One-Step Assembly of a Chiral Palladium Bis(Acyclic Carbene) Complex and Its Unexpected Oxidation to a Bis(amidine) Complex

Yoshitha A. Wanniarachchi, and LeGrande M. Slaughter*

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078 USA email: <u>lms@chem.okstate.edu</u>

SUPPLEMENTARY INFORMATION

CONTENTS

Experimental	p. S2
Details of X-ray crystallographic analyses	p. S4
Computational details	p. S6
Optimized geometries of conformational isomers of 3 and GAUSSIAN03 archive files	p. S7
References	p. S25

EXPERIMENTAL

General Considerations. All manipulations were performed under air unless otherwise noted. Anhydrous DMF and acetonitrile were purchased in septum-sealed bottles from Acros and were used as received. Dichloromethane (Pharmco) was washed with concentrated H₂SO₄, water, and aqueous NaHCO₃, and then distilled from P₂O₅ prior to use. Hexanes (Pharmco) and diethyl ether (Acros) were distilled from Na/benzophenone ketyl prior to use. NMR solvents were purchased from Cambridge Isotopes Laboratories. CD_3CN and $DMSO-d_6$ were dried by stirring over activated 4Å molecular sieves followed by vacuum distillation at room temperature. CD₂Cl₂ was dried similarly and then stored over and distilled from P₂O₅ before use. All other reagents were purchased from Aldrich or Acros and used as received. **p-**Trifluoromethylphenylisocyanide was synthesized via a phase-transfer Hofmann reaction.¹ (COD)PdCl₂,² iodosobenzene,³ and methylisocyanide⁴ were prepared by literature procedures. NMR spectra were recorded on Varian GEMINI 2000 (300 MHz) and Unity INOVA (400 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks (¹³C, ¹H) or to calibrated external standards (¹⁹F, ³¹P). IR spectra were acquired from Nujol mulls on a Nicolet Protégé 460 FT-IR spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

cis-Bis(*p*-trifluoromethylphenylisocyanide)palladium Dichloride (1). To a solution of *p*-trifluoromethylphenylisocyanide (133 mg, 0.78 mmol) in 10 mL of dichloromethane was added (COD)PdCl₂ (100 mg, 0.35 mmol). The reaction mixture was stirred under air at 25 °C for 10 min. Layering of hexanes onto the solution resulted in precipitation of **1** as colorless crystalline plates. The product was collected by filtration and dried under vacuum. Yield: 130 mg, 72%. Larger reaction scales gave product containing significant amounts of unreacted arylisocyanide. Thus, several reactions were run in parallel to prepare larger quantities of **1**. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.79 (AB, *J*=8.6, *C*=8.9 Hz, *ortho,meta*-H). ¹³C NMR (101 MHz, CD₃CN): δ 133.4 (q, ²*J*_{CF}=33.5 Hz, Ar *para*), 129.4 (s, Ar *ipso*), 129.1 (s, Ar *ortho*), 128.1 (q, ³*J*_{CF}=3.8 Hz, Ar *meta*), 124.3 (q, ¹*J*_{CF}=272 Hz, *C*F₃), ArNC not detected. ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -63.8 (s). IR (Nujol): v_{max}/cm⁻¹ 2241, 2221. Anal. Calc. for C₁₆H₈Cl₂F₆N₂Pd: C, 36.99; H, 1.55; N, 5.39 %. Found: C, 36.70; H, 1.33; N, 5.31 %.

Chiral (Racemic) Bis(carbene)palladium Dichloride (3). To a stirred solution of **1** (885 mg, 1.7 mmol) under Ar in 70 mL of dichloromethane at 25 °C was slowly added N,N'-dimethyl-1,2-diaminocyclohexane **2** (244 μ L, 220 mg, 1.55 mmol) as a solution in 12 mL of dichloromethane, using a syringe pump set at an addition rate of 12 mL h⁻¹. The solution was stirred for a further 2 h at room temperature, during which time a light yellow precipitate formed. ¹H NMR analysis of the solid at this point showed it to be analytically pure **3**, but the following procedure was followed to obtain maximum yield. The solvent was removed under vacuum, anhydrous acetonitrile (30 mL) was added to the solid residue, and the mixture was heated at reflux under Ar for 2 h. The pale yellow precipitate was collected by filtration, washed with acetonitrile, and dried under vacuum. Yield: 661 mg, 65 %. For reaction scales of ~70 mg **3**, the product could be obtained pure in up to 55% yield simply by stirring a mixture of **1** and **2** for 3 h in ~5 mL of anhydrous acetonitrile under N₂ in a stopcock-sealed ampule, followed by heating to 80 °C for 2 h and filtration of the solid precipitate. However, this method resulted in impure samples of **3** for reaction scales >100 mg. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.62 (1H, s, N*H*), 9.05 (1H, s,

N*H*), 8.25 (2H, d, *J*=8.3 Hz, Ar), 7.71 (2H, d, *J*=7.7 Hz, Ar), 7.55 (2H, d, *J*=8.3 Hz, Ar), 7.42 (1H, m, ^cHex ipso C*H*), 7.19 (2H, d, *J*=7.7 Hz, Ar), 3.68 (1H, m, ^cHex ipso C*H*), 3.20 (3H, s, NC*H*₃), 3.10 (3H, s, NC*H*₃), 2.36-2.22 (1H, m, ^cHex), 2.22-2.08 (1H, m, ^cHex), 2.04-1.78 (4H, m, ^cHex), 1.63-1.38 (2H, m, ^cHex). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 190.3 (carbene), 184.4 (carbene), 144.4 (Ar *ipso*), 143.6 (Ar *ipso*), 125.6 (q, ²*J*_{CF} =31.2 Hz, Ar *para*), 125.4 (q, ³*J*_{CF} =4.1 Hz, Ar *meta*), 124.8 (q, ²*J*_{CF} =32.5 Hz, Ar *para*), 124.4 (q, ³*J*_{CF} =3.8 Hz, Ar *meta*), 124.2 (q, ¹*J*_{CF} =272 Hz, CF₃), 124.2 (q, ¹*J*_{CF} =272 Hz, CF₃), 123.8 (Ar *ortho*), 123.5 (Ar *ortho*), 67.9 (NCH₃), 66.9 (NCH₃), 40.7 (^cHex), 31.7 (^cHex), 31.4 (^cHex), 29.9 (^cHex), 25.3 (^cHex), 24.6 (^cHex). ¹⁹F NMR (282 MHz, DMSO-*d*₆): δ -61.28 (s), -61.32 (s). Anal. Calc for C₂₄H₂₆Cl₂F₆N₄Pd: C, 43.56; H, 3.96; N, 8.47 %. Found: C, 43.41; H, 3.93; N, 8.63 %.

Bis(amidine)palladium Dichloride (4). Bis(carbene) palladium complex **3** (100 mg, 0.151 mmol) and iodosobenzene (66 mg, 0.30 mmol) were measured into a glass NMR tube fitted with a sealable valve. Anhydrous DMF (1.2 mL) was added to the NMR tube under nitrogen, and the tube was sealed with a teflon stopcock. The mixture was shaken under nitrogen for 3 d to obtain an orange, crystalline product. The solid was filtered off under air, washed with 5 mL of DMF and 5 mL of dichloromethane, and dried in vacuo. Yield: 69 mg, 69%. Significantly lower yields were obtained if only 1 equiv of iodosobenzene was used. The insolubility of **4** in all common solvents prevented characterization by NMR. Crystallographic indexing confirmed the composition of the crystals (see below). In addition, the decomposition point range of a sample of **4** obtained by PhIO oxidation (230-235 °C) was compared with that of a sample of **4** prepared by air oxidation of **3** (235-248 °C). The higher onset of decomposition in the latter case was attributed to the larger size of the crystals. In both samples, decomposition produced a black char along with a trace of colorless crystalline material whose melting behavior was consistent with free bis(amidine) **5**. Anal. Calc for $C_{24}H_{24}Cl_2N_4F_6Pd$: C, 43.68; H, 3.67; N, 8.49 %. Found: C, 43.59; H, 3.56; N, 8.61 %.

Bis(amidine) (5). To a solution of bis(amidine) palladium complex 4 (100 mg, 0.151 mmol) in 10 mL of DMF was added methylisocyanide (21 µL, 0.38 mmol), and the mixture was stirred for 12 h at room temperature. The solvent was then evaporated under vacuum, and the residue was dried under vacuum for 12 h. The residue was taken up in 10 mL of a 20:80 mixture of hexane and diethyl ether and filtered through celite. The volume of the filtrate was reduced under vacuum, the solution was cooled to 0 °C, and hexane was added to maximize crystal formation. Filtration afforded pale yellow crystals of 5, which were dried in vacuo for 3 h. Yield: 49 mg, 67%. Note: compound 5 was initially isolated from a similar reaction using 2 equiv AgBF₄ in conjunction with methylisocyanide, in an attempt to prepare a bis(methylisocyanide) derivative of Pd complex 4. ¹H NMR (300 MHz, C₆D₆): δ 7.26 (4H, d, J=8.1 Hz, Ar), 6.35 (4H, d, J=8.1 Hz, Ar), 2.68 (6H, s, NCH₃), 2.63-2.46 (2H, m, ^cHex), 1.58-1.38 (2H, m, ^cHex), 1.38-1.18 (2H, m, ^cHex), 0.79-0.54 (4H, m, ^cHex). ¹³C NMR (101 MHz, C₆D₆): δ 152.8 (NC=N), 148.0 (s, Ar *ipso*), 125.7 (q, ${}^{3}J_{CF}$ =3.8 Hz, Ar *meta*), 125.7 (q, ${}^{1}J_{CF}$ =271 Hz, *C*F₃), 123.7 (q, ${}^{2}J_{CF}$ =32.1 Hz, Ar para), 121.6 (s, Ar ortho), 59.9 (NCH₃), 29.9 (°Hex), 28.4 (°Hex), 23.8 (°Hex). Anal. Calc. for C₂₄H₂₄N₄F₆: C, 59.75; H, 5.01; N, 11.61 %. Found: C, 59.46; H, 4.73; N, 11.42 %. Melting point range 179-182 °C.

DETAILS OF X-RAY CRYSTALLOGRAPHIC ANALYSES

General Considerations. X-ray diffraction data for **3**, **4**, and **5** were collected on a Bruker SMART APEX II diffractometer with a CCD detector using a combination of ϕ and ω scans. A Bruker Kryoflex liquid nitrogen cooling device was used for low-temperature data collections. Data integration employed the Bruker SAINT software package.⁵ All X-ray diffraction experiments employed graphite-monochromated Mo K α radiation (λ =0.71073 Å). Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software suite.⁶ Non-hydrogen atoms were assigned anisotropic temperature factors, with hydrogen atoms included in calculated positions (riding model). Specific refinement details are given below. Supplementary crystallographic data for **3**, **4**, and **5** have been deposited in CIF format with the Cambridge Crystallographic Data Centre and can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

X-ray Crystallographic Analysis of 3. Slow evaporation of a concentrated methanol solution of **3** afforded colorless rod-shaped crystals. Three crystals were screened, and all showed weak reflections at higher angles and diffraction patterns suggestive of non-merohedral twinning. The crystals decomposed within 10 min of removal from the solvent if not coated in Paratone N oil in a nylon loop and placed in a stream of liquid nitrogen. A full data set was collected for the strongest-diffracting crystal at 100(2) K. The program CELL NOW⁷ was used to identify two twin domains having identical unit cells from a set of 1404 reflections. A two-component integration of the full data was performed with SAINT⁵ using the orientation matrices determined by CELL NOW, and the data were scaled and merged with TWINABS.⁸ The structure was solved on one twin component, and final refinement was performed on both twin components. Two methanol molecules per asymmetric unit were located in the difference Fourier map and refined as part of the model. Due to weak intensity at higher angles, only data to $2\theta = 46.6$ were used in refinement. Refined formula $C_{24}H_{26}Cl_2F_6N_4Pd\cdot 2CH_3OH$, M = 725.87, crystal size 0.55 x 0.05 x 0.02 mm, triclinic, space group P-1, a = 8.0588(4) Å, b = 14.0376(8)Å, c = 14.1642(8) Å, $\alpha = 84.861(4)^{\circ}$, $\beta = 85.869(4)^{\circ}$, $\gamma = 74.662(4)^{\circ}$, U = 1537.11(15) Å³, Z = 2, $D_c = 1.568 \text{ g cm}^{-1}, \mu = 0.844 \text{ mm}^{-1}, T = 100(2) \text{ K}, 2\theta_{\text{max}} = 46.5^{\circ}, 9760 \text{ total reflections}, 4285$ independent ($R_{int} = 0.057$). Final R1 [$I > 2\sigma(I)$] = 0.0510, wR2 (all data) = 0.1141, largest difference peak and hole 0.717 and -0.694 eÅ⁻³, refined ratio of twin components 0.55:0.45, twin law 1.00 0.00 0.00 0.92 -1.00 0.00 0.25 0.00 -1.00. Deposition number CCDC 625246.

X-ray Crystallographic Analysis of 4. A concentrated DMSO solution of complex 3 was allowed to stand for 30 d under air, and deep orange crystals of 4 formed. A rectangular plate was immersed in Paratone N oil in a nylon loop and cooled to 100(2) K for X-ray diffraction analysis. The structure was solved in the orthorhombic space group *Pnma*, and the direct methods solution indicated an asymmetric unit consisting of one-half of the complex, with palladium located on a crystallographic mirror plane. Locations of difference Fourier peaks suggested a disorder model in which both enantiomers of 4 occupy the same crystallographic position, each with 50% occupancy, which refined successfully. Pd1, Cl1, N1, C1 and the *p*-(CF₃)Ph group have identical coordinates and thermal parameters for the two enantiomers, while each of the other atoms has 50% occupancy and belongs to only one enantiomer. Enantiomer 1 contains N2 C3 C4 C5 C6 C7A C8A C9A N3A C3A and associated hydrogens, where "A" denotes the reflection of a 50%-occupied atom of the asymmetric unit across the mirror plane

(equivalent position x, 1/2-y, z). Enantiomer 2 contains N3 C3 C7 C8 C9 C4A C5A C6A N2A C2A and associated hydrogens. An alternative model was tested involving a 50:50 racemic twin in the space group *Pna2*₁ with an asymmetric unit containing the entire molecule, but this model did not refine as well and displayed unreasonable thermal parameters, including some non positive definite (NPD) atoms. Standard restraints were applied to bond lengths and thermal parameters of the disordered atoms to aid refinement. Refined formula C₂₄H₂₄Cl₂F₆N₄Pd, *M* = 659.77, crystal size 0.27 x 0.15 x 0.04 mm, orthorhombic, space group *Pnma*, *a* = 12.8242(6) Å, *b* = 24.6468(13) Å, *c* = 8.0601(4) Å, *U* = 2547.6(2) Å³, *Z* = 4, *D_c* = 1.720 g cm⁻¹, μ = 1.004 mm⁻¹, *T* = 100(2) K, 2 θ_{max} = 56.6°, 16960 total reflections, 3226 independent (*R*_{int} = 0.049). Final *R*1 [*I*>2 σ (*I*)] = 0.0342, *wR*2 (all data) = 0.0782, largest difference peak and hole 0.743 and -0.585 eÅ⁻³. Deposition number CCDC 625247.

Crystallographic Indexing of a Sample of 4 Prepared in Bulk. Because of the insolubility of 4 and the resulting inability to obtain NMR data, crystallographic evidence was sought to ensure that preparative samples of 4 were chemically identical to the crystals formed upon oxidation of **3** in DMSO (see above) Bulk samples of **4** prepared by iodosobenzene oxidation of **3** in DMF contained many crystals that appeared to be of sufficient size for single-crystal X-ray diffraction analysis. However, all crystals tested were weakly diffracting and showed more spots than expected for the known structure of 4. Analysis of diffraction patterns with CELL NOW^7 identified multiple orientations of a single unit cell in all tested crystals, diagnostic of nonmerohedral twinning. CELL NOW was used to determine unit cell parameters for three crystals from a single batch having different sizes and shapes, and in each case the cell parameters matched those of the fully determined structure of 4 (see above) within one standard deviation. A sample of 4 from this same batch was sent for elemental analysis, confirming the expected ratios of elements (see above). One crystal was carefully cut with a scalpel along fault lines visible under a polarized light microscope and subjected to a full X-ray crystallographic data collection at 25 °C. The solved structure was identical within error to the structure of 4 obtained from the differently grown crystals, although refinement was poor: $R1=0.176 [I>2\sigma(I)]$ and wR2=0.499 (all data).

X-ray Crystallographic Analysis of 5. Slow evaporation of a cyclohexane solution of **5** afforded pale yellow block-shaped crystals. A suitable crystal was mounted on a hollow glass fiber with epoxy, and a full data collection was performed at 24(2) °C. A suitable model was obtained from the structure solution, but it refined poorly. The program ROTAX⁹ was employed to check for twinning, and a twin law consistent with pseudomerohedral twinning was identified. Refinement as a two-component twin led to convergence of the model. To model apparent disorder in the CF₃ groups, the groups were restrained to near-threefold symmetry and treated as rotationally disordered between two orientations. The refined occupancy ratios for the two CF₃ orientations were 64:36 for F1-F3 and 60:40 for F4-F6. Low-temperature data could not be obtained, because an apparent phase transition at cryogenic temperatures caused the diffraction to degrade over the course of a data collection. Refined formula C₂₄H₂₄F₆N₄, M = 482.47, crystal size 0.17 x 0.17 x 0.11 mm, monoclinic, space group $P2_1/n$, a = 7.1121(3) Å, b = 11.9950(5) Å, c = 26.9486(11) Å, $\beta = 90.481(3)^\circ$, U = 2298.89(17) Å³, Z = 4, $D_c = 1.394$ g cm⁻¹, $\mu = 0.118$ mm⁻¹, T = 297(2) K, $2\theta_{max} = 43.9^\circ$, 11851 total reflections, 2813 independent ($R_{int} = 0.041$). Final *R*1 [$I > 2\sigma(I)$] = 0.0480, wR2 (all data) = 0.1363, largest difference peak and hole 0.131 and -0.130

COMPUTATIONAL DETAILS

Density functional theoretical (DFT) calculations were performed with the GAUSSIAN03 quantum chemistry package¹⁰ using the B3LYP hybrid functional.¹¹ Palladium and main group elements were described using the relativistic effective core potentials (ECPs) and valence basis sets (VBSs) of Stevens,¹² denoted CEP-31G in GAUSSIAN03. ECPs include all core electrons for main group elements. For palladium, a semi-core approximation is used with valence and outermost core electrons explicitly calculated. The valence basis sets of heavy main group elements were augmented with d polarization functions using the Extrabasis keyword, with exponents of 0.8 for C, N, and F and an exponent of 0.75 for Cl. Thus, main group atoms are described with VBSs of double- ζ -plus-polarization. For palladium, a triple- ζ treatment of the valence *n*d, (*n*+1)s, and (*n*+1)p orbitals is employed. This ECP/VBS combination, denoted SBK(d) in the literature, has been reported to reliably model structural and energetic properties of a wide range of transition metal organometallic complexes in conjunction with suitable DFT methods.¹³

For the C_l conformation of **3**, DFT geometry optimization was performed using atomic coordinates from the x-ray structure of **3** as an input geometry. For C_2 conformations of **3**, geometric manipulations were performed on the x-ray geometry using GAUSSVIEW¹⁴ to attain the desired starting stereochemistry about the carbene units, and the structures were preoptimized by molecular mechanics calculations using the Universal Force Field (UFF) of Rappé et al¹⁵ as implemented in GAUSSIAN03. The UFF-optimized geometries were then submitted for geometry optimization and frequency calculations at the B3LYP/SBK(d) level of theory. Optimizations were performed on all degrees of freedom, and all optimized structures were verified as true minima with no imaginary frequencies. Calculated thermodynamic quantities utilized unscaled vibrational frequencies derived from the energy Hessian. In addition to the lowest energy C_2 conformation shown in Fig. 2b and Fig. S2, two other possible C_2 isomers of complex 3 were optimized (Figs. S3, S4). A fourth C_2 conformation was optimized by UFF calculations and was found to be destabilized by 29 kcal mol⁻¹ relative to the x-ray geometry by this method (Fig. S5). However, this input geometry did not optimize to a C_2 -symmetric structure at the B3LYP/SBK(d) level of theory, but instead gave rise to a C_1 conformation lying slightly higher in enthalpy than the x-ray geometry (Fig. S6). Structural diagrams and relative energies of optimized geometries are presented below, along with tabulations of relevant geometric parameters and GAUSSIAN03 archive files for the B3LYP/SBK(d) geometry optimizations.

Supplementary Material (ESI) for Chemical Communications # This journal is (c) The Royal Society of Chemistry 2007



Fig. S1. B3LYP/SBK(d) optimized geometry of C_1 conformation of **3** (**3a**) starting from x-ray atomic coordinates

	Calculated value	Experimental value
		(from x-ray structure)
distances (A)	1 0 5 7	
$C_{carbene}$ -N(H) (left)	1.357	1.346(7)
$C_{carbene}$ -N(H) (right)	1.364	1.350(8)
$C_{carbene}$ -N(Me) (left)	1.361	1.331(7)
C _{carbene} -N(Me) (right)	1.357	1.333(7)
$Pd-C_{carbene}$ (left)	2.028	1.975(6)
Pd-C _{carbene} (right)	2.022	1.985(6)
Pd-Cl (left)	2.3990	2.3942(16)
Pd-Cl (right)	2.4164	2.3901(16)
angles $(^{0})$		
N-Castan-N (left)	116.0	117 5(5)
N-Casthene-N (right)	115.6	116.0(6)
N(Me) sum of angles (left)	360.0	359 1(9)
N(Me) sum of angles (right)	359.8	360 0(9)
N(H) sum of angles (left)	360.0	359.9
N(H) sum of angles (right)	359.4	360.1
C-Pd-C	85.1	82.3(2)
C-Pd-Cl (left)	89.02	91.90(17)
C-Pd-Cl (right)	89.93	93 62(18)
Cl-Pd-Cl	95.00	91.39(6)
1 (2)		
torsion angles (°)	2.5	10.2(0)
$N-C_{carbene}-N-C_{Me}$ (left)	-2.7	-10.3(8)
$N-C_{carbene}-N-C_{Me}$ (right)	-7.0	-3.3(8)
$N-C_{carbene}-N-C_{cyclohex}$ (left)	179.8	180.8(5)
$N-C_{carbene}-N-C_{cyclohex}$ (right)	178.9	178.5(5)
$N-C_{carbene}-N(H)-C_{Ar}$ (left)	175.6	189.2(6)
N-C _{carbene} -N(H)-C _{Ar} (right)	185.8	175.9(5)
$Cl-Pd-C_{carbene}-N(H)$ (left)	-80.8	-82.1(5)
$Cl-Pd-C_{carbene}-N(H)$ (right)	86.4	82.9(5)

Table S1. Comparison of calculated versus experimental geometric parameters for C_1 configuration of **3**. Calculated values are from B3LYP/SBK(d) optimized geometry (**3a**).

Gaussian03 archive file for geometry optimization of 3a

```
1\1\GINC-OUANTUM\FOpt\RB3LYP\Gen\C24H26Cl2F6N4Pd1\LMS\07-May-2007\0\\# OPT
FREQ=NORAMAN B3LYP/CEP-31G EXTRABASIS 5D 7F
GEOM=CONNECTIVITY\\Chiral Pd dicarbene b3lvp/cep-31g(d)\\0.1\Pd.-0.4862531141.-
1.6724595931,-0.5256926808\C,-0.5352833041,-
1.6068952348,1.5005588187\C,1.5227484921,-1.7281315244,-0.3038190109\Cl,-
2.8844990974,-1.7288464897,-0.5408066046\Cl,-0.2456605835,-2.3263401657,-
2.8394891437\N,-0.7461809656,-0.5634144986,2.3421725498\H,-0.7154941938,-
0.7414024798,3.3471388067\C,-0.0965716085,-2.9515568116,3.5500957865\H,0.6619399772,-
2.2542334188,3.9518417496\H,0.2304512702,-3.9695722396,3.784896491\H,-1.0569173238,-
2.7809415878,4.0698418438\C,3.6273362722,-2.8662133904,0.3235387909\H,4.0953926273,-
2.678078864,-0.6577930068\H.3.9322237531,-3.8674626869,0.6513324538\H.4.0157302827,-
2.137838423,1.0603798909\C,-0.0097908619,-3.9598829579,1.1706719495\H,-0.6758565997,-
3.7882891583,0.3161037343\C,1.4577534534,-4.0756408221,0.6491088679\H,2.0668872823,-
4.4472341713,1.4944739818\C,1.4921987931,-5.1249689306,-0.4978160287\H,0.8753101254,-
4.7449053619,-1.3289268887\H,2.5245269986,-5.219357327,-0.8781111673\C,0.9844521213,-
6.5047231501,-0.007795828\H,1.6967119124,-6.918787644,0.7321455252\H,0.9606072239,-
7.2088148684,-0.8562123406\C,-0.4188593708,-6.3985510474,0.6363153256\H,-
0.7241724294,-7.373787111,1.0519551664\H,-1.1623925731,-6.1262810379,-
0.1323471391\C,-0.4346922157,-5.3303149685,1.7607496112\H,-1.4484996366,-
5.2371445513,2.1840728669\H,0.2430873419,-5.655773481,2.5722440165\N,2.3264407793,-
0.6656043339.-0.597246665\H.3.3169680565.-0.7068846952.-0.3553290524\N.-
0.2412689425,-2.7982253342,2.0882935396\N,2.1491579531,-2.807230823,0.2291100198\C,-
0.9868613537,0.8200376414,2.0528057327\C,-0.8234525985,1.7159164087,3.1456491828\H,-
0.5271083139,1.3367837085,4.1294229322\C,-1.0414805747,3.0975584404,2.9726916949\H,-
0.9243097721,3.7796264091,3.8165587625\C,-1.4160672652,3.5906252299,1.6977435305\C,-
1.5818824151.2.696682752.0.6111643702\H.-1.8894412461.3.0737284433.-0.3648731799\C.-
1.3825462612,1.3089566555,0.7835484688\H,-1.5636110253,0.6240023821,-0.04278449\C,-
1.591389218,5.0878588854,1.5022974714\C,1.915557473,0.6388691803,-
1.0593508988\C,2.4542533483,1.7663803166,-
0.3883531532\H,3.1062075704,1.6304739474,0.4796991893\C,2.1312701006,3.0712538624,-
0.824168596\H,2.53924726,3.939899797,-0.3055962103\C,1.268342243,3.2395445799,-
1.9333626075\C,0.7347564328,2.1099665303,-2.6030589682\H,0.0815438823,2.2408886975,-
3.4683839964\F,-2.4267658582,5.3865612341,0.4737266599\F,-
2.0926151707.5.6937822928.2.6201134504\F,-
0.4006040202, 5.7118023804, 1.2358517794 \\ F, 0.9359621583, 4.7486018548, -3.7616987497 \\ F, -3.7616977497 \\ F, -3.76179747 \\ F, -3.7617974749747 \\ F, -3.76179747 \\ F, -3.76177747 \\ F, -3.76177747 \\ F, -
0.4073189981.4.9476730923.-2.0496746463\C.1.0639981183.0.8042273535.-
2.1782676707\H,0.6777484654,-0.0668550672,-2.7099452548\C,0.8758152719,4.6319347972,-
2.4033985188\F,1.6767757448,5.6019432974,-1.8823751249\\Version=IA32L-
G03RevC.02\State=1-A\HF=-493.258125\RMSD=4.430e-09\RMSF=3.700e-
```

06\Dipole=4.4096891,-2.9700492,4.785457\PG=C01 [X(C24H26Cl2F6N4Pd1)]\\@

Supplementary Material (ESI) for Chemical Communications # This journal is (c) The Royal Society of Chemistry 2007



Fig. S2. B3LYP/SBK(d) optimized geometry of lowest energy C₂ conformation of 3 (3b)

 ΔH°_{f} relative to 3a = +17.9 kcal mol⁻¹

 ΔG°_{f} relative to **3a** = +16.8 kcal mol⁻¹

distances (Å)	
C _{carbene} -N(H)	1.348
C _{carbene} -N(Me)	1.396
Pd-C _{carbene}	2.027
Pd-Cl	2.400
angles (°)	
N-C _{carbene} -N	119.61
N(Me) sum of angles	351.4
N(H) sum of angles	358.5
C-Pd-C	84.0
C-Pd-Cl	89.15
Cl-Pd-Cl	98.43
torsion angles (°)	
N-C _{carbene} -N-C _{Me}	-148.8
N-C _{carbene} -N-C _{cvclohex}	64.4
$N-C_{carbene}-N(H)-C_{Ar}$	10.7
$Cl-Pd-C_{carbene}-N(H)$	46.6

 Table S2.
 Calculated geometric parameters for 3b from B3LYP/SBK(d) optimized geometry.

Gaussian03 archive file for 3b

-2007\0\\# opt freq=NoRaman b3lyp/cep-31g extrabasis 5d 7f geom=connectivity\\PdDicarbene C2 #1

 $DFT\0,1\Pd,0.0858005618,0.000344214,0.0880555565\C,0.1702173743,0.098397165,2.111359902\C,2.1064339083,-0.0977809786,0.2218776336\C1,-2.3053466805,-0.0977809786,0.221877636\C1,-2.3053466805,-0.0977809786,0.221877636\C1,-2.3053466805,-0.0977809786,0.221877636\C1,-2.3053466805,-0.0977809786,0.221877636\C1,-2.3053466805,-0.0977809786,0.221877638\C1,-2.3053466805,-0.0977809786,0.221877638\C1,-2.3053466805,-0.0977809786,0.221877638\C1,-2.3053466805,-0.0977809786,0.29786,0.$

 $1.2278362295, 2.1652249622 \ C, 1.3536144522, 2.2302389878, 2.240078389 \ H, 0.5325166122, 2.4847492977, 1.5580919392 \ H, 2.3060754676, 2.3176101131, 1.6909966484 \ H, 1.3586381583, 2.9568358457, 3.0691391905 \ C, 2.2061050291, -2.2297076093, 1.4079204493 \ H, 1.6338262621, -2.2297076093, 2.407826493 \ H, 2.338262621, -2.2297076093, 2.4079204493 \ H, 2.338262621, -2.2297076093, 2.4078264493 \ H, 2.338262621, -2.2297076093, 2.407826493 \ H, 2.338262621, -2.2297076093, 2.4078264493 \ H, 2.407844493 \ H, 2.4078264493 \ H, 2.40784493$

0.1918494336,2.3565979328\H,3.8326840386,0.7374470898,1.9874437789\C,4.4858837127,-1.0275927347,3.0403690569\H,4.0604552885,-1.9654916918,3.4381968288\H,5.248834939,-1.3061269636,2.2949302726\C,5.1318883666,-

 $0.2257618562, 4.1992707839 \ H, 5.6478680931, 0.6609381982, 3.787060323 \ H, 5.9030074346, -0.8428577802, 4.6902020243 \ C, 4.0725170473, 0.2259443337, 5.2330890673 \ H, 4.5444943778, 0.8429627971, 6.0160137986 \ H, 3.6477668814, -0.8429627971, -0.94396 \ H, 3.6477668814, -0.9496 \ H, 3.64776688$

 $0.6607617656, 5.7387857436 \ (C, 2.9297964406, 1.0278860607, 4.5590063843 \ (H, 2.1659497138, 1.3064146328, 5.3035293362 \ (H, 3.3379555508, 1.965788406, 4.1434878809 \ (N, 2.8069722875, 0.7975733535, -0.5024805595 \ (H, 2.1954445322, 1.2284872158, -0.5024805595 \ (H, 2.1954445322, -0.5024805595 \ (H, 2.195445322, -0.5024805595 \ (H, 2.195445322, -0.5024805595 \ (H, 2.195445595 \ (H, 2.1954445322, -0.5024805595 \ (H, 2.19545322, -0.5024805595 \ (H, 2.1954445322, -0.5024805595 \ (H, 2.19545322, -0.5024805595 \ (H, 2.195452, -0.5024805595$

1.2131102718\N,1.111733761,0.8746565192,2.7897179447\N,2.7615619079,-

1.3630151495,-1.6905495711,6.8838552725\C,-0.8339045474,-

0.678571378\C,5.2200949328,0.0969600447,-0.4150271836\H,4.9516828528,-0.8909452195,-0.0454980225\C,6.570427016,0.4178166653,-0.6734431485\H,7.3482265687,-0.3248859393,-0.4867322365\C,6.9150361759,1.6909078423,-1.1943742968\C,5.9040994339,2.6439873742,-1.4751990132\H,6.1653737708,3.6175546468,-1.8932258473\F,-1.9657891498,-

0.962006709,9.0841315933\F,-2.5992830296,-2.9752350974,8.4826313579\F,-0.4960471042,-2.5748082354,8.9331611446\F,8.5435924814,2.9760530159,-

```
2.3906571136 \\ F, 8.9429319096, 2.5740769729, -0.2773897018 \\ C, 4.5531798002, 2.3253412552, -1.2201282205 \\ H, 3.7682998135, 3.0522798254, -1.4454174756 \\ C, 8.3784645784, 2.0483870389, -1.2201282205 \\ C, 8.3784645784, -1.4454174756 \\ C, 8.3784645784, -1.445417456 \\ C, 8.3784645784, -1.445447456 \\ C, 8.3784645784, -1.445447456 \\ C, 8.3784645784, -1.445447456 \\ C, 8.3784645784, -1.445447456 \\ C, 8.3784645784, -1.44547456 \\ C, 8.3784645784, -1.44547456 \\ C, 8.3784645784, -1.4454745647456 \\ C, 8.3784645784, -1.4454745647456 \\ C, 8.3784645784, -1.4454745647456 \\ C, 8.3784645784, -1.44547456 \\ C, 8.37
```

G03RevD.02\State=1-A\HF=-493.2288824\RMSD=4.414e-09\RMSF=1.424e-

06\Thermal=0.\Dipole=3.4393576,-0.0000036,3.5244636\PG=C01

[X(C24H26Cl2F6N4Pd1)]\\@



Fig. S3. B3LYP/SBK(d) optimized geometry of second C_2 conformation of **3** (**3c**)

 ΔH°_{f} relative to 3a = +25.4 kcal mol⁻¹ ΔG°_{f} relative to 3a = +25.0 kcal mol⁻¹

<u></u>	
distances (Å)	
C _{carbene} -N(H)	1.353
C _{carbene} -N(Me)	1.405
Pd-C _{carbene}	2.015
Pd-Cl	2.396
angles (°)	
N-C _{carbene} -N	111.26
N(Me) sum of angles	351.1
N(H) sum of angles	359.8
C-Pd-C	84.7
C-Pd-Cl	90.89
Cl-Pd-Cl	96.10
torsion angles (°)	
N-C _{carbene} -N-C _{Me}	-149.1
N-C _{carbene} -N-C _{cyclohex}	64.3
N-C _{carbene} -N(H)-C _{Ar}	187.8
Cl-Pd-C _{carbene} -N(H)	69.9

 Table S3.
 Calculated geometric parameters for 3c from B3LYP/SBK(d) optimized geometry.

Gaussian03 archive file for 3c

1\1\CASCAM01-COMPUTE-1-10\FOpt\RB3LYP\Gen\C24H26Cl2F6N4Pd1\TOMC\05-May-2007\0\\# opt freq=NoRaman b3lyp/cep-31g extrabasis 5d 7f geom=connectivity\\PdDicarbene 2nd C2 conformation DFT\\0.1\Pd.-0.2197859315.0.0031197802.-0.2263727714\C.-0.1589784648,-0.0852611491,1.7859110755\C,1.7893603559,0.0891831104,-0.0970337818\Cl,-2.5780139937,0.4240057062,-0.1740763641\Cl,-0.0879806038,-0.4151992199,-2.5819361615\N,-0.6978929142,-1.0835253921,2.5234178779\H,-0.5902683751,-0.9706142158,3.5359121271\C,0.7817194887,2.1458800732,2.1749253143\H,-0.1232823223,2.4130386691,1.6159505139\H,1.6633325473,2.3811780251,1.5547103129\H,0. 8189386344,2.7622764401,3.0870604195\C,2.1438235779,-2.1432370594,0.8542778571\H,1.4942044182,-2.3788326577,1.7143716499\H,3.0535730531,-2.7606406249,0.9213284884\H,1.6151833654,-2.4088203025,-0.0692264776\C,1.9241318005,0.084803976,3.1260056555\H,1.6426301697,-0.9240609779,3.4655680489\C,3.0574980586,-0.084200381,2.0303964305\H,3.4073872308,0.9246024674,1.7616053884\C,4.2598961361,-0.8502278839,2.636775355\H,3.9479787969,-1.8666558139,2.9338965975\H,5.0421010241,-0.9635091049,1.866852597\C,4.8141405211,-0.1073082161,3.8788108931\H,5.2217520651,0.8737654496,3.5710824029\H,5.6540876639,-0.6798360232,4.3067999365\C,3.7117129987,0.1043309596,4.9445400261\H,4.1114272998,0. 6755950186,5.7991508273\H,3.3893160812,-0.8768271939,5.3404420412\C,2.4900036863,0.8490701438,4.349090223\H,1.6940219168,0.9 624119522.5.1047514218\H.2.7986033912.1.8654803605.4.0484671143\N.2.5458748155.1.087 1390514,-0.6095309969\H,3.5539902684,0.9730281781,-0.467552386\N.0.6904057758.0.7204247312.2.5623746116\N.2.5355440198.-0.718090579,0.7776037501\C,-1.4898540765,-2.2283324306,2.1785063816\C,-2.1498335978,-2.868076879,3.2634478437\H,-2.064926301,-2.4615923208,4.276528434\C,-2.939237718,-4.0147144827.3.0415850773\H.-3.4520309867.-4.4950138262.3.8764298343\C.-3.069888549.-4.528081342,1.7270218023\C,-2.4096464531,-3.8929341477,0.6459449314\H,-2.5190464838,-4.2780324969,-0.3689867646\C,-1.6129287396,-2.7487719712,0.8651476613\H,-1.1265027022,-2.2664305853,0.0190324973\C,-3.8692903486,-5.8005256606,1.4914491081\C,2.2293740684,2.23304219,-1.4117071145\C,0.9215369985,2.7551702708,-1.5787634951\H,0.0588528264,2.2734142231,-1.1217490371\C,0.7308331776,3.9002716763,-2.3814092127\H,-0.2793633894,4.2866694602,-2.5248354371\C,1.8344364643,4.5347127806,-3.0040333891\C,3.1431975851,4.0196725144,-2.8293414641\H.3.9955096.4.4994368071.-3.3130599752\F.-4.4060063486.-5.8524054418,0.2433019883\F,-3.0919316805,-6.9210362925,1.6273989989\F,-4.8938532265,-5.9363260544,2.3813082465\F,1.7328569607,6.9275883139,-3.0261567683\F,2.554323625,5.946515669,-4.8003557797\C,3.3368092802,2.8720573538,-2.0339150819\H,4.3459506054,2.4642804074,-1.9150774624\C,1.6272502935,5.8081357807,-3.8097154794\F,0.399787839,5.8594386412,-4.3922913648\\Version=AM64L-G03RevD.02\State=1-A\HF=-493.2170123\RMSD=3.811e-09\RMSF=2.243e-06\Thermal=0.\Dipole=4.9785069,-0.0054062,5.1504265\PG=C01 [X(C24H26Cl2F6N4Pd1)]\\@

Supplementary Material (ESI) for Chemical Communications # This journal is (c) The Royal Society of Chemistry 2007



Fig. S4. B3LYP/SBK(d) optimized geometry of third C_2 conformation of 3 (3d)

 ΔH°_{f} relative to **3a** = +32.8 kcal mol⁻¹

$$\Delta G^{\circ}_{f}$$
 relative to **3a** = +31.2 kcal mol⁻¹

distances (Å)	
$C_{carbene}$ -N(H)	1.345
C _{carbene} -N(Me)	1.418
Pd-C _{carbene}	2.008
Pd-Cl	2.399
angles (°)	
N-C _{carbene} -N	110.19
N(Me) sum of angles	345.6
N(H) sum of angles	359.8
C-Pd-C	82.4
C-Pd-Cl	91.6
Cl-Pd-Cl	96.0
torsion angles (°)	
N-C _{carbene} -N-C _{Me}	142.3
N-C _{carbene} -N-C _{cyclohex}	-81.0
N-C _{carbene} -N(H)-C _{Ar}	176.9
Cl-Pd-C _{carbene} -N(H)	-75.4

 Table S4.
 Calculated geometric parameters for 3d from B3LYP/SBK(d) optimized geometry.

Gaussian03 archive file for 3d

1\1\CASCAM01-COMPUTE-1-9\FOpt\RB3LYP\Gen\C24H26Cl2F6N4Pd1\TOMC\06-May-2007\0\\# opt freq=NoRaman b3lyp/cep-31g extrabasis 5d 7f geom=connectivity\\Chiral Pd dicarbene 3rd C2 DFT\\0,1\Pd,-0.2606964207,0.0097858853,-0.2901771377\C,-0.2003877182,0.1344156633,1.7134613252\C,1.7312648164,-0.1290102325,-0.0743104599\Cl,-2.6481565837,-0.228976295,-0.2699345176\Cl,-0.0528137323,0.2635871305,-2.6670991383\N,-0.5491020558,1.1891750569,2.4710446938\H,-0.3903191874,1.0412193692,3.4739247703\C,0.1522074799,-2.22946448,2.1443795468\H,-0.9286778692,-2.3169149281,1.97405715\H,0.4257941898,-2.8738734297,2.9962177262\H,0.6815373092,-2.5846888251,1.2433364147\C,2.147768203,2.2296885789,0.3275283132\H,2.0622141616,2.3 252911507,-0.7626574835\H,2.9799662105,2.8664187179,0.6707035081\H,1.2107562097,2.5877263467,0. 7880361081\C,1.9535335319,-0.6334841192,2.7961592751\H,2.4549230577,-1.5286098894,2.3839398472\C,2.6473650099,0.617379664,2.1627224322\H,2.2032849271,1.5 121170102,2.6368635313\C,4.1606590485,0.5980305585,2.520026702\H,4.6239661504,-0.2948643777,2.059150156\H,4.6373873391,1.4775125163,2.05659651\C,4.4094202003,0.582 0620239,4.0468987925\H,4.0319709182,1.5218733044,4.4918113919\H,5.4937543747,0.54819 64846,4.2468333384\C,3.694899838,-0.6231509656,4.6998110829\H,3.8099346459,-0.5978272961,5.7966369432\H,4.1617062906,-1.5635937221,4.3515010118\C,2.1919846507,-0.6266576479,4.3327777358\H,1.6870818446,-1.5059669367,4.7656920598\H,1.7022380667,0.2663910241,4.7651216932\N,2.5070699568,-1.1869171316,-0.3694162107\H,3.4953406847,-1.0469536065,-0.1315228605\N.0.4818261676,-0.8284360309.2.4995123277\N.2.4673413748.0.8241608671.0.6738563155\C.-1.1917757144,2.4414359159,2.1831670036\C,-1.4579016627,3.2600862299,3.3152418609\H,-1.1868608953,2.918114081,4.3193689661\C,-2.0871520256,4.5114849544,3.1563675446\H,-2.2976162961,5.1327038048,4.0283482124\C,-2.4513138134,4.947541433,1.8579611572\C,-2.1868651205,4.1302104695,0.7307968199\H,-2.4800824412,4.4581018481,-0.2675727036\C,-1.5561199879.2.8761915524.0.8839740931\H.-1.3859716239.2.2510911974.0.0100443264\C.-3.079908034,6.3218262186,1.6773172079\C,2.262336455,-2.433403468,-1.0405525535\C,0.993169438,-2.8563705031,-1.5095591872\H,0.1129071463,-2.2256760363,-1.4055494742\C,0.8817514507,-4.1057107583,-2.1581183039\H,-0.0924615912,-4.4244785691,-2.531643765\C,2.0205662511,-4.9300030173,-2.3372365888\C,3.2889949872,-4.5056916043,-1.8685259423\H.4.1705530466,-5.1322492134,-2.0129151181\F,-3.8703006432,6.3884917158,0.573526653\F,-3.8448005653,6.6790177217,2.7484919214\F,-2.1310760654.7.2992998833.1.5390463828\F.3.0061443964.-6.6592230355.-3.6681116389\F,1.6633572723,-7.2814250174,-2.0574988883\C,3.4061978736,-3.2590260517.-1.2210180706\H.4.3880088046.-2.9261066072.-0.8690341632\C,1.8809200819,-6.2994109983,-2.986570291\F,0.8415640857,-6.354257166,-3.8607697425\\Version=AM64L-G03RevD.02\State=1-A\HF=-493.2045061\RMSD=6.475e-09\RMSF=1.011e-06\Thermal=0.\Dipole=4.4955627,-0.0302289,4.8621944\PG=C01 [X(C24H26Cl2F6N4Pd1)]\\@



Fig. S5. Molecular mechanics (UFF) optimized geometry of fourth C_2 conformation of **3** (**3e**). When used as an input geometry for B3LYP/SBK(d) optimization, a C_1 configuration resulted (**3f**, see below).

 ΔH°_{f} relative to **3a** (from UFF calculation) = +29.1 kcal mol⁻¹

distances (Å)	
$C_{carbene}$ -N(H)	1.356
C _{carbene} -N(Me)	1.359
Pd-C _{carbene}	2.053
Pd-Cl	2.313
angles (°)	
N-C _{carbene} -N	121.79
N(Me) sum of angles	352.4
N(H) sum of angles	360.0
C-Pd-C	85.9
C-Pd-Cl	92.0
Cl-Pd-Cl	90.1
torsion angles (°)	
N-C _{carbene} -N-C _{Me}	137.6
N-C _{carbene} -N-C _{cyclohex}	-74.1
N-C _{carbene} -N(H)-C _{Ar}	-18.04
Cl-Pd-C _{carbene} -N(H)	-69.4

 Table S5.
 Calculated geometric parameters for 3e from UFF optimized geometry.

Gaussian03 archive file for 3e

1\1\GINC-OUANTUM\FOpt\UFF\ZDO\C24H26Cl2F6N4Pd1\LMS\08-Mar-2007\0\\# OPT UFF GEOM=CONNECTIVITY\\c2 4th conformation\\0,1\Pd,0.0717840409,0.0490951477,-0.0727987512\C.0.4926307306.2.0313417911.-0.4009008827\C.1.5679832677.-0.3397911996.-1.423275292\Cl,-1.5948244018,0.5695560605,1.4440413819\Cl,-0.3471022649,-2.2043726731,0.2359201337\N,-0.4172176791,2.7926312498,-1.0581290234\H,-1.3039696825,2.3306878305,-1.3586239851\C,2.3967698642,2.1962453063,1.0193720572\H,1.7475811656,2.6310261301.1. 8103598717\H,3.3854611095,2.6980878093,1.0812805611\H,2.5306473373,1.1112647685,1.21 45559931\C,0.3106957461,0.0317029964,-3.4107459852\H,0.1630469338,-1.0664654047,-3.5023595611\H,0.4199151546,0.4436897481,-4.4361790303\H,-0.5871778357,0.4807867319,-2.9357670239\C.2.7176155686.2.300102087.-1.4656542505\H.3.5767584644.1.6510693137.-1.1816740991\C,2.0914439067,1.6771809511,-2.7701995456\H,1.2889737503,2.3733794186,-3.1039651042\C,3.1456100966,1.6415158709,-3.8957155468\H,3.9788412519,0.964049586,-3.6169726849\H,2.6886519971,1.2514442181,-4.8301910222\C,3.7165831585,3.03595246,-4.1719950208\H,2.9119085578,3.7036789807,-4.5516141002\H,4.499332511,2.9619584266,-4.9574299785\C,4.3310699824,3.6339858157,-2.9035390374\H,4.6953654334,4.6607363587,-3.1229209529\H,5.2028831113,3.021857915,-2.5829185914\C,3.2976984961,3.6954406821,-1.7743771292\H,3.7849931028,4.1120793091,-0.8671295948\H,2.4848670485,4.3894585932,-2.0722119913\N,2.7215924812,-0.8971640858,-0.9782212352\H,2.7886840041,-1.1152575543,0.0405527051\N,1.7960974917,2.4008169246,-0.3005867277\N.1.5023454013.0.3193186118,-2.6094264869\C,-0.2293499789.4.1797900418,-1.3781045407\C,-0.6585817331,4.6641850945,-2.6197319431\H,-1.1124749243,3.9919196992,-3.3371420844\C,-0.4805934226,6.0093288633,-2.9533258642\H,-0.8046390136,6.3596568679,-3.9256768353\C,0.1120781826,6.8979185343,-2.0413307149\C.0.5148938251,6.4164974964,-0.782390044\H.0.9647416289,7.0755805007,-0.0514294466\C,0.3384482393,5.0700950881,-0.4513423767\H.0.6417699337,4.7239279291,0.5280661925\C,0.2973068883,8.3424066281,-2.4320848367\C,3.8537323528,-1.186426801,-1.8128075114\C,3.6911835907,-1.7404248272,-3.0936158471\H,2.7031436661,-1.9644877288,-3.4738882083\C,4.8057338544,-2.0121629471,-3.8921239415\H,4.6478804382,-2.4284627852,-4.8785267603\C,6.10292916,-1.7487227245,-3.4159033765\C,6.2608450407,-1.221761744,-2.1236198314\H,7.250596566,-1.0175376691,-1.7339685862\F,0.8907916503,9.0757371299,-1.4190047385\F,1.09904594,8.4152964161,-3.5567309815\F,-0.9339511657,8.9031141728,-2.7190850765\F.8.0242944859.-0.844032483.-4.4466368929\F.8.1391353217.-2.9293287882.-3.6034124517\C,5.1456213829,-0.9525438187,-1.3260102264\H,5.2856913394,-0.5408797249,-0.3342857238\C,7.3247815644,-2.0218537699,-4.2562209459\F,6.9897375744,-2.5410806745,-5.4950149449\\Version=IA32L-G03RevC.02\HF=0.1658494\RMSD=0.000e+00\RMSF=2.628e-05\Dipole=0..0.0\PG=C01 [X(C24H26Cl2F6N4Pd1)]\\@



Fig. S6. B3LYP/SBK(d) optimized geometry of an alternative C_1 conformation of **3** (**3f**), which resulted from using UFF-optimized C_2 conformation **3e** as an input geometry

 ΔH°_{f} relative to 3a = +1.2 kcal mol⁻¹

 ΔG°_{f} relative to 3a = -0.39 kcal mol⁻¹

distances (Å)	
C _{carbene} -N(H) (left)	1.373
C _{carbene} -N(H) (right)	1.364
C _{carbene} -N(Me) (left)	1.347
C _{carbene} -N(Me) (right)	1.366
$Pd-C_{carbene}$ (left)	2.015
Pd-C _{carbene} (right)	2.061
Pd-Cl (left)	2.400
Pd-Cl (right)	2.409
<u>angles (°)</u>	
N-C _{carbene} -N (left)	121.4
N-C _{carbene} -N (right)	119.0
N(Me) sum of angles (left)	359.7
N(Me) sum of angles (right)	359.3
N(H) sum of angles (left)	358.6
N(H) sum of angles (right)	351.9
C-Pd-C	89.6
C-Pd-Cl (left)	86.18
C-Pd-Cl (right)	89.69
Cl-Pd-Cl	93.76
torsion angles (°)	
$N-C_{carbene}-N-C_{Me}$ (left)	7.7
N-C _{carbene} -N-C _{Me} (right)	16.6
N-C _{carbene} -N-C _{cyclohex} (left)	-178.9
N-C _{carbene} -N-C _{cvclohex} (right)	-153.1
$N-C_{carbene}-N(H)-C_{Ar}$ (left)	39.4
N-C _{carbene} -N(H)-C _{Ar} (right)	31.8
$Cl-Pd-C_{carbene}-N(H)$ (left)	-55.3
Cl-Pd-C _{carbene} -N(H) (right)	38.7

Table S6. Calculated geometric parameters for 3f from B3LYP/SBK(d) optimized geometry.

Gaussian03 archive file for 3f

1\1\CASCAM01-COMPUTE-1-10\FOpt\RB3LYP\Gen\C24H26Cl2F6N4Pd1\TOMC\10-May-2007\0\\# opt freq=NoRaman b3lyp/cep-31g extrabasis 5d 7f geom=connectivity\\Pd dicarbene 4th C2 conformation DFT resubmit/\0,1\Pd,1.0637539696,-2.2880652933,2.0689071933\C,0.5977377993,-1.0918563147,3.6224918037\C,2.7006737681,-1.1021449234,1.6643177992\Cl,-1.057380626,-3.3425615573,2.4520087518\Cl,1.5286147472,-3.5818111206,0.0911437807\N,-0.5941395277,-0.4182332716,3.5220486338\H,-1.2417054262,-0.9419705342,2.9180017555\C,1.0353149981,-0.167670282,5.900569713\H,-0.0573771415,-0.1137668115,5.9727537972\H,1.4394933854,0.8586225013,5.8835315034\H,1.4105928032,-0.6849921621,6.7903780782\C,4.1410789919,0.8769369849,2.2330236093\H,3.6428598051,1. $369211168.1.3898523797 \land H.5.2053533055.0.7371326824.1.9805836865 \land H.4.0733640243.1.538$ 552878,3.112347065\C,2.6850732369,-1.712118775,4.6457350051\H,2.4505529982,-2.6198849322,4.0711110557\C,3.8102030219,-0.9409952586,3.9033955876\H,4.07669737,-0.0642725467,4.520959089\C,5.0635111211,-1.8537796524,3.7667078628\H,4.7930260653,-2.7070266892,3.1195063132\H,5.8668982636,-1.2957788424,3.2558169838\C,5.5604494253,-2.3723772957,5.1362773323\H,5.9279821692,-1.5244489228,5.7446980883\H,6.4161558201,-3.0518809489,4.9863063085\C,4.4211893632,-3.0945874787,5.890442527\H,4.7598690794,-3.4134476014,6.890361901\H,4.1298110769,-4.0079610449,5.341857584\C,3.1911195311,-2.1652403645,6.0392551827\H,2.3786563938,-2.6986302774,6.5602523946\H,3.4777409281,-1.2981021141,6.6616691779\N,2.8479603613,-0.8465970513,0.3323486258\H,2.2494205203,-0.3901934616,2.5611939843\C,-0.9715022673,0.9141959829,3.8576933932\C,-2.3458308252,1.1877702852,4.1045868352\H,-3.0713891342,0.3706110017,4.0874444875\C,-2.766078276.2.5067332455.4.3773708518\H.-3.8202819855.2.7126252166.4.5709194065\C.-1.8148013027,3.5589294102,4.4193381039\C,-0.4473304971.3.2917733144.4.157628643\H.0.2803967407.4.1055365184.4.1693552156\C.-0.0276274237,1.9759058998,3.8668525726\H,1.0176555173,1.7766703709,3.6223567711\C,-2.2668247781,4.9876636374,4.6732726423\C,4.0200937581,-0.4152670889,-0.3963636838\C.5.2921794956,-0.9820684572,-0.1365830973\H.5.3983682679,-1.7445356643,0.637052926\C,6.4103186837,-0.5842268755,-0.9024131257\H,7.3919231756,-1.0183598576,-0.7036225162\C,6.2508006139,0.3710222638,-1.9381939875\C,4.9724715174,0.9152762002,-2.2218869999\H,4.8511513502,1.6413416576,-3.0276456378\F,-1.3208356613,5.713784793,5.3378420143\F,-2.5218549213,5.6631065098,3.511560057\F,-3.4101039748,5.0431036921,5.4120870923\F,7.6277823067,-0.0889892841,-3.8462679591\F.7.3192224584.2.0113531538.-3.3182593879\C.3.8582258307.0.5236384634.-1.4461478912\H,2.8689473517,0.940887675,-1.648426829\C,7.4490725179,0.7607863128,-2.7923129642\F,8.612119819,0.7425368067,-2.0791967595\\Version=AM64L-G03RevD.02\State=1-A\HF=-493.2560929\RMSD=6.330e-09\RMSF=3.960e-06\Thermal=0.\Dipole=2.6105778,2.5981292,3.3826882\PG=C01

[X(C24H26Cl2F6N4Pd1)]\\@

REFERENCES

- 1 (a) G. W. Gokel, R. P. Widera and W. P. Weber, *Org. Synth.*, 1976, **55**, 96-99; (b) D. P. Curran, H. Liu, H. Josien and S. B. Ko, *Tetrahedron*, 1996, **52**, 11385-11404.
- 2 D. Drew, J. R. Doyle and A. G. Shaver, *Inorg. Synth.*, 1972, **13**, 52-53.
- 3 H. Saltzman and J. G. Sharefkin, Org. Synth., 1963, 43, 60-61.
- 4 R. E. Schuster, J. E. Scott and J. Casanova, *Org. Synth.*, 1966, **46**, 75-77.
- 5 Bruker, *SAINT-plus*, Version 6.29, Bruker AXS, Madison, WI, USA, **2001**.
- 6 G. M. Sheldrick, *SHELXTL*, Version 6.14, Bruker AXS, Madison, WI, USA, **2000**.
- 7 G. M. Sheldrick, *CELL NOW*, Bruker AXS, Madison, WI, USA, **2004**.
- 8 G. M. Sheldrick, *TWINABS*, Version 1.05, Bruker AXS, Madison, WI, USA, **2002**.
- 9 S. Parsons and R. O. Gould, *ROTAX*, University of Edinburgh, Edinburgh, UK, **2003**.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03, Revisions C.02, D.02*, Gaussian, Inc., Wallingford, CT, **2004**.
- 11 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, 1998, **B37**, 785-789.
- 12 M. Krauss, W. J. Stevens, H. Basch and P. G. Jasien, *Can. J. Chem.*, 1992, **70**, 612-630.
- (a) M. T. Benson, T. R. Cundari, M. L. Lutz and S. O. Sommerer, in *Reviews in Computational Chemistry*, eds. D. Boyd and K. Lipkowitz, Wiley, New York, 1996, vol. 8, pp. 145-202; (b) A. S. Veige, L. M. Slaughter, E. B. Lobkovsky, P. T. Wolczanski, N. Matsunaga, S. A. Decker and T. R. Cundari, *Inorg. Chem.*, 2003, 42, 6204-6224; (c) R. G. Bergman, T. R. Cundari, A. M. Gillespie, T. B. Gunnoe, W. D. Harman, T. R. Klinckman, M. D. Temple and D. P. White, *Organometallics*, 2003, 22, 2331-2337.
- 14 R. Dennington, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell and R. Gilliland, *GAUSSVIEW*, Version 3.08, Semichem, Inc., Shawnee Mission, KS, **2003**.
- 15 A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035.