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Conformational analyses of the five-membered palladacycles derived from 1-(1′-naphthyl)ethyldiphenylphosphine and its arsenic analogue

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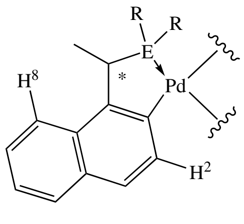
Abstract—The conformational behaviors of the five-membered palladacycles derived from the ligands, 1-(1′-naphthyl)ethyldiphenylphosphine and 1-(1′-naphthyl)ethyldiphenylarsine were determined from their *O*,*O*′-acetylacetonate complexes. Despite the possibilities of both palladacycles to exist in both δ and λ conformations, these palladacycles were noted to be conformationally rigid and only one of these was adopted in both the solid state and in solution ($CDCl_3$), as supported from their X-ray molecular structures and 2-D ^1H–^1H ROESY NMR studies, respectively.

1. Introduction

Chiral cyclopalladated compounds have continued to receive attention for the variety of their applications. They were used as agents for: (i) asymmetric syntheses (catalytic and stoichiometric);[1–13] (ii) chiral derivatizing agents for chiral discrimination and the determinations of enantiomeric excesses;[14–22] (iii) optical resolutions.[23–33] Among the pool of the accessible chiral cyclopalladated reagents, *N*,*N*-dimethyl-1-(1′-naphthyl)ethylaminate palladacycle **1** is probably the most commonly utilized. We have previously shown it to be a chiral auxiliary for the syntheses of optically active phosphines of various functionalities.[9–13,34–37] This is significant, since the metal complexes of enantiomerically pure phosphines are valuable as reagents for homogenous asymmetric catalysis.[38,39] The versatility of the above mentioned aminate palladacycle originates from two important unique features present within the chiral backbone: Firstly, the system possesses a strong electronic discrimination as a result of 'antisymbiosis'.[40,41] Secondly, the NMe_2 groups[42] and the H(2) proton[43] help to convey the stereochemical information from the conformationally rigid five-membered palladacycle. This latter observation was confirmed from solid state studies[41] as well as from NMR studies.[36,43] As the presence of a stable geometry within a chiral ligand is an important consideration in the rational design of Lewis acid systems for successful asymmetric applications,[44,45] the conformational rigidity of this chiral aminate system must therefore be highlighted. To note, the related chiral *N*,*N*-dimethyl-1-(phenyl)ethylaminate and *N*,*N*-dimethyl-1-(2′-naphthyl)ethylaminate palladacycles were generally regarded as less efficient[29,30,46,47] systems for optical resolutions because of the inherent lack of the crucial conformational locking that is present in **1**.



1: E = N, R = Me
2: E = P, R = Ph
3: E = As, R = Ph

As a part of our continued interest in developing novel chiral templates of this type, we have previously reported on the development of the analogous diphenylphosphino- **2** and diphenylarsino- **3** based palladacycles in the optically active forms.[48] In designing chiral Lewis acids for future use as catalysts or auxiliaries for asymmetric transformations, the necessity to first assess the stereochemical

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behaviors of these systems is significant and cannot be undermined.[49,50] Herein, we report the results of the studies of the conformational characteristics of these newly developed five-membered palladacycle systems **2** and **3**, in both solid state and in solution.

2. Results and discussion

The palladacycle systems **2** and **3** were prepared in optically active forms as the chloride-bridged dimeric complexes **2a** and **3a**.[48] Solution conformational studies of these systems were carried out using 2-D ^{1}H–^{1}H ROESY NMR spectroscopy to probe into the three dimensional structure of these chelates. For this purpose, these chloride-bridged dimers had to be transformed into derivatives suitable for such studies. Complexes **2a** and **3a** themselves were unsuitable for such studies because of the poorly resolved proton NMR resonance that they present. The broadness of these signals were directly attributed to the existence of the dimer as a mixture of two rapidly exchanging *syn* and *anti* regioisomers in solution (Scheme 1), in a manner that was also noted for the analogous chloride-bridged dimer of palladacycle **1**.[51] This fluxional behavior was observed on **2a** by variation temperature ^{31}P NMR spectroscopy. In Figure 1, the complex is presented as two broad singlets at room temperature (300 K) at δ 62.3 and 62.5. An improved peak resolution and a general downfield shift of the signals were observed upon cooling and a coalescence of both peaks was noted at 253 K. Curiously, heating the NMR sample from 300 to 328 K led to further broadening of the signals.

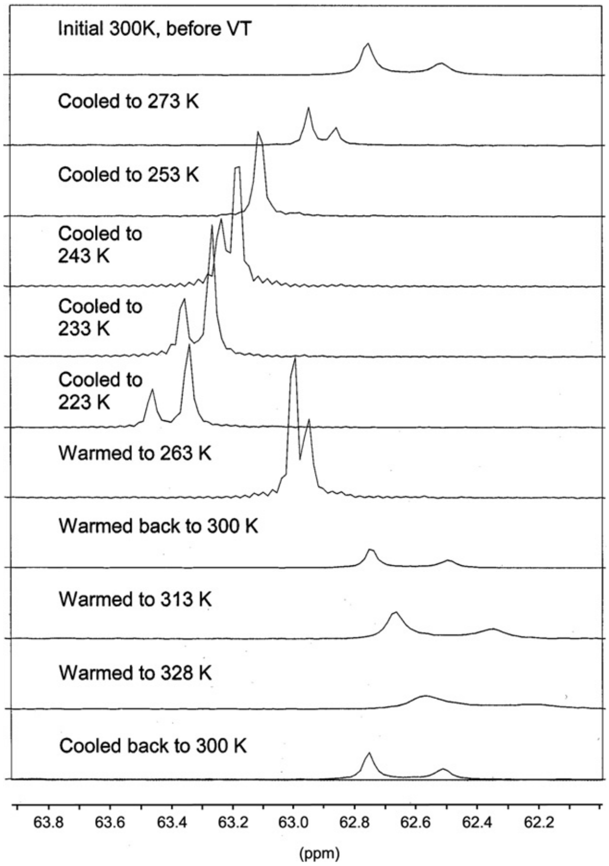
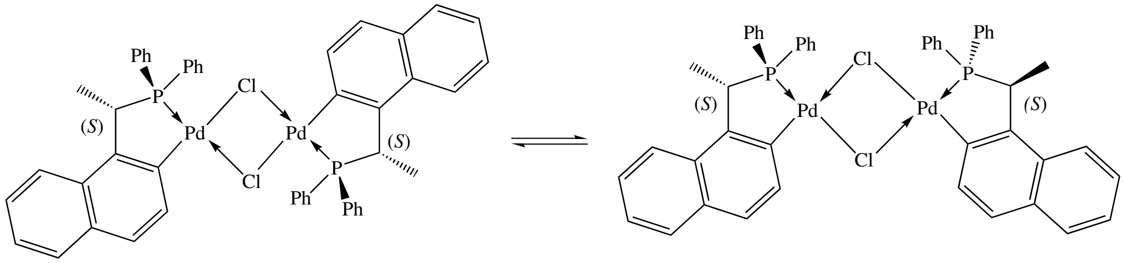


Figure 1. VT ^{31}P NMR spectra of (*S*,*S*)-**2a**.

Therefore, for the above solution NMR studies, the monomeric β-diketonate derivatives **2b** and **3b** were used. The choice of this derivative was made mainly because of the simplicity of the ^{1}H NMR spectroscopic signals that the *O*,*O*′-acetylacetonate ligand could present. It possesses only protons from the aliphatic groups and so the absence of any aromatic protons within the β-diketonate framework will therefore not contribute to the complexity at the aromatic region of the ^{1}H NMR spectrum, a region one can expect to be dominated by the large bulk of aromatic protons originating from the palladacycle. This ligand may prove preferable to other available ancillary ligands for NMR characterization of palladacycles, such as the commonly used triphenylphosphine because of the possibility of generating a mixture of *cis*- and *trans*-geometric isomers that could further complicate the assignment of signals. This problem can be especially severe for palladacycles that possess poor regioselectivities. The *O*,*O*′-acetylacetonate chelate, which is C_2 symmetrical, is free from this drawback. In addition, the preparations of these derivatives are straightforward. They involve direct mixing of dimers (*S*,*S*)-**2**–**3a** with the acetylacetonate salt (Scheme 2) while the isolation of products, (*S*)-**2c** and (*S*)-**3c** is technically simple. These products were obtained as pale yellow needles with $[\alpha]_D = +594$ (*c* 0.5, CH_2Cl_2) and $[\alpha]_D = +391$ (*c* 0.4, CH_2Cl_2), respectively.

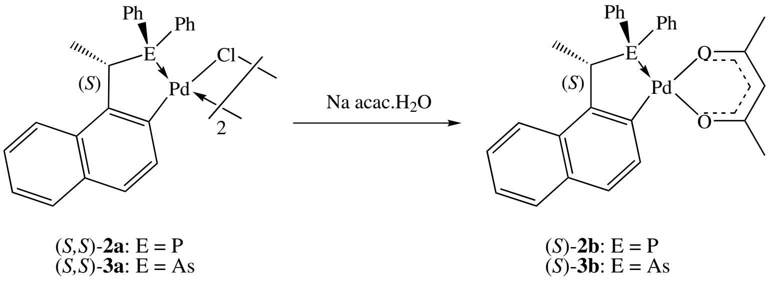
As illustrated by the Sawhorse and Newman representations in Figure 2, the puckered five-membered palladacycle could assume either the λ or δ conformation. The significant difference lies in the relative orientations of the α-



anti-(*S*,*S*)-**2a**

syn-(*S*,*S*)-**2a**

Scheme 1. Interconversion of the *anti*- and *syn*-(*S*,*S*)-**2a** regioisomers.



Scheme 2. Preparation of (S)-**2b** and (S)-**3b**.

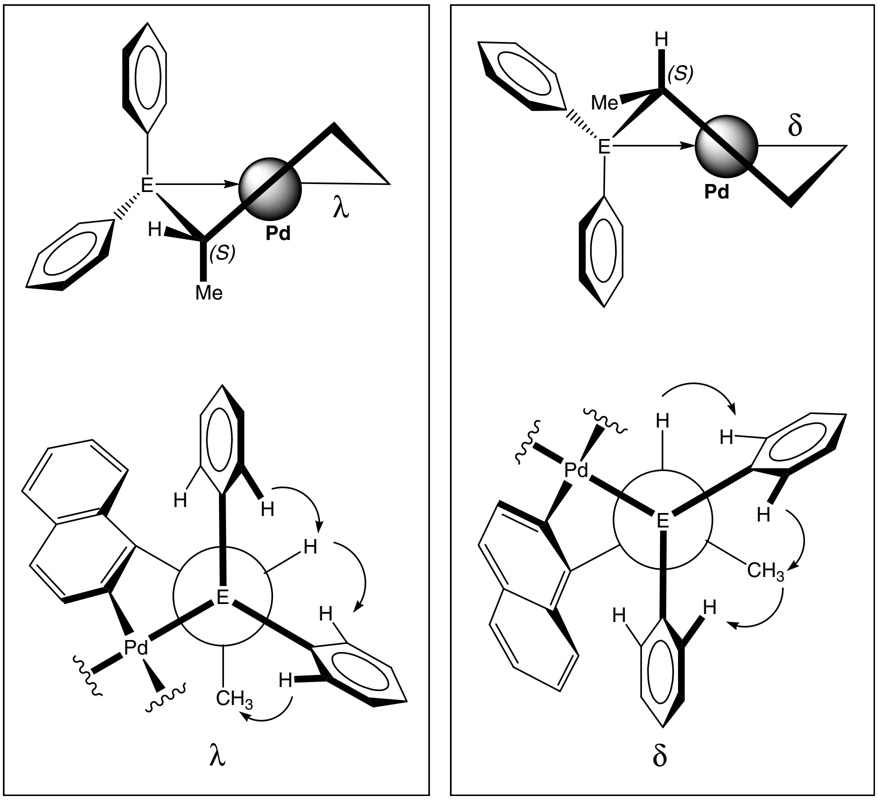


Figure 2. Sawhorse and Newman projections of the two possible conformations of the five-membered palladacycle with (*S*)-configuration.

C*H* proton and the α-C*Me* group. In the λ conformation for the (S_c) palladacycle, the former takes up the equatorial location while the latter substituent is located axially.

The solid state X-ray diffraction studies of complexes (*S*)-**2b** and (*S*)-**3b** were performed and their respective molecular structures are depicted in Figures 3 and 4. Selected bond lengths and angles are presented in Table 1. Notably, both structures share similar structural features. From the studies, the absolute (*S*)-configurations at the stereogenic centers were confirmed from the Flack's parameter of −0.02(3) for (*S*)-**2b** and 0.04(1) for the arsenic analogue. Expectedly, the five atoms of each palladacycle ring do not lie on the same plane but are located in a manner that gives a puckered arrangement. This is supported by a few facts. First, the mean intrachelate palladacycle torsion angle was 19.4° for (*S*)-**2b** and 18.9° for (*S*)-**3b**. The extent of the ring twisting is moderate by comparison of this parameter with those of similarly cyclopalladated phosphines. Second, the heterodonor E atom of each palladacycle was vertically displaced from its PdCCC plane. These were found to be 0.6543 and 0.7088 Å, respectively. Importantly, the α-C*Me* substituent is essentially disposed in the axial orientation in both palladacycles. The C(11)–C(12) bond was determined to subtend an angle of 4.6° and 5.2° to the normal of the mean coordination plane (m.c.pl.) for the phosphine and arsine complexes correspondingly. Furthermore, the axial location of the α-C*Me* substituent was further confirmed from the torsion angle of 154° and 151.6° correspondingly for the four atoms of C(12)–C(11)–E(1)–C(19). As the methyl substituent is located axially for the stereogenic α-C atom with the absolute (*S*)-configuration, both palladacycle rings must therefore assume the λ conformation. The possible steric interaction between the methyl substituent with the aromatic H(8) proton as the main factor in controlling the observed

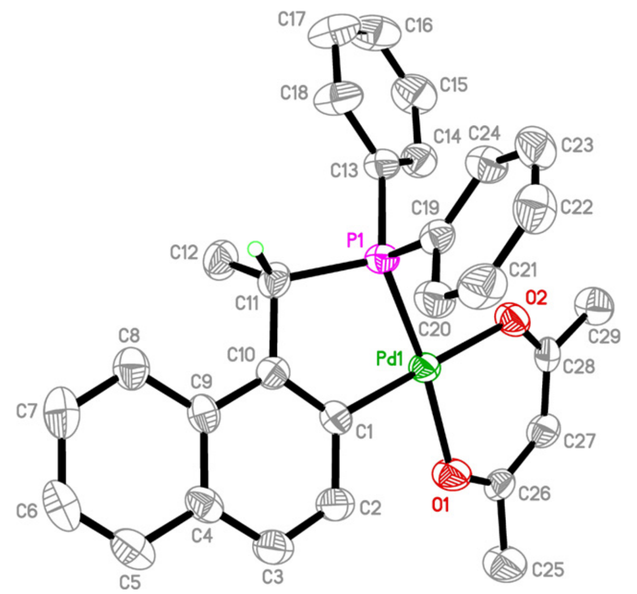


Figure 3. X-ray molecular structure of (*S*)-**2b**.

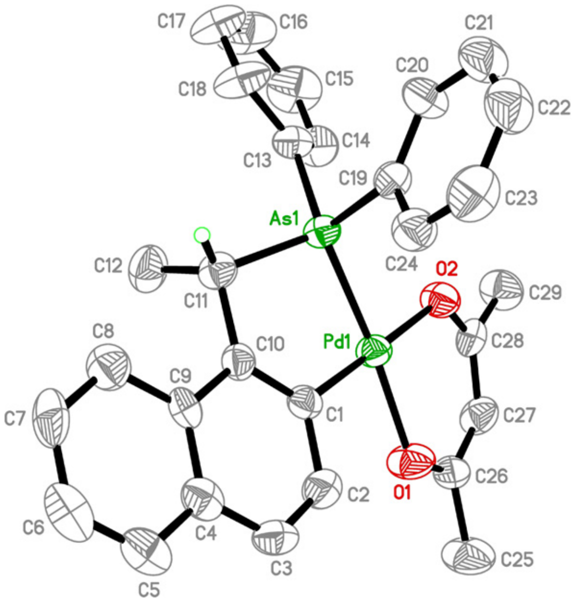


Figure 4. X-ray molecular structure of (*S*)-**3b**.

Table 1. Selected bond lengths (Å) and angles (°) of (*S*)-**2b** and (*S*)-**2c**

(*S*)-**2b**		(*S*)-**2c**	
Pd(1)–C(1)	2.006(4)	Pd(1)–C(1)	2.011(6)
Pd(1)–P(1)	2.200(1)	Pd(1)–As(1)	2.300(1)
Pd(1)–O(1)	2.073(3)	Pd(1)–O(1)	2.053(4)
Pd(1)–O(2)	2.104(3)	Pd(1)–O(2)	2.102(4)
P(1)–C(11)	1.837(4)	As(1)–C(11)	1.951(6)
C(10)–C(11)	1.510(5)	C(10)–C(11)	1.509(8)
C(1)–C(10)	1.384(5)	C(1)–C(10)	1.380(8)
P(1)–C(13)	1.813(4)	As(1)–C(13)	1.937(6)
P(1)–C(19)	1.828(4)	As(1)–C(19)	1.940(6)
C(11)–C(12)	1.539(5)	C(11)–C(12)	1.525(8)
C(1)–Pd(1)–P(1)	80.2(1)	C(1)–Pd(1)–As(1)	80.4(2)
C(1)–Pd(1)–O(1)	91.2(1)	C(1)–Pd(1)–O(1)	91.9(2)
P(1)–Pd(1)–O(2)	100.49(7)	As(1)–Pd(1)–O(2)	98.7(1)
O(1)–Pd(1)–O(2)	88.1(1)	O(1)–Pd(1)–O(2)	89.0(2)
Pd(1)–C(1)–C(10)	123.4(3)	Pd(1)–C(1)–C(10)	125.4(4)
C(1)–C(10)–C(11)	117.9(3)	C(1)–C(10)–C(11)	119.5(5)
C(10)–C(11)–P(1)	103.7(2)	C(10)–C(11)–As(1)	103.3(4)

palladacycle conformation is relevant here. This is explained by a consideration of the short H(8)–H(11) [(*S*)-**2b**: 2.234 Å; (*S*)-**3b**: 2.174 Å], and H(8)–C(12) contacts [(*S*)-**2b**: 3.024 Å; (*S*)-**3b**: 2.994 Å]. As a comparison, the latter distances are comparable to the sum of the van der Waal's radii of 3.0 Å for C and H atoms. Therefore, it is reasonable to suppose that in the alternate and unfavorable δ(*S*)-conformation in which the α-C*H* proton and the α-C*Me* group have exchanged positions, the resulting H(8)–C(12) close proximity would lead to a more severe congestion. However the roles of the P/As–Ph rings in affecting the conformational behavior seem insignificant. This conclusion is made on the basis of the significant variation of the shortest Ph_{eq}–H(11) and Ph_{ax}–H(11) distances between each *O*,*O*′-acetylacetonate derivative with its parent chloro-bridged dimer (*S*,*S*)-**2a** or **3a**, an indication of the abilities of these Ph rings to assume different rotameric states. For phosphapalladacycle **2**, the variations were found to be 0.870 and 0.693 Å for Ph_{eq}–H(11) as well as 0.892 and 0.806 Å for Ph_{ax}–H(11). Two values can be applied for each comparison since the parent dimer (*S*,*S*)-**2a** consists of two crystallographically independent halves with minor dissimilarities in their structural parameters. Likewise, the respective variations in distances of 0.544 and 0.836 Å as well as 0.939 and 0.729 Å were determined for the arsenic analogue **3**.

In solution ($CDCl_3$), the ^{1}H NMR signals were assigned using a combination of 2D ^{1}H–^{1}H COSY and ROESY NMR spectroscopic methods. Apart from the existence of ^{1}H–^{31}P couplings that were applicable to the α-C*H*, –*Me* and the aromatic protons of the diphenylphosphino group in (*S*)-**2b**, the ^{1}H NMR spectra of both compounds were similar. An unexpected but significant coupling with $J_{PH} = 3.8$ Hz was detected for the relatively low field H(2) proton (δ 8.10). The 2D ^{1}H–^{1}H ROESY NMR spectra of (*S*)-**2b** and (*S*)-**3b** have been expanded for clarity in Figures 5 and 6, respectively. From both spectra, the H(8) proton was immediately recognized from its NOE contacts with the α-C*H* proton and the α-C*Me* group (interactions C and D). Moreover, while the α-C methyl protons were observed to sterically interact with only one set of *ortho*-PPh protons (interaction A), the methine proton on the same carbon atom was seen to interact with both sets of *ortho*-PPh protons (interactions B and E). This NOE picture can only be satisfied by the λ-conformation for the (*S*)-palladacycle, as illustrated by the Newman projection in Figure 2. By this conformation, the α-C methyl group must thus take up an axial position while the methine proton on the same carbon atom must be equatorially oriented. In addition, the sequence of the signals for both sets of *ortho*-PPh protons may thus be assigned from an axial *ortho*-EPh at a high field to an equatorial *ortho*-EPh at a low field. It is important to note the absence of an NOE contact between the methyl group and the axial *ortho*-EPh protons as it indicates a conformational rigidity of the palladacycle ring. This interaction, if present to-

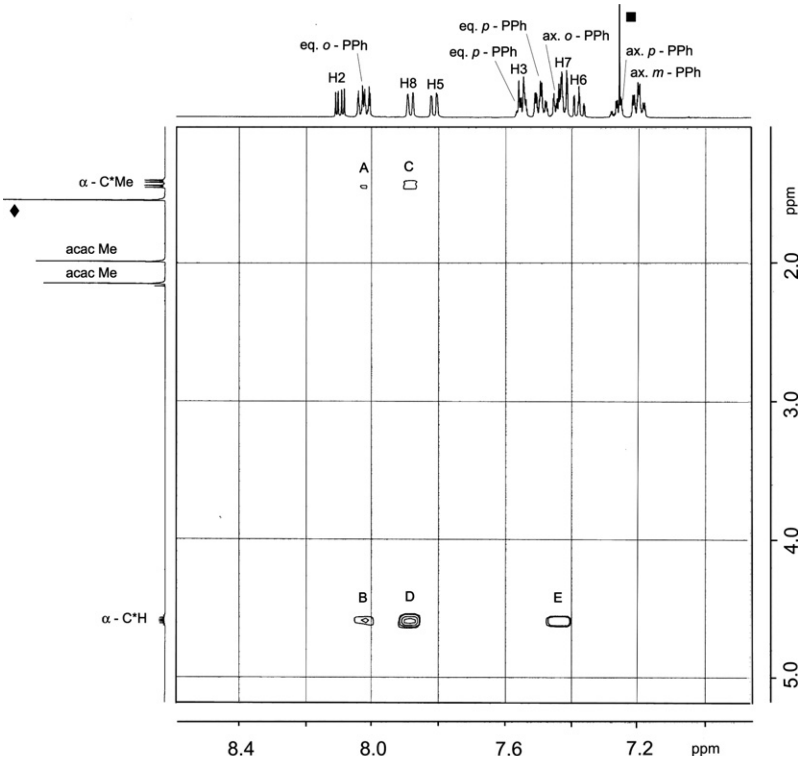


Figure 5. Expanded 2D ^{1}H–^{1}H ROESY NMR spectrum ($CDCl_3$) of (*S*)-**2b**. Selected NOE interactions: A, eq. *o*-PPh–α-CMe; B, eq. *o*-PPh–α-CH; C, H^8–α-CMe; D, H^8–α-CH; E, ax. *o*-PPh–α-CH. Solvent signals: ■, $CDCl_3$; ◆, H_2O.

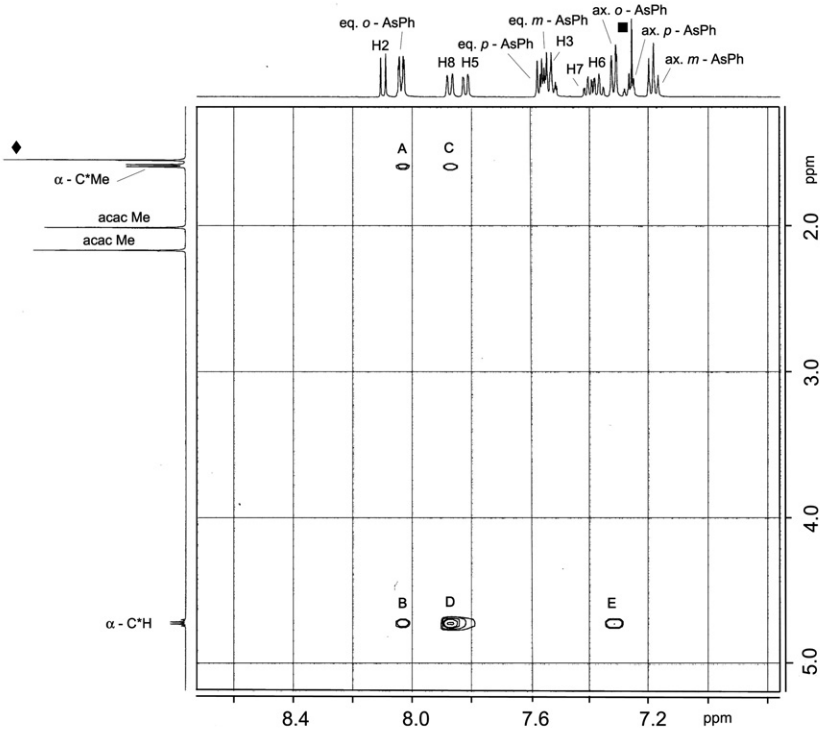


Figure 6. Expanded 2D ^{1}H–^{1}H ROESY NMR spectrum ($CDCl_3$) of (*S*)-**3b**. Selected NOE interactions: A, eq. *o*-AsPh–α-CMe; B, eq. *o*-AsPh–α-CH; C, H^8–α-CMe; D, H^8–α-CH; E, ax. *o*-AsPh–α-CH. Solvent signals: ■, $CDCl_3$; ◆, H_2O.

gether with the NOE interactions A–E however, would then imply a non-rigid conformational state for the palladacycle ring as the adoption of both λ and δ conformations then becomes feasible. When 2D ^{1}H–^{1}H ROESY NMR spectroscopic studies were carried out at a higher temperature of 328 K for both complexes, similar NOE patterns were observed. This implies that both systems are conformationally rigid not only at room temperature, but also at elevated temperatures, to at least 328 K in the same solvent.

3. Conclusion

Palladacycles **2** and **3** have been shown to be conformationally rigid in both the solid state as well as in solution ($CDCl_3$), such that their respective α-*Me* groups are axially located. Investigations on the applications of these two stereochemically well-defined palladacycles in various asymmetric transformations are currently underway.

4. Experimental

The ^1H NMR spectra of (*S*)-**2b** and (*S*)-**3b** were recorded on a Bruker AMX 500 NMR spectrometer while the $^{31}P\{^1H\}$ NMR spectrum of (*S*)-**2b** was recorded at 202 MHz on the same spectrometer. ^1H and $^{31}P\{^1H\}$ NMR chemical shifts were referenced relative to $SiMe_4$ and 85% H_3PO_4, respectively. The phase sensitive ROESY NMR experiments were acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $\gamma B_1/2\pi = 5000$ Hz and then transformed into 1024 × 1024 points using a sine bell weighting functions in both dimensions. Melting points were determined on a Büchi melting point B-545 apparatus and are uncorrected. Optical rotations were measured on the specified solution in a 1 cm or 1 dm cell at 25 °C with a Perkin–Elmer 341 Polarimeter. Infrared spectra were performed on a Bio-Rad FTS 3000MX (Excalibur Series) spectrometer. Elemental analyses and single crystal X-ray diffraction studies were performed by the staff of Elemental Analysis Laboratory and X-ray Diffraction Laboratory, respectively, of the Department of Chemistry at the National University of Singapore. The starting materials, di-μ-chlorobis[(*S*)-1-[1′-(diphenylphosphosphino)ethyl]naphthyl-C^2,*P*]-dipalladium(II), (*S*,*S*)-**2a**, and di-μ-chlorobis[(*S*)-1-[1′-(diphenylarsino)ethyl]naphthyl-C^2,*As*]dipalladium(II), (*S*,*S*)-**3a** were used as prepared as reported earlier.[48]

4.1. Preparation of (acetylacetonato-*O*,*O*′){(*S*)-1-[1-(diphenylphosphino)ethyl]naphthyl-C^2,*P*}palladium(II), (*S*)-2b

Sodium acetylacetonate monohydrate (0.029 g, 0.2080 mmol) was added to an acetone suspension (3 mL) of (*S*,*S*)-**2a** (0.100 g, 0.104 mmol) while the mixture was stirred vigorously for 16 h at room temperature, after which it was filtered through a short plug of Celite to give a pale yellow filtrate. The product was crystallized as fine, pale yellow needles upon concentration of the filtrate, mp 241–243 °C dec; 0.105 g (92.9% yield). $[\alpha]_D = +594$ (*c* 0.5, CH_2Cl_2); Anal. Calcd for $C_{29}H_{27}O_2PPd$: C, 63.9; H, 5.0. Found: C, 63.8; H, 5.3. IR (KBr, *v*, cm^{-1}) 1578 (s), 1560 (s), 1516 (s) (C═O, C–H, C═C of acac moiety); ^1H NMR ($CDCl_3$) δ 1.43 (dd, 3H, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 18.6$ Hz, PCH*Me*), 1.99 (s, 3H, *Me* from acac moiety), 2.15 (s, 3H, *Me* from acac moiety), 4.59 (dq, 1H, $^3J_{HH} = 7.1$ Hz, $^2J_{PH} = 13.0$ Hz, PC*H*Me), 5.45 (s, 1H, C*H* from acac moiety); 7.18–7.22 (m, 2H, ax. *m*-PPh), 7.25–7.29 (m, 1H, ax. *p*-PPh), 7.38 (m, 1H, H^6), 7.42–7.46 (overlapping m, 3H, H^7, ax. *o*-PPh), 7.47–7.51 (m, 2H, eq. *m*-PPh), 7.53–7.57 (overlapping m, 2H, H^3, *p*-PPh), 7.81 (dd, 1H, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 0.9$ Hz, H^5), 7.89 (d, 1H, $^3J_{HH} = 7.9$ Hz, H^8), 8.00–8.05 (m, 2H, eq. *o*-PPh), 8.10 (dd, 1H, $^3J_{HH} = 8.6$ Hz, $^4J_{PH} = 3.8$ Hz, H^2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 57.6 (s).

4.2. Preparation of (acetylacetonato-*O*,*O*′){(*S*)-1-[1-(diphenylarsino)ethyl]naphthyl-C^2,*As*} palladium(II), (*S*)-3b

Sodium acetylacetonate monohydrate (0.010 mg, 0.070 mmol) was added to an acetone suspension (3 mL) of (*S*,*S*)-**3a** (0.037 g, 0.035 mmol) and the mixture was stirred vigorously for 16 h at room temperature. The resulting suspension was filtered through a short plug of Celite to give a pale yellow filtrate. The product was crystallized as fine yellow needles upon concentration of the filtrate, mp (dec) 251–253 °C dec; $[\alpha]_D = +391$ (*c* 0.4, CH_2Cl_2); 0.041 g (74.6% yield). Anal. Calcd for $C_{29}H_{27}AsO_2Pd$: C, 59.2; H, 4.6. Found: C, 59.1; H, 4.5. IR (KBr, *v*, cm^{-1}) 1576 (s), 1560 (s), 1513 (s) (C═O, C–H, C═C of acac moiety); ^1H NMR ($CDCl_3$) δ 1.59 (d, 3H, $^3J_{HH} = 7.3$ Hz, AsCH*Me*), 2.02 (s, 3H, *Me* from acac moiety), 2.17 (s, 3H, *Me* from acac moiety), 4.72 (q, 1H, $^3J_{HH} = 7.3$ Hz, AsC*H*Me), 5.46 (s, 1H, C*H* from acac moiety), 7.18 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 7.3$ Hz, ax. *m*-AsPh), 7.27 (tt, 1H, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, ax. *p*-AsPh), 7.32 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.3$ Hz, ax. *o*-AsPh), 7.35–7.38 (m, 1H, H^6), 7.39–7.42 (m, 1H, H^7), 7.51–7.58 (overlapping m, 4H, H^3, eq. *m*-AsPh, eq. *p*-AsPh), 7.82 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.3$ Hz, H^5), 7.87 (d, 1H, $^3J_{HH} = 8.3$ Hz, H^8), 8.03 (dd, 2H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz, eq. *o*-AsPh), 8.09 (d, 1H, $^3J_{HH} = 8.8$ Hz, H^2).

4.3. X-ray diffraction studies of complexes (*S*)-2b and (*S*)-3b

Crystal data for both complexes and a summary of the crystallographic analyses are given in Table 2. Diffraction

Table 2. Crystallographic data for complexes (*S*)-**2b** and (*S*)-**2c**

	(*S*)-**2b**	(*S*)-**2c**
Formula	$C_{29}H_{27}O_2PPd$	$C_{29}H_{27}AsO_2Pd$
M	544.88	588.83
Space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
Crystal system	Orthorhombic	Orthorhombic
a/Å	12.6232(13)	12.7499(6)
b/Å	13.3669(13)	13.4202(6)
c/Å	14.4999(14)	14.6409(6)
V/Å^3	2446.6(4)	2505.15(19)
Z	4	4
T/K	223(2)	295(2)
λ/Å	0.71073	0.71073
μ/mm^{-1}	0.848	2.075
R_1 (obs data)[a]	0.0399	0.0534
wR_2 (obs data)[b]	0.0721	0.0867
Flack parameter	−0.02(3)	0.036(14)

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $wR_2 = \sqrt{\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

data were collected on a Siemens SMART CCD diffractometer with Mo K_α radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied and refinements by full-matrix least-squares were based on SHELXL 93.[52] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at a fixed distance from the carbon atoms and were assigned fixed thermal parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-634581 [for (*S*)-**2b**] and CCDC-634582 [for (*S*)-**3b**]. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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References

1. Longmire, J. M.; Zhang, X.; Shang, M.. *Organometallics* **1998**, *17*, 4374–4378.
2. Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881–5884.
3. Stark, M. A.; Jones, C. J.; Richards, C. J. *Organometallics* **2000**, *19*, 1282–1291.
4. Kirsch, S. F.; Overman, L. E. *J. Am. Chem. Soc.* **2005**, *127*, 2866–2867.
5. Overman, L. E.; Remarchuk, T. P. *J. Am. Chem. Soc.* **2002**, *124*, 12–13.
6. Hollis, T. K.; Overman, L. E. *Tetrahedron Lett.* **1997**, *38*, 8837–8840.
7. Leung, P. H.; Ng, K. H.; Li, Y. X.; White, A. J. P.; Williams, D. J. . *Chem. Commun.* **1999**, *23*, 2346–2435.
8. Takenaka, K.; Uozumi, Y. *Org. Lett.* **2004**, *6*, 1833–1835.
9. Qin, Y.; Lang, H.; Vittal, J. J.; Tan, G.-K.; Selvaratnam, S.; White, A. J. P.; Williams, D. J.; Leung, P.-H. *Organometallics* **2003**, *22*, 3944–3950.
10. Aw, B.-H.; Leung, P.-H. *Tetrahedron: Asymmetry* **1994**, *5*, 1167–1170.
11. He, G.; Loh, S.-K.; Vittal, J. J.; Mok, K. F.; Leung, P.-H. *Organometallics* **1998**, *17*, 3931–3936.
12. Liu, X.; Mok, K. F.; Leung, P.-H. *Organometallics* **2001**, *20*, 3918–3926.
13. Leung, P. H.; Qin, Y.; He, G.; Mok, K. F.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2001**, 309–314.
14. Böhm, A.; Seebach, D. *Helv. Chim. Acta* **2000**, *83*, 3262–3278.
15. Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K. *Tetrahedron: Asymmetry* **2000**, *11*, 2907–2916.
16. Albert, J.; Granell, J.; Muller, G.; Sainz, D.; Font-Bardia, M.; Solans, X. *Tetrahedron: Asymmetry* **1995**, *6*, 325–328.
17. Moncarz, J. R.; Laritcheva, N. F.; Glueck, D. S. *J. Am. Chem. Soc.* **2002**, *124*, 13356–13357.
18. Levrat, F.; Stoeckli-Evans, H.; Engel, N. *Tetrahedron: Asymmetry* **2002**, *13*, 2335–2344.
19. Chooi, S. Y. M.; Leung, P.-H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529–532.
20. Dunina, V. V.; Kuz'mina, L. G.; Kazakova, M. Yu.; Grishin, Yu. K.; Veits, Yu. A.; Kazakova, E. I. *Tetrahedron: Asymmetry* **1997**, *8*, 2537–2545.
21. Lopez, C.; Bosque, R.; Sainz, D.; Solans, X.; Font-Bardia, M. *Organometallics* **1997**, *16*, 3261–3266.
22. Kyba, E. P.; Rines, S. P. *J. Org. Chem.* **1982**, *47*, 4800–4801.
23. Kurita, J.; Usuda, F.; Yasuike, S.; Tsuchiya, T.; Tsuda, Y.; Kiuchi, F.; Hosoi, S. *Chem. Commun.* **2000**, 191–192.
24. He, G.; Mok, K. F.; Leung, P.-H. *Organometallics* **1999**, *18*, 4027–4031.
25. Brown, J. M.; Hulmes, D. I.; Layzell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673–1674.
26. Kwong, F. Y.; Yang, Q.; Mak, T. C. W.; Chan, A. S. C.; Chan, K. S. *J. Org. Chem.* **2002**, *67*, 2769–2777.
27. McCarthy, M.; Guiry, P. J. *Tetrahedron* **1999**, *55*, 3061–3070.
28. Ng, J. K.-P.; Li, Y.; Tan, G.-K.; Koh, L. L.; Vittal, J. J.; Leung, P. H. *Inorg. Chem.* **2005**, *44*, 9874–9886.
29. Alcock, N. W.; Brown, J. M.; Hulmes, D. L. *Tetrahedron: Asymmetry* **1993**, *4*, 743–756.
30. Valk, J.-M.; Claridge, T. D. W.; Brown, J. M. *Tetrahedron: Asymmetry* **1995**, *6*, 2597–2610.
31. Lacey, P. M.; McDonnell, C. M.; Guiry, P. J. *Tetrahedron Lett.* **2000**, *41*, 2475–2478.
32. Albert, J.; Cadena, J. M.; Granell, J.; Muller, G.; Panyella, D.; Sañudo, C. *Eur. J. Inorg. Chem.* **2000**, 1283–1286.
33. Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260.
34. Leung, P.-H.; Loh, S. K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1996**, 4443–4448.
35. Leung, P. H.; Siah, S.-Y.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 893–899.
36. Aw, B.-H.; Hor, T. S. A.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; Mcfarlane, W.; Leung, P.-H.; Chan, S.-H. *Inorg. Chem.* **1997**, *36*, 2138–2146.
37. Song, Y.; Mok, K. F.; Leung, P.-H. *Inorg. Chem.* **1998**, *37*, 6399–6401.
38. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley-Interscience: New York, 1994.
39. Parshall, G. W.; Ittel, S. D. *Homogenous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992.
40. Leung, P.-H.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1406–1410.
41. Chooi, S. Y. M.; Hor, T. S. A.; Leung, P.-H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494–1500.
42. Chooi, S. Y. M.; Tan, M. K.; Leung, P.-H.; Mok, K. F. *Inorg. Chem.* **1994**, *33*, 3096–3103.
43. Aw, B.-H.; Selvaratnam, S.; Leung, P.-H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753–1762.
44. Hollis, T. K.; Odenkirk, W.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron* **1993**, *49*, 5415–5430.
45. Liu, D.; Li, W.; Zhang, X. *Tetrahedron: Asymmetry* **2004**, *15*, 2181–2184.
46. Allen, D. A.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007–1014.
47. Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876–7886.
48. Ng, J. K.-P.; Tan, G.-K.; Vittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2003**, *42*, 7674–7682.
49. Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423–2426.
50. Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905–912.
51. Hockless, D. C. R.; Gugger, P. A.; Leung, P.-H.; Mayadunne, R. C.; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083–4094.
52. Sheldrick, G. M. SHELXL 93*, Program for Crystal Structure*; University of Gottingham: Germany, 1993.