

Journal of Organometallic Chemistry, 438 (1992) 343–351
 Elsevier Sequoia S.A., Lausanne
 JOM 22829

Palladium(II) complexes with the cyclometallated $C-Y-N(sp^2)-Pd-C(sp^2)$ ring ($Y = N, C$) and (R)-(+) -hydroxy-methylene camphor

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(Received December 31, 1991)

Abstract

The reactions between the cyclopalladated chloro-dimers $\{[Pd(L^{\mu})(\mu-Cl)]_2\}$ ($HL^1 = 2,6$ -dimethylazobenzene, $HL^2 = 4,4'$ -dimethoxyazobenzene, $HL^3 = 4$ -ethoxy-4'-heptanoylazobenzene, $HL^4 = 5$ -(1-hexyl)-2-[[4'-(1-undecyloxy)phenyl]pyrimidine) and the optically pure $K[(R)-(+)MC]$ salt ((*R*)-(+)MC = (*R*)-(+) -bicyclo[2,2,1]-heptan-2-onate-3-(hydroxymethylene)-1,7,7'-trimethyl) give the corresponding mononuclear $\{Pd(L^{\mu})(R)-(+)MC\}$ complexes 1–4. NMR and circular dichroism data account for diastereoisomeric mixtures which consist of two complexes differing in the 7,7' dimethyl bridge being above or below the palladium coordination plane. The relative abundance of diastereoisomers has been estimated by NMR spectroscopy.

Introduction

Cyclopalladated complexes, whose chemistry has been recently reviewed by Ryabov [1], are currently under investigation for different applications [2,3]. The synthesis of such compounds is usually achieved by reaction of the appropriate ligand HL with a source of palladium(II) [1]. The organometallic species obtained have formulae $\{[Pd(L)(\mu-X)]_2\}$, and molecular structures with two five-membered palladacycles bridged by two X groups (X = halide or acetate). Moreover, the complexes react readily with potential monodentate or polydentate ligands, so that they are useful starting materials for the preparation of neutral or cationic mononuclear cyclopalladated derivatives [1,2,4–7].

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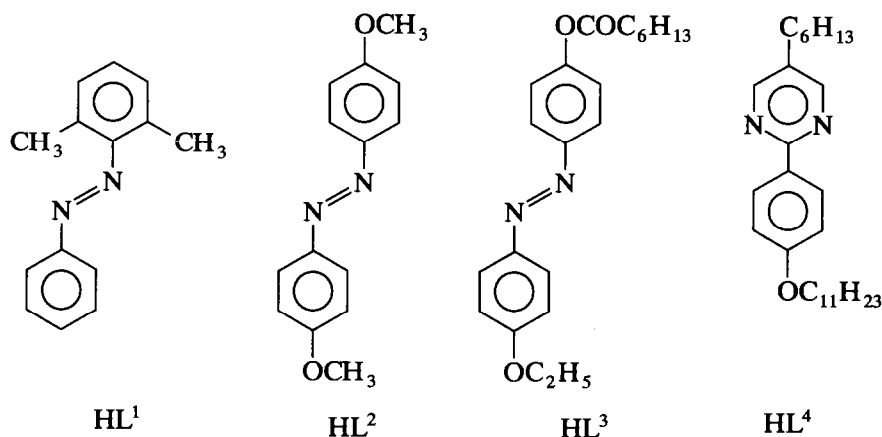


Fig. 1. Compounds HLⁿ.

Ortho-palladated neutral mononuclear species, containing chelating acetylacetonate are very easy to prepare [6,8,9]. To investigate chiral cyclopalladated complexes, we considered (*R*)-(+)-bicyclo[2,2,1]-heptan-2-one-3-(hydroxymethylene)-1,7,7'-trimethyl (or hydroxymethylenecamphor, thereafter reported as (*R*)-(+)-HMC), whose acetylacetonato-like coordination chemistry has been previously reported [10]. Here we describe the synthesis and characterization of new compounds formed by (*R*)-(+)-HMC and the Pd(Lⁿ) palladacycles arising from the HLⁿ molecules shown in Fig. 1.

Experimental

General procedures

All manipulations were carried out in dioxygen-free atmosphere. IR spectra were recorded for KBr pellets on a Perkin-Elmer 1330 spectrometer. NMR measurements were performed on a Bruker AC-200 spectrometer (CDCl₃, standard SiMe₄) using standard pulse sequences [11] for JMOD and two-dimensional experiments; mixing times of 2 s were used for NOESY measurements. Circular dichroism spectra were recorded on a Jobin-Yvonne Dichrographe III using chloroform as solvent, with concentrations of 0.5 mg mL⁻¹. Elemental analyses were carried out by the Microanalysis Laboratory of the Dipartimento di Chimica, Università della Calabria, Italy.

Preparation of compounds

The standard chemicals (Aldrich Chemical Co.) were used as supplied. (*R*)-(+)-Camphor (Fluka A.G.) was vacuum-distilled before use. [Pd(PhCN)₂Cl₂] [12] and the chloro-bridged cyclopalladated dimers [(Pd(L¹)μ-Cl)₂] (I) [13], [(Pd(L²)μ-Cl)₂] (II) [14], [(Pd(L³)μ-Cl)₂] (III) [15], and [(Pd(L⁴)μ-Cl)₂] (IV) [16], were prepared as previously reported.

(*R*)-(+)-Bicyclo[2,2,1]-heptan-2-one-3-(hydroxymethylene)-1,7,7'-trimethyl-camphor, (*R*)-(+)-HMC, was prepared from (*R*)-(+)-camphor according to the literature method [17]; its optical rotation index agreed with the reported values [17].

Preparation of Tl[(R)-(+)-MC]. To a solution of freshly distilled (R)-(+)-HMC (2.5 g, 14.2 mmol) in absolute ethanol (30 mL), thallos ethoxyde (1 mL, 14.0 mmol) was added. The homogeneous solution gave a white precipitate after stirring for 5 min. The precipitate was filtered, washed with diethyl ether and vacuum dried. Quantitative yield was obtained.

Synthesis of the {Pd(Lⁿ)[(R)-(+)-MC]} complexes (1–4). The preparative procedure was the same for each of the homologous {Pd(Lⁿ)[(R)-(+)-MC]} complexes 1–4, and therefore as an example, only the synthesis of 1 is described.

{Pd(L¹)[(R)-(+)-MC]} (1): [Pd(L¹)(μ-Cl)]₂ (0.18 mmol) was added to a stirred solution of Tl[(R)-(+)-MC] (0.36 mmol) in ethanol (5 mL). The mixture was stirred at room temperature overnight and the TlCl filtered off. The filtrate was concentrated *in vacuo* and the precipitate which formed by addition of diethyl ether (unreacted products) filtered off. The solution, after removing the solvent, gave the desired product as a yellow solid in 45% yield. Anal. Found: C, 59.60; H, 5.48; N, 5.69. C₂₅H₂₈N₂O₂Pd calc.: C, 60.67; H, 5.70; N, 5.66%.

Colours, yields and analytical data for the other complexes are as shown below.

{Pd(L²)[(R)-(+)-MC]} (2): Yellow solid. Anal. Found: C, 56.53; H, 5.41; N, 5.23. C₂₅H₂₈N₂O₄Pd calc.: C, 56.99; H, 5.36; N, 5.32%. Yield: 50%.

{Pd(L³)[(R)-(+)-MC]} (3): Yellow solid. Anal. Found: C, 59.66; H, 6.29; N, 4.28. C₃₂H₄₀N₂O₅Pd calc.: C, 60.14; H, 6.31; N, 4.38%. Yield: 48%.

{Pd(L⁴)[(R)-(+)-MC]} (4): Yellow solid. Anal. Found: C, 65.40; H, 8.03; N, 3.92. C₃₈H₅₆N₂O₃Pd calc.: C, 65.65; H, 8.12; N, 4.03%. Yield: 52%.

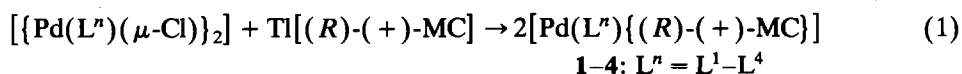
Results and discussion

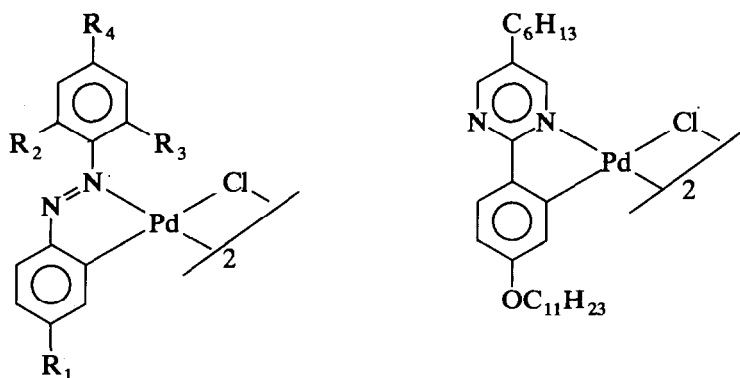
Synthesis of (R)-(+)-camphorate complexes

The bridged dichloro-compounds [{Pd(L)(μ-Cl)]₂ can be converted into mononuclear species containing both the cyclopalladated L and a monoanionic chelating ligand, by a reaction which involves halogen-bridge cleavage and displacement of the chlorine atom [6,7]. The (R)-(+)-MC complexes were obtained similarly. The HLⁿ starting materials were selected in order to prevent the formation of mixtures of metallated compounds. Thus, for HL¹, HL² and HL⁴ the C(sp²)-H bonds which can provide the required five-membered Pd(C,N) metallacycle are structurally equivalent; for HL³, the position of metallation should be determined by the activating ethoxy substituent because the cyclopalladation reaction is electrophilic attack by the palladium centre [1].

Complexes I–IV have the molecular structures of Fig. 2. For compound III, the ¹H NMR spectrum confirms the presence of only one isomer, while 2D ¹H NMR NOESY measurements indicate that metallation occurs selectively on the aromatic ring bearing the OC₂H₅ substituent [18].

The reaction of complexes I–IV with the thallium salt of the optically pure (R)-(+)-hydroxymethylenecamphor (eq. 1) gave yellow products whose elemental analyses were in agreement with derivatives of general formula [Pd(Lⁿ)[(R)-(+)-MC]].





I: $R_1 = R_4 = \text{H}$; $R_2 = R_3 = \text{CH}_3$

II: $R_1 = R_4 = \text{OCH}_3$; $R_2 = R_3 = \text{H}$

III: $R_1 = \text{OC}_2\text{H}_5$; $R_2 = R_3 = \text{H}$; $R_4 = \text{OCOC}_6\text{H}_{13}$

IV

Fig. 2. Sketch of the molecular structures of complexes I–IV.

The IR spectra of 1–4 display a strong absorption at about 1620 cm^{-1} diagnostic of chelating (*R*)-(+)-MC [10].

In principle, reaction 1 affords pairs of diastereoisomers since the 7,7' dimethyl bridge of the (*R*)-(+)-MC ligand can be above or below the coordination plane of the square-planar complexes. This would lead to structures with the hydrogen atom *ortho* to the palladated carbon atom and the hydrogen atom of the acetylacetonate backbone being mutually *cis* (A) or *trans* (B) (Fig. 3).

Spectral analysis

The actual stereochemistry of the products 1–4 was investigated by NMR and circular dichroism spectroscopy. Relevant ^1H NMR and ^{13}C NMR data are listed in Table 1 and 2.

The assignment of ^1H and ^{13}C NMR spectra of all the title compounds is not trivial due to the large number of signals and much overlapping. Assignment is greatly simplified by 2d methods (namely ^1H 2D NOESY and $^1\text{H}/^{13}\text{C}$ 2D correlations), through a combined analysis of ^1H and ^{13}C resonance spectra. For instance, in the case of the ^{13}C spectrum of 3, the number of the signals (more than the expected 32) and the regular variation in their relative intensities, indicate the presence of two species in different abundances.

Using $\text{Tl}[(R)\text{-}(+)\text{-MC}]$ as a reference, we assign the methyne signals at δ 167.0 and 170.9 to carbon C(1) and C(1') (where hereafter ' indicates the signals of the lesser isomer). The corresponding protons are expected to be singlets resonating in the range 7–8 ppm. One singlet is in fact found in the ^1H spectrum at δ 7.63, the second (of lower intensity) being hidden by other resonances at δ 8.05. This is clear from the integrated areas and a further analysis of the aromatic spin systems (see later), and is unambiguously proved by $^1\text{H}/^{13}\text{C}$ correlation measurements.

The assignment of protons a, b, c (at δ 7.07, 6.76 and 7.82, respectively) is straightforward on the basis of the multiplicities, ^1H 2D COSY, and ^1H 2D

Table 2

Carbon-13 NMR data for complexes 1–4 ^a

Compound	δ										
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C _a	C _b	C _c
1A	166.3	177.9	47.9	28.5	30.3	58.1	202.0	51.3	n.a.	n.a.	n.a.
1B	171.9						198.8	53.2			
2A	167.1	117.5	48.0	28.6	30.5	58.3	201.7	51.7	115.16	112.9	129.9
2B	170.9	117.3					199.4	52.7			
3A	167.0	117.6	47.9	n.a.	n.a.	58.3	201.8	51.7	115.8	113.3	130.8
3B	170.9	117.4					199.3	52.7	115.4		
4A	167.9	117.7	48.2	n.a.	n.a.	57.9	201.3	51.6	114.9	112.9	127.3
4B	170.5						58.3	199.8	52.3	114.2	

^a In CDCl₃ at 298 K and at 50.3 MHz. n.a., not assigned.

NOESY measurements. The proton signals of the free aromatic ring form a pseudo AA'BB' spin system and are grouped in two sets of multiplets centred at δ 8.05 and 7.19. Since neither set of signals shows an NOE effect with respect to the closest protons of the side chain ($-\text{OCOCH}_2-$ at δ 2.6) no further distinction can be made.

The other assignments (Table 1) result from the comparison with the NMR data for $\text{Ti}[(R)\text{-}(+)\text{-MC}]$ and for $\{\text{Pd}(\text{L}^n)(\mu\text{-Cl})_2\}$ and from the $^1\text{H}/^{13}\text{C}$ 2D correlations. It is worth noting that the ^1H NMR spectrum of the lesser isomer is almost coincident with that of the greater, only two signals (1' and a') being clearly differentiated, indicating a great similarity between their corresponding stereostructures.

The other assignments are shown in Tables 1 and 2. Apart from a few obvious differences, due to different substituents, all the spectra are strikingly similar. In each case: (i) resonances from two distinct complexes are observed; the relative intensities range from 2.5/1 for **1** to 1.2/1 for **4**; (ii) the ^1H spectrum of the lesser isomer is almost coincident with that of the greater; (iii) the ^1H and ^{13}C spectra of the lesser and more abundant isomer show similar shift trends. This, together with the elemental analyses indicate that all the samples are mixtures of isomeric complexes having very similar stereostructures.

The 2D ^1H NOESY spectrum of **4** (Fig. 4) leads to the following conclusions: (i) NOE is observed between the proton 1 at δ 7.61 and proton a at δ 7.12 and (ii) NOE is found between proton 1' at δ 7.98 and the signal at δ 8.62, attributed to the pyrimidine proton d', *ortho* to the coordinated nitrogen. Since the Overhauser factor is an indication of the proximity of the interacting nuclei, our findings require that the more abundant and lesser isomers of **4** have *A* and *B* structures, respectively. The lack of resolution in the ^1H spectra has prevented similar measurements for the other complexes.

Figure 5 shows the circular dichroism spectra of the diastereoisomeric mixtures of complexes 1–4. The CD spectra are very similar around 315 nm, with an intense positive transition for all the four samples. Compounds **1**, **2** and **3** also show a positive Cotton effect of lower intensity around 440 nm, almost absent in the CD spectrum of **4**. In addition, **3** exhibits a pronounced shoulder at 360 nm.

As the complex $\text{Ti}[(R)\text{-}(+)\text{-MC}]$ displays a pronounced positive Cotton effect at 315 nm, it seems probable that this transition should involve essentially $(R)\text{-}(+)\text{-MC}$

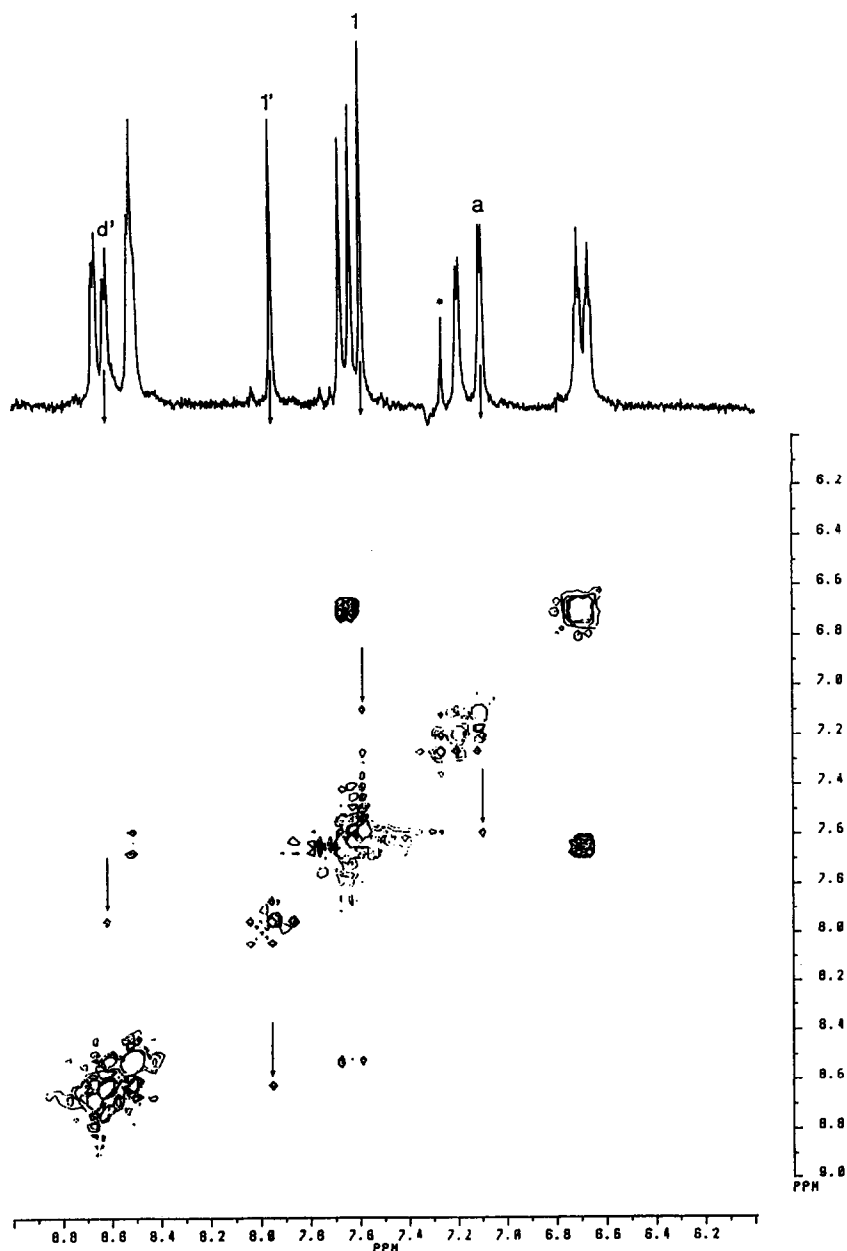


Fig. 4. Section of 2D NOESY ^1H NMR spectrum (200.13 MHz, CDCl_3 , 298 K) for complex 4. * indicates impurity.

and reflect the chirality of the hydroxymethylene camphor itself, because no other elements of dissymmetry are present. In **1**, **2** and **3**, the transitions associated with a Cotton effect in the 400–500 nm region should be related to $d-d$ or to charge-transfer transitions involving the metal; thus the sign and the intensity of the Cotton effect should reflect not only the chirality of the ligand but also the

$$\frac{\epsilon_1 - \epsilon_r}{dm^3 mol^{-1} cm^{-1}}$$

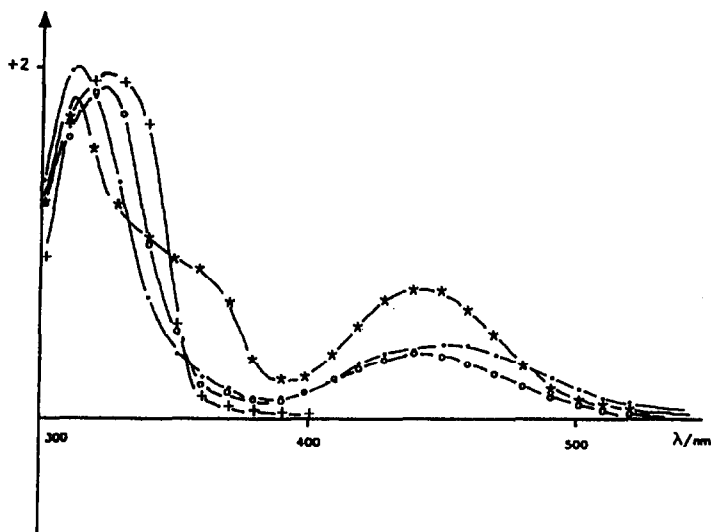


Fig. 5. CD spectra of: 1 (*—*), 2 (●—●), 3 (○—○), 4 (+—+).

intrinsic chirality of the metal chromophore and be related to the diastereoisomeric composition of the complexes. There is indeed a relationship between the diastereoisomeric excess (d.e.), accessible by NMR spectroscopy, and the intensity of the Cotton effect around 440 nm. Compound 1, obtained in a 43% d.e., shows the highest Cotton effect at 440 nm; in compounds 2 and 3, a lower d.e. corresponds to a decrease of the Cotton effect in the same region. In contrast, compound 4, which shows a moderate 9% d.e., gives a CD spectrum almost superimposable on that of $Tl[(R)\text{-}(+)\text{-MC}]$, without any significant Cotton effect around 440 nm.

Since the complexity and the overlapping of the signals exhibited by the 1H NMR spectra prevented NOE experiments on 1–3, computer modelling has been considered. The molecular modelling software [19] used allows an evaluation of the interatomic distances. None of the complexes 1–4, either for A or B geometry, showed steric constraints which account with certainty for the diastereoisomeric mixtures detected. Therefore, the source of the observed stereodiscrimination probably originates in effects which we are not able to identify.

Acknowledgments

This work was supported by the Italian CNR (Consiglio Nazionale delle Ricerche) under the cover of Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate and Ministero dell'Università e della Ricerca Scientifica e Tecnologica. We thank Johnson Matthey Ltd. for a generous loan of $PdCl_2$.

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