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ARTICLE TYPE

Substituent-controlled preference of carbonyl group–metal coordination in d⁸ metal complexes with non-symmetric pentadentate ligands. Structural and stereochemical aspects†‡

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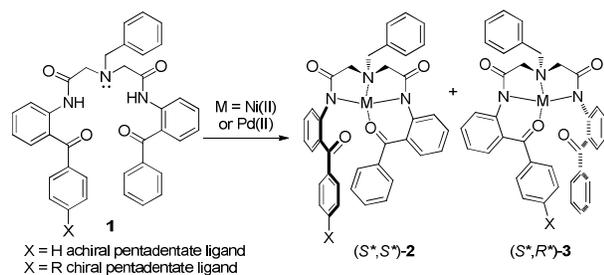
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Chirally switchable Ni(II) and Pd(II) complexes were synthesized and fully characterized by X-ray crystallography and additionally by spectroscopic means (NMR and MS). The syntheses and
10 characterizations of their ligands are also reported. It was found that control of the stereochemical preference between (*S**,*S**) and (*S**,*R**) diastereomers by substituent modification of the ligand sidearms was possible in the solid state with the preferred atomic coordinations of the sidearms consistent with
15 expectations based on the electron-withdrawing properties of the substituent *-o*-CF₃ group. The dilemma arising in terms of assigning the absolute configuration descriptors resulting from selecting between
20 strictly following only the covalent bonds of the ligand, or disregarding the nature of the bonds altogether and thus bringing the coordinate bonds into consideration, to determine the stereochemical priority sequence is hereby resolved by declaring that the latter option is to be preferred. The results obtained here provide clear indication that sidearm substitution of the Ni(II) and Pd(II) complexes need not disturb
macromolecular stereochemical arrangements leading to quasidiastereomeric relationships. This permits
the design of molecular systems sensitive to external stimuli with predictable macromolecular structure.

Introduction

Coordination compounds play an important role in the design and synthesis of molecules that can organize into supramolecular assemblies possessing useful chemical and physical properties.¹
25 One of the major challenges in this field is to attain a fine balance between structural predictability and coordination flexibility, thereby allowing the compounds to be responsive to external stimuli.² In this respect, one successful approach has been based on the application of ligands containing carbonyl groups
30 specifically intended to be weakly coordinating.³ Recently, we introduced a new molecular system based on the coordination of achiral pentadentate ligands with d⁸ metals (Scheme 1).⁴



Scheme 1 Formation of diastereomerically switchable complexes **2** and **3** from achiral and chiral ligands **1**.

The innovative feature of this system is that the coordination of the achiral ligand **1** (X = H) with Ni(II) or Pd(II) results in the

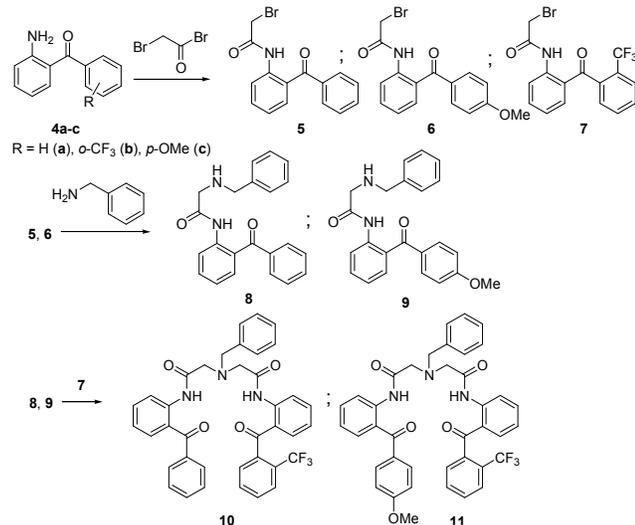
generation of two elements of chirality: the stereogenic center located at the benzylamine nitrogen, and the stereogenic axis
40 arising from the restricted rotation of the uncoordinated *N*-(*o*-benzophenone) amide moiety about the N–C_i bond. The switch between diastereomers (*S**,*S**)-**2** and (*S**,*R**)-**3** occurs *via* the carbonyl de-coordination/coordination step resulting in inversion of the stereogenic center chirality whilst retaining the same sense
45 of the axial chirality. It should be noted that due to the structural rigidity of complexes **2** and **3**, this process occurs with near complete (>99%) stereoselectivity. Due to the *cis* and *trans* relationship of the benzyl and uncoordinated *N*-(*o*-benzophenone) amide groups, diastereomers (*S**,*S**)-**2** and (*S**,*R**)-**3** differ in
50 stability. However, this difference is rather minute as both diastereomers can be randomly obtained in the solid state purely by chance.^{5a} In the current study, to further advance this molecular system in terms of some predictability, we considered introducing electron-withdrawing or -donating substituents to
55 influence the preference for coordination of the *N*-(*o*-benzophenone) amide carbonyls. During design of the corresponding ligands, we also realized that we will be faced with an interesting stereochemical dilemma as the ligands **1** bearing a substituent X = R thereby already possess a stereogenic center,
60 also located at the same nitrogen atom that is rendered chiral upon complexation. The coordination of such chiral ligands with d⁸ metals can thus result in unconventional stereochemical assignments taking into account the priority dictated by covalent vs. coordination bonds, an aspect which seemingly remains to be

properly clarified. The results described herein will, in addition to having far reaching implications in the deeper understanding of the correlation between stereochemistry and the presence of substituents on the switchable framework of molecules **2** and **3**, potentially lead to a general approach for rational control of their coordination properties.

Results and discussion

Building on our modular approach⁵ for the design of various tetra- or pentadentate ligands and the corresponding Ni(II) complexes, we prepared from a set of 2-aminobenzophenones **4a–c** a series of compounds **5–7** (Scheme 2) encompassing the unsubstituted benzophenone moiety (**5**) as well as compounds bearing electron-donating *para*-methoxy, *-p*-OMe, (**6**) and electron-withdrawing *ortho*-trifluoromethyl, *-o*-CF₃, (**7**) groups. Derivatives **5–7** were obtained in high yields *via* simple reaction of **4a–c** with bromoacetyl bromide, respectively. Bromides **5** and **6** were then used in a simple reaction with benzylamine to produce the secondary amines **8** and **9**, respectively, also in high yield. Finally, secondary amines **8** and **9** were transformed to the pentadentate ligands **10** and **11**, respectively, by alkylation with the *-o*-CF₃ group-containing bromide **7**. To prevent possible quaternization of the benzylamine nitrogen, the reactions were conducted in acetonitrile in the presence of Hünig's base,⁶ thus facilitating isolation of compounds **10** and **11** in high yields.

The ligands **10** and **11** are, in principle at least, chiral, as the benzylamine nitrogen atom, the stereogenic center, bears four

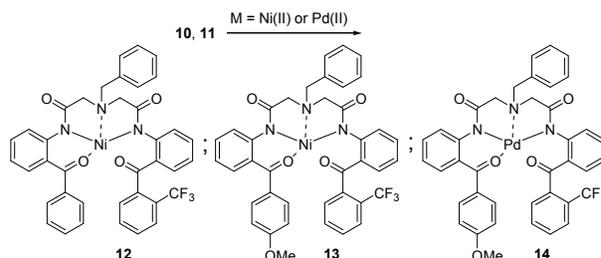


Scheme 2 Synthesis of pentadentate ligands **10** and **11**.

distinct substituents including the unshared pair of electrons. Furthermore, the capability of the carbonyl oxygen atom of the benzophenone moiety containing the *-o*-CF₃ group is expected to be diminished towards coordination with a metal due to the strong electron-withdrawing effect of this group, deliberately located by design in an *ortho* position. To generate the corresponding Ni(II) complexes, pentadentate ligands **10** and **11** were heated in methanol at 60–70 °C for several hours together with Ni(NO₃)₂·6H₂O and NaOH (Scheme 3). Upon completion, the red-colored Ni(II) complexes **12** and **13** were isolated by filtration from ice water and, interestingly, were stable enough to

be further purified by column chromatography over silica gel.

For the preparation of the corresponding Pd complex, it was found that Pd(OAc)₂ as the metal source gave the best result. The reaction was also conducted in methanol but using triethylamine as the base. The formation of the Pd(II) complex **14** occurred at a much higher rate and the reaction was complete in almost half the time. Filtration using celite pad was found to be necessary to remove the excess Pd residue, and following column chromatography through a short column of silica gel, the target Pd(II) complex **14** was obtained in quantitative yield.



Scheme 3 The Ni(II) complexes **12** and **13** and the Pd(II) complex **14**.

The complexes **12–14** were only very poorly soluble in suitable solvents, thus precluding their comprehensive analysis by NMR, especially with the consequent unavailability of ¹³C acquisition. With appreciable conformational mobility including the flexible benzyl moiety, fluxional motion of the heteroatom rings formed by coordination to the metal, and other bond rotations *etc.*, in addition to the chiral switching arising from the de-coordination/coordination steps of the carbonyl oxygen atoms to the metal, the NMR spectra were either extremely broad or contained multiple resonances from the various contributing species. Nevertheless, reasonable ¹H and ¹⁹F NMR data were attained at various temperatures and were consistent with the expected structures.

However, the dynamics clearly indicate the potential for facile switching between the diastereomers and the solution-state dynamic NMR behavior remains an area for future study, particularly in conjunction with molecular modeling which could enable the identification of the various contributing species and the likely transitions in effect. It was beyond the scope of the present work to conduct variable-temperature measurements for the purposes of extracting thermodynamic data on the transformations at hand, but clearly chiral switching must be a principle process in effect based on the magnitude of the energies involved. An interesting point is that the δ_F of the coalesced signal for the *-CF*₃ group for complexes **12–14** is essentially identical in all three cases (–61 ppm), thus pertaining to at least some dominance of the species where the carbonyl oxygen in the ligand arm bearing the *-CF*₃ group is not coordinated to the metal, otherwise it could be expected that differences in δ_F s would be apparent—notwithstanding some quite improbable coincidences in δ_F and equilibria positions.

Nevertheless, from the NMR data, it was clear that the introduction of electron-withdrawing or -donating substituents on the sidearms in ligands **10** and **11** was insufficient for providing a predictable, overwhelmingly biased coordination of a particular carbonyl group in solution. The next step therefore was to ascertain if an overwhelmingly predominant coordination mode was forthcoming in the solid state. For this, X-ray

crystallographic analysis was conducted on crystals of complex **12** grown from a $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ solution. The structure is presented in Fig. 1 and the details of data collection and refinement are summarized in Table 1.

In the crystallographic unit of complex **12**, both enantiomers (*S,S*) and (*R,R*) are present, though only the former is depicted in Fig. 1. Most importantly, as was intentionally designed, the

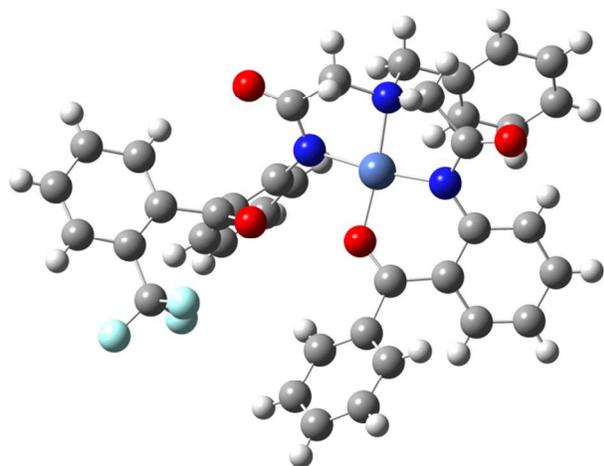


Fig. 1 X-ray structure of complex **12**; only the (*S,S*)-enantiomer is shown from the unit cell containing both enantiomers.

electron-deficient carbonyl oxygen atom of the $-o\text{-CF}_3$ group-containing benzophenone moiety is not coordinated to the metal. This result therefore is in concert with expectations given the strong electron-withdrawing properties of the $-\text{CF}_3$ group.

According to CIP priority rules,⁷ and considering only the covalent bonds involved, the first point of difference between the substituents of the benzylamine nitrogen atom for differentiation purposes occurs at the *ortho* position of the benzophenone phenyl rings, thereby giving priority to the $-o\text{-CF}_3$ group-containing arm. However, its carbonyl is not coordinated to the Ni and we argue that the first point of difference for stereochemical differentiation purposes should be considered from the point of view of the coordinated and non-coordinated carbonyl oxygen atoms, whereby it is the former that would then yield priority naming rights. The problem is that the CIP priority rules⁷ do not explicitly indicate the manner in which assignment should be considered as they do not say anything about the type of bonds involved. It is fully conceivable that different workers could follow different bond pathways and thus end up with different stereochemical assignments, as would be the case here. This deficiency, however, can be rectified by declaring that the convention that should be followed is that, rather than strictly following only the covalent bonds of the ligand, the nature of the bonds involved should be disregarded altogether. This then brings into consideration the coordinate bonds as we recommend.

Accordingly, following our declaration, the assignment of the absolute stereochemistry of the stereogenic nitrogen atom for the structure depicted in Fig. 1 is therefore *S* based on the sequence:

Table 1 Summary of crystal data for complexes **12–14**

	12	13	14
Formula	$\text{C}_{38}\text{H}_{28}\text{F}_3\text{N}_3\text{NiO}_4$	$\text{C}_{39}\text{H}_{30}\text{F}_3\text{N}_3\text{NiO}_5$	$\text{C}_{39}\text{H}_{30}\text{F}_3\text{N}_3\text{PdO}_5$
<i>M</i>	706.34	736.36	784.06
Temperature/K	291(2)	291(2)	293(2)
Wavelength/Å	0.71073	0.71073	1.54186
Crystal size/mm	$0.28 \times 0.24 \times 0.22$	$0.28 \times 0.24 \times 0.22$	$0.09 \times 0.02 \times 0.02$
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	<i>P1</i>	<i>P1</i>	<i>Pbca</i>
<i>a</i> /Å	11.869(2)	9.648(4)	10.9428(2)
<i>b</i> /Å	11.874(3)	13.897(6)	23.9074(4)
<i>c</i> /Å	14.3120(18)	16.270(7)	26.1834(5)
α /°	74.121(2)	66.870(7)	–
β /°	78.329(3)	74.393(7)	–
γ /°	79.1460(10)	87.648(8)	–
<i>V</i> /Å ³	1880.9(7)	1927.0(14)	6849.9(2)
<i>Z</i>	2	2	8
<i>D_c</i> /Mg m ⁻³	1.311	1.300	1.521
<i>F</i> (000)	768	780	3184
θ Range for data collection/°	1.80–26.00	2.20–26.00	4.75–68.17
Index ranges, <i>hkl</i>	–12 to 14, –14 to 14, –8 to 17	–11 to 11, –9 to 17, –16 to 20	–13 to 13, –28 to 28, –31 to 31
Reflections unique/observation	10366/7258	10590/7415	74634/6252
Goodness-of-fit on <i>F</i> ²	1.039	0.980	1.109
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)], <i>R</i> 1, <i>wR</i> 2	0.0572, 0.1342	0.0552, 0.0954	0.0584, 0.1344
<i>R</i> indices (all data), <i>R</i> 1, <i>wR</i> 2	0.0735, 0.1395	0.0853, 0.1010	0.0997, 0.1883
Largest diff. peak, hole/e Å ⁻³	0.325, –0.270	0.559, –0.421	1.308, –1.081

Ni(II) > coordinated C=O > non-coordinated C=O > benzyl group. To the best of our knowledge, structure **12** is the first unequivocal example where the formation of a coordinate bond can introduce a dilemma regarding the stereochemical priority sequence for assignment purposes from consideration of the types of bonds involved (*viz.* only covalent bonds *vs.* any type of bond). By this convention, the *-o*-CF₃ group-containing complex (*S,S*)-**12** and its unsubstituted analog (*S,S*)-**2** (Scheme 1) have the same allocated stereochemistry and, therefore presumably, might possess not only similar physicochemical functional properties, but could also share similar chiroptical properties as well, which would hence be a convenient outcome of the naming system.

Crystals of complex **13** with *-o*-CF₃ and *-p*-OMe groups on each arm were grown from CH₂Cl₂ solution and the resulting X-ray crystallographic structure is presented in Fig. 2. The details of data collection and refinement of complex **13** are summarized in Table 1. In this case too the crystallographic unit is also composed of a pair of enantiomers of absolute configuration (*S,S*) and (*R,R*) (portrayed).

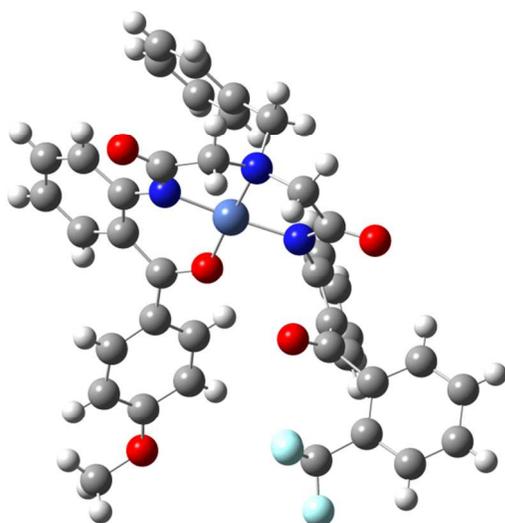


Fig. 2 X-ray structure of complex **13**; only the (*R,R*)-enantiomer is shown from the unit cell containing both enantiomers.

Similarly by intentional design, the more electron-rich carbonyl oxygen atom conjugated with the electron-donating *-p*-OMe group is coordinated to Ni in the solid state. This result again is in concert with expectations given the strong electron-withdrawing properties of the *-o*-CF₃ group for the ligand arm containing it. The labeling of the absolute configuration of the two enantiomers of **13** was likewise based on the priority of the coordinated carbonyl oxygen atom over the non-coordinated carbonyl oxygen atom. Hence, for the structure depicted in Fig. 2, the absolute stereochemistry of the stereogenic nitrogen atom is deemed to be *R*.

Finally, to attain a broader sense of generality, crystals of the Pd(II) complex **14** were also prepared from an ethyl acetate–hexane solution. The X-ray crystallographic structure of **14** is presented in Fig. 3. The details of data collection and refinement of complex **14** are summarized in Table 1. However, in contrast to the Ni(II) complexes **12** and **13**, the crystallographic unit of

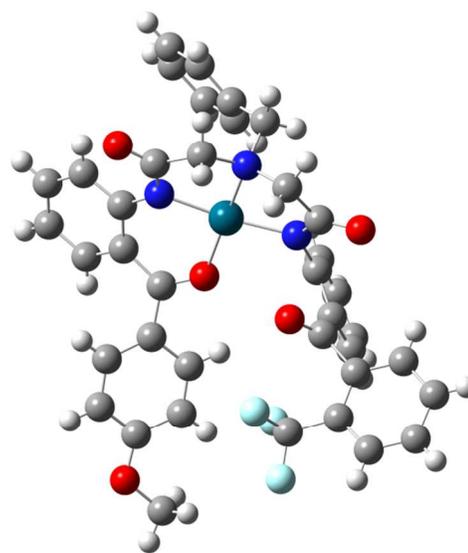


Fig. 3 X-ray structure of complex **14**; only the (*R,R*)-enantiomer is shown from the unit cell containing both enantiomers.

Pd(II) complex **14** is composed of eight molecules arranged in four sets of (*S,S*) and (*R,R*) enantiomeric pairs. Importantly though, in line with complexes **12** and **13**, the less electron-rich carbonyl oxygen atom, depleted by the electron-withdrawing effect of the *-o*-CF₃ group, is not coordinated to the metal. The absolute configuration of the stereogenic nitrogen atom in the molecule depicted in Fig. 3, was denoted, as previously for complexes **12** and **13**, on the basis of giving priority to the coordinated *-p*-OMe group-containing arm, and hence is deemed to be *R*.

Thus, there is a consistent general trend observed within this study in that the carbonyl oxygen of the more electron rich arm of the ligand coordinates to the metal in the solid state, as was anticipated. Furthermore, the *cis* isomers were not observed at all—and thus only the enantiomers (*S,S*) and (*R,R*) were present representing the *trans* isomers. Hence the stereochemistry can be effectively controlled by intentional design.

These results lead to the preeminent question, what are the stereochemical relationships between the unsubstituted complexes **2** and **3**, the monosubstituted complex **12** and the disubstituted derivatives **13** and **14**? In our opinion, the closest concept in the literature is the concept of quasienantiomers, defined as constitutionally different yet closely related chemical species possessing very similar chemical and physicochemical properties.⁸ In an entirely analogous manner therefore, we shall apply the term *quasidiastereomers* to describe the relationships between, for example, compounds (*S,R*)-**12** and (*R,R*)-**14**.

Experimental

NMR experimental

NMR spectra were acquired using a Bruker Avance NMR spectrometer equipped with a 5-mm normal configuration dual coil probe with z-gradient capability at a field strength of 9.4 T operating at 400, 100 and 376 MHz for ¹H, ¹³C and ¹⁹F nuclei, respectively, at 25 °C (other temperatures as indicated for the

complexes **12–14**) with samples contained in CDCl₃ (in CD₂Cl₂ for the complexes **12–14**). The chemical shifts of ¹H and ¹³C nuclei are reported relative to TMS incorporated as an internal standard ($\delta = 0$ ppm for both ¹H and ¹³C) and externally to CF₃CO₂H in CDCl₃ [2–3% v/v] at 25 °C for ¹⁹F ($\delta = -78.5$ ppm). General NMR experimental details have been previously described.⁹

X-ray experimental

The crystal data and details of data collection are given in Table 1. The data were collected on a Siemens SMART CCD diffractometer {graphite-monochromated Mo-K α radiation, ω -scan technique, $\lambda = 0.71073$ (complexes **12** and **13**) or 1.54186 (complex **14**) Å} at 291 (complexes **12** and **13**) or 293 (complex **14**) K. The structures were solved by direct methods using SHELXS-97¹⁰ and were refined on F^2 using SHELXL-97.¹¹ All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². Depictions of the X-ray derived structures in Figs 1–3 were produced using the GUI GaussView.¹²

Synthesis

General procedure for the preparation of *N*-(2-benzoylphenyl)-2-bromoacetamides 5–7 by the condensation of 2-aminobenzophenone and bromoacetyl bromide. A solution of bromoacetyl bromide (44.38 g, 225 mmol) in CH₃CN (2 mL/gram of bromoacetyl bromide) was slowly added to a slurry of the appropriate 2-aminobenzophenone **4** (19.72 g, 100 mmol) and potassium carbonate (69.11 g, 500 mmol) in CH₃CN (250 mL). The reaction was stirred at ambient temperature on a water bath for 1 hour and upon completion as indicated by TLC, the CH₃CN was evaporated under vacuum. Water (200 mL) was then added and the crude mixture extracted with CH₂Cl₂ (3 × 200 mL). The organic portions were combined, dried and concentrated under vacuum to afford the corresponding α -bromoamide **5–7** in 98% yield and greater than 99% chemical purity.

***N*-(2-benzoylphenyl)-2-bromoacetamide (5).** ¹H NMR δ 4.03 (2 H, s), 7.16 (1 H, m), 7.47–7.53 (2 H, m), 7.59–7.64 (3 H, m), 7.72–7.75 (2 H, m), 8.60 (1 H, dd, $J = 8.9, 1.2$ Hz), 11.50 (1 H, bs). ¹³C NMR δ 29.5, 121.5, 123.1, 124.1, 128.4, 130.0, 132.7, 133.6, 134.2, 138.3, 139.5, 165.3, 199.3. ESI-MS m/z 340 amu [M + Na]⁺. Mp 94–95 °C.

2-bromo-*N*-(2-(4-methoxybenzoyl)phenyl)acetamide (6). ¹H NMR δ 3.90 (3 H, s), 4.01 (2 H, s), 6.98 (2 H, m), 7.17 (1 H, m), 7.56–7.62 (2 H, m), 7.75–7.78 (2 H, m), 8.54 (1 H, dd, $J = 8.6, 1.1$ Hz), 11.23 (1 H, bs). ¹³C NMR δ 29.6, 55.6, 113.7, 121.7, 123.1, 125.0, 130.6, 132.7, 132.8, 133.4, 138.9, 163.5, 164.8, 197.3. ESI-MS m/z 370 amu [M + Na]⁺. Mp 127–128 °C.

2-bromo-*N*-(2-(2-(trifluoromethyl)benzoyl)phenyl)acetamide (7). ¹H NMR δ 4.07 (2 H, s), 7.07 (1 H, m), 7.31 (1 H, dd, $J = 8.0, 1.7$ Hz), 7.37–7.40 (1 H, m), 7.60–7.68 (3 H, m), 7.77–7.82 (1 H, m), 8.78 (1 H, dd, $J = 8.5, 1.0$ Hz), 12.09 (1 H, bs). ¹³C NMR δ 29.6, 120.7, 122.2, 123.1, 123.5 (qt, $J_{F,C} = 273.9$ Hz), 126.8 (qt, $J_{F,C} = 3.8$ Hz), 127.9 (qt, $J_{F,C} = 32.3$ Hz), 128.0, 130.2, 131.6, 134.9, 135.9,

138.0 (qt, $J_{F,C} = 2.1$ Hz), 140.9, 165.6, 199.4. ESI-MS m/z 408 amu [M + Na]⁺. Mp 87–88 °C.

General procedure for the alkylation of *N*-(2-benzoylphenyl)-2-bromoacetamides with benzylamine to yield the corresponding *N*-(2-benzoylphenyl)-2-(benzylamino)acetamides 8 and 9. To a flask containing **5** or **6** (50 mmol) and CH₃CN (1 mL/gram of **5** or **6**), was added benzylamine (2.5 eq). The reaction mixture was stirred at 60–70 °C until the starting material **5** or **6** had been completely consumed as indicated by TLC (hexane/AcOEt, 4 : 1). The solvent was then removed under reduced pressure and water added to the residue followed by extraction with CH₂Cl₂ (× 3). The organic portions were combined and dried over anhydrous MgSO₄. After filtration and removal of the solvent followed by column chromatography over silica gel, compound **8** or **9** was obtained in 97–99% yield.

***N*-(2-Benzoylphenyl)-2-(benzylamino)acetamide (8).** ¹H NMR δ 3.47 (2 H, s), 3.88 (2 H, s), 7.09–7.14 (1 H, m), 7.24–7.31 (3 H, m), 7.42–7.45 (2 H, m), 7.42–7.64 (5 H, m), 7.77–7.80 (1 H, m), 8.65 (1 H, dd, $J = 8.3, 0.6$ Hz), 11.70 (1 H, bs). ¹³C NMR δ 52.8, 54.0, 121.7, 122.4, 124.8, 127.3, 128.4, 128.5, 130.2, 132.7, 132.9, 133.7, 138.5, 139.2, 139.3, 171.4, 198.4. ESI-MS m/z 367 amu [M + Na]⁺. Mp 80–81 °C.

***N*-(2-(4-Methoxybenzoyl)phenyl)-2-(benzylamino)acetamide (9).** ¹H NMR δ 3.44 (2 H, s), 3.84 (2 H, s), 3.90 (3 H, s), 6.96–6.99 (2 H, m), 7.10–7.15 (1 H, m), 7.23–7.33 (3 H, m), 7.40–7.43 (2 H, m), 7.51–7.58 (2 H, m), 7.80–7.83 (2 H, m), 8.59 (1 H, dd, $J = 8.3, 0.4$ Hz), 11.44 (1 H, bs). ¹³C NMR δ 52.8, 54.0, 55.6, 113.6, 121.8, 122.4, 125.9, 127.3, 128.5, 128.6, 130.8, 132.0, 132.8, 133.0, 138.7, 139.2, 163.5, 171.2, 196.7. ESI-MS m/z 375 amu [M + H]⁺.

General Procedure for the syntheses of ligands 10 and 11.

A solution of compound **8** or **9** (10 mmol) in CH₃CN (10 mL) was added to compound **7** (1.1 eq) and *N*-ethyl-*N*-isopropylpropan-2-amine (1.5 eq). The reaction mixture was stirred at 60–70 °C until compound **8** or **9** had been completely consumed as indicated by TLC (hexane/AcOEt, 3 : 1). After evaporation of the solvent, aqueous NH₄Cl was added to the residue and the organic layer extracted with CH₂Cl₂ (× 3). The organic portions were combined and dried over anhydrous MgSO₄. After removal of the solvent followed by column chromatography over silica gel, the desired ligand **10** or **11** was obtained in 93–95% yield.

Ligand 10. ¹H NMR δ 3.47 (2 H, s), 3.48 (2 H, s), 3.95 (2 H, s), 6.84–6.89 (2 H, m), 7.02 (1 H, m), 7.11 (1 H, m), 7.21–7.67 (17 H, m), 7.78–7.80 (1 H, m), 8.15 (1 H, d, $J = 8.2$ Hz), 8.76 (1 H, dd, $J = 8.3$ Hz), 10.75 (1 H, bs), 12.11 (1 H, bs). ¹³C NMR δ 58.6, 59.1, 59.8, 121.0, 122.2, 122.5, 122.8, 123.4, 123.6 (qt, $J_{F,C} = 274.4$ Hz), 126.8 (qt, $J_{F,C} = 4.1$ Hz), 127.4, 127.8, 127.8 (qt, $J_{F,C} = 32.5$ Hz), 128.2, 128.3, 128.6, 129.7, 130.0, 130.1, 131.6, 132.0, 132.6, 132.9, 134.8, 135.9, 136.6, 137.9, 138.1, 138.2 (qt, $J_{F,C} = 2.0$ Hz), 141.2, 169.4, 170.1, 197.6, 199.2. ESI-MS m/z 672 amu [M + Na]⁺. Mp 56–57 °C.

Ligand 11. ¹H NMR δ 3.46 (2 H, s), 3.48 (2 H, s), 3.84 (3 H, s), 3.93 (2 H, s), 6.84–6.89 (2 H, m), 7.02 (1 H, ddd, $J = 8.2, 6.0,$

1.2 Hz), 7.12 (1 H, dt, $J = 7.6, 1.1$ Hz), 7.21–7.49 (9 H, m), 7.55–7.70 (5 H, m), 7.77–7.80 (1 H, m), 8.10 (1 H, d, $J = 7.6$ Hz), 8.75 (1 H, dd, $J = 8.4, 0.8$ Hz), 10.53 (1 H, bs), 12.10 (1 H, bs). ¹³C NMR δ 55.5, 58.5, 59.0, 59.7, 113.6, 121.0, 122.3, 122.5, 123.1, 123.4, 123.6 (qt, $J_{F,C} = 273.9$ Hz), 126.7 (qt, $J_{F,C} = 3.8$ Hz), 127.8, 127.9 (qt, $J_{F,C} = 32.3$ Hz), 128.2, 128.3, 128.6, 129.7, 130.0, 130.5, 131.3, 131.5, 132.2, 132.6, 134.8, 135.9, 136.7, 137.3, 138.2 (qt, $J_{F,C} = 2.0$ Hz), 141.1, 163.4, 169.3, 170.1, 196.0, 199.2. ESI-MS m/z 702 amu [M + Na]⁺. Mp 58–60 °C.

Syntheses of Ni(II) complexes 12 and 13. To a flask containing ligand **10** or **11** (0.86 mmol), Ni(NO₃)₂·6H₂O (0.75 g, 2.58 mmol) and 5 mL of MeOH, was added NaOH (0.21 g, 5.16 mmol). The reaction mixture was stirred at 60–70 °C under a N₂ atmosphere. After 8 h, the reaction mixture was poured into ice water and left until complete precipitation had occurred. The red solid was filtered off and washed with water. After column chromatography through a short column of silica gel, the desired Ni(II) complexes **12** or **13** were obtained.

Ni(II) complex 12. ¹H NMR (–80 °C, major species) δ 3.32 (1 H, d, $J = 15.6$ Hz), 3.67 (1 H, d, $J = 16.1$ Hz), 3.99 (1 H, d, $J = 15.7$ Hz), ~4.09 (2 H, vbs), 4.27 (1 H, d, $J = 16.3$ Hz), 6.92–7.86 (19 H, m), 8.06 (1 H, bd, $J = 8.5$ Hz), 8.20 (2 H, bd, $J = 7.4$ Hz). ¹⁹F NMR (35 °C) δ –61.08.

Ni(II) complex 13. ¹H NMR (35 °C) δ ~3.30 (2 H, vb), ~3.74 (3 H, vb), 3.79 (3 H, s), ~4.10 (1 H, vb), 6.75–7.06 (4 H, m), 7.16–7.80 (15 H, m), 7.87–7.98 (2 H, m). ¹⁹F NMR (35 °C) δ –60.89.

Synthesis of Pd(II) complex 14. To a flask containing ligand **11** (0.10 g, 0.17 mmol), Pd(OAc)₂ (0.077 g, 0.34 mmol) and 5 mL of MeOH, was added triethylamine (0.059 mL, 0.43 mmol). The reaction mixture was stirred at 60–70 °C for 4.5 h whilst being monitored by TLC (acetone/CHCl₃, 1 : 4). The reaction mixture was then filtered through Celite with the aid of acetone for the removal of Pd residue. After removal of the solvent followed by column chromatography through a short column of silica gel, the desired Pd(II) complex **14** was obtained in quantitative yield. ¹H NMR (35 °C) δ ~3.61 (1 H, vbd), 3.62 (1 H, bd, $J = 15.2$ Hz), 3.77–3.97 (2 H, vb), 3.82 (3 H, s), 3.93 (1 H, bd, $J = 15.4$ Hz), ~4.05 (1 H, vbd, $J = \sim 10.5$ Hz), 6.87–7.03 (4 H, m), 7.15–7.39 (6 H, m), 7.48–7.88 (11 H, m). ¹⁹F NMR (35 °C) δ –60.96.

Conclusions

The dilemma arising, as demonstrated in this work, in terms of assigning the absolute configuration descriptors resulting from selecting between strictly following only the covalent bonds of the ligand, or disregarding the nature of the bonds altogether and thus bringing the coordinate bonds into consideration, to determine the stereochemical priority sequence is hereby resolved by declaring that the latter option is to be preferred. The results obtained here provide a clear indication that substituents need not disturb macromolecular stereochemical arrangements leading to quasideastereomeric relationships and allow for the structural design of systems sensitive to external stimuli, a work we are rigorously pursuing at present. Finally, the results markedly demonstrate that coordination, and thus the stereochemistry, can

be controlled in the solid state by the electronic properties of the substituents introduced into the coordinating sidearms.

The potential for facile switching between the diastereomers in the solution-state as vehemently indicated by the dynamic NMR behavior remains an area for future study. The atomic coordinates on hand from the X-ray crystal structure determinations will provide for an indispensable starting point for molecular modeling calculations, as has been amply demonstrated before.¹³

Acknowledgements

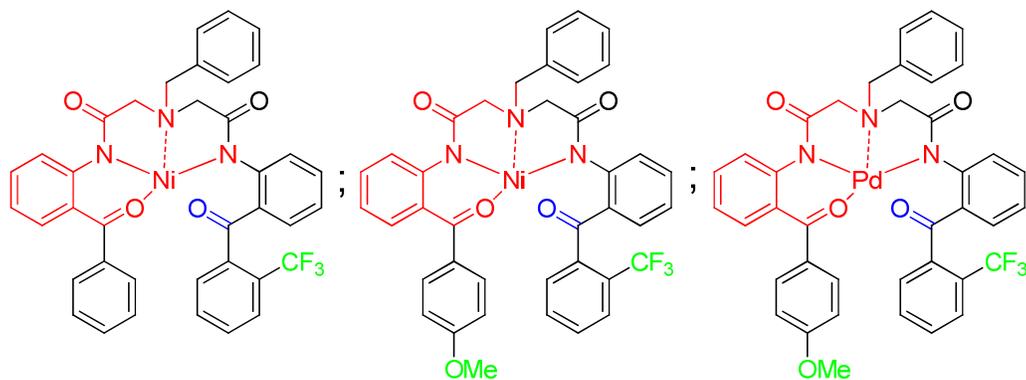
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- † Crystal structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC): deposit numbers CCDC-951881 (12), CCDC-951882 (13) and CCDC-951883 (14).
- ‡ Electronic Supplementary Information (ESI) available: NMR spectral data for compounds 5–14; X-ray data for Ni(II) complexes 12 and 13 and the Pd(II) complex 14. See DOI: 10.1039/b000000x/
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TOC entry:



The sidearm substitution of chirally switchable Ni(II) and Pd(II) complexes permits stereochemical inclinations to be controlled in the solid state.