Reversible Ligand Pairing and Sorting Processes Leading to Heteroligated Palladium(II) Complexes with Hemilabile Ligands

Pirmin A. Ulmann,[†] Chad A. Mirkin,*[,†] Antonio G. DiPasquale,[‡] Louise M. Liable-Sands,[‡,§] and Arnold L. Rheingold[‡]

Department of Chemistry and the International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093, and Chemistry Department, Widener University, One University Place, Chester, Pennsylvania 19013

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Halide-induced ligand pairing and sorting processes have been observed in the context of Pd(II) complexes with hemilabile P,S and P,O ligands. Mixing of the ligands $Ph_2PCH_2CH_2SMe$ (**7**) and $Ph_2PCH_2CH_2SPh$ (**8**) with a Pd(II) precursor in CH_2Cl_2 results in a mixture of [(**7**)$_2$ClPd]Cl, [(**8**)$_2$Cl$_2$Pd], and [(**7**)(**8**)ClPd]Cl complexes at 20 °C. This equilibrium can be driven toward the heteroligated structure [(**7**)(**8**)ClPd]Cl by (1) cooling the mixture or (2) precipitation with hexanes, leading to the exclusive formation of semiopen heteroligated complex *cis*-[κ^2-(**7**)-κ^1-(**8**)ClPd]Cl (**9a**), as confirmed by a single-crystal X-ray diffraction study and solid state CPMAS $^{31}P\{^1H\}$ NMR spectroscopy. Dissolution of **9a** in CH_2Cl_2 leads to the original mixture of complexes, which illustrates the reversible nature of this ligand pairing and sorting process. Similar processes occur when a combination of P,S and P,O ligands is used. The semiopen heteroligated complexes can be chemically manipulated in a reversible fashion to form closed complexes, allowing for control of the relative position and flexibility between neighboring substituents in these "tweezer"-like structures. Control experiments suggest these ligand sorting and pairing processes occur via a halide-induced ligand rearrangement (HILR) reaction.

Introduction

The synthesis of supramolecular structures based on coordination chemistry has led to a variety of new materials and compounds with novel shapes and reactivities.[1] These structures are frequently based on rigid ligands, resulting in highly symmetric coordination assemblies. When multiple ligands are mixed together that can form supramolecular structures by coordination to transition metal ions, ligand self-pairing behavior[2a−i] or the formation of mixtures of both self-paired (homoligated) and complementary paired (heteroligated) structures[2j,k] is frequently observed (Scheme 1). The exclusive formation of heteroligated **AMB** structures[2h,i,3] via thermodynamically controlled reactions has been less frequently reported in supramolecular coordination chemistry and in many cases requires a template guest molecule.[3c−e] The ability to form **AMB** structures offers a convenient way to control the relative position of two different functional groups, appended to ligands **A** and **B**, in one coordination complex, especially if aligned cofacially in a "tweezer"-like fashion (Scheme 2). Such heteroligated structures can be synthesized on the basis of the weak-link approach (WLA)[1c,h,4] and the halide-induced ligand rearrangement (HILR) reaction[1i,5] (Scheme 2). Since hemilabile P,X (X = S, O) ligands are used, the relative distance and flexibility between the functional sites can be regulated *in situ* using small

* To whom correspondence should be addressed. Fax: (1) 847-467-5123. E-mail: chadnano@northwestern.edu.
† Northwestern University.
‡ University of California, San Diego.
§ Widener University.

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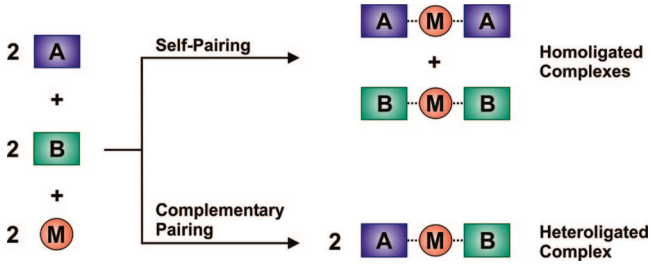
Scheme 1. Homoligated and Heteroligated Complexes Based on Ligands A and B and Metal Ion M[a]



[a] Ligands **A** and **B** belong to the same ligand class (e.g. pyridine, phosphine, etc.). Additional ancillary ligands may be bound to **M**.

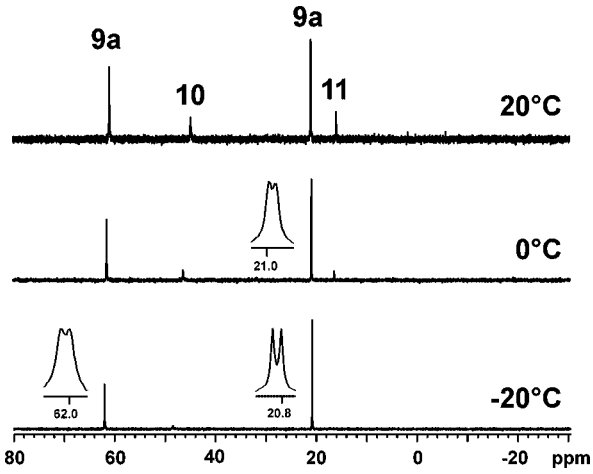


Figure 1. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra (121.5 MHz) of **9a** dissolved in CD_2Cl_2.

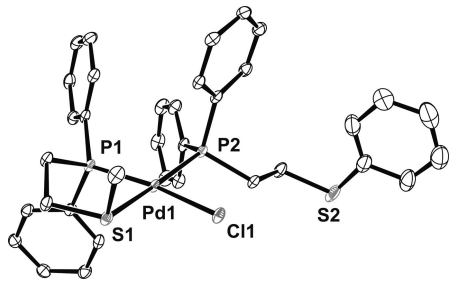


Figure 2. ORTEP diagram of complex **9a**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−P1 2.2540(12), Pd1−P2 2.3110(13), Pd1−S1 2.3674(13), Pd1−Cl1 2.3468(12), P1−Pd1−P2 97.87(4), S1−Pd1−Cl1 85.55(4), P2−Pd1−Cl1 90.67(4), P1−Pd1−S1 86.13(4), P1−Pd1−Cl1 171.35(3), P2−Pd1−S1 172.30(3).

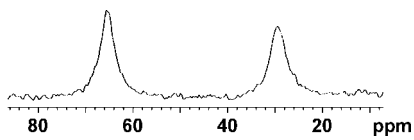


Figure 3. Solid state $^{31}P\{^{1}H\}$ CPMAS NMR spectrum (161.8 MHz) of **9a** (spinning sidebands are not shown).

ancillary ligands via selective cleavage of the M−X bonds. On the basis of this regulation capability, which is inherent to complexes prepared via the WLA, biomimetic allosteric coordination complexes and catalytic signal amplification systems have been developed in homoligated (**AMA**) systems.[1h,7]

Thus far, heteroligated rearrangement processes are known for Rh(I)-P,S_{Aryl}-P,O_{Aryl}[5,6] and Pt(II)-P,S_{Alkyl}-P,S_{Aryl}[8] complexes (**3**−**6**, Scheme 2). These assembly processes occur spontaneously and are independent of the order of addition of the respective ligands. It has been shown that various functional groups, including metalated porphyrins,[6] are compatible with the HILR reaction. Herein we describe an unusual ligand pairing and sorting process that results in the formation of heteroligated Pd(II) complexes. These complexes exist in the solid state and in solution at low temperature, but spontaneously establish an equilibrium between homoligated and heteroligated species in solution at room temperature.

Results and Discussion

Synthesis of Heteroligated Pd(II)-P,S_{Alkyl}-P,S_{Aryl} Complexes 9a,b and 12. When P,S_{Alkyl} ligand **7**, P,S_{Aryl} ligand **8**, and $[Pd(COD)Cl_2]$ (COD: 1,5-cyclooctadiene) are combined in CH_2Cl_2, heteroligated semiopen complex **9a** forms as the major product (Scheme 3, Figure 1). It can be isolated and separated from the COD byproduct via precipitation with hexanes. Homoligated complexes **10** and **11**, which have been characterized previously,[9−11] also form as determined by $^{31}P\{^{1}H\}$ NMR spectroscopy in CD_2Cl_2. Upon cooling to −20 °C, the $^{31}P\{^{1}H\}$ NMR resonance associated with **10** almost disappears and the

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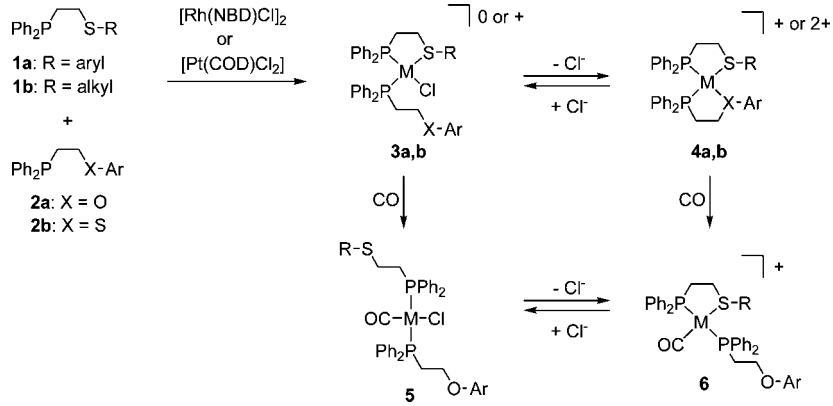
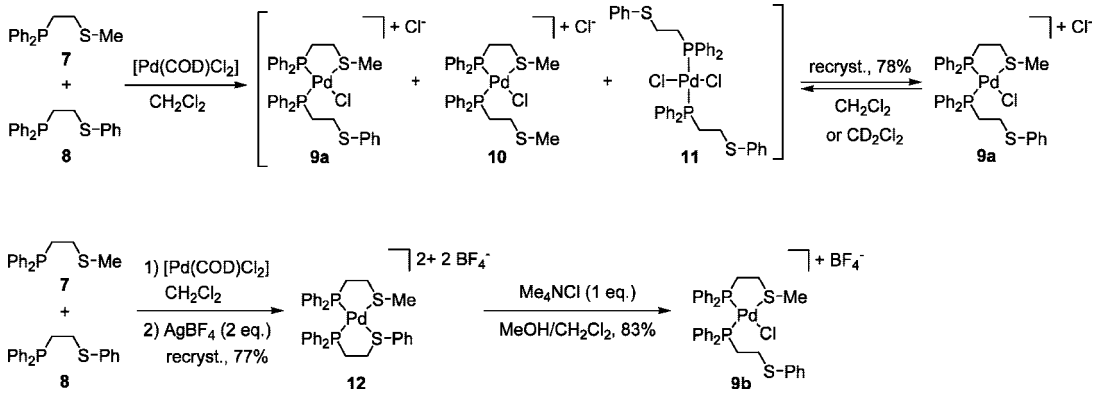
(10) Compound **10** exhibits only one $^{31}P\{^{1}H\}$ NMR resonance due to an exchange process between the two phosphines that is fast on the NMR timescale.[9]
(11) Examples of related Pd(II)-P, X (X = S, N, O) complexes: (a) Munk, V. P.; Sadler, P. J. *Chem. Commun.* **2004**, 1788–1789. (b) Habtemariam, A.; Watchman, B.; Potter, B. S.; Palmer, R.; Parsons, S.; Parkin, A.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1306–1318. (c) Eisenberg, A. H.; Ovchinnikov, M. V.; Mirkin, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 2836–2837. (d) Escriche, L.; Muñoz, J. A.; Kivekäs, R.; Sillampää, R.; Casabó, J. *Eur. J. Inorg. Chem.* **2002**, *2002*, 3258–3263. (e) Clot, O.; Wolf, M. O.; Patrick, B. O. *J. Am. Chem. Soc.* **2001**, *123*, 9963–9973. (f) Eisenberg, A. H.; Dixon, F. M.; Mirkin, C. A.; Stern, C. L.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 2052–2058. (g) Dervisi, A.; Jenkins, R. L.; Malik, K. M. A.; Hursthouse, M. B.; Coles, S. *Dalton Trans.* **2003**, 1133–1142. (h) Hou, D.-R.; Lin, T.-C.; Hsieh, T.-Y.; Cheng, M.-C.; Peng, S.-M.; Liu, S.-T. *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *108*, 61–73. (i) Sanger, A. R. *Can. J. Chem.* **1983**, *61*, 2214–2219. (k) Zotti, G.; Pilloni, G.; Rigo, P.; Martelli, M. *J. Electroanal. Chem.* **1981**, *124*, 277–284. (l) Dyer, G.; Workman, M. O.; Meek, D. W. *Inorg. Chem.* **1967**, *6*, 1404–1407. (m) Fritz, H. P.; Gordon, I. R.; Schwarzhans, K. E.; Venanzi, L. M. *J. Chem. Soc.* **1965**, 5210–5216.

Scheme 2. Formation of Heteroligated Rh(I) and Pt(II) Complexes[a]



[a] **3a**, **4a**: M = Rh(I), X = O, R = aryl; **3b**, **4b**: M = Pt(II), X = S, R = alkyl; **5**, **6**: M = Rh(I), R = aryl; Ar: aryl, counterion: BF_4^-, NBD: 2,5-norbornadiene, COD: 1,5-cyclooctadiene.

Scheme 3. Formation of Heteroligated Pd(II)-P,S_{Alkyl}-P,S_{Aryl} Complexes



resonance associated with **11** disappears completely, but both resonances reappear upon warming to 20 °C. For **9a**, the two resonances assigned to the two P ligands at δ 62.0 (d, $^2J_{P-P}$ = 3 Hz) and 20.8 (d, $^2J_{P-P}$ = 4 Hz) exhibit coupling to each other at −20 °C. Slow recrystallization by layering of the reaction mixture with hexanes results in colorless needles (78% yield) that consist of **9a**, according to a single-crystal X-ray diffraction study (Figure 2) and elemental analysis.

In order to gain more information on the crystallization process of compound **9a**, a mixture of **9a**, **10**, and **11** (Figure 1), formed upon dissolution of analytically pure compound **9a** in CD_2Cl_2, was subjected to precipitation with hexanes and isolation of the pale yellow powder by vacuum removal of solvent, resulting in pure **9a**, as evidenced by solid state $^{31}P\{^1H\}$ CPMAS NMR spectroscopy (Figure 3). Indeed, only two resonances at δ 65.7 (s) and 29.5 (s), consistent with **9a** being the only product in the solid state, are observed. Therefore, the precipitation procedure does not simply lead to a selective crystallization of **9a** from the mixture of components, but rather involves a shift in the equilibrium from **9a**, **10**, and **11** to exclusively **9a** upon precipitation/crystallization.

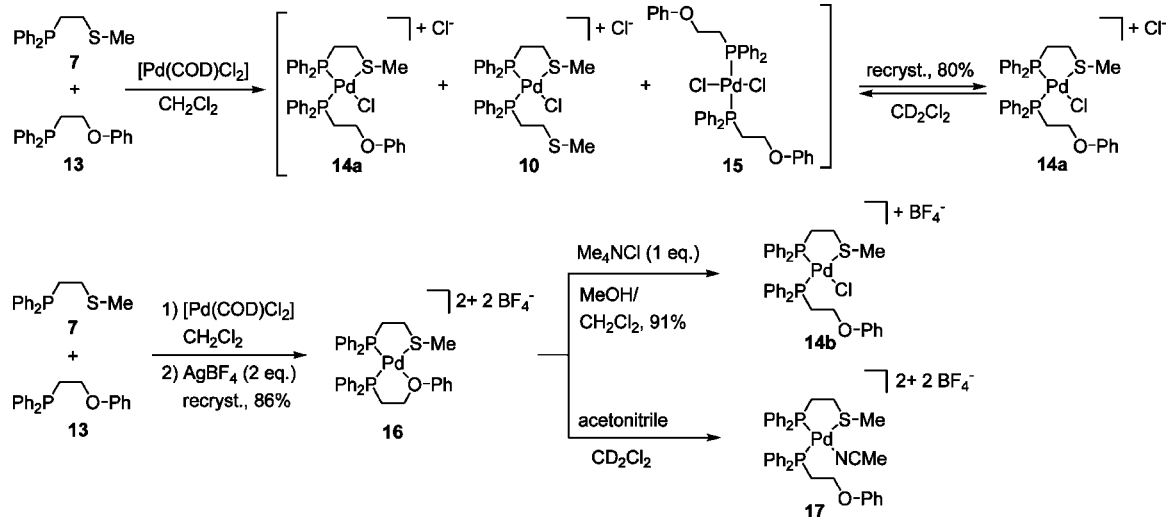
These results indicate that the relative distribution between complexes **9a**, **10**, and **11** is thermodynamically controlled and mediated by a dynamic equilibration process in solution.

Closed heteroligated complex **12** (Scheme 3) can be formed in one-pot fashion by reacting ligands **7** and **8** with [Pd(COD)Cl_2] with subsequent Cl^- abstraction. Recrystallization of the product from hexanes gave **12** (77% yield) and crystals suitable for single-crystal X-ray diffraction (Figure 4). Complex **12** can be reopened to selectively give semiopen complex **9b** using Me_4NCl (1 equiv) in MeOH/CH_2Cl_2. The presence of BF_4^- as the counterion in **9b** instead of chloride (**9a**) results in the stabilization of the heteroligated semiopen compound in solution. Addition of acetonitrile, which is known to coordinate to Pd(II) with moderate strength,[11f] does not open complex **12**, a reflection of the more tightly bound thioether ligands.

Formation of Heteroligated Pd(II)-P,S_{Alkyl}-P,O_{Aryl} Complexes 14a,b, 16, and 17. Mixing of P,S ligand **7** and P,O ligand **13** with [Pd(COD)Cl_2] in CH_2Cl_2, followed by the removal of COD via precipitation with hexanes, predominantly leads to heteroligated complex **14a** (Scheme 4). Indeed, $^{31}P\{^1H\}$ NMR spectroscopy of the solution exhibits resonances at δ 61.2 (s) and 22.3 (s), assigned to **14a**, and two minor resonances at δ 44.8 (s) and 12.9 (s) assigned to complexes **10** and **15**. Complex **10** is known[9,10] and complex **15** has been synthesized via a separate route and fully characterized in solution and by single-crystal X-ray diffraction in the solid state (Figure 5). At −20 °C, resonances assigned to **10** and **15** are less intense, but observable (see Experimental Section). Slow recrystallization results in a pale yellow solid (80% yield) with an elemental composition that is consistent with semiopen complex **14a**. $^{31}P\{^1H\}$ CPMAS NMR spectroscopy in the solid state measured on material obtained via precipitation of a CH_2Cl_2 solution of the mixture (**14a**, **10**, **15**) with hexanes, followed by concentration *in vacuo*, exhibits resonances at δ 63.9 (s) and 33.4 (s), diagnostic of **14a**.

Closed complex **16** can be formed in 86% yield in a one-pot procedure by mixing ligands **7** and **13** with [Pd(COD)Cl_2] followed by the addition of the Cl^--abstracting agent, $AgBF_4$ (Scheme 4). Single crystals of **16**, suitable for X-ray analysis,

Scheme 4. Formation of Heteroligated Pd(II)-P,S_{Alkyl}-P,O_{Aryl} Complexes



were formed by the slow evaporation method (see Experimental Section and Figure 6). Complex **16** can be reopened selectively with Me_4NCl (1 equiv) in $MeOH/CH_2Cl_2$, giving semiopen complex **14b**, or with excess acetonitrile,[11f] resulting in complex **17**, according to ^1H and $^{31}P\{^1H\}$ NMR and FT-IR spectroscopies.

These results show that the HILR reaction, in the context of the ligands studied, occurs independent of the heteroatom in the more weakly binding hemilabile ligand, which suggests that the binding strength of this ligand can be systematically varied to discriminate between small ancillary ligands of different kinds, as shown for acetonitrile.

Crystal Structures 9a, 12·CH_2Cl_2, 15, and 16. All crystal structures exhibit distorted tetracoordinate square-planar geometries with respect to the metal ion. In structure **9a** (Figure 2), the two P,S ligands coexist as five-membered κ^2-P,S_{Alkyl} chelated and unchelated forms. While one chloride ion binds to Pd(II) with a bond length of 2.35 Å, the other chloride ion is present as an outer-sphere counterion with a Pd−Cl distance of 4.71 Å. Fully chelated κ^2-P,S_{Alkyl}/κ^2-P,X_{Aryl} structures **12**·CH_2Cl_2 (X = S, Figure 4) and **16** (X = O, Figure 6) are similar to each other, with the notable exception that the *cis*-oriented S-methyl and S-phenyl groups in **12**·CH_2Cl_2 exhibit an *anti* relationship, while the *cis*-oriented S-methyl and O-phenyl groups in structure **16** assume a *syn* relationship. Structure **15** (Figure 5) exhibits a *trans* relationship between the two unchelated κ^1-P,O_{Aryl} groups with an *anti* relationship between the bulky P*Ph*$_2$ groups. Further crystallographic data are presented in Table 1.

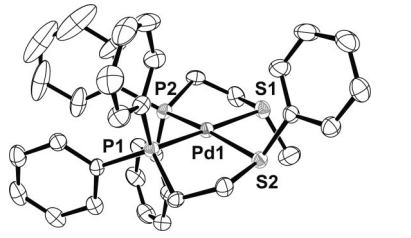
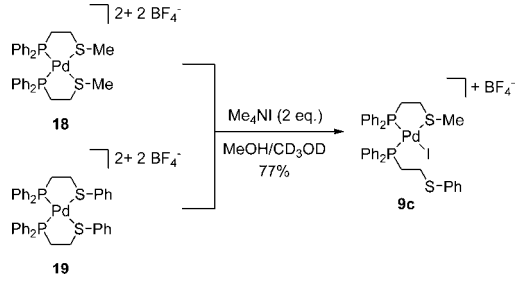


Figure 4. ORTEP diagram of complex **12**·CH_2Cl_2. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms, solvent molecules, and anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−P1 2.2778(11), Pd1−P2 2.2720(12), Pd1−S1 2.3588(12), Pd1−S2 2.3814(12), P1−Pd1−P2 98.36(4), S1−Pd1−S2 91.12(4), P1−Pd1−S2 85.51(4), P2−Pd1−S1 85.37(4), P1−Pd1−S1 175.47(4), P2−Pd1−S2 171.82(4).

Scheme 5. Formation of Heteroligated Complex 9c upon Iodide Addition to Homoligated Complexes 18 and 19



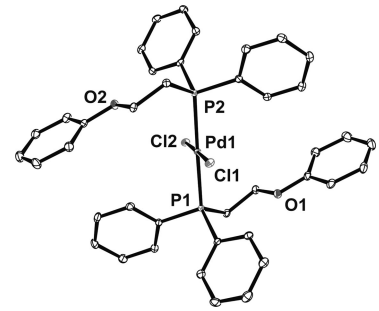


Figure 5. ORTEP diagram of complex **15**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−P1 2.3172(7), Pd1−P2 2.3291(7), Pd1−Cl1 2.2998(6), Pd1−Cl2 2.2996(6), P1−Pd1−Cl1 94.10(2), P1−Pd1−Cl2 84.96(2), P2−Pd1−Cl1 85.48(2), P2−Pd1−Cl2 95.46(2), P1−Pd1−P2 179.03(3), Cl1−Pd1−Cl2 178.73(3).

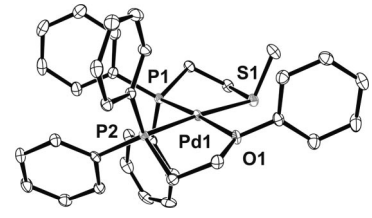


Figure 6. ORTEP diagram of complex **16**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−P1 2.2291(6), Pd1−P2 2.2790(7), Pd1−S1 2.3881(8), Pd1−O1 2.1601(16), P1−Pd1−P2 97.47(2), S1−Pd1−O1 95.48(5), P1−Pd1−O1 176.35(5), P2−Pd1−S1 175.09(2), P1−Pd1−S1 86.66(2), P2−Pd1−O1 80.26(5).

Table 1. Crystallographic Data for 9a, 12·CH_2Cl_2, 15, and 16

	9a	12·CH_2Cl_2	15	16
formula	$C_{35}H_{36}Cl_2P_2PdS_2$	$C_{36}H_{38}B_2Cl_2F_8P_2PdS_2$	$C_{40}H_{38}Cl_2O_2P_2Pd$	$C_{35}H_{36}B_2F_8OP_2PdS$
fw	760.00	947.64	789.94	846.66
color, habit	colorless plate	colorless blade	yellow block	colorless plate
cryst dimens [mm]	0.12 × 0.10 × 0.05	0.22 × 0.10 × 0.08	0.28 × 0.16 × 0.10	0.34 × 0.30 × 0.18
space group	$P\bar{1}$	$C2/c$	$P2(1)$	$P\bar{1}$
cryst syst	triclinic	monoclinic	monoclinic	triclinic
a [Å]	9.835(5)	37.697(4)	9.9937(6)	11.0292(6)
b [Å]	12.815(7)	13.4866(12)	18.6424(11)	13.0562(7)
c [Å]	14.592(8)	17.6277(17)	10.6535(6)	13.6416(7)
α [deg]	102.884(7)	90	90	84.9740(10)
β [deg]	107.206(7)	115.2870(10)	116.0850(10)	66.6040(10)
γ [deg]	94.910(7)	90	90	88.5070(10)
V [Å^3]	1689.7(16)	8103.3(13)	1782.65(18)	1795.86(17)
Z	2	8	2	2
D_{calcd} [g cm^{-3}]	1.494	1.554	1.472	1.566
radiation (λ, D [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
F(000)	776	3824	808	856
2θ range [deg]	3.02 to 56.00	2.38 to 41.68	4.26 to 56.18	3.14 to 56.68
abs coeff [mm^{-1}]	0.950	0.836	0.795	0.734
T [K]	100(2)	100(2)	100(2)	100(2)
no. of measd reflns	19 458	16 887	15 992	23 757
no. of indep reflns	7347	4239	6983	8101
refinement method	full-matrix least-squares on F^2			
GOF on F^2	1.048	1.066	1.010	1.017
final R indices [$I > 2\sigma(I)$]	R1 = 0.0425, wR2 = 0.1015	R1 = 0.0351, wR2 = 0.0856	R1 = 0.0245, wR2 = 0.0559	R1 = 0.0342, wR2 = 0.0760
R indices (all data)	R1 = 0.0570, wR2 = 0.1096	R1 = 0.0413, wR2 = 0.0891	R1 = 0.0281, wR2 = 0.0583	R1 = 0.0488, wR2 = 0.0821
largest diff. peak and hole [e·Å^{-3}]	1.270 and −1.211	0.477 and −0.991	0.497 and −0.336	1.145 and −0.759

Confirmation of the Halide-Induced Ligand Rearrangement (HILR) Reaction in Pd(II) Complexes. To confirm that the formation of heteroligated complexes occurs spontaneously in the presence of halide ions via a ligand rearrangement process, ligands **7** and **8** (1 equiv each) were separately mixed with [Pd(COD)Cl_2] (0.5 equiv each) in CD_2Cl_2, and the formation of complexes **10**[9] and **11**[9] was confirmed via $^{31}P\{^1H\}$ NMR spectroscopy. These two solutions were mixed rapidly, and an additional $^{31}P\{^1H\}$ NMR spectrum was acquired after 15 min, which exhibited major resonances corresponding to heteroligated structure **9a** as well as minor resonances for **10** and **11**. This experiment illustrates that the HILR reaction occurs via a ligand dissociation/reassociation process, which leads to a mixture that consists predominantly of heteroligated species. In an additional experiment, complexes **18** (1 equiv) and **19** (1 equiv) (Scheme 5) were mixed in CH_2Cl_2 in the absence of any halide ions, and no reaction was observed after 18 days, according to $^{31}P\{^1H\}$ NMR spectroscopy. Compounds **18** and **19** also showed no reactivity in CH_3OH/CD_3OD (10:1 v/v) after 2.5 h, whereas the formation of heteroligated complex **9c** was observed upon addition of Me_4NI (2 equiv) after 30 min, according to $^{31}P\{^1H\}$ NMR spectroscopy and high-resolution ESI-MS. These experiments show the crucial role of halide ions for the formation of heteroligated species via ligand rearrangement processes.

Conclusions

Thermodynamically controlled pairing and sorting processes that favor complementary combinations are well known in biological or organic supramolecular assemblies (e.g., pairing of nucleobases), but are still relatively rare in supramolecular coordination chemistry. The results obtained thus far show that the HILR reaction consistently results in the spontaneous formation of heteroligated species with various d^8 transition metal ions [Rh(I),[5,6] Pt(II),[8] Pd(II)]. In the case of the Pd(II) complexes, these ligand pairing and sorting processes are reversible, as evidenced by the dynamic equilibrium established with the homoligated complexes in solution at elevated temperatures. One can control this process through the choice of counterion and stabilize the heteroligated structures with non- or weakly coordinating counterions such as BF_4^-. This "toolbox" of reactions will be useful in studying and regulating the cooperative interactions between different functionalities in tweezer complexes that derive from this novel ligand pairing and sorting process.[1i]

Experimental Section

General Methods/Instrument Details. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere glovebox. CH_2Cl_2, acetonitrile, and hexanes were dried and purified through activated alumina columns as described by Grubbs et al. prior to use.[12] All solvents were degassed with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All other chemicals were used as received from Aldrich Chemical Co. or prepared according to literature procedures (**7**,[8] **8**,[13] **13**[14]). ^1H NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 300 MHz and referenced to residual proton resonances in deuterated solvents. $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 282.5 MHz and referenced relative to an external $CFCl_3$ (in $CDCl_3$) standard. Solution $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 121.5 MHz and referenced relative to an external 85% H_3PO_4 standard. The NMR probe temperature was calibrated using methanol (−20 to 20 °C) before variable-temperature measurements.[15] Solid state $^{31}P\{^1H\}$ CPMAS (cross-polarization magic-angle spinning) NMR spectra were recorded on a 400 MHz Varian FT-NMR system with a wide bore magnet and a T3 MAS probe (HPC mode) at 161.8 MHz, with 3.3 μs proton pulse width, a contact time of 5 ms, a recycle delay of 30 s, and a spin rate of 10 000 s^{-1}. Chemical shifts were referenced with respect to an external 85% H_3PO_4 standard by referencing the resonance for external solid $NH_4H_2PO_4$ to 0.8 ppm. All chemical shifts are reported in ppm. FT-IR spectra were recorded in solution using a Thermo Nicolet Nexus 670 FT-IR spectrometer with a NaCl cell

(12) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
(13) Dubois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011–1015.
(14) Singewald, E. T.; Shi, X.; Mirkin, C. A.; Schofer, S. J.; Stern, C. L. *Organometallics* **1996**, *15*, 3062–3069.
(15) Raiford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51*, 2050–2051.

(cell length = 0.1 mm). Electrospray ionization (ESI) mass spectra were recorded on a Micromass Quatro II triple quadrupole mass spectrometer or an Agilent LC/MS MSD1100 mass spectrometer. MALDI-TOF mass spectra were recorded on an Applied Biosystems Voyager-DE STR at the Mass Spectrometry Laboratory of the University of Illinois, Urbana−Champaign, IL. High-resolution elecrospray ionization mass spectra (ESI-HRMS) were recorded on an Agilent 6210 TOF LC/MS spectrometer. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ, or the Microanalytical Laboratory of the University of Illinois, Urbana−Champaign, IL.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2SPh$)ClPd]Cl, 9a.** A solution of [Pd(COD)Cl_2] (44.3 mg, 0.155 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SPh$ (**8**) (50.0 mg, 0.155 mmol, 1 equiv) in CH_2Cl_2 (2 mL) at 24 °C. The solution was yellow. After 5 min, a solution of $Ph_2PCH_2CH_2SMe$ (**7**) (40.4 mg, 0.155 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise, and the yellow reaction mixture was stirred for 1 h. Recrystallization from CH_2Cl_2/hexanes resulted in **9a** as a colorless solid (92.0 mg, 78%). CPMAS $^{31}P\{^1H\}$ NMR (161.8 MHz, 22 °C): δ 65.7 (s), 29.5 (s). Anal. Calcd for $C_{35}H_{36}Cl_2P_2PdS_2$: C, 55.31; H, 4.77. Found: C, 55.43; H, 4.73. Crystals of **9a** suitable for single-crystal X-ray diffraction were obtained by slow diffusion of hexanes into the reaction mixture (colorless plates). The following characterization data are for a mixture of **9a**, **10**, and **11** in solution, which forms upon dissolution of **9a** in CD_2Cl_2, as described in the prior sections, Scheme 3 and Figure 1. ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.52−7.05 (m, arom.), 3.66 (br s, aliph.), 3.32 (br s, aliph.), 3.09 (br s, aliph.), 2.90 (br s, aliph.), 2.78−2.42 (m, aliph.). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 61.0 (s, **9a**), 44.9 (s, **10**), 21.1 (s, **9a**), 16.1 (s, **11**); 0 °C: δ 61.5 (s, **9a**), 46.4 (s, **10**), 21.0 (d, $^2J_{P-P}$ = 3 Hz, **9a**), 16.4 (s, **11**); −20 °C: δ 62.0 (d, $^2J_{P-P}$ = 3 Hz, **9a**), 48.4 (s, **10**), 20.8 (d,$^2J_{P-P}$ = 4 Hz, **9a**). The temperature equilibration period between insertion of the NMR tube and acquisition of variable-temperature NMR spectra was approximately 5 min. $^{31}P\{^1H\}$ NMR spectroscopic resonances for **10**[9] and **11**[9] were measured separately at the respective temperatures and are consistent with the corresponding assignments within 0.1 ppm. MS (ESI, CH_2Cl_2): m/z = 723.5 $[M - Cl]^+$.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2SPh$)ClPd]BF_4, 9b.** A solution of Me_4NCl (1.9 mg, 0.018 mmol, 1 equiv) in MeOH (anhydrous, 1 mL) was added to a solution of compound **12** (15.0 mg, 0.0174 mmol, 1 equiv) in CH_2Cl_2 (1 mL), resulting in a yellow solution. $^{31}P\{^1H\}$ NMR spectroscopy after 15 min showed predominantly complex **9b**. The reaction mixture was concentrated *in vacuo*, dissolved in CH_2Cl_2 (2 mL), followed by the addition of hexanes until the solution became turbid (ca. 1 mL). Filtration and concentration *in vacuo* resulted in **9b** (11.7 mg, 83%) as a pale yellow powder. ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.95−7.21 (m, 25H, arom.), 3.22−3.02 (m, 2H, CH_2), 2.93 (d, J = 4.5 Hz, 3H, CH_3), 2.77−2.68 (m, 4H, CH_2), 2.59−2.55 (m, 2H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 62.6 (d, $^2J_{P-P}$ = 7 Hz), 22.5 (d, $^2J_{P-P}$ = 5 Hz). $^{19}F\{^1H\}$ NMR (282.5 MHz, CD_2Cl_2, 22 °C): δ −152.86 (s, $^{10}BF_4$), −152.91 (s, $^{11}BF_4$). MS (ESI, MeOH): m/z 723.0 $[M - BF_4]^+$, 344.0 $[M - BF_4 - Cl]^{2+}$. Anal. Calcd for $C_{35}H_{36}ClP_2PdS_2BF_4$: C, 51.81; H, 4.47. Found: C, 52.08; H, 4.49.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^2-($Ph_2PCH_2CH_2SPh$)Pd]$(BF_4)_2$, 12.** A solution of [Pd(COD)Cl_2] (88.5 mg, 0.310 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SPh$ (**8**) (100.0 mg, 0.310 mmol, 1 equiv) in CH_2Cl_2 (2 mL) at 24 °C. After 5 min, a solution of $Ph_2PCH_2CH_2SMe$ (**7**) (80.7 mg, 0.310 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise, and the reaction mixture was stirred for 1 h. After addition of $AgBF_4$ (120.7 mg, 0.620 mmol, 2 equiv), the reaction solution turned cloudy yellow. After 1 h, the reaction solution was filtered through Celite. Recrystallization from CH_2Cl_2/hexanes (slow diffusion) resulted in **12**·1/2CH_2Cl_2 as a pale yellow powder (216.7 mg, 77%). ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.80−7.77 (m, 2H, arom.), 7.58−7.44 (m, 23H, arom.), 3.4−2.9 (m, 8H, CH_2), 2.57 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 62.4 (s). MS (ESI, CH_2Cl_2): m/z 775.3 $[M - BF_4]^+$, 344.2 $[M - 2\ BF_4]^{2+}$. Anal. Calcd for $C_{35}H_{36}B_2F_8P_2PdS_2$·1/2$CH_2Cl_2$: C, 47.10; H, 4.12. Found: C, 47.42; H, 3.93. A residual amount of CH_2Cl_2 was observed via ^1H NMR spectroscopy in $CDCl_3$ upon drying *in vacuo*. Crystals of **12**·CH_2Cl_2 suitable for single-crystal X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **12** in CH_2Cl_2 (colorless blades). Addition of acetonitrile (5 μL, 0.1 mmol, 20 equiv) to **12** (5.0 mg, 0.0058 mmol, 1 equiv) in CD_2Cl_2 (0.75 mL) at 24 °C resulted in no opening of complex **12** after 2 h, according to $^{31}P\{^1H\}$ NMR spectroscopy.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2OPh$)ClPd]Cl, 14a.** A solution of [Pd(COD)Cl_2] (65.8 mg, 0.230 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SMe$ (**7**) (60.0 mg, 0.231 mmol, 1 equiv) in CH_2Cl_2 (2 mL) at 24 °C. The solution was yellow. After 5 min, a solution of $Ph_2PCH_2CH_2OPh$ (**13**) (70.6 mg, 0.230 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise, and the orange reaction mixture was stirred for 1 h. Recrystallization from CH_2Cl_2/hexanes resulted in **14a** as a slightly yellow powder (137.4 mg, 80%). CPMAS $^{31}P\{^1H\}$ NMR (161.8 MHz, 22 °C): δ 63.9 (s), 33.4 (s). Anal. Calcd for $C_{35}H_{36}Cl_2OP_2PdS$: C, 56.50; H, 4.88. Found: C, 56.46; H, 4.63. The following characterization data are for a mixture of **14a**, **10**, and **15** in solution, which forms upon dissolution of **14a** in CD_2Cl_2, as described in the previous sections and Scheme 4. ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.91−7.89 (m, arom.), 7.72−7.41 (m, arom.), 7.11−7.06 (m, arom.), 6.92−6.87 (m, arom.), 4.42−4.32 (m, aliph.), 3.83 (br s, aliph.), 3.46 (br s, aliph.), 3.29 (br s, aliph.), 3.29−3.10 (m, aliph.), 2.98−2.8 (m, aliph.). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 61.2 (s, **14a**), 44.8 (s, **10**), 22.3 (s, **14a**), 12.9 (s, **15**); 0 °C: δ 61.9 (d, $^2J_{P-P}$ = 2 Hz, **14a**), 46.4 (s, **10**), 26.1 (s, minor unidentified species), 22.8 (d, $^2J_{P-P}$ = 2 Hz, **14a**), 12.9 (s, **15**); −20 °C: δ 62.4 (d, $^2J_{P-P}$ = 2 Hz, **14a**), 48.3 (s, **10**), 26.4 (s, minor unidentified species), 23.2 (d, $^2J_{P-P}$ = 2 Hz, **14a**), 12.6 (s, **15**). The temperature equilibration period between insertion of the NMR tube and acquisition of variable-temperature NMR spectra was approximately 5 min. $^{31}P\{^1H\}$ NMR spectroscopic resonances for **10**[9] and **15** were measured separately at the respective temperatures and are consistent with the corresponding assignments within 0.2 ppm. MS (ESI, CH_2Cl_2): m/z 707.2 $[M - Cl]^+$.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2OPh$)ClPd]BF_4, 14b.** A solution of Me_4NCl (1.9 mg, 0.018 mmol, 1 equiv) in MeOH (anhydrous, 1 mL) was added to a solution of compound **16** (15.0 mg, 0.0177 mmol, 1 equiv) in CH_2Cl_2 (1 mL), resulting in a yellow solution. $^{31}P\{^1H\}$ NMR spectroscopy after 15 min indicated completion of the reaction. The reaction mixture was concentrated *in vacuo*, dissolved in CH_2Cl_2 (2 mL), followed by filtration and concentration *in vacuo*, resulting in **14b** (12.8 mg, 91%) as a light red powder. ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.9−7.24 (m, 20H, arom.), 7.06−7.00 (m, 2H, arom.), 6.85−6.82 (m, 3H, arom.), 4.43−4.33 (m, 2H, OCH_2), 3.13−3.05 (m, 4H, CH_2), 2.91 (d, J = 4.5 Hz, 3H, CH_3), 2.68−2.52 (m, 2H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 63.7 (d, $^2J_{P-P}$ = 6 Hz), 25.4 (d, $^2J_{P-P}$ = 6 Hz). $^{19}F\{^1H\}$ NMR (282.5 MHz, CD_2Cl_2, 22 °C): δ −152.95 (s, $^{10}BF_4$), −153.01 (s, $^{11}BF_4$). HRMS (ESI, MeOH): m/z 707.0694 $[M - BF_4]^+$.

***trans*-[κ^1-($Ph_2PCH_2CH_2OPh$)$_2Cl_2Pd$], 15.** [Pd(COD)Cl_2] (25.0 mg, 0.0876 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added to a solution of $Ph_2PCH_2CH_2OPh$ (**13**) (53.7 mg, 0.175 mmol, 2 equiv) in CH_2Cl_2 (2 mL), resulting in a yellow solution. After 1 h, the reaction solution was layered with hexanes (slow recrystallization), resulting in yellow crystals of **15** (65.0 mg, 94%). ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.77−7.71 (m, 8H, arom.), 7.50−7.39

(m, 12H, arom.), 7.23−7.18 (m, 4H, arom.), 6.98−6.88 (m, 2H, arom.), 6.78−6.71 (m, 4H, arom.), 4.30−4.24 (m, 4H, OCH_2), 3.02−2.96 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 25.7 (s, minor unidentified species), 13.0 (s, **15**); 0 °C: δ 26.0 (s, minor unidentified species), 12.8 (s, **15**); −20 °C: δ 26.3 (s, minor unidentified species), 12.5 (s, **15**). MS (ESI, CH_2Cl_2): *m*/*z* 753.1 $[M - Cl]^+$. Anal. Calcd for $C_{40}H_{38}Cl_2O_2P_2Pd$: C, 60.81; H, 4.85. Found: C, 60.60; H, 4.75. Crystals of **15** suitable for single-crystal X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **15** in CH_2Cl_2 (yellow blocks).

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^2-($Ph_2PCH_2CH_2OPh$)Pd](BF_4)$_2$, 16.** A solution of [Pd(COD)Cl_2] (82.2 mg, 0.288 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SMe$ (**7**) (75.0 mg, 0.288 mmol, 1 equiv) in CH_2Cl_2 (2 mL) at 24 °C. After 5 min, a solution of $Ph_2PCH_2CH_2OPh$ (**13**) (88.2 mg, 0.288 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise, and the orange reaction mixture was stirred for 1 h. After addition of $AgBF_4$ (112.1 mg, 0.576 mmol, 2 equiv), the reaction solution turned cloudy yellow. After 1 h, the reaction solution was filtered through Celite, followed by recrystallization from CH_2Cl_2/hexanes (slow diffusion), resulting in **16** as a slightly orange powder (209.3 mg, 86%). ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.67−7.49 (m, 24H, arom.), 7.14−7.09 (m, 1H, arom.), 4.42−4.15 (m, 2H, OCH_2), 3.55−3.05 (m, 4H, CH_2), 2.95−2.4 (m, 2H, CH_2), 2.14 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 63.9 (s), 51.4 (s). MS (MALDI-TOF, DHB): *m*/*z* 670.8 $[M - H - 2\ BF_4]^+$. Anal. Calcd for $C_{35}H_{36}B_2F_8OP_2PdS$: C, 49.65; H, 4.29. Found: C, 49.72; H, 4.20. Crystals of **16** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of hexanes into a solution of **16** in 1,2-dichloroethane (colorless plates).

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2OPh$)(acetonitrile)Pd](BF_4)$_2$, 17.** Compound **16** (7.5 mg, 0.0089 mmol, 1 equiv) was dissolved in CD_2Cl_2 (1 mL), followed by the addition of acetonitrile (3 μL, 0.06 mmol, 6 equiv). $^{31}P\{^1H\}$ NMR spectroscopy of the light yellow solution after 15 min showed quantitative formation of **17**. ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.63−7.18 (m, 20H, arom.), 7.05−6.93 (m, 2H, arom.), 6.65−6.62 (m, 3H, arom.), 4.14−4.08 (m, 2H, OCH_2), 3.25−3.21 (m, 2H, CH_2), 3.15−2.9 (m, 2H, CH_2), 2.79 (d, J = 4.8 Hz, 3H, CH_3), 2.70−2.67 (m, 2H, CH_2), 1.97 (s, ca. 20H, CH_3CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 64.3 (d, $^2J_{P-P}$ = 5 Hz), 22.5 (d, $^2J_{P-P}$ = 5 Hz). MS (MALDI-TOF, DHB): *m*/*z* 670.8 [M − acetonitrile − H − 2 BF_4]$^+$. FT-IR (CD_2Cl_2): ν_{CN} 2303 (metal bound acetonitrile), 2197 (free acetonitrile) cm^{-1}. Addition of 1 equiv of acetonitrile to **16** led to only a partial opening of the complex. The compound was not isolated in the solid state due to loss of acetonitrile upon solvent removal.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)$_2$Pd](BF_4)$_2$, 18.** A solution of [Pd(COD)Cl_2] (54.8 mg, 0.192 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SMe$ (**7**) (100.0 mg, 0.384 mmol, 2 equiv) in CH_2Cl_2 (2 mL) at 24 °C. The solution was orange. After 15 min, $AgBF_4$ (74.8 mg, 0.384 mmol, 2 equiv) was added, and the cloudy light yellow reaction mixture was stirred for 1 h. Precipitation with hexanes, filtration through Celite, followed by extraction of the precipitate with CH_2Cl_2 (25 mL) and concentration *in vacuo* resulted in **18** as a yellow powder (153.4 mg, 99.8%). ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.9−7.40 (m, 20H, arom.), 3.6−2.95 (m, 8H, CH_2), 2.78 (d, J = 3.9 Hz, 6H, CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 61.5 (s). MS (ESI, MeOH): *m*/*z* 313.0, $[M - 2\ BF_4]^{2+}$. Anal. Calcd for $C_{30}H_{34}B_2F_8P_2PdS_2$: C, 45.00; H, 4.28. Found: C, 44.64; H, 4.15. $^{31}P\{^1H\}$ NMR data are consistent with the perchlorate derivative of **18** reported in ref 9.

***cis*-[κ^2-($Ph_2PCH_2CH_2SPh$)$_2$Pd](BF_4)$_2$, 19.** A solution of [Pd(COD)Cl_2] (13.3 mg, 0.0466 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added dropwise to a stirring solution of $Ph_2PCH_2CH_2SPh$ (**8**) (30.0 mg, 0.0931 mmol, 2 equiv) in CH_2Cl_2 (2 mL) at 24 °C. The solution was yellow. After 15 min, $AgBF_4$ (18.1 mg, 0.0930 mmol, 2 equiv) was added and the cloudy yellow reaction mixture was stirred for 1 h. Precipitation with hexanes, filtration through Celite, followed by extraction of the precipitate with CH_2Cl_2 (25 mL) and concentration *in vacuo* resulted in **19**·3/4CH_2Cl_2 as a light yellow powder (42.8 mg, 93%). ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): δ 7.75−7.05 (m, 30H, arom.), 3.28−3.26 (m, 4H, SCH_2), 3.15−3.05 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ 62.9 (s). MS (ESI, MeOH): *m*/*z* 375.0 $[M - 2\ BF_4]^{2+}$. Anal. Calcd for $C_{40}H_{38}B_2F_8P_2PdS_2$·3/4$CH_2Cl_2$: C, 49.51; H, 4.03. Found: C, 49.64; H, 3.73. A residual amount of CH_2Cl_2 was observed via ^1H NMR spectroscopy in $CDCl_3$ upon drying *in vacuo*. $^{31}P\{^1H\}$ NMR data are consistent with the perchlorate derivative of **19** reported in ref 9.

Control Experiments for HILR Reaction. Formation of Heteroligated Complex 9a from Homoligated Complexes 10 and 11. Complex **10** was formed by the addition of a solution of [Pd(COD)Cl_2] (4.5 mg, 0.016 mmol, 0.5 equiv) in CD_2Cl_2 (0.75 mL) to **7** (8.1 mg, 0.031 mmol, 1 equiv). Complex **11** was formed by the addition of a solution of [Pd(COD)Cl_2] (4.5 mg, 0.016 mmol, 0.5 equiv) in CD_2Cl_2 (0.75 mL) to **8** (10.0 mg, 0.031 mmol, 1 equiv). $^{31}P\{^1H\}$ NMR spectra for **10** and **11** were consistent with ref 9 and assignments in Figure 1. These two solutions were mixed, and a $^{31}P\{^1H\}$ NMR spectrum was acquired after 15 min, showing a mixture of **9a** (major component), **10**, and **11**.

Formation of Heteroligated Complex 9c from Homoligated Complexes 18 and 19. Complexes **18** (10.4 mg, 0.0130 mmol, 1 equiv) and **19** (12.0 mg, 0.0130 mmol, 1 equiv) were dissolved in MeOH (anhydrous, 10 mL) and stirred, resulting in a yellow solution. After 1 h, a solution of Me_4NI (5.2 mg, 0.0259 mmol, 2 equiv) in CD_3OD (1 mL) was added to the reaction solution, resulting in the formation of an orange solution. $^{31}P\{^1H\}$ NMR spectroscopy after 30 min indicated the formation of heteroligated complex **9c**. The solvent was removed *in vacuo*, CH_2Cl_2 (2 mL) was added to the residue, and the solution was filtered, followed by removal of solvent *in vacuo*, resulting in **9c** (24.2 mg, 77%) as an orange solid.

***cis*-[κ^2-($Ph_2PCH_2CH_2SMe$)-κ^1-($Ph_2PCH_2CH_2SPh$)IPd]BF_4, 9c.** ^1H NMR (300 MHz, CD_3OD, 22 °C): δ 7.82−7.23 (m, 25H, arom.), 3.3−3.05 (m, 2H, CH_2), 3.0 (s, 3H, CH_3), 2.95−2.6 (m, 6H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 22 °C): δ 61.9 (s), 17.3 (s). $^{19}F\{^1H\}$ NMR (282.5 MHz, CD_3OD, 22 °C): δ −154.32 (s, $^{10}BF_4$), −154.37 (s, $^{11}BF_4$). HRMS (ESI, MeOH): *m*/*z* 814.9812 $[M - BF_4]^+$.

X-ray Crystallography. Crystallographic data are collected in Table 1. Crystals were mounted on Cryoloops with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

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Supporting Information Available: Crystallographic data for **9a**, **12**·CH_2Cl_2, **15**, and **16** in cif format are available free of charge via the Internet at http://pubs.acs.org.

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