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Conformational Behavior and Coordination Chemistry of 2,11-Dithia[3.3]*ortho*cyclophane with Platinum Group Metals

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The compound 2,11-dithia[3.3]*ortho*cyclophane (L) is a mesocyclic dithioether that can act as a bidentate ligand in different conformations. In the ionic heteroleptic complexes [PtL(η^4-cod)][CF_3SO_3]$_2$ (**1**), [RhL(η^4-cod)][CF_3SO_3] (**2**), and [IrL(η^4-cod)][CF_3SO_3] (**3**) (cod = 1,5-cyclooctadiene), L is coordinated in the *anti I* conformation both in solution and in the solid state, as revealed by an X-ray diffraction study of complex **1**. However, in complexes [PdL-(PPh_3)$_2$][SO_3CF_3]$_2$ (**4**) and [PtL(PPh_3)$_2$][SO_3CF_3]$_2$ (**5**), L exhibits two different conformations: *anti I* and *anti II* in a 40:60 ratio, as observed by ^{1}H and ^{31}P NMR spectroscopy, with no exchange up to 90 °C. The homoleptic complexes [PdL_2][SO_3CF_3]$_2$ (**6**) and [PtL_2][SO_3CF_3]$_2$ (**7**), with two ligands bound to the metal, display two isomers in solution, one of them with L in conformations *anti I–anti II* and the other with conformations *anti II–anti II* with a 75:25 ratio. The X-ray structure of **6** showed only the presence of the *anti II–anti II* isomer in the solid state. All complexes were synthesized by the reaction of a suitable chloride complex with 2 equiv of silver triflate and 1 equiv of L.

Introduction

Particular attention has been recently devoted to the design and syntheses of metal−cyclophane complexes because of their unique molecular properties and potential applications as anion[1] and molecular[2] sensors, molecular receptors,[3] electron-transfer assemblies,[4] and conductive polymers.[5] Initially, the coordination chemistry of cyclophanes was dominated by metal−arene compounds, the so-called metallocenophanes;[6] however, incorporation of heteroatoms into the alkane bridges[7] has greatly expanded the scope of this area, and the synthesis of novel complexes using azacyclophanes,[8] selenacyclophanes,[9] thiacyclophanes,[10] and mixed aza-thiacyclophanes[11] as ligands has grown steadily.

During the design of cyclophane ligands, it must be noted that the conformational preferences of uncoordinated and coordinated cyclophanes are necessarily very different. Usually, a variety of conformational changes are required to achieve coordination, and this is often greatly influenced by the electronic properties of the metal ion.[12−14] Our group

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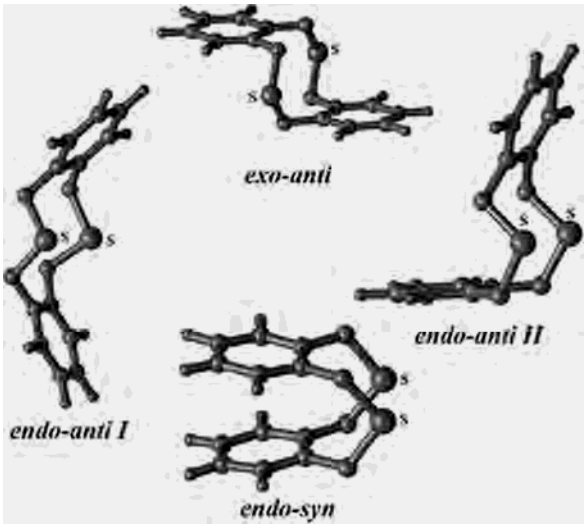

Figure 1. Different conformations of 2,11-dithia[3.3]*ortho*cyclophane (L). Benzylic hydrogens are omitted for clarity.

has been studying the coordination chemistry of thiacyclophanes and their application to molecular recognition.[15−19] In particular, we are interested in the factors controlling their conformational behavior.

A convenient synthesis of the thiacyclophane 2,11-dithia-[3.3]*ortho*cyclophane (L) has been reported,[20] and molecular mechanics calculations have shown that the minimum energy conformer has an *anti* structure with *exo* oriented sulfur atoms.[21] This is also the conformation observed in the solid state by X-ray crystallography.[21] Thus L, like many cyclic thioethers, with the notable exception of the preorganized 9S3,[22] shows a conformational preference for an *exo* arrangement of S atoms both in solution and in the solid state.[23] Therefore, in order for chelation to occur, it is necessary for donor atoms to reorient from an *exo* to an *endo* arrangement.[24] In the *endo* conformation, three isomers exist, which are potentially capable of chelating a metal: *anti I*, *anti II*, and *syn* (see Figure 1).

According to molecular mechanics calculations, the *syn* isomer has the highest energy of the three conformations and is therefore the least likely to be observed in metal complexes.[21,25] The conformation *anti I* is slightly more stable than the *anti II*; however, it is sterically very demanding and probably can only be observed when nonbulky ligands are bound to the metal. It is possible, however, for the ligand to adopt the alternative conformation, *anti II*, thereby allowing coordination of bulky ligands at the metal, as was previously reported by Hanton and Kemmit for a series of Ru(II) complexes.[25]

With the aim to further understand the factors controlling the conformational preferences of the cyclophanes upon coordination, thiacyclophanes in general and 2,11-dithia[3.3]-*ortho*cyclophane in particular, we are extending this work to the platinum group metals rhodium, palladium, iridium, and platinum which prefer a square planar geometry.

Experimental Section

All reagents were purchased from Aldrich and used as received. The starting complexes $[M(\mu\text{-Cl})(\eta^4\text{-cod})]_2$ (M = Rh, Ir) were acquired from Strem Chemical Co. The ligand (L) 2,11-dithia[3.3]-*ortho*cyclophane[20] and the complexes $[PtCl_2(\eta^4\text{-cod})]$,[26] $[MCl_2(PPh_3)_2]$[27] (M = Pd, Pt), $[Pd(MeCN)_4][CF_3SO_3]_2$,[28] and $[Pt(EtCN)_4][CF_3SO_3]_2$[29] were prepared by published methods. All reactions were carried out under an atmosphere of N_2(g) using Schlenk techniques, and the solvents were degassed prior to use. Microanalyses were performed using a Fisons EA1108 instrument. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 500.1 (Bruker 500 MHz), 75.4 (Varian 300 MHz), and 202.5 (Bruker 300 MHz), respectively, locked onto the deuterated solvent. FAB mass spectra were obtained on a JEOL JMS-SX102A. Molecular mechanics calculations were performed using the MM3 force field under the graphic interface Spartan.[30]

$[Pt(S_2C_{16}H_{16})(\eta^4\text{-cod})][CF_3SO_3]_2$ (1). To a solution of the complex $[PtCl_2(\eta^4\text{-cod})]$ (100 mg, 0.27 mmol) in chloroform (50 cm^3) was added 2 equiv of $AgCF_3SO_3$ (137 mg, 0.54 mmol). The mixture was stirred for 3 h and then filtered through Celite to remove AgCl. To the resulting solution was added, with stirring, 1 equiv of L (72.8 mg, 0.27 mmol). The precipitated white solid was filtered and washed with chloroform. Yield: 130 mg (56%). ^{1}H NMR (CD_3CN, 300 K): δ (ppm) 7.59 (m, aromatic, L), 5.39 (br, CH, cod, ^{195}Pt satellite doublet at 5.46 and 5.32, $^2J_{H-Pt}$ = 70.0 Hz), 5.13 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, L, ^{195}Pt satellite at 5.19 and 5.07, $^3J_{H-Pt}$ = 60.0 Hz), 4.99 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, L), 1.68 (m, CH_2, cod). ^{13}C{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 133.0 (s, aromatic, L), 131.9 (s, aromatic, L), 131.3 (s, aromatic, L), 115.5 (s, CH, cod, ^{195}Pt satellite doublet at 116.3 and 114.8, $^1J_{C-Pt}$ = 113.3 Hz,), 42.4 (s, benzylic, L), 30.0 (s, CH_2, cod). MS FAB$^+$ Calcd for $[Pt(S_2C_{16}H_{16})(\eta^4\text{-cod})][CF_3SO_3]^+$: 724. Found: 724. Anal. Calcd for $C_{26}H_{28}F_6O_6PtS_4$: C, 35.7; H, 3.2; S, 14.7. Found: C, 35.5; H, 3.0; S, 14.7.

$[Rh(S_2C_{16}H_{16})(\eta^4\text{-cod})][CF_3SO_3]$ (2). To a solution of the complex $[RhCl(\eta^4\text{-cod})]_2$ (100 mg, 0.20 mmol) in acetone (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (104 mg, 0.40 mmol). The mixture was stirred for 4 h and then filtered through Celite to remove AgCl. To the resulting solution was added, with stirring, 2 equiv of L (110 mg, 40 mmol). This mixture was stirred further for 4 h. The

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volume was reduced to ca. half in vacuo, and then, *n*-hexane was added. The precipitated yellow solid was filtered and washed with *n*-hexane. Yield: 198 mg (77%). ^{1}H NMR (CD_3CN, 300 K): δ (ppm) 7.55 (m, aromatic, L), 4.84 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, L), 4.74 (dd, $^2J_{H-H}$ = 12.9 Hz, $^3J_{H-Rh}$ = 1.8 Hz, benzylic, L), 3.98 (m, CH, cod), 1.65 (m, CH_2, cod). ^{13}C{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 136.1 (s, aromatic, L), 131.9 (s, aromatic, L), 130.4 (s, aromatic, L), 89.6 (d, $^1J_{C-Rh}$ = 11.3 Hz, CH, cod), 41.3 (s, benzylic, L), 30.8 (s, CH_2, cod). MS FAB$^+$ Calcd for [Rh($S_2C_{16}H_{16}$)-(η^4-cod)]$^+$: 483. Found: 483. Anal. Calcd for $C_{25}H_{28}F_3O_3RhS_3$: C, 47.5; H, 4.5; S, 15.2. Found: C, 47.1; H, 4.3; S, 15.8.

[Ir($S_2C_{16}H_{16}$)(η^4-cod)][CF_3SO_3] (3). To a solution of the complex [IrCl(η^4-cod)]$_2$ (100 mg, 0.15 mmol) in acetone (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (76.5 mg, 0.30 mmol). The mixture was stirred for 6 h and then was filtered through Celite to remove AgCl. To the resulting solution was added, with stirring, 2 equiv of L (82 mg, 30 mmol). This mixture was stirred further for 12 h. The volume was reduced to ca. half in vacuo, and then, *n*-hexane was added. The precipitated red solid was filtered and washed with *n*-hexane. Yield: 160 mg (74%). ^{1}H NMR (CD_3CN, 300 K): δ (ppm) 7.40 (m, aromatic, L), 4.95 (d, $^2J_{H-H}$ = 13.1 Hz, benzylic, L), 4.71 (d, $^2J_{H-H}$ = 13.1 Hz, benzylic, L), 3.52 (m, CH, cod), 1.33 (m, CH_2, cod). ^{13}C{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 134.5 (s, aromatic, L), 130.8 (s, aromatic, L), 129.5 (s, aromatic, L), 74.9 (s, CH, cod), 42.6 (s, benzylic, L), 30.5 (s, CH_2, cod). MS FAB$^+$ Calcd for [Ir($S_2C_{16}H_{16}$)(η^4-cod)]$^+$ 573. Found: 573. Anal. Calcd for $C_{25}H_{28}F_3IrO_3S_3$: C, 41.6; H, 3.9; S, 13.3. Found: C, 41.1; H, 3.5; S, 13.4.

[Pd($S_2C_{16}H_{16}$)(PPh_3)$_2$][CF_3SO_3]$_2$ (4). To a solution of the complex [$PdCl_2$(PPh_3)$_2$] (100 mg, 0.14 mmol) in acetonitrile (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (73.2 mg, 0.28 mmol). The mixture was stirred in the dark for 6 h and then was filtered through Celite to remove AgCl. To the resulting mixture was added, with stirring, 1 equiv of L (38.8 mg, 0.14 mmol) and stirred for a further 4 h. The solvent was then removed in vacuo yielding a yellow solid. Yield: 150 mg (88%). ^{1}H{^{31}P} NMR (CD_3CN, 300 K): δ (ppm) 7.89 (q, aromatic, L), 7.79 (q, aromatic, L), 7.69 (m, aromatic, PPh_3), 7.55 (m, aromatic, PPh_3), 7.47 (m, aromatic, PPh_3), 7.43 (q, aromatic, L), 7.35 (m, aromatic, PPh_3), 7.30 (q, aromatic, L), 7.01 (m, aromatic, PPh_3), 5.0 (d, $^2J_{H-H}$ = 13.3 Hz, benzylic, *anti I*), 4.7 (d, $^2J_{H-H}$ = 13.8 Hz, benzylic *anti II*), 4.5 (d, $^2J_{H-H}$ = 13.3 Hz, benzylic, *anti I*), 4.2 (d, $^2J_{H-H}$ = 13.8 Hz, benzylic, *anti II*), 4.1 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti II*), 3.4 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti II*). ^{31}P{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 32.7 (s, *anti II*), 29.5 (s, *anti I*). ^{13}C{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 134.8, (s, aromatic), 134.3 (m, aromatic), 133.7 (s, aromatic) 133.3 (s, aromatic), 133.1 (s, aromatic), 133.0 (s, aromatic), 132.9 (s, aromatic), 132.8 (s, aromatic), 131.0 (s, aromatic), 130.6 (s, aromatic), 130.1 (s, aromatic), 129.6 (m, aromatic), 42.2 (s, benzylic, *anti I*), 39.2 (s, benzylic, *anti II*), 34.8 (s, benzylic, *anti II*). MS FAB$^+$ Calcd for [Pd($S_2C_{16}H_{16}$)(PPh_3)$_2$][CF_3SO_3]$^+$: 1051. Found: 1051. Anal. Calcd for $C_{54}H_{46}F_6O_6P_2PdS_4$: C, 54.0; H, 3.9; S, 10.7. Found: C, 54.1; H, 3.6; S, 10.5.

[Pt($S_2C_{16}H_{16}$)(PPh_3)$_2$][CF_3SO_3]$_2$ (5). To a solution of the complex [$PtCl_2$(PPh_3)$_2$] (150 mg, 0.19 mmol) in acetonitrile (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (97.5 mg, 0.38 mmol). The mixture was stirred in the dark for 24 h and then was filtered through Celite to remove AgCl. To the resulting mixture was added, with stirring, 1 equiv of L (51.7 mg, 0.19 mmol), and this mixture stirred for a further 24 h. The solvent was then removed in vacuo yielding a white solid. Yield: 210 mg (86%). ^{1}H{^{31}P} NMR (CD_3CN, 300 K): δ (ppm) 7.78 (q, aromatic, L), 7.69 (q, aromatic, L), 7.62 (m, aromatic, PPh_3), 7.54 (q, aromatic, L), 7.45 (m, aromatic, PPh_3), 7.41 (q, aromatic, L), 7.35 (m, aromatic, PPh_3), 7.28 (q, aromatic, L), 7.22 (m, aromatic, PPh_3), 7.14 (q, aromatic, L), 6.89 (m, aromatic, PPh_3), 4.74 (d, $^2J_{H-H}$ = 13.5 Hz, benzylic, *anti I*), 4.41 (d, $^2J_{H-H}$ = 13.5 Hz, benzylic, *anti I*), 4.37 (d, $^2J_{H-H}$ = 13.8 Hz, benzylic, *anti II*), 4.13 (d, $^2J_{H-H}$ = 13.8 Hz, benzylic, *anti II*), 4.09 (d, $^2J_{H-H}$ = 13.0 Hz, benzylic, *anti II*), 3.28 (d, $^2J_{H-H}$ = 13.0 Hz, benzylic, *anti II*). ^{31}P{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 15.7 (s, ^{195}Pt satellite doublet at 23.5 and 7.9, $^1J_{P-Pt}$ = 3159 Hz, *anti II*), 12.5 (s, ^{195}Pt satellite doublet at 20.3 and 4.6, $^1J_{P-Pt}$ = 3179 Hz, *anti I*). ^{13}C{^{1}H} NMR (CD_3CN, 300 K): δ (ppm) 134.7, (s, aromatic), 134.5 (m, aromatic), 133.7 (s, aromatic) 133.1 (s, aromatic), 133.0 (s, aromatic), 132.9 (s, aromatic), 132.8 (s, aromatic), 131.2 (s, aromatic), 130.6 (s, aromatic), 130.5 (s, aromatic), 130.2 (s, aromatic), 129.5 (m, aromatic), 43.5 (s, benzylic, *anti I*), 40.9 (s, benzylic, *anti II*), 36.2 (s, benzylic, *anti II*). MS FAB$^+$ Calcd for [Pt($S_2C_{16}H_{16}$)(PPh_3)$_2$][CF_3SO_3]$^+$: 1141. Found: 1141. Anal. Calcd for $C_{54}H_{46}F_6O_6P_2PtS_4$: C, 50.3; H, 3.6; S, 9.9. Found: C, 49.4; H, 3.5; S, 10.1.

[Pd($S_2C_{16}H_{16}$)$_2$][CF_3SO_3]$_2$ (6). Method A. To a solution of the complex [Pd(MeCN)$_4$][CF_3SO_3]$_2$ (100 mg, 0.18 mmol) in acetonitrile (20 cm^3) was added 2 equiv of L (96 mg, 0.36 mmol) under stirring. The mixture was stirred for a further 4 h and then the solvent removed in vacuo yielding a yellow solid. Yield: 157 mg (94%).

Method B. To a suspension of the complex [$PdCl_2$($S_2C_{16}H_{16}$)][31] (100 mg, 0.22 mmol) in acetone (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (114 mg, 0.44 mmol). The mixture was stirred for 2 h in the dark and then filtered through Celite to remove AgCl. To the resulting solution was added, with stirring, 1 equiv of L (61 mg, 0.22 mmol), and this mixture stirred for a further 2 h. The precipitated yellow solid was filtered and washed with dichloromethane. Yield: 164 mg (79%). ^{1}H NMR (CD_3CN, 300 K): δ (ppm) 7.69 (m, aromatic), 7.57 (m, aromatic), 7.51 (m, aromatic), 7.44 (m, aromatic), 7.32 (m, aromatic), 7.17 (m, aromatic), 6.98 (m, aromatic), 4.84 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.70 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.66 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.53 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.31 (d, $^2J_{H-H}$ = 13.5 Hz, benzylic, *anti II*−*anti II*), 4.18 (d, $^2J_{H-H}$ = 13.9 Hz, benzylic, *anti I*−*anti II*), 4.02 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti II*−*anti II*), 3.77 (d, $^2J_{H-H}$ = 12.6 Hz, benzylic, *anti I*−*anti II*), 3.46 (d, $^2J_{H-H}$ = 13.5 Hz, benzylic, *anti II*−*anti II*), 3.21 (d, $^2J_{H-H}$ = 13.9 Hz, benzylic, *anti I*−*anti II*), 3.15 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti II*−*anti II*), 2.85 (d, $^2J_{H-H}$ = 12.6 Hz, benzylic, *anti I*−*anti II*). ^{13}C NMR (CD_3CN, 300K): δ (ppm) 136.2 (s, aromatic), 135.7 (s, aromatic), 133.6 (s, aromatic), 133.5 (s, aromatic), 133.2 (s, aromatic), 132.4 (m, aromatic), 132.3 (s, aromatic), 132.2 (s, aromatic), 132.0 (s, aromatic), 130.7 (s, aromatic), 129.9 (s, aromatic), 43.0 (s, benzylic, *anti I*−*anti II*), 42.3 (s, benzylic, *anti I*−*anti II*), 40.1 (s, benzylic, *anti I*−*anti II*), 39.8 (s, benzylic, *anti II*−*anti II*), 35.2 (s, benzylic, *anti II*−*anti II*), 34.6 (s, benzylic, *anti I*−*anti II*). MS FAB$^+$ Calcd

(31) [MCl_2($S_2C_{16}H_{16}$)] M = Pd, Pt: To a solution of the corresponding salt K_2[MCl_4] in an acetone−water mixture was added a solution of L in dichloromethane. The mixture was stirred vigorously for 24 h at room temperature. The precipitated solid was isolated by filtration, washed with water, acetone, and dichloromethane, and dried in vacuo. [$PdCl_2$($S_2C_{16}H_{16}$)] yield: 94%. Anal. Calcd for $C_{16}H_{16}Cl_2PdS_2$: C, 42.7; H, 3.6; S, 14.3. Found: C, 42.4; H, 3.9; S, 13.8. FT-IR (KBr, cm^{-1}): 2937(m), 1490(m), 1454(s), 1241(m), 779(s), 664(m). Far-IR (polyethylene, cm^{-1}): 343, 321, 298, 282. [$PtCl_2$($S_2C_{16}H_{16}$)], yield: 85%. Anal. Calcd for $C_{16}H_{16}Cl_2PtS_2$: C, 35.7; H, 3.0; S, 11.9. Found: C, 35.8; H, 3.1; S, 12.1. FT-IR (KBr, cm^{-1}): 2940(m), 1490-(m), 1456(s), 1241(m), 779(s), 658(s). Far-IR (polyethylene, cm^{-1}): 337, 323, 310, 308.

for $[Pd(S_2C_{16}H_{16})_2][CF_3SO_3]^+$: 799. Found: 799. Anal. Calcd for $C_{34}H_{32}F_6O_6PdS_6$: C, 43.0; H, 3.4; S, 20.3. Found: C, 42.2; H, 3.8; S, 20.5.

$[Pt(S_2C_{16}H_{16})_2][CF_3SO_3]_2$ (7). Method A. To a solution of the complex $[Pt(EtCN)_4][CF_3SO_3]_2$ (100 mg, 0.14 mmol) in dichloromethane (50 cm^3) was added 2 equiv of L (76 mg, 0.28 mmol) with stirring. The mixture was stirred for a further 24 h and then the solvent removed in vacuo yielding a white solid. Yield: 135 mg (93%).

Method B. To a suspension of the complex $[PtCl_2(S_2C_{16}H_{16})]$[31] (100 mg, 0.19 mmol) in acetone (20 cm^3) was added 2 equiv of $AgCF_3SO_3$ (95.4 mg, 0.37 mmol). The mixture was stirred for 40 h in the dark and then was filtered through Celite to remove AgCl. To the resulting solution was added, with stirring, 1 equiv of L (51 mg, 0.19 mmol). This solution was stirred for a further 24 h, and then, the solvent was removed in vacuo yielding a white solid. Yield: 158 mg (82%). ^1H NMR (CD_3CN, 300 K): δ (ppm) 7.65 (m, aromatic), 7.62 (m, aromatic), 7.54 (m, aromatic), 7.45 (m, aromatic), 7.27 (m, aromatic), 7.16 (m, aromatic), 7.12 (m, aromatic), 6.95 (m, aromatic), 4.97 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.79 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.77 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.62 (d, $^2J_{H-H}$ = 13.2 Hz, benzylic, *anti I*−*anti II*), 4.51 (d, $^2J_{H-H}$ = 14.1 Hz, benzylic, *anti II*−*anti II*), 4.36 (d, $^2J_{H-H}$ = 14.0 Hz, benzylic, *anti I*−*anti II*), 4.20 (d, $^2J_{H-H}$ = 12.7 Hz, benzylic, *anti II*−*anti II*), 3.97 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti I*−*anti II*), 3.51 (d, $^2J_{H-H}$ = 14.1 Hz, benzylic, *anti II*−*anti II*), 3.29 (d, $^2J_{H-H}$ = 14.0 Hz, benzylic, *anti I*−*anti II*), 3.24 (d, $^2J_{H-H}$ = 12.7 Hz, benzylic, *anti II*−*anti II*), 2.95 (d, $^2J_{H-H}$ = 12.9 Hz, benzylic, *anti I*−*anti II*). ^{13}C NMR (CD_3CN, 300 K): δ (ppm) 135.2 (s, aromatic), 134.7 (s, aromatic), 132.8 (s, aromatic), 132.4 (s, aromatic), 132.1 (s, aromatic), 131.5 (s, aromatic), 131.3 (m, aromatic), 131.2 (s, aromatic), 131.0 (s, aromatic), 129.8 (s, aromatic), 129.0 (s, aromatic), 43.8 (s, benzylic, *anti I*−*anti II*), 42.7 (s, benzylic, *anti I*−*anti II*), 41.2 (s, benzylic, *anti I*−*anti II*), 40.8 (s, benzylic, *anti II*−*anti II*), 35.8 (s, benzylic, *anti II*−*anti II*), 35.0 (s, benzylic, *anti I*−*anti II*). MS FAB$^+$ Calcd for MS $[Pt(S_2C_{16}H_{16})_2][CF_3SO_3]^+$: 889. Found: 889. Anal. Calcd for $C_{34}H_{32}F_6O_6PtS_6$: C, 39.3; H, 3.1; S, 18.5. Found: C, 39.9; H, 3.7; S, 18.6.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a Siemens SMART/CCD diffractometer. Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. The systematic absences in the diffraction data and the determined unit-cell parameters were uniquely consistent for the reported space group. Diffracted data were corrected for absorption using the SADABS program. SHELXTL 5.03 Program Library[32] was used for the structure solution, and refinement was based on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions. Crystallographic data and refinement parameters are summarized in Table 1.

Structure Determination of $[Pt(S_2C_{16}H_{16})(\eta^4\text{-cod})][CF_3SO_3]_2$ (1). Colorless crystals were grown by slow evaporation of an acetonitrile solution of the complex. The structure was solved by direct methods and refined with full-matrix least-squares methods. This resulted in $R(F_o)$ = 2.77% and $R_w(F_o^2)$ = 7.24% at final convergence. A goodness-of-fit calculation resulted in a value of 1.027. Selected bond distances and angles are summarized in Table 3. Listings of atomic positional parameters, nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as Supporting Information.

Structure Determination of $[Pd(S_2C_{16}H_{16})_2][CF_3SO_3]_2$ (6). Orange crystals were grown by slow evaporation of an acetonitrile solution of the complex. The structure was solved by direct methods and refined with full-matrix least-squares methods. A molecule of acetonitrile is present in the unit cell. This resulted in $R(F_o)$ = 5.82% and $R_w(F_o^2)$ = 9.13% at final convergence. A goodness-of-fit calculation resulted in a value of 1.115. Selected bond distances and angles are summarized in Table 4. Listings of atomic positional parameters, nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as Supporting

Table 1. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $[PtL(\eta^4\text{-cod})][SO_3CF_3]_2$ (**1**) and $[PdL_2][SO_3CF_3]_2$·MeCN (**6**)

	1	**6**
formula	$C_{26}H_{28}F_6O_6PtS_4$	$C_{36}H_{32}F_6NO_6PdS_6$
fw	873.83	987.39
a, Å	11.0874(21)	9.4421(5)
b, Å	11.5019(22)	21.7356(11)
c, Å	13.4237(25)	19.1037(10)
α, deg	82.617(3)	
β, deg	70.159(3)	
γ, deg	66.268(3)	
cryst syst	triclinic	orthorhombic
space group	*P*1	*Pbcn*
V, Å^3	1474.0(3)	3920.6(4)
ρ(calcd), g cm^{-3}	1.969	1.673
Z	2	4
μ (mm^{-1})	5.122	0.868
λ, Å	0.71073	0.71073
T (K)	293	193
$R(F_o)$, % (all data)[a]	2.77	5.82
$R_w(F_o^2)$, % (all data)[a]	7.24	9.13

[a] $R(F_o) = \sum||F_o| - |F_c|/\sum|F_o||$, $R_w(F_o^2) = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Table 2. NMR Spectroscopic Data for the Benzylic Groups in Complexes

complex	conformation	δ ^1H, ppm ($^2J_{H_a-H_e}$, Hz)	δ ^{13}C, ppm
$[PtL(\eta^4\text{-cod})][CF_3SO_3]_2$ (**1**)	*anti I*	5.13, 4.99 (13.2)	42.4
$[RhL(\eta^4\text{-cod})][CF_3SO_3]$ (**2**)	*anti I*	4.84, 4.74 (12.9)	41.3
$[IrL(\eta^4\text{-cod})][CF_3SO_3]$ (**3**)	*anti I*	4.95, 4.71 (13.1)	42.6
$[PdL(PPh_3)_2][CF_3SO_3]_2$ (**4**)	*anti I*	5.00, 4.53 (13.3)	42.2
	anti II	4.70, 4.16 (13.8)	39.2
		4.07, 3.40 (12.9)	34.8
$[PtL(PPh_3)_2][CF_3SO_3]_2$ (**5**)	*anti I*	4.74, 4.41 (13.5)	43.5
	anti II	4.37, 4.13 (13.8)	40.9
		4.09, 3.28 (13.0)	36.2
$[PdL_2][CF_3SO_3]_2$ (**6**)	*anti I*−*anti II*	4.84, 4.66 (13.2)	43.0
		4.70, 4.53 (13.2)	42.3
		4.18, 3.21 (13.9)	40.1
		3.77, 2.85 (12.6)	34.6
	anti II−*anti II*	4.31, 3.46 (13.5)	39.8
		4.02, 3.15 (12.9)	35.2
$[PtL_2][CF_3SO_3]_2$ (**7**)	*anti I*−*anti II*	4.97, 4.77 (13.2)	43.8
		4.79, 4.62 (13.2)	42.7
		4.36, 3.29 (14.0)	41.2
		3.97, 2.95 (12.9)	35.0
	anti II−*anti II*	4.51, 3.51 (14.1)	40.8
		4.20, 3.24 (12.7)	35.8

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[PtL(\eta^4\text{-cod})][SO_3CF_3]_2$ (**1**)

Pt−S1	2.370(6)	Pt−C18	2.233(16)
Pt−S2	2.349(5)	Pt−C21	2.21(2)
Pt−C17	2.219(13)	Pt−C22	2.19(2)
S1−Pt−S2	95.4(2)	C18−Pt−C21	81.9(7)
S2−Pt−C21	87.2(6)	C18−Pt−C17	34.2(7)

(32) Siemens Analytical Instrument Division, Madison, WI, 1997.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[PdL_2][SO_3CF_3]_2$ (**6**)[a]

Pd−S1	2.338(1)	Pd−S2	2.332(1)
S1−C1	1.833(4)	S2−C8	1.835(4)
S1−C16	1.839(5)	S2−C9	1.855(4)
S1−Pd−S2	95.04(4)	S1−Pd−S1A	85.06(4)
C1−S1−Pd	103.65(15)	C16−S1−Pd	112.31(14)

[a] Symmetry transformations used to generate equivalent atoms: #A, $-x$, y, $-z + {}^3/_2$.

Scheme 1. Syntheses of Heteroleptic cod Complexes

$$[MCl_2(\eta^4\text{-cod})] \xrightarrow[-2AgCl,\ L]{2\ AgCF_3SO_3} [ML(\eta^4\text{-cod})][CF_3SO_3]_n \xleftarrow[-2AgCl,\ L]{2\ AgCF_3SO_3} [MCl(\eta^4\text{-cod})]_2$$

M=Pd, Pt; n = 2, M = Pt, **1**; n = 1, M = Rh, **2**; or Ir, **3**; M=Rh, Ir

Information. The molecule lies on a 2-fold crystallographic axis, such that one cyclophane ligand generates a second.

Results and Discussion

Syntheses and Characterization of Heteroleptic Cyclooctadiene Complexes. Treatment of $[MCl_2(\eta^4\text{-cod})]$ (M = Pd or Pt) and $[M(\mu\text{-Cl})(\eta^4\text{-cod})]_2$ (M= Rh or Ir) with 2 equiv of silver triflate in chloroform, acetone, or acetonitrile provides a convenient source of the $[M(\eta^4\text{-cod})]^{n+}$ moiety, which reacts readily with L to form air stable ionic heteroleptic complexes $[PtL(\eta^4\text{-cod})][SO_3CF_3]_2$ (**1**), $[RhL(\eta^4\text{-cod})][SO_3CF_3]$ (**2**), and $[IrL(\eta^4\text{-cod})][SO_3CF_3]$ (**3**), as is shown in Scheme 1.

All attempts to obtain $[PdL(\eta^4\text{-cod})][SO_3CF_3]_2$ resulted in isolation of the homoleptic complex $[PdL_2][SO_3CF_3]_2$ (**6**), probably because of the weakness of the Pd−olefin bond compared with that of the platinum equivalent.[33]

Elemental analyses were in agreement with the proposed formula, and in positive ion mode FAB mass spectrometry, the fragments $[PtL(\eta^4\text{-cod})][SO_3CF_3]^+$ for **1** (m/z = 724), $[RhL(\eta^4\text{-cod})]^+$ for **2** (m/z = 483), and $[IrL(\eta^4\text{-cod})]^+$ for **3** (m/z = 573) were detected with the expected isotopic distribution. This unambiguously established the presence of cod, L, and the metal in each complex. NMR spectra of these complexes show resonances in the regions δ = 3.52−5.39 ppm and δ = 1.33−1.68 ppm which were assigned to the CH and CH_2 of the cyclooctadiene ring, respectively. The aromatic protons of L appear between 7.4 and 7.59 ppm, and benzylic protons, in 4.71−5.13 ppm. The benzylic region of the spectrum is the most informative, concerning the conformation of the ligand in the complex. ^{1}H and ^{13}C NMR data for the benzylic groups are presented in Table 2.

The benzylic region consists of one signal in the ^{13}C NMR spectrum and two doublets in ^{1}H NMR spectrum. This information establishes that the cyclophane is rigidly bound in the *anti I* conformation with C_{2v} symmetry, and so, it has four equivalent benzylic carbon atoms, each one containing two nonequivalent protons which are axial and equatorial with respect to the cyclophane ring, generating an AB system. Molecular mechanics calculations are in agreement with the conformational preference for the *anti I* conformation of L in this class of complexes.

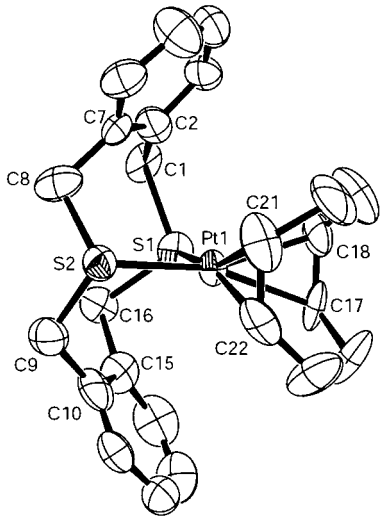

Figure 2. Perspective ORTEP drawing of $[PtL(\eta^4\text{-cod})]^+$, showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

Scheme 2. Syntheses of Heteroleptic PPh_3 Complexes

$$[MCl_2(PPh_3)_2] \xrightarrow[-2\ AgCl,\ L]{2\ AgCF_3SO_3} [M(L)(PPh_3)_2][CF_3SO_3]_2$$

M = Pd, **4**; or Pt, **5**

It is interesting that ^{1}H NMR spectra of both $[PtL(\eta^4\text{-cod})][SO_3CF_3]_2$ (**1**) and $[RhL(\eta^4\text{-cod})]$ $[SO_3CF_3]$ (**2**) exhibit couplings between the metal center (^{195}Pt and ^{103}Rh) and one of the protons at the benzylic groups. Because the axial protons of the cyclophane ring are formally *trans* to the metal, we have tentatively assigned these coupling constants ($^3J_{Rh-H}$ = 1.8 Hz and $^3J_{Pt-H}$ = 60.0 Hz) to the M−S−C−H_{axial} (M = Pt or Rh) bond.

X-ray Structure of $[PtL(\eta^4\text{-cod})][SO_3CF_3]_2$ (1). In the asymmetric unit, there coexist two very slightly different molecules of **1**. Figure 2 clearly shows that the Pt atom has square planar geometry and the conformation of the ligand is *anti I*. The S−Pt−S angle of 95.4(2)° deviates slightly from that expected for square planar coordination. The average Pt−S distance of 2.36(1) Å compares with previously reported Pt−S(thioether) bond distances.[34] The average Pt−C bond distance of 2.21(2) Å is similar to the distance reported for analogous complexes.[35] Relevant bond and angles are shown in Table 3.

Syntheses and Characterization of Heteroleptic Phosphine Complexes. Reaction of the neutral complexes $[MCl_2(PPh_3)_2]$ (M = Pd or Pt) with 2 equiv of silver triflate in MeCN followed by the addition of 1 equiv of L produced the complexes $[PdL(PPh_3)_2][SO_3CF_3]_2$ (**4**) and $[PtL(PPh_3)_2][SO_3CF_3]_2$ (**5**), as is shown in Scheme 2.

Both complexes are air stable, yellow (**4**) and white (**5**) solids, with the expected elemental composition. The fragments $[PdL(PPh_3)_2][SO_3CF_3]^+$ (m/z = 1051 for **4**) and $[PtL(PPh_3)_2][SO_3CF_3]^+$ (m/z = 1141 for **5**) with the appropriate

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(34) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365−414.

(35) Ferguson, G.; Gallagher, J. F.; McAlees, A. J.; McCrindle, R. *Organometallics* **1997**, *16*, 1053−1057.

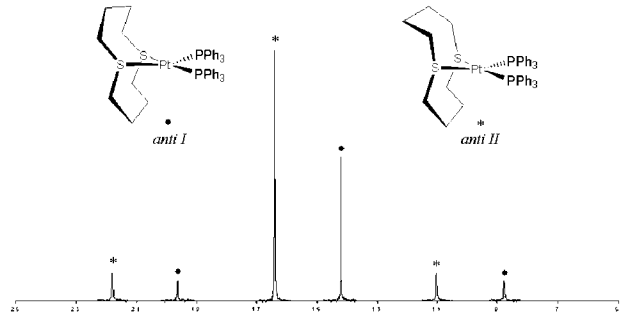

Figure 3. ^{31}P NMR of $[PtL(PPh_3)_2][SO_3CF_3]_2$. Key: dots indicate *anti I*; asterisks indicate *anti II*. Aromatic rings are omitted for clarity. Assignations are based on ^{1}H−^{31}P NMR experiments.

Scheme 3. Syntheses of Homoleptic Complexes

$$[M(S)_4][CF_3SO_3]_2 \xrightarrow{2\ L} [M(L)_2][CF_3SO_3]_2 \xleftarrow[-2\ AgCl,\ L]{2\ AgCF_3SO_3} [MCl_2L]$$

M = Pd, S = MeCN; M = Pt, S = EtCN

M = Pd, **6**; or Pt, 7

isotopic distribution were observed by positive ion mode FAB mass spectrometry. ^{1}H{^{31}P} NMR spectra display overlapped signals corresponding to the aromatic protons of the triphenylphosphine and L and six doublets, for each compound, between 3.40−5.00 (**4**) and 3.28−4.74 ppm (**5**) due to the benzylic hydrogens. ^{13}C NMR spectra exhibit three signals in the benzylic zone, as is summarized in Table 2.

The complex NMR spectra show the presence of a mixture of two isomers with cyclophane ligands L bound in two different conformations: *anti I*, which is symmetrical and originates one signal in the ^{13}C NMR spectrum and two doublets in the ^{1}H NMR spectrum, and *anti II*, which being nonsymmetrical gives rise to a pair of signals in the ^{13}C NMR spectrum and the remaining four doublets observed in the ^{1}H NMR spectrum. A 40:60 proportion, for both complexes, was estimated on the basis of the integral values. Additional COSY and HETCOR experiments were used to confirm the assignations.

The presence of both isomers is clearly observed by ^{31}P NMR spectroscopy (Figure 3). The spectra exhibit two signals for **4** at 29.5 (*anti I*) and 32.7 ppm (*anti II*) and for **5** at 12.5 (*anti I*) and 15.7 ppm (*anti II*), with Pt satellites of 3179 and 3159 Hz, respectively. The conformational assignment is based on the known relative abundance of each identified isomer by ^{1}H NMR.

^{1}H NMR spectra also display couplings between some benzylic hydrogens and phosphorus, which disappear on irradiation of the phosphorus atoms. Variable temperature NMR experiments in nitromethane-d_3 up to 95 °C showed no exchange between isomers. The presence of two isomers, in these kinds of complexes, can be rationalized as being due to the relatively close values in energy for both conformations of the cyclophane, as determined by molecular mechanics calculations, and the higher steric requirements of the triphenylphosphine ligand as compared to that of the cyclooctadiene ligand, although electronic effects also can play a role.

Syntheses and Characterization of Homoleptic Complexes. The compounds $[ML_2][CF_3SO_3]_2$ (M = Pd, **6**; M = Pt, **7**) were synthesized in high yield as shown in Scheme 3. The neutral complexes $[MCl_2L]$ (M = Pd or Pt) were also used as starting materials for these syntheses; however, low solubility prevented its full characterization.[31]

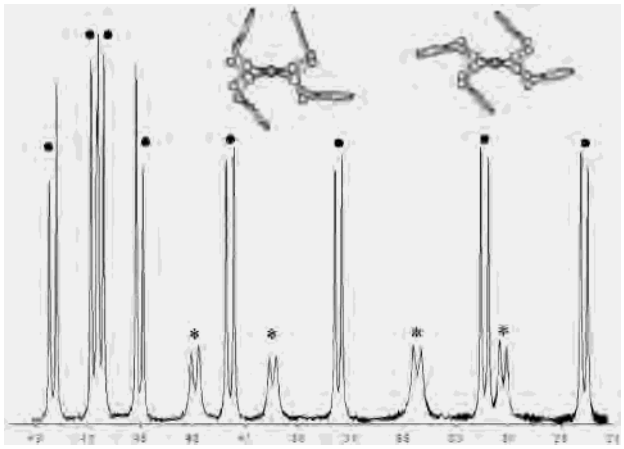

Figure 4. ^{1}H NMR spectrum of the benzylic region for $[PdL_2][SO_3CF_3]_2$ (**6**). Key: dots indicate *anti I*−*anti II*; asterisks indicate *anti II*−*anti II*.

Both complexes are air stable, yellow (**6**) and white (**7**) solids, with good solubility and stability in organic polar solvents, especially in acetonitrile and nitromethane. The microanalyses are in agreement with the proposed formula. The FAB$^+$ mass spectra of these complexes display the presence of the ions $[ML_2][CF_3SO_3]^+$ (m/z = 799 for **6**; m/z = 889 for **7**) with the expected isotopic distribution, establishing the presence of two ligands by each metallic atom.

The solution ^{1}H NMR spectra show signals in two regions corresponding to the aromatic and the benzylic protons. The benzylic region is shown in Figure 4. By their number and position, ^{1}H and ^{13}C signals can be divided in two groups, corresponding to two different isomers. One isomer, corresponding to cyclophane L in the *anti I*−*anti II* conformation with C_s symmetry, has four different benzylic groups generating four signals in the ^{13}C NMR spectrum and eight doublets in the ^{1}H NMR spectrum, whereas the other isomer with the conformation *anti II*−*anti II* has C_{2h} symmetry and thus only two different benzyl groups, generating two signals in ^{13}C NMR spectrum and four doublets in ^{1}H NMR spectrum, as is observed in Figure 4. The ratio of isomers is 80:20 and appears to be independent of the metal ion. The higher stability of the *anti I*−*anti II* conformation was also suggested by molecular mechanics calculations.

X-ray Structure of $[PdL_2][SO_3CF_3]_2$ (6). The single-crystal X-ray structure of **6** (Figure 5) shows the Pd atom in a square planar geometry with a 2-fold rotation axis at the metal generating two equivalent ligands. The conformation of both ligands is *anti II*. This geometry might be preferred because of a better molecular packing in the crystals. The S−Pd−S angle of 95.04(4)° deviates slightly from that expected for square planar coordination and contrasts with the 90.4(1)° observed in the ruthenium complexes for this cyclophane in the same conformation.[19] The Pd−S distance of 2.335(4) Å compares well with that previously reported for other Pd−S(thioether) bond distances.[34] No interactions

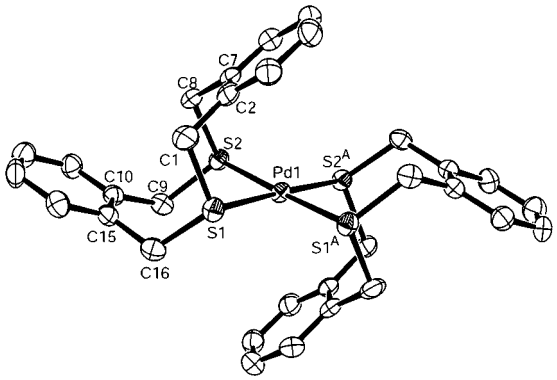

Figure 5. Perspective ORTEP drawing of cation $[PdL_2]^{2+}$, showing the atom-numbering scheme. Ellipsoids are given at 50% probability. Hydrogen atoms are omitted for clarity.

between the aromatic rings were observed in the solid state. Relevant bond and angles are shown in Table 4.

Conclusions

The thiacyclophane 2,11-dithia[3.3]*ortho*cyclophane is a flexible bidentate ligand that, when coordinated, can adopt two different conformations: *anti I* and *anti II*. No evidence has been found for the presence of conformation *syn*, in agreement with the relatively high energy suggested by molecular mechanics calculations for this arrangement.

Heteroleptic cod derivatives $[ML(\eta^4\text{-cod})][CF_3SO_3]_n$ (n = 1 for M = Rh and Ir; n = 2 for M = Pt) have the chelating ligand with *anti I* configuration. Whereas replacement of cod for the larger PPh_3 ligand in the complexes $[ML(PPh_3)_2][CF_3SO_3]_2$ (M = Pd and Pt) gives rise to mixtures of two isomers, the thiacyclophane has *anti I* (ca. 40% abundance) and *anti II* (ca. 60% abundance) conformations. Similarly homoleptic compounds $[ML_2][CF_3SO_3]_2$ (M = Pd and Pt) also display a pair of isomers in which the thiacyclophane ligands have *anti I*−*anti II* (ca. 80% abundance) or *anti II*−*anti II* (ca. 20% abundance) configurations.

In all cases, the relative proportions of isomers appear to be independent of the metallic center. Although mesocyclic ring inversion could provide a mechanism for isomer exchange, no evidence was found in this work for such a process.

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Supporting Information Available: X-ray crystallographic file in CIF format for complexes **1** and **6**. This material is free of charge via the Internet at http://pubs.acs.org

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