Optical Resolution of Cyclo-palladated (Dimethylaminomethyl)ferrocene†

Takao Komatsu, Matsuo Nonoyama,* and Junnosuke Fujita
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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Cyclo-palladated (dimethylaminomethyl)ferrocene has been resolved into optically pure enantiomers *via* the (*S*)-proline derivatives. The absolute configuration is assumed by comparing the circular dichroism spectrum with that of similarly cyclo-palladated (*S*)-[1-(dimethylamino)ethyl]ferrocene of the known configuration. Several optically active derivatives of the cyclo-palladated (dimethylaminomethyl)ferrocene have been prepared and characterized.

Cyclo-metallated compounds are important intermediates for synthesizing ortho-disubstituted aromatic compounds as well as heterocycles.[1-7] 1,2-Disubstituted ferrocenes can be chiral and optically active ferrocenes recently attract much attention.[8-11] They are usually prepared from optically active derivatives but the method is somewhat troublesome.[8] Cyclo-palladated ferrocenes easily react to afford various 1,2-disubstituted ferrocenes.[4,5] If the cyclo-palladated ferrocenes are resolved efficiently into optically pure isomers, the resolved isomers can be useful intermediates to synthesize optically active ferrocenes. An optically active cyclo-palladated ferrocene so far known is the one prepared from optically active [1-(dimethylamino)ethyl]ferrocene (abbreviated as Hdaef).[12] We have succeeded in resolving cyclo-palladated (dimethylaminomethyl)ferrocene (Hdamf) *via* the derivative of (*S*)-proline. In this paper the resolution and some optically active derivatives obtained from the resolved complex are described. The abbreviations used in this paper are given in the footnote of Table 1.

Experimental

Measurements. Electronic spectra were recorded on a Hitachi 323 spectrophotometer and circular dichroism (CD) spectra on a JASCO J-20 spectropolarimeter. Optical rotations at 589 nm were determined by a JASCO DIP-4 polarimeter at 23 °C. ^{1}H NMR spectra were measured with a JEOL PMX-60 spectrometer (60 MHz). Tetramethylsilane (TMS) was used as an internal standard for chloroform-*d* solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for water-d_2 and dimethyl-d_6 sulfoxide solutions. Infrared spectra in the regions of 5000—400 cm^{-1} and 700—200 cm^{-1} were obtained by a JASCO A-3 and a Hitachi EPI-L spectrophotometer, respectively, using Nujol and hexachlorobutadiene mulls. Electric conductances of 10^{-3} mol/dm^3 methanol solutions were measured with a Tōa CM-6A conductometer at 25 °C.

Syntheses. The complexes, $[PdCl(damf)]_2$,[13] (*R*)-$[PdCl(S\text{-daef})]_2$,[12] and (*R*)-[Pd(*S*-daef)(acac)][12] were prepared by the methods reported. Analytical results and melting points of the new and related complexes are summerized in Table 1.

[Pd(damf)(S-pro)]. A suspension of 7.68 g (10.0 mmol) of $[PdCl(damf)]_2$ in 100 cm^3 of acetone was mixed with an aqueous solution (100 cm^3) containing 2.30 g (20.0 mmol) of (*S*)-proline and 2.00 g (20.0 mmol) of potassium hydrogencarbonate and the mixture was stirred for 5 h at room temperature. The solution was filtered and the filtrate was concentrated to a small volume under reduced pressure to give yellow precipitate. The precipitate was washed with a mixture of water–acetone (1:1) and dried *in vacuo*. Yield, 6.74 g (73%).

Separation of Diastereomers of [Pd(damf)(S-pro)]. To a hot chloroform solution (200 cm^3) of 7.5 g of [Pd(damf)(*S*-pro)] was added 800 cm^3 of hot acetone and the solution was cooled to room temperature to give 2.9 g of crystals. The crystals were recrystallized from 750 cm^3 of a mixture of chloroform–acetone (1:4) to give 2.0 g of leaf-like crystals, (+)-[Pd(damf)(*S*-pro)], with a specific rotation of $[\alpha]=+356°$ (*c* 0.04, CH_3OH).

The complex obtained by evaporating the mother liquor was repeatedly recrystallized from a mixture of chloroform–cyclohexane (1:4) to form needles, (−)-[Pd(damf)(*S*-pro)], with a specific rotation of $[\alpha]=-206°$ (*c* 0.08, CH_3OH).

(+)-[PdCl(damf)]$_2$. A dichloromethane solution (40 cm^3) of 464 mg (1.0 mmol) of (+)-[Pd(damf)(*S*-pro)] was mixed with 40 cm^3 of 0.06 mol/dm^3 hydrochloric acid and the mixture was vigorously shaken for 2 h. The dichloromethane phase was separated, washed three times with 10 cm^3 of water, and mixed with 10 cm^3 of methanol. Upon concentration under reduced pressure red precipitate was obtained. The precipitate was washed with a small amount of methanol and dried in air. Yield, 195 mg (51%). $[\alpha]=+664°$ (*c* 0.15, CH_2Cl_2).

(+)-[Pd(damf)(acac)]. This complex was prepared by the method reported for (*R*)-[Pd(*S*-daef)(acac)][12] using (+)-$[PdCl(damf)]_2$. Yield, 43%. $[\alpha]=+494°$ (*c* 0.04, CH_3OH).

(+)-[Pd(damf)(en)]BF_4. A mixture of 200 mg (0.43 mmol) of (+)-[Pd(damf)(*S*-pro)], 82 mg (1.33 mmol) of ethylenediamine, and 140 mg (1.27 mmol) of sodium tetrafluoroborate in 20 cm^3 of water was stirred for 4 h at room temperature to give red crystals, which were washed with a small amount of methanol and dried in air. Yield, 120 mg (56%). $[\alpha]=+99°$ (*c* 0.05, CH_3OH).

(R)-*[Pd(S-daef)(en)]BF_4.* This complex was prepared by a method similar to that above using (*R*)-[PdCl(*S*-daef)]$_2$.[12] Yield, 39%. $[\alpha]=-23°$ (*c* 0.056, CH_3OH).

(−)-[Pd(damf)(diphos)]PF_6. A mixture of 93 mg (0.20 mmol) of (+)-[Pd(damf)(*S*-pro)] and 80 mg (0.20 mmol) of 1,2-bis(diphenylphosphino)ethane in 5 cm^3 of ethanol was refluxed for 1 h with stirring and filtered. To the filtrate was added a solution of 80 mg (0.48 mmol) of sodium hexafluorophosphate in 2 cm^3 of ethanol with stirring and the mixture was allowed to stand at room temperature. Reddish brown precipitate was collected, washed with a small amount of ethanol, and dried in air. The product was recrystallized from ethanol. Yield, 148 mg (81%). $[\alpha]=-8.8°$ (*c* 0.14, CH_3OH).

(+)-[Pd(damf)(diars)]PF_6. This complex was prepared from (+)-[Pd(damf)(*S*-pro)] and 1,2-bis(diphenylar-

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Table 1. Melting points and analytical results for the complexes[a)]

Complex	Mp/°C[b)]	Found(Calcd) (%)		
		C	H	N
$[PdCl(damf)]_2$*	172(dec)	40.42(40.67)	4.12(4.20)	3.56(3.65)
[Pd(damf)(*S*-pro)]	151(dec)	46.50(46.73)	5.43(5.23)	6.18(6.05)
(+)-$[Pd(damf)(en)]BF_4$[e)]	165(dec)	36.22(36.37)	5.01(4.88)	8.52(8.48)
(−)-$[Pd(damf)(diphos)]PF_6$[d)]	169	52.77(52.52)	4.45(4.52)	1.85(1.57)
(+)-$[Pd(damf)(diars)]PF_6$[e)]	164	47·95(47.81)	3.74(4.12)	1.42(1.43)
(+)-$[Pd(damf)(py)_2]PF_6$[f)]	137—141	41.93(42.33)	4.19(4.17)	6.43(6.44)
(+)-[Pd(damf)(acac)]	119—124	48.15(48.30)	5.21(5.18)	3.22(3.13)
[PdCl(damf)(py)]	148(dec)	46.32(46.59)	4.37(4.78)	6.06(6.04)
[PdBr(damf)(py)]	147	42.54(42.51)	4.19(4.36)	5.54(5.51)
(+)-(*R*)-$[PdCl(S\text{-daef})]_2$**	155	41.92(42.25)	4.65(4.56)	3.89(3.52)
(−)-(*S*)-$[PdCl(S\text{-daef}]_2$**	146—148	42.29(42.25)	4.56(4.56)	3.44(3.52)
(+)-(*R*)-[Pd(*S*-daef)(acac)]**	124—125	49.59(49.43)	5.72(5.45)	3.37(3.04)
(−)-(*R*)-$[Pd(S\text{-daef})(en)]BF_4$	160(dec)	37.58(37.72)	5.20(5.14)	8.45(8.25)

a) Abbreviations used in this paper are as follows; Hdamf = (dimethylaminomethyl)ferrocene, Hdaef = [1-(dimethylaminomethyl)ferrocene, S-Hpro = (S)-proline, en = ethylenediamine, diphos = 1,2-bis(diphenylphosphino)ethane, diars = 1,2-bis(diphenylarsino)ethane, Hacac = acetylacetone, and py = pyridine. b) dec = decomposition. Molar electric conductances of 10^{-3} mol/dm^3 methanol solutions at 25 °C, Λ/Ω, cm^2/mol. c) 98. d) 104. e) 63. f) 94. * and **: See Refs. 13 and 12, respectively.

sino)ethane by a method similar to the above. Yield, 136 mg (69%). $[\alpha]=+49°$ (*c* 0.10, CH_3OH).

(+)-[Pd(damf)(py)$_2$]PF$_6$. A mixture of 230 mg (0.50 mmol) of (+)-[Pd(damf)(*S*-pro)], 160 mg (2.0 mmol) of pyridine, and 250 mg (1.5 mmol) of sodium hexafluorophosphate in 20 cm^3 of ethanol was heated with stirring for 2 h and filtered. The filtrate was concentrated to *ca.* 2.5 cm^3 and stored in a refrigerator for a few days. Yellow precipitate was collected, washed with ethanol, and dried in air. Yield, 150 mg (46%). $[\alpha]=+194°$ (*c* 0.17, CH_3OH).

[Pd(X)(damf)(py)] (X=Cl and Br). A mixture of 230 mg (0.30 mmol) of $[PdCl(damf)]_2$ and 100 mg (1.3 mmol) of pyridine in 30 cm^3 of dichloromethane was stirred at room temperature for 30 min. The resulting solution was filtered and 10 cm^3 of ethanol was added to the filtrate. Upon concentration yellow crystals (X=Cl) were obtained, which were washed with a small amount of ethanol and dried in air. Yield, 190 mg (68%).

The yellowish brown bromo complex was prepared by metathesis of the chloro complex with excess lithium bromide in hot ethanol. Yield, 73%.

Results and Discussion

A pair of diastereomers of [Pd(damf)(*S*-pro)] are efficiently separated by solubility difference (Fig. 1). In the ^{1}H NMR spectra, the less soluble isomer, (+)-[Pd(damf)(*S*-pro)], in a mixture of chloroform–acetone (1:4) shows sharp signals of the N–CH_3 at 2.87 (s) and 3.09 (s) ppm and that of the C_5H_5 group at 4.23 (s), while the other, (−)-[Pd(damf)(*S*-pro)], at 2.87 (s) and 3.14 (s), and at 4.15 (s), respectively (Table 2). The sharp signals are used as an indication of complete separation of the isomers. The electronic spectra of the two are very similar, while the CD spectra are nearly enantiomeric to each other (Fig. 2). This suggests that the two are a pair of diastereomers resulting from the planar chirality. The geometrical isomer (*trans-N,N*) shown in Fig. 1 is assumed,

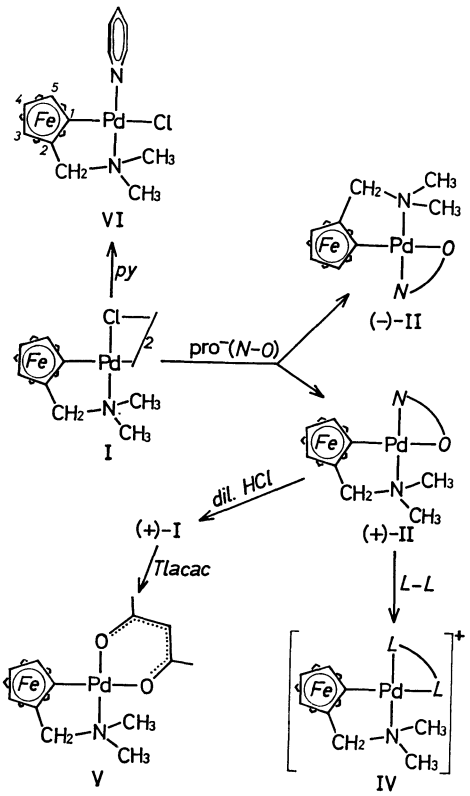


Fig. 1. Cyclo-palladated (dimethylaminomethyl)ferrocene and its derivatives. L–L in IV is en, diphos, diars, or 2py.

since a similar ortho-palladated complex, (*N,N*-dimethylbenzylamine-2*C,N*)(*N*-phenylsalicylideneaminato)-palladium(II)[14] has a *trans-N,N* structure.

A reaction of (+)-[Pd(damf)(*S*-pro)] with dilute hydrochloric acid regenerates the original dimer, (+)-$[PdCl(damf)]_2$. The absorption and CD spectra are

Table 2. Representative signals of ^{1}H NMR spectra of some of the complexes in $CDCl_3$ (δ in ppm from internal TMS)[a]

Complex	$N(CH_3)_2$		Ferrocenyl-H
$[PdCl(damf)]_2$	2.91 s,	3.05 s	4.31 s (C_5H_5)
			4.36[b] (3-H)
			4.00 m (4,5-H)
(+)-[Pd(damf)-(*S*-pro)]	2.87 s,	3.09 s	4.23 s (C_5H_5)
(−)-[Pd(damf)-(*S*-pro)]	2.87 s,	3.14 s	4.15 s (C_5H_5)
(+)-[Pd(damf)-(en)]BF_4	2.68 s,	2.88 s	4.20 s (C_5H_5)
(−)-[Pd(damf)-(diphos)]PF_6	2.46 b,	2.81 b	3.75 s (C_5H_5)
(+)-[Pd(damf)-(diars)]PF_6	2.76 s,	3.09 s	3.79 s (C_5H_5)
(+)-[Pd(damf)-(acac)][c]	2.82 s,	3.03 s	4.18 s (C_5H_5)
			4.25[b] (3-H)
			4.01 m (4,5-H)
[PdCl(damf)(py)]	2.98 s,	3.23 s	4.20 s (C_5H_5)
			4.12 d (3-H)
			3.93 t (4-H)
			3.24 d (5-H)
[PdBr(damf)(py)]	3.01 s,	3.29 s	4.19 s (C_5H_5)
			4.11 d (3-H)
			3.92 t (4-H)
			3.18 d (5-H)

a) s=singlet, d=doublet, t=triplet, m=multiplet, and b=broad. b) Overlapped by the signal of C_5H_5. c) CH_3 of acac resonates at 1.95 s and 1.99 s ppm and methine-H of acac at 5.29 s.

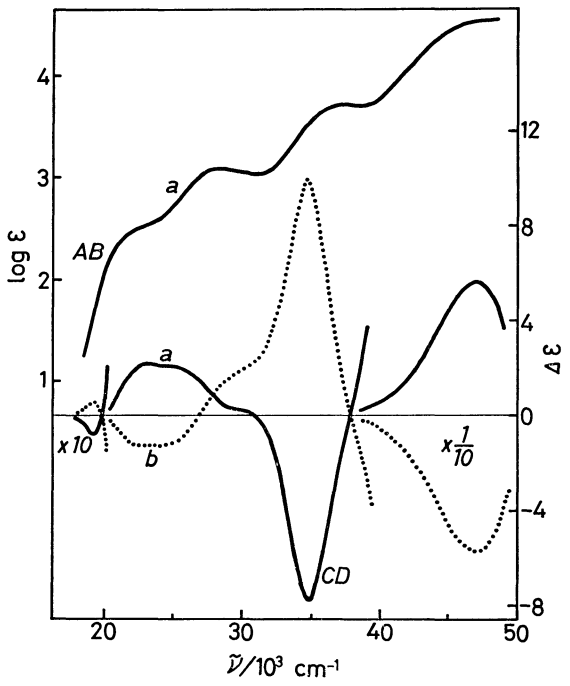


Fig. 2. Absorption (AB) and CD spectra of methanol solutions of a: (+)-[Pd(damf)(*S*-pro)] and b: (−)-[Pd(damf)(*S*-pro)].

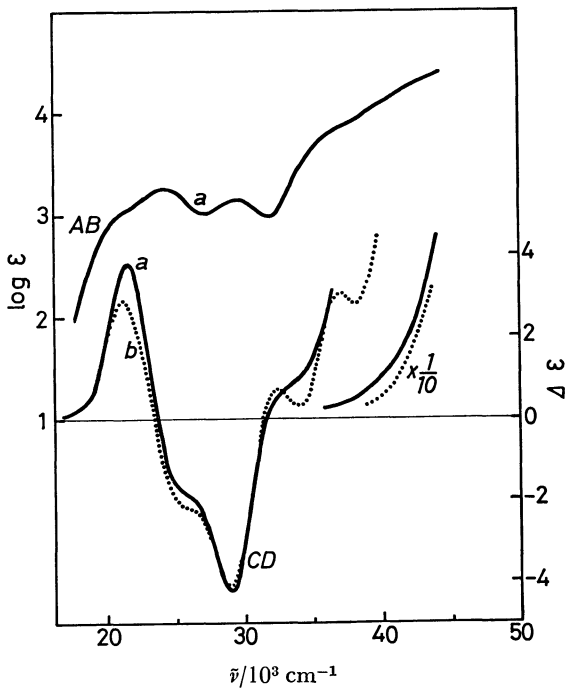


Fig. 3. Absorption (AB) and CD spectra of dichloromethane solutions of a: (+)-[PdCl(damf)]$_2$ and b: (*R*)-[PdCl(*S*-daef)]$_2$.

shown in Fig. 3 together with the CD spectrum of (+)-(*R*)-[PdCl(*S*-daef)]$_2$.[12] The similarlity in CD spectra suggests that (+)-[PdCl(damf)]$_2$ has the same absolute configuration *R* for the ferrocene moiety.

From the separated isomer, (+)-[Pd(damf)(*S*-pro)], the optically active complexes, $[Pd(damf)(L\text{-}L)]^+$ are derived, where L-L are en, diphos, diars, and 2py (Table 1 and Fig. 1). The (+)-[Pd(damf)(acac)] complex was obtained from (+)-[PdCl(damf)]$_2$. Some of the ^{1}H NMR spectral data are given in Table 2.

The CD spectra of (+)-[Pd(damf)(en)]BF_4 and (+)-[Pd(damf)(acac)] are compared with those of (*R*)-[Pd(*S*-daef)(en)]BF_4 and (*R*)-[Pd(*S*-daef)(acac)], respectively (Fig. 4). The absolute configuration of the enantiomer (*S*)-[Pd(*R*-daef)(acac)] has been determined by the X-ray method.[15] The results also show that the absolute configuration of the ferrocene moiety in (+)-[Pd(damf)(en)]BF_4 and (+)-[Pd(damf)(acac)] is *R*. The CD spectra of the other complexes are shown in Fig. 5.

The cyclo-palladated (dimethylaminomethyl)ferrocene complexes change the CD spectra remarkably depending on the kind of ligands (L-L) (Figs. 2—5) and there seems to be no regularity among the spectra. The diphos and diars complexes are a unique pair to give similar spectra. Nevertheless a shoulder absorption observed at *ca.* 22000 cm^{-1} for all the complexes appears to arise mainly from d-d transitions of the iron(II) ion, since the free Hdamf ligand gives a band due to the d-d transitions at 22300 cm^{-1} (ε=107).[16] The CD extremes corresponding to this shoulder (Figs. 2—5) are always positive and the positive extremes seem to be a representative of a (*R*)-ferrocenyl group. A chiral ferrocenylphosphine, (+)-(*R*)-[2-(dimethylaminomethyl)-1-ferrocenyl] diphenylphosphine (VII)

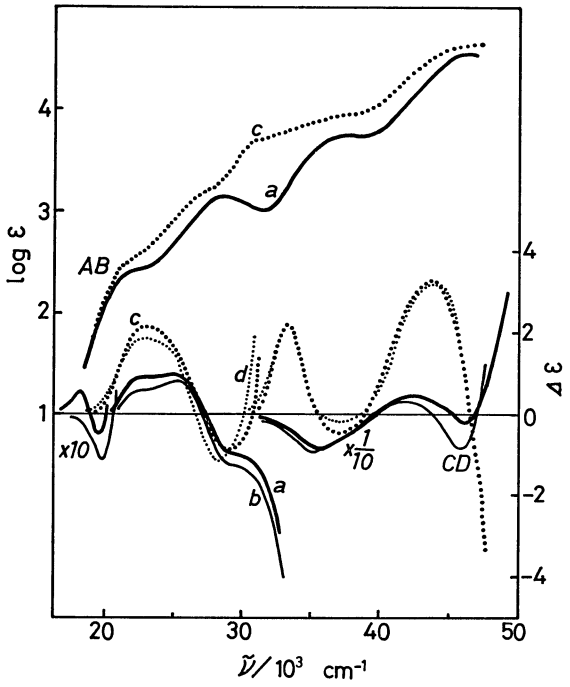


Fig. 4. Absorption (AB) and CD spectra of methanol solution of a: (+)-[Pd(damf)(en)]BF_4, b: (*R*)-[Pd(*S*-daef)(en)]BF_4, c: (+)-[Pd(damf)(acac)], and d: (*R*)-[Pd(*S*-daef)(acac)].

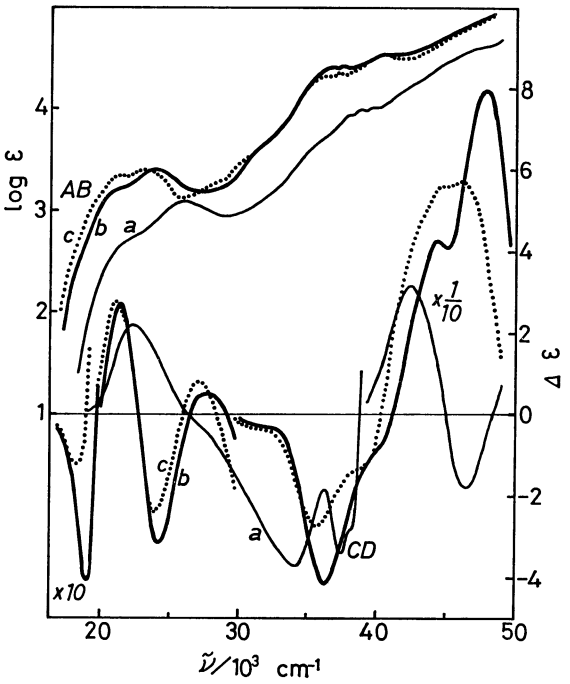
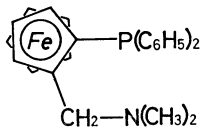


Fig. 5. Absorption (AB) and CD spectra of methanol solutions of a: (+)-[pd(damf)$(py)_2$]PF_6, b: (−)-[Pd(damf)(diphos)]PF_6, and c: (+)-[Pd(damf)-(diars)]PF_6.

has recently been reported to show a positive CD extreme in this region;[10,11] $\Delta\varepsilon = +0.52$ at 21800 cm^{-1}.

The protons of unsubstituted cyclopentadienyl rings of (−)-[Pd(damf)(diphos)]PF_6 and (+)-[Pd(damf)-(diars)]PF_6 resonate at a considerably higher field than those of the other complexes (Table 2). The properly oriented phenyl rings of diphos and diars are expected to bring about the shielding effect by



VII

their magnetic anisotropy.[17] In the ^1H NMR spectra of [PdCl(damf)(py)] and [PdBr(damf)(py)] a doublet at a very high field (3.23 (Cl) and 3.18 (Br) ppm) is observed in contrast to those of the other complexes. The doublet can be assigned to 5-H of the substituted cyclopentadienyl ring since this proton should be shielded by the ring current of the coordinated pyridine (Fig. 1, VI), when [PdX(damf)(py)] (X=Cl and Br) has a *trans-N,N, trans-C,X* arrangement like other ortho-palladated complexes, [PdX(C–N)(py)] (C–N= ortho-palladated ligand).[1,18] The structure is supported by appearance of a low frequency ν(Pd–Cl) band at 268 cm^{-1}.[19]

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