal to the PdPC(2) plane [P–Pd–C(2)–C(1) = ω_1 = 100.7 (4)°]. The short N(1)···C(12) and N(2)···C(6) contacts [2.73 (1) and 2.69 (1) Å] are relieved by deformations of the N–C–C angles at C(1) and C(7) and by twisting of the phenyl rings out of the $N_2C(1)$ and $N_2C(7)$ planes [N(2)–N(1)–C(1)–C(6) = −4.2 (5)° and N(1)–N(2)–C(7)–C(12) = 3.7 (5)°]. The narrowing of the C(1)–C(2)–C(3) angle to 115.5 (4)° as a result of the attachment of C(2) to Pd is similar to that found in *trans*-$[PdCl(C_6H_4\text{-}2\text{-}N{=}NPh)(PEt_3)_2]$.[8]

The geometry of the PCy_3 ligand is unexceptional. The cyclohexyl rings display chair conformations, the mean C–C bond length is 1.520 (4) Å, C–C–C bond angles are close to tetrahedral [109.1 (5)–113.4 (6)°], and |C–C–C–C| torsion angles are 53.4 (6)–57.6 (5)°. The P–C bonds [mean length 1.851 (8) Å] are equatorial to each ring.

The most significant interligand contact is that of 3.18 (1) Å between C(2) and C(C1). This arises from the orientation of the PCy_3 ligand which is such that the bonds P–C(C1) and Pd–C(2) are nearly coplanar [C(2)–Pd–P–C(C1) = ω_2 = −5.9 (2)°]. We have calculated the molecular potential energy[9] of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$ as a function of the torsion angles ω_1 and ω_2 in order to aid interpretation of the NMR data for this and related complexes (see below). The principal minima in the molecular potential energy occur at ω_1 = 110° and ω_2 = −10°, corresponding to the conformation found in the crystal, and at ω_1 = −100° and ω_2 = −10°, corresponding roughly to a rotation of the C_6H_4-2-N=NPh ligand by 180° about the Pd–C(2) bond. Intermediate values of ω_1 give high potential energies and unacceptably close interligand contacts whatever the value of ω_2. The calculations thus suggest that stable conformations of the molecule require the C_6H_4-2-N=NPh ligand to be roughly normal to the PdPC(2) plane and that the barrier to interconversion between the two low-energy conformers by rotation about the Pd–C(2) bond is considerable. Even if PCy_3 is replaced by a less sterically demanding phosphine, such as PMe_3, the barrier to rotation about Pd–C(2) is still substantial. In this case, however, the calculated molecular energy is insensitive to rotation of the PMe_3 ligand about the Pd–P bond.

NMR Spectroscopic Studies. Addition of 1 mol equiv of PMe_2Ph or PEt_2Ph (L) to a C_7D_8 solution of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)]$ in a 5-mm NMR tube generates the new derivatives $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)L]$, analogous to the PCy_3 complex described above and those of PEt_3 and P-*n*-Bu_3 reported previously.[4] Their

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Table III. Variable-Temperature $^{13}C\{^1H\}$ NMR Data[a] for the Complexes $[Pd(C_6H_4\text{-}2\text{-}X)(\eta^5\text{-}C_5H_4R)L]$ in C_7D_8 Solution

R	X	L	temp (°C)	δ (J_{PC}, Hz) C_5H_4R	 L
CH_3	N=NPh	PEt_3	−50	92.40 (s), 93.27 (s), 97.47 (s), 98.72 (s), 110.81 (d, 6.6, ipso), 14.21 (d, 3.8)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 17.85 (d, 28.9); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 7.69 (d, 5.0)
H	N=NPh	PMe_2Ph	−70	96.37 (d)	17.37 (d, 31.0), 18.59 (d, 30.5)
			−10	96.52 (d, 2.8)	18.3 (br d, 27.5)
CH_3	N=NPh	PMe_2Ph	−80	93.35 (s), 94.35 (s), 97.72 (s), 99.00 (s), 110.98 (d, 7.9, ipso), 14.07 (s)	17.33 (d, 32.5), 18.13 (d, 30.2)
			0	94.12 (br s), 97.92 (s), 98.3 (v br), 111.26 (d, 6.7, ipso), 13.9 (br s)	17.8 (v br)
H	N=NPh	PEt_2Ph	−70	96.37 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 18.61 (d, 30.2), 21.57 (d, 26.6); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 8.04 (s), 8.09 (s)
			0	96.67 (d, 2.7)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ obscured by CD_3 signal; $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 8.16 (s)
CH_3	N=NPh	PEt_2Ph	−70	93.44 (s), 94.21 (s), 98.08 (s), 99.25 (s), 110.86 (d, 8.1, ipso), 14.16 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 19.39 (d, 33.0), 21.15 (d, 32.3); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 8.06 (s), 8.22 (s)
			+30	94.44 (br), 98.95 (br), ipso carbon not observed, 14.08 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 20.86 (d, 28.9); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 8.23 (s)
CH_3	N=NPh	PCy_3	+23	94.29 (s), 94.90 (s), 99.09 (s), 99.82 (s), 111.76 (d, 7.8, ipso), 14.29 (s)	
$SiMe_3$	N=NPh	PMe_2Ph	−70	98.73 (s), 99.72 (d, 9.8), 100.71 (s), 101.99 (s), 106.84 (s), 0.66 (s)	17.25 (d, 32.8), 17.88 (d, 31.9)
			0	99.86 (s), 100.13 (s), 101.17 (v br), 107.28 (s, ipso), 0.8 (s)	17.98 (br d, 31.3)
$SiMe_3$	N=NPh	PEt_2Ph	−70	99.08 (s), 99.58 (s), 100.41 (s), 101.92 (s), 106.34 (s, ipso), 0.44 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 18.05 (d, 30.3), 21.3 (d, ~30, partly obscured by CD_3 signal); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 7.77 (s), 7.86 (s)
			+30	100.10 (br), 101.18 (br), 107.21 (s, ipso), 0.51 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ obscured by CD_3 signal; $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 8.09 (s)
H	CH=NCH_3	PMe_2Ph	−70[b]	96.28 (s)	17.19 (d, 32.6)[c]
			+20	96.65 (s)	17.82 (d, 31.7)
H	CH=NCH_3	PEt_2Ph	−70[d]	96.32 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 19.11 (d, 30.2), 19.38 (d, 25.4); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 7.82 (s), 7.90 (s)
			0	96.62 (s)	$\mathrm{P}\mathit{C}\mathrm{H_2}$ at 19.96 (d, 28.4); $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$ at 7.98 (s)

[a] Recorded at 75.4 MHz and referenced to CD_3 at 20.40 ppm. [b] $\mathrm{N}\mathit{C}\mathrm{H_3}$ at δ 48.81 (s). [c] The methyl signals appear to be coincident. [d] $\mathrm{N}\mathit{C}\mathrm{H_3}$ at δ 48.81 (s).

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data are listed in Tables II and III. At temperatures near −70 °C, it is clear from the ^1H and $^{13}C\{^1H\}$ spectra that the two methyl or ethyl phosphine substituents are magnetically nonequivalent, and therefore no plane of symmetry containing the Pd–P bond exists. ^1H NMR measurements of this type have often been used to establish solution conformations, particularly for PMe_2Ph complexes,[10] but to our knowledge this is the first report of the use of $^{13}C\{^1H\}$ NMR spectroscopy for such analyses. These observations are entirely compatible with the 2-(phenylazo)phenyl ligand lying out of the PPdC(aryl) plane in solution, as it does in the tricyclohexylphosphine complex in the solid state.

At −10 °C, both the ^1H and $^{13}C\{^1H\}$ NMR spectra of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)L]$ indicate that the phosphine alkyls are now magnetically equivalent. This presumably comes about by rapid (on the NMR time scale) rotation or oscillation of the aryl group about its Pd–C bond between the two calculated potential energy minima. Retention of couplings between phosphorus and the C_5-ring carbons and hydrogens precludes a dissociative route being responsible for the apparent equivalences.

Since an important contribution to the rotational barriers for the aryl groups arises from the ortho substituents,[10] we have extended our observations to 2-[(methylimino)methyl]phenyl complexes. Treatment of $[Pd(C_6H_4\text{-}2\text{-}CH{=}NMe)(\eta^5\text{-}C_5H_5)]$[11] with PMe_2Ph or PEt_2Ph produces the new 2-(iminomethyl)phenyl complexes $[Pd(C_6H_4\text{-}2\text{-}CH{=}NMe)(\eta^5\text{-}C_5H_5)L]$, for which NMR data are given in Tables II and III. The PMe_2Ph and PEt_2Ph derivatives again exhibit magnetically nonequivalent alkyl (phosphine) groups at −70 °C, indicating a similar conformation to the 2-(phenylazo)phenyl complexes. Above 0 °C the alkyl groups are magnetically equivalent, indicative of rotation or oscillation of the aryl group.

To confirm that the same phenomenon exists with the more symmetrical phosphines PEt_3 and PCy_3, we have introduced an element of dissymmetry into the cyclopentadienyl ring. The methylcyclopentadienyl complex $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4Me)]$ was prepared from the reaction of $[Pd_2(C_6H_4\text{-}2\text{-}N{=}NPh)_2(\mu\text{-}Cl)_2]$ with NaC_5H_4Me, generated in situ from C_5H_5Me and NaOEt in ethanol. The (trimethylsilyl)cyclopentadienyl complex $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4SiMe_3)]$ was prepared similarly by using $LiC_5H_4SiMe_3$, generated by treating $C_5H_5SiMe_3$ with *n*-butyllithium in hexane solution. Both complexes form air-stable, black crystals that dissolve readily in organic solvents to produce intense green-purple solutions. Addition of 1 mol equiv of PEt_3, PMe_2Ph, PEt_2Ph, or PCy_3 to a C_7D_8 solution of the methylcyclopentadienyl complex, or of PMe_2Ph or PEt_2Ph to a C_7D_8 solution of the (trimethylsilyl)cyclopentadienyl complex, produces the species $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4R)L]$; NMR data for these novel compounds are presented in Tables II and III.

The C_5H_4R complexes with PMe_2Ph or PEt_2Ph give rise to analogous spectroscopic observations as far as the

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Table IV. ^{1}H NMR Coalescence Temperatures[a] and $\Delta G^\ddagger$ Values[b] for the Complexes $[Pd(C_6H_4\text{-}2\text{-}X)(\eta^5\text{-}C_5H_4R)L]$ in C_7D_8 Solution

R	X	L	T_c (K)	$\Delta G^\ddagger$ (kcal/mol)
H	N=NPh	PMe_2Ph	225	11.8
CH_3	N=NPh	PMe_2Ph	245	12.7
$SiMe_3$	N=NPh	PMe_2Ph	226	11.9
H	N=NPh	PEt_2Ph	235	11.4
H	N=NPh	PEt_2Ph[c]	224	11.1
CH_3	N=NPh	PEt_2Ph	225	12.5
$SiMe_3$	N=NPh	PEt_2Ph	273	13.5
H	CH=NMe	PMe_2Ph	252	13.1
H	CH=NMe	PEt_2Ph	244	12.9

[a] Measured for the phosphine methyl groups in each case. [b] Obtained by means of the equation $\Delta G^\ddagger = 0.004\,57T_c(9.97 + \log T_c/\Delta\delta)$.[14] [c] In CD_2Cl_2 solution.

phosphine alkyl groups are concerned, but the presence of the ring substituents provides another probe of asymmetry even with nondiastereotopic phosphines. Thus, in $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4R)L]$ (R = Me, L = PEt_3, PMe_2Ph, PEt_2Ph, or PCy_3; R = $SiMe_3$, L = PMe_2Ph or PEt_2Ph) the C_5H_4 ring gives rise to four ^{1}H and five ^{13}C resonances at low temperature. Similar observations have been made for optically active rhenium[12] and ruthenium[13] methylcyclopentadienyl complexes. In our complexes each carbon resonance appears as a singlet, with the exception of the ipso carbon which exhibits coupling to phosphorus. As the temperature is raised, the four ^{1}H signals gradually merge into two, and at 0 °C or above only two ^{1}H and three ^{13}C resonances are detected for the PEt_3, PMe_2Ph, and PEt_2Ph complexes. Even at +23 °C, however, $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4Me)(PCy_3)]$ exhibits five carbon resonances for the C_5H_4 unit, indicating that rotation about the Pd–C(aryl) bond is still hindered at this temperature with the more bulky PCy_3 ligand. Above this temperature, decomposition of the complex occurs.

We have determined coalescence temperatures for each of the PMe_2Ph and PEt_2Ph complexes by monitoring the ^{1}H methyl signals. These, together with $\Delta G^\ddagger$ values calculated at the coalescence temperature,[14] are given in Table IV. The temperature dependence and small chemical shift differences for the PMe_2Ph complexes may lead to small errors in $\Delta G^\ddagger$, but this is not the case for the PEt_2Ph complexes. For $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4R)(PEt_2Ph)]$ (R = H, Me, $SiMe_3$) $\Delta\delta$ is at least 7 times greater than the chemical shift variation over a 100 °C temperature range in C_7D_8. For $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PEt_2Ph)]$ in CD_2Cl_2 solution, coalescences of the CH_3 signals in the ^{1}H NMR spectrum and of the CH_2 resonances in the $^{13}C\{^1H\}$ NMR spectrum (where the peak separation is greater) lead to consistent $\Delta G^\ddagger$ values. Thus, there is a steady increase in the coalescence temperature and $\Delta G^\ddagger$ in the order $C_5H_5 < C_5H_4Me < C_5H_4SiMe_3$ for the PEt_2Ph complexes. There is also a small solvent effect on changing from C_7D_8 to CD_2Cl_2. The increasing $\Delta G^\ddagger$ with the size of the cyclopentadienyl substituent is to be expected, since the presence of a substituent will cause greater hindrance to rotation about the Pd–C(aryl) bond.

Experimental Section

Table V. Crystallographic Data for $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_5)(PCy_3)]$

formula	$C_{35}H_{47}N_2PPd$
fw, amu	633.1
cryst system	orthorhombic
space group	*Pbca*
a, Å	11.958 (1)
b, Å	19.079 (2)
c, Å	28.247 (3)
V, Å^3	6444.5 (12)
Z	8
F(000), electrons	2656
d(calcd), g cm^{-3}	1.305
μ(Mo Kα), cm^{-1}	6.4
transmissn on *F*	0.85–1.16
intensity measurements	
scan type	$\theta/2\theta$
scan width ($\Delta\omega$), deg	1.2
max counting time, s	120
2θ range, deg	4–50
q[a]	0.03
unique reflectns	6123
final refinement	
reflectns used (*n*) [$I \geq 3\sigma(I)$]	3252
refined parameters (p)	352
max shift/error	0.018
R[b]	0.029
R_w[c]	0.036
S[d]	1.6
weights, *w*	σ^{-2}(F)
$\lvert\Delta\rho\rvert$, electrons	0.40

[a] Manojlovič-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 2427. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [d] $S = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$.

NMR spectra were recorded on a Varian XL-300 spectrometer operating in the Fourier Transform mode. Probe temperatures were calibrated by using the temperature-dependent chemical shift differences of the ^{1}H resonances of methanol.[15] Microanalyses were performed at the University of Glasgow, the Institut de Quimica Bio-Organica de Barcelona (C.S.I.C.), and Galbraith Microanalytical Laboratories, Knoxville, TN. The compounds $[Pd_2(C_6H_4\text{-}2\text{-}N{=}NPh)_2(\mu\text{-}Cl)_2]$,[16] $[Pd_2(C_6H_4\text{-}2\text{-}CH{=}NMe)_2(\mu\text{-}Cl)_2]$,[11] $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta\text{-}C_5H_5)]$,[4] and $[Pd(C_6H_4\text{-}2\text{-}CH{=}NMe)(\eta\text{-}C_5H_5)]$[11] were prepared as described previously. Methylcyclopentadiene was distilled following the method of Reynolds and Wilkinson.[17] Cyclopentadienyltrimethylsilane was prepared by treating C_5H_6 successively with *n*-butyllithium then Me_3SiCl in ether. After filtration and solvent removal it was used without futher purification.

Preparation of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4Me)]$. To a solution of sodium ethoxide (5.6 mmol, prepared from 0.13 g of sodium) in ethanol (50 mL) was added freshly distilled methylcyclopentadiene (2.0 mL), followed by $[Pd_2(C_6H_4\text{-}2\text{-}N{=}NPh)_2(\mu\text{-}Cl)_2]$ (1.5 g, 2.3 mmol). The solution slowly developed a deep blue-green color. Stirring was continued for 3 days, then unreacted $[Pd_2(C_6H_4\text{-}2\text{-}N{=}NPh)_2(\mu\text{-}Cl)_2]$ (0.2 g, identified by its infrared spectrum) was removed by filtration. Removal of the solvent from the filtrate left a black semisolid. Extraction with petroleum, followed by slow evaporation of the solvent at −30 °C in vacuo, gave the product as a black powder (0.4 g, 35%). Anal. Calcd for $C_{18}H_{16}N_2Pd$: C, 58.9; H, 4.4; N, 7.6. Found: C, 59.0; H, 4.5; N, 7.6. ^{1}H NMR (C_7D_8, −50 °C): δ 5.39 (apparent triplet, J_{HH} = 2.2 Hz), 5.47 (apparent triplet, J_{HH} = 2.2 Hz), 1.79 (CH_3). $^{13}C\{^1H\}$ NMR: C_5H_4 at δ 95.18, 97.85, 110.85 (ipso); CH_3 at δ 13.15; phenyl carbons at δ 123.71, 124.14, 125.52, 128.65, 129.78, 131.55, 140.02, 154.25, 162.31, 182.82.

Preparation of $[Pd(C_6H_4\text{-}2\text{-}N{=}NPh)(\eta^5\text{-}C_5H_4SiMe_3)]$. A hexane solution of *n*-butylithium (5.5 mL, 1.5 M) was added to a stirred solution of $Me_3SiC_5H_5$ (3.0 mL) in diethyl ether (50 mL). A white precipitate formed. $[Pd_2(C_6H_4\text{-}2\text{-}N{=}NPh)_2(\mu\text{-}Cl)_2]$ (2.0

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Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)]

	x/a	y/b	z/c	U,[a] Å^2
Pd	0.20196 (3)	0.17287 (1)	0.16674 (1)	0.042
P	0.21638 (9)	0.27560 (5)	0.12731 (4)	0.043
N(1)	0.3501 (3)	0.0778 (2)	0.1001 (1)	0.055
N(2)	0.4149 (3)	0.0397 (2)	0.0783 (1)	0.067
C(1)	0.2374 (4)	0.0798 (2)	0.0826 (2)	0.052
C(2)	0.1605 (4)	0.1208 (2)	0.1082 (2)	0.048
C(3)	0.0516 (4)	0.1223 (2)	0.0899 (2)	0.057
C(4)	0.0232 (4)	0.0881 (3)	0.0491 (2)	0.071
C(5)	0.1012 (5)	0.0503 (3)	0.0239 (2)	0.082
C(6)	0.2078 (4)	0.0442 (3)	0.0417 (2)	0.071
C(7)	0.5275 (4)	0.0407 (2)	0.0950 (2)	0.053
C(8)	0.6027 (5)	0.0019 (3)	0.0685 (2)	0.074
C(9)	0.7135 (4)	0.0007 (3)	0.0812 (2)	0.078
C(10)	0.7509 (4)	0.0383 (3)	0.1192 (2)	0.074
C(11)	0.6752 (4)	0.0763 (3)	0.1460 (2)	0.071
C(12)	0.5636 (4)	0.0777 (2)	0.1341 (2)	0.062
C(A1)	0.1077 (4)	0.3378 (2)	0.1471 (2)	0.053
C(A2)	0.1251 (4)	0.3661 (2)	0.1972 (2)	0.061
C(A3)	0.0300 (5)	0.4154 (3)	0.2115 (2)	0.083
C(A4)	−0.0818 (5)	0.3805 (3)	0.2076 (2)	0.102
C(A5)	−0.1021 (4)	0.3520 (3)	0.1588 (2)	0.094
C(A6)	−0.0078 (4)	0.3030 (3)	0.1429 (2)	0.068
C(B1)	0.3485 (3)	0.3198 (2)	0.1423 (1)	0.046
C(B2)	0.4522 (4)	0.2734 (2)	0.1382 (2)	0.053
C(B3)	0.5536 (4)	0.3093 (2)	0.1589 (2)	0.067
C(B4)	0.5742 (4)	0.3803 (3)	0.1360 (2)	0.090
C(B5)	0.4723 (4)	0.4263 (2)	0.1395 (2)	0.086
C(B6)	0.3684 (4)	0.3910 (2)	0.1184 (2)	0.063
C(C1)	0.2013 (4)	0.2704 (2)	0.0616 (1)	0.056
C(C2)	0.1562 (5)	0.3350 (3)	0.0349 (2)	0.083
C(C3)	0.1320 (6)	0.3147 (3)	−0.0163 (2)	0.105
C(C4)	0.2304 (7)	0.2843 (4)	−0.0413 (2)	0.119
C(C5)	0.2778 (5)	0.2225 (3)	−0.0145 (2)	0.097
C(C6)	0.3032 (4)	0.2419 (2)	0.0369 (2)	0.065
C(R1)	0.2322 (5)	0.0821 (3)	0.2189 (2)	0.079
C(R2)	0.3083 (4)	0.1307 (4)	0.2322 (2)	0.086
C(R3)	0.2454 (6)	0.1907 (3)	0.2465 (2)	0.077
C(R4)	0.1330 (5)	0.1714 (3)	0.2459 (2)	0.067
C(R5)	0.1249 (4)	0.1058 (2)	0.2278 (2)	0.066

[a] U is the mean latent root of the anisotropic displacement tensor.

g, 3.1 mmol) was added as a solid, and stirring was continued for 2 h, during which time a deep blue-black color developed. The solution was filtered, and the solvent was removed under reduced pressure. The oily residue was crystallized from petroleum ether to give the product as dark purple crystals (1.3 g, 50%). Anal. Calcd for $C_{20}H_{22}N_2PdSi$: C, 56.5; H, 5.2; N, 6.6. Found: C, 56.6; H, 5.2; N, 6.4. ^{1}H NMR (C_7D_8, 22 °C): δ 5.60 (apparent triplet, J_{HH} = 2.0 Hz), 5.82 (apparent triplet, J_{HH} = 2.0 Hz), 0.09 ($SiMe_3$). $^{13}C\{^1H\}$ NMR: C_6H_4 at δ 100.01, 100.14, 110.46 (ipso); $SiMe_3$ at δ 0.43; phenyl carbons, at δ 123.88, 124.25, 125.74, 128.66, 130.04, 131.83, 154.73, 162.62, 180.97.

Preparation of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)]. Tricyclohexylphosphine (0.16 g, 0.57 mmol) was added to a hexane solution (10 mL) of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)] (0.20 g, 0.57 mmol) under argon. The solvent was removed after 3 h, and the residue was washed with hexane (5 mL) to give a deep blue solution and a red-brown solid. The latter was dissolved in petroleum ether, and cooling to −30 °C gave the product as red crystals (0.20 g, 56%). Anal. Calcd for $C_{35}H_{47}N_2PPd$: C, 66.4; H, 7.5; N, 4.4. Found: C, 66.3; H, 7.5; N, 4.3. ^{1}H NMR (CD_2Cl_2, 23 °C): δ 5.64 (d, J_{PH} = 3.0 Hz, Cp). $^{13}C\{^1H\}$ NMR: δ(C) 97.01 (d, J_{PC} = 3.8 Hz, Cp), 115.05, 123.31, 123.60, 127.88, 129.27, 130.19, 143.19, 148.78 (d, J_{PC} = 10.9 Hz), 153.51, 160.98. $^{31}P\{^1H\}$ NMR: δ(P) 49.91. Crystals suitable for X-ray structure determination were obtained by recrystallization from petroleum ether at −30 °C.

Reaction of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)] with PEt_2Ph. The complex (20.8 mg, 0.0605 mmol) was weighed into a 5-mm NMR tube fitted with a rubber septum. The tube was evacuated and then filled with argon, and toluene-d_8 (0.4 mL) was introduced by syringe. After the complex dissolved to give a deep blue-black solution, PEt_2Ph (10.5 μL, 0.0603 mmol) was added and the solution became dark brown. The tube was then transferred to the NMR probe, which had been precooled to −50 °C, and the complex [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PEt_2Ph)] was examined in situ.

The other complexes of the type [Pd(C_6H_4-2-X)(η^5-C_5H_4R)L] were generated similarly. NMR data for the complexes [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)L] (L = P-*i*-Bu_3 or $P(CH_2Ph)_3$) are as follows. [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(P-*i*-Bu_3)]: ^{1}H NMR (C_7D_8, +24 °C) C_5H_5 at δ 5.76 (d, J_{PH} = 1.3 Hz); $^{31}P\{^1H\}$ NMR δ(P) 24.7. [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5){$P(CH_2Ph)_3$}]: ^{1}H NMR (C_7D_8, −20 °C) C_5H_5 at δ 5.21 (d, J_{PH} 1.6 Hz), PCH_2 at δ 2.75; $^{31}P\{^1H\}$ NMR δ(P) 26.8.

X-ray Structure Analysis of [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)]. The experimental and computational procedures have been described in detail elsewhere.[18] Pertinent details of this analysis are presented in Table V. All X-ray measurements were made at 22 ± 1 °C by using an Enraf-Nonius CAD4F diffractometer and graphite-monochromated Mo X-rays (λ = 0.71069 Å). The specimen was a red plate, 0.52 × 0.36 × 0.12 mm.

The unit-cell dimensions were determined by a least-squares treatment of the setting angles of 22 high-angle reflections. The intensities were corrected for background, *Lp*, and absorption effects. *R*(internal) = 0.033 for averaging the intensities of 1404 reflections measured more than once. The space group was determined from the systematic absences.

The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares. In the final calculations anisotropic displacement parameters were adjusted for Pd, P, N, and C atoms. H atoms were constrained to ride on their attached C atoms with C–H = 0.96 Å and $U(H) = 1.2U_{iso}(C)$. Neutral atom scattering factor and anomalous dispersion corrections were taken from ref 19. All calculations were performed on a GOULD 32/27 minicomputer using the locally developed GX system.[20] Final coordinates of non-hydrogen atoms are presented in Table VI.

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Registry No. [Pd_2(C_6H_4-2-N=NPh)$_2$(μ-Cl)$_2$], 14873-53-1; [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_4Me)], 114762-97-9; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4SiMe_3$)], 114762-98-0; [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)], 85453-00-5; [Pd(C_6H_4-2-CH=NCH_3)(η^5-C_5H_5)], 39015-52-6; [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PCy_3)], 114762-99-1; [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PEt_2Ph)], 114763-00-7; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4CH_3$)(PEt_3)], 114763-01-8; [Pd(C_6H_4-2-N=NPh)(η^5-C_5H_5)(PMe_2Ph)], 114763-02-9; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4CH_3$)(PMe_2Ph)], 114763-03-0; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4CH_3$)(PEt_2Ph)], 114763-04-1; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4CH_3$)(PCy_3)], 114763-05-2; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4SiMe_3$)(PMe_2Ph)], 114763-06-3; [Pd(C_6H_4-2-N=NPh)(η^5-$C_5H_4SiMe_3$)(PEt_2Ph)], 114763-07-4; [Pd(C_6H_4-2-CH=NCH_3)(η^5-C_5H_5)(PMe_2Ph)], 114763-08-5; [Pd(C_6H_4-2-CH=NCH_3)(η^5-C_5H_5)(PEt_2Ph)], 114763-09-6; $Me_3SiC_5H_5$, 25134-15-0; methylcyclopentadiene, 26519-91-5.

Supplementary Material Available: Anisotropic displacement parameters (Table VII) and hydrogen atom parameters (Table VIII) (3 pages); a listing of final $|F_o|$ and $|F_c|$ values (Table IX) (14 pages). Ordering information is given on any current masthead page.

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