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Novel heteroleptic *cis*-(C^N)$_2$Pd(II) chelates for the preparation of enantiopure planar chiral cyclopalladated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine†

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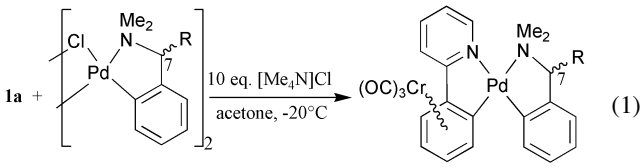
In the presence of large amounts of [Me$_4$N]Cl, the reaction of ortho-chloromercurated 2-[(η^6-phenyl)tricarbonylchromium]pyridine with μ-chloro cyclopalladated aromatic compounds yields a series of new heteroleptic heterodinuclear *cis*-(C^N)$_2$Pd(II) complexes, which are valuable precursors of planar chiral cyclopalladated (η^6-arene)Cr(CO)$_3$ complexes.

Recently, the facile ortho-mercuration of various (η^6-arene)Cr(CO)$_3$ complexes bearing endogenous ligands was reported.[1] When treated with inorganic sources of palladium the described mercurated products showed an interesting propensity to exchange the Hg(II) center for Pd(II) and form a new set of palladated (η^6-arene)Cr(CO)$_3$ complexes.[1] We decided to probe other organometallic sources of Pd(II) with the aim of designing a specific methodology of synthesis of planar chiral metallated (η^6-arene)Cr(CO)$_3$ complexes.

In this regard, heteroleptic bis-chelated Pd(II) complexes can be of help for the resolution of racemates of planar asymmetric Pd(II) complexes.[2] Herein, we report the unprecedented synthesis of dinuclear asymmetric heteroleptic Pd(II) complexes from Hg(II) derivative **1a** (Scheme 1) as well as their use in the preparation of enantiopure **2** and **3**.

Treatment of model ortho-chloromercurated complex **1a** with ortho-palladated compounds **4a–4c** [3] (eqn. 1) in the



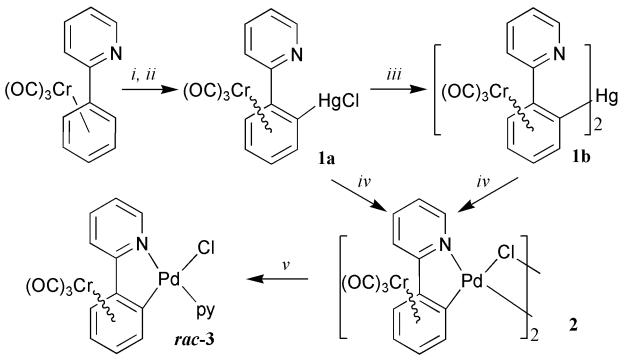
(1)

4a, R= H
4b, (7*S*), R= Me
4c, (7*R*), R= Me

rac-**5a**, R= H
(p*R*,7*S*)-*endo*-**5b**; (p*S*,7*S*)-*exo*-**5b**
(p*S*,7*R*)-*endo*-**5c**; (p*R*,7*R*)-*exo*-**5c**

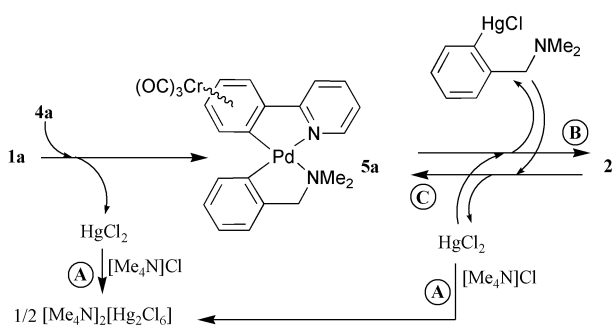
presence of a large excess of [Me$_4$N]Cl afforded the corresponding dinuclear heteroleptic Pd(II) complexes **5a** (62%), **5b** (70% conv., d.r. = 1.3:1 in favor of *endo*-**5b**) and **5c** (65% conv., d.r. = 1.3:1 in favor of *endo*-**5c**).

In this reaction, the chloride ion was introduced in large amounts in order to force the trapping of $HgCl_2$, which is formed in the course of the transmetallation process leading to complexes **5a–c**. Mercuric chloride reacts with Cl^- to yield the corresponding insoluble adduct $[Me_4N]_2[Hg_2Cl_6]$.[4] Several pathways were observed depending on the presence (or not) of $HgCl_2$ in the medium. We noticed that in the absence of chloride ion, the transmetallation process led directly to complex **2** and



Scheme 1 *i*: Hg(OAc)$_2$, EtOH, 50 °C; *ii*: $CaCl_2$, EtOH; *iii*: [Me$_4$N]Cl, acetone, rt; *iv*: Pd(MeCN)$_2$Cl$_2$, acetone, −20 °C; *v*: pyridine, rt.

eventually *rac*-**3** upon quenching with pyridine. Both **1b** and **1a** were able to yield compound **5a** when treated with **4a** in the presence of large amounts of chloride. In the absence of chloride, the treatment of **1a** with **4a–4c** led, after quenching with pyridine, to *rac*-**3** in *ca.* 50% yield. Complex **1b** treated with **4b–4c** afforded, after quenching with pyridine, a mixture containing *rac*-**3** and low amounts of the heteroleptic Pd(II) complexes **5b–5c**, which could readily be converted to **2** and **3** upon sequential treatment with $HgCl_2$ and pyridine. These results suggest that the heteroleptic Pd(II) complexes **5a–5c** are the primary products of the reaction between **1a** and the cyclopalladated substrates **4a–4c**. Complex **2** is formed only if $HgCl_2$ is present in sufficient amounts to efficiently attack the bis-chelated Pd(II) centre by a process probably similar to that evidenced a few years ago by van Koten and Pfeffer for simple mononuclear homo and heteroleptic Pt(II) and Pd(II) bis-chelates.[5] In this reaction the electrophilic mercury center is assumed to bind to the more basic ligand of the bis-chelate, *ie*.



Scheme 2 Possible pathways for the reaction between **1a** and **4a**: (A) the trapping of $HgCl_2$ in the presence of Cl^-, (B) reaction of **5a** with $HgCl_2$ in the absence of Cl^-, (C) a possible back-reaction of **2** with the released chloro-mercurated benzylamine derivative in the presence of Cl^-.

† Electronic supplementary information (ESI) available: preparation procedures, spectroscopic data for **5a–c**, NMR and CD spectra for (p*R*)-**3** and (p*S*)-**3**, crystal data for **5b**, **5c**, (p*R*)-**3** and (p*S*)-**3**.

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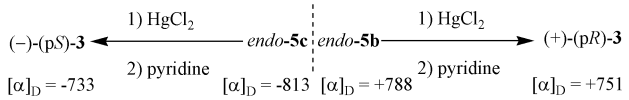
the benzylamine derivative. Scheme 2 outlines the possible evolution of the reaction between **1a** and **4a** in the presence or absence of chloride ion in the medium.

Diastereomers **5b**, as well as **5c**, were found to co-crystallise in the monoclinic system and their pseudo centro-symmetric lattice to fit the $P2_1$ space group (see supplementary information†).‡ These distorted square planar Pd(II) bis-chelates encompass three types of chirality: centered, planar and helical.[6] We succeeded in separating the diastereomers **5b** by low temperature chromatography on silica gel (see the photographs in the supplementary information†), to yield a pure sample of *endo*-**5b** and a mixture containing *exo*-**5b** and various decomposition products such as 2-[(η^6-phenyl)$Cr(CO)_3$]pyridine. A similar treatment was applied to **5c**. Complex *endo*-**5b** and its mirror image *endo*-**5c**, were sequentially treated with $HgCl_2$ and pyridine (Scheme 3) to yield two enantio-enriched (+) and (−) samples of **3** respectively.



Scheme 3 Conversion of bis-chelated complexes into enantiopure (+) and (−)-**3**. Specific rotations were determined in CH_2Cl_2 solutions (20 °C, c = 0.04).

The enantiomeric purity of compounds (−)-**3** and (+)-**3** was then determined using salts [nBu$_3$NH][Λ-TRISPHAT] or [nBu$_4$N][Δ-TRISPHAT][7] as diamagnetic NMR chiral shift agents.[8] In a first set of experiments these salts were added to a solution of *rac*-**3** (1:4 d_6-acetone/C_6D_6). This induced a 1:1 split of the signal of one ortho proton of the Cr-bound arene ($\Delta\delta$ = 0.1 ppm). Then, compounds (−)-**3** and (+)-**3** were treated under the same conditions and their spectra displayed only one signal (δ = 4.25 ppm and 4.15 ppm, ^3J = 5.7 Hz) suggesting that each sample can be considered as highly enantio-enriched (*ee* > 96%) (Fig. 1).

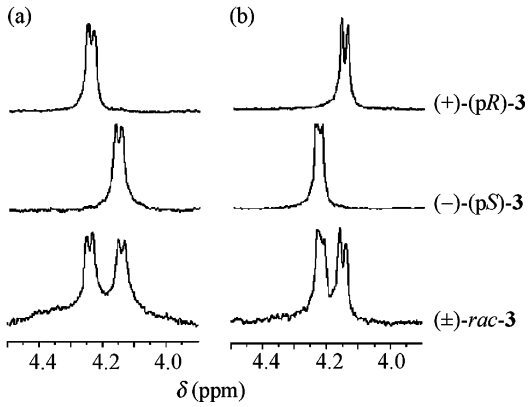


Fig. 1 ^{1}H NMR spectra (20 °C, 300 MHz, 1:4 d_6.acetone in C_6D_6) of the two enantiomers of **3** (1.52 mM) and the racemate in the presence of: (a) [nBu$_3$NH][Λ-TRISPHAT] (6.08 mM), (b) [nBu$_4$N][Δ-TRISPHAT](6.08 mM).

Fortunately, both enantiomers could be crystallised and their absolute structure determined by X-ray diffraction analyses.‡ Enantiomer (+)-**3** was found to crystallise with one disordered molecule of CH_2Cl_2 in the monoclinic system and its lattice to fit the $P2_1$ space group: the molecular structure reveals a p*R* configuration at the ipso carbon bearing the palladium atom (see the supplementary material†). A p*S* configuration was found for (−)-**3**·CH_2Cl_2, which crystallises in the orthorhombic system with a lattice fitting the $P2_12_12_1$ space group.

In conclusion, we have described a new efficient method of synthesis of heteroleptic Pd(II) bis-chelate and have demonstrated the high potential of heteroleptic Pd(II) complexes displaying planar asymmetry for the synthesis of enantiopure samples of a palladated (η^6-arene)$Cr(CO)_3$ complex.

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Notes and references

‡ *Crystal data* for **5b**: $C_{48}H_{44}N_4O_6Cr_2Pd_2$, M = 1089.70, monoclinic, $P2_1$, a = 11.1217(3) Å, b = 17.0324(4) Å, c = 11.5570(3) Å, β = 102.118(5) °, V = 2140.45(9) Å^3, Z = 2, D_c = 1.69 g cm^{-3}, μ = 1.377 mm^{-1}, F(000) = 1096, λ(MoKα) = 0.71073 Å, T = 173 K, orange, dimension 0.20 × 0.14 × 0.14. A total of 12332 reflections were collected with 2.5 < θ < 30.03. R = 0.030, R_w = 0.046, GOF = 1.046, maximum residual electron density 0.424 eÅ^{-3}. 4310 unique reflections had intensities I > 3σ(I). CCDC 198824. See http://www.rsc.org/suppdata/cc/b2/b211873d/ for crystallographic files in CIF or other electronic format.

For **5c**: $C_{48}H_{44}N_4O_6Cr_2Pd_2$, M = 1089.70, monoclinic, $P2_1$, a = 11.1267(2) Å, b = 17.0317(3) Å, c = 11.5572(2) Å, β = 102.140(5) °, V = 2141.19(6) Å^3, Z = 2, D_c = 1.69 g cm^{-3}, μ = 1.376 mm^{-1}, F(000) = 1096, λ(MoKα) = 0.71073 Å, T = 173 K, orange, dimension 0.18 × 0.14 × 0.10. A total of 10295 reflections were collected with 2.5 < θ < 30.02. R = 0.023, R_w = 0.028, GOF = 0.941, maximum residual electron density 0.372 eÅ^{-3}. 5557 unique reflections had intensities I > 3σ(I). CCDC 198825.

For (p*S*)-**3**: $C_{20}H_{15}N_2O_3Cl_3CrPd$, M = 596.11, orthorhombic, $P2_12_12_1$, a = 18.0316(3) Å, b = 18.0653(3) Å, c = 6.6008(1) Å, V = 2150.19(6) Å^3, Z = 4, D_c = 1.84 g cm^{-3}, μ = 1.739 mm^{-1}, F(000) = 1176, λ(MoKα) = 0.71073 Å, T = 173 K, orange, dimension 0.20 × 0.08 × 0.03 mm. A total of 6317 reflections were collected with 2.5 < θ < 30.03. R = 0.030, R_w = 0.036, GOF = 1.037, maximum residual electron density 0.893 eÅ^{-3}. 5347 unique reflections had intensities I > 3σ(I). CCDC 198827.

For (p*R*)-**3**: $C_{20}H_{15}N_2O_3CrPd$, M = 596.11, monoclinic, $P2_1$, a = 6.4747(2) Å, b = 12.4324(3) Å, c = 14.0935(5) Å, β = 96.103(5) °, V = 1128.04(6) Å^3, Z = 2, D_c = 1.75 g.cm^{-3}, μ = 1.658 mm^{-1}, F(000) = 588, λ(MoKα) = 0.71073 Å, T = 173 K, color, dimension 0.20 × 0.16 × 0.10. A total of 6353 reflections were collected with 2.5 < θ < 30.04. R = 0.040, R_w = 0.057, GOF = 1.129, maximum residual electron density 1.137 eÅ^{-3}. 2879 unique reflections had intensities I > 3σ(I). The disordered molecule of CH_2Cl_2 solvate was not refined. CCDC 198826.

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