

CHIRAL HETEROCYCLIC LIGANDS

III *. A STRUCTURAL STUDY OF THE CYCLOPALLADATION OF (4*S*, 7*R*)-7,8,8-TRIMETHYL-1-PHENYL-4,5,6,7-TETRAHYDRO-4,7-METHANO-1*H*-INDAZOLE

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Summary

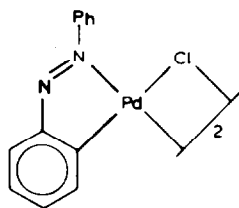
Reaction of the ligand (4*S*, 7*R*)-7,8,8-trimethyl-1-phenyl-4,5,6,7-tetrahydro-4,7-methano-1*H*-indazole, LH=V, with lithium tetrachloropalladate gives a *trans*-Pd(LH)₂Cl₂ complex, which on further reaction undergoes cyclopalladation to [PdLCl]₂. These compounds were characterised spectroscopically and their structures confirmed by single crystal X-ray analyses, with refinement to *R* values of 0.028 and 0.036 respectively.

Introduction

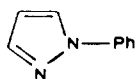
Since the discovery by Cope and Siekman [1] that azobenzene undergoes cyclopalladation to give the chloro-bridged dimer I numerous related complexes have been reported [2–7]. Although the preparations, properties and applications to organic synthesis [8] of such cyclopalladated compounds have been extensively reviewed, studies of the mechanism of formation of these compounds have been less common. The most commonly accepted mechanism for the formation of I is that proposed by Parshall [9]. However for the cyclopalladation [10–12] of 1-phenylpyrazole (II) it has been proposed [10] that the reaction proceeds via the intermediate III, which is in turn converted to the dimer IV. However the intermediate III was not fully characterised owing to loss of some of the ligand II on drying of the complex.

We are currently involved in a study of the synthesis and complexing abilities of a series of chiral polydentate ligands which incorporate nitrogen-heterocycles fused to a bornane skeleton [13,14]. As part of this study we examined the reaction of

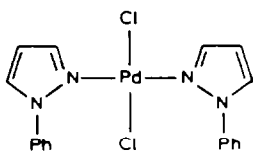
* For part II see ref. 14.



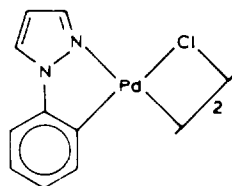
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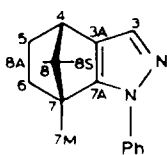
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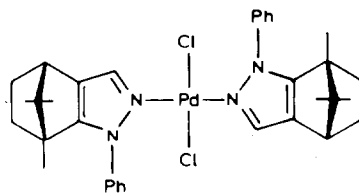
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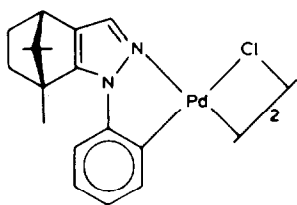
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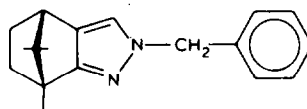
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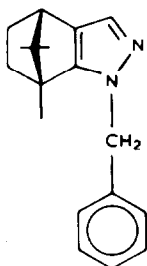
(VI)



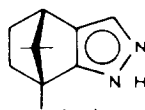
(VII)



(VIII)



(IX)



(X)

lithium tetrachloropalladate with (4*S*, 7*R*)-7,8,8-trimethyl-1-phenyl-4,5,6,7-tetrahydro-4,7-methano-1*H*-indazole (V), a chiral derivative of II, and obtained a stable *trans*-PdL₂Cl₂ complex, analogous to III, which on further reaction underwent cyclopalladation to give a chloro-bridged dimer analogous to IV. We herein report spectroscopic and X-ray crystallographic studies of these compounds.

Results and discussion

The ligand V was prepared from hydroxymethylene camphor and phenyl hydrazine as previously reported [15]. Reaction of V with lithium tetrachloropalladate in methanol produced the bis-complex VI, whose structure follows from its infrared spectrum (780 and 700 cm⁻¹, monosubstituted benzene ring; 340 cm⁻¹, *trans*-PdCl₂ [12]), NMR spectra (Table 1) and combustion analysis. Reaction of VI with additional lithium tetrachloropalladate gave the cyclopalladated dimer VII for which the infrared (740 cm⁻¹) and NMR spectra (Table 1) showed the presence of an *ortho*-disubstituted benzene ring. A notable feature of the ¹H NMR spectra of VI and VII is the significant shifts in the position of the C(7)-methyl proton chemical shifts. Relative to the free ligand V the resonance for these protons shifts upfield in VI and downfield in VII. These shifts can be rationalised on the basis of the

TABLE 1
¹³C AND ¹H NMR CHEMICAL SHIFTS FOR V-IX

¹³ C	V	VI	VII	VIII	IX
C(3)	132.9	135.3	132.4	121.6	131.2
C(3A)	130.4	130.0	130.4	not obs.	129.1
C(4)	47.2	47.7	47.2	47.3	47.6
C(5)	27.8	27.2	27.3	27.8	27.8
C(6)	33.7	33.5	33.6	33.8	33.4
C(7)	63.4	62.8	63.2	60.6	62.8
C(7A)	153.2	158.0	152.7	166.2	not obs.
C(8)	53.1	53.8	55.5	50.2	52.3
C(7M)	12.2	11.2	15.1	10.8	11.3
C(8S)	19.7	19.2	19.7	19.2	19.6
C(8A)	20.3	20.3	20.3	20.6	20.3
C(1')	140.2	138.0	143.3	138.1	138.2
C(2')	124.2	128.2	142.1	127.0	126.7
C(3')	128.7	128.7	134.6	128.5	128.6
C(4')	127.2	129.4	125.0	127.4	127.5
C(5')	128.7	128.7	124.4	128.5	128.6
C(6')	124.2	128.2	112.1	127.0	126.7
CH ₂				55.1	53.9
¹ H	V	VI	VII	VIII	IX
7-CH ₃	1.15	0.83	1.62	1.33	1.17
<i>syn</i> -8-CH ₃	0.78	0.70	0.82	0.70	0.73
<i>anti</i> -8-CH ₃	0.92	0.83	0.97	0.95	0.87
4-H	2.82	2.76	2.85	2.73	2.75
3-H	7.32	7.28	7.48	6.87	7.18
Ph-H	7.43	7.57	6.8-7.6	7.0-7.4	7.0-7.4
CH ₂				5.25	5.32

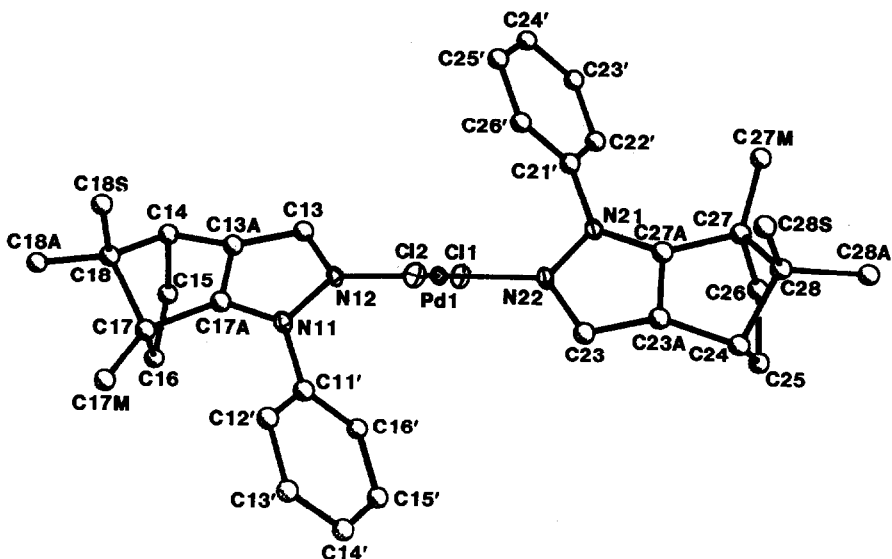


Fig. 1. Perspective view and atom labelling of VI. Hydrogen atoms omitted for clarity.

conformation of the phenyl ring since in the complex VI the phenyl ring is expected to be approximately orthogonal to the pyrazole ring with the result that the C(7)-methyl protons lie above the shielding plane of the phenyl ring. In the cyclopalladated compound VII however the phenyl ring is constrained to be coplanar with the pyrazole ring and in this orientation the C(7)-methyl protons lie in the deshielding plane of the phenyl ring.

In order to confirm the structures of VI and VII single crystal X-ray structure determinations were carried out. Figures 1 and 2 show perspective views and atom labelling of the structures of VI and VII respectively. Tables 2 and 3 list bond lengths and angles respectively with standard deviations in parentheses. The structure of VI (Fig. 1) is confirmed as the *trans*-PdL₂Cl₂ complex analogous to the previously proposed [10] intermediate III in the cyclopalladation of II. The coordination about the palladium atom is square planar (maximum deviation from the mean plane: 0.016 Å) with Pd–Cl and Pd–N bond lengths similar to those in previously reported related *trans*-PdL₂Cl₂ complexes [16–20]. The two pyrazole rings are planar (maximum deviations from the mean planes: 0.008 and 0.008 Å) and inclined to the palladium coordination mean plane at angles of 52.6 and 61.6°. The two phenyl rings are planar (maximum deviations from the mean planes: 0.011 and 0.013 Å) and inclined to the corresponding pyrazole ring mean planes at angles of 52.4 and 51.1°. These small torsional angle differences are the only features which destroy the non-crystallographic two-fold symmetry of the complex. The bonding within the bornyl framework is normal [13,14]. All intermolecular contacts between non-hydrogen atoms are > 3.4 Å.

The structure of VII (Fig. 2) is confirmed as the cyclopalladated chloro-bridged dimer in which the chelate rings are *trans*-related. The coordination about both palladium atoms is square planar. The Pd–Cl bonds *trans* to the Pd–C bonds are longer than those *trans* to the Pd–N bonds. Similar *trans* effects have been noted in

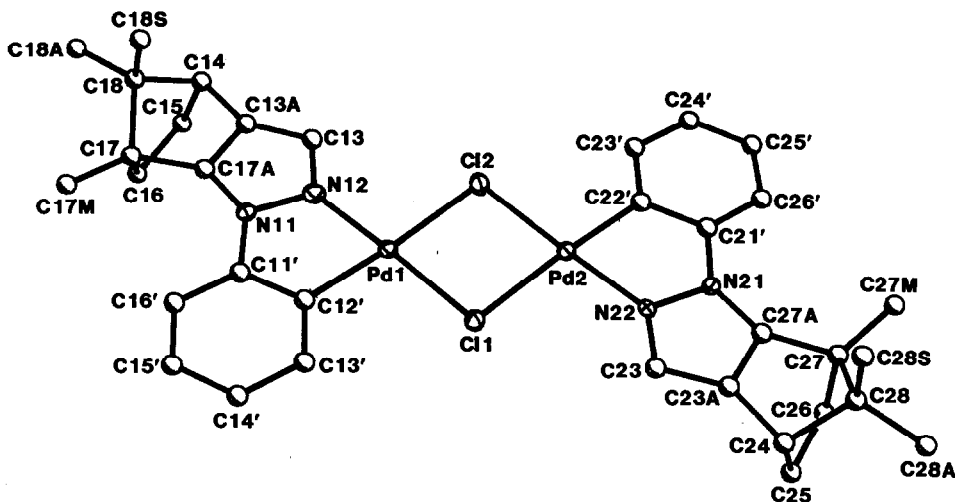


Fig. 2. Perspective view and atom labelling of VII. Hydrogen atoms omitted for clarity.

closely related structures [21,22]. The Pd–C bond lengths are almost identical to those found in the only other report of bis-chloro-bridged dimers having only Pd–C (sp^2) σ bonds [22]. However the Pd–Pd separation (3.447(1) Å) and Pd–N bond

TABLE 2
BOND LENGTHS (Å)

	VI	VII		VI	VII
Pd(1)–Cl(1)	2.301(1)	2.329(2)	Pd(1)–Cl(2)	2.302(1)	2.443(2)
Pd(1)–N(12)	2.011(2)	1.958(6)	Pd(1)–C(12')		1.969(6)
Pd(2)–Cl(1)		2.456(2)	Pd(2)–Cl(2)		2.321(2)
Pd(1/2)–N(22)	2.007(2)	1.990(6)	Pd(2)–C(22')		1.963(6)
N(11)–N(12)	1.369(4)	1.381(8)	N(11)–C(17A)	1.339(4)	1.345(8)
N(11)–C(11')	1.442(4)	1.440(8)	N(12)–C(13)	1.345(4)	1.349(10)
C(13)–C(13A)	1.386(4)	1.377(10)	C(13A)–C(14)	1.513(4)	1.515(10)
C(13A)–C(17A)	1.376(5)	1.366(9)	C(14)–C(15)	1.558(4)	1.532(9)
C(14)–C(18)	1.558(5)	1.555(10)	C(15)–C(16)	1.551(5)	1.556(10)
C(16)–C(17)	1.569(4)	1.557(9)	C(17)–C(17A)	1.523(4)	1.531(9)
C(17)–C(17M)	1.516(5)	1.519(11)	C(17)–C(18)	1.587(5)	1.576(10)
C(18)–C(18A)	1.527(5)	1.528(11)	C(18)–C(18S)	1.529(5)	1.535(11)
C(11')–C(12')	1.378(5)	1.383(9)	C(11')–C(16')	1.384(5)	1.383(9)
C(12')–C(13')	1.393(6)	1.393(9)	C(13')–C(14')	1.370(6)	1.398(10)
C(14')–C(15')	1.396(6)	1.390(10)	C(15')–C(16')	1.396(5)	1.374(10)
N(21)–N(22)	1.369(4)	1.371(7)	N(21)–C(27A)	1.361(4)	1.367(9)
N(21)–C(21')	1.426(4)	1.417(9)	N(22)–C(23)	1.342(5)	1.324(9)
C(23)–C(23A)	1.379(4)	1.394(10)	C(23A)–C(24)	1.509(5)	1.468(11)
C(23A)–C(27A)	1.378(5)	1.395(10)	C(24)–C(25)	1.563(5)	1.562(11)
C(24)–C(28)	1.562(4)	1.546(10)	C(25)–C(26)	1.562(5)	1.535(11)
C(26)–C(27)	1.564(5)	1.563(11)	C(27)–C(27A)	1.505(4)	1.505(10)
C(27)–C(27M)	1.510(5)	1.517(10)	C(27)–C(28)	1.586(5)	1.586(10)
C(28)–C(28A)	1.536(5)	1.522(11)	C(28)–C(28S)	1.520(5)	1.520(10)
C(21')–C(22')	1.382(5)	1.402(9)	C(21')–C(26')	1.386(5)	1.348(10)
C(22')–C(23')	1.390(5)	1.397(9)	C(23')–C(24')	1.369(6)	1.371(10)
C(24')–C(25')	1.379(6)	1.374(10)	C(25')–C(26')	1.397(5)	1.388(11)

TABLE 3
BOND ANGLES (°) FOR VI AND VII

	VI	VII		VI	VII
Cl(1)–Pd(1)–Cl(2)	179.6(1)	87.6(1)	Cl(1)–Pd(1)–N(12)	87.6(1)	177.0(2)
Cl(2)–Pd(1)–N(12)	92.8(1)	95.3(2)	Cl(1)–Pd(1)–N(22)/C(12')	91.5(1)	97.3(2)
Cl(2)–Pd(1)–N(22)/C(12')	88.1(1)	174.8(2)	N(12)–Pd(1)–N(22)/C(12')	178.4(1)	79.7(3)
Cl(1)–Pd(2)–Cl(2)		87.5(1)	Cl(1)–Pd(2)–N(22)		95.5(2)
Cl(2)–Pd(2)–N(22)		176.8(2)	Cl(1)–Pd(2)–C(22')		176.0(2)
Cl(2)–Pd(2)–C(22')		96.4(2)	N(22)–Pd(2)–C(22')		80.6(2)
Pd(1)–Cl(1)–Pd(2)		92.2(1)	Pd(1)–Cl(2)–Pd(2)		92.7(1)
N(12)–N(11)–C(17A)	108.9(3)	109.7(5)	N(12)–N(11)–C(11')	119.1(3)	111.5(5)
C(17A)–N(11)–C(11')	130.2(3)	138.7(6)	Pd(1)–N(12)–N(11)	125.4(2)	118.2(4)
Pd(1)–N(12)–C(13)	126.9(2)	135.2(5)	N(11)–N(12)–C(13)	107.5(2)	106.6(6)
N(12)–C(13)–C(13A)	108.9(3)	108.5(6)	C(13)–C(13A)–C(14)	145.7(3)	144.5(7)
C(13)–C(13A)–C(17A)	106.1(3)	108.1(6)	C(14)–C(13A)–C(17A)	106.7(3)	107.0(6)
C(13A)–C(14)–C(15)	104.5(3)	105.7(6)	C(13A)–C(14)–C(18)	99.8(3)	100.4(5)
C(15)–C(14)–C(18)	101.6(3)	101.6(5)	C(14)–C(15)–C(16)	103.8(3)	102.4(5)
C(15)–C(16)–C(17)	104.4(3)	105.4(5)	C(16)–C(17)–C(17A)	103.0(3)	102.6(3)
C(16)–C(17)–C(17M)	114.9(3)	113.1(6)	C(17A)–C(17)–C(17M)	120.6(3)	122.6(6)
C(16)–C(17)–C(18)	100.7(3)	99.4(5)	C(17A)–C(17)–C(18)	97.5(2)	98.5(5)
C(17M)–C(17)–C(18)	117.0(3)	117.1(6)	N(11)–C(17A)–C(13A)	108.7(3)	107.1(6)
N(11)–C(17A)–C(17)	140.6(3)	143.8(6)	C(13A)–C(17A)–C(17)	109.2(3)	108.6(6)
C(14)–C(18)–C(17)	94.6(3)	94.4(5)	C(14)–C(18)–C(18A)	113.6(3)	112.7(6)
C(17)–C(18)–C(18A)	113.6(3)	114.8(6)	C(14)–C(18)–C(18S)	113.6(3)	113.2(6)
C(17)–C(18)–C(18S)	113.4(3)	113.7(6)	C(18A)–C(18)–C(18S)	113.6(3)	107.7(6)
N(11)–C(11')–C(12')	119.7(3)	114.3(5)	N(11)–C(11')–C(16')	117.9(3)	112.6(6)
C(12')–C(11')–C(16')	122.4(3)	123.0(6)	Pd(1)–C(12')–C(11')		116.2(5)
Pd(1)–C(12')–C(13')		125.9(5)	C(11')–C(12')–C(13')	118.0(4)	117.9(6)
C(12')–C(13')–C(14')	121.4(4)	119.5(6)	C(13')–C(14')–C(15')	119.7(4)	121.1(7)
C(14')–C(15')–C(16')	120.1(4)	119.5(7)	C(11')–C(16')–C(15')	118.4(4)	119.0(6)
N(22)–N(21)–C(27A)	108.6(3)	107.8(5)	N(22)–N(21)–C(21')	120.9(3)	114.1(5)
C(27A)–N(21)–C(21')	129.5(3)	138.0(6)	Pd(1/2)–N(22)–N(21)	125.4(2)	115.7(4)
Pd(1/2)–N(22)–C(23)	126.9(2)	135.4(5)	N(21)–N(22)–C(23)	107.2(2)	108.9(5)
N(22)–C(23)–C(23A)	110.1(3)	109.7(6)	C(23)–C(23A)–C(24)	147.7(3)	146.7(7)
C(23)–C(23A)–C(27A)	105.9(3)	105.4(7)	C(24)–C(23A)–C(27A)	106.2(3)	106.9(6)
C(23A)–C(24)–C(25)	104.5(3)	104.3(6)	C(23A)–C(24)–C(28)	99.8(3)	101.8(6)
C(25)–C(24)–C(28)	101.6(3)	102.4(6)	C(24)–C(25)–C(26)	103.2(3)	101.8(6)
C(25)–C(26)–C(27)	104.5(3)	106.1(6)	C(26)–C(27)–C(27M)	115.2(3)	115.6(6)
C(26)–C(27)–C(27A)	102.4(2)	101.3(6)	C(27M)–C(27)–C(27A)	120.2(3)	123.3(6)
C(26)–C(27)–C(28)	101.1(3)	100.1(6)	C(27M)–C(27)–C(28)	117.1(2)	114.7(6)
C(27A)–C(27)–C(28)	97.6(3)	98.2(5)	N(21)–C(27A)–C(23A)	108.2(3)	108.2(6)
N(21)–C(27A)–C(27)	141.6(3)	142.9(6)	C(23A)–C(27A)–C(27)	109.9(3)	108.0(6)
C(24)–C(28)–C(27)	94.5(2)	94.0(5)	C(24)–C(28)–C(28A)	112.9(3)	113.2(6)
C(27)–C(28)–C(28A)	113.1(3)	112.9(6)	C(24)–C(28)–C(28S)	114.0(3)	113.5(6)
C(27)–C(28)–C(28S)	113.3(3)	114.5(6)	C(28A)–C(28)–C(28S)	108.5(2)	108.4(6)
N(21)–C(21')–C(22')	119.9(3)	114.3(6)	N(21)–C(21')–C(26')	118.8(3)	123.9(6)
C(22')–C(21')–C(26')	121.3(3)	121.8(7)	Pd(2)–C(22')–C(21')		115.3(5)
Pd(2)–C(22')–C(23')		127.3(5)	C(21')–C(22')–C(23')	119.1(3)	117.5(6)
C(22')–C(23')–C(24')	120.0(4)	120.5(6)	C(23')–C(24')–C(25')	121.2(4)	120.5(7)
C(24')–C(25')–C(26')	119.6(4)	119.7(7)	C(21')–C(26')–C(25')	118.8(4)	119.9(7)

lengths are somewhat shorter than reported for these cyclopalladated dimethylbenzylamine derivatives, but the Pd–N bond lengths are similar to those reported for other palladium bonds to *sp*²-nitrogens. The two pyrazole and two benzene rings are

all planar (maximum deviations from the mean planes: 0.007, 0.004, 0.006 and 0.011) and all approximately coplanar with one another. Thus the molecule possesses a non-crystallographic approximate two-fold rotation axis. The bonding geometry of the bornyl group is similar to that in VI. All intermolecular interactions between non-hydrogen atoms are $> 3.5 \text{ \AA}$.

Having established the structures of VI and VII and since the corresponding 2-pyridylmethyl derivative readily forms a 1:1 complex with PdCl_2 [14] we examined the reactions of the related ligands VIII and IX with lithium tetrachloropalladate. Phase transfer catalysed [14,23] benzylation of the parent indazole produced the two isomers VIII and IX (distinguished by their ^{13}C NMR spectra; Table 1) in a ratio of 3/1, consistent with the more rapid alkylation of N_2 [14]. However reaction of VIII and IX with lithium tetrachloropalladate did not produce cyclopalladated complexes under the same reaction conditions as does V. This is consistent with the known [24–26] greater difficulty in effecting cyclometalation reactions that result in formation of a six-membered ring compared to those which form a five-membered metallocycle.

Experimental

Infrared and ultraviolet spectra were recorded on Shimadzu IR27G and Varian DMS 100 spectrophotometers respectively. ^1H and ^{13}C NMR spectra were recorded on Varian T60 and CFT20 spectrometers respectively, for CDCl_3 solutions with Me_4Si as internal standard. Mass spectra were recorded on an A.E.I. MS902 spectrometer. Optical rotations were recorded with a JASCO ORD/CD-5 spectropolarimeter. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 P.F.₂₅₄ silica gel. The following compounds were prepared according to the literature procedure: V [15] and X [27].

Preparation of VI

To a solution of palladium(II) dichloride (0.10 g, 0.56 mmol) and lithium chloride (0.08 g, 1.9 mmol) in methanol (30 ml) was added a methanolic solution of V (0.29 g, 1.15 mmol). After 30 min the resulting yellow precipitate of VI was collected. Yield 60%. (Found: C, 59.8; H, 5.9; N, 8.2. $\text{C}_{34}\text{H}_{40}\text{N}_4\text{Cl}_2\text{Pd}$ calcd.: C, 59.9; H, 5.9; N, 8.2%) ^1H and ^{13}C NMR see Table 1. $\nu(\text{KBr})$ 770, 700 (monosubstituted benzene), 340 cm^{-1} (*trans*- PdCl_2). $\lambda_{\text{max}}(\text{CHCl}_3)$ 420 nm (ϵ 333 $M^{-1} \text{ cm}^{-1}$). $\lambda(\Delta\epsilon)$ 422 (+0.60), 379 (+0.23), 334 nm (+0.96 $M^{-1} \text{ cm}^{-1}$). $\lambda([M])$ 460 (–306), 399 (–2590), 360 nm (–1360° $M^{-1} \text{ m}^{-1}$).

Crystals suitable for X-ray crystal study were obtained by recrystallization from benzene.

Preparation of VII

A solution of palladium(II) dichloride (0.045 g, 0.25 mmol) and lithium chloride (0.04 g, 0.95 mmol) in methanol (20 ml) was added to a solution of VI (0.17 g, 0.25 mmol) in methanol (80 ml). The resulting solution was stirred at room temperature for 3 d during which time VII was deposited as a yellow powder. Yield 82%. (Found: C, 50.9; H, 4.9; N, 6.7. $\text{C}_{34}\text{H}_{38}\text{N}_4\text{Cl}_2\text{Pd}_2 \cdot \text{H}_2\text{O}$ calcd.: C, 50.8; H, 5.0; N, 7.0%). ^1H and ^{13}C NMR see Table 1. $\nu(\text{KBr})$ 740 cm^{-1} (*ortho*-disubstituted

benzene). $\lambda(\text{CHCl}_3)$ 338(sh) nm (ϵ 3150 M^{-1} cm^{-1}). $\lambda(\Delta\epsilon)$ 327 nm ($+3.78 M^{-1}$ cm^{-1}). $\lambda([\text{M}])$ 350 ($+15700$), 314 nm ($+9450 M^{-1}$ m^{-1}).

Crystals suitable for X-ray crystal study were obtained by recrystallization from benzene.

Phase-transfer catalysed benzylation of X

A mixture of benzyl chloride (0.36 g, 2.8 mmol), (4*S*, 7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1*H*(2*H*)-indazole (X) (0.50 g, 2.8 mmol), 40% aqueous sodium hydroxide (10 ml), 40% aqueous tetrabutyl ammonium hydroxide (6 drops) and benzene (80 ml) was stirred and refluxed for 7 h and then stirred at room temperature overnight. The organic layer was then separated, dried (Na_2SO_4) and evaporated under reduced pressure to yield an oil, shown by ^1H NMR to be a 3/1 mixture of two isomers. Yield 90%. The oil was then absorbed onto a silica radial chromatographic plate and elution with ether/petroleum ether (1/5) afforded the major isomer (4*S*, 7*R*)-2-benzyl-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole (VIII) as an oil, which slowly crystallized. m.p. 39–40°C. (Found: M^+ , 266.1782. $\text{C}_{18}\text{H}_{22}\text{N}_2$ calcd.: M^+ , 266.1783). ^1H and ^{13}C NMR see Table 1. ν_{max} (smear) 2950, 1450, 1390, 1370, 730, 700 cm^{-1} . Further elution afforded the minor isomer (4*S*, 7*R*)-1-benzyl-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1*H*-indazole (IX) as an oil. (Found: M^+ , 266.1782. $\text{C}_{18}\text{H}_{22}\text{N}_2$ calcd.: M^+ , 266.1783). ^1H and ^{13}C NMR see Table 1. ν_{max} (smear) 2950, 1450, 1440, 740, 700 cm^{-1} .

TABLE 4
CRYSTAL DATA AND X-RAY EXPERIMENTAL DETAILS

Compound	VI	VII
Formula	$\text{C}_{34}\text{H}_{40}\text{N}_4\text{Cl}_2\text{Pd}$	$\text{C}_{34}\text{H}_{38}\text{N}_4\text{Cl}_2\text{Pd}_2$
M_{rel}	682.1	786.4
a (Å)	9.882 (4)	7.901 (2)
b (Å)	12.880 (3)	17.589 (2)
c (Å)	13.541 (5)	11.363 (2)
β (°)	108.48 (3)	94.54 (2)
V (Å ³)	1634.6	1574.2
Space group	$P2_1$	$P2_1$
Z	2	2
D_c (g cm^{-3})	1.39	1.66
D_m (g cm^{-3})	1.38	1.64
λ (Å)	0.71069	0.71069
F (000)	704	792
μ (cm^{-1})	7.45	13.29
Radiation	Mo- K_α	Mo- K_α
Temperature (°C)	-140	-150
Crystal size (mm)	0.85 × 0.55 × 0.18	0.41 × 0.13 × 0.10
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{\text{max}}$ (°)	55	55
Unique reflections	3941	3953
Observed reflections	3797	3117
Discrimination	$I > 3\sigma(I)$	$I > 3\sigma(I)$
g	0.0003	0.0007
R	0.028	0.036
R_w	0.041	0.043

Crystallography

Table 4 lists crystal data and X-ray experimental details for VI and VII. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo- K_{α} radiation. The measured densities were determined by flotation in acidic zinc bromide solutions. Cell parameters were determined by least-squares

TABLE 5

ATOM COORDINATES ^a AND TEMPERATURE FACTORS ^b FOR VI AND VII

Atom	VI				VII			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^c	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^c
Pd(1)	9958.1(2)	5000 ^d	7508.5(2)	17(1)	9463.1(6)	5000 ^d	7211.3(4)	21(1)
Pd(2)					5752.5(6)	4128.3(3)	7883.4(4)	21(1)
Cl(1)	8603(1)	6488(1)	7251(1)	28(1)	8083(2)	3875(1)	6631(2)	31(1)
Cl(2)	11329(1)	3518(1)	7775(1)	26(1)	7155(2)	5241(1)	8471(2)	36(1)
N(11)	7768(3)	3406(2)	6392(2)	21(1)	12234(7)	6060(3)	7156(5)	22(2)
N(12)	8122(3)	4192(2)	7108(2)	20(1)	10700(7)	5939(4)	7630(5)	28(2)
C(13)	7078(3)	4260(3)	7545(2)	20(1)	10433(9)	6545(4)	8320(7)	30(2)
C(13A)	6070(3)	3499(2)	7123(2)	21(1)	11772(8)	7041(4)	8261(6)	24(2)
C(14)	4563(3)	3131(3)	6969(2)	25(1)	12589(9)	7758(4)	8779(6)	25(2)
C(15)	3666(3)	3615(3)	5909(3)	28(1)	14045(8)	7491(4)	9652(6)	24(2)
C(16)	4214(3)	3047(3)	5100(3)	30(1)	15289(8)	7122(4)	8823(6)	25(2)
C(17)	5360(3)	2265(3)	5764(3)	25(1)	14455(9)	7242(4)	7548(6)	25(2)
C(17A)	6542(3)	2976(3)	6408(2)	23(1)	12880(8)	6734(4)	7528(5)	17(2)
C(17M)	5699(4)	1368(3)	5155(3)	34(1)	15717(10)	7200(5)	6609(6)	35(2)
C(18)	4697(3)	1981(3)	6654(3)	28(1)	13568(10)	8032(4)	7723(6)	28(2)
C(18A)	3268(4)	1416(3)	6256(3)	41(1)	14782(11)	8688(5)	8052(7)	37(3)
C(18S)	5690(4)	1327(3)	7529(3)	38(1)	12394(11)	8284(5)	6653(7)	45(3)
C(11')	8503(3)	3326(3)	5629(2)	23(1)	12627(7)	5456(4)	6367(5)	18(2)
C(12')	8957(3)	2370(3)	5403(3)	30(1)	11444(7)	4875(4)	6281(5)	20(2)
C(13')	9594(4)	2316(4)	4622(3)	36(1)	11751(8)	4259(4)	5558(6)	26(2)
C(14')	9806(4)	3188(4)	4112(3)	40(1)	13239(9)	4241(4)	4969(6)	29(2)
C(15')	9365(4)	4153(4)	4367(3)	36(1)	14403(9)	4835(4)	5075(7)	32(2)
C(16')	8694(3)	4225(3)	5130(2)	27(1)	14093(8)	5447(4)	5778(6)	26(2)
N(21)	12189(3)	6553(2)	8645(2)	20(1)	2977(6)	3087(3)	7971(4)	18(2)
N(22)	11770(3)	5827(2)	7869(2)	22(1)	4477(6)	3179(3)	7457(4)	19(2)
C(23)	12692(3)	5877(3)	7326(2)	23(1)	4731(9)	2578(4)	6792(5)	24(2)
C(23A)	13723(3)	6614(3)	7754(2)	24(1)	3383(9)	2070(4)	6843(6)	29(2)
C(24)	14998(3)	7214(3)	7676(3)	26(1)	2743(9)	1299(4)	6590(7)	31(2)
C(25)	14394(4)	8313(3)	7284(3)	32(1)	3193(10)	852(5)	7761(7)	37(2)
C(26)	13969(4)	8758(3)	8218(3)	28(1)	2012(10)	1226(5)	8601(7)	36(2)
C(27)	14412(3)	7892(3)	9069(2)	22(1)	943(9)	1826(4)	7848(6)	26(2)
C(27A)	13393(3)	7027(3)	8587(2)	21(1)	-733(8)	2038(4)	8302(7)	30(2)
C(27M)	14586(4)	8248(3)	10165(3)	34(1)	2295(9)	2404(4)	7602(6)	28(2)
C(28)	15779(3)	7425(3)	8856(3)	27(1)	804(9)	1413(4)	6604(6)	28(2)
C(28A)	17004(3)	8211(3)	9041(3)	34(1)	-178(10)	669(5)	6610(7)	38(3)
C(28S)	16351(4)	6454(3)	9487(3)	36(1)	42(10)	1899(5)	5590(6)	32(2)
C(21')	11550(3)	6593(3)	9452(2)	22(1)	2595(8)	3685(4)	8742(6)	22(2)
C(22')	11149(3)	7537(3)	9756(3)	27(1)	3813(7)	4267(4)	8839(5)	19(2)
C(23')	10555(3)	7563(3)	10560(3)	35(1)	3524(8)	4874(4)	9591(6)	25(2)
C(24')	10347(3)	6658(4)	11022(3)	36(1)	2101(9)	4890(4)	10207(7)	32(2)
C(25')	10732(4)	5712(3)	10716(3)	35(1)	921(8)	4316(4)	10080(6)	31(2)
C(26')	11369(3)	5675(3)	9930(2)	27(1)	1178(9)	3712(5)	9327(7)	33(2)

^a ($\times 10^4$). ^b ($\text{\AA}^2 \times 10^3$). ^c $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. ^d Origin defining coordinate.

refinement, the setting angles of 25 accurately centered reflections ($2\theta > 35^\circ$) being used. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects and empirical absorption corrections, based on azimuthal ψ -scans, were applied. The space groups followed from systematic absences and the chiral nature of the complexes. In addition the data for VI showed pseudo-absences of an A-centring, which were subsequently explained by the pseudo-symmetric location of the palladium atom at $0, y, 3/4$.

The structures were solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. The absolute configuration employed was that consistent with the known [28] absolute configuration of (+)-camphor from which the ligand was synthesised. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [29].

Final atom coordinates are listed in Table 5. Tabulations of structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the authors.

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