Metallocryptophanes | Very Important Paper |

VIP The Chemo- and Stereoselective Formation of Pallado- and Platinocryptophanes

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Dedicated to Professor Dr. Jean-Pierre Sauvage on the occasion of his 75th birthday

Abstract: Cyclotricyanobenzylene (CTB) **1** was resolved by HPLC on chiral stationary phase and the absolute configurations of its enantiomers were determined. Optically-active pallado- and platinocryptophanes assembled separately from (+)-**1** and (–)-**1**, and the optical properties of $[M_3(dppp)_3((+)-1)_2](OTf)_6$ and $[M_3(dppp)_3((-)-1)_2](OTf)_6$ ($M = Pd$ and Pt ; $dppp = 1,3$ -bis(di-phenylphosphanyl)propane) were studied by polarimetry and electronic circular dichroism (ECD). The enantiomerization barriers of the metallocryptophanes depend only weakly on the

nature of the metal. TD-DFT calculations demonstrated the occurrence of induced ECD effects from the optically active CTB **1** to the metal complex fragments. Comparison of the 1H NMR spectra of the optically-pure and racemic metallocryptophanes confirmed that the latter formed diastereoselectively and enantioselectively. Self-assembly of metallocryptophanes from two different CTBs (**1** and **2**) gave clear evidence of chemoselectivity for the process, using 1H NMR spectroscopy and ESI-MS.

Introduction

Inherently chiral molecular containers feature cavities, the dissymmetry of which is imprinted in the whole structure.^[1] Among hollow molecular receptors exhibiting this property, cryptophanes occupy a prominent place.^[2] These spheroidal compounds can exist in achiral, *syn*, and chiral, *anti* configurations (Figure 1).^[3] Chiral cryptophanes are made from face-to-face connected homochiral cyclotribenzylene (CTB) concave subunits and were shown to exhibit outstanding chiral recognition properties.^[4] Traditionally, chiral cryptophanes are constructed using the so-called template strategy,^[3a,5] starting from a CTB with tethered benzylic alcohol pendants as precursors of

the second CTB. The stereochemical outcome of the reaction (achiral *syn* or chiral *anti* configuration) depends on the nature and length of the three bridges connecting the two CTBs in the cryptophane.^[3c,3e] CTBs and chiral cryptophanes were resolved either by fractional crystallization or chromatography of the diastereomeric mixtures resulting from the chemical modification of the enantiomers with an optically active agent,^[3c,6] by analytical^[7] and preparative^[8] HPLC of the racemate on optically active phases, and by thermodynamic dynamic resolution.^[9]

Figure 1. The chemical structures of prototypical chiral (*anti*) cryptophane-A (*M,M* enantiomer) and *meso* (*syn*) cryptophane-B for comparison.

A few examples of cryptophanes obtained by self-assembly were reported. Dynamic covalent bonds,^[10] hydrogen bonding interactions,^[11] and coordination bonds^[8,12] were all used to generate cryptophanes by tripod-tripod [1+1] coupling of CTBs either directly^[11] or through bridging subunits,^[8,10,12] but these approaches did not systematically lead to *anti*-cryptophanes. Recently however, we accounted for the stereoselective formation of chiral cryptophanes from cyclotricyanobenzylene

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caps (CTB **1**, Figure 2) and connectors derived from the $[M(dppp)(OTf)_2]$ complexes ($M = Pd$ or Pt ; dppp is 1,3-bis(di-phenylphosphanyl)propane).^[12c] In these so-called metallo-cryptophanes the coordination sphere of the square-planar metal cation complex fragments $[M(dppp)]^{2+}$ is completed by the *N*-coordinating carbonitrile substituents of **1**. More recently, Hardie and co-workers showed that cyclotriguaiacylene (CTG) derivatives carrying 4-pyridyl substituents (via a carbonyl or a methylene spacer) formed predominantly *anti*-metallo-cryptophanes when $[Pd(dppp)]^{2+}$ ^[12d] or $[Ir(ppy)_2(MeCN)_2]^+$ ^[12e] (*ppy* = 2-phenylpyridinato) were used as metal complex bridging fragment.

Figure 2. Structural formulae and chirality descriptors of the enantiomers of CTB **1** and CTB **2**.

Our initial investigations used racemic **1** for the generation of pallado- and platinocryptophane racemates.^[12c] We now focus at first on the self-assembly of the corresponding optically active metallocryptophanes from the separated enantiomers of the CTB component **1**, as well as on the investigation of the chiroptical properties of these molecular assemblies. The characterization of $[M_3(dppp)_3((+)-1)_2](OTf)_6$ and $[M_3(dppp)_3((-)-1)_2](OTf)_6$ ($M = Pd$ and Pt) by 1H NMR spectroscopy will allow us to provide a chemical demonstration that the self-assembly of these metallocryptophanes produces the *anti* diastereomers. Therefore, the generation of pallado- and platinocryptophanes from racemic CTB **1** proceeds through enantioselective self-sorting. In our preliminary investigation,^[12c] we had also shown that mixing $[Pd(dppp)]^{2+}$ and CTBs **1** and **2** (Figure 2) in 3:1:1 ratio proceeded through chemoselective self-sorting, as the homoleptic metallocryptophanes $[Pd_3(dppp)_3(1)_2]^{6+}$ and $[Pd_3(dppp)_3(2)_2]^{6+}$ were obtained at the expense of the elusive $[Pd_3(dppp)_3(1)_2]^{6+}$. Therefore, the second major point of the present study will concern a complete investigation, by 1H NMR spectroscopy and mass spectrometry, of the chemoselective self-sorting effect in the self-assembly of pallado- and platinocryptophanes.

Results and Discussion

Electronic Absorption Spectroscopy and Stability of the Metallocryptophanes in Solution

In an earlier study, the metallocryptophanes were identified and characterized in solution by 1H NMR spectroscopy in chlorinated solvents (CD_2Cl_2 , $CDCl_3$, and $C_2D_2Cl_4$) at millimolar concentrations.^[12c] The investigation of their spectroscopic properties in the UV/Visible range, including electronic absorption and circular dichroism (ECD), requires to know the stability in solution of these metallo-organic assemblies at lower concentrations. Comparison of the spectra in the millimolar range in

CH_2Cl_2 (1.22 and 1.02 mM for the palladocryptophane and the platinocryptophane, respectively) with those in the 0.1 mM range (3.11 and 0.93×10^{-4} M for the palladocryptophane and the platinocryptophane, respectively) showed that the relative differences at the maximum absorbance were no greater than 7.5 % (Figures S1–S2). The latter were used in the subsequent experiments and discussion. We also recorded the spectra of the separated components CTB **1** and $[M(dppp)(OTf)_2]$ ($M = Pd$ and Pt), and calculated the spectra of their virtual mixtures in 2:3 stoichiometric ratio (Figures S3–S4). The evolution of the spectra of the metallocryptophanes upon increasing dissociation into their separated components was calculated from 0 to 100 % using 10 % increments. The corresponding plots are shown in Figure 3a and Figure 3c. Both present an isosbestic point, at 236 and 240 nm for the pallado- and platinocryptophanes, respectively. Next, we performed dilution experiments of solutions of the metallocryptophanes, in the range 3.11×10^{-4} – 5.52×10^{-6} M (Pd) and 9.27×10^{-5} – 5.83×10^{-6} M (Pt). The raw spectra (Figures S5–S6) were corrected for concentrations, and, in order to eliminate dilution errors, each of the isosbestic points found in the simulations of the dissociation of the metallocryptophanes was imposed on the experimental spectra. The corresponding plots are shown in Figure 3b and Figure 3d for the pallado- and platinocryptophanes, respectively. In the case of $[Pd_3(dppp)_3(1)_2](OTf)_6$, two maxima at 245 and 345 nm with an inflexion at ca. 273 nm were observed at higher concentration (0.3 mM). As the solution was diluted down to 5.52×10^{-6} M, the highest energy maximum shifted to 235 nm, the lowest energy maximum to 351 nm, while a new maximum at 276 nm progressively took the place of the inflexion point in the same region. Noteworthy, the electronic spectrum of $[Pd(dppp)(OTf)_2]$ shows maxima at 357 and 276 nm. The changes observed upon diluting a solution of $[Pd_3(dppp)_3(1)_2](OTf)_6$ down to 5.52×10^{-6} M therefore agree qualitatively with the release of $[Pd(dppp)(OTf)_2]$ and quasi-complete dissociation. The electronic absorption spectrum of $[Pt_3(dppp)_3(1)_2](OTf)_6$ shows a maximum at 247 nm for 9.27×10^{-5} M, which, upon dilution down to 5.83×10^{-6} M, shifts to the blue while decreasing in intensity. At this lowest concentration explored, the maximum has moved to higher energy (236 nm) with respect to the isosbestic point. However, according to the comparison with the simulated spectra shown in Figure 3c, the system is far from complete dissociation, the estimated ratio between the platinocryptophane and its separated components lying between 7:3 and 6:4. In conclusion, comparison of the two series of spectra shows that the metallocryptophanes are stable down to concentrations of ca. 1.5×10^{-4} M for palladium and ca. 0.5×10^{-4} M for platinum. The electronic absorption data of the metallocryptophanes are collected in Table 1.

Resolution and Chiroptical Properties of CTB **1**

As the nitrile function cannot be reversibly derivatized, which is a prerequisite for chemical resolution, separation of the enantiomers of *rac*-**1** was best performed by HPLC on a chiral stationary phase. (*S,S*)-Whelk-O1 column using heptane/di-

Figure 3. Calculated changes of the electronic absorption spectra of virtual mixtures of $[\text{M}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$, $[\text{M}(\text{dppp})(\text{OTf})_2]$ and CTB **1**, the latter in 3:2 ratio, from 100:0 to 0:100 by 10 % increments: (a) $\text{M} = \text{Pd}$, (c) $\text{M} = \text{Pt}$. Changes in the electronic absorption spectra of solutions of $[\text{M}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ upon dilution in CH_2Cl_2 : (b) $\text{M} = \text{Pd}$, (d) $\text{M} = \text{Pt}$. Concentrations are given in M.

Table 1. UV/Vis isotropic and CD absorption spectra in CH_2Cl_2 .

Compound	λ [nm] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$])	λ [nm] ($\Delta\epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$])
(+)- 1	238 (53000), 246 (47000), ^[a] 277 (2200), 288 (2200)	233 (100), 250 (−94)
$[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$	245 (148500), 345 (20100)	239 (+227), 259 (−39), 288 (+32), 347 (+6) ^[b]
$[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$	247 (161000)	244 (+134), 263 (+128), 295 (+19) ^[c]

[a] Shoulder. [b] Values measured for $[\text{Pd}_3(\text{dppp})_3((+)\mathbf{1})_2](\text{OTf})_6$ (see text). [c] Values measured for $[\text{Pt}_3(\text{dppp})_3((+)\mathbf{1})_2](\text{OTf})_6$ (see text).

chloromethane, 30:70 at 1 mL min^{-1} as eluent gave satisfactory results: $R_{t1} = 7.5 \text{ min}$, $R_{t2} = 9.3 \text{ min}$, enantioselectivity and resolution being 1.39 and 4, respectively. CTBs (+)-**1** and (−)-**1** were both obtained in 30 % yield with ees > 97 %. The $[\alpha]_D^{25}$ values (CH_2Cl_2 , $c = 0.027$ and 0.026) were +526 and −523 for the first (i.e. (+)-**1**) and second (i.e. (−)-**1**) eluted enantiomers, respectively (Scheme 1). The electronic absorption spectra of the enantiomers are superposed in Figure 4a. They show a broad

band with a maximum at $\lambda = 238 \text{ nm}$ ($\epsilon = 53000 \text{ M}^{-1} \text{cm}^{-1}$) and a residual absorbance between 260 and 290 nm. The separated enantiomers show mirror-image ECD traces (Figure 4b). In the case of (+)-**1** for example, the ECD shows a couplet with consecutive positive and negative maxima at 233 nm ($\Delta\epsilon = 100 \text{ M}^{-1} \text{cm}^{-1}$) and 250 nm ($\Delta\epsilon = -94 \text{ M}^{-1} \text{cm}^{-1}$) followed by weak maxima with positive $\Delta\epsilon$ values at 279 and 288 nm. The enantiomerization^[13] kinetics of (−)-**1** in CH_2Cl_2 was studied by

Scheme 1. Asymmetric synthesis of the optically-active cryptophanes from the resolved enantiomers (*P*)-**1** and (*M*)-**1**.

monitoring the decrease of the enantiomeric excess by chiral HPLC. Data processing gave $k_{\text{enant}} = 1.7 \times 10^{-6} \text{ s}^{-1}$ at 40 °C, which translates into $t_{1/2} = 56$ hours in these conditions. The corresponding inversion barrier of the crown is $\Delta G^\ddagger = 26.65 \text{ kcal mol}^{-1}$ (Figure S7). This value is in keeping with those reported in the case of various CTBs.^[13] For example, for cyclotriarylsilene, $\Delta G^\ddagger_{\text{enant}} = 27.1 \text{ kcal mol}^{-1}$ at 25 °C in CHCl_3 .^[2a] Therefore, changing electron-withdrawing (–CN) for electron-releasing (–OMe) substituents does not significantly affect the enantiomerization barriers, as noted previously for other substituents.^[2a] The rate constant for the inversion process is also about 10^{-8} – 10^{-7} s^{-1} , which corresponds to a decrease of the optical rotation of 1 % within a 12–48 h period of time in solution at 25 °C.^[14]

Figure 4. (a) Electronic absorption and (b) ECD spectra of the separated enantiomers (+)-**1** (first eluted; green curves) and (–)-**1** (second eluted; red, dotted curves) of CTB **1** in CH_2Cl_2 at 25 °C.

The range of substituents of known optically active CTBs is relatively limited (OH, OMe and other alkoxy radicals, I, Br, OC(O)CH_3 , H), but all have positive spectroscopic moments (*SM*) with respect to H, ranging from 34 to 0 $\text{cm}^{-1/2} \text{ M}^{-1/2}$.^[15] As $SM(\text{CN}) = -19 \text{ cm}^{-1/2} \text{ M}^{-1/2}$, it is useful to note that (+)-**1** and (–)-**1** are optically active CTB derivatives carrying a substituent with a negative *SM*, which is unprecedented.^[16] These compounds offer therefore the unique opportunity to test the exciton chirality method used earlier for assigning the absolute configurations of chiral CTBs.^[6c,17] The latter indeed often show bisignate ECD bands in the 230–260 nm and 260–310 nm ran-

ges, which result from exciton coupling between the B_{1u} and B_{2u} transition dipole moments of the three aryl chromophores, respectively ($\pi \rightarrow \pi^*$ transitions). When the γ and γ' carbon atoms carry substituents with different *SM*, the B_{2u} transition dipole moments are rotated from their basic position parallel to the CTB axis by an angle, the value of which defines the sequence of signs of the related couplet. A band with two weak $\Delta\epsilon$ maxima (resp. minima) corresponding to those of the electronic absorption spectra can be seen in the B_{2u} regions of (+)-**1** (resp. (–)-**1**). Clearly, no stereochemical information can be obtained from this B_{2u} pattern.^[18] Interestingly however, it was recognized that the bisignate sequence of the B_{1u} transition couplet, usually in the 230–260 nm range, could be considered as a fingerprint (or invariant)^[19] of the chirality sense within a given family of cryptophane^[6g] and hemicyptophane^[20] derivatives for which the B_{2u} and B_{1u} transitions were equally affected. This was, for example, typically the case for (–)-cyclotriarylsilene (CTA) and (–)-cyclotriphenylene (CTP). Both carry oxygen atoms at the γ carbon atoms and show a negative-positive couplet from short to long wavelength in the B_{1u} region,^[6c] a characteristic feature of the *P* configuration. The ECD spectrum of (–)-**1** in the B_{1u} region shows the same sequence as the ECD spectrum of (–)-CTA, albeit with a larger $\Delta\epsilon$ maximum value (100 $\text{M}^{-1} \text{ cm}^{-1}$).

The ECD spectrum of (*M*)-**1** in CH_2Cl_2 , obtained by TD-DFT computation at the CAM-B3LYP-D3 level of theory using the 6-311+G(d,p) basis set, is represented in Figure S8. The calculated pattern is positive-negative bisignate from high to low energy. Considering a 10–15 nm hypsochromic offset, the theoretical spectrum of (*M*)-**1** matches well with the experimental spectrum of (+)-**1** (Figure 4b). The $[\alpha]_D^{25}$ values obtained by TD-DFT calculations (Table 2) also support this assignment. Therefore,

Table 2. Optical rotations $[\alpha]_\lambda^{25}$ of the compounds of this study in CH_2Cl_2 at various wavelengths (λ , nm).

Compound	$c^{[a]}$	$[\alpha]_\lambda^{25}$				
		589	578	546	436	365
(+)- 1	0.027	+526	+552	+615	+1144	+2026
(–)- 1	0.026	–523	–550	–612	–1112	–1996
(<i>M</i>)-(+)- 1 ^[b]	–	+618	+646	+739	+1303	+2156
$[\text{Pd}_3(\text{dppp})_3((+)\text{-1})_2]^{6+}$	0.197	+193	+205	+239	+498	–
$[\text{Pd}_3(\text{dppp})_3((+)\text{-1})_2]^{6+}$	0.135	–216	–227	–265	–559	–
$[\text{Pt}_3(\text{dppp})_3((+)\text{-1})_2]^{6+}$	0.224	+208	+217	+253	+502	+996
$[\text{Pt}_3(\text{dppp})_3((+)\text{-1})_2]^{6+}$	0.228	–208	–218	–255	–504	–1001

[a] g/100 cm^3 . [b] Obtained by TD-DFT calculations at the CAM-B3LYP-D3 level of theory, using the 6-311+G(d,p) basis set on the (*M*) enantiomer.

in spite of the fact that their substituents have opposite spectroscopic moments (-19 and $31 \text{ cm}^{-1/2} \text{ M}^{-1/2}$ for CN and OMe, respectively), $(-)$ -CTA and $(-)$ -**1** have the same absolute configuration, i.e. *P*. This situation is not unique, as inversion of the B_{1u} CD couplet by comparison with the expected sequence has been observed previously, in particular in the case of bromine ($SM = 4 \text{ cm}^{-1/2} \text{ M}^{-1/2}$) which has a much stronger effect on the B_{1u} than the B_{2u} transition.^[21]

Chiroptical Properties of the Palladocryptophanes Based on (+)-**1** and (–)-**1**

$[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ (resp. $[\text{Pd}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$) was prepared by reaction of $(+)\text{-}\mathbf{1}$ (resp. $(-)\text{-}\mathbf{1}$) with $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ in 2:3 ratio in CH_2Cl_2 . The $[\alpha]_D^{25}$ values (CH_2Cl_2 , $c = 0.197$ and 0.135) were $+193$ and -216 for $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pd}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$, respectively. The electronic absorption and ECD spectra of the enantiomers in CH_2Cl_2 are superposed in Figure 5a and Figure 5b, respectively. As they were recorded at concentrations of $9.4 \times 10^{-5} \text{ M}$ and $7.9 \times 10^{-5} \text{ M}$, respectively, these spectra correspond to species that are slightly dissociated (20 % for $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ and ca. 30 % for $[\text{Pd}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$, see Figure S9). The ECD spectra show mirror-image traces. For example $>80\%$ pure $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ shows a positive-negative couplet with a maximum at 239 nm ($\Delta\epsilon = 227 \text{ M}^{-1} \text{ cm}^{-1}$) and a minimum at 259 nm ($\Delta\epsilon = -39 \text{ M}^{-1} \text{ cm}^{-1}$) followed by a maximum at 288 nm ($\Delta\epsilon = 32 \text{ M}^{-1} \text{ cm}^{-1}$) and very weak features around 347 nm ($\Delta\epsilon = +6 \text{ M}^{-1} \text{ cm}^{-1}$). The kinetics of enantiomerization of $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ in CHCl_3 was studied by monitoring the decrease of $[\alpha]_D^{25}$. In these conditions, the enantiomerization rate constant is $k_{\text{enanti}} = 3.75 \times 10^{-6} \text{ s}^{-1}$ ($t_{1/2} = 25.7$ hours) and the associated activation barrier at 55°C is $\Delta G^\ddagger = 27.45 \text{ kcal mol}^{-1}$ (Figure S10).

Chiroptical Properties of the Platinocryptophanes Based on (+)-**1** and (–)-**1**

$[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ (resp. $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$) was prepared by reaction of $(+)\text{-}\mathbf{1}$ (resp. $(-)\text{-}\mathbf{1}$) with $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ in 2:3 ratio in CH_2Cl_2 . The $[\alpha]_D^{25}$ values (CH_2Cl_2 , $c = 0.224$ and 0.228) were $+208$ and -208 for $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$, respectively. The electronic absorption spectra of the enantiomers of the platinocryptophanes are shown in Figure 5c and their ECD spectra in Figure 5d. These spectra were recorded at concentrations of 1.02×10^{-4} and $1.03 \times 10^{-4} \text{ M}$, respectively. Therefore, they correspond to species that are very weakly dissociated (10 % for $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ and ca. 0 % for $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$, see Figure S11). The latter are mirror-images of each other. As an example, $>90\%$ pure $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ shows only positive differential absorption with maxima at 244 nm ($\Delta\epsilon = 134 \text{ M}^{-1} \text{ cm}^{-1}$) and 263 nm ($\Delta\epsilon = 128 \text{ M}^{-1} \text{ cm}^{-1}$), and a shoulder at 295 nm ($\Delta\epsilon = 19 \text{ M}^{-1} \text{ cm}^{-1}$). The enantiomerization kinetics of $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ was also studied in CHCl_3 at 55°C , but by monitoring the rotatory power at 365 nm . The enantiomerization rate constant was $k_{\text{enanti}} = 1.96 \times 10^{-6} \text{ s}^{-1}$ ($t_{1/2} = 49$ hours), the corresponding enantiomerization barrier being $\Delta G^\ddagger = 27.87 \text{ kcal mol}^{-1}$ at 55°C (Figure S12).

To sum up, the enantiomerization barriers of $(+)\text{-}\mathbf{1}$ and of the corresponding palladium and platinum complexes $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2]^{6+}$ and $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2]^{6+}$ range from $26.65 \text{ kcal mol}^{-1}$ at 40°C to $27.87 \text{ kcal mol}^{-1}$ at 55°C , which is in keeping with the average magnitude of the enantiomerization barriers of CTBs.^[2a,14] Moreover, the relative difference between the enantiomerization barriers $\Delta G^\ddagger$ of the palladium and platinum cryptophanes is only 1.5 %. This indicates that, within experimental error, the $\Delta G^\ddagger$ values of the metallocryptophanes do not depend on the nature of the metal. This suggests that the enantiomerization rates are not controlled by the lability of the metal-nitrogen bonds, but reflect the stereochemical stability

Figure 5. (a) Electronic absorption and (b) ECD spectra of the optically active metallocryptophanes $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ (green curves) and $[\text{Pd}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$ (red, dotted curves). (c) Electronic absorption and (d) ECD spectra of the optically active metallocryptophanes $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$ (green curves) and $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$ (red, dotted curves). All solutions in CH_2Cl_2 at 25°C .

of the CTB component. As a consequence, these experiments allowed us to set a maximum value for the energy necessary to break Pt–N(carbonitrile) bonds to ca. 27 kcal mol^{−1}.

TD-DFT Computations of the Electronic and ECD Spectra of [Pd₃(dppp)₃((P)-1)₂]⁶⁺ and [Pt₃(dppp)₃((P)-1)₂]⁶⁺

The experimental CD spectra of covalent cryptophanes could be analyzed, in the regions corresponding to the two forbidden transitions of the benzene ring, B_{1u} (230–260 nm) and B_{2u} (275–300 nm), by application of the Kuhn–Kirkwood exciton mechanism to the coupling of six equivalent oscillators in the D₃ molecular point group.^[17b,17c] At the zero-order, the B_{1u} and B_{2u} transitions are each split into three components, one A₂ along the C₃ symmetry axis and two non-degenerate E in the plane normal to this axis, the number and signs of Cotton effects being determined by the energy differences between those components. This generally results into a conservative bisignate couplet for B_{1u} and a variable sequence of a maximum of three bands for B_{2u}. For example, in dioxane, the ECD of (+)-cryptophane-A shows a negative-positive sequence of Cotton effects at 238.5 and 252.0 nm (B_{1u} region), and two positive Cotton effects at 277.5 and 299.0 nm (B_{2u} region). Whereas the ECD spectrum of [Pd₃(dppp)₃((-)-1)₂]⁶⁺ shows the expected bisigned couplet in the B_{1u} region, this is not the case of the platinum analogue, for which a strong negative band at 263 nm presumably hides the low-energy component of the B_{1u} couplet.

In order to get a deeper insight into the ECD spectra of the metallocryptophanes, TD-DFT computations were performed at the CAM-B3LYP-D3 level of theory. Figure 6 compares the calculated electronic absorption spectra and ECD profiles of [Pd₃(dppp)₃((-)-1)₂]⁶⁺ and [Pt₃(dppp)₃((-)-1)₂]⁶⁺ at λ > 200 nm in vacuo. The former shows a strong absorption at 227 nm and shoulders at 266 and ca. 338 nm. Its ECD spectrum consists of a negative-positive exciton couplet from short to long wavelength in the B_{1u} region of CTB **1**, with a minimum at 222 nm, inversion at 250 nm, and a maximum at 262 nm. By contrast, the calculated electronic absorption spectrum of the platinum cryptophane shows a single broad band at 232 nm and a negative ECD band in the same region, with a single minimum at 249 nm. These calculations account reasonably well for the differences of the experimental electronic absorption and ECD profiles of the palladium and the platinum metallocryptophanes shown in Figure 5a–d. At first glance, these latter differences were surprising, because the chirogenic subunits, i.e. the CTB caps **1**, are the same in both cryptophanes, which differ only by the nature of the bridging metal cations. Therefore, we focused our interest into the models [M(dppp)(PhCN)₂]²⁺ (M = Pd or Pt) of the bridging metal complex fragments of the metallocryptophanes.

The calculated electronic absorption spectrum of [Pd(dppp)(PhCN)₂]²⁺ shows sequences of absorption in three regions with a maximum at 235 nm and two broad shoulders at 250–270 and 335 nm, whereas the calculated electronic absorption spectrum of the corresponding platinum complex shows a broad absorption at 235 nm and a shoulder at 282 nm (Figures S13–S14). The higher energy absorption regions ex-

Figure 6. Calculated (a) electronic absorption and (b) ECD spectra of [Pd₃(dppp)₃((P)-1)₂]⁶⁺ (blue lines) and [Pt₃(dppp)₃((P)-1)₂]⁶⁺ (red lines). Continuous, bold lines: variation of the oscillator strength *f* in (a) and rotational strength *R*_{rot} in (b); vertical lines are calculated according to the CAM-B3LYP-D3 functional. Compare with Figure 2b and Figure 2d (red, dotted lines).

cepted, these features reproduce well the differences observed in the experimental electronic absorption spectra of the Pd- and Pt-cryptophanes, respectively, indicating that they originate from transitions pertaining to the corresponding [M(dppp)(PhCN)₂]²⁺ chromophores. Interestingly, optimization of the geometrical structures of the Pd(II) and Pt(II) complexes showed that they converged towards chiral conformations (Figures S15–S16). Their computed ECD spectra (Figures S13–S14) show some discrepancies compared to the experimental ECD spectra of the corresponding metallocryptophanes (Figure 5b and Figure 5d), e.g. a positive Cotton effect at about 350 nm in spite of a negative one. In order to probe the origin of these differences, the three [Pd(dppp)(PhCN)₂]²⁺ cations were extracted from the optimized structure of the [Pd₃(dppp)₃((-)-1)₂]⁶⁺ cation, keeping the geometry frozen (except for hydrogen atoms used to saturate broken bonds) and ECD spectra were calculated. As shown in Figure S17, the sum of the ECD spectra of the three dications and (P)-**1** resembles now the spectrum of [Pd₃(dppp)₃((-)-1)₂]⁶⁺. As a consequence, the ECD profiles of the metallocryptophanes are dominated by transitions centered on the metal complex bridging fragments and are sensitive to the geometry of these units.

A list of electronic transitions involving natural transition orbitals^[22] and restricted to those contributing to the lowest energy excited states, because they are the most relevant for describing the differences between the pallado- and platinocryptophanes, is given in Table 3, together with the corresponding excitation energies and oscillator strengths. In the case of

Table 3. Calculated transitions involving metal orbitals, together with corresponding NTO qualitative character.

[Pd ₃ (dppp) ₃ (1) ₂] ⁶⁺				[Pt ₃ (dppp) ₃ (1) ₂] ⁶⁺			
NTO n°	λ [nm] ^[a]	f ^[b]	Transition ^[c]	λ [nm] ^[a]	f ^[b]	Transition ^[c]	
1	351.0	0.270	d _{z²} → d _{x²-y²}	290.2	0.105	d _{z²} → d _{x²-y²}	
2	293.6	0.007	d _{xz} + π(PPh) → d _{x²-y²}	253.3	0.165	ε(Pt) ^[d] + π(PPh) + π(CTB) → ε(Pt) ^[d] + π*(CTB)	
3	289.2	0.045	d _{yz} + π(2 PPh) → d _{x²-y²}	252.2	0.005	d _{xz} + π(PPh) → d _{x²-y²}	
4	285.2	0.023	d _{yz} + π(PPh) + π(PPh ₂) → d _{x²-y²}	251.0	0.030	ε(Pt) ^[d] + π(PPh) + π(PPh ₂) + π*(CTB) → ε(Pt) ^[d] + 2π*(CTB)	
5	281.7	0.206	d _{xy} + π(PPh) + π(PPh ₂) → d _{x²-y²}	249.9	0.035	ε(Pt) ^[d] + π(2 PPh) + π(CTB) → ε(Pt) ^[d] + 2π*(CTB)	
6	277.4	0.025	ε(Pd) ^[d] + π(PPh) + π(PPh ₂) → d _{x²-y²}	249.3	0.024	ε(Pt) ^[d] + π(2 PPh) + π(CTB) → ε(Pt) ^[d] + π*(CTB)	
7	272.2	0.273	ε(Pd) ^[d] + π(2 PPh ₂) → d _{x²-y²}	248.1	0.092	d _{xz} + π(2PPh) → d _{x²-y²}	
8	268.1	0.078	ε(Pd) ^[d] + π(2 PPh ₂) → d _{x²-y²}	245.9	0.008	d _{xz} + π(2 PPh) → d _{x²-y²} + π*(CTB) + π*(PPh)	
9	264.7	0.128	ε(Pd) ^[d] + π(2 PPh ₂) → d _{x²-y²}	245.5	0.015	ε(Pt) ^[d] + π(2 PPh) → d _{x²-y²} + π*(CTB) + π*(PPh)	
10	261.0	0.032	ε(Pd) ^[d] + π(PPh) + π(PPh ₂) → d _{x²-y²}	244.9	0.051	d _{xz} + π(2 PPh) → d _{x²-y²} + π*(2 PPh)	
11				242.3	0.096	d _{xy} + π(PPh) + π(2 PPh) → d _{x²-y²} + π*(2 PPh)	
12				241.9	0.025	ε(Pt) ^[d] + π(PPh) + π(2 PPh) → d _{x²-y²} + π*(2 PPh)	

[a] Excitation energies. [b] Oscillator strength. [c] Natural transition orbitals (see ref.^[22]). [d] Minor contribution.

[Pd₃(dppp)₃(-)-1)₂]⁶⁺, the weak lowest energy band of the experimental spectrum at 345 nm corresponds to the HOMO-LUMO d-d transition in the square planar ligand field, the band at 287 nm originates from a mixture of higher energy d-d and LMCT (dppp → d_{x²-y²}) transitions, while the band at 259 nm has mainly LMCT character. In the case of [Pt₃(dppp)₃(-)-1)₂]⁶⁺, d-d transitions are shifted to higher energy by comparison with the palladocryptophane, hence it is the lowest energy band observed at 295 nm that corresponds to the d_{z²} → d_{x²-y²} transition. The band with a maximum at 263 nm has very little d-d character. It results mainly from π → π* transitions from orbitals localized on two adjacent dppp and CTB phenyl groups to the LUMO of the latter. Pictorial representations of the natural transition orbitals relevant to this discussion are reproduced in Figure 7.

Figure 7. Plots of the natural transition orbitals. They correspond to transitions that involve the [M(dppp)(nitrile)₂]²⁺ metal complex fragments undergoing ICD. a) "particle" NTO1 (d_{x²-y²}). b) "hole" NTO1 (d_{z²}). c) "particle" NTO2 (CTB π*). d) "hole" NTO2 (PPh π and CTB π).

The ECD spectra of the metallocryptophanes are very different in nature from those of the optically active CTB precursors (+)-1 and (-)-1 of this study, and covalent cryptophanes.

Whereas the spectral features of the latter compounds directly result from the dissymmetry of the CTB chromophores and their mutual arrangement, respectively, those of the former show patterns that are a consequence of induced circular dichroism (ICD) effects.^[23] In the case of the metallocryptophanes, the dissymmetry of the homochiral CTB caps is transferred mechanically (by a twist) to the metal complex bridging fragments, imparting them with a chiral conformation, which is detected by ECD. Related effects have nevertheless been observed in the case of optically active covalent cryptophanes, the ECD spectra of which being shown to be very sensitive to encapsulated substrates, including solvent molecules,^[17b] as well as to the surroundings (i.e. bulk solvent,^[6f] counterions^[24]). Whereas the basic ECD patterns resulted mainly from the dissymmetry of the CTB chromophores, encapsulation-induced changes in the ECD spectra were ascribed to modifications of the conformations of the atom chains bridging the CTB caps.^[19,25] An important and early recognized dependence of the ECD on the conformation of the cryptophanes is the effect of the twist angle 2γ on the separation of the E levels. As it is much larger when 2γ = 0° (eclipsed conformation) than in the case of 2γ = 60° (staggered conformation), for which these levels appear as quasi-degenerate, the bisignate couplet of the B_{1u} transition has been considered as an ECD signature of the staggered conformation of covalent D₃ cryptophanes in solution.^[17b] This applies as well to the metallocryptophanes of this study, because the bisignate couplet is clearly observed in the B_{1u} region of the ECD spectra of the palladium enantiomers. It is interesting, in this respect, that a quasi-perfect staggered conformation had also been observed in the X-ray crystal structures of the metallocryptophanes (2γ = 57(3)° for both Pd and Pt).^[12c]

¹H NMR Spectroscopy of the Enantiomerically Pure Metallocryptophanes

In earlier experiments, the metallocryptophanes were formed from racemic CTB 1 (*rac*-1).^[12c] The assemblies were examined by ¹H NMR spectroscopy. In the case of platinum, the spectrum of the reaction mixture in dichloromethane showed two sets of signals in ca. 95:5 ratio, which were assigned to the diastereomeric forms of [Pt₃(dppp)₃(1)₂]⁶⁺, that is, the racemic form *anti*-

Figure 8. Stacked plot of the ^1H NMR spectra (600 MHz, CD_2Cl_2 , 300 K) of (a) $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2](\text{OTf})_6$, (b) $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2](\text{OTf})_6$, and (c) the platino-cryptophane synthesized from the racemic mixture of CTB $\mathbf{1}$ (*rac*- $\mathbf{1}$). Proton labels are shown in Scheme 1.

$[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$, and the *meso* form *syn*- $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$. Clearly, these forms do not exchange in dichloromethane at the chemical shift timescale. In our previous work,^[12c] we tentatively assigned the major diastereomer to the *anti*- $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$ on the basis of the X-ray crystal structure of $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$, which showed that the cryptophane had crystallized as a racemate. However, solution analysis could not allow us to distinguish between the diastereomers, because enantiotopic pairs of protons of the $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ complex precursor become diastereotopic both in the *anti*- and *syn*- $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$ assemblies. Figure 8 shows a stacked plot of the ^1H NMR spectra of $[\text{Pt}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2]^{6+}$, $[\text{Pt}_3(\text{dppp})_3((-)\text{-}\mathbf{1})_2]^{6+}$, and *rac*- $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$, altogether as their triflate salts. The spectra of the optically pure metallocryptophanes are identical with each other, which indicates that these complexes are diastereomerically pure, as only one set of signals can be identified. Moreover, these spectra are identical to the sub-spectrum corresponding to the major diastereomer in the spectrum of $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$. This result confirms without ambiguity that the major diastereomer obtained upon mixing $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ and *rac*- $\mathbf{1}$ in 3:2 ratio was indeed the racemic mixture of the chiral metallocryptophanes *anti*- $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$.

In turn, the case of palladium is less clear-cut. The ^1H NMR spectrum at 300 K of the product resulting from mixing $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ and *rac*- $\mathbf{1}$ in 3:2 ratio in CDCl_3 was very similar, in terms of resolution, to what was observed in the case of platinum. However only a single set of signals could be identified, attesting for the complete diastereoselectivity of the

molecular assembly at the ^1H chemical shift timescale. By contrast, the situation was very different in CD_2Cl_2 , as the same set of signals showed relatively broad shapes at the same temperature (Figure S18 and Figure 9a and Figure 9c). This attested to the occurrence of exchange phenomena at the same timescale. Cooling down the solution led to gradual sharpening of most of the signals (with a maximum at 250–260 K), with concomitant intensity decrease at the expense of a new set of signals, which corresponded to a major species below 210 K. These observations were interpreted in terms of the temperature-dependent interconversion of the *anti* and *syn* diastereomers of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$, the ratio changing from 100:0 to 37:63 as the temperature was lowered from 300 to 200 K. By contrast, the ^1H NMR spectrum of the optically active assembly $[\text{Pd}_3(\text{dppp})_3((+)\text{-}\mathbf{1})_2]^{6+}$ in CD_2Cl_2 at 300 K showed (Figure 9b and Figure 9d) sharpened signals (γ -H and a-H excepted) by comparison with the spectrum of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$, attesting that exchange phenomena were no longer possible. Cooling down the solution broadened mainly the signals of o,o'-H, $r_{\text{A,B}}$ -H and s-H of the dppp ancillary ligands, while those of γ -H and a-H of the CTB components sharpened. Within the temperature range examined only one species was present in solution. Most significantly, its signals corresponded to those of the species identified in the 300 K ^1H NMR spectrum of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$. This demonstrates that the self-assembly of $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ and *rac*- $\mathbf{1}$ in 3:2 ratio in CD_2Cl_2 also produces the chiral, *anti* form of the metallocryptophane, and that the species which builds up gradually as the temperature is lowered is the corresponding *meso*, *syn* diastereomer.

Figure 9. Stacked plots showing the evolution of the ^1H NMR spectra (600 MHz, CD_2Cl_2) of (a) and (c) $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$; (b) and (d) $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ upon lowering the temperature from 300 to 200 K. Proton labels are shown in Scheme 1.

In our 2016 study, we had recorded the high temperature evolution of the ^1H NMR spectra in $\text{C}_2\text{D}_2\text{Cl}_4$ of both complexes $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ (Figures S19 and S20).^[12c] We had observed the appearance of new, small intensity signals, in particular a singlet at 4.05 ppm. Noticeably, the signal was also detected in the room-temperature ^1H NMR spectrum of CTB *rac-1* in $\text{C}_2\text{D}_2\text{Cl}_4$ and its intensity gradually increased upon heating the sample up to 410 K (Figure S21). It is characteristic of the methylene protons of a saddle conformation, which are all equivalent because of a pseudo-rotation process.^[26] Besides a high field shifted doublet at 7.30 ppm, the signals in the aromatic region are partially obscured by those of the crown conformation. In the case of the metallocryptophanes, the intensity of the CH_2 signal started to increase when the sample temperature was 360 K for $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$, and 389 K for $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$. These observations attest to the increased lability of the palladium–nitrile bond by comparison with the platinum–nitrile bond. In addition, the released CTB **1** undergoing crown/saddle isomerization does not form a cryptophane and remains in solution where it is detected.

Investigations of Metallocryptophane Assembly by Mass Spectrometry

The pallado- and platinocryptophanes assembled from CTBs **1** and **2** had not been investigated by mass spectrometry so far.

Spectra of all four metallocryptophanes were acquired in this study by electrospray orthogonal time-of-flight (microTOF-Q) mass spectrometry in the positive mode. Samples were freshly prepared in chlorinated solvents ($\text{C}_2\text{H}_2\text{Cl}_4$ or CH_2Cl_2) at the concentrations used for recording the ^1H NMR spectra (ca. 10^{-3} M), as the molecular peaks were weaker at 10^{-4} M in the case of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$, for example. The spectra and isotopic simulations of the peak clusters can be found in the Supporting Information (Figures S22–S32). The data and peak assignments are collected in Table 4. In all four cases, the most intense signal arises from the $[\text{M}(\text{dppp})(\text{OTf})]^+$ cation, at $m/z = 667.00$ for $\text{M} = \text{Pd}$ and 756.07 for $\text{M} = \text{Pt}$. The $[\text{M}(\text{dppp})(\text{Cl})]^+$ cation at $m/z = 555.02$ ($\text{M} = \text{Pd}$) and 643.08 ($\text{M} = \text{Pt}$), possibly formed via capture of chloride from the solvent, is also noteworthy. Other fragments resulting from dissociation of the metal complex bridging subunits are $[\text{Pt}(\text{dppp})(\text{OH})]^+$ at $m/z = 624.12$ for the platinocryptophanes, and in the case of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$, $[\text{Pd}(\text{dppp})(\text{OH})(\text{H}_2\text{O})]^+$ ($m/z = 573.03$), the chlorido-bridged $[\text{Pd}_2(\text{dppp})(\text{Cl})_2(\text{OTf})]^+$ dimer ($m/z = 1256.99$) and the ion cluster $[\text{Pd}(\text{dppp})\text{Cl}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})]^+$ ($m/z = 680.94$), the latter showing the second most intense signal. The molecular peaks of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pd}_3(\text{dppp})_3(\mathbf{2})_2](\text{OTf})_6$ are relatively intense and correspond to a doubly-charged species at $m/z = 1421.61$ for the former and at 1512.16 for the latter.

With regard to the corresponding platinocryptophanes, the most intense molecular peaks are also the doubly-charged species. In addition, very weak singly-charged species can be ob-

Table 4. ESI mass spectrometry data of [Pd₃(dppp)₃(1)₂](OTf)₆ and [Pt₃(dppp)₃(1)₂](OTf)₆.

Palladocryptophanes			Platinocryptophanes		
Intensity ranking ^[a]	Measured <i>m/z</i> ^[b]	Assignment	Intensity ranking ^[a]	Measured <i>m/z</i> ^[b]	Assignment
1 (1)	667.00	[Pd(dppp)(OTf)] ⁺	1 (2)	756.07	[Pt(dppp)(OTf)] ⁺
2	680.94	[Pd(dppp)Cl ₂ (H ₂ O) ₄ (H ₃ O)] ⁺			
3 (6)	1421.61 (1512.16)	[Pd ₃ (dppp) ₃ (CTB) ₂ (OTf) ₄] ²⁺	3 (1)	1554.21 (1644.74)	[Pt ₃ (dppp) ₃ (CTB) ₂ (OTf) ₄] ²⁺
4 (2)	555.02	[Pd(dppp)(Cl)] ⁺	2 (3)	643.08	[Pt(dppp)(Cl)] ⁺
5 (5)	647.99 (1230.44)		5 (6)	633.60	
6	573.03	[Pd(dppp)(Cl)(H ₂ O)] ⁺	6 (4)	624.12	[Pt(dppp)(OH)] ⁺
7	1256.99	[Pd ₂ (dppp) ₂ (Cl) ₂ (OTf)] ⁺	7 (5)	1397.19	
8 (3)	1013.13 (1102.17)	[Pd ₂ (dppp) ₂ (CTB) ₂ (OTf) ₂] ²⁺	8 (9)	1102.20 (1192.23)	[Pt ₂ (dppp) ₂ (CTB) ₂ (OTf) ₂] ²⁺
9	2175.21	[Pd ₂ (dppp) ₂ (CTB) ₂ (OTf) ₃] ⁺	(8)	1415.16	
w (4)	898.42 (958.12)	[Pd ₃ (dppp) ₃ (CTB) ₂ (OTf) ₃] ³⁺	4 (7)	986.82 (1046.51)	[Pt ₃ (dppp) ₃ (CTB) ₂ (OTf) ₃] ³⁺
			w (w)	3258.36 (3436.43)	[Pt ₃ (dppp) ₃ (CTB) ₂ (OTf) ₃] ⁺

The number in parentheses gives [a] the ranking of the corresponding signal for the related [M₃(dppp)₃(2)₂](OTf)₆ cage, and [b] the mass of the associated fragment.

served at *m/z* = 3258.36 and 3436.43 in the case of [Pt₃(dppp)₃(1)₂](OTf)₆ and [Pt₃(dppp)₃(2)₂](OTf)₆, respectively. Also observed in all four cases are weak signals corresponding to metallocryptophane fragments, which display the composition [M₂(dppp)₂(CTB)₂(OTf)_{*n*}]^{(4-*n*)+} (M = Pd, Pt; CTB = **1** or **2**; *n* = 2 or 3). Noteworthy, no trace of singly-bridged CTB dimer was detected. This indicates that, at the concentrations used, the metallocryptophanes are in equilibrium with doubly-bridged CTB dimers, which result from the loss of only one [M(dppp)]²⁺ subunit.

Stereoselective and Chemoselective Self-Sorting in the Metallocryptophane Self-Assembly

To sum up, this study confirms our previous conjecture that the metallocryptophanes self-assembled stereoselectively, affording the chiral *anti*-forms (stereoselective self-assembly).^[12c] Assuming that the enthalpies of formation of the palladocryptophanes under thermodynamic control do not depend on the strain, but rely mainly on the strength of the Pd–N(nitrile) bond, the entropic term should be a determining factor. The reactivity in solution of racemic CTB **1** in the presence of [Pd(dppp)(OTf)₂] is reminiscent of the recently reported TFA-catalyzed condensation of the racemate of triaminotriphenylquinacene with a bis(salicylaldehyde), which led to the [2+3] imine homochiral cages with a maximal diastereoselective ratio of 86:14 in 1,4-dioxane.^[27] This outcome was analyzed in terms of the entropic advantage resulting from the excess of distinct chiral products (enantiomeric pair) by comparison with the achiral ones (*meso* form). Such an explanation holds true in our case as well. Indeed, let us consider the equilibrium between *syn*- and *anti*-[Pd₃(dppp)₃(1)₂](OTf)₆ shown in Equation (1). The corresponding equilibrium constants *K*_{sa} and *K*_{as} obey Equation (2) in which [*syn*] and [*anti*] stand for the relative concentrations of *syn*- and *anti*-[Pd₃(dppp)₃(1)₂](OTf)₆, respectively.

$$\ln(K_{\text{sa}}) = -\ln(K_{\text{as}}) = \ln([\text{anti}]/[\text{syn}]) = -\Delta H_{\text{sa}}/RT + \Delta S_{\text{sa}}/R \quad (2)$$

The values of *K*_{sa} at various temperatures could be determined by integration of three pairs of signals for better accuracy: α'-H (*syn*) and γ-H (*anti*), a-H (*syn* and *anti*), and e-H (*syn* and *anti*) (Figure S33). Three van't Hoff plots of ln ([*anti*]/[*syn*]) = f(1/*T*) were obtained, one for each pair of protons (Figure S34–S36). Linear regression analyses allowed us to obtain three corroborating values of Δ*H*_{sa} and Δ*S*_{sa}, which were averaged to Δ*H*_{sa} = 3.52(8) kcal mol^{−1} and Δ*S*_{sa} = 16.3(3) cal mol^{−1} K^{−1} for the conversion of *syn*- to *anti*-[Pd₃(dppp)₃(1)₂](OTf)₆. Therefore, whereas the formation of *anti*-[Pd₃(dppp)₃(1)₂](OTf)₆ is controlled above 215.3 K by entropy (positive variation) as expected (Δ*G*_{sa} = −1.3 kcal mol^{−1} at 298.15 K), the formation of *syn*-[Pd₃(dppp)₃(1)₂](OTf)₆ is controlled by enthalpy (negative variation for the reverse process) at temperatures below 215.3 K. The equilibrium constant of *anti*-[Pd₃(dppp)₃(1)₂](OTf)₆ in CH₂Cl₂ at 298.15 K is therefore *K*_{sa} = 1/*K*_{as} = exp(−Δ*G*_{sa}/*RT*) ≈ 10.

In our former study,^[12c] we had investigated by ¹H NMR spectroscopy in 1,1,2,2-tetrachloroethane (C₂D₂Cl₄) the assembly of the palladocryptophanes starting from an equimolecular racemic mixture of two different CTBs, *rac*-**1** and *rac*-**2**, the latter featuring methoxy substituents at the γ positions. Mixing [Pd(dppp)(OTf)₂], *rac*-**1** and *rac*-**2** in 3:2 ratio had afforded a 1:1 mixture of the palladocryptophanes of homogeneous CTB composition [Pd₃(dppp)₃(1)₂](OTf)₆ and [Pd₃(dppp)₃(2)₂](OTf)₆ (Figure S37). We repeated this experiment in the case of platinum, using the same CTBs and [Pt(dppp)(OTf)₂]. Dichloromethane was chosen as solvent, as this medium provided the best spectral resolution. A stacked plot of the spectra of [Pt₃(dppp)₃(1)₂](OTf)₆ and [Pt₃(dppp)₃(2)₂](OTf)₆ prepared individually in the same conditions, and the spectrum of the mixture resulting from the combination of [Pt(dppp)(OTf)₂], *rac*-**1** and *rac*-**2** in 3:2 ratio is displayed in Figure S38. It shows that the mixture contains mainly the homoleptic platinocryptophanes *anti*-[Pt₃(dppp)₃(1)₂](OTf)₆ and *anti*-[Pt₃(dppp)₃(2)₂](OTf)₆, the former being accompanied by minor amounts of the *syn* form, as usually observed in this solvent. Interestingly, additional signals of weak intensities could be assigned to the mixed CTB platinocryptophane, [Pt₃(dppp)₃(1)(2)](OTf)₆: a doublet for α-H(**1**), a doublet of doublets for γ-H(**1**), a singlet for

α' -H(**2**) and α -H(**2**), two doublets for a-H(**1**) and a-H(**2**), and a singlet for the Me(**2**) protons, respectively. In the ROESY spectrum of the mixture (Figure S39), a correlation between the singlet of the Me group and the singlet of α -H(**2**) confirms that these signals originate from protons of the CTB **2** incorporated into the heteroleptic platinocryptophane. In addition, there is a weak inter-component correlation between the protons of the OMe(**2**) substituent of CTB **2** and the γ -H(**1**) proton of CTB **1**. Integration of the signals of the γ protons (6 H) of *anti*-[Pt₃(dppp)₃(**1**)₂]⁶⁺, α' protons (6 H) of *syn*-[Pt₃(dppp)₃(**1**)₂]⁶⁺, α protons (6 H) of [Pt₃(dppp)₃(**2**)₂]⁶⁺, and γ -H(**1**) protons (3 H) of [Pt₃(dppp)₃(**1**)(**2**)]⁶⁺, shows that the distribution of the platinocryptophanes is ca. 37, 43, and 20 %, respectively. Therefore, the ratios of the homoleptic platinocryptophanes vs. the heteroleptic assembly also departs from the statistical one, i.e. 25:25:50. A VT experiment was performed in C₂D₂Cl₄, in which *syn*-[Pt₃(dppp)₃(**1**)₂]⁶⁺ is not formed.^[12c] At 298 K the distribution of the platinocryptophanes is 40, 52, and 8 % for [Pt₃(dppp)₃(**1**)₂]⁶⁺, [Pt₃(dppp)₃(**1**)₂]⁶⁺, and [Pt₃(dppp)₃(**1**)(**2**)]⁶⁺, respectively. Heating to 338 K switches this distribution to 37, 47, and 16 %, in favor of the heteroleptic system. The initial distribution between the platinocryptophanes is recovered upon cooling the reaction mixture to 298 K, which indicates that the three components are in thermodynamic equilibrium, as indicated by Equation (3). The variation of the formation constant (K_{scr}) of the heteroleptic metallocryptophane [Pt₃(dppp)₃(**1**)(**2**)](OTf)₆ with the temperature [Equation (4)] was calculated by measuring the relative integrations of the following protons (Figures S40–S42): γ -H, α -H, α 2-H and γ 1-H for [Pt₃(dppp)₃(**1**)₂](OTf)₆, [Pt₃(dppp)₃(**2**)₂](OTf)₆, and [Pt₃(dppp)₃(**1**)(**2**)](OTf)₆, respectively. A linear regression analysis gives $\Delta H_{scr} = 8.9(0.6)$ kcal mol⁻¹ and $\Delta S_{scr} = 23(2)$ cal mol⁻¹ K⁻¹, which implies that the formation of the heteroleptic metallocryptophane would be favored at temperatures above 387 K (114 °C).

$$\ln(K_{scr}) = \ln \frac{[\text{Pt}_3(\text{dppp})_3(\mathbf{1})(\mathbf{2})](\text{OTf})_6^2}{[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6 [\text{Pt}_3(\text{dppp})_3(\mathbf{2})_2](\text{OTf})_6} = -\Delta H_{scr}/RT + \Delta S_{scr}/R \quad (4)$$

The reaction of a mixture of [M(dppp)(OTf)₂] (M = Pd or Pt) and the CTBs **1** and **2** in 3:1:1 ratios was finally investigated by positive ESI mass spectrometry. The results are illustrated in Figure 10 and Figures S43–S44. In the case of M = Pd, the most intense signals are still those of the complex species deriving from [Pd(dppp)]²⁺, including [Pd(dppp)(OTf)]⁺ and [Pd(dppp)(Cl)]⁺. They are followed by the signals at $m/z = 1421.63$ and 1512.16 of the doubly-charged ions [Pd₃(dppp)₃(**1**)₂(OTf)₄]²⁺ and [Pd₃(dppp)₃(**2**)₂(OTf)₄]²⁺, which correspond to the genuine homoleptic metallocryptophanes. Much weaker signals at 1466.65 and 928.11 can be attributed to the doubly- and triply-charged ions [Pd₃(dppp)₃(**1**)(**2**)(OTf)₄]²⁺ and [Pd₃(dppp)₃(**1**)(**2**)(OTf)₃]³⁺ of the genuine heteroleptic metallocryptophane. These observations show that the homoleptic metallocryptophanes are formed predominantly over the heteroleptic ones, which is in agreement

with the ¹H NMR spectroscopy experiments. Switching the in-source collision induced dissociation (ISCID) energy from 0 to 10 eV did not change these conclusions, except that [Pd₃(dppp)₃(**1**)₂](OTf)₆ showed up only as the dinuclear metallo-cryptophane fragment [Pd₂(dppp)₂(**1**)₂(OTf)_n]⁽⁴⁻ⁿ⁾⁺. Interestingly, in the case of M = Pt (dichloromethane and 10 eV ISCID energy), the results were significantly different from those obtained in the palladium series (Figure 10). Whereas the most intense signals of the platinocryptophanes at $m/z = 1554.71$ and 1644.74 remained those of the doubly-charged ions of the homoleptic systems [Pt₃(dppp)₃(**1**)₂](OTf)₆ and [Pt₃(dppp)₃(**2**)₂](OTf)₆, respectively, the relative intensity of the signal at $m/z = 1599.72$ corresponding to the doubly-charged ion of the heteroleptic platinocryptophane [Pt₃(dppp)₃(**1**)(**2**)](OTf)₆ was much higher in intensity than its palladium analogue. Although the overall sensitivity of the response of platinocryptophanes was higher than that of palladocryptophanes, this result suggests that the heteroleptic systems are formed in the highest proportion in the latter case.

Self-Sorting

The present study now allows us to confirm that the hypothesis of homochiral self-sorting^[28] we had put forward is actually correct. The complexes [M₃(dppp)₃(**1**)₂]⁶⁺ and [M₃(dppp)₃(**2**)₂]⁶⁺ (M = Pd and Pt) characterized in the NMR experiments are indeed both in the chiral, *anti* configuration. Actually, a total of 10 distinct species would have been expected upon mixing (*P*)-**1**, (*M*)-**1**, (*P*)-**2**, and (*M*)-**2** with [M(dppp)(OTf)₂]: In addition to the two *D*₃-homochiral pairs of enantiomers of *anti*-[M₃(dppp)₃(**1**)₂]⁶⁺ and *anti*-[M₃(dppp)₃(**2**)₂]⁶⁺ observed, other possible palladocryptophanes would be the C_{3h}-heterochiral *syn*-[M₃(dppp)₃(**1**)₂]⁶⁺ and *syn*-[M₃(dppp)₃(**2**)₂]⁶⁺, the C₃-pseudo-homochiral pair of *anti*-[M₃(dppp)₃(**1**)(**2**)]⁶⁺, and the C₃-pseudo-heterochiral pair of *syn*-[M₃(dppp)₃(**1**)(**2**)]⁶⁺ (Table 5 and Figure S45). The degree of self-sorting has been defined as $M = p_0/p$, the ratio between the population p_0 of all the theoretically possible distinct metallocryptophanes and the population p of those experimentally observed.^[29] In the case of the palladocryptophanes, $M = 10/4 = 2.5$. In the case of the platinocryptophanes, assuming that only *anti*-[Pt₃(dppp)₃(**1**)(**2**)]⁶⁺ is observed in addition to *anti*-[Pt₃(dppp)₃(**1**)₂]⁶⁺ and *anti*-[Pt₃(dppp)₃(**2**)₂]⁶⁺, $M = 10/6 = 1.67$.

So far, we only examined the entropy increase in the eyes of the maximization of the number of distinguishable reaction products. A positive entropy variation can also be a consequence of the increased symmetry of the products, because of the lower number of differing orientations which can be obtained by rotations (ΔS_{rot}).^[30] Theoretically, on the basis of the symmetry numbers^[31] collected in Table 5, the two enantiomeric pairs of *anti*-[M₃(dppp)₃(**1**)₂]⁶⁺ and *anti*-[M₃(dppp)₃(**2**)₂]⁶⁺, as well as *syn*-[M₃(dppp)₃(**1**)₂]⁶⁺ and *syn*-[M₃(dppp)₃(**2**)₂]⁶⁺ should be equally favored, but the pairs of *anti*-[M₃(dppp)₃(**1**)(**2**)]⁶⁺ and *syn*-[M₃(dppp)₃(**1**)(**2**)]⁶⁺, which have lower symmetry numbers should be disfavored by comparison with the former.

Another factor is ligand preorganization. Of structural nature, it makes variations of entropy of complexation, due to the re-

Figure 10. Positive ESI mass spectrum of the mixture resulting from combining $[\text{Pd}(\text{dppp})(\text{OTf})_2]$, CTB **1** and CTB **2** in 3:1:1 ratio in dichloromethane.

Table 5. Symmetry numbers (σ)^[a] of all the possible palladocryptophanes.

Palladocryptophane	Configuration ^[b]	Point group	σ
$[\text{Pd}_3(\text{dppp})_3(\text{M-1})_2]^{6+}$	<i>anti</i>	D_3	6
$[\text{Pd}_3(\text{dppp})_3(\text{P-1})_2]^{6+}$	<i>anti</i>	D_3	6
$[\text{Pd}_3(\text{dppp})_3(\text{M-2})_2]^{6+}$	<i>anti</i>	D_3	6
$[\text{Pd}_3(\text{dppp})_3(\text{P-2})_2]^{6+}$	<i>anti</i>	D_3	6
$[\text{Pd}_3(\text{dppp})_3(\text{M-1})(\text{P-1})]^{6+}$	<i>syn</i>	C_{3h}	6
$[\text{Pd}_3(\text{dppp})_3(\text{M-2})(\text{P-2})]^{6+}$	<i>syn</i>	C_{3h}	6
$[\text{Pd}_3(\text{dppp})_3(\text{M-1})(\text{P-2})]^{6+}$	<i>anti</i>	C_3	3
$[\text{Pd}_3(\text{dppp})_3(\text{P-1})(\text{M-2})]^{6+}$	<i>anti</i>	C_3	3
$[\text{Pd}_3(\text{dppp})_3(\text{M-1})(\text{M-2})]^{6+}$	<i>syn</i>	C_3	3
$[\text{Pd}_3(\text{dppp})_3(\text{P-1})(\text{P-2})]^{6+}$	<i>syn</i>	C_3	3

[a] Calculated according to ref.^[30b] [b] Note that, due to the priority rules in the Cahn-Ingold-Prelog system, *M-1* and *P-2* (resp. *P-1* and *M-2*) are pseudo-homomers, whereas *M-1* and *M-2* (resp. *P-1* and *P-2*) are pseudo-enantiomers.

striction of the degrees of freedom of the ligands, less positive, hence less unfavorable if their conformation does not change significantly upon complexation. Relying on the geometrical parameters obtained from the X-ray crystal structures of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$,^[12c] we believe

that preorganization is involved to a significant extent in the formation of both homoleptic and heteroleptic metallocryptophanes.

In the light of these considerations, whereas the *anti*-metallocryptophanes are clearly favored over the *syn*-metallocryptophanes [Equation (1)] by a higher number of distinct stereoisomers, the fact that the spontaneous formation of $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})(\mathbf{2})]^{6+}$ at the expense of $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$ and $[\text{Pt}_3(\text{dppp})_3(\mathbf{2})_2]^{6+}$ [Equation (3)] is under entropic control above 387 K in $\text{C}_2\text{D}_2\text{Cl}_4$ must find other explanations. Until now we have neglected solvent effects, as the factors we have invoked hold true primarily in the gas phase. A possible explanation in the context of solvent effects could be a less structured solvation sphere around the heteroleptic metallocryptophane by comparison with the homoleptic systems.

The stereochemical outcome of the assembly of $[\text{Pd}_3(\text{dppp})_3(\text{CTB})_2]^{6+}$ and $[\text{Pt}_3(\text{dppp})_3(\text{CTB})_2]^{6+}$ (CTB = *rac-1* or *rac-2*) is very similar to the most recent observations of Hardie and co-workers, who used CTBs carrying 4-pyridyl metal binding units connected via carbonyl or methylene bridges to the

CTG scaffold, in conjunction with either achiral $[\text{Pd}(\text{dppp})]^{2+}$ ^[12d] or chiral $[\text{Ir}(\text{ppy})_2(\text{MeCN})_2]^+$ ^[12e] as metal complex bridging fragments. Particular to the latter case, chiral self-sorting within the metallocryptophanes concerned both CTB ligands and $[\text{Ir}(\text{ppy})_2]^+$ bridges, a feature that was ascertained by the use of enantiomerically pure components.

In this context, it is relevant to note that all of these results are in contrast with the self-discrimination between heterochiral CTBs^[8,12b] or subphthalocyanine^[32] CTB analogues functionalized with 4-pyridyl ligands. Moreover, Lützen et al. showed that rigid bridging ligands based on 2,8-difunctionalized chiral Tröger's base formed $[\text{M}_2\text{L}_2]^{4+}$ rhomboidal complexes diastereoselectively also in the achiral *meso* C_{2h} -symmetric form, whatever the nature of the coordinating groups (nitrile^[33a] or pyridine^[33b]). An explanation of the preference for homochiral assemblies was raised in a recent review in which different models were developed for the analysis of dimers made from chiral components.^[34] In particular, the "corner model" applies to structures in which the corners are occupied by the assembling metal cations. The metallocryptophanes $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$ and $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2]^{6+}$ are more compact than those constructed from CTBs carrying pyridyl ligand subunits. Therefore, their stereochemistry is best explained by the repulsive-corner model in which homochirality is a means to avoid unfavorable steric interactions between the ancillary ligands. The heterochirality of the larger and less crowded metallocryptophanes is rationalized by the attractive-corner model.

Conclusions

Optically active covalent cryptophanes have been extensively documented for decades, which is far to be the case of those obtained by self-assembly, whatever the approach used. The present work concerned the study of the chiroptical properties of metallocryptophanes, that is, cryptophanes that are assembled using metal complex fragments as connectors between the two homochiral CTB components.

This study has allowed us (i) to demonstrate in conclusive manner that the self-assembly process was highly stereoselective, leading to the chiral, *anti* form of the metallocryptophanes; and (ii) to delineate the peculiarities of metallocryptophanes with reference to their covalent analogues. As far as the second point is concerned, metallocryptophanes are endowed with dynamic properties, the degree of which depends upon the lability of the coordination bonds involved in the assembly. A direct consequence of this is their propensity to enantiomerize. Notably, the process is controlled by the rate of enantiomerization of the CTB component, not its rate of exchange at the metal cation, the latter being faster than the former. Remarkable chiroptical properties of the metallocryptophanes are the observed ICD effects from the optically-active CTB component to the achiral bridging metal complex fragments. Evidence for these ICDs have been obtained by TD-DFT calculations at the CAM-B3LYP-D3 level of theory. They demonstrated, in particular, that the ICD affected the d–d transitions of the metal assemblers in the square planar ligand field.

In the work preceding this study, we had employed racemic CTBs for the self-assembly of the metallocryptophanes. On the basis of the comparison of the solution ^1H NMR spectra of the pallado- and platinocryptophanes, and the analysis of their XRD structures, we had theorized that the multi-component reactions were stereoselective, leading to the preferential (Pt) or exclusive (Pd) formation of the chiral, *anti* forms of the metallocages. Working in the optically active series allowed us to rule out the formation of the *meso*, *syn* form of the metallocryptophanes, and to confirm our initial hypothesis. It is interesting to put this work in the more general context of the problem of self-sorting, as expressed by Wu and Isaacs.^[28b] As observed in many other cases, the stereoselectivity of the self-assembly of metallocryptophanes using the palladium or platinum nitrile bond is likely controlled by entropy rather than enthalpy, by selecting the family of stereoisomers containing the highest number of distinct species.

Experimental Section

General information. CTB $\mathbf{1}$,^[12c] $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ ^[35] and $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ ^[35] were prepared according to literature procedures. $\text{C}_2\text{D}_2\text{Cl}_4$ and CD_2Cl_2 were used as received. CH_2Cl_2 was distilled from CaH_2 prior to use in dilution experiments. ^1H NMR experiments were performed using a Bruker Avance II 600 MHz spectrometer and a Bruker Avance III 400 MHz spectrometer.

Dilution experiments. UV/Visible spectra were measured either with an Agilent 8453E single beam spectrophotometer at the millimolar concentration level using a 5 mm quartz cuvette equipped with a 4.9 mm quartz wedge from Thuet B France, or with a Cary 5000 double beam spectrophotometer from Agilent Technologies at lower concentrations using 1, 2, or 10 mm quartz cuvettes. The mother solutions of $[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ and $[\text{Pt}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$ were prepared as follows. For the ca. 10^{-3} M solutions, $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (2.98 mg, 3.65×10^{-6} mol) and CTB $\mathbf{1}$ (0.83 mg, 2.40×10^{-6} mol) were mixed in CH_2Cl_2 (0.66 mL). After stirring, the solution was diluted to 1 mL in a calibrated vial to obtain a final concentration of 1.22×10^{-3} M. $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ (2.77 mg, 3.06×10^{-6} mol) and CTB $\mathbf{1}$ (0.70 mg, 2.04×10^{-6} mol) were mixed in CH_2Cl_2 (0.66 mL). After stirring, the solution was diluted to 1 mL in a calibrated vial to obtain a final concentration of 1.02×10^{-3} M. For the ca. 10^{-4} M and more dilute solutions, $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (3.81 mg, 4.66×10^{-6} mol) and CTB $\mathbf{1}$ (1.07 mg, 3.10×10^{-6} mol) were mixed in CH_2Cl_2 (0.69 mL). After 4 h, the solution was transferred into a 5 mL volumetric flask to make a 3.11×10^{-4} M stock solution. $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ (4.21 mg, 4.65×10^{-6} mol) and CTB $\mathbf{1}$ (1.08 mg, 3.13×10^{-6} mol) were mixed in CH_2Cl_2 (0.69 mL). After 4 h, the solution was transferred into a 5 mL volumetric flask to make a 3.10×10^{-4} M stock solution, which was used for the dilution studies.

Mass spectrometry experiments.

$[\text{Pd}_3(\text{dppp})_3(\mathbf{1})_2](\text{OTf})_6$. A slurry of $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (3.05 mg, 3.73×10^{-6} mol) in the minimum of $\text{C}_2\text{D}_2\text{Cl}_4$ was added to a stirred suspension of CTB $\mathbf{1}$ (0.86 mg, 2.49×10^{-6} mol), in $\text{C}_2\text{D}_2\text{Cl}_4$ in a vial. The mixture gradually clarified with a final concentration of 1.88×10^{-3} M (0.66 mL).

$[\text{Pd}_3(\text{dppp})_3(\mathbf{2})_2](\text{OTf})_6$. A slurry of $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (1.85 mg, 2.26×10^{-6} mol) in the minimum of $\text{C}_2\text{D}_2\text{Cl}_4$ was added to a stirred suspension of CTB $\mathbf{2}$ (0.65 mg, 1.49×10^{-6} mol), in $\text{C}_2\text{D}_2\text{Cl}_4$ in a vial.

The mixture gradually clarified with a final concentration of 1.35×10^{-3} M (0.56 mL).

[Pt₃(dppp)₃(1)₂](OTf)₆. A slurry of [Pt(dppp)(OTf)₂] (3.27 mg, 3.61×10^{-6} mol) in the minimum of CD₂Cl₂ was added to a stirred suspension of CTB **1** (0.81 mg, 2.35×10^{-6} mol), in CD₂Cl₂ in a vial. The mixture gradually clarified with a final concentration of 1.82×10^{-3} M (0.66 mL).

[Pt₃(dppp)₃(2)₂](OTf)₆. A slurry of [Pt(dppp)(OTf)₂] (3.24 mg, 3.58×10^{-6} mol) in the minimum of CD₂Cl₂ was added to a stirred suspension of CTB **2** (1.04 mg, 2.39×10^{-6} mol), in CD₂Cl₂ in a vial. The mixture gradually clarified with a final concentration of 1.81×10^{-3} M (0.66 mL).

Electronic absorption spectra of the mixtures of [M(dppp)(OTf)₂] and CTB **1 in 3:2 ratio.** CTB **1** (1.02 mg, 2.95×10^{-6} mol) was dissolved in CH₂Cl₂ (100 mL). An aliquot of the solution was transferred into a 10 mm quartz cuvette, and its electronic absorption spectrum recorded. Similarly, [Pd(dppp)(OTf)₂] (3.65 mg, 4.47×10^{-6} mol) and [Pt(dppp)(OTf)₂] (4.00 mg, 4.42×10^{-6} mol) were dissolved separately in CH₂Cl₂ (100 mL each). Their electronic absorption spectra were recorded in the same conditions. The individual data sets were processed with the Microsoft Excel software to calculate the virtual spectra of non-interacting 3:2 mixtures by applying the formula $\{3 \epsilon_{\lambda}([M(dppp)(OTf)_2]) + 2 \epsilon_{\lambda}(\mathbf{1})\} = f(\lambda)$.

Resolution of CTB **1.** Chromatographic separation of both enantiomers was performed by HPLC using a (S,S)-Whelk-O1 column from Regis and Co. (250 × 10 mm) operating at room temperature, the hexane/dichloromethane, 30:70 v/v binary mixture as mobile phase, a 5 mL min⁻¹ flow-rate, and a UV detection at 220 nm. The optical purities were checked by analytical chiral HPLC. About 17 mg of compound **1** were dissolved in CH₂Cl₂ (63 mL). 210 injections of 300 μL were performed every 3.5 min. The first eluted fraction was collected between 5.7 and 6.2 min, and the second one between 6.5 and 6.9 min, affording 5.5 mg of (+)-**1** with ee > 97 % and 5.5 mg of (–)-**1** with ee > 97 %. The enantioenriched CTBs were stored at –18 °C prior to use.

Small scale formation of the optically active metallocryptophanes. Freshly prepared [M(dppp)(OTf)₂] (M = Pd or Pt) and (+)-**1** or (–)-**1** were mixed in 3:2 ratio in 0.66 mL CD₂Cl₂ at room temperature in a closed vial. The initial suspension turned into a pale yellow solution after several minutes, which was further stirred for at least 1 h. The solution was then transferred into a 5 mm NMR tube and checked by ¹H NMR spectroscopy. In the case of M = Pt, it was necessary to readjust the amount of [Pt(dppp)(OTf)₂], as ca. 18 % of (+)-**1** or (–)-**1** remained unreacted after 1 h. When quantitative complex formation was ascertained by ¹H NMR, the solvent was allowed to evaporate naturally, the solid residue was dried in vacuo at room temperature and stored at –18 °C before further measurements.

[Pd₃(dppp)₃(+)-1**]₂](OTf)₆.** 1.19×10^{-6} mol from [Pd(dppp)(OTf)₂] (2.92 mg, 3.57×10^{-6} mol) and CTB (+)-**1** (0.82 mg, 2.37×10^{-6} mol).

[Pd₃(dppp)₃(–)-1**]₂](OTf)₆.** 1.16×10^{-6} mol from [Pd(dppp)(OTf)₂] (2.84 mg, 3.57×10^{-6} mol) and CTB (–)-**1** (0.80 mg, 2.37×10^{-6} mol).

[Pt₃(dppp)₃(+)-1**]₂](OTf)₆.** 1.22×10^{-6} mol from [Pt(dppp)(OTf)₂] (3.31 mg, 3.65×10^{-6} mol) and CTB (+)-**1** (0.71 mg, 2.04×10^{-6} mol).

[Pt₃(dppp)₃(–)-1**]₂](OTf)₆.** 1.24×10^{-6} mol from [Pt(dppp)(OTf)₂] (3.37 mg, 3.72×10^{-6} mol) and CTB (–)-**1** (0.72 mg, 2.08×10^{-6} mol).

Electronic absorption spectroscopy, circular dichroism and polarimetry. ECD and UV/Vis spectra were measured on a JASCO J-

815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2 °C. A cell of 1 mm optical pathlength was used. The CD spectrometer was purged with dinitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing. Optical rotations $[\alpha] = 100 \alpha l^{-1} c^{-1}$, expressed in 10⁻¹ deg cm² g⁻¹ (l in dm and c in g/100 cm³), were measured at 25 °C on a 241 Perkin-Elmer polarimeter equipped with a double-jacketed 10 cm cell, a sodium (589 nm) and a mercury (578, 546, 436, and 365 nm) lamp.

Kinetics of enantiomerization.

CTB **1.** About 0.35 mg of an enantioenriched sample of (–)-**1** was heated in about 25 mL of CH₂Cl₂ at 40 °C. 10 μL were taken and then injected on an analytical (S,S)-Whelk-O1 column using heptane/dichloromethane, 30:70 as mobile phase, a 1 mL min⁻¹ flow-rate, and a UV detection at 240 nm.

[Pd₃(dppp)₃(+)-1**]₂](OTf)₆.** About 0.5 μmol of complex was heated in about 1 mL of CHCl₃ at 55 °C in the double-jacketed cell of the polarimeter while monitoring the decrease of the rotary power at 436 nm.

[Pt₃(dppp)₃(+)-1**]₂](OTf)₆.** The same procedure as for the Pd complex was applied, using about 0.152 μmol of the complex and a detection wavelength of 365 nm.

Self-sorting experiment of the pallado- and platinumcryptophanes.

Palladocryptophanes. A suspension of [Pd(dppp)(OTf)₂] (3.08 mg, 3.77×10^{-6} mol) in the minimum of C₂D₂Cl₄ was added to a stirred suspension of CTB **1** (0.42 mg, 1.22×10^{-6} mol) and CTB **2** (0.51 mg, 1.17×10^{-6} mol) in C₂D₂Cl₄ in a vial. The mixture gradually clarified to give a 1.90×10^{-3} M solution (0.66 mL). It was checked after 2 h by ¹H NMR spectroscopy prior to ESI-MS experiments.

Platinocryptophanes. A suspension of [Pt(dppp)(OTf)₂] (3.25 mg, 3.59×10^{-6} mol) in the minimum of CD₂Cl₂ was added to a stirred suspension of CTB **1** (0.41 mg, 1.19×10^{-6} mol) and CTB **2** (0.53 mg, 1.22×10^{-6} mol) in CD₂Cl₂ in a vial. The mixture gradually clarified to give a 1.81×10^{-3} M solution (0.66 mL). It was checked after 2 h by ¹H NMR spectroscopy prior to ESI-MS experiments.

Computations. Quantum chemistry calculations were performed at the Density Functional Theory level with the Gaussian09 software, Revision D.01.^[36] The CAM-B3LYP functional was used, together with Grimme's GD3 dispersion correction.^[37] Geometry optimization on the *M* enantiomer of CTB **1** was performed using the 6-311+G(d,p) basis set. Solvent (CH₂Cl₂) effects were taken into account through a PCM model. Frequency calculations were performed to check that the true energy minimum was obtained (no imaginary frequency). Time-dependent DFT calculations were then performed in order to compute the ECD spectra (144 excited states were solved and a 0.125 eV UV/Vis peak half-width at half height was used in GaussView to display the spectrum). Optical rotations were also calculated at the same level of theory (reported in Table 1) and allowed us to identify the absolute configuration of (+)-**1** as *M*.

Starting geometries of the [Pd₃(dppp)₃(–)-**1**]₂⁶⁺ and [Pt₃(dppp)₃(–)-**1**]₂⁶⁺ cations were taken from the corresponding experimentally determined X-ray crystal structures (absolute configuration of the CTB units is *P*). In a first step, the geometries of the isolated cations were optimized using the 6-31G(d,p) and Def2-SVP basis sets for C, H, P, N atoms, and the Pd or Pt metal center, respectively. For Pd and Pt, effective core potentials were also used to model

the effect of the core electrons (taken from the EMSL Basis Set library).^[38] Frequency calculations were then performed in order to check that true energy minima were attained. Time-Dependent DFT calculations were done using the previously obtained geometries by employing the same functional, but with larger basis sets including diffuse functions (6-31+G(d,p) for C, H, P, and N atoms, and Def2-SVPD for Pd and Pt atoms). For each cation, 72 excited states were solved, and the ECD spectra were simulated using the GaussView software, using a UV/Vis peak half-width at half height of 0.3 eV. Natural Transition Orbitals^[23] were then calculated and displayed with GaussView software.

The same procedure was used to optimize the geometry of [Pd(dppp)(PhCN)₂]²⁺ and [Pt(dppp)(PhCN)₂]²⁺ cations, and to calculate the corresponding ECD spectra. The [Pd₃(dppp)₃((-)-1)]⁶⁺ cation was decomposed in its three [Pd(dppp)(PhCN)₂]²⁺ moieties, saturating broken bonds with hydrogen atoms, which were then optimized at the same level of theory than previous calculations, keeping the rest of the geometry frozen. TD-DFT was finally used to simulate the ECD spectra of these three constrained dications, together with the one of uncomplexed (*P*)-1.

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Metallocryptophanes

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VIP

**The Chemo- and Stereoselective
Formation of Pallado- and Platino-
cryptophanes**

Metallocryptophanes were assembled from optically pure cyclo[3]tricyanotriphenylene (CTB) **1** and $[\text{M}(\text{dppp})-(\text{OTf})_2]$ ($\text{M} = \text{Pd}$ and Pt), and their chiroptical properties were studied experimentally and theoretically, providing

evidence of ICD effects. As shown by ^1H NMR spectroscopy and ESI mass spectrometry, the reaction proceeds stereoselectively and chemoselectively when a second CTB is involved in the self-assembly.

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