Novel Chiral and Achiral NCN Pincer Complexes Based on 1,3-Bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene

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Received September 13, 2002

NCN pincer ligands based on 1,2,4-triazole and their corresponding palladium(II) complexes have been synthesized by the reaction of 1,3-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene derivatives with palladium(II) acetate. All compounds are *ortho*,*ortho*-metalated. Chiral complexes were obtained by using pincer ligands with substituents on the arms. The chiral complexes are conformationally rigid up to 150 °C.

Introduction

Transition metal complexes containing pincer-type ligands,[1] named after the particular coordination mode of these ligands, have attracted increasing interest owing to the unusual properties of the metal centers imparted by the pincer ligand. An excellent review on the platinum-group pincer complexes was published by van Koten in 2001.[2] Pincer ligands share a common feature in that the central atom of the pincer belongs to either a benzene ring (XCX type) or a pyridine ring (XNX type). These kinds of complexes have several sites that can be modified which will affect the properties of the metal center: the pendant ligands, the atoms connecting the extremes of the pincer with the aromatic ring, and the substituents on the aromatic ring. The first of these sites has been widely modified as evident by the following examples where CCC,[3] CNC,[4] CNS,[5] NNN,[6] NCN,[7] PCP,[8] PNP,[9] PCN,[10] OCO,[11] SCS,[12] SNS,[13] and SPS[14] pincer ligands have been reported in recent years. CCC and CNC pincer ligands usually bind the metal through carbene atoms generated from imidazolium salts,[3,4] while other azole systems such as pyrazole[7c,f] have been used for NCN ligands. The most commonly used metal is palladium but platinum, nickel, iridium, tin, molybdenum, osmium, rhodium, ruthenium, and cobalt have also been used for different applications. A recent paper highlighting the utility of bifunctional pincer complexes as building blocks for polymetallic materials has been published.[15] The atoms connecting the extremes of the pincer with the aromatic ring are appropriate sites to create stereogenic centers. Thus, some C_2 complexes have been synthesized with the aim of using these systems in chiral catalysis.[16] Chiral catalysts have also been prepared by using chiral oxazoline as a substructure bearing the extreme atoms of the pincer[17] and by using disubstituted ferrocene as a substructure bearing the central atom of the pincer.[18] The latter site can act as a remote electronic tuner or as an anchoring site, a feature that has also been

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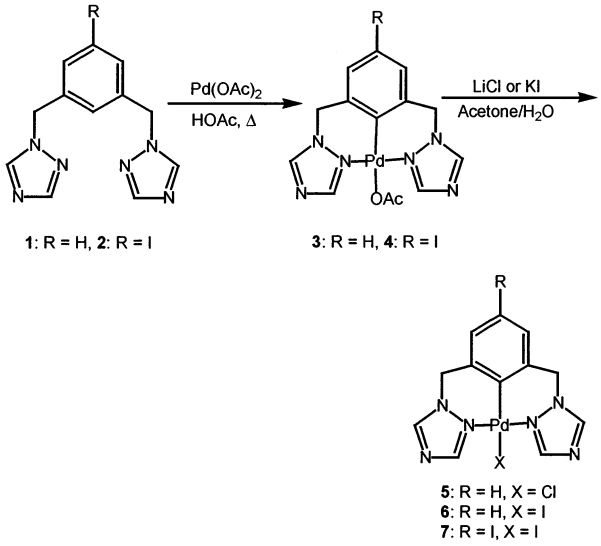
10.1021/om020764i CCC: $25.00
Publication on Web 01/07/2003

Scheme 1. Synthesis of Achiral Complexes



employed in some studies on the synthesis of dendritic catalysts.[19]

The 1,2,4-triazole ring has proven to be a suitable system for metal coordination by both nitrogen lone pairs and prior carbene formation.[20] This heterocyclic system also has one more nitrogen atom and this may have interesting effects on the metal-binding stability, which is claimed as an important factor in terms of the catalytic activity of these compounds.[3] Moreover, the 1,2,4-triazole ring would have an additional uncoordinated nitrogen atom that would be able to coordinate to other metal atoms, giving rise to interesting heterobinuclear complexes. In this paper we report the first NCN pincer ligands based on the 1,2,4-triazole system and also the Pd(II) complexes of these ligands. In addition, substitution on the carbon atom connecting the extremes of the pincer with the aromatic ring afforded chiral complexes.

Results and Discussion

Synthesis of Achiral Complexes. Starting materials for the synthesis of the achiral complexes were *m*-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene **1** (btmb) and its iodo derivative **2** (ibtmb). These compounds were prepared in 48% and 50% yields, respectively, by reaction of the corresponding *m*-bis(bromomethyl)benzene derivative[21] with use of Phase-Transfer Catalysis techniques.[22]

The reactions of compounds **1** and **2** with $Pd(OAc)_2$ in refluxing acetic acid[7f] yielded the pincer-type complexes **3** and **4** (Scheme 1), which, after evaporation of acetic acid, were dissolved in acetone/water (see the Experimental Section) and stirred with an excess of lithium chloride or potassium iodide to give compounds **5** [PdCl(btmp)] (80%), **6** [PdI(btmp)] (85%), and **7** [PdI(ibtmp)] (94%).

The ^1H and ^{13}C NMR spectra of complexes **5**−**7** show only one type of signal for the two heterocycles and the two methylene bridges as a result of the fluxional equilibrium shown below. All NMR data agree with an *ortho*,*ortho*-palladated pattern. Thus, the ^{13}C NMR signals for C−Pd are unique for each compound and the ^1H NMR signals for the hydrogen atoms of the benzene ring are a multiplet (3H) for compounds **5** and **6** and a singlet (2H) for compound **7**.

The structure of **6** was confirmed by X-ray crystal studies. The molecular structure, atomic numbering scheme, and relevant geometric parameters are shown in Figure 1a.

Complex **6** is chiral, with two molecules per asymmetric unit corresponding to the two enantiomers. The palladium atom is bound to four atoms, the two nitrogen atoms from the two triazole groups, the carbon of the phenyl ring, and the iodide atom, in a distorted-square-planar coordination, the mean deviation from the coordination plane being 0.42(1) Å. The plane of the aromatic ring is twisted, 36.6(2)° and 36.2(2)° for Pd1 and Pd2, respectively, out of the plane of the palladium coordination plane, similar to other complexes.[7f] The fused six-membered metallacycles show a boat conformation, as usual for this kind of complex.

The Pd−C and Pd−N distances and angles are in reasonable agreement with the values published for related structures.[7f] Pd−I distances [2.709(1) and 2.734(1) Å for Pd1 and Pd2, respectively] are slightly longer than the predicted value of 2.64 Å (based upon r(Pd(II) = 1.31 Å and r(I) = 1.33 Å),[23] probably due to the trans influence of the carbon atom. These long Pd−I distances have also been reported for similar complexes.[24]

The crystal is stabilized by an extensive hydrogen-bonding network. The geometric features of the hydrogen bond network are shown in Figure 1b. Hydrogen bond interactions between iodine or nitrogen atoms and C−H groups have been reported.[25]

Study of the Dynamic Behavior of Compounds 5 and 6. The ^1H NMR spectra of compounds **5**, **6**, and **7** show a singlet for the four protons of the methylene bridges, suggesting an equilibrium between the two enantiomers (Scheme 2). We represent the pincers here using a projection similar to that proposed by van Koten for bis(aminomethyl)-NCN pincers.[2] In an effort to verify this dynamic behavior, variable-temperature ^1H NMR experiments were performed on compounds **5** and **6** with DMF-d_7 as solvent. In these complexes the two metallacyclic rings present boat conformations and a rapid boat-to-boat equilibrium on the NMR time scale was observed at room temperature. Thus, the signal due to the methylene protons appeared as a singlet. At low temperature this inversion process is slow on the NMR time scale and the methylene protons are no longer equivalent but are observed as an AB system.

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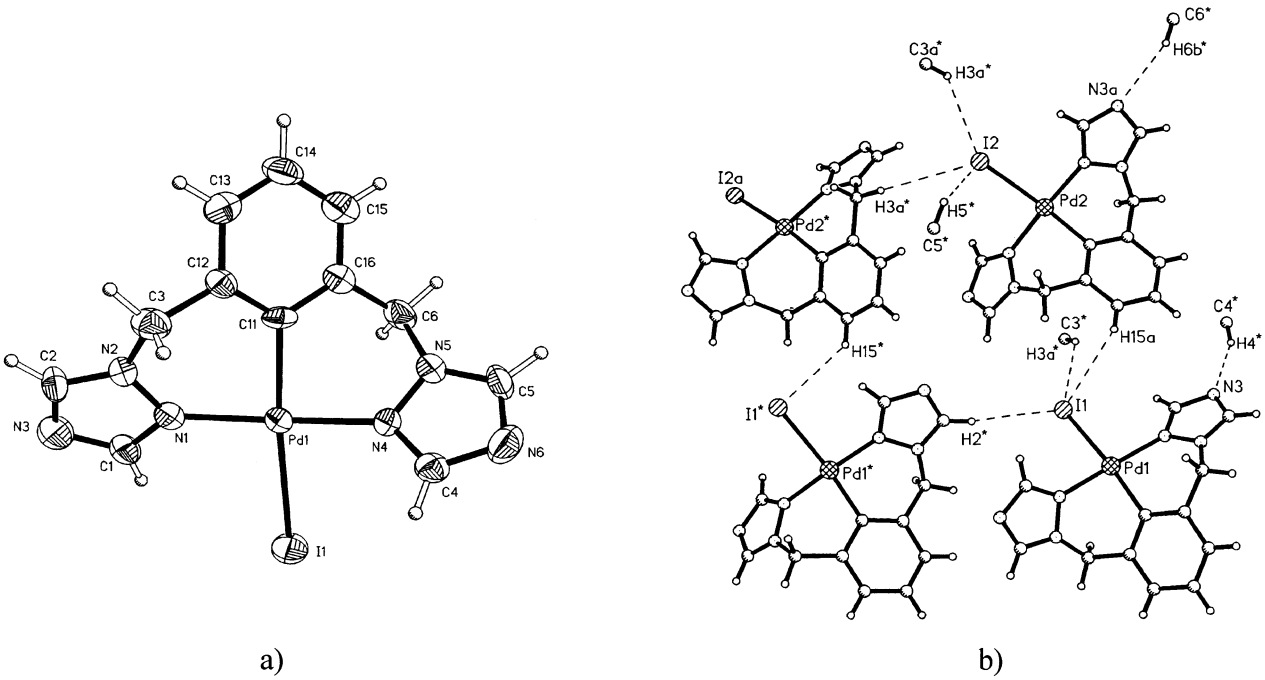


a) b)

Figure 1. (a) Molecular structure and atom-labeling scheme for [PdI(btmp)] (**6**), with thermal ellipsoids at 50% probability, and selected bond lengths (Å) and angles (deg): Pd1−I1 2.710(1), Pd2−I2 2.734(1), Pd1−N1 2.019(6), Pd2−N1a 2.037(6), Pd1−N4 2.007(6), Pd2−N4a 2.020(6), Pd1−C11 2.018(7), Pd2−C11a 2.005(7), I1−Pd1−N1 94.7(2), I2−Pd2−N1a 94.1(2), I1−Pd1−N4 88.8(2), I2−Pd2−N4a 89.4(2), N1−Pd1−C11 89.4(3), N1a−Pd2−C11a 89.7(3), N4−Pd1−C11 87.9(3), N4a−Pd2−C11a 87.4(3). (b) Dashed lines represent hydrogen bonds in compound **6**. An asterisk indicates a different asymmetric unit.

Scheme 2. Boat-to-Boat Equilibrium of [PdCl(btmp)] (5) and [PdI(btmp)] (6)

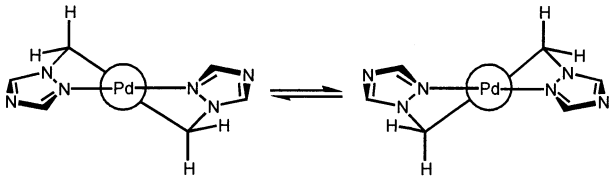


Table 1. Activation Parameters and Geminal Coupling Constants

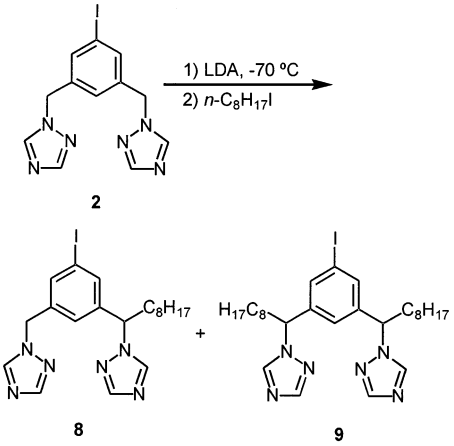
compd	T_c (K)	$\Delta G^{\#}$ (kJ/mol)[26]	$^2J_{HH}$ (Hz)[a]
5	239	48.1 ± 0.3	14.8
6	271	55.2 ± 0.3	14.1

[a] Determined in DMF-d_7 at 215 K for **5** and at 233 K for **6**.

Coalescence temperature, free energy values[26] ($\Delta G^{\#}$), and geminal coupling constants are summarized in Table 1. $\Delta G^{\#}$ values for compounds **5** and **6** are similar to those reported by Hartshorn and Steel for pincer complexes based on pyrazole; however, coalescence temperatures for our pincer complexes based on 1,2,4-triazole are lower when compared with pyrazole ones.

Synthesis of Chiral Complexes. As indicated above, we were interested in preparing chiral pincer-type complexes derived from *m*-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzenes. With this aim in mind we modified the arm of the pincer with *n*-octyl substituents, which will also provide an increased solubility of the complexes. We used the procedure reported by Moreno-Mañas[27] for the alkylation of the methylene bridge of

Scheme 3. Synthesis of Precursors of Arm-Alkylated Ligands



N-benzyl-1*H*-1,2,4-triazole. Compound **2** was deprotonated with LDA in dry THF at −78 °C and the anion was treated with *n*-octyl iodide. Products substituted in the methylene groups were obtained as oils (Scheme 3).

Treatment of 1.5 mmol of **2** with an excess of LDA (4 mmol) and *n*-octyl iodide (4.5 mmol) gave compound **9** (*rac*/*meso*-ibtnb) as the major product (60% of **9** and 9% of **8**). On the other hand, compound **8** (*rac*-itmtnb) was the major product (70% of **8** and 5% of **9**) when LDA was not used in excess (2 mmol of **2**, 0.75 mmol of LDA, and 4.5 mmol of *n*-octyl iodide). Compound **8** was obtained as a racemic mixture and compound **9** as a 1:1 mixture of the *rac* (*R*,*R* + *S*,*S*) and *meso* (*R*,*S*) diaste-

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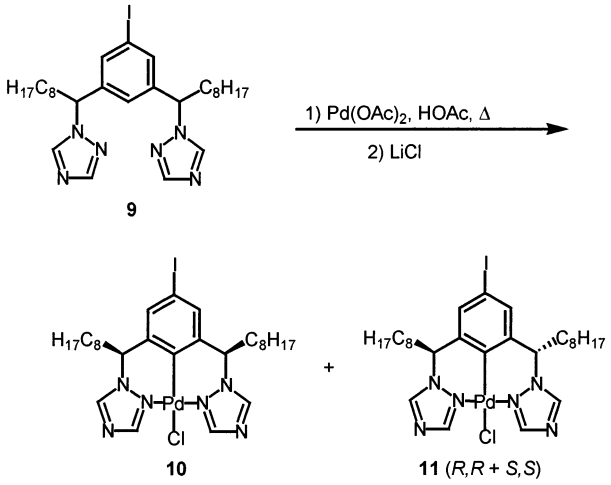
Scheme 4. Synthesis of Chiral Complexes *meso*-[PdCl(ibtnp)] (10) and *rac*-[PdCl(ibtnp)] (11)



reoisomers. Unfortunately, separation of the diastereoisomers has proved unsuccessful to date.

The ^{1}H and ^{13}C NMR spectra of compound **8** clearly show that only one octyl group is present and a nonsymmetric structure was obtained. The ^{1}H NMR spectrum contains a doublet-of-doublets (5.20 ppm) due to the methine group and one broad singlet (5.28 ppm) due to the methylene bridge bonded to 1,2,4-triazole and benzene. In addition, there are two multiplets (2.01−2.13, 2.32−2.45 ppm) arising from the two diastereotopic protons of the first methylene group of the octyl chain. All protons from benzene and the two different 1,2,4-triazole rings are also present. These facts indicate that the octyl group is bonded to the arm.

The ^{13}C NMR spectra confirm that the molecule is asymmetric: two sets of signals are present for the 1,2,4-triazole rings, the carbon atoms of the methine and methylene groups are different, and the ortho and meta (from the iodine) carbon signals are duplicated.

^{1}H and ^{13}C NMR spectra indicate that both stereoisomers **9** (*meso* and *rac*) are symmetrical. Thus, in the ^{1}H NMR spectrum all methine protons show the same chemical shift and appear as a doublet-of-doublets (5.20 ppm). In addition, the same chemical shifts are observed for both octyl groups, although the two diastereotopic protons of the first methylene group of the octyl chains appear as two multiplets (2.00−2.13, 2.32−2.44 ppm). These facts again indicate that the octyl groups are bonded to the arms. The existence of the two diastereoisomers was confirmed by the duplication of the NMR signals corresponding to H4 and H2(H6) of the benzene and H5 of the triazole ring, as well as of C4 and C2(C6) of the benzene ring.

Heating a mixture of diastereoisomers **9** (*meso* + *rac*) under reflux with palladium(II) acetate in acetic acid, followed by treatment with lithium chloride, gave the corresponding pincer-type complexes **10** and **11** (Scheme 4) in 20% and 60% yield, respectively, after tedious purification by column chromatography. Compound **10** is the diastereoisomer (*R*,*S*)-[PdCl(ibtnp)], although it behaves as a *meso* form because of the fluxional equilibrium described below, and **11** is a racemic mixture (*R*,*R* + *S*,*S*) *rac*-[PdCl(ibtnp)].

The ^{1}H and ^{13}C NMR chemical shifts of the signals for **10** and **11** are very similar (see Experimental Section) and their assignment is not easy. To perform a structural assignment it was necessary to perform variable-temperature experiments. (*R*,*S*)-[PdCl(ibtnp)] (**10**) has two enantiomeric structures that are in a boat-to-boat equilibrium (Scheme 5). At room temperature this equilibrium is fast on the NMR time scale with all H3 and H5 protons of the heterocycle, and the methine protons each show only one signal. At low temperature the equilibrium is slow on the NMR time scale and the signals of these three protons (−20 °C for methine groups and −50 °C for H3 and H5 of the 1,2,4-triazoles) are duplicated with an integral ratio of 1:1 for each of the three pairs of signals.

Scheme 5. Boat-to-Boat Equilibrium of *meso*-[PdCl(ibtnp)] (10)

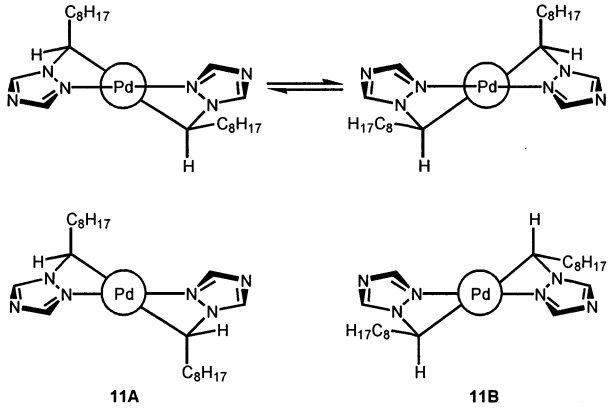


Figure 2. Proposed pseudoaxial and pseudoequatorial conformations of *rac*-[PdCl(ibtnp)] (**11**).

Table 2. Activation Parameters of (*R*,*S*)-[PdCl(ibtnp)] (10)

group	T_c (K)	$\Delta G^{\#}$ (kJ/mol)[26]
NC*H*C_8H_{17}	271	55.2 ± 0.3
H3 (1,2,4-triazole)	250	52.7 ± 0.4
H5 (1,2,4-triazole)	250	52.7 ± 0.4

The activation energy of this fluxional process has been determined by examining the coalescence temperature of the 1,2,4-triazole ring protons and the methine protons. The thermodynamic parameters are summarized in Table 2. The presence of both pseudoequatorial and pseudoaxial *n*-octyl groups does not represent any important effect on the activation energy of the process.

For *rac*-[PdCl(ibtnp)] (**11**) there are two possible structures (**11A** and **11B**, Figure 2); one of these contains the two octyl groups in positions that are termed pseudoaxial (**11A**) and the other structure has the two octyl groups in pseudoequatorial positions (**11B**)—a situation that results in two conformations of different energy. If this equilibrium exists, it would be expected that two different sets of signals with integrals other than 1:1 would be observed at low temperature. However, when the temperature of the ^{1}H NMR probe was decreased to as low as −60 °C ($CDCl_3$), duplication of the signals was not observed in any case. When the spectrum was registered at temperatures up to 150 °C (DMSO-d_6) any change was observed. These facts indicate that, in the range of −60 to 150 °C and within the limits of NMR detection, a boat-to-boat equilibrium does not exist and that the structure is conformationally rigid with only one product present.

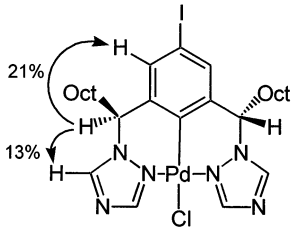


Figure 3. NOE values for *rac*-[PdCl(ibtnp)] (**11**).

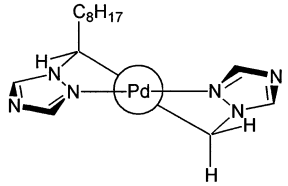
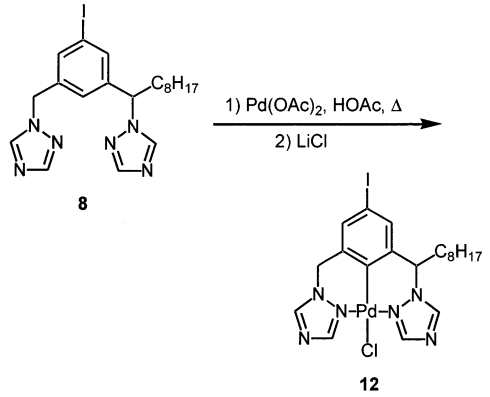


Figure 4. Proposed conformation for *rac*-[PdCl(itmtnp)] (**12**).

Scheme 6. Synthesis of Chiral Complex *rac*-[PdCl(itmtnp)] (12)



A variety of experiments were performed in an effort to determine the nature of the conformation present at room temperature (Figure 3). The methine protons show a NOE effect of 13% with H5 of the 1,2,4-triazole rings and 21% with H3 of the benzene ring. Moreover, the absence of a NOE between the first methylene protons of the octyl groups and H5 of 1,2,4-triazole rings or H3 of the benzene was noted.

These results indicate that the methine protons are in pseudoequatorial positions and the octyl groups are in pseudoaxial positions (**11A**).

Reaction of compound **8** with palladium(II) acetate in acetic acid under reflux gave rise to a new pincer complex **12** *rac*-[PdCl(itmtnp)] in 40% yield (Scheme 6).

The structure of compound **12** was determined by ^{1}H and ^{13}C NMR spectroscopy. Both spectra showed a set of duplicate signals, indicating a nonsymmetric structure. In a similar way to compounds **10** and **11** the C−Pd signal appears at 137.2 ppm, as expected for an *ortho*,*ortho*-palladated carbon. When the ^{1}H NMR spectrum was recorded at low (−60 °C) and high (150 °C) temperature, the natures of the signals did not change. As explained above, these results agree with the existence of a conformationally rigid structure up to 150 °C. A pseudoaxial configuration for the octyl group (Figure 4) was confirmed by NOE experiments: the methine proton has a NOE of 10% with H3 of the 1,2,4-triazole ring and 15% with H3 of the benzene ring. In addition, there is no NOE effect between the first methylene of the octyl group and H3 of the 1,2,4-triazole ring or H3 of benzene.

The significant degree of stability for the pseudoaxial conformations may be explained by considering the lower steric interactions between the octyl chain and the heterocycle and benzene moieties when compared with pseudoequatorial disposition.

Conclusions

Pincer-type complexes based on 1,2,4-triazole systems with palladium(II) have been synthesized. Substitution on the arms of the pincer ligands allowed the synthesis of chiral and achiral complexes. Chiral complexes, both mono- and disubstituted, are conformationally rigid up to 150 °C. This feature makes these palladium(II) complexes attractive compounds for catalysis.

Complexes having an additional functional group have also been obtained. These systems allow the opportunity to incorporate new functionalities or to envisage the synthesis of dendritic catalysts.

Experimental Section

Solvents were purified by distillation from appropriate drying reagents before use. All materials were obtained from Acros or Aldrich and were used without purification—except for *n*-octyl iodide, which was dried over an activated alumina column and stored under an argon atmosphere with the exclusion of light. When necessary, work was carried out with use of standard Schlenk techniques under an atmosphere of dry argon.

Melting points were determined in capillary tubes on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer. Fast Atom Bombardment (FAB) mass spectrometry (using *m*-NBA as matrix) and Electron Impact (EI) (working at 70 V and 200 °C) were performed on a VG Autospec instrument belonging to Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid. NMR spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts are expressed in parts per million (δ) relative to TMS as internal standard. The resonances of compounds were assigned by difference NOE and Hetcor experiments.

Variable-temperature experiments were performed by registering successive spectra in the range from −60 to 150 °C. Spectra were initially recorded each 25 °C and the temperature gap was reduced to 1 °C at the proximity of the coalescence temperature. Activation energy values were obtained as indicated in ref 25.

1,3-Bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (1). A mixture of 1,3-bis(bromomethyl)benzene (3.96 g, 15 mmol), 1*H*-1,2,4-triazole (2.40 g, 35 mmol), aqueous sodium hydroxide (40%, 12 mL), and tetrabutylammonium bromide (0.48 g, 1.5 mmol) in toluene (38 mL) was placed in a 100-mL round-bottomed flask fitted with a reflux condenser. The reaction mixture was heated for 6 h at 80 °C. The reaction mixture was allowed to cool to room temperature and the organic layer was separated and the residue extracted with dichloromethane (4 × 50 mL). The combined organic phases were dried over anhydrous sodium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2, ethyl acetate/methanol, 20:1) and crystallized from ethyl acetate/hexane. Yield: 1.73 g, 48%. Colorless crystals. Mp: 109−110 °C. ^{1}H NMR ($CDCl_3$): δ 5.34 (s, 4H, CH_2), 7.17 (s, 1H, H2 benzene), 7.23 (d, J = 7.5 Hz, 2H, H4 and H6 benzene), 7.39 (t, J = 7.5 Hz, 1H, H5 benzene), 7.97 (s, 2H, H3 triazole), 8.11 (s, 2H, H5 triazole). ^{13}C NMR ($CDCl_3$): δ 53.0 (CH_2), 127.2

(C2 benzene), 128.0 (C4 and C6 benzene), 129.7 (C5 benzene), 135.6 (C1 and C3 benzene), 143.1 (C5 triazole), 152.2 (C3 triazole). Anal. Calcd for $C_{12}H_{12}N_6$ (240.26): C, 59.99; H, 5.03; N, 34.98. Found: C, 59.77; H, 5.05; N, 34.58.

1-Iodo-3,5-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (2). 1-Iodo-3,5-bis(bromomethyl)benzene[21] (1.17 g, 3 mmol), 1*H*-1,2,4-triazole (0.48 g, 7 mmol), anhydrous potassium carbonate (0.97 g, 7 mmol), powdered potassium hydroxide (0.39 g, 7 mmol), tetrabutylammonium bromide (97 mg, 0.3 mmol), and toluene (30 mL) were placed in a 50-mL round-bottomed flask. The mixture was heated under reflux for 38 h. The crude reaction mixture was filtered and the solid residue was extracted with dichloromethane (4 × 25 mL). The combined organic phases were dried over anhydrous sodium sulfate. The product was purified by column chromatography on silica gel. Elution with ethyl acetate/methanol (19:1) afforded the pure product as a colorless solid. Yield: 0.55 g, 50%. Mp: 156−158 °C (ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$): δ 5.28 (s, 4H, CH_2), 7.11 (s, 1H, H4 benzene), 7.57 (s, 2H, H2 and H6 benzene), 8.00 (s, 2H, H3 triazole), 8.12 (s, 2H, H5 triazole).^{13}C NMR ($CDCl_3$): δ 52.2 (CH_2), 95.2 (CI), 126.5 (C4 benzene), 136.9 (C2 and C6 benzene), 137.6 (C3 and C5 benzene), 143.2 (C5 triazole), 152.6 (C3 triazole). Anal. Calcd for $C_{12}H_{11}IN_6$ (366.16): C, 39.36; H, 3.03; N, 22.95. Found: C, 39.29; H, 3.04; N, 22.60.

[PdCl(btmp)] (5). This method is based on that described by Hartshorn and Steel[7f] and is representative of the general procedure for *ortho*-metalation in this work. A solution of 1,3-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (**1**) (360 mg, 1.5 mmol) and palladium acetate (336 mg, 1.5 mmol) in acetic acid (15 mL) was heated under reflux for 16 h under an argon atmosphere in a 50-mL Schlenk tube. The solvent was removed under reduced pressure and a solution of lithium chloride (318 mg, 7.5 mmol) in acetone/water (3:2, 15 mL) was added. The resulting solution was stirred at room temperature for 48 h. The product precipitated and was filtered off. The colorless solid was washed twice with water (5 mL). Yield: 0.46 g, 80%. Mp: > 260 °C (methanol). ^{1}H NMR (DMSO-d_6): δ 5.57 (s, 4H, CH_2), 7.06−7.17 (m, 3H, benzene), 8.43 (s, 2H, H3 triazole), 8.98 (s, 2H, H5 triazole). ^{13}C NMR (DMSO-d_6): δ 54.6 (CH_2), 124.9 and 126.9 (C3, C4, and C5 benzene), 134.9 (C2 and C6 benzene), 139.3 (CPd), 145.1 (C5 triazole), 153.6 (C3 triazole). MS(FAB): m/*z* 727 [$2M^+ + 2 - Cl$], 345 [$M^+ - Cl$]. Anal. Calcd for $C_{12}H_{11}ClN_6Pd$ (381.13): C, 37.82; H, 2.91; N, 22.05. Found: C, 37.97; H, 2.91; N, 21.83.

[PdI(btmp)] (6). The general method described for the synthesis of compound **5** was followed with use of 1,3-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (**1**) (480 mg, 2 mmol), palladium acetate (449 mg, 2 mmol), and acetic acid (45 mL). The acetic acid was evaporated and a solution of potasium iodide (1.66 g, 10 mmol) in acetone/water (3:2, 50 mL) was added. The resulting solution was stirred for 48 h at room temperature. The product precipitated and was filtered off. The red solid was washed twice with water (5 mL). Yield: 0.80 g, 85%. Mp: 255−256 °C dec (acetonitrile). ^{1}H NMR (DMSO-d_6): δ 5.59 (s, 4H, CH_2), 7.08−7.19 (m, 3H, benzene), 8.63 (s, 2H, H3 triazole), 8.99 (s, 2H, H5 triazole). ^{13}C NMR (DMSO-d_6): δ 54.4 (CH_2), 125.2 and 127.0 (C3, C4, and C5 benzene), 134.8 (C2 and C6 benzene), 142.5 (CPd), 145.2 (C5 triazole), 156.6 (C3 triazole). MS(FAB): *m*/*z* 819 [$2M^+ + 2 - I$], 473 [$M^+ + 1$], 345 [$M^+ - I$]. Anal. Calcd for $C_{12}H_{11}IN_6Pd$ (472.58): C, 30.50; H, 2.35; N, 17.78. Found: C, 30.63; H, 2.44; N, 17.99.

[PdI(ibtmp)] (7). The general method described for the synthesis of compound **5** was followed with use of 1-iodo-3,5-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (**2**) (450 mg, 1.23 mmol), palladium acetate (276 mg, 1.23 mmol), and acetic acid (35 mL). The acetic acid was evaporated and a solution of potasium iodide (1.03 g, 6.15 mmol) in acetone/water (1:1, 35 mL) was added. The resulting solution was stirred for 48 h at room temperature. The product precipitated and was filtered off. The red solid was washed twice with water (5 mL). Yield: 0.69 g, 94%. Mp: >270 °C. ^{1}H NMR (DMSO-d_6): δ 5.56 (s, 4H, CH_2), 7.56 (s, 2H, H3 and H5 benzene), 8.62 (s, 2H, H3 triazole), 8.95 (s, 2H, H5 triazole). ^{13}C NMR (DMSO-d_6): δ 53.5 (CH_2), 90.0 (CI), 134.8 (C3 and C5 benzene), 137.3 (C2 and C6 benzene), 142.4 (CPd), 145.4 (C5 triazole), 156.6 (C3 triazole). MS(FAB): *m*/*z* 471 [$M^+ - I$]. Anal. Calcd for $C_{12}H_{10}I_2N_6Pd\cdot H_2O$ (616.49): C, 23.38; H, 1.96; N, 13.63. Found: C, 23.03; H, 1.92; N,13.23.

***rac*-1-Iodo-3-(1*H*-1,2,4-triazol-1-ylmethyl)-5-[1-(1*H*-1,2,4-triazol-1-yl)nonyl]benzene (8).** To a solution of 1-iodo-3,5-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene **(2)** (0.73 g, 2 mmol) in THF (30 mL) in a flame-dried 100-mL Schlenk tube under an argon atmosphere with stirring at −78 °C was slowly added by syringe a 2.0 M solution of LDA (0.38 mL, 0.75 mmol) in THF/hexane. The slurry reddish-brown reaction mixture was stirred for 1 h at this temperature. A previously prepared solution of *n*-octyl iodide (0.82 mL, 4.5 mmol) in THF (30 mL), cooled to −78 °C, was added dropwise to the reaction mixture. The mixture was stirred for 1 h at −78 °C and was allowed to warm to room temperature overnight. The clear yellow solution was quenched with saturated aqueous ammonium chloride solution (20 mL) and dichloromethane (20 mL) was added. The organic layer was separated and washed with saturated aqueous ammonium chloride solution (3 × 50 mL) and then dried over sodium sulfate. The solvent was evaporated to give a clear yellow oil. The product was purified by column chromatography on silica gel. Elution with ethyl acetate afforded the pure product as a colorless oil. Yield: 0.25 g, 70% (5% of **9** was also obtained). ^{1}H NMR ($CDCl_3$): δ 0.87 (pseudo-t, J = 6.8 Hz, 3H, $CHCH_2(CH_2)_6CH_3$), 1.19−1.31 (m, 12H, $CHCH_2(CH_2)_6CH_3$), 2.01−2.13 (m, 1H) and 2.32−2.45 (m, 1H) ($CHCH_2(CH_2)_6CH_3$), 5.20 (dd, J = 9 Hz, J = 6.5 Hz, 1H, $CHCH_2(CH_2)_6CH_3$), 5.28 (br s, 2H, NCH_2), 7.20 (br s, 1H, H4 benzene), 7.52 (br s, 1H) and 7.65 (br s, 1H) (H2 and H6 benzene), 7.98 (s, 1H, H3 triazole), 7.99 (s, 1H, H3 triazole), 8.12 (s, 1H, H5 triazole), 8.13 (s, 1H, H5 triazole). ^{13}C NMR ($CDCl_3$): δ 14.0 ($CHCH_2(CH_2)_6CH_3$), 22.5, 26.2, 28.8, 29.0, 29.1, 31.6 ($CHCH_2(CH_2)_6CH_3$), 35.1 ($CHCH_2(CH_2)_6CH_3$), 52.2 (NCH_2), 63.5 ($CHCH_2(CH_2)_6CH_3$), 95.0 (CI), 125.6 (C4 benzene), 136.0 and 136.5 (C2 and C6 benzene), 137.4 (C3 benzene), 142.3 (C5 benzene), 142.5 (C5 triazole), 143.2 (C5 triazole), 152.2 (C3 triazole), 152.4 (C3 triazole). Anal. Calcd for $C_{20}H_{27}IN_6$ (478.38): C, 50.22; H, 5.69; N, 17.57. Found: C, 50.37; H, 5.74; N, 17.51.

***rac/meso*-1-Iodo-3,5-bis[1-(1*H*-1,2,4-triazol-1-yl)nonyl]-benzene (9).** The same method as used in the preparation of compound **8** was followed with use of 1-iodo-3,5-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (0.55 g, 1.5 mmol), 2 M LDA (2 mL, 4 mmol), and octyl iodide (0.82 mL, 4.5 mmol). Compound **9** was obtained as an oil in 60% yield (0.53 g) (9% of **8** was also obtained). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 6.9 Hz, 12H, $CHCH_2(CH_2)_6CH_3$), 1.17−1.28 (m, 48H, $CHCH_2(CH_2)_6CH_3$), 2.00−2.13 (m, 4H) and 2.32−2.44 (m, 4H) ($CHCH_2(CH_2)_6CH_3$), 5.20 (dd, J = 9.0 Hz, J = 6.3 Hz, 4H, $CHCH_2(CH_2)_6CH_3$), 7.267 (br s, 1H, H4 benzene) and 7.272 (br s, 1H, H4 benzene), 7.61 (s, 2H, H2 and H6 benzene), 7.62 (s) (2H, H2 and H6 benzene), 7.98 (s, 4H, H3 triazole), 8.11 (s, 2H, H5 triazole), 8.12 (s, 2H, H5 triazole). ^{13}C NMR ($CDCl_3$): δ 14.0 ($CHCH_2(CH_2)_6CH_3$), 22.6, 26.2, 28.9, 29.1, 29.2, 31.7 ($CHCH_2(CH_2)_6CH_3$), 35.1 ($CHCH_2(CH_2)_6CH_3$), 35.2 ($CHCH_2(CH_2)_6CH_3$), 63.59 ($CHCH_2(CH_2)_6CH_3$), 63.6 ($CHCH_2(CH_2)_6CH_3$), 94.9 (CI), 124.86 (C4 benzene), 124.9 (C4 benzene), 135.7 (C2 and C6 benzene), 135.74 (C2 and C6 benzene), 142.2 (C3 and C5 benzene), 142.5 (C5 triazole), 152.1 (C3 triazole). MS(EI): *m*/*z* 590 [M^+]. Anal. Calcd for $C_{28}H_{43}IN_6$ (590.59): C, 56.94; H, 7.34; N, 14.23. Found: C, 56.65; H, 7.49; N, 13.94.

(*R*,*S*)-[PdCl(ibtnp)] (10) and *rac*-[PdCl(ibtnp)] (11). The general method described for the synthesis of compound **5** was followed using *rac*/*meso*-1-iodo-3,5-bis(1*H*-1,2,4-triazol-1-yl-nonyl)benzene (**9**) (184 mg, 0.31 mmol), palladium acetate (70 mg, 0.31 mmol), and acetic acid (10 mL). The acetic acid was

evaporated and a solution of lithium chloride (66 mg, 1.56 mmol) in dichloromethane/water (1:1, 20 mL) was added. The resulting solution was stirred for 6 h at room temperature. Water (20 mL) was added to the solution and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3 × 20 mL) and the combined organic phases were dried over anhydrous sodium sulfate. The solvent was removed and the brown residue was extracted with hot diethyl ether (4 × 20 mL). Diastereoisomers were separated by column chromatography on silica gel with use of hexane/ethyl acetate (4:1) as eluent: TLC hexane/ethyl acetate (1:1). Compound **11** was obtained in the first fraction as a yellow solid: 68 mg, 60% yield. Additional purification was not necessary, although the product could be crystallized from dichloromethane/hexane. Compound **10** was obtained in the second fraction as a yellow solid: 22 mg, 20% yield. Additional purification of this product was desirable, although decomposition products were obtained after chromatography.

Analytical Data for (*R*,*S*)-[PdCl(ibtnp)] (10). ^{1}H NMR ($CDCl_3$): δ 0.83−0.89 (m, 6H, $CHCH_2(CH_2)_6CH_3$), 1.26 (br s, 24H, $CHCH_2(CH_2)_6CH_3$), 2.48−2.60 (m, 4H, $CHCH_2(CH_2)_6CH_3$), 5.51 (br s, 2H, $CHCH_2(CH_2)_6CH_3$), 7.35 (s, 2H, H3 and H5 benzene), 8.26 (s, 2H, H5 triazole), 8.56 (s, 2H, H3 triazole). ^{13}C-NMR ($CDCl_3$): δ 14.08 ($CHCH_2(CH_2)_6CH_3$), 14.1 ($CHCH_2(CH_2)_6CH_3$), 22.6, 22.7, 26.5, 29.1, 29.2, 29.3, 31.7, 31.9 ($CHCH_2(CH_2)_6CH_3$), 37.4 ($CHCH_2(CH_2)_6CH_3$), 66.2 (br s, $CHCH_2(CH_2)_6CH_3$), 89.2 (CI), 133.6 (br s, CPd, C3 and C5 benzene), 141.0 (C2 and C6 benzene), 142.4 (C5 triazole), 154.4 (C3 triazole).

Analytical Data for *rac*-[PdCl(ibtnp)] (11). Mp: 246−250 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.84−0.88 (m, 6H, $CHCH_2(CH_2)_6CH_3$), 1.13−1.26 (m, 24H, $CHCH_2(CH_2)_6CH_3$), 2.41−2.53 (m, 2H) and 2.71−2.84 (m, 2H) ($CHCH_2(CH_2)_6CH_3$), 5.26 (dd, J = 9 Hz, J = 6.3 Hz, 2H, $CHCH_2(CH_2)_6CH_3$), 7.35 (s, 2H, H3 and H5 benzene), 8.28 (s, 2H, H3 triazole), 8.68 (s, 2H, H5 triazole). ^{13}C NMR: δ 14.1 ($CHCH_2(CH_2)_6CH_3$), 22.6, 26.4, 28.7, 29.1, 29.3, 31.9 ($CHCH_2(CH_2)_6CH_3$), 39.8 ($CHCH_2(CH_2)_6CH_3$), 67.6 ($CHCH_2(CH_2)_6CH_3$), 88.9 (CI), 134.8 (CPd), 135.3 (C3 and C5 benzene), 141.3 (C2 and C6 benzene), 143.5 (C5 triazole), 154.9 (C3 triazole). MS(FAB): m/z 1425 [2 M^+ − Cl + 1], 695 [M^+ − Cl]. Anal. Calcd for $C_{28}H_{42}ClIN_6Pd$ (731.45): C, 45.98; H, 5.79; N, 11.49. Found: C, 45.91; H, 5.86; N, 11.83.

***rac*-[PdCl(itmtnp)] (12).** The general method described for the synthesis of compound **5** was followed with use of compound **8** (96 mg, 0.20 mmol), palladium acetate (46 mg, 0.20 mmol), and acetic acid (15 mL). The acetic acid was evaporated and a solution of lithium chloride (42 mg, 1.02 mmol) in dichloromethane/water (1:1, 20 mL) was added. The resulting solution was stirred for 6 h at room temperature. Water (20 mL) was added to the solution and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum and the residue was purified by column chromatography, using a mixture of hexane/ethyl acetate as eluent followed by elution with ethyl acetate. A yellow solid was obtained and this was recrystallized from dichloromethane/hexane. Yield 49 mg, 40%. Mp: 183−185 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J = 6.6 Hz, 3H, $CHCH_2(CH_2)_6CH_3$), 1.16−1.29 (m, 12H), 2.42−2.54 (m, 1H) and 2.70−2.82 (m, 1H) ($CHCH_2(CH_2)_6CH_3$), 2.70−2.82 (m, 1H, $CHCH_2(CH_2)_6CH_3$), 5.18 (A of ABq, J = 14.5 Hz, 1H, NCH_2), 5.28 (t, J = 7.5 Hz, 2H, $CHCH_2(CH_2)_6CH_3$), 5.51 (B of ABq, J = 14.5 Hz, 1H, NCH_2), 7.36 (br s, 1H, H3 benzene), 7.41 (br s, 1H, H5 benzene), 8.30 (s, 1H, H5 triazole), 8.35 (s, 1H, H5 triazole), 8.62 (s, 1H, H3 triazole), 8.63 (s, 1H, H3 triazole). ^{13}C NMR: δ 14.1 ($CHCH_2(CH_2)_6CH_3$), 22.6, 26.4, 28.7, 29.1, 29.2, 31.7 ($CHCH_2(CH_2)_6CH_3$), 39.9 ($CHCH_2(CH_2)_6CH_3$), 55.1 (NCH_2), 67.4 ($CHCH_2(CH_2)_6CH_3$), 89.1 (CI), 135.3 and 135.4 (C3 and C5 benzene), 136.5 (C2 benzene), 137.2 (CPd), 141.1 (C6 benzene), 143.5 (C5 triazole), 143.6 (C5 triazole), 154.8 (C3 triazole), 154.9 (C3 triazole). MS(FAB): m/z 1203 [2 M^+ − Cl + 1], 583 [M^+ − Cl]. Anal. Calcd for $C_{20}H_{26}ClIN_6Pd$ (619.24): C, 38.79; H, 4.23; N, 13.57. Found: C, 39.12; H, 3.89; N, 13.21.

Table 3. Crystal Data and Structure Refinement for [PdI(btmp)] (6)

formula	$C_{24}H_{22}I_2N_{12}Pd_2$
fw	945.14
T (K)	293(2)
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	19.254(2)
b (Å)	8.222(2)
c (Å)	18.454(1)
β (deg)	108.2(2)
V (Å^3)	2775.2(4)
Z	4
Dc (g cm^{-3})	2.262
μ (mm^{-1})	3.561
F(000)	1792
cryst dimens (mm^3)	0.4 × 0.2 × 0.12
θ range (deg)	1.11 to 24.97
hkl ranges	$-20 \le h \le 20$, $0 \le k \le 9$, $0 \le l \le 22$
data/parameters	5011/361
goodness-of-fit on F^2	1.001
final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0394$; $wR_2 = 0.0798$
largest diff peak (eÅ^{-3})	0.610/−0.709

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

X-ray Structure Determination for [PdI(btmp)] (6). Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator Mo Kα radiation (λ = 0.71073 Å) using an $\omega/2\theta$ scan technique. The final unit cell parameters were determined from 25 well-centered and refined by the least-squares method. The space group was determined from the systematic absences and this was vindicated by the success of the subsequent solutions and refinements. The structures were solved by direct methods with the SHELXS computer program[28] and refined on F^2 by full-matrix least-squares (SHELXL-97).[29] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor with use of a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 3.

Acknowledgment. The authors gratefully acknowledge the Junta de Comunidades de Castilla−La Mancha (JCCM) for their financial support (project PAI-02-016). J.G. also acknowledges JCCM for a grant.

Supporting Information Available: Variable-temperature NMR experiments for compounds **5**, **6**, and **10**; NOE-difference spectra for compounds **11** and **12**; and details of data collection, refinement, atom coordinates, anisotropic displacement parameters, hydrogen bond network, and bond lengths and angles for complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020764I

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