



Syntheses and Characterization of Optically Active Cyclopalladated Compounds containing Ferrocenyl units.

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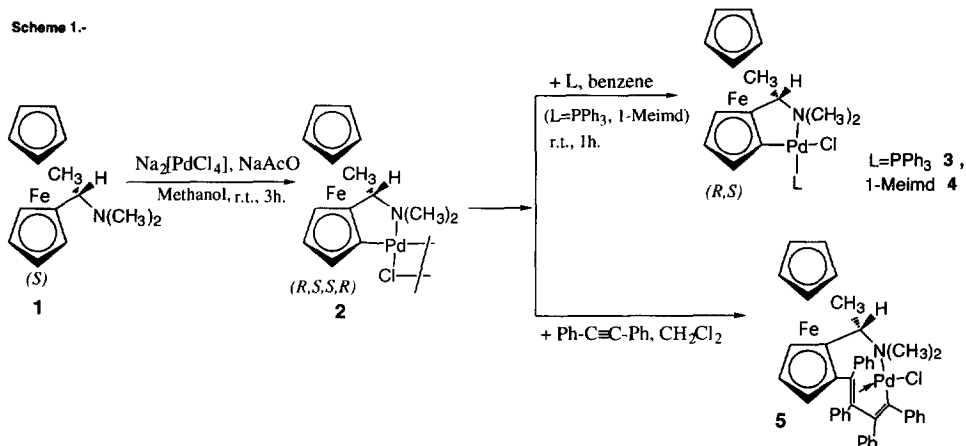
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Abstract.- The diastereoselective cyclopalladation of (*S*)-(-)-*N,N*-dimethyl-1-ferrocenylethylamine **1** produces (*R,S,S,R*)-(+)-[Pd{[(η^5 -C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η^5 -C₅H₅)}(μ-Cl)]₂ **2**. The absolute configuration of this complex has been determined by X-ray diffraction. Reactivity studies on the "Pd(μ-Cl)₂Pd" units and the σ(Pd-C) bond in compound **2** have been also undertaken and have allowed to isolate (*R,S*)-(+)-[Pd{[(η^5 -C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η^5 -C₅H₅)}Cl(L)] L= PPh₃ **3** or 1-Meimd **4** and [Pd{[(PhC=CPh)₂(η^5 -C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η^5 -C₅H₅)}Cl] **5**. Copyright © 1996 Elsevier Science Ltd

Despite the prochiral nature of monosubstituted ferrocenes ¹, cyclopalladation of the amine: [(η^5 -C₅H₅)Fe{ η^5 -C₅H₄-CH₂-N(CH₃)₂}] ² or the ferrocenylimines: [(η^5 -C₅H₅)Fe{ η^5 -C₅H₄-C(R)=N-R'}] {with R=H, Me or Ph} ³ have yielded unambiguously racemates. In order to improve the enantiomeric excess of these processes, several strategies based on the addition of chiral aminoacids in the reaction media, have been used, but in none of the cases was the isolation of the enantiomerically pure 1,2-disubstituted derivative achieved.⁴ On this basis we decided to elucidate whether the use of an optically active ligand with a stereogenic centre in between the N-donor atom and the substituted C₅H₄ ring would allow to induce preferentially the activation of one of the two *ortho* σ(C-H) bonds of the ferrocenyl moiety. In this paper we report the diastereoselective cyclopalladation of the (*S*)-(-)-*N,N*-dimethyl-1-ferrocenylethylamine **1**. This substrate reacts at room temperature with Na₂[PdCl₄] and Na(CH₃COO)·3H₂O in a 1:1:1 molar ratio, giving (*R,S,S,R*)-(+)-[Pd{[(η^5 -C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η^5 -C₅H₅)}(μ-Cl)]₂ **2**. Complex **2** is a stable dark solid and has been characterized by ¹H-NMR spectroscopy and X-ray diffraction. The structure consists of discrete molecules of *cis*- [Pd{[(η^5 -C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η^5 -C₅H₅)}(μ-Cl)]₂ packed by van der Waals forces (Fig.1). The two halves of the molecule are in a *cis*-arrangement and exhibit identical planar chirality, thus indicating that the presence of the stereogenic carbon in the starting material induces the activation of only one of the two *ortho* C-H bonds.

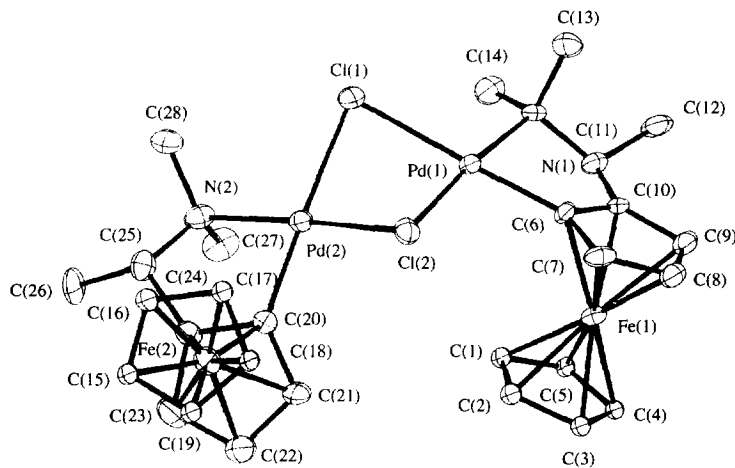
Scheme 1.-



It is well known⁵ that lithiation of 1, which occurs through a cyclic mechanism, also proceeds with substantial asymmetric induction {e.e. =92%}, and in this case the major isomer arises from the activation of the *ortho*-position conformationally opposite to the methyl at the stereogenic carbon. The cyclopalladation process, where no evidence of the formation of any other isomer were detected by ¹H-NMR {500MHz}, proceeds through the enantiotopic hydrogen activation of the other *ortho*-C-H bond, being disfavoured by the C-CH₃ ferrocenyl interaction that would be involved.

Figure 1.- Molecular structure and atom labeling scheme for complex 2.

Selected structural data: bond lengths: Pd(1)-N(1): 2.096(6), Pd(2)-N(2): 2.145(7), Pd(1)-Cl(1): 2.478(2), Pd(2)-Cl(2): 2.486(2), Pd(1)-C(6): 1.928(6) and Pd(2)-C(20): 1.916(8)Å; bond angles: Cl(1)-Pd-Cl(2): 86.13(7) and Cl(2)-Pd(2)-Cl(1): 85.89(7)



Crystal data: a = 10.911(2), b = 27.240(3), c = 9.863(2)Å, α = β = γ = 90.0.

Details of the refinement: -15 ≤ h ≤ 15; 0 ≤ k ≤ 38 and 0 ≤ l ≤ 13

Number of reflections collected 8553 { from 2.01 to 30.01 }.

Final R-values: R1 = 0.0487, wR2 = 0.1109 { for I > 2σ(I) }, and R1 = 0.0903 and wR2 = 0.2316 { all data }.

Addition of triphenylphosphine or 1-methylimidazole to benzene suspensions of 2 produces the cleavage of the μ-Cl-bridges giving: (R,S,-)-(+)-[Pd{[(η⁵-C₅H₃)-CH(CH₃)-N(CH₃)₂]Fe(η⁵-C₅H₅)}Cl(L)] { with L = PPh₃ 3

or 1-MeImd **4**) (Scheme 1). ^{31}P -NMR spectra of **3** agrees with a *trans* arrangement between the phosphine ligand and the nitrogen³. Double insertion of $\text{PhC}\equiv\text{CPh}$ into the $\sigma(\text{Pd}-\text{C}_{\text{sp}^2}, \text{ferrocene})$ bond of **2** also yields: $[\text{Pd}\{[(\text{PhC}=\text{CPh})_2(\eta^5\text{-C}_5\text{H}_3)\text{-C}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]\text{5}$.

The results reported here have allowed the diastereoselective isolation of the enantiomeric complex: $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$ and to study its reactivity. According to previous work on the applications of cyclopalladated complexes⁶, compound **2** appears to be not only a good substrate for the syntheses of other optically active 1,2 derivatives (*i.e.* by insertion of other small molecules such CO), but also as an auxiliary reagent for the resolution of optically active phosphines or for the determination of enantiomeric excesses. Further work on this area is currently under study.

Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics de la Universitat de Barcelona. Routine ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were recorded at 20°C on a GEMINI-200MHz spectrophotometer using CDCl_3 (99.8%) and $\text{Si}(\text{CH}_3)_4$ as solvent and internal standard respectively. The ^1H -NMR of **2** was recorded using CD_2Cl_2 (99.8%) as solvent using a Varian-500 MHz instrument. $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectrum of **3** was recorded with a BRUKER 250-DXR spectrometer (32.8MHz), using CHCl_3 as solvent and $\text{P}(\text{OCH}_3)_3$ as standard. The optical rotations of the complexes ($c = 0.1\text{g}/100\text{ml}$) in CH_2Cl_2 , were determined at 20°C using a Perkin Elmer 241-MC polarimeter. Ligand **1** was obtained from Aldrich and used as received.

Preparation of the compounds:

(*R,S,S,R*)- (+)- $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$ **2**.- 0.441 g (1.5 mmol) of $\text{Na}_2[\text{PdCl}_4]$, 0.204 g (1.5 mmol) of $\text{Na}(\text{CH}_3\text{COO})\cdot 3\text{H}_2\text{O}$ and 1.5 mmol of **1** were suspended in 15 ml of methanol. The reaction mixture was stirred at 20°C for 3 h. The orange solid **2** formed was then filtered and air-dried. (Yield: 66%). Anal.(%) Calcd for $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Fe}_2\text{Pd}_2$ (found): C, 42.33 (42.2); H, 4.53 (4.5) and N, 1.76 (1.8) %. ^1H -NMR (in ppm) for **2**: 4.23 and 4.30 (Cp); 3.85 and 3.87 (H^3), 4.01 and 4.02 (H^4); 4.07 and 4.12 (H^5); 2.87, 2.80, 2.61 and 2.57 (N- CH_3); 1.18 and 1.17 (CH_3) and 4.43 and 4.49 (-CH-). For (**2** + *py-d*₅): 4.12 (Cp); 3.26 (H^3), 3.85 (H^4), 4.09 (H^5); 3.02 and 2.63 (N- CH_3); 1.18 and 1.17 (CH_3) and 4.38 (-CH-). $[\alpha]_{20^\circ\text{C}} = +291$.

(*R,S*)-(+)- $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{L})]$ (L= PPh_3 **3** or 1-MeImd **4**).- 0.1 mmol of triphenylphosphine or 1-methylimidazole were added to a benzene suspension (20 ml) of **2** (0.1mmol). The mixture was stirred at 20°C for 2 h. The undissolved materials were removed by filtration and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then treated with *n*-hexane (ca. 10 ml) and stirred at room temperature for 15 min. The solid **3** or **4** formed was filtered and air-dried. (Yield: 82 and 75%). **3**: Anal.(%) Calcd. for: $\text{C}_{32}\text{H}_{33}\text{NFePdPCl}$ (found): C, 58.20 (58.4), H, 5.02 (5.1) and N, 2.12 (2.0) %. ^1H -NMR (in ppm): 3.88 (Cp and H^5); 3.76 (H^3); 3.92 (H^4); 3.07 and 2.75 (N- CH_3); 1.30 (CH_3), 4.02(-CH-) and 7.30-7.50 (C_6H_5). ^{31}P -NMR: 40.18ppm. $[\alpha]_{20^\circ\text{C}} = +142$. **4**: Anal.(%) Calcd. for: $\text{C}_{18}\text{H}_{24}\text{FePdN}_3\text{Cl}$ (found): C, 45.02 (45.1); H, 5.00 (4.9) and N, 8.75 (8.8)%. ^1H -NMR (in ppm): 4.13 (Cp); 3.56 (H^3); 3.88 (H^4); 4.06(H^5); 2.97 and 2.57 (N- CH_3); 1.19 (CH_3), 4.32(-CH-) and 3.68, 6.76, 7.40 and 7.98 (1-MeImd). $[\alpha]_{20^\circ\text{C}} = +78$.

(*R,S*)- $[\text{Pd}\{[(\text{C}_6\text{H}_5\text{-C}=\text{C-C}_6\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_3)\text{-CH}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]\text{5}$.- 0.200 g (0.25 mmol) of **2**, were suspended in 15 ml of CH_2Cl_2 , and then a solution of $\text{PhC}\equiv\text{CPh}$ (0.178 g, 1 mmol) in CH_2Cl_2 (10 ml), was added dropwise. The mixture was stirred at room temperature for 2.5 hours. The undissolved materials were filtered. The filtrate was allowed to evaporate to ca. 5 ml., and then treated with *n*-hexane (ca. 5

ml.). The solid **5** formed was collected and air-dried. (Yield: 72 %). Anal (%) Calcd. for: $C_{42}H_{38}FePdNCl \cdot CH_2Cl_2$ (found): C, 61.74 (61.7); H, 4.97(5.0) and N, 1.67 (1.7) %. 1H -NMR (in ppm): 3.78 (Cp); 4.02 (H³); 4.10 (H⁴); 4.02 (H⁵); 3.46 and 2.38 (N-CH₃); 0.832 (CH₃), 3.12 (-CH-) and 6.80-7.60 (C₆H₅).

Crystal Structure Determination and Refinement.- A prismatic crystal of **2** was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections in the range $8 \leq \Theta \leq 12$ and refined by least squares method. Intensities were collected with a graphite monochromatized Mo, K α radiation, using ω -2 Θ scan-technique. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz polarization and absorption corrections were made. The structure was solved by Patterson synthesis using SHELXS ⁷ and refined by full-matrix least-squares method with SHELX96 ⁸, using 8479 reflections (very negative intensities were not assumed). The function minimized was $\sum w | |F_o|^2 - |F_c|^2 |$, where $w = \{ \sigma^2(I) + (0.0677P)^2 \}^{-1}$, and $P = (|F_o|^2 + 2 |F_c|^2) / 3$. f , f' and f'' were taken from *International Tables of X-ray Crystallography* ⁹. The two unsubstituted C₅H₅ rings of the ferrocenyl moieties were found in disordered positions. These groups were refined with planar constrained geometry {with C-C bond lengths = 1.39Å} and isotropically. The chirality of the structure was defined from the Flack coefficient ¹⁰ {0.03(4) for the given results}. The positions of 26 H-atoms were computed and refined with an overall isotropic temperature factor using a riding model. The goodness of fit on F² was 0.998.

Acknowledgements.-We are indebted to the D.G.Y.C.I.T (Grant N. PB93-0804) for financial support.

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