Chiral Mono- and Bis-annelated Cyclopentadienyl Ligands Derived from Tartaric Acid: Synthesis of [(η^5-Cyclopentadienyl)RuCl(cod)] and [(η^5-Cyclopentadienyl)(η^6-benzene)Ru]PF_6 Derivatives

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The synthesis of chiral mono- and bis-annelated 1,3-cyclopentadienes derived from tartaric acid, a chiral pool starting material, is described. In addition to known functionalized chiral 1,3-cyclopentadienes, new derivatives have also been structurally characterized by X-ray crystallographic and NMR spectroscopic studies. Neutral and cationic ruthenium(II) complexes, containing a mono-annelated chiral cyclopentadienyl ligand (**1**), have been successfully prepared. The X-ray crystal structure of [(η^5-Cp′)Ru(η^6-benzene)]-[PF_6], Cp′ = **1**, has been determined.

Introduction

Transition metal complexes containing chiral η^5-indenyl, η^5-fluorenyl, and η^5-cyclopentadienyl (Cp) ligands are widely used in asymmetric synthesis.[1] There are many examples of such complexes being used as catalysts for stereoselective hydrogenation,[2] carboalumination,[3] olefin polymerization[4] particularly with chiral zirconocenes,[5] and carbon−carbon bond forming reactions.[6] The chiral pool provides a rich source of chirality for such ligands. Indeed, menthyl- and related terpenyl-derived η^5-cyclopentadienyl ligands have been used in several transition metal complexes, e.g., Pd,[7] Rh,[8] Ru,[9] Co,[10] Zr,[11] Ti,[12] and Fe.[13] The incorporation of chirality into the cyclopentadienyl ligand can be achieved in a number of ways. A useful approach involves the preparation of a fused bicyclic chiral auxiliary derived from camphor,[14] tartrate,[15] nopol,[16] and other terpenes.[17]

We describe in this report the preparation of annelated cyclopentadienyl ligands **1** and **2**, derived from tartaric acid **3**, the synthesis of which turned out to be nontrivial in our hands, but could be accomplished in synthetically useful yields through *careful* choice of reaction conditions (Figure 1). The preparation of mono-annelated diol **8** and bis-annelated tetra-alcohol **9** derivatives provides scope for the introduction of various substituents and potential for use in hydrogen-bonded networks. Two ruthenium(II) complexes (**15** and **16**) containing ligand **1** have also been prepared.

Results and Discussion

Our initial studies focused on chiral annelated 1,3-cyclopentadiene **1**, first prepared by Halterman and co-workers through reaction of sodium cyclopentadienide (NaCp) with 2,3-*O*-isopropylidene-(*S*,*S*)-threitol ditosylate **4**.[15b,18] Heller and co-workers later found that careful purification of the crude reaction mixture also provided the bis-annelated cyclopentadiene **2**.[15a] While the yield of **2** was low (4%), compound **1** could be isolated and treated further with NaH, followed by addition of **4**, affording **2** in an overall yield of 25%. In terms of application, both **1** and **2** were deprotonated using LDA and reacted with [$Co(PPh_3)_3Cl$] in the presence of 1,5-cyclooctadiene to give chiral cobalt complexes of the type [(η^5-Cp′)Co(cod)] (Cp′ refers to the chiral cyclopentadienyl group).[15a]

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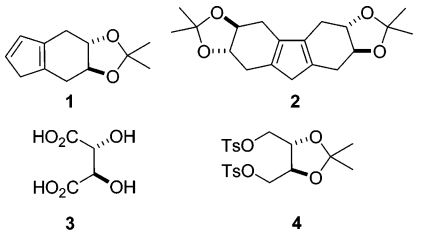


Figure 1. Mono-annelated ligand **1** and bis-annelated ligand **2**, and their synthetic precursors.

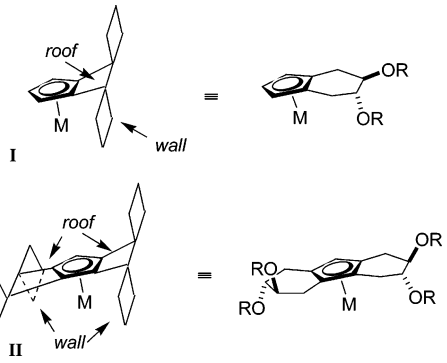


Figure 2. Potential chiral transition metal cyclopentadienyl complexes.

Our interest in these compounds was driven by the need to prepare novel nonracemic η^5-cyclopentadienyl transition metal complexes[19] containing ligands **1** and **2** and novel ligand assemblies possessing greater steric hindrance about the oxygen atoms (I and II, Figure 2).

After several attempts at preparing compounds **1** and **2** it was determined that the *key* conditions required for successful annelation of 1,3-cyclopentadiene with **4** were (1) rigorous oxygen- and moisture-free conditions; (2) slow and consistent addition of the ditosylate to a NaCp solution in THF (over 1 h); (3) slow removal of EtOAc *in vacuo* after workup without additional heating (essential); (4) use of a basic workup, 0.5 M $NaHCO_3$, until the organic layer is neutral; and (5) rapid column chromatography on silica gel.[20] Using these conditions we were able to prepare **1** and **2** in 20% and 3.4% yields, respectively. As part of this study, we were able to successfully crystallize the mono-annelated compound **1** from diethyl ether/hexane, which could be characterized by X-ray analysis (Figure 3).

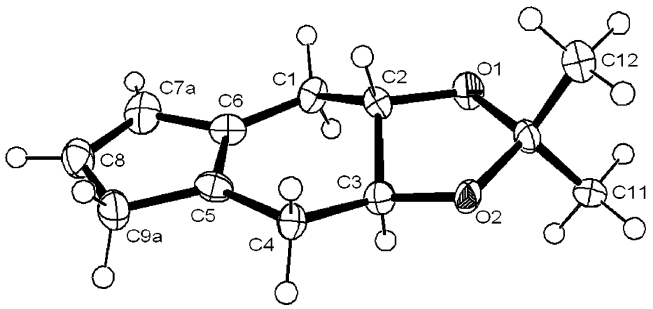


Figure 3. ORTEP plot of **1** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)−C(2) = 1.489(11); C(5)−C(6) = 1.358(12); C(2)−C(3) = 1.499(9); C(2)−O(1) = 1.441(8).

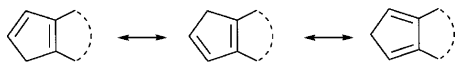
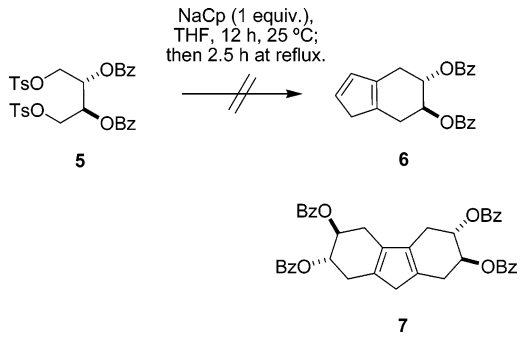


Figure 4. Resonance forms for **1**.

Scheme 1. Attempted Synthesis of 6 and 7 from Ditosylate 5



The X-ray structure reveals a 1:1 mixture of two isomeric forms (I and II, Figure 4), where the C5−C6 double bond is retained (identical by NMR spectroscopy). The higher energy isomer III (contains two bridgehead C sp^2 atoms)[15a] is not observed crystallographically. In all previous studies,[15] **1** has been depicted as isomer III. The ^{13}C NMR spectrum of **1** (in $CDCl_3$) shows four alkenyl carbon signals (δ 136.8, 136.3, 133.6, and 132.5). Isomer III possesses symmetry; thus only two alkenyl carbon signals would be seen if this were the correct form. The dihedral angle for O1−C2−C3−O2 is 42.3°, which is conformationally restricted by the cyclic acetal group.

The annelation of ditosylate **5**, using the conditions described *vide supra*, was also attempted (Scheme 1). Treatment of **5** with NaH failed to give the desired dibenzoate **6** or tetrabenzoate **7** (**5** was consumed and some ester decomposition was seen).

The difference in reactivity of **4** relative to **5** in the annelation reaction can be in part attributed to C2−C3 restricted bond rotation in **4**. In **5**, C2−C3 bond rotation will be dominated by steric effects, thus lowering the concentration of the reactive rotamer required for intramolecular S_N2 attack.

Derivatization of compounds **1** and **2** is possible. For example, careful hydrolysis of **1** provides diol **8** in 87% yield (Scheme 2). Subsequent treatment of **8** with benzoyl chloride or acetic anhydride in the presence of pyridine affords dibenzoate **6** and diacetate **10** in 75% and 95% yields, respectively. Similarly, the equivalent bis-annelated compound **9** could be prepared by careful hydrolysis of **2** (64%). Esterification with benzoyl chloride or acetic anhydride gave **7** and **11**, in 44% and 98% yields, respectively.

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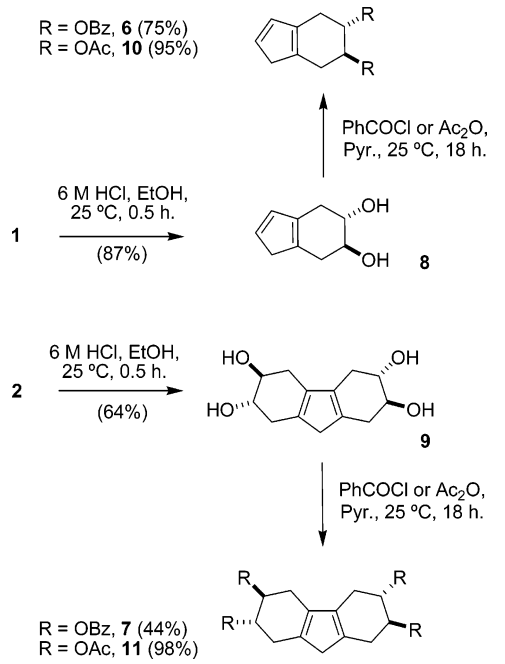
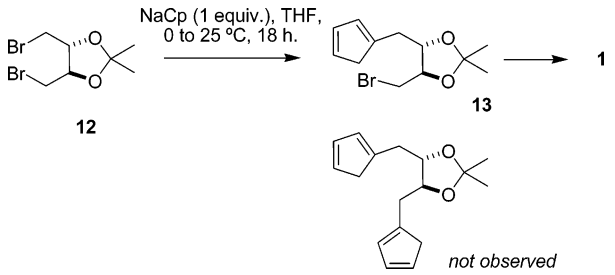
Scheme 2. Synthesis of Derivatized Cyclopentadienyl Compounds



Scheme 3. Detection of Mono-bromide 13 by GC/MS



We anticipated that dibromide **12** would be more reactive than ditosylate **4**. Compound **12** was prepared by reaction of **4** with 2 equiv of LiBr in DMSO at 80 °C for 3 h. The reaction of **12** with NaCp gave compound **1** in a similar yield to **4**. The advantage of using the dibromide reagent negates the difficulties associated with removal of large quantities of the tosyl salt/tosic acid byproducts during the reaction workup. Interestingly for the first time we detected the intermediate product, mono-bromide **13** (ca. 25%, by GC/MS), although this decomposes on workup (Scheme 3).

Compounds **8**, **9**, and **10** crystallize from CH_2Cl_2/ether (1:5, v/v) solutions. The point made *vide supra* about the correct structural form for **1** is mirrored in ^{13}C NMR spectra of compounds **6**, **8**, and **10** and the X-ray analysis of the latter two. The dihedral angles for the O−C−C−O fragment is interesting to compare in these structures. For the diol derivatives **8** and **9** the equivalent dihedral angles are 53.02° and 53.04°, respectively. The hydroxyl substituents occupy equatorial positions on the six-membered ring. In contrast, for diacetate **10** the dihedral angle O1−C7−C8−O3 is 175.41°. Here, the acetoxy substituents occupy axial positions on the six-membered ring. Moreover the arrangement of the acetoxy substituents in **10** supports the model depicted in Figure 2. Finally, in each of the three structures the six-membered ring fragments exhibit half-chair conformations.

Anticipating that Ru(II) complexes [(η^5-Cp′-**1**)RuCl(cod)] (**15**) and [(η^5-Cp′-**1**)(η^6-C_6H_6)Ru]PF_6 (**16**) could be useful in asymmetric catalysis, their preparation was next investigated

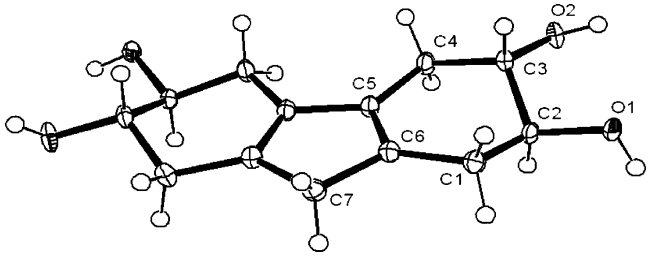


Figure 5. ORTEP plot of **9** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(6)−C(7) = 1.5066(19); C(5)−C(6) = 1.347(2); C(1)−C(6) = 1.4953(18); C(2)−O(1) = 1.4298(15); C(2)−C(3) = 1.5282(19).

(Scheme 4). The chiral ligands described above possess only one homotopic face for complexation; thus single diastereoisomeric complexes are expected.[15a]

Initial synthetic routes[21] failed for these complexes containing all the chiral cyclopentadienyl ligands detailed above. Major side-reactions involve ruthenocene formation (ca. 40−50% yields); where EtOH or MeOH were used as mandatory solvents, formation of Ru(II) products **17a** and **17b**,[22] respectively, hindered many attempts (Scheme 5).

For the synthesis of **15**, attention was placed on a procedure described for [(η^5-Cp)RuCl(cod)] and related derivatives by Singleton and co-workers.[23] Treatment of [RuH(cod)(NH_2-NMe_2)$_3$]PF_6, formed by reaction of [$RuCl_2$(cod)]$_n$ with *N*,*N*-dimethylhydrazine in water/MeOH, with the TlCp′ salt of **1** in acetone at reflux gave intermediate hydride complex [(η^5-Cp′-**1**)RuH(cod)] as an off-white solid in 64% yield, which was sensitive to light. Treatment of [(η^5-Cp′-**1**)RuH(cod)] with CCl_4 (purity >99%) gave complex **15** as golden yellow flakes in modest yield (from two runs in 37% and 42% yields, respectively). This yield dropped dramatically if the CCl_4 was not doubly distilled. Using the method[24] described by Zhang et al. the TlCp′ salt of **1** reacted with [(η^6-C_6H_6)$RuCl_2$]$_2$ in acetonitrile, affording the intermediate complex [(η^5-Cp′-**1**)(η^6-C_6H_6)RuCl] (not isolated), which was reacted directly with NH_4PF_6 in MeOH to give chiral complex **16** in 32% yield.

Complex **16** crystallized from CH_2Cl_2, allowing an X-ray structure to be obtained (Figure 7). The structure is in the *P*2 space group ($Z = 4$). It is almost in the higher symmetry *P*2/*c* space group; the chiral bridgehead carbons, C13, C14, etc., break the symmetry. The all *S*-configuration is known from the synthesis and confirmed by anomalous dispersion. Use of the higher symmetry *P*2/*c* space group, which would contain enantiomers, gave a much poorer *R* factor, etc. Two molecules of CH_2Cl_2 from crystallization were disordered, and a two-site model for the carbons was used for structure refinement (occupancy for each carbon site being allowed to refine). The cyclohexyl fragment of the ligand is essentially the same as the free ligand **1**; the dihedral angle O1−C13−C14−O2 of 42.97° is similar to the equivalent dihedral angle in **1** (O1−C2−C3−O2, *vide supra*).

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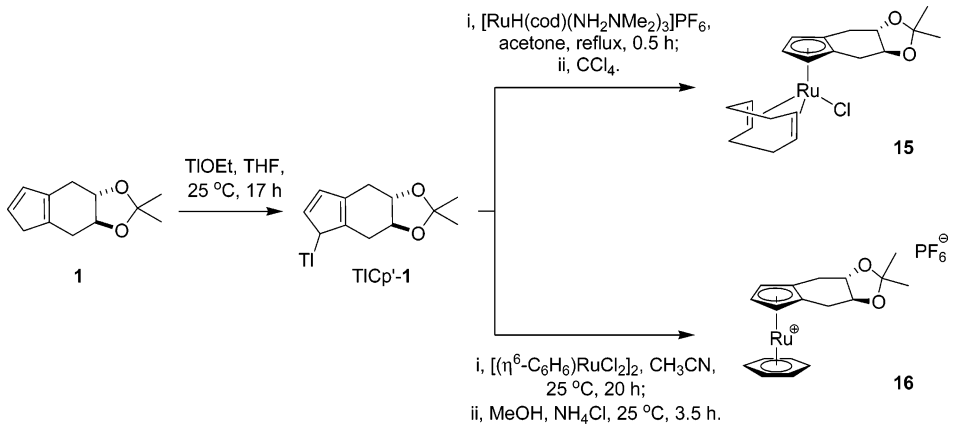
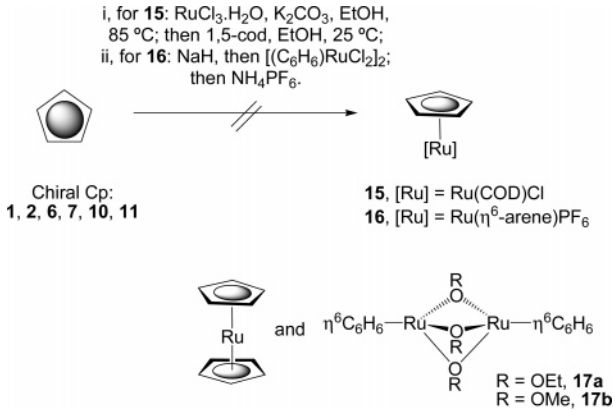
Scheme 4. Synthesis of Neutral and Cationic Ruthenium(II) Complexes



Scheme 5. Complexation of Chiral Cyclopentadienyl Ligands to Ruthenium Using Classical Synthetic Methods



Conclusion

In summary, important reaction conditions have been described for the preparation of mono- and bis-annelated cyclopentadienyl ligands derived from the chiral pool starting material tartaric acid. Some useful functionalized cyclopentadienyl derivatives, and neutral and cationic ruthenium(II) complexes of cyclopentadienyl **1**, have been synthesized.

Experimental Section

General Procedures. 2,3-*O*-Isopropylidene-(*R*,*R*)-threitol ditosylate **4** (prepared on a 0.5 mol scale),[25] 2,3-*O*-isopropylidene-(*R*,*R*)-threitol dibromide **12**,[26] $[RuCl_2(cod)]_n$,[27] and $[RuH(cod)(NH_2NMe_2)_3]PF_6$[23] were prepared according to literature procedures. All other reagents and metal precursors were purchased from Sigma-Aldrich or Strem Chemicals. Solvents were dried where necessary using standard procedures prior to use and stored under an argon atmosphere. Nitrogen gas was oxygen-free and was dried immediately prior to use by passage through an 80 cm column containing sodium hydroxide pellets and silica. Argon gas was used directly via balloon transfer or on a Schlenk line. TLC analysis was performed routinely using Merck 5554 aluminum-backed silica plates or Macherey-Nagel polygram ALOX N/UV254 aluminum oxide-coated plastic sheets. Compounds were visualized using UV light (254 nm) and a basic aqueous solution of potassium permanganate or acidic DNP (dinitrophenol hydrazine). GC parameters: Analysis was performed using a Varian CP-3800 GC equipped with a CP-8400 autosampler. Separation was achieved using a DB-1 column (30 m × 0.32 mm, 0.25 μm film thickness) with carrier gas flow rate of 3 mL min^{-1} and a temperature ramp from 50 to 250 °C at 20 °C min^{-1}. The injection volume was 1 μL with a split ratio of 50. Mass spectrometry was carried out using a Fisons Analytical (VG) Autospec instrument. ^1H NMR spectra were recorded at 400 MHz using a JEOL ECX 400 spectrometer or 500 MHz on a Bruker AV 500 spectrometer; ^{31}P NMR spectra at 202 MHz (^1H decoupled). Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

Preparation of (3a*S*,8a*S*)-4,5,8,8a-Tetrahydro-2,2-dimethyl-3a*H*-indeno[5,6-*d*][1,3]dioxole (1) and Bis-annelated Compound 2. A 1 L three-necked round-bottomed flask was fused with sodium hydride (3.52 g, 60%, 88 mmol). This was washed with pentane (3 × 10 mL). THF (200 mL), followed by freshly distilled cyclopentadienyl (2.64 g, 3.3 mL, 40.0 mmol), was added and the mixture stirred for 10 min at room temperature. Gas evolution incurred and the suspension turned from a white to a pink color after 3 min. A solution of 2,3-*O*-isopropylidene-(*S*,*S*)-threitol ditosylate (20.66 g, 43.9 mmol) in THF (100 mL) was added. The mixture was stirred for 12 h at room temperature and then heated at reflux for 2.5 h. The mixture was allowed to cool, and 0.5 M HCl (40 mL) was added followed by ethyl acetate (100 mL). The organic layer was then washed with 0.5 M $NaHCO_3$ (3 × 40 mL), dried over anhydrous $MgSO_4$, and filtered and the solvent removed *in vacuo*. Column chromatography on silica gel (20:1, pentane/diethyl ether) afforded **1** (1.68 g, 20%) as a pale yellow solid; further elution with (10:1 pentane/diethyl ether) gave **2** as a colorless solid (0.48 g, 3.4%). Data for **1**: mp 44−45, lit.[18a] 44.0−44.5; [found: C, 75.4; H, 8.55; $C_{12}H_{16}O_2$ requires C, 74.97; H, 8.39]; $[\alpha]_D^{20}$ 122.5 (*c* 2.62, EtOH), lit.[18a] 113.1 (*c* 0.275, EtOH); ν_{max} (neat) 2922, 1460, 1375, 1232, 1136, 1075 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.20−6.29 (2H, m, (CH_2CH═CH), 3.61−3.76 (2H, m, (OC*H*C*H*O), 2.62−2.92 (2H, m, (C*H*$CH_2)_2$), 1.40 (6H, s, ($CH_3)_2$C); δ_C (100.6 MHz, $CDCl_3$) 136.8, 136.3, 133.6, 132.5, 110.2, 43.0, 30.1, 29.2, 27.14, 27.08; *m*/*z* (CI) 193 (MH^+), 152, 135, 117. Data for **2**: mp 154−156, lit.[15a] 155−156; [found: C, 71.9; H, 8.3; $C_{19}H_{26}O_4$ requires C, 71.67; H, 8.23%]; $[\alpha]_D^{20}$ +232.6 (*c* 1, $CHCl_3$) lit.[15a] $[\alpha]_D^{20}$ +235.85 (*c* 1, $CHCl_3$); ν_{max} (neat) 2922, 1376, 1234, 1140, 1105 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.73−3.80 (4H, m, 2 × OC*H*C*H*O), 2.20−2.80 (10H, m, (C═CCH_2C═C) and 2 × ($CHCH_2)_2$), 1.45 (12H, s, 2 × ($CH_3)_2$C); δ_C (100.6 MHz, $CDCl_3$) 136.2, 136.0, 110.4, 77.6, 44.0, 30.4, 27.8, 27.2; *m*/*z* (EI) 318 (M^+), 243, 205, 129.

Preparation of (2*S*,3*S*)-1,4-Ditolylsulfonylbutane-2,3-dibenzoate (5). (2*S*,3*S*)-1,4-Ditolylsulfonylbutane-2,3-diol was prepared

(25) Carmack, M.; Kelley, C. J. *J. Org. Chem.* **1968**, *33*, 2171.
(26) Townsend, J. M.; Blount, J. F.; Chu Sun, R.; Zawoiski, S.; Valentine, D., Jr. *J. Org. Chem.* **1980**, *45*, 2995.
(27) Albers, M. O.; Ashworth, T. V.; Oosthizen, H. E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 69.

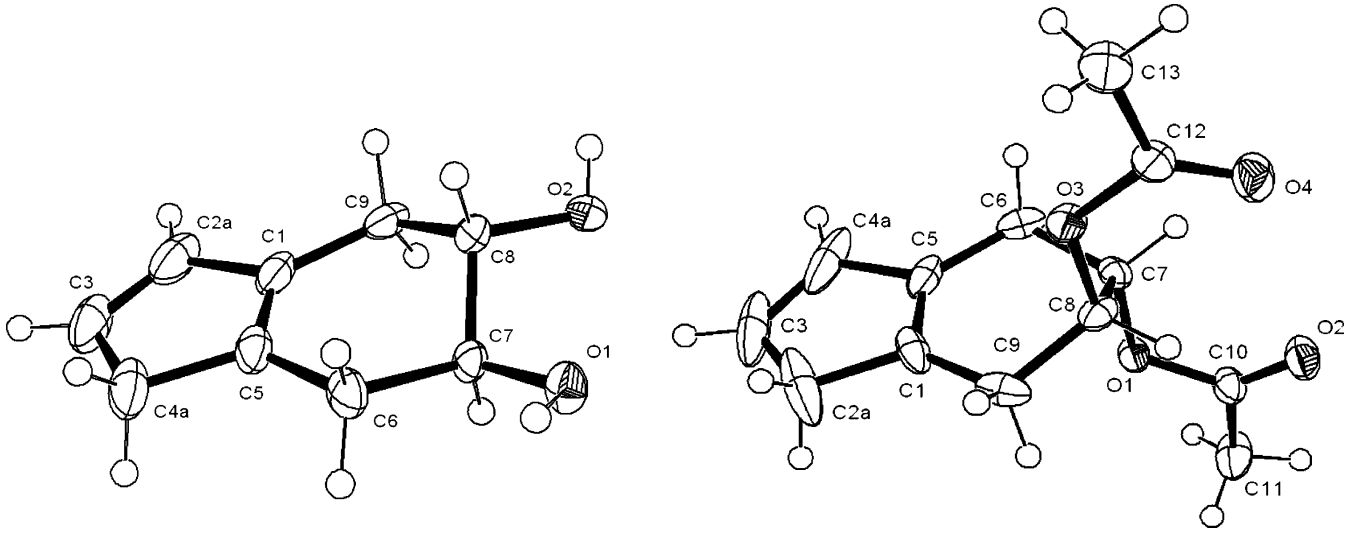


Figure 6. ORTEP plots of diol **8** and diacetate **10** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances for **8** (Å): C(1)−C(5) = 1.341(5); C(5)−C(6) = 1.500(5); C(6)−C(7) = 1.517(4); C(7)−O(1) = 1.424(4); C(7)−C(8) = 1.523(4). Selected distances for **10** (Å): C(1)−C(5) = 1.339(3); C(5)−C(6) = 1.483(3); C(6)−C(7) = 1.511(2); C(7)−O(1) = 1.4571(16); C(7)−C(8) = 1.520(2); C(10)−O(1) = 1.3484(16).

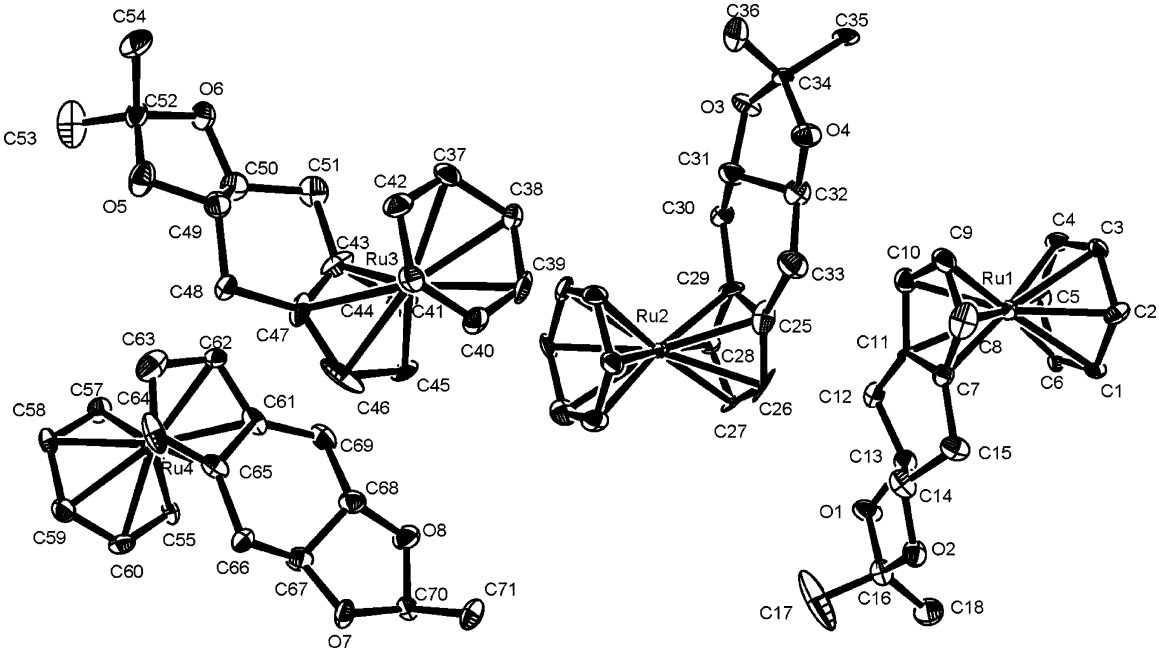


Figure 7. ORTEP plot of **16** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. The PF_6 anion and a CH_2Cl_2 molecule are omitted for clarity. Selected distances (Å): C(1)−Ru(1) = 2.211(8); C(2)−Ru(1) = 2.204(9); C(3)−Ru(1) = 2.223(8); C(4)−Ru(1) = 2.220(8); C(5)−Ru(1) = 2.242(8); C(6)−Ru(1) = 2.204(8); C(7)−Ru(1) = 2.225(7); C(9)−Ru(1) = 2.142(9); C(13)−C(14) = 1.503(9); C(13)−O(1) = 1.436(7); C(14)−O(2) = 1.418(9).

according to the literature.[28] To a solution of the diol (18.0 g, 41.8 mmol) in pyridine (200 mL) was added benzoyl chloride (58.77 g, 0.418 mol) at 0 °C. The mixture was allowed to warm to room temperature and further stirred overnight. The resulting precipitate was filtered and washed with water (2 × 100 mL). The crude ditosylate was recrystallized from $CHCl_3$, affording the product as a white fluffy solid (22.8 g, 85%): mp 188−190 [found: C, 59.9; H, 4.96; $C_{32}H_{30}O_{10}S_2$ requires C, 60.18; H, 4.73]; $[\alpha]_D^{20}$ −17.0 (*c* 0.5, $CHCl_3$); ν_{max} (Nujol) 2919, 1715, 1460, 1366, 1176 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.88 (4H, m, Ar), 7.70 (4H, d *J* 8.2 Hz, Ar*H*), 7.52−7.58 (2H, m, Ar*H*), 7.35−7.44 (4H, m, Ar*H*), 7.17 (4H, d *J* 8.2, Ar*H*), 5.54−5.56, (2H, m, 2 × C═OOC*H*), 4.31−4.35 (4H, m, 2 × CH_2), 2.31, (6H, s, 2 × CH_3); δ_C (100.6 MHz, $CDCl_3$) 165.5, 145.6, 133.9, 132.2, 130.2, 130.1, 128.7, 128.9, 128.2, 69.1, 66.7, 21.3; *m*/*z* (CI) 656 (MNH_4^+), 467, 416, 312, 190, 105; $C_{32}H_{30}O_{10}S_2$ requires 638.1280, found 638.1289.

Preparation of (5*S*,6*S*)-4,5,6,7-Tetrahydro-1*H*-indene-5,6-dibenzoate (6). To a solution of compound **8** (0.165 g, 1.084 mol) in pyridine (3 mL) was added benzoyl chloride (0.381 g, 2.71 mol). The mixture was stirred overnight. Ethyl acetate (40 mL) was then added and washed with 0.5 M HCl (10 mL) and water (10 mL). The crude solution was dried over anhydrous $MgSO_4$ and filtered and the solvent removed *in vacuo*. Column chromatography on silica gel (20:1, pentane/diethyl ether) afforded the product as a colorless gum (0.294 g, 75%): $[\alpha]_D^{20}$ +135.67 (*c* 1.95, $CHCl_3$); ν_{max} (Nujol) 1720, 1278, 1113, 709 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.78−7.90 (4H, m, Ar*H*), 7.20−7.40 (6H, m, Ar*H*), 6.23−6.25 (2H, m, CH_2CH═C*H*), 5.55−5.62 (2H, m, OC*HCH*O), 2.50−3.00

(28) Zhang, S.-Q.; Zhang, S.-Y.; Feng, R. *Tetrahedron: Asymmetry* **1991**, *2*, 173.

Table 1. X-ray Data for 1, 8, 9, 10, and 16

	1	8	9	10	16
empirical formula	$C_{12}H_{16}O_2$	$C_9H_{12}O_2$	$C_{13}H_{18}O_4$	$C_{13}H_{16}O_4$	$C_{37}H_{44}Cl_2F_{12}O_4P_2Ru_2$
fw	192.25	152.19	238.27	236.26	1115.70
temperature/K	100(2)	115(2)	115(2)	115(2)	115(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*C*2	*P*1	*C*2	*P*2(1)	*P*2
a/Å	19.719(5)	5.0093(9)	19.5862(19)	8.5111(9)	23.2056(11)
b/Å	7.3842(19)	5.7478(10)	6.9648(7)	6.6500(7)	8.1184(4)
c/Å	15.748(4)	13.953(3)	8.4605(8)	10.6084(11)	23.2436(11)
α/deg	90	97.094(4)	90	90	90
β/deg	113.273(5)	98.241(4)	97.906(2)	100.347(2)	110.3650(10)
γ/deg	90	93.637(4)	90	90	90
volume/Å^3	2106.5(9)	393.19(12)	1143.16(19)	590.66(11)	4105.2(3)
Z	8	2	4	2	4
density (calc)/Mg m^{-3}	1.212	1.285	1.384	1.328	1.805
absorp coeff/mm^{-1}	0.081	0.090	0.102	0.098	1.038
cryst size/mm^3	0.27 × 0.10 × 0.02	0.28 × 0.13 × 0.02	0.23 × 0.20 × 0.06	0.18 × 0.17 × 0.16	0.20 × 0.13 × 0.06
no. of reflns collected	8462	2654	5935	6711	42 845
no. of indep reflns	2031	2174	2826	3339	20 334
R(int)	0.0621	0.0143	0.0230	0.0268	0.0304
goodness of fit	1.132	1.060	1.054	1.058	1.029
R [$I > 2\sigma(I)$]	0.0760	0.0462	0.0385	0.0453	0.0493
wR (F^2), all data	0.0983	0.0610	0.0403	0.0489	0.0710

(6H, m, 2 × C*H*C*H*$_2$ and C*H*$_2$CH═CH); δ_C (100.6 MHz, $CDCl_3$) 166.0, 133.0, 132.9, 129.5, 128.2, 71.5, 71.4, 42.9, 30.0, 29.1; *m*/*z* (CI) 378 (MNH_4^+), 239, 52; $C_{23}H_{24}NO_4$ requires 378.1705, found 378.1709.

Preparation of (5*S*,6*S*)-4,5,6,7-Tetrahydro-1*H*-indene-5,6-diol (8). To a solution of **1** (0.5 g, 2.60 mmol) in ethanol (10 mL) was added 2 M HCl (1.5 mL). The mixture was stirred for 1 h. KOH (0.17 g) was then added and the mixture stirred for 30 min. The organic layer was extracted with ethyl acetate (2 × 40 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, and filtered and the solvent removed *in vacuo*. Column chromatography on silica gel (1:1, pentane/ethyl acetate) afforded the product as a white solid (0.346 g, 87%): mp 110−111; [found: C, 70.6; H, 8.0; $C_9H_{12}O_2$ requires C, 71.03; H, 7.95]; $[\alpha]_D^{20}$ +140.0 (*c* 1, $CHCl_3$); ν_{max} (Nujol) 2928, 2850, 1458, 1378 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.22−6.24 (2H, m, CH_2CH═CH), 3.72−3.78 (2H, m, HOC*H*C*H*O), 2.20−2.79 (6H, m, 2 × CHC*H*$_2$ and C*H*$_2$CH═CH), 1.98 (2H, s, 2 × OH); δ_C (100.6 MHz, $CDCl_3$) 136.0, 135.8, 133.4, 131.9, 72.8, 42.9, 32.9, 31.9; *m*/*z* (CI) 153 (MH^+), 135; $C_9H_{12}O_2$ requires 153.0916, found 153.0917.

Preparation of (2*S*,3*S*,6*S*,7*S*)-2,3,4,5,6,7,8,9-Octahydro-1*H*-fluorene-2,3,6,7-tetraol (9). To a solution of **2** (0.633 g, 1.99 mmol) in ethanol (10 mL) was added 2 M HCl (2 mL) and the solution stirred for 30 min. The resulting precipitate was filtered and washed with diethyl ether (2 × 50 mL), affording the product as a white powder (0.30 g, 64%): mp 184−185 [found: C, 64.93; H, 7.71; $C_{13}H_{18}O_4$ requires C, 65.53; H, 7.61]; $[\alpha]_D^{20}$ +176.0 (*c* 0.6 DMSO); ν_{max} (Nujol) 2954, 2927, 2854, 1460, 1376 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.55−4.59 (4H, m, 2 × HOC*H*C*H*OH), 3.39−3.48 (4H, m, 4 × O*H*), 1.82−2.60 (10H, m, 2 × HOCH(CHC*H*$_2$)C*H*$_2$ and C═CC*H*$_2$C═C); δ_C (100.6 MHz, $CDCl_3$) 135.3, 135.6, 70.9, 70.7, 43.1, 32.4, 30.0; *m*/*z* (CI) 239 (M^+), 221; $C_{13}H_{18}O_4$ requires 239.1283; found 239.1280.

Preparation of (5*S*,6*S*)-4,5,6,7-Tetrahydro-1*H*-indene-5,6-diacetate (10). To a solution of **8** (0.250 g, 1.643 mol) in pyridine (2 mL) was added Ac_2O (0.838 g, 8.213 mmol). The mixture was stirred overnight. Methanol (10 mL) was added and the solvent removed *in vacuo*. Column chromatography on silica gel (10:1, pentane/diethyl ether) afforded the product as a pale yellow solid (0.368 g, 95%): mp 84−87; [found: C, 66.0; H, 7.0; $C_{13}H_{16}O_4$ requires C, 66.09; H, 6.83]; $[\alpha]_D^{20}$ +106.0 (*c* 0.67, $CHCl_3$); ν_{max} (Nujol) 2915, 1742, 1460, 1372, 1247 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.15−6.23 (2H, m, CH_2CH═CH), 5.09−5.13 (2H, m, C*H*$_2$CH═CH), 2.72−2.80 (4H, m, 2 × CHC*H*$_2$), 2.25−2.55 (2H, m, 2 × CHC*H*$_2$), 1.99 (6H, s, 2 × CH_3); δ_C (100.6 MHz, $CDCl_3$) 170.4, 134.9, 134.8, 133.1, 132.0, 70.5, 70.4, 42.9, 29.6, 28.7, 21.1; *m*/*z* (CI) 254 (MNH_4^+), 177, 116; $C_{13}H_{20}NO_4$ requires 254.1392, found 254.1392.

Preparation of (2*S*,3*S*,6*S*,7*S*)-2,3,4,5,6,7,8,9-Octahydro-1*H*-fluorene-2,3,6,7-tetraacetate (11). To a suspension of **9** (30.0 mg, 0.126 mmol) in pyridine (1 mL) was added acetic anhydride (0.130 g, 0.12 mL, 1.27 mol). The mixture was stirred for 3 days. Methanol was added and the solvent removed under reduced pressure. Column chromatography on silica gel (10:1, hexane/ethyl acetate) afforded the title compound as a white solid (50 mg, 98%): mp 168−169 [found: C, 62.03; H, 6.40; $C_{21}H_{26}O_8$ requires C, 62.06; H, 6.45]; $[\alpha]_D^{20}$ +150.8 (*c* 1.0); ν_{max} (Nujol) 2922, 1743, 1460, 1376, 1244 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.03−5.15 (4H, m, 2 × AcOC*H*C*H*OAc), 2.12−2.80 (10H, m, 4 × CHC*H*$_2$ and C═CC*H*$_2$), 1.98 (12H, s, 4 × C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$) 170.3, 134.1, 133.5, 70.2, 70.0, 43.4, 29.6, 26.9, 21.0; *m*/*z* (CI) 424 (MNH_4^+), 347, 287, 227, 166; $C_{21}H_{30}O_8N$ requires 424.1971, found 424.1963.

Preparation of (2*S*,3*S*,6*S*,7*S*)-2,3,4,5,6,7,8,9-Octahydro-1*H*-fluorene-2,3,6,7-tetrabenzoate (7). To a suspension of **9** (30.0 mg, 0.126 mmol) in pyridine (1 mL) was added benzoyl chloride (0.142 g, 1.01 mmol), and the mixture was stirred overnight. Ethyl acetate (50 mL) was then added, and the organic mixture washed with water (10 mL). The crude product was dried over anhydrous $MgSO_4$ and filtered and the solvent removed *in vacuo*. Column chromatography on silica gel (8:1, pentane/diethyl ether) afforded the title compound as a white solid (36 mg, 44%): mp 102−105 [found: C, 73.37; H, 6.77; $C_{41}H_{34}O_8$ requires C, 73.30; H, 6.78; crystallized with two molecules of $(CH_3CH_2)_2O$]; $[\alpha]_D^{20}$ +161.8 (*c* 0.5); ν_{max} (Nujol) 2940, 2903, 2855, 1722, 1461, 1376, 1275 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.88−7.90 (8H, m, Ar*H*), 7.23−7.49 (12H, m, Ar*H*), 5.52−5.55 (4H, m, 2 × OC*H*C*H*O), 2.42−3.05 (10H, m, 4 × CHC*H*$_2$ and C═CC*H*$_2$); δ_C (100.6 MHz, $CDCl_3$) 166.1, 134.2, 133.5, 133.6, 133.0, 130.1, 129.6, 128.4, 128.3, 71.4, 71.3, 43.5, 30.1, 27.5; *m*/*z* (FAB) 677 (MNa), 479, 433, 326, 176, 239, 52; $C_{41}H_{34}O_8Na$ requires 677.2151, found 677.2159.

Preparation of ThalliumCp′-1. A solution of TlOEt (1.945 g, 7.82 mmol, 1.01 equiv) in THF (2 mL) was added to a solution of MCp′H (1.5 g, 7.81 mmol, 1 equiv) in THF (17 mL) at room temperature in a drybox. After stirring for 17 h, ca. 10 mL of the solvent was removed *in vacuo*. The resulting off-white precipitate was collected on a sintered glass filter (under N_2) and washed with small amounts of toluene (5 × 5 mL). The light brown solid was

dried *in vacuo*, is air-sensitive (stored in the drybox), and was used without any further purification (2.1 g, 68%).

Preparation of Ruthenium(II) Complex 15. A suspension of [(η^4-C_8H_{12})-RuH(NH_2NMe_2)$_3$][PF_6] (0.5 g, 0.93 mmol) and TlCp′-**1** (0.40 g, 1.02 mmol) in dry and degassed acetone was heated to reflux for 0.5 h. After cooling to room temperature, the air-sensitive solution was filtered through a pad of Celite under N_2 and the solvent removed *in vacuo*. The sticky residue was extracted with dry and degassed pentane (30 mL) to give a yellow solution of [(η^5-**1**)Ru(cod)H]. Then CCl_4 (89 μL, 0.93 mmol, 1 equiv) was added, and a golden solid precipitated immediately. The solution was allowed to stir for a further 5 min and then filtered in air to yield [(η^5-Cp′-**1**)RuCl(cod)] (150 mg, 37%): mp 135−136 °C; $[\alpha]_D^{20}$ −30.0 (*c* 0.23, toluene); ν_{max} (KBr) 1454, 1437, 1379, 1232, 1137, 1079, 848, 789, 510 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.11 (1H, m), 4.95 (1H, m), 4.68 (1H, m), 4.44 (2H, m), 4.11 (1H, m), 3.96 (1H, m), 3.71 (1H, m), 3.41 (1H, m), 2.85 (1H, m), 2.73 (2H, m), 2.56 (1H, m), 2.36 (1H, s), 2.24 (3H, m), 2.09 (3H, m), 1.89 (2H, m), 1.42 (3H, s), 1.41 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) 128.7, 111.1, 105.0, 100.3, 91.8, 87.4, 80.5, 80.4, 80.4, 77.4, 76.4, 75.2, 33.6, 31.0, 29.0, 28.7, 28.0, 27.7, 27.1, 26.9, 26.0, 24.6; *m*/*z* (FAB) 402 (MH^+, 100%).

Preparation of Ruthenium(II) Complex 16. The cyclopentadienyl thallium salt TlCp′-**1** (1.0 g, 2.5 mmol) was added to a suspension of [(η^6-C_6H_6)$RuCl_2$]$_2$ (0.629 g, 1.26 mmol) in acetonitrile (50 mL). After stirring at room temperature for 20 h, the reaction mixture was filtered through Celite, and the filtrate was washed with acetonitrile (4 × 10 mL). The solution was concentrated to dryness and the residue dissolved in methanol (40 mL). Solid NH_4-PF_6 (0.4 g, 2.5 mmol) was added to this solution, whereupon the product precipitated. After 3.5 h of stirring, the reaction mixture was filtered, affording an orange solid identified as [(η^6-C_6H_6)-$RuCl_2(OMe)_3$] (18% based on [(η^6-C_6H_6)$RuCl_2$]$_2$).[2] The remaining filtrate was reduced in volume to give a white precipitate, which was collected on a frit by cannula filtration under N_2. The remaining solid was washed with methanol (3 × 20 mL) and then diethyl ether (1 × 20 mL), affording [(η^5-Cp′-**1**)RuCl(η^6-C_6H_6)]PF_6 isolated as a white solid, after drying *in vacuo* (0.41 g, 32%): mp 221−222 °C; $[\alpha]_D^{20}$ +22.8 (*c* 0.29, acetone) (circular dichroism measurements in acetonitrile reveals only one enantiomer); ν_{max} (KBr) 1442, 1380, 1232, 1135, 833, 727, 561 cm^{-1}; δ_H (400 MHz, CD_3OCD_3) 6.38 (6H, s), 5.50 (1H, m), 5.54 (1H, m), 5.41 (1H, t, J = 2.5 Hz) 4.02 (1H, ddd, J = 5.2, J = 9.1, J = 10.7 Hz), 3.69 (1H, ddd, J = 5.9, J = 9.1, J = 11.5 Hz), 3.05 (2H, m), 2.84 (1H, m), 2.56 (1H, dd, J = 10.7, J = 15.1 Hz), 1.41 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CD_3OCD_3) 113.3, 101.6, 99.7, 89.6, 81.6, 81.1, 79.9, 79.7, 78.7, 29.70, 28.9, 28.3, 28.2; δ_P (161 MHz, CD_3OCD_3) −143.7 (septet, $^1J_{PF}$ = 708 Hz); *m*/*z* (LRCI) 371 (MH^+, 100%); $C_{18}H_{22}O_2Ru^+$ 371.059, found from isotopic distribution (nominal mass calculation).

Data for compounds **1** (CCDC 644840), **8** (CCDC 644837), **9** (CCDC 644838), **10** (CCDC 644836), and **16** (CCDC 644839) are available through the Cambridge Crystallographic Database Centre.

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Supporting Information Available: The X-ray coordinates and associated data tables are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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