74. Synthesis, Structure, and 2D-NMR Studies of Novel Chiral (η^3-Allyl)palladium(II) Complexes Containing the Bidentate Ligand Sparteine

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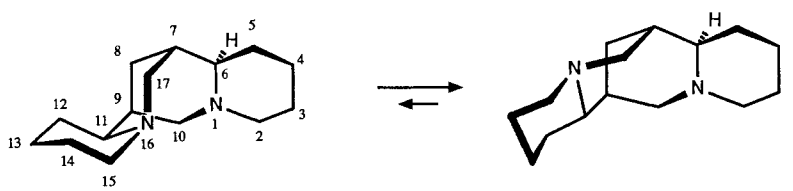
Novel cationic allylpalladium(II) complexes containing the alkaloid (−)-sparteine (**1**) as a bidentate ligand have been prepared. Two of them, [η^3-(cyclohex-2-enyl)] (sparteine)palladium(II) hexafluorophosphate ([Pd(η^3-C_6H_9)(sparteine)][PF_6]; **3b**) and (sparteine)[η^3-(1,1,3-triphenylallyl)]palladium(II) trifluoromethanesulfonate ([Pd(η^3-$Ph_2CCHCHPh$)(sparteine)][CF_3SO_3]; **3c**) were characterized by X-ray diffraction. The application of 2D-NMR methods (COSY and NOESY) affords a correlation between the solid-state and solution structures for complex **3c**.

1. Introduction. – η^3-Allyl complexes of Pd(II) are of fundamental importance in organometallic chemistry [1] and constitute key intermediates in several Pd-mediated organic transformations [2]. A number of such complexes stabilized by tertiary-phosphine ligands have been used as effective catalyst precursors in the so-called allylic alkylation reaction [3], where the allyl ligand undergoes attack by a suitable nucleophile. The use of allylpalladium complexes containing chiral chelating diphosphines as catalysts has been developed to a synthetic methodology for the formation of optically active allylic derivatives by several research groups [4]. Many of the synthetic efforts rely upon crystallographic work to support their structural ideas; however, 2D-NMR methods have been revealed in recent years as powerful tools for the study of the structure and dynamic behavior of allylpalladium complexes in solution [5].

In contrast to the enormous amount of work produced over the last decades on phosphine-containing allylpalladium complexes, the corresponding compounds stabilized by tertiary-amine ligands have been rather neglected. The readily available alkaloid (−)-sparteine (**1**; see *Scheme 1*) has been shown to be an effective chelating ligand, in

Scheme 1. *Preferred Conformations of (−)-Sparteine* (**1**)



1 all-chair conformation

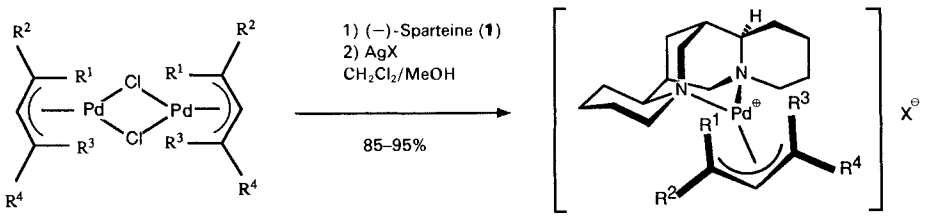
1 one-boat conformation

particular for first-row transition metals [6]. It has also been applied as a source of chiral information in several types of asymmetric reactions [7].

As part of our research program on chiral transition-metal complexes and their use in asymmetric synthesis [8], we decided to study the coordination ability of (−)-sparteine in allylpalladium chemistry. We report herein the preparation of novel Pd(II) complexes containing this bidentate amine ligand, their X-ray crystal structure, and 2D NMR studies. The parent compound **3a** was found to show some catalytic activity in asymmetric allylic alkylation [9].

2. Results and Discussion. – 2.1. *Synthesis.* Cationic (η^3-allyl)(sparteine)palladium(II) complexes **3** are readily prepared from the corresponding dimeric (allyl)chloropalladium complexes **2** *via* abstraction of the Cl-ligand by Ag^+ in the presence of a slight excess of (−)-sparteine (**1**; see *Scheme 2*). They can be isolated in high yield as their air-stable crystalline $[PF_6]^-$ or $[CF_3SO_3]^-$ salts.

Scheme 2



2a $R^1 = R^2 = R^3 = R^4 = H$, $X = [PF_6]^-$
b $R^1 - R^3 = -(CH_2)_3-$, $R^2 = R^4 = H$, $X = [PF_6]^-$
c $R^1 = R^2 = R^4 = Ph$, $R^3 = H$, $X = (CF_3SO_3]^-$

3a $R^1 = R^2 = R^3 = R^4 = H$, $X = [PF_6]^-$
b $R^1 - R^3 = -(CH_2)_3-$, $R^2 = R^4 = H$, $X = [PF_6]^-$
c $R^1 = R^2 = R^4 = Ph$, $R^3 = H$, $X = [CF_3SO_3]^-$

2.2. *Solid-State Structure.* The crystal and molecular structure of the complexes **3b** and **3c** was determined by X-ray analysis. ORTEP views [10] of the cations are shown in *Figs. 1* and *2*, and relevant bond distances and angles for both complexes are given in *Tables 1* and *2*, respectively. Both complexes are monomeric and show the expected overall geometric features with the sparteine molecule acting as a bidentate ligand in its all-chair conformation and the η^3-coordination mode for the allyl moieties. The rigid sparteine ligand is qualitatively found to occupy a hemispherical portion of the space around the Pd-atom. This is illustrated in *Fig. 3* which shows a space-filling model of complex **3b**.

Complex **3b** crystallizes in the orthorhombic space group $P2_12_12_1$ with three independent molecules in the unit cell. No significant differences in the bonding parameters exist between these three molecules so that the general features discussed below apply to all three molecules. The Pd–C and Pd–N bond lengths are found to be very similar to those previously observed by *Hegedus et al.* [11] in the cation of the complex salt ($[Pd(\eta^3\text{-}C_3H_5)(tmen)][Pd(\eta^3\text{-}C_3H_5)Cl_2]$ and by *Murrall* and *Welch* [12] in $[Pd\{\eta^3\text{-}(1\text{-}Ph\text{-}C_3H_4)\}(tmen)][BF_4]$[1]). The conformation of the six-membered cyclohexenyl ligand is best described as boat-like and *exo* with respect to the sparteine. A similar conformation is found in the complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_6H_9)(CO)]$ [13]. The preferred adoption of a boat- *vs.* a

[1]) *N,N,N',N'*-Tetramethylethylenediamine = tmen.

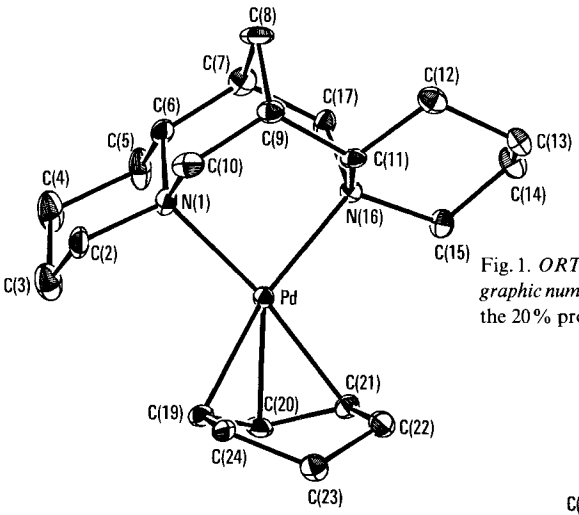


Fig. 1. *ORTEP View of cation* **3b**, *showing the crystallographic numbering scheme and the vibrational ellipsoids* (at the 20% probability level)

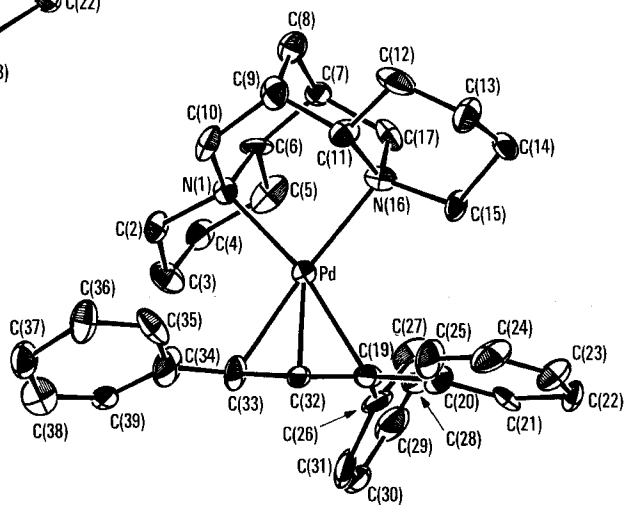


Fig. 2. *ORTEP View of cation* **3c**, *showing the crystallographic numbering scheme and the vibrational ellipsoids* (at the 20% probability level)

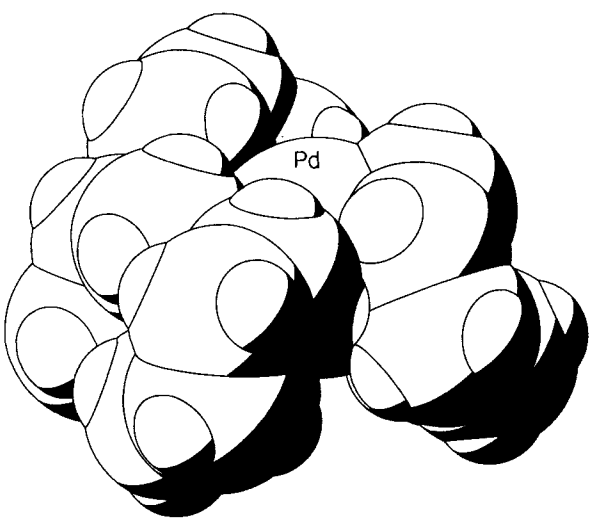


Fig. 3. *Space-filling model of cation* **3b**, *showing the space requirement of sparteine around the Pd-center*

Table 1. *Relevant Interatomic Distances* [Å] *and Angles* [°] *in* **3b**[a])

Molecule	**A**[b])	**B**[b])	**C**[b])
Pd–N(1)	2.14(1)	2.17(1)	2.15(1)
Pd–N(16)	2.16(1)	2.16(1)	2.17(1)
Pd–C(19)	2.14(2)	2.14(1)	2.16(2)
Pd–C(20)	2.09(2)	2.14(2)	2.09(2)
Pd–C(21)	2.14(2)	2.16(2)	2.14(2)
C(19)–C(20)	1.46(2)	1.41(3)	1.44(2)
C(20)–C(21)	1.40(2)	1.44(3)	1.39(2)
N(1)–Pd–N(16)	85.7(5)	86.0(5)	86.0(4)
N(1)–Pd–C(19)	102.8(6)	102.6(6)	103.0(5)
N(1)–Pd–C(20)	138.6(6)	136.8(6)	138.2(5)
N(1)–Pd–C(21)	164.0(5)	164.8(6)	163.0(6)
N(16)–Pd–C(19)	169.4(6)	168.5(5)	169.7(6)
N(16)–Pd–C(20)	133.6(6)	135.7(6)	134.4(5)
N(16)–Pd–C(21)	103.4(5)	102.9(6)	102.4(6)
C(19)–C(20)–C(21)	111(1)	113(2)	116(1)
C(20)–C(19)–C(24)	123(1)	122(2)	120(2)
C(20)–C(21)–C(22)	124(1)	121(2)	119(2)

[a]) E.s.d.'s on the last significant digit are given in parentheses.
[b]) **A**, **B**, and C refer to the three independent molecules in the unit-cell.

Table 2. *Relevant Interatomic Distances* [Å] *and Angles* [°] *in* **3c**[a])

Pd–N(1)	2.21(1)	Pd–N(16)	2.19(2)
Pd–C(19)	2.25(1)	Pd–C(32)	2.17(2)
Pd–C(33)	2.19(2)	C(19–C(20)	1.48(3)
C(19)–C(26)	1.48(3)	C(19)–C(32)	1.37(3)
C(32)–C(33)	1.43(3)	C(33)–C(34)	1.41(3)
N(1)–Pd–N(16)	86.1(5)	N(1)–Pd–C(19)	162.9(8)
N(1)–Pd–C(32)	137.4(7)	N(1)–Pd–C(33)	100.9(6)
N(16)–Pd–C(19)	107.8(6)	N(16)–Pd–C(32)	132.1(6)
N(16)–Pd–C(33)	168.5(7)	C(19)–C(32)–C(33)	122(2)
C(32)–C(33)–C(34)	120(2)	C(20)–C(19)–C(32)	115(2)
C(26)–C(19)–C(32)	121(2)	C(20)–C(19)–C(26)	119(2)

[a]) E.s.d.'s on the last significant digit are given in parentheses.

chair-like conformation by the η^3-cyclohexenyl ligand appears to be dictated by inter-ligand steric effects. A chair-like arrangement would lead to a substantial steric interaction between the axial H-atom at C(23) and the sparteine ligand (see also discussion in [13]).

Complex **3c** presents some more interesting structural features. It crystallizes in the hexagonal space group $P6_5$ which is rather rare for organic or organometallic compounds [14]. *Fig. 4* illustrates the esthetically appealing hexagonal symmetry around the crystallographic c-axis. Due to the three bulky Ph substituents on the allyl ligand, some distortions in the coordination sphere of the Pd-atom are observed. All bond lengths to Pd are 0.03 to 0.11 Å longer than in **3b**. The two inter-ligand angles N(1)–Pd–C(33) and N(16)–Pd–C(19) (100.0 (6) and 107.8 (6)°, resp.) are significantly different when compared to those found in **3b** and in the two tmen complexes mentioned above. Furthermore, an angle of 19° is found between the planes Pd–N(1)–N(16) and Pd–C(19)–C(33),

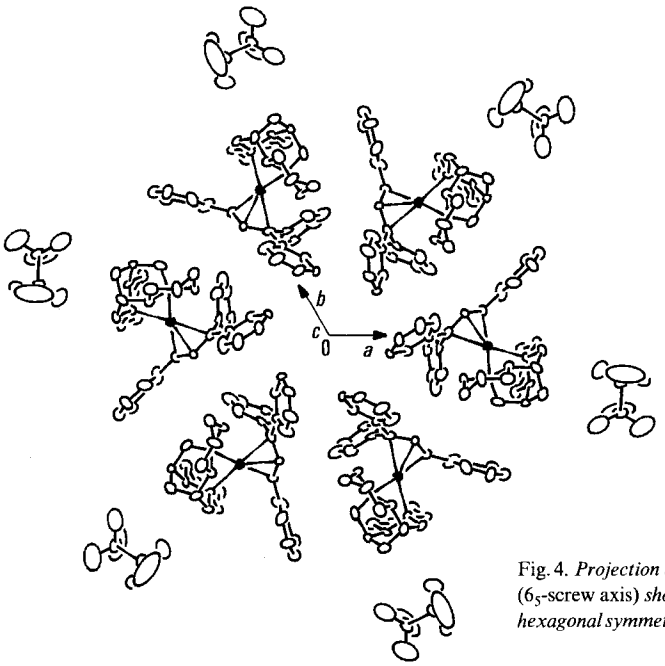


Fig. 4. *Projection along the crystallographic* c*-axis* (6_5-screw axis) *showing the crystal packing and the hexagonal symmetry* (space group $P6_5$) *of complex* **3c**

constituting an important deviation from the pseudo square planar geometry around the Pd(II) center. This is also illustrated by the fact that C(32) and C(33) lie above the PdN_2 plane (distance 0.58 (2) and 0.34 (2) Å, resp.), whereas C(19) lies below it (distance 0.38 (2) Å). The allyl ligand (plane C(19)–C(32)–C(33)) also forms an angle of 72° with the former defined PdN_2 plane (C(32)–H vector 'leaning' toward Pd). This distortion, also sustained by the fact that the central allylic C-atom is closer to the Pd-atom than the other two C-atoms, has been previously observed in $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ [15] and in the complex $[Pd(S,S\text{-chiraphos})(\eta^3\text{-}C(xylyl)_2CHCHPh)][BPh_4]$[2]) [16], the latter containing an allyl ligand with the same substitution pattern as the one in **3c**. The same distortion leads to a 'bending-away' of the *'anti'*-Ph group[3]) from the Pd-atom, whereas the two *'syn'*-Ph groups[3]) are tilted towards the metal center.

This tilting is also responsible for *a*) the non-coplanarity of C(20) and C(34) with the allyl moiety (distances of these two atoms from the C(19)–C(32)–C(33) plane: 0.24 and 0.15 Å, resp.) and *b*) for the observation of short inter-ligand distances between the allyl fragment and sparteine (C(2)–C(34) 3.27 and C(20)–C(15) 3.16 Å). The unique *'anti'*-Ph group is not parallel to the allyl moiety (the angle between the planes C(19)–C(32)–C(33) and C(26–31) being 68°). This seems to be dictated by the vicinity of the 'outer'[4]) sparteine ring N(1)–C(6).

The allyl ligand is coordinated to the metal atom in the orientation which results in the (*S*)-configuration at C(33), and this in turn correlates with the observed absolute config-

[2]) (*S,S*)-Chiraphos = (*S,S*)-2,3-bis(diphenylphosphino)butane.

[3]) The descriptors *'syn'* and *'anti'* are used for positions relative to the allyl proton H–C(32).

[4]) The rings containing C(2)–C(5) and C(12)–C(15), respectively, are referred to as 'outer', whereas the two central cyclic fragments as 'inner' rings.

uration of the product obtained by nucleophilic attack of $Na[CH(COOMe)_2]$ on this C-atom [9].

Finally, it is interesting to observe that the orientation of the allyl ligand relative to sparteine in **3c** is opposite to the one found in **3b** (*i.e.* upon superimposition of the sparteine ligands of the two complexes, the H–C(32) vector in **3c** points in the opposite direction of the corresponding H–C(20) vector in **3b**).

2.3. *NMR Spectroscopy.* The interesting solid-state structural features of complex **3c** prompted us to study its structure in solution by NMR. The ^{1}H-NMR spectroscopy of **3c** is complicated by the nature of the ligands and consequently reveals a spectrum with at least sixteen different aliphatic and allylic absorptions, many of these arising from overlapping resonances (see *Figs. 5* and *6*). We have used ^{13}C,^{1}H correlation in connection with COSY and NOESY 2D ^{1}H-NMR methods to assign key aspects of the allyl moiety in three dimensional space. The philosophy of our approach for **3c** may be summarized as follows: *a*) the ^{13}C,^{1}H correlation pin-points the allyl protons *via* readily recognized [17] ^{13}C-signals, *e.g.* the central allyl C-atom. Moreover, nonequivalent geminal protons, which often have very different chemical shifts, are thus assigned pairwise to a single C-atom. *b*) ^{1}H-COSY spectroscopy locates ^{1}H-spins which are spin-spin coupled to immediate neighbors (geminal or vicinal). *c*) ^{1}H-NOESY measurements allow the recognition of ^{1}H-spins which are close in space and most importantly identifies close inter-ligand contacts.

The Ph rings of the allyl moiety provide anisotropic shielding areas [18] which result in marked upfield shifts in properly positioned sparteine protons which are remote from the metal. Since both sides of sparteine and the allyl ligands are nonequivalent, potential isomers exist; however, only one form exists in solution. To identify this species, it was necessary not only to distinguish the two 'sides' of each ligand, but to place them relative to each other. The following observations are important for the assignement:

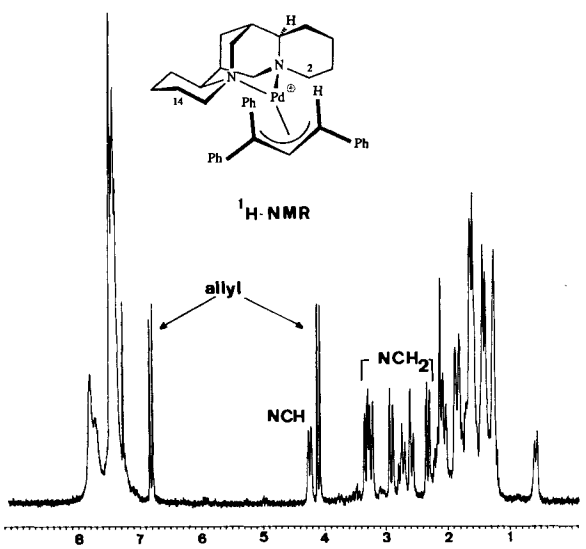
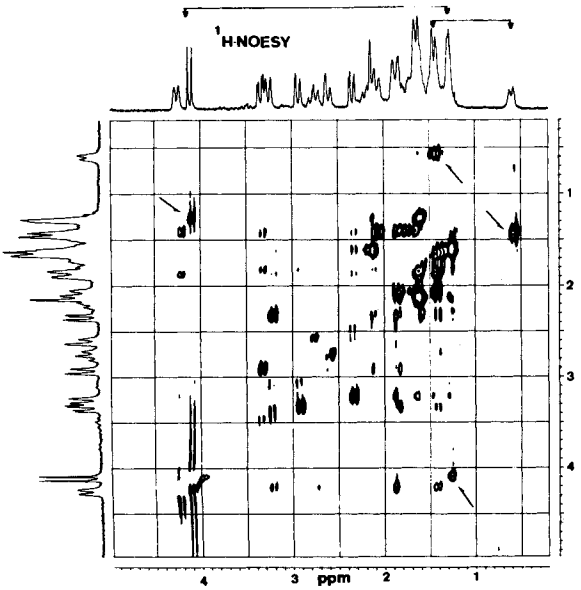
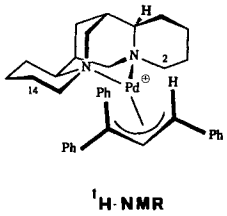


Fig. 5. *^{1}H-NMR spectrum* ($CDCl_3$, 200 MHz) *of complex* **3c**





^{1}H-NMR

Fig. 6. *Phase-sensitive NOESY ^{1}H-NMR spectrum* (0–5 ppm region; $CDCl_3$, 300 MHz) *of complex* **3c**

1) The *'anti'* allyl proton H–C(33) reveals a strong NOE, in both 1D and 2D spectra, to one aliphatic proton of a CH_2 group bound to two C-atoms, (*i.e.* C–CH_2–C). Both the solid-state structure and molecular models suggest this unknown proton to be H_{ax}–C(3) and not H_{ax}–C(14). This NOE is due to the (*R*)-configuration at C(6) bringing H–C(3) close to the allyl ligand. This presumed H–C(3) is adjacent to a CH_2N, as shown by both ^{1}H-COSY and NOE experiments. This adjacent CH_2N is shifted to relatively high field, *ca.* 1.60 ppm, due to the presence of the unique *'anti'*-Ph group which is twisted out of the allyl plane *(vide supra)*. These observations identify the 'outside' six-membered ring close to the Ph–C(33) side of the allyl ligand.

2) As shown in *Figs. 5* and *6*, there is an aliphatic one-proton resonance at *ca.* 0.55 ppm again arising from 1H of a C–CH_2–C fragment which is also immediately adjacent to a CH_2N group. We assign this unusually high-field proton to H_{ax}–C(14) and attribute its chemical shift to proximity to *'syn'*-Ph–C(19). ^{1}H-NMR spectra of sparteine, [Pd-(η^3-C_3H_5)(sparteine)][PF_6] (**3a**), and **3b** do not show this relatively high-field shift. There is no significant inter-ligand NOE to an allyl proton from H–C(14). With this starting point, COSY and NOESY measurements allow key assignments in the second 'outside' six-membered ring close to Ph_2C(19).

It now remains to assign the two 'inner' ring fragments, $NCHCHCH_2N$, which differ in three-dimensional space primarily with respect to the *'syn'*- and *'anti'*-Ph rings at C(19). There is a strong hint concerning this assignment for the following reasons:

3) One of the CH_2N protons of one fragment is shifted by at least 0.5 ppm to high field relative to the other three, presumably due to the *'anti'*-Ph at C(19).

4) The δ's of the ^{1}H- and ^{13}C-signals for the two CHN moieties are very different ($\Delta\delta$, *ca.* 6 ppm for C and *ca.* 2 ppm for H). This is a consequence of the differing coordination capabilities of the two terminal allyl C-atoms, *i.e.*, C(33) coordinates better than C(19) [16] [19], with presumed resulting differences in bonding to N(1) and N(16), respectively

[20]. This latter point is worth noting as the crystallography reveals practically equivalent Pd–N separations, presumably due to the relatively large experimental errors.

There are two further points worthy of mention in connection with the solution structure: we estimate [21] that the allyl H–C(33) to H_{ax}–C(3) distance is most likely $\leqslant 2.7$ Å, based on our previous experience with inter-ligand allyl NOE's, and there is likely to be the same forward distortion of the *'syn'*-Ph substituents, in solution, as found in the solid-state structure, since the high-field shifts of the axial protons at C(3) and C(14) are very pronounced. The analogous positions in a methallylpalladium(II) complex, *e.g.*, $[Pd(CH_2C(CH_3)CH_2)(\text{nitrogen chelate})]^+$ have the *'syn'*-protons twisted toward, and the *'anti'*-protons twisted away from the Pd-atom [21–23].

The results discussed above strongly suggest that complex **3c** adopts a preferred structure in solution which is very similar to the one observed in the solid state. In particular, the strong NOE's described can be best explained invoking the same type of distortions as observed in the crystal.

From the present study, we do not have any evidence that complex **3c** undergoes π-σ-π equilibria on the NMR time-scale at room temperature. In contrast, this type of dynamic behavior has been observed and studied for the analogous complex containing (*S,S*)-chiraphos[2]) instead of sparteine as chelating ancillary ligand [24].

Experimental Part

General. All reactions with air- or moisture-sensitive materials were carried out under Ar using standard *Schlenk* techniques. Freshly distilled solvents (CH_2Cl_2 from powdered CaH_2, Et_2O from Na/benzophenone ketyl and MeOH from NaOMe) were used throughout. (–)-Sparteine (**1**, *Sigma*) was distilled under reduced pressure and stored under Ar. M.p.: in open capillaries; *Büchi-510* melting-point apparatus; uncorrected. Optical rotations. *Perkin-Elmer-241* polarimeter, 10-cm-cells. ^{1}H- and ^{13}C-NMR spectra: *AC-200* and *AM-300 Bruker* instruments using 5-mm selective ^{1}H and 5-mm QNP probeheads; the sample was degassed by the freeze-thaw method; chemical shifts δ in ppm relative to Me_4Si, J values in Hz; recording of the HETCOR spectrum as a 4k by 1k data matrix using the standard *Bruker* software, the FID's were treated with an exponential multiplication ($LB = 1$ in f_1, $LB = 4$ in f_2) to obtain the final data set. ^{1}H-phase sensitive NOESY spectrum: as a 2k by 2k data matrix using square cosine bells in both f_1 and f_2 as window functions; mixing time 0.7 s as in previous NOESY spectra with similar molecules (unpublished results); standard *Bruker* software was used. Elemental analyses were performed by the analytical research services of *Ciba-Geigy AG*. Complexes **2b** [25] and **2c** [4b] were prepared according to published procedures, **2a** was purchased from *Johnson-Matthey* and recrystallized before use.

(η^3-Allyl)(sparteine)palladium(II) Hexafluorophosphate ($[Pd(\eta^3\text{-}C_3H_5)(\text{sparteine})][PF_6]$; **3a**). Sparteine (1 ml, 4.25 mmol; **1**) was added to a soln. of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (707 mg, 1.93 mmol; **2a**) in CH_2Cl_2 (30 ml). A soln. of Ag $[PF_6]$ (977 mg, 3.86 mmol) in MeOH (10 ml) was added and the mixture stirred in the dark for 1 h. The finely divided precipitate of AgCl was filtered off on a *Celite* plug. Slow addition of Et_2O (50 ml) to the filtrate induced crystallization. The crystals were washed with Et_2O and pentane and dried *in vacuo:* 1.88 g (92%). $[\alpha]_D^{22} = -67$ ($c = 1.035$, CH_2Cl_2). M.p. 215–218° (dec.). ^{1}H-NMR ($CDCl_3$, 300 MHz, r.t.): 1.17–3.82 (complex *m*, 28 H); 4.00 (br. *d*, $J = 12.5$, 1H); 4.25 (br. *d*, $J = 11.5$, 1H); 5.82–6.03 (*m*, 1H). Anal. calc. for $C_{18}H_{31}F_6N_2PPd$: C 41.04, H 5.93, N 5.32, F 21.64, P 5.88; found: C 41.11, H 5.93, N 5.33, F 21.60, P 5.85.

[η^3-(Cyclohex-2-enyl)](sparteine)palladium(II) hexafluorophosphate ($[Pd(\eta^3\text{-}C_6H_9)(\text{sparteine})][PF_6]$; **3b**) was prepared in a similar way starting from **2b** (4 g, 8.9 mmol) and **1** (4.3 ml, 18 mmol) in CH_2Cl_2 (150 ml), and $Ag[PF_6]$ (4.53 g, 17.9 mmol) in MeOH (100 ml). After filtering off the AgCl, the product separated first as an oil, upon addition of Et_2O (200 ml). It was converted to crystalline material on cooling under vigorous stirring. Filtration and washing with Et_2O and pentane yielded 9.64 g (95%). M.p. > 145° (dec. without melting). ^{1}H-NMR $CDCl_3$, 300 MHz, r.t.): 1.09–2.31 (complex *m*, 22 H); 2.61 (*td*, $J = 12, 4, 1$ H); 2.89 (br. *d*, $J = 12.5$, 1 H); 2.97 (*dd*, $J = 14, 3, 1$ H); 3.23 (br. *d*, $J = 12$, 1 H); 3.32 (*dd*, $J = 12, 4, 1$ H); 3.45–3.92 (complex *m*, 5 H); 4.48 (*t*, $J = 6$, 1 H); 4.72 (*t*, $J = 6$, 1 H); 5.98 (*t*, $J = 7.5$, 1 H). Anal. calc. for $C_{21}H_{35}F_6N_2PPd$: C 44.49, H 6.22, N 4.94, F 20.11, P 5.46; found: C 44.51, H 6.27, N 4.91, F 20.05, P 5.35.

(Sparteine)[η^3-(1,1,3-triphenylallyl)]palladium(II) Trifluoromethanesulfonate ([Pd(η^3-$Ph_2CCHCHPh$)-(sparteine)][CF_3SO_3]; **3c**). This complex was prepared following a similar procedure as described above, starting from **2c** (2 g, 2.43 mmol) and **1** (1.15 g, 4.9 mmol) dissolved in CH_2Cl_2 (200 ml) and Ag[CF_3SO_3] (1.14 g; 4.4 mmol) in MeOH (10 ml). After filtering off the AgCl and concentrating the soln. *in vacuo* to 50 ml, the product was obtained as orange microcrystalline material upon addition of Et_2O (100 ml) and cooling to 5° overnight: 3.15 g (85%). M.p. 199–200° (dec.). $[\alpha]_D^{22} = -176$ ($c = 0.285$, CH_2Cl_2). NMR: *Table 3*, *Figs. 5* and *6*. Anal. calc. for $C_{37}H_{43}F_3N_2O_3PdS$: C 58.54, H 5.71, F 7.51, N 3.69, S 4.22; found: C 58.38, H 5.66, F 7.52, N 3.61, S 4.28.

Table 3. *Selected ^1H- and ^{13}C-NMR Chemical Shifts of Complex* **3c**

H–C(32)	6.78	H–C(33)	4.09
H–C(2)	1.60 (2 H)	H–C(10)	2.92, 3.32
H_{ax}–C(3)	1.24	H–C(11)	2.12
H_{eq}–C(3)	1.60	H_{eq}–C(14)	1.39
H–C(4)	1.40 (2 H)	H_{ax}–C(14)	0.55
H–C(6)	4.25	H_{ax}–C(15)	2.69
H–C(7)	1.87	H_{eq}–C(15)	2.61
H–C(9)	1.81	H–C(17)	3.18, 2.30
C(32)	106.2	C(33)	69.2
C(2)	61.0	C(10)	48.4
C(3)	*ca.* 26.0	C(11)	63.2
C(6)	69.9	C(14)	19.7
C(7), C(9)	34.3, 34.1	C(15)	62.3
C(17)	64.4		

X-Ray Structure Analyses of **3b** *and* **3c**. Crystal data and aquisition parameters for both compounds are given in *Table 4*. Crystals suitable for X-ray diffraction of both complexes were grown by slow diffusion of MeOH into a concentrated CH_2Cl_2 soln. at 4°. The crystals used for the measurements were imbedded in and fixed to a *Lindemann* capillary with *Araldit Rapid* glue. Space-group and cell-constants determination as well as collection of intensity data were effected on a *Philips-PW-1100* diffractometer. The $\theta/2\theta$ scan mode was used. There was no

Table 4. *Crystal Data and Experimental Conditions Associated with Data Collection for* **3b** *and* **3c**

Complex	**3b**	**3c**
Molecular formula	$C_{21}H_{35}F_6N_2PPd$	$C_{37}H_{43}F_3N_2O_3PdS$
Formula weight	566.88	759.22
Crystal system	orthorhombic	hexagonal
Space group	$P2_12_12_1$	$P6_5$
a [Å]	47.537 (4)	24.296 (2)
b [Å]	15.835 (2)	$= a$
c [Å]	9.068 (1)	10.980 (1)
V [Å^3]	6826	5614
Z	12	6
Calc. density [g/cm^3]	1.655	1.347
Cryst. dimensions [mm]	0.70 × 0.35 × 0.15	0.69 × 0.20 × 0.10
Temperature [°C]	−55 (±4)	20 (±2)
Radiation	Mo$K\alpha$1	Mo$K\alpha$1
λ [Å] (graphite monochrom.)	0.70926	0.70926
2θ Range [°]	6–54	6–40
Scan time [s]	$\leqslant 30$	$\leqslant 42$
Scan width [°]	0.84	1.4
No. of reflections	8361	11295
No. of non-zero reflections ($I > 2\sigma(F_o)$)	7384	1778
Final R factor	0.073	0.057

significant intensity variation for three standard reflections measured every 2 h. The structures were solved by the heavy-atom methods using the program SHELX 76 [26]. The H-atoms could not be localized. Block-diagonal-least-squares refinements were carried out with anisotropic temperature factors for Pd, P, and F (**3b**) and for Pd (**3c**). Final positional parameters and a complete list of bond distances and angles for both complexes have been deposited with the *Cambridge Crystallographic Data Centre*.

REFERENCES

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, California, 1987, Chapt. 19.

[2] For reviews, see a) J. Tsuji, 'Organic Synthesis with Palladium Compounds', Springer, Berlin, 1980; b) B.M. Trost, T.R. Verhoeven, in 'Comprehensive Organometallic Chemistry, Eds. G. Wilkinson, F.G.A. Stone, and E.W. Abel, Pergamon, London, 1984, Vol. 8, p. 799.

[3] For a review, see B.M. Trost, *Acc. Chem. Res.* **1980,** *13,* 3845.

[4] For a review, see G. Consiglio, R.M. Waymouth, *Chem. Rev.* **1989,** *89,* 257; see also a) T. Hayashi, M. Kumada, in 'Asymmetric Synthesis, Ed. J.D. Morrison, Academic Press, Orlando, FL, 1985, Vol. 5, p. 147, and ref. cit. therein; b) P.R. Auburn, P.B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985,** *107,* 2033; c) B.M. Trost, D.J. Murphy, *Organometallics* **1985,** *4,* 1143.

[5] a) P.S. Pregosin, C. Amman, *Pure Appl. Chem.* **1989,** *61,* 1771; b) E. Cesarotti, M. Grassi, L. Prati, F. Demartin, *J. Organomet. Chem.* **1989,** *370,* 407.

[6] a) E. Boschmann, G.A. Nypaver, J.P. Majors, S.M. Ealy, M. van Horn, *J. Coord. Chem.* **1978,** *7,* 141; b) R. Kuroda, S.F. Mason, *J. Chem. Soc., Dalton Trans.* **1977,** 371; c) E. Boschmann, L.M. Wienstock, M. Carmack, *Inorg. Chem.* **1974,** *13,* 1297; d) S.F. Mason, R.D. Peacock, *J. Chem. Soc., Dalton Trans.* **1973,** 226.

[7] a) H. Kageyama, K. Miki, Y. Kai, N. Kasai, Y. Okamoto, H. Yuki, *Bull. Chem. Soc. Jpn.* **1984,** *57,* 1189; b) M. Guetté, J. Capillon, J.-P. Guetté, *Tetrahedron* **1973,** *29,* 3659; c) B.M. Trost, T.J. Dietsche, *J. Am. Chem. Soc.* **1973,** *95,* 8200; d) R.A. Kretchmer, *J. Org. Chem.* **1972,** *37,* 2744; e) H. Nozaki, T. Aratani, T. Toraya, R. Noyori, *Tetrahedron* **1971,** *27,* 905.

[8] A. Togni, S.D. Pastor, G. Rihs, *Helv. Chim. Acta* **1989,** *72,* 1471, and ref. cit. therein.

[9] a) A. Togni, G. Rihs, Poster at the Sixth International Symposium on Homogeneous Catalysis 1988, Vancouver, Canada; b) A. Togni, manuscript in preparation.

[10] C.K. Johnson, Program ORTEP II, ORNL-5138, Oak Ridge Natl. Lab. [Rep.], U.S., 1976.

[11] L.S. Hegedus, B. Åkermark, D.J. Olsen, O.P. Anderson, K. Zetterberg, *J. Am. Chem. Soc.* **1982,** *104,* 697.

[12] N.W. Murrall, A.J. Welch, *J. Organomet. Chem.* **1986,** *301,* 109.

[13] M. Crocker, M. Green, C.E. Morton, K.R. Nagle, A.G. Orpen, *J. Chem. Soc., Dalton Trans.* **1985,** 2145.

[14] a) A.D. Mighell, V.L. Himes, J.D. Rodgers, *Acta Crystallogr., Sect. A* **1983,** *39,* 737; b) J. Donohue, *ibid.* **1985,** *41,* 203.

[15] A.E. Smith, *Acta Crystallogr.* **1965,** *18,* 331.

[16] D.H. Farrar, N.C. Payne, *J. Am. Chem. Soc.* **1985,** *107,* 2054.

[17] a) K. Vrieze, H.C. Volger, P.W.N.M. van Leeuwen, *Inorg. Chim. Acta Rev.* **1969,** 109; b) A. Musco, R. Pontellini, M. Grassi, A. Sironi, S.V. Meille, H. Rüegger, C. Ammann, P.S. Pregosin, *Organometallics* **1986,** *7,* 2130; c) C. Ammann, P.S. Pregosin, H. Rüegger, M. Grassi, *Magn. Reson. Chem.* **1989,** *27,* 355.

[18] E.D. Becker, 'High Resolution NMR', Academic Press, New York, 1980, pp. 73–74.

[19] B. Åkermark, B. Kratenberger, S. Hansson, *Organometallics* **1987,** *6,* 620.

[20] M. Grassi, S.V. Meille, A. Musco, R. Pontellini, A. Sironi, *J. Chem. Soc., Dalton Trans.* **1989,** 615, and ref. cit. therein.

[21] A. Albinati, C. Ammann, P.S. Pregosin, submitted to *Organometallics.*

[22] J.E. Gozum, D.M. Palina, J.A. Jensen, G.S. Girolami, *J. Am. Chem. Soc.* **1988,** *110,* 2688.

[23] T. Clark, C. Rohde, P.v.R. Schleyer, *Organometallics* **1983,** *3,* 1344.

[24] P.B. Mackenzie, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1985,** *107,* 2046.

[25] B.M. Trost, P.E. Strege, L. Weber, T.J. Fullerton, T.J. Dietsche, *J. Am. Chem. Soc.* **1978,** *100,* 3407.

[26] G.M. Sheldrick, 'SHELX 76, Crystal Structure Analysis Package', Univ. of Cambridge, England, 1976.