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Article

Solvent and Temperature Induced Switching Between Structural Isomers of Rh^I Phosphinoalkyl Thioether (PS) Complexes

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To develop functional systems based on the weak-link approach (WLA), it is important to understand how solvent and ligand binding strength alter the coordination geometry of complexes formed from this method. A series of phosphinoalkyl thioether (PS) hemilabile ligands with varying electron donating abilities were synthesized and incorporated into homoligated $Rh^I(PS)_2Cl$ complexes to help understand the effects of solvent and ligand binding strength on the preferred coordination modes. The switching between closed and semiopen structural isomers of these $Rh^I(PS)_2Cl$ complexes was studied by variable temperature ^{31}P NMR spectroscopy in different solvent mixtures of CH_2Cl_2 and tetrahydrofuran (THF) to obtain thermodynamic parameters ($\Delta G°$, $\Delta H°$, $T\Delta S°$, and K_{eq}). The isomers differ in the position of the chloride counterion. In the closed isomer, the Cl^- anion occupies the outer coordination sphere, while in the semiopen isomer, the Cl^- has moved inner sphere and displaced one of the Rh−S bonds. The closed isomer is favored in CH_2Cl_2 and the semiopen isomer is favored in THF. The preference for either isomer at equilibrium depends on the solvent polarity, based upon the E_T^N solvent polarity scale, as was determined from 15 different solvents, with more polar solvents favoring the closed isomer. The isomer preference also depends on the electron donating ability of the group attached to the sulfur of the PS ligand, with electron donating groups favoring the closed isomers and electron withdrawing groups favoring the semiopen isomers. The formation of the semiopen isomer from the closed isomer is entropically favored but enthalpically disfavored under all conditions studied. Elucidation of the principles and environments that determine the equilibrium between the two isomers will aid in the design of functional complexes prepared by the WLA.

Introduction

The weak-link approach (WLA) is a method for preparing macrocyclic, tweezer, and triple-decker coordination complexes,[1,2] which behave as allosteric enzyme mimics that can be used in ELISA- and PCR-like signal amplification and detection schemes for small molecules and elemental ions.[3,4] In the WLA, flexible hemilabile ligands containing chelating metal binding sites consisting of a diphenylphosphine moiety and a second heteroatom metal binder (PX, where X = O, S, or N) are combined with tetra-coordinate metal ions, such as Rh^I, Pt^{II}, Pd^{II}, or Cu^I, to form supramolecular coordination complexes such as macrocycles and tweezers.[1] Homoligated complexes, in which the two ligands bound to the metal center are identical, have previously been interconverted between two coordination geometries, open (**1**) and closed (**2**), through small molecule reactions that occur at metal centers (Scheme 1A).[1] In this process, the weaker metal-heteroatom bonds are cleaved by incoming small molecule ligands (such

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(1) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (b) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825–837. (c) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618–1629. (d) Wiester, M. J.; Mirkin, C. A. *Inorg. Chem.* **2009**, *48*, 8054–8056. (e) Wiester, M. J.; Ulmann, P. U.; Mirkin, C. A., *Angew. Chem., Int. Ed.* **2010**, DOI: 10.1002/anie.201000380.

(2) Reviews on other coordination chemistry approaches for preparing supramolecular assemblies: (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975–982. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369–378. (c) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521–537.

(3) (a) Gianneschi, N. C.; Cho, S.-H.; Nguyen, S. T.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5503–5507. (b) Oliveri, C. G.; Gianneschi, N. C.; Nguyen, S. T.; Mirkin, C. A.; Stern, C. L.; Wawrzak, Z.; Pink, M. *J. Am. Chem. Soc.* **2006**, *128*, 16286–16296. (c) Yoon, H. J.; Heo, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 14182–14183. (d) Yoon, H. J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 11590–11591. (e) Ulmann, P. A.; Braunschweig, A. B.; Lee, O.-S.; Wiester, M. J.; Schatz, G. C.; Mirkin, C. A. *Chem. Commun.* **2009**, 5121–5123.

(4) Other examples of synthetic allosteric systems and enzyme mimics: (a) Thordarson, P.; Bijsterveld, E. J. A.; Elemans, J. A. A. W.; Kasak, P.; Nolte, R. J. M.; Rowan, A. E. *J. Am. Chem. Soc.* **2003**, *125*, 1186–1187. (b) Pall, T.; Ruud, G. E. C.; Johannes, A. A. W. E.; Paul, J. T.; Johan, V.; Alan, E. R.; Roeland, J. M. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 4755–4759. (c) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251–254. (d) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Science* **2007**, *316*, 85–88. (e) Veling, N.; Thomassen, P. J.; Thordarson, P.; Elemans, J. A. A. W.; Nolte, R. J. M.; Rowan, A. E. *Tetrahedron* **2008**, *64*, 8535–8542.

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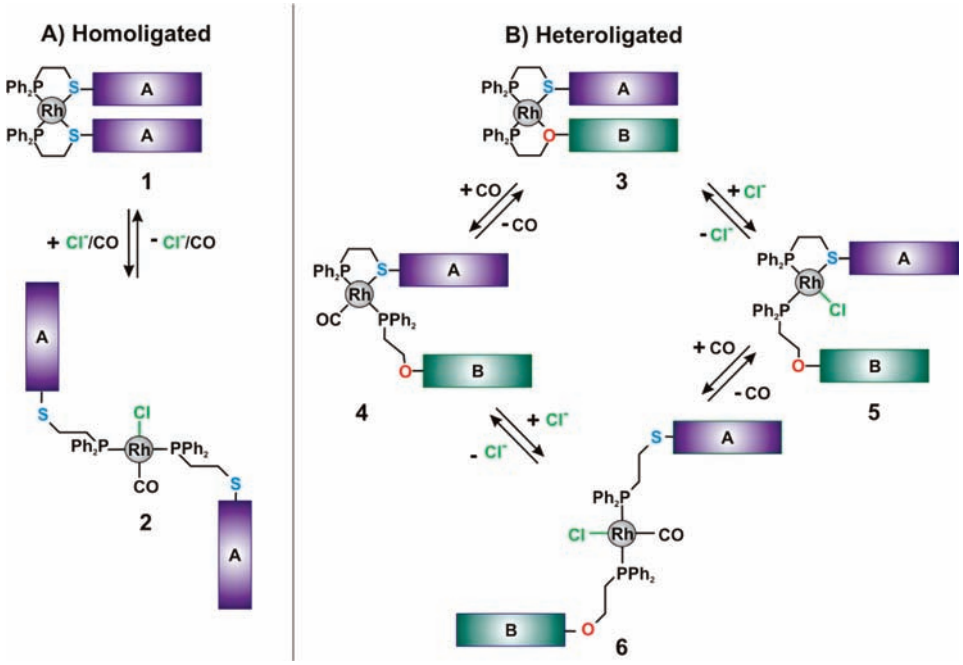
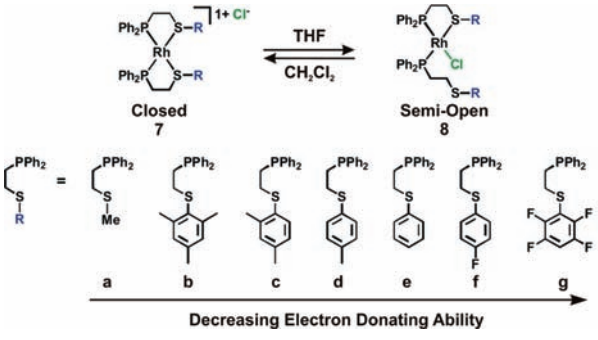
Scheme 1. (A) Homoligated Tweezer Complexes Formed via the WLA and (B) Heteroligated Tweezer Complexes Formed via the WLA and HILR Reaction, Where **A** and **B** Are Two Different Functional Groups



as Cl^-, CO, MeCN, or CN^-), while the stronger phosphine-metal bonds remain intact, resulting in more flexible open structures. Heteroligated complexes, in which two different ligands (either PS/PO or PS/PS′; PS, phosphinoalkyl thioether) are complexed to the metal, also can be prepared by the WLA and a halide-induced ligand rearrangement (HILR) reaction,[5] and interconverted between multiple geometries (**3**−**6**) through small molecule reactions that occur at the metal hinge sites (Scheme 1B). If only one of the metal-heteroatom bonds is cleaved, the molecule adopts a semiopen conformation (**4** and **5**, Scheme 1B), termed the semiopen isomer.[1c] WLA complexes have only been interconverted between different geometries by the addition or removal of small molecules,[1] whereas other dynamic molecular systems[6a−e] have been actuated by changes in solvent,[7a] temperature,[7b] or irradiation,[7c] as well as by the addition of small molecules.[7d,e]

While Cl^- is often utilized with complexes prepared by the WLA as a structural regulatory ligand that binds to the metal center to create more flexible open structures, in some cases Cl^- is present as a counterion.[1,3] This indicated to us that under certain conditions Cl^- may move from outer to inner sphere coordination or vice versa, thereby interconverting the two closed and semiopen structural isomers (eq 1). Herein we report the observation that by altering solvent and temperature we can induce the opening and closing of various homoligated $Rh^I(PS)_2Cl$ complexes as a result of the Cl^- anions moving from the outer to inner sphere of the coordination complex (eq 1). When designing functional architectures based on the WLA, it is important to understand how different environmental conditions and ligand properties affect the geometry and ultimately the performance of those systems. Because the coordination geometry is central to all of the functional complexes prepared via the WLA, we have systematically studied the thermodynamic basis for this switching by variable temperature (VT) ^{31}P NMR spectroscopy and related the preference of the Cl^- anion for inner and outer sphere coordination to solvent polarity and electron donating ability of the thioether ligands. Taken together, these complexes are excellent model systems for understanding how to design the much more sophisticated and complicated WLA catalysts and allosteric enzyme mimics.



(1)

(5) (a) Ovchinnikov, M. V.; Brown, A. M.; Liu, X.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2004**, *43*, 8233–8235. (b) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 14316–14317. (c) Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4207–4209. (d) Jeon, Y. M.; Heo, J.; Brown, A. M.; Mirkin, C. A. *Organometallics* **2006**, *25*, 2729–2732. (e) Ulmann, P. A.; Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A.; Di Pasquale, A. G.; Rheingold, A. L. *Chem.—Eur. J.* **2007**, *13*, 4529–4534. (f) Oliveri, C. G.; Heo, J.; Nguyen, S. T.; Mirkin, C. A.; Wawrzak, Z. *Inorg. Chem.* **2007**, *46*, 7716–7718. (g) Oliveri, C. G.; Nguyen, S. T.; Mirkin, C. A. *Inorg. Chem.* **2008**, *47*, 2755–2763.

(6) (a) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477–487. (b) Feringa, B. L. *Acc. Chem. Res.* **2001**, *34*, 504–513. (c) Braunschweig, A. B.; Northrop, B. H.; Stoddart, J. F. *J. Mater. Chem.* **2006**, *16*, 32–44. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191. (e) Olson, M. A.; Braunschweig, A. B.; Ikeda, T.; Fang, L.; Trabolsi, A.; Slawin, A. M. Z.; Khan, S. I.; Stoddart, J. F. *Org. Biomol. Chem.* **2009**, *7*, 4391–4405.

(7) (a) Leigh, D. A.; Morales, M. Á. F.; Pérez, E. M.; Wong, J. K. Y.; Saiz, C. G.; Slawin, A. M. Z.; Carmichael, A. J.; Haddleton, D. M.; Brouwer, A. M.; Buma, W. J.; Wurpel, G. W. H.; León, S.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 3062–3067. (b) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1216–1221. (c) Irie, M. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 917–926. (d) Marlin, D. S.; Cabrera, D. G.; Leigh, D. A.; Slawin, A. M. Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 1385–1390. (e) Marlin, D. S.; Cabrera, D. G.; Leigh, D. A.; Slawin, A. M. Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 77–83.

Experimental Section

General Methods. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert-atmosphere glovebox unless otherwise noted. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), diethyl ether, and hexanes were purified according to published methods.[8] Chlorocyclohexane, 2,4,6-trimethylpyridine, 1,2-dimethoxyethane, diethylene glycol dimethyl ether, methyl acetate, triethylene glycol dimethyl ether, 1,1,2,2-tetrachloroethane, dibromomethane, 1-decanol, 1-nonanol, and 2-chlorophenol were purchased from Alfa Aesar, dried over 4 Å molecular sieves and deoxygenated prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. All other chemicals were used as received from Aldrich Chemical Co. or TCI America unless otherwise stated.

All NMR spectra were recorded on a Bruker Avance III 400 MHz FTNMR spectrometer, and all chemical shifts are reported in parts per million. ^{1}H NMR spectra were referenced relative to residual solvent proton resonances in deuterated solvents. $^{31}P\{^1H\}$ and ^{31}P (161 MHz) spectra were referenced relative to an external 85% H_3PO_4 standard. $^{13}C\{^1H\}$ (101 MHz) spectra were referenced relative to residual solvent resonances. $^{19}F\{^1H\}$ (376 MHz) spectra were referenced relative to an external $CFCl_3$ in $CDCl_3$ standard. High resolution atmospheric pressure photoionization mass spectra (APPIMS) and high resolution electrospray ionization mass spectra (ESIMS) were recorded on an Agilent 6210 LC-TOF with an Agilent 1200 HPLC introduction mass spectrometer system.

Preparation of PS Ligands. Ligands **a**−**g** were prepared according to literature methods.[5c] A general procedure for the preparation of these compounds is given below.

2-Chloroethyldiphenylphosphine (0.34 g, 1.4 mmol, 1.0 equiv), cesium carbonate (0.88 g, 2.8 mmol, 2.0 equiv), and the appropriate thiol precursor (1.4 mmol, 1.0 equiv) were added to 25 mL of acetonitrile in a 50 mL Schlenk flask. The solution was degassed with nitrogen for 10 min and then heated under reflux for 16 h. The solution was cooled to room temperature, and all subsequent purification was performed in air. The solution was filtered through a fine fritted funnel, and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (3 × 50 mL). The organic layers were collected, dried over $MgSO_4$, and the solvent was removed under vacuum to yield a colorless oil. The compound was further purified on a silica gel column (CH_2Cl_2) and recrystallized from pentane to yield a white powder.

(2-(Methylthio)ethyl)diphenylphosphine (a). ^{1}H NMR (CD_2Cl_2), δ = 7.39−7.47 (m, Ph_2P, 10 H), 2.59 (m, PCH_2CH$_2$S, 2 H), 2.39 (m, PCH$_2$CH_2S, 2 H), 2.13 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 138.2 (d, J_{C-P} = 13.8 Hz, Ar*C*), 132.6 (d, J_{C-P} = 18.8 Hz, Ar*C*), 128.6 (s, Ar*C*), 128.5 (d, J_{C-P} = 6.6 Hz, Ar*C*), 30.6 (d, J_{C-P} = 21.5 Hz, *C*H$_2$), 28.2 (d, J_{C-P} = 14.6 Hz, *C*H$_2$), 15.2 (s, *C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −16.4 (s). APPIMS (*m*/*z*): Calcd: 261.0861 $[M+H]^+$. Found: 261.0865.

(2-(Mesitylthio)ethyl)diphenylphosphine (b). ^{1}H NMR (CD_2Cl_2), δ = 7.31 (m, Ph_2P, 10 H), 6.92 (s, Ar*H*, 2 H), 2.65 (m, PCH_2CH$_2$S, 2 H), 2.42 (s, CH_3, 6 H), 2.25 (s, CH_3, 3 H), 2.23 (m, PCH$_2$CH_2S, 2 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 142.9 (s, Ar*C*), 138.3 (s, Ar*C*), 138.0 (d, J_{C-P} = 16.7 Hz, Ar*C*), 132.5 (d, J_{C-P} = 18.7 Hz, Ar*C*), 129.5 (s, Ar*C*), 128.9 (s, Ar*C*), 128.6 (s, Ar*C*), 128.4 (d, J_{C-P} = 6.5 Hz, Ar*C*), 31.4 (d, J_{C-P} = 20.7 Hz, *C*H$_2$), 28.0 (d, J_{C-P} = 15.2 Hz, *C*H$_2$), 21.7 (s, *C*H$_3$), 20.7 (s, *C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −16.4 (s). APPIMS (*m*/*z*): Calcd: 365.1487 $[M+H]^+$. Found: 365.1474.

(2-(2,4-Dimethylphenylthio)ethyl)diphenylphosphine (c). ^{1}H NMR (CD_2Cl_2), δ = 7.10−7.43 (br m, Ph_2P, 10 H), 7.08 (d, J_{H-H} = 8.1 Hz, Ar*H*, 1 H), 7.03 (s, Ar*H*, 1 H), 6.95 (br d, Ar*H*, 1 H), 2.89 (m, PCH_2CH$_2$S, 2 H), 2.35 (m, PCH$_2$CH_2S, 2 H), 2.32 (s, CH_3, 3H), 2.29 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 138.4 (s, Ar*C*), 138.0 (d, J_{C-P} = 13.6 Hz, Ar*C*), 136.2 (s, Ar*C*), 132.6 (d, J_{C-P} = 18.8 Hz, Ar*C*), 131.2 (s, Ar*C*), 131.0 (s, Ar*C*), 129.7 (s, Ar*C*), 128.7 (s, Ar*C*), 128.5 (d, J_{C-P} = 6.6 Hz, Ar*C*), 127.1 (s, Ar*C*), 30.0 (d, J_{C-P} = 22.0 Hz, *C*H$_2$), 28.9 (d, J_{C-P} = 15.0 Hz, *C*H$_2$), 20.6 (s, *C*H$_3$), 20.1 (s, *C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −17.3 (s). APPIMS (*m*/*z*): Calcd: 351.1331 $[M+H]^+$. Found: 351.1318.

(2-(*p*-Tolylthio)ethyl)diphenylphosphine (d). ^{1}H NMR (CD_2Cl_2), δ = 7.33−7.39 (br m, Ph_2P, 10 H), 7.16 (d, J_{H-H} = 8.4 Hz, Ar*H*, 2 H), 7.09 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2 H), 2.91 (m, PCH_2CH$_2$S, 2 H), 2.33 (m, PCH$_2$CH_2S, 2 H), 2.30 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 137.9 (d, J_{C-P} = 13.8 Hz, Ar*C*), 136.4 (s, Ar*C*), 132.7 (d, J_{C-P} = 18.8 Hz, Ar*C*), 132.1 (s, Ar*C*), 130.0 (s, Ar*C*), 129.6 (s, Ar*C*), 128.7 (s, Ar*C*), 128.5 (d, J_{C-P} = 6.6 Hz, Ar*C*), 30.8 (d, J_{C-P} = 22.3 Hz, *C*H$_2$), 28.1 (d, J_{C-P} = 15.1 Hz, *C*H$_2$), 20.7 (s, *C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −16.4 (s). APPIMS (*m*/*z*): Calcd: 337.1174 $[M+H]^+$. Found: 337.1166.

(2-(Phenylthio)ethyl)diphenylphosphine (e). ^{1}H NMR (CD_2Cl_2), δ = 7.33−7.41 (br m, Ph_2P, 10 H), 7.17−7.27 (br m, Ar*H*, 5 H), 2.96 (m, PCH_2CH$_2$S, 2 H), 2.36 (m, PCH$_2$CH_2S, 2 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 137.9 (d, J_{C-P} = 13.8 Hz, Ar*C*), 136.0 (s, Ar*C*), 132.7 (d, J_{C-P} = 18.8 Hz, Ar*C*), 129.1 (s, Ar*C*), 128.9 (s, Ar*C*), 128.8 (s, Ar*C*), 128.5 (d, J_{C-P} = 6.6 Hz, Ar*C*), 126.0 (s, Ar*C*), 30.1 (d, J_{C-P} = 22.7 Hz, *C*H$_2$), 28.1 (d, J_{C-P} = 15.1 Hz, *C*H$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −17.2 (s). APPIMS (*m*/*z*): Calcd: 323.1023 $[M+H]^+$. Found: 323.1009.

(2-(4-Fluorophenylthio)ethyl)diphenylphosphine (f). ^{1}H NMR (CD_2Cl_2), δ = 7.38−7.42 (br m, Ph_2P, 10 H), 7.31 (m, Ar*H*, 2 H), 7.05 (d, J_{H-H} = 7.0 Hz, Ar*H*, 2 H), 2.97 (m, PCH_2CH$_2$S, 2 H), 2.39 (m, PCH$_2$CH_2S, 2 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 161.8 (d, J_{C-F} = 244.4 Hz, Ar*C*), 137.8 (d, J_{C-P} = 13.8 Hz, Ar*C*), 132.6 (d, J_{C-P} = 18.8 Hz, Ar*C*), 132.4 (d, J_{C-F} = 8.0 Hz, Ar*C*), 130.9 (s, Ar*C*), 128.7 (d, J_{C-F} = 9.5 Hz, Ar*C*), 128.5 (d, J_{C-P} = 6.6 Hz, Ar*C*), 115.9 (d, J_{C-P} = 21.9 Hz, Ar*C*), 31.4 (d, J_{C-P} = 22.4 Hz, *C*H$_2$), 28.1 (d, J_{C-P} = 15.2 Hz, *C*H$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −16.6 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ = −116.3 (s, Ar*F*). APPIMS (*m*/*z*): Calcd: 341.0924 $[M+H]^+$. Found: 341.0912.

Diphenyl(2-(2,3,5,6-tetrafluorophenylthio)ethyl)phosphine (g). ^{1}H NMR (CD_2Cl_2), δ = 7.34−7.40 (br m, Ph_2P, 10 H), 7.08 (m, Ar*H*, 1 H), 2.98 (m, PCH_2CH$_2$S, 2 H), 2.32 (m, PCH$_2$CH_2S, 2 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 147.7 (m, Ar*C*), 145.3 (m, Ar*C*), 137.4 (d, J_{C-P} = 13.7 Hz, Ar*C*), 132.6 (d, J_{C-P} = 19.0 Hz, Ar*C*), 128.9 (s, Ar*C*), 128.6 (d, J_{C-P} = 6.7 Hz, Ar*C*), 114.8 (t, J_{C-F} = 20.7 Hz, Ar*C*), 106.0 (t, J_{C-F} = 22.9 Hz, Ar*C*), 31.2 (d, J_{C-P} = 21.6 Hz, *C*H$_2$), 28.9 (d, J_{C-P} = 16.2 Hz, *C*H$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −16.4 (s). $^{19}F\{^1H\}$ NMR −134.37 (m, Ar*F*), −139.00 (m, Ar*F*). APPIMS (*m*/*z*): Calcd: 395.0641 $[M+H]^+$. Found: 395.0630.

Preparation of $Rh^I(PS)_2Cl$ Tweezer Complexes. Closed isomers, **7a**−**f**, and semiopen isomers, **8b**−**g**, were all prepared by the same method; the general procedure for their preparation is given below.

A solution of the appropriate PS ligand (0.39 mmol, 1.0 equiv) in THF (5 mL) was added to a solution of $[Rh(COE)_2Cl]_2$ (0.072 g, 0.099 mmol, 0.25 equiv) in THF (5 mL) via pipet over 10 min. The solution was stirred at room temperature for 2 h. The orange solution was concentrated under vacuum, and the orange solid was precipitated by the addition of hexanes (10 mL). Filtering through Celite with subsequent hexane washes (3 × 5 mL) resulted in pure semiopen complex. The semiopen isomer could be quantitatively converted to the closed isomer by removal of THF under vacuum followed by addition of CH_2Cl_2.

[($Ph_2PCH_2CH_2SCH_3$)$_2$Rh][Cl] (7a). ^{1}H NMR (THF-d_8), δ = 7.27−7.40 (br m, Ph_2P, 12 H), 7.17−7.25 (br m, Ph_2P, 8 H), 2.73 (br s, CH_3, 6 H), 2.62 (br m, PCH_2CH_2S, 8 H). $^{31}P\{^1H\}$ NMR (THF-d_8) δ = 64.3 (d, J_{Rh-P} = 160.4 Hz). ESIMS (*m*/*z*): Calcd: 623.0627 $[M-Cl]^+$. Found: 623.0639.

(8) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

***cis*-[κ^2-($Ph_2PCH_2CH_2S(2,4,6\text{-}(CH_3)_3C_6H_2)$)-$\kappa^1$-($Ph_2PCH_2CH_2S(2,4,6\text{-}(CH_3)_3C_6H_2)$) ClRh] (8b).** ^{1}H NMR (THF-d_8), δ = 7.57 (br m, Ph_2P, Ar*H*, 4 H), 7.08−7.30 (br m, Ph_2P, Ar*H*, 12 H), 6.84−6.93 (br m, Ph_2P, Ar*H*, 8 H), 3.03 (br m, PCH_2CH_2S, 2 H), 2.76 (br m, PCH_2CH_2S, CH_3, 6 H), 2.39 (br m, PCH_2CH_2S, CH_3, 10 H), 2.23 (br m, PCH_2CH_2S, CH_3, 8 H). ^{31}P{^{1}H} NMR (THF-d_8) δ = 71.4 (dd, J_{Rh-P} = 138.4 Hz, J_{P-P} = 31.5 Hz), 34.3 (dd, J_{Rh-P} = 128.7 Hz, J_{P-P} = 32.8 Hz). ESIMS (*m*/*z*): Calcd: 831.1879 [M−Cl]$^+$. Found: 831.1874.

***cis*-[κ^2-($Ph_2PCH_2CH_2S(2,4\text{-}(CH_3)_2C_6H_3)$)-$\kappa^1$-($Ph_2PCH_2CH_2S(2,4\text{-}(CH_3)_2C_6H_3)$) ClRh] (8c).** ^{1}H NMR (THF-d_8), δ = 7.20 (br m, Ph_2P, Ar*H*, 8 H), 6.95 (br m, Ph_2P, Ar*H*, 6 H), 6.82 (br m, Ph_2P, Ar*H*, 8 H), 6.72 (br m, Ph_2P, Ar*H*, 2 H), 6.63 (br m, Ph_2P, Ar*H*, 2 H), 2.54 (br m, PCH_2CH_2S, 2 H), 2.13 (br m, PCH_2CH_2S, CH_3, 6 H), 1.99 (br m, PCH_2CH_2S, CH_3, 4 H), 1.86 (br m, PCH_2CH_2S, CH_3, 2 H), 1.50 (br m, PCH_2CH_2S, CH_3, 2 H), 1.23 (br m, PCH_2CH_2S, CH_3, 4 H). ^{31}P{^{1}H} NMR (THF-d_8) δ = 70.9 (dd, J_{Rh-P} = 135.9 Hz, J_{P-P} = 30.3 Hz), 31.3 (dd, J_{Rh-P} = 127.5 Hz, J_{P-P} = 31.5 Hz). ESIMS (*m*/*z*): Calcd: 803.1566 [M−Cl]$^+$. Found: 803.1564.

***cis*-[κ^2-($Ph_2PCH_2CH_2S(4\text{-}(CH_3)C_6H_4)$)-$\kappa^1$-($Ph_2PCH_2CH_2S(4\text{-}(CH_3)C_6H_4)$)ClRh] (8d).** ^{1}H NMR (THF-d_8), δ = 7.80 (br m, Ph_2P, Ar*H*, 4 H), 7.63 (br m, Ph_2P, Ar*H*, 8 H), 7.40 (br m, Ph_2P, Ar*H*, 6 H), 7.27 (br m, Ph_2P, Ar*H*, 10 H), 3.08 (br m, PCH_2CH_2S, 2 H), 2.56 (br m, PCH_2CH_2S, 2 H), 2.48 (br, CH_3, 3 H), 2.31 (br m, PCH_2CH_2S, 2 H), 1.91 (br m, PCH_2CH_2S, 2 H), 1.68 (br, CH_3, 3 H). ^{31}P{^{1}H} NMR (THF-d_8) δ = 71.5 (dd, J_{Rh-P} = 135.2 Hz, J_{P-P} = 29.1 Hz), 30.8 (dd, J_{Rh-P} = 125.0 Hz, J_{P-P} = 25.5 Hz). ESIMS (*m*/*z*): Calcd: 775.1258 [M−Cl]$^+$. Found: 775.1272.

***cis*-[κ^2-($Ph_2PCH_2CH_2SPh$)-κ^1-($Ph_2PCH_2CH_2SPh$)ClRh] (8e).** ^{1}H NMR (THF-d_8), δ = 7.77 (br m, Ph_2P, Ar*H*, 4 H), 7.48 (br m, Ph_2P, Ar*H*, 8 H), 7.29−7.24 (br m, Ph_2P, Ar*H*, 10 H), 7.13 (br m, Ph_2P, Ar*H*, 8 H), 3.01 (br m, PCH_2CH_2S, 2 H), 2.45 (br m, PCH_2CH_2S, 2 H), 2.17 (br m, PCH_2CH_2S, 2 H), 1.77 (br m, PCH_2CH_2S, 2 H). ^{31}P{^{1}H} NMR (THF-d_8) δ = 73.2 (dd, J_{Rh-P} = 135.9 Hz, J_{P-P} = 27.9 Hz), 32.8 (dd, J_{Rh-P} = 125.0 Hz, J_{P-P} = 27.9 Hz). ESIMS (*m*/*z*): Calcd: 747.0940 [M−Cl]$^+$. Found: 747.0937.

***cis*-[κ^2-($Ph_2PCH_2CH_2S(4\text{-}F_1\text{-}C_6H_4)$)-$\kappa^1$-($Ph_2PCH_2CH_2S(4\text{-}F_1\text{-}C_6H_4)$)ClRh] (8f).** ^{1}H NMR (THF-d_8), δ = 7.75 (br m, Ph_2P, Ar*H*, 4 H), 7.44 (br m, Ph_2P, Ar*H*, 8 H), 7.23 (br m, Ph_2P, Ar*H*, 4 H), 7.10 (br m, Ph_2P, Ar*H*, 6 H), 7.00 (br m, Ph_2P, Ar*H*, 6 H), 2.91 (br m, PCH_2CH_2S, 4 H), 2.40 (br m, PCH_2CH_2S, 4 H). ^{19}F{^{1}H} NMR (THF-d_8) δ = −118.3 (br m, Ar*F*). ^{31}P{^{1}H} NMR (THF-d_8) δ = 74.6 (dd, J_{Rh-P} = 137.1 Hz, J_{P-P} = 30.3 Hz), 35.5 (dd, J_{Rh-P} = 127.5 Hz, J_{P-P} = 30.3 Hz). ESIMS (*m*/*z*): Calcd: 783.0757 [M−Cl]$^+$. Found: 783.0738.

***cis*-[κ^2-($Ph_2PCH_2CH_2S(2,3,5,6\text{-}F_4\text{-}C_6H_1)$)-$\kappa^1$-($Ph_2PCH_2CH_2S(2,3,5,6\text{-}F_4\text{-}C_6H_1)$) ClRh] (8g).** ^{1}H NMR (THF-d_8), δ = 7.80 (br m, Ph_2P, Ar*H*, 5 H), 7.31−7.46 (br m, Ph_2P, Ar*H*, 13 H), 7.16 (br m, Ph_2P, Ar*H*, 4 H), 3.65 (br m, PCH_2CH_2S, 2 H), 2.89 (br m, PCH_2CH_2S, 2 H), 2.64 (br m, PCH_2CH_2S, 4 H). ^{19}F{^{1}H} NMR (THF-d_8) δ = −133.4 (m, Ar*F*), −136.5 (m, Ar*F*), −141.6 (m, Ar*F*), −141.9 (m, Ar*F*). ^{31}P{^{1}H} NMR (THF-d_8) δ = 71.3 (dd, J_{Rh-P} = 133.5 Hz, J_{P-P} = 30.3 Hz), 33.1 (dd, J_{Rh-P} = 132.3 Hz, J_{P-P} = 31.5 Hz). ESIMS (*m*/*z*): Calcd: 891.0186 [M−Cl]$^+$. Found: 891.0200.

General Procedure for VT NMR Experiments. All samples were prepared in an inert atmosphere glovebox and sealed under nitrogen in NMR tubes with J. Young valves. The NMR samples were prepared by adding 0.5 mL of a stock solution containing between 0 and 100% THF-d_8 in CD_2Cl_2 to 15−20 mg of the $Rh^I(PS)_2Cl$ complex. The samples were allowed to equilibrate for 10 min in the NMR after the temperature reading from the thermocouple stabilized to within 0.1 K. The temperature of the probe was determined by using either neat methanol (for temperatures between 170 and 300 K) or neat ethylene glycol (for temperatures between 300 and 312 K) using the following equations: for methanol, $T = -23.832\Delta^2 - 29.46\Delta + 403.0$ (where Δ is the shift difference (ppm) between the CH_3 and O*H* peak) and for ethylene glycol, $T = (4.637 - \Delta)/0.009967$ (where Δ is the shift difference (ppm) between the CH_2 and O*H* peak). K_{eq} was determined from the integration of the appropriate resonances in the ^{31}P NMR spectra corresponding to the closed and semiopen isomers.

Results and Discussion

Homoligated $Rh^I(PS)_2Cl$ complexes (**7a**−**f** and **8b**−**g**, eq 1) were prepared to evaluate the influence of the electron withdrawing/donating ability of the ligand, solvent effects, and temperature on the equilibrium between the two possible isomers, closed (**7**) and semiopen (**8**), where the Cl^- anion is outer or inner sphere, respectively. PS ligands **a**−**g** (eq 1), which contain substituents on the thioether that vary in their electron donating/withdrawing ability, were synthesized in one step from commercially available thiols and (2-chloroethyl)diphenylphosphine by refluxing the reaction mixture in acetonitrile in the presence of cesium carbonate. The substituents on the ligands (R) span a range of electron donating ability, from the strongly electron withdrawing tetrafluorophenyl (**g**) to the electron donating methyl (**a**). The $Rh^I(PS)_2Cl$ complexes were prepared in THF by adding 4 equiv of ligand to 1 equiv of $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) followed by precipitation with hexanes. They were characterized by ^{1}H, ^{31}P{^{1}H}, ^{19}F{^{1}H} NMR spectroscopy, high resolution mass spectrometry, and in some cases in the solid state by single crystal X-ray diffraction studies, and all data are consistent with their proposed structural formulations.

All crystal structures exhibit a distorted tetracoordinate square-planar geometry with respect to the metal ion (Figures 1−5). The semiopen isomers exhibit *cis*-P-Rh-P coordination environments, where one PS ligand is present as a five-membered κ^2-PS chelate and the second PS ligand is present in a κ^1-PS unchelated form, with the chloride ion occupying the fourth coordination site of the Rh^I center (Figures 1, 2, 4, and 5). The solid state structures of the semiopen isomers **8c**,**d**,**f**,**g** contain two different Rh−P bonds lengths, with the Rh1−P1 bond being around 0.05 Å shorter than the Rh1−P2 bond in all structures (Table 1). The shorter length of the Rh1−P1 bond is most likely a result of the P1 phosphorus atom being a part of the five-membered PS chelate. The stronger *trans* effect of the thioether, compared to chloride, may also contribute to the shortening of the Rh1−P1 bond. The solid state structures of semiopen isomers **8c**,**d**,**f**,**g** only exhibit two significant differences in bond lengths. The largest difference among the structures is between the Rh1−S1 bonds of **8f** and **8g**, with the former being 0.043 Å longer than the latter (Table 1). In addition, the Rh1−P1 bond of **8g** is 0.010 Å longer than the analogous bond in **8d**. All other bonds are within 0.009 Å of each other (Table 1). In the closed isomer **7e** (Figure 3), both PS ligands are chelated to the Rh^I in a κ^2-PS fashion with a *cis*-P-Rh-P coordination environment, and the chloride ion is present as an outer-sphere counterion with a Rh−Cl distance of 7.57 Å. The smaller P2−Rh1−S1 angle in the closed isomer, 161°, as compared to the semiopen isomers, around 174°, is more distorted from an ideal square-planar geometry, which is possibly a result of the increased steric congestion around the Rh^I center when both PS ligands are chelated to the metal as is **7e** (further crystallographic data are presented in the Supporting Information). Taken together, these data show

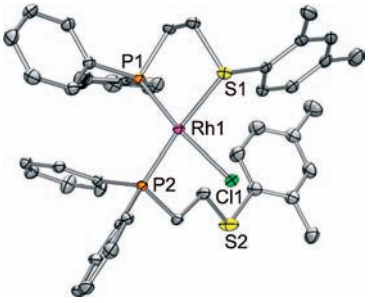


Figure 1. X-ray crystal structure of semiopen isomer **8c**, with thermal ellipsoids drawn at 50% probability. The crystal of **8c** was grown by slow diffusion of diethyl ether into a THF solution of **8c**. Hydrogen atoms have been omitted for clarity. Pink = Rh, Yellow = S, Orange = P, Green = Cl.

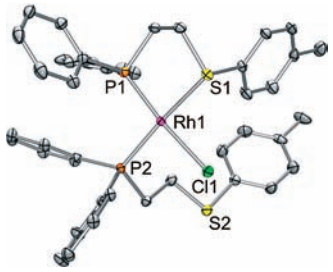


Figure 2. X-ray crystal structure of semiopen isomer **8d**, with thermal ellipsoids drawn at 50% probability. The crystal of **8d** was grown by slow diffusion of diethyl ether into a THF solution of **8d**. Hydrogen atoms have been omitted for clarity. Pink = Rh, Yellow = S, Orange = P, Green = Cl.

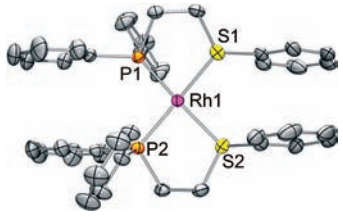


Figure 3. X-ray crystal structure of closed isomer **7e**, with thermal ellipsoids drawn at 50% probability. The crystal of **7e** was grown by slow diffusion of pentane into a CH_2Cl_2 solution of **7e**. Hydrogen atoms and non-coordinating counterions have been omitted for clarity. Pink = Rh, Yellow = S, Orange = P.

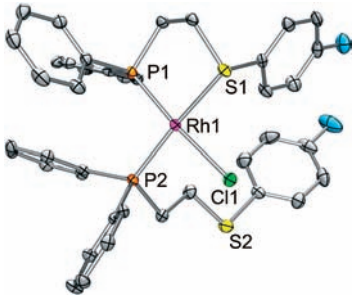


Figure 4. X-ray crystal structure of semiopen isomer **8f**, with thermal ellipsoids drawn at 50% probability. The crystal of **8f** was grown by slow diffusion of diethyl ether into a THF solution of **8f**. Hydrogen atoms have been omitted for clarity. Pink = Rh, Yellow = S, Orange = P, Green = Cl, Light Blue = F.

that the structures are remarkably similar in the solid state, lending themselves to reasonable comparisons (vide infra).

Room temperature ^{31}P NMR spectra of the $Rh^I(PS)_2Cl$ complex made from ligand **b**, show that the closed isomer (**7b**) is the only isomer present in CD_2Cl_2, while in THF-d_8 only

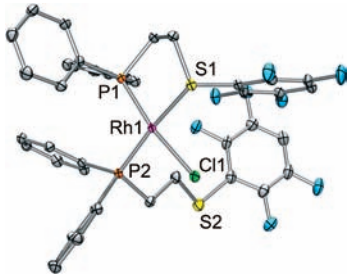


Figure 5. X-ray crystal structure of semiopen isomer **8g**, with thermal ellipsoids drawn at 50% probability. The crystal of **8g** was grown by slow diffusion of diethyl ether into a THF solution of **8g**. Hydrogen atoms have been omitted for clarity. Pink = Rh, Yellow = S, Orange = P, Green = Cl, Light Blue = F.

Table 1. Selected Bond Lengths (Å) and Angles (deg)

	8c	8d	7e	8f	8g
Rh1−P1	2.1949(6)	2.1895(3)	2.2325(9)	2.1903(6)	2.1996(4)
Rh1−P2	2.2463(7)	2.2486(3)	2.2325(9)	2.2477(6)	2.2539(4)
Rh1−S1	2.3537(7)	2.3551(3)	2.3100(9)	2.3592(6)	2.3160(4)
Rh1−S2	na	na	2.3100(9)	na	na
Rh1−Cl1	2.4006(6)	2.3918(3)	na	2.3976(6)	2.3924(3)
P1−Rh1−P2	98.88(2)	97.657(12)	98.18(5)	97.33(2)	99.689(13)
P1−Rh1−S1	86.83(2)	87.397(12)	85.59(3)	86.95(2)	86.993(13)
P1−Rh1−S2	na	na	161.72(3)	na	na
P1−Rh1−Cl1	172.81(2)	174.220(11)	na	174.82(2)	170.728(13)
P2−Rh1−S1	174.27(2)	174.062(11)	161.72(3)	175.24(2)	173.006(13)
P2−Rh1−S2	na	na	85.59(3)	na	na
P2−Rh1−Cl1	87.93(2)	87.775(11)	na	87.72(2)	89.315(13)
S1−Rh1−S2	na	na	96.45(4)	na	na

the semiopen isomer (**8b**) is observed, indicating that the coordination of the Cl^- is strongly influenced by solvent. To study this effect further, the equilibria distribution between semiopen and closed isomers were measured in a series of different solvents. Complexes **7b** and **8b** were used in these studies because the two mesityl ligands provide enhanced solubility and therefore access to more solvents, and the equilibrium distribution between the two isomers was observed to be strongly influenced by solvent polarity, as determined by the E_T^N solvent polarity scale.[9] This scale is based upon a solvatochromatic shift in the absorption spectra of 2,6-dipenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (diphenyl betaine), a dye molecule that is zwitterionic in the ground state and less polar in the excited state because of charge redistribution, and the scale ranges from 0.0 for tetramethylsilane to 1.0 for water.[9] Solvents were chosen such that they spanned a range of polarities from 0.009 to 0.741.[9] The ^{31}P NMR spectra of complexes **7b** and **8b** were obtained in 15 solvents at room temperature, and the percentage of semiopen **8b** was plotted as a function of solvent polarity (Figure 6). The two different coordination environments of the two isomers can be distinguished by their resonances in the ^{31}P NMR spectra, with the closed isomer **7b** exhibiting a doublet around δ 61−66 and the semiopen isomer **8b** exhibiting two doublets of doublets around δ 71−75 and δ 31−35, corresponding to the phosphines of the chelated and non-chelated ligands, respectively (Figure 8).[10] Although, the solvents chosen vary in physical properties from coordinating to

(9) (a) Dimroth, K.; Reichardt, C. *Fresenius' Z. Anal. Chem.* **1966**, *215*, 344–350. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.

(10) (a) Sanger, A. R.; Lobe, C. G.; Weiner-Fedorak, J. E. *Inorg. Chim. Acta* **1981**, *53*, L123–L124. (b) Sanger, A. R. *Can. J. Chem.* **1983**, *61*, 2214–2219.

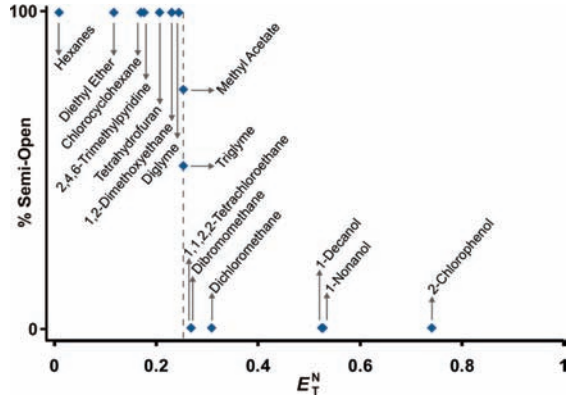


Figure 6. Effect of solvent polarity on the ratio of semiopen **8b** to closed **7b**. The dashed line is at 0.253.

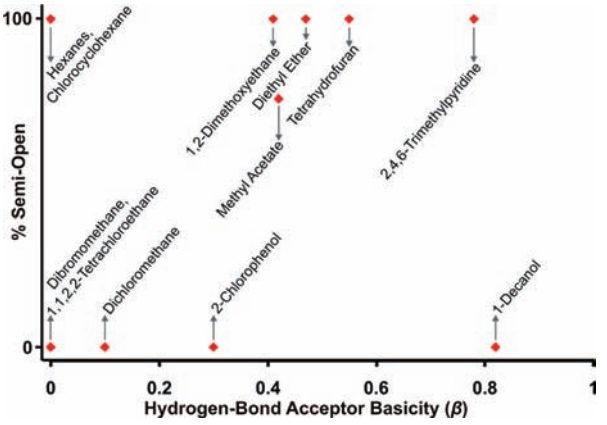


Figure 7. Effect of hydrogen-bond accepting basicity (β) of the solvent on the preference for either isomer. No reported values for 1-nonanol, diglyme, or triglyme could be found.

non-coordinating, hydrogen bond donating/accepting, protic and aprotic, solvent polarity seems to be the most significant factor affecting the preference for one isomer over the other. In all solvents less polar than diethylene glycol dimethyl ether (diglyme), which has an E_T^N value of 0.244, only the semiopen isomer, **8b**, was observed in the ^{31}P NMR spectra (Figure 6). In contrast, only the closed isomer, **7b**, was observed in all solvents more polar than 1,1,2,2-tetrachloroethane, which has an E_T^N value of 0.269. Only in the case of the two solvents with polarities between these two values, methyl acetate and triethylene glycol dimethyl ether (triglyme) (which both have E_T^N values of 0.253), were both isomers observed in solution at room temperature. The difference in the ratios of **7b** to **8b** in methyl acetate and triglyme may result from the $Rh^I(PS)_2Cl$ complex being more sensitive to small changes in polarity in this region than the dye molecule used to calculate E_T^N values, diphenyl betaine, which gives the same value for methyl acetate and triglyme. Interestingly, the switch in preference for one isomer takes place over a remarkably narrow polarity range (0.244−0.269), and does not seem to show a significant dependence on any other physical properties of the solvents. The same trend is seen with other solvent polarity scales (Z and π^*), although fewer values for different solvents have been reported for such scales (see Supporting Information).[11]

(11) (a) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887. (b) Marcus, Y. *Chem. Soc. Rev.* **1993**, *22*, 409–416. (c) Zou, H.; Zhang, Y.; Lu, P. *Anal. Chim. Acta* **1995**, *310*, 461–471. (d) El-Sayed, M.; Spange, S. *J. Phys. Chem. B* **2007**, *111*, 7224–7233.

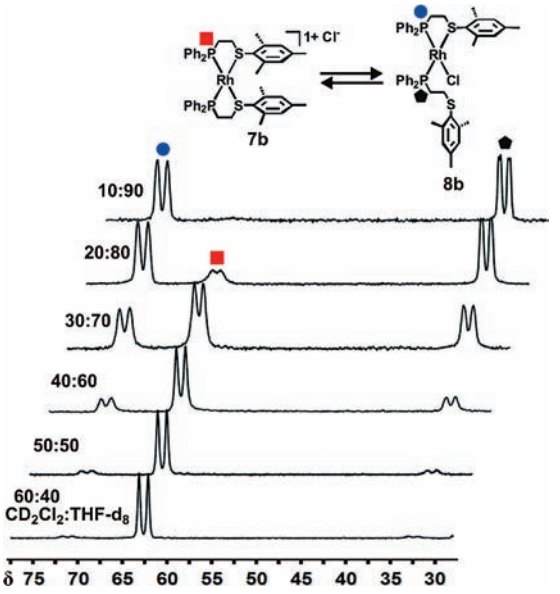


Figure 8. ^{31}P NMR spectra of **7b** and **8b** in different solvent mixtures of CD_2Cl_2 and THF-d_8 at 298 K. Spectra are shifted by 2.5 ppm.

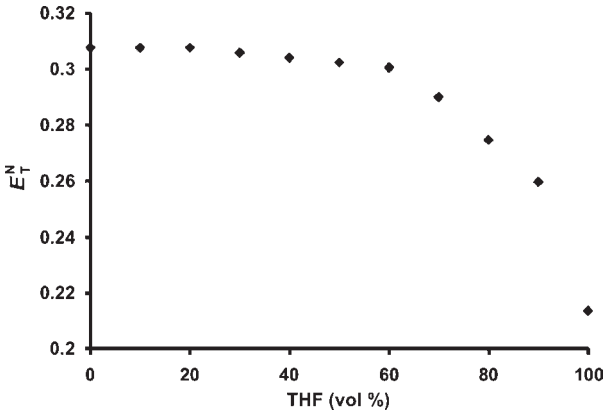


Figure 9. Polarity of different solvent ratios of THF and CH_2Cl_2.

It should also be noted that no correlation was observed between isomer preference and hydrogen-bond accepting basicity (β) (Figure 7), hydrogen-bond donating acidity (α), or dielectric constant of the solvents, although not all hydrogen-bond donating acidities α values for the solvents used in this study are known (see Supporting Information).[11] Interestingly, the two solvents of choice for working with WLA complexes historically have been CH_2Cl_2 and THF,[1,3,5] which happen to fall on opposite sides of the value of solvent polarity defining preference for inner or outer sphere Cl^- coordination (Figure 6).

To further understand the origin of the preference for the closed isomer in more polar solvents and the semiopen isomer in less polar solvents, the switching between the closed and semiopen isomers, **7b** and **8b**, was studied by ^{31}P NMR spectroscopy in different solvent mixtures of CD_2Cl_2 and THF-d_8 (Figure 8). The absorption spectra of diphenyl betaine in different solvent mixtures of CH_2Cl_2 and THF were taken and used to calculate E_T^N values for the solvent mixtures (Figure 9 and Supporting Information).[12] The

(12) (a) Balakrishnan, S.; Easteal, A. J. *Aust. J. Chem.* **1981**, *34*, 943–947. (b) Balakrishnan, S.; Easteal, A. J. *Aust. J. Chem.* **1981**, *34*, 933–941. (c) Langhals, H. *Angew. Chem., Int. Ed.* **1982**, *21*, 724–733.

solvent polarity values measured were 0.213 for THF and 0.308 for CH_2Cl_2, which match well with literature values (0.207 and 0.309, respectively).[9] The polarity of the solution does not change as the amount of THF relative to CH_2Cl_2 increases from 0 to 20%, and only the closed isomer **7b** is observed in the ^{31}P NMR spectra. In this range, the value of E_T^N remains constant at 0.308 (Figure 9). There is a slight decrease in the polarity of the solution as the amount of THF increases from 20 to 60%, E_T^N values decrease from 0.308 to 0.301, and a small amount of **8b** begins to appear in the ^{31}P NMR spectra at 40% THF-d_8 (Figure 8). A dramatic decrease in the polarity of the solvent mixture occurs as the amount of THF increases from 60 to 100%, as evidenced by decreasing E_T^N values from 0.301 to 0.213, and **8b** begins to dominate the equilibrium. In solvent mixtures between 50 and 80% THF-d_8, the range at which the E_T^N value decreases significantly, both isomers can be observed in solution. For solvent mixtures above 80% THF-d_8, only the semiopen isomer is observed by ^{31}P NMR spectroscopy at room temperature, because the E_T^N value defining the preference for outer sphere Cl^- coordination has been exceeded. The range of solvent polarities where both isomers (**7b** and **8b**) are observed in mixtures of CD_2Cl_2 and THF-d_8 (0.275−0.302) is slightly shifted from the solvent polarity range for the pure solvents (0.244−0.269) where both isomers are observed (Figure 6). The size of this window is very similar for both cases, 0.027 for CD_2Cl_2 and THF-d_8 solvent mixtures and 0.025 for the pure solvents, indicating that the preference for one isomer switches over a very narrow range of solvent polarity. The 0.03 shift in the range of solvent polarities where both isomers are observed in solution between the pure solvents as compared to the binary CH_2Cl_2: THF solvent mixtures may result from the preferential solvation of the Rh^I complex or the diphenyl betaine in the solvent mixtures.[13] These results have clear implications for functional systems involving the WLA. If one wants to take advantage of through space interactions between the two ligands in a closed tweezer-like complex, one should use solvents more polar than dibromomethane, while using a solvent with a slightly lower polarity, such as diglyme, will result in a semiopen complex, with little communication between the ligands.

The electron donating/withdrawing ability of the PS ligands also likely influences the equilibrium distribution between the two isomers. To quantitatively compare the effects of the electronic contribution of the ligand on the equilibrium between the two possible isomers, the thermodynamic parameters (K_{eq}, $\Delta G°$, $\Delta H°$, and $T\Delta S°$) for the interconversion between the closed and semiopen isomers were determined by VT ^{31}P NMR spectroscopy in mixtures of CD_2Cl_2 and THF-d_8. The ^{31}P NMR spectra were taken over a temperature range of 170 to 312 K, and the relative integration of the resonances corresponding to the complexes with different coordination geometries was used to calculate K_{eq} at each temperature (Figure 10). When calculating K_{eq}, the concentration of chloride counterions in the outer coordination sphere was assumed to be equal to the concentration of the closed isomer. Van't Hoff plots were used to estimate $\Delta H°$ and $T\Delta S°$.[14]

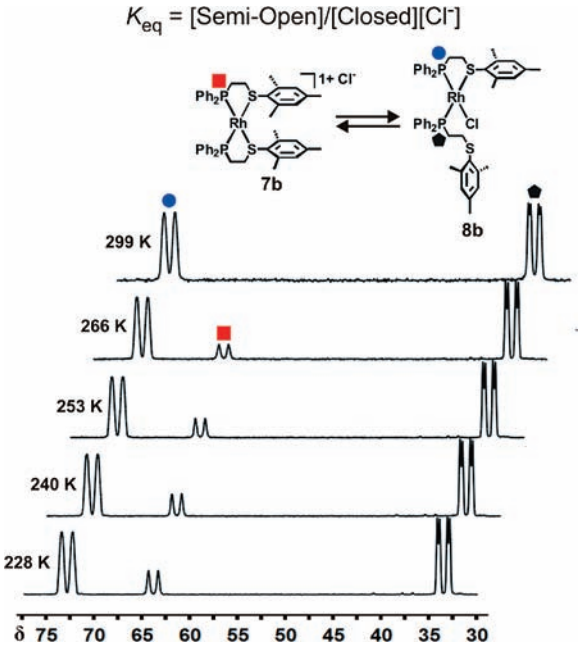


Figure 10. ^{31}P NMR spectra of **7b** and **8b** at various temperatures in THF-d_8. Spectra are shifted by 2.5 ppm.

Indeed, interconversion between the two isomers can be observed by measuring the intensities of the peaks corresponding to **7b** and **8b** in THF-d_8 in the their ^{31}P NMR spectra as a function of temperature. At 299 K, only the resonances corresponding to the semiopen isomer, **8b**, are observed (Figure 10), however, upon cooling the solution, the resonance corresponding to the closed isomer, **7b**, is first observed at 285 K, and then increases in relative intensity compared to resonances for the semiopen isomer as the temperature is progressively decreased. In THF-d_8, K_{eq} increases as the temperature increases, indicating that the movement of Cl^- to the inner coordination sphere is endothermic. It should be noted that the resonances for both isomers do not shift or broaden significantly over the temperature range where switching is observed, indicating that the two complexes are exchanging slowly on the NMR time scale. $\Delta H°$ and $T\Delta S°$ were determined from a van't Hoff plot of the different K_{eq} values obtained as a function of temperature, neglecting the changes in solvent heat capacity (Figure 11),[14] and were found to be 2.7 ± 0.2 and 8.8 ± 0.3 kcal/mol, respectively, at 298 K, signifying that the formation of the semiopen isomer from the closed isomer is entropically favored, but enthalpically disfavored. Because only the semiopen complex is observed by NMR spectroscopy at 298 K in THF-d_8, the value of K_{eq} had to be calculated from $\Delta H°$ and $T\Delta S°$ and was found to be $2.9 \times 10^4 \pm 9 \times 10^3$ M^{-1} at 298 K. Using these values, $\Delta G°$ was found to be −6.1 ± 0.3 kcal/mol in favor of the semiopen isomer in THF-d_8.

The equilibria between the closed (**7b**) and semiopen (**8b**) isomers were also investigated by VT ^{31}P NMR spectroscopy as a function of CD_2Cl_2 and THF-d_8 solvent ratio to understand how $\Delta G°$, $\Delta H°$, $T\Delta S°$, and K_{eq} change with solvent polarity (Figure 8). These experiments were run in triplicate to determine the uncertainty associated with each value. As discussed above, in solvent mixtures containing less than 40% THF-d_8, only the closed isomer (**7b**) could be observed

(13) (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003. (b) Marcus, Y. *Solvent Mixtures: Properties and Selective Solvation*; Marcel Dekker: New York, 2002.

(14) (a) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* **1966**, *62*, 539–547. (b) Stauffer, D. A.; Barrans, R. E.; Dougherty, D. A. *J. Org. Chem.* **1990**, *55*, 2762–2767.

Table 2. Thermodynamic Parameters for the Switching between the Closed and Semi-Open Isomers of Complexes **7b** and **8b**, Respectively, at 298 K[a,b]

complex	solvent ratio (CD_2Cl_2:THF-d_8)	K_{eq} (M^{-1})	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)	$T\Delta S°$ (kcal/mol)
7b,**8b**	60:40	3.5 ± 0.8	-0.7 ± 2.6	13.1 ± 1.9	13.8 ± 1.8
	50:50	9 ± 3	-1.3 ± 1.6	11.4 ± 1.1	12.7 ± 1.1
	40:60	31 ± 17	-2.0 ± 2.3	13.3 ± 1.7	15.3 ± 1.6
	30:70	150 ± 18	-3.0 ± 0.2	9.4 ± 0.2	12.4 ± 0.2
	20:80	$3 \times 10^3 \pm 1 \times 10^3$	-4.7 ± 0.3	8.1 ± 0.2	12.8 ± 0.3
	10:90	$1.6 \times 10^4 \pm 6 \times 10^3$	-5.7 ± 0.4	7.2 ± 0.2	13.0 ± 0.3
	0:100	$2.9 \times 10^4 \pm 9 \times 10^3$	-6.1 ± 0.3	2.7 ± 0.2	8.8 ± 0.3

[a] Enthalpy and entropy values were obtained by neglecting the solvent heat capacity $-\Delta Cp°$.[14] [b] Thermodynamic parameters were extrapolated from van't Hoff plots (Figure 11). Uncertainties were determined by a least-squares analysis from three different samples.

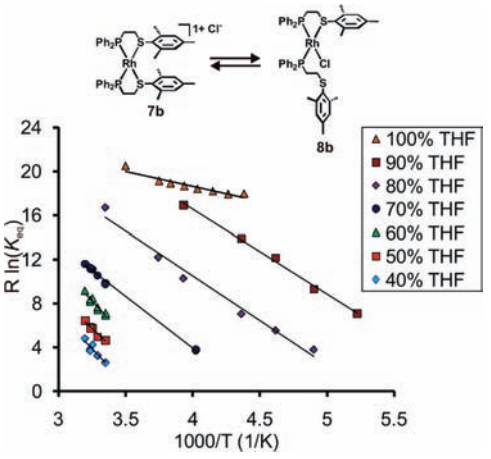


Figure 11. van't Hoff plots of **7b** and **8b** in different solvent mixture of CD_2Cl_2 and THF-d_8.

in the ^{31}P NMR spectra at all temperatures investigated. In solutions of 40−100% THF-d_8 in CD_2Cl_2 both isomers, closed (**7b**) and semiopen (**8b**), are present in solution, and the equilibrium thermodynamic parameters could be determined for each solvent mixture. As the amount of THF-d_8 increases relative to CD_2Cl_2 from 40 to 60%, the values of $\Delta G°$, $\Delta H°$, and $T\Delta S°$ remain almost constant, within the uncertainty of the experiment (Table 2). This is consistent with the observation that the E_T^N value does not vary significantly over this range, and therefore no change in the equilibrium position is expected. In contrast, as the amount of THF-d_8 increases above 60%, $\Delta H°$ decreases with increasing THF-d_8 concentration, from 13.3 ± 1.7 kcal/mol in 60% THF-d_8 to 2.7 ± 0.2 kcal/mol in 100% THF-d_8, indicating that the enthalpic cost in going from the closed to semiopen isomer decreases as the solvent polarity decreases. This is most likely the result of the neutral semiopen isomer being favored because the less polar solvent mixture is less able to solvate the ions. The values of $T\Delta S°$ remain consistent within the uncertainty of the experiment in all mixtures of THF-d_8 and CD_2Cl_2, with the values fluctuating around 13 kcal/mol. The value of $T\Delta S°$ in 100% THF-d_8 is significantly less than the corresponding values calculated for the solvent mixtures, 8.8 ± 0.3 kcal/mol, possibly a result of the less polar THF-d_8 forming a less ordered solvent shell around the ions or fewer solvent molecules being able to solvate the ions, because of the slightly larger size of THF-d_8 as compared to CD_2Cl_2, which produces a lower entropic contribution when liberated (Table 2). The changes in K_{eq}, $\Delta G°$, $\Delta H°$, and $T\Delta S°$ can be explained by considering the plot of solvent ratio to polarity: no significant changes in the E_T^N values are seen between ratios of 100:0 and 60:40, CD_2Cl_2/THF-d_8, which corresponds to the point when polarity begins to change. Similarly, no change in the equilibrium position is observed until the solvent ratio of 60:40, CD_2Cl_2/THF-d_8 is surpassed, strongly suggesting this change is the result of changes in polarity. From 70 to 100% THF-d_8, there is a large decrease in solvent polarity and also a decrease observed in the values of $\Delta H°$ and $T\Delta S°$. Interestingly, formation of the semiopen isomer from the closed isomer is entropically favored in all solvent mixtures of THF-d_8 and CD_2Cl_2. The favorable entropic changes could arise because the charged closed complex and counterion have an ordered solvation sphere, while the resulting neutral semiopen complex produces considerable less ordering of the solvent.[15] The positive enthalpy in all solvent mixtures is most likely a result of the difference in energies between the Rh−S bond, which is broken, and Rh−Cl bond, which is formed, with the former being stronger. It is also likely that there is some contribution to the positive enthalpy from the energy required for solvent reorganization.

The switching between inner and outer sphere Cl^- coordination of $Rh^I(PS)_2Cl$ complexes **7c**−**f** and **8c**−**f** in different solvent mixtures of THF-d_8 and CD_2Cl_2 was also studied by VT ^{31}P NMR spectroscopy (Table 3). No error values are reported because of the excessive experimental time to run these in triplicate, although the uncertainties can be approximated from those calculated for complexes **7b**,**8b**. It should be noted that no switching was observed for the complexes formed with the most electron donating (**a**) and most electron withdrawing (**g**) ligands. For all solvent ratios and temperatures investigated, only the closed isomer **7a** and only the semiopen isomer **8g** were observed by ^{31}P NMR spectroscopy, indicating that strongly electron donating ligands favor the closed isomer, and strongly electron withdrawing ligands favor the semiopen isomer. For some of the complexes **7c**−**f** and **8c**−**f**, switching was only observed at temperatures between 170−180 K in 100% THF-d_8, close to the freezing point of THF, limiting the range over which switching could be studied as well as the magnitude of the observed changes in the ^{31}P NMR spectra, and thus increasing the experimental error beyond the acceptable limit. To compare the thermodynamic parameters of these complexes, we chose to investigate switching in 80 and 90% THF-d_8 because in this region there is a significant change in polarity and as a consequence, the equilibrium position. For complexes **7c**−**f** and **8c**−**f**, $\Delta H°$ decreases as the amount of THF-d_8 increases, similar to complexes **7b** and **8b**, signifying that there is a lower enthalpy of reaction in less polar solvent mixtures, consistent with the hypothesis that less polar solvent mixtures cannot shield the charges between the Rh^I complex and the Cl^- counterion.

(15) Basolo, F.; Johnson, R. C. *Coordination Chemistry: The Chemistry of Metal Complexes*; W. A. Benjamin, Inc.: New York, 1964.

Table 3. Thermodynamic Parameters for the Switching between the Closed and Semi-Open Isomers of Complexes **7b**−**f** and **8b**−**f**, Respectively, at 298 K[a,b]

complexes	solvent ratio (CD_2Cl_2:THF-d_8)	K_{eq} (M^{-1})	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)	$T\Delta S°$ (kcal/mol)
7b,**8b**	20:80	3×10^3	−4.7	8.1	13
	10:90	1.6×10^4	−5.7	7.2	13
7c,**8c**	20:80	1×10^3	−4.1	8.0	12
	10:90	1.2×10^4	−5.6	6.7	12
7d,**8d**	20:80	2×10^3	−4.5	7.5	12
	10:90	3×10^3	−4.7	6.2	11
7e,**8e**	20:80	2.7×10^6	−8.8	7.2	16
	10:90	4.7×10^4	−6.4	5.9	12
7f,**8f**	20:80	2.8×10^6	−8.8	6.4	15
	10:90	1.7×10^4	−5.8	5.9	12

[a] Enthalpy and entropy values were obtained by neglecting the solvent heat capacity $-\Delta Cp°$.[14] [b] Thermodynamic parameters were extrapolated from van't Hoff plots (see Supporting Information).

Although for reactions involving **7c**,**d** and **8c**,**d**, respectively, the values of $T\Delta S°$ do not vary significantly as the amount of THF-d_8 increases, for reactions involving complexes **7e**,**f** and **8e**,**f**, respectively, the values of $T\Delta S°$ are 3−4 kcal/mol larger in 80% THF-d_8 than in 90% THF-d_8. These data show that the reaction is always entropically favored, but there is no obvious reason for the abrupt change in magnitude of $T\Delta S°$ for **7e**,**f** and **8e**,**f**. $\Delta H°$ also can be compared between complexes to correlate the electron donating/withdrawing abilities of the ligands to the preference of one isomer over the other and the strength of the Rh−S bond. As mentioned above, for the complexes with the most electron donating and withdrawing groups on the ligands, only the closed isomer **7a** and semiopen isomer **8g** were observed for all solvent ratios and temperatures investigated. In both 80 and 90% THF-d_8 similar trends are observed for $\Delta H°$ as the electron donating ability of the substituents on the sulfur are changed. $\Delta H°$ can be compared among the different complexes at each solvent ratio to quantify the differences in the enthalpic cost of breaking the Rh−S bond as a result of changing the electron donating ability of the ligand. As the energy required to form the Rh−Cl bond is nearly identical in all cases and the energy associated with solvent reorganization should be similar in all cases, the change in this parameter should only reflect differences in strength of the Rh−S bond. There is a decrease in $\Delta H°$ as the electron withdrawing ability of the ligands decreases, $\Delta H°_{\mathbf{b}} > \Delta H°_{\mathbf{c}} > \Delta H°_{\mathbf{d}} > \Delta H°_{\mathbf{e}} > \Delta H°_{\mathbf{f}}$, signifying that it requires less energy to break the Rh−S bond when more electron withdrawing ligands are present (Table 3).

Conclusion

In conclusion, the switching between closed and semiopen structural isomers of $Rh^I(PS)_2Cl$ complexes has been studied by VT ^{31}P NMR spectroscopy. This switching is reversible and depends upon the solvent polarity, the solvent ratio, the temperature, and the group attached to the sulfur of the PS ligand. These results suggest that when designing functional systems using the WLA, it is necessary to understand the effects of solvent, temperature, and the balance between counterion coordination and the electron donating ability of the ligand to predict the coordination geometry under experimental conditions. As a consequence of these studies one can anticipate the solvent polarity, ligand, or temperature needed to achieve a desired coordination geometry. If a closed geometry is desired, a more polar solvent and electron donating ligands should be used, whereas less polar solvents, such as THF, and electron withdrawing ligands favor the semiopen geometry. This study focused on Rh^I homoligated tweezer-like complexes; however, the results are likely extendable to the more sophisticated and complicated WLA catalysts and allosteric enzyme mimics.

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Supporting Information Available: Tables of crystallographic data, UV/vis spectra of diphenyl betaine, ^{31}P VT NMR spectra, and van't Hoff plots. This material is available free of charge via the Internet at http://pubs.acs.org.