

Phosphine Ligand Binding and Catalytic Activity of Group 10-14 Heterobimetallic Complexes

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ABSTRACT: Heterobimetallic complexes have attracted much interest due to their broad range of structures and reactivities as well as unique catalytic abilities. Additionally, these complexes can be utilized as single-source precursors for the synthesis of binary intermetallic compounds. An example is the family of bis(pyridine-2-thiolato)dichloro-germanium and tin complexes of group 10 metals (Pd, Pt). The reactivity of these heterobimetallic complexes is highly tunable through substitution of the group 14 element as well as the neutral ligand bound to the transition metal. Here, we study the binding energies of three different phosphorous-based ligands, PR₃ (R = Bu, Ph, OPh) by density functional theory (DFT) and restricted Hartree-Fock (RHF) methods. The PR₃ ligand binding energies follow the trend of PBU₃ > PPh₃ > P(OPh)₃, in agreement with their sigma-bonding ability. These results are confirmed by ligand exchange experiments monitored with ³¹P NMR spectroscopy, in which a weaker binding PR₃ ligand is replaced with a stronger one. Further, we demonstrate that the heterobimetallic complexes are active catalysts in the Negishi coupling reaction, where stronger binding PR₃ ligands inhibit access to an active site at the metal center. Similar strategies could be applied to other complexes to better understand their ligand binding energetics and predict their reactivity as both precursors and catalysts.

INTRODUCTION

Pincer complexes are structurally diverse inorganic molecules with a distinct balance of stability and reactivity, often resulting in unique catalytic activity. Pincer complexes are widely used as catalysts for Mizoroki-Heck, Suzuki-Miyaura, Sonogashira, Hiyama, and Negishi coupling reactions, among others.^{1,2,3} For example, Pd pincer complexes bearing S-donor atoms, commonly referred to as SCS or SNS complexes—depending on the specific central donor atom—have been studied for the Mizoroki-Heck cross coupling—*i.e.*, the reaction between an unsaturated halide or triflate and an alkene, the Suzuki-Miyaura cross coupling—between a boronic acid and an organohalide,⁴ and C-S diarylthioetherification—the reaction between a disulfide and an organohalide.⁵ Other examples include bis(N-heterocyclic thione) (NHT) Pd complexes as catalysts for the Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira cross-coupling reactions—the latter between a terminal alkyne and an aryl- or vinyl-halide.⁶

Recently, hetero-element pincer ligands built around heavier main group elements and their complexes with Ni, Pd, or Pt have attracted interest because of their unique bonding and reactivity. For example, PALP pincer complexes of Ni have been synthesized and studied for C-X, H-H, and C-H bond activation as well as intramolecular aryl transfer.⁷ PTrP (Tr = Al, Ga, or In) pincer complexes of Pd

have been studied as catalysts for the hydrosilylation of CO₂.⁸ PSiP, PSiN, and NSiN pincer complexes have been studied for Si-H bond activation, C-H borylation of arenes, hydrocarboxylation of allenes, dehydrogenative borylation, fluorosilane activation, and hydroborylation of CO₂.^{9,10,11,12} A PGeP pincer complex of Pd has been studied as a catalyst for the hydrocarboxylation of allenes¹³ and the hydrometallation of ethylene.¹⁴ The heterobimetallic bonding interaction between the group 14 element (E = Ge or Sn, sometimes referred to as “tetrel”) and Ni, Pd, or Pt in SES and PEP complexes has been studied.^{15,16,17,18,19,20,21,22,23} PEP (E = Si, Ge, Sn) complexes of Pd were demonstrated to be active catalysts for a reductive aldol-type reaction.²⁴ PSnP complexes of group 10 metals undergo Sn-Cl bond activation and alkyl transfer.²⁵ PSbP complexes of Pd act as water compatible F⁻ ion sensors.²⁶ PSbP complexes of Pt undergo photoreductive elimination of Cl in both solution and in the solid-state.²⁷ Some of these complexes have also been applied to alkyne activation, enyne cyclization, intramolecular hydroarylation, and the catalytic addition of pyrrole and thiophenes to alkynes.^{28,29,30,31} PBiP complexes of group 10 metals were also reported.^{32,33,34,35}

Another emerging application of heterobimetallic complexes supported by hetero-element pincers is their use as

single-source precursors to intermetallic nanocrystals.^{36,37,38} In a recent study, varying the monodentate donor ligands (phosphine or phosphite) bound to SES complexes lead to different nanocrystalline products upon thermolysis.³⁶ This suggests that the reactivity of the heterobimetallic [EPd] core can be fine-tuned by ligand substitution.³⁶ This observation bears promise beyond the use of similar complexes as molecular precursors, as these could also become a potentially tunable class of homogeneous catalysts. Nonetheless, the use of such heterobimetallic complexes as catalysts is relatively underexplored.

In this study, we use a combination of computational and experimental methods to measure the relative binding affinity of different phosphorous-based ligands on the heterobimetallic [EM] core in a family of bis(pyridine-2-thiolato)dichloro-element complexes of group 10 metals. These have the general formula $\text{Cl}_2\text{E}(\mu\text{-PyS})_2\text{M-PR}_3$, where E = Ge or Sn; M = Pd or Pt, and R = Ph, OPh, or Bu (Figure 1). Using complementary computational methods, we estimate the relative strength of the Pd- PR_3 binding interaction in these complexes. Using solution-phase ³¹P NMR and UV-Vis absorption spectroscopies, we study the exchange of the different tertiary phosphine and phosphite ligands onto the heterobimetallic [EPd]PR₃ core. Finally, we demonstrate that the heterobimetallic complexes are active catalysts in the Negishi coupling reaction between ethyl-*o*-iodobenzoate and cyclohexyl zinc chloride.

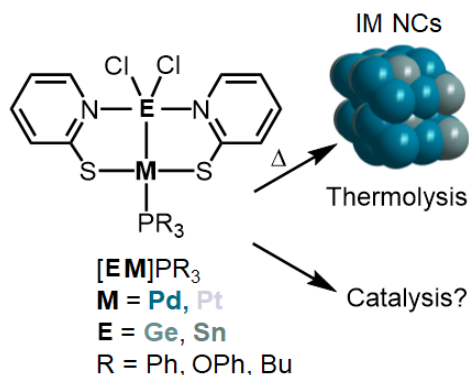


Figure 1. Bis(pyridine-2-thiolato)dichloro-group 14 complexes of group 10 metals and their demonstrated or potential applications. [EM] denotes the heterobimetallic $\text{Cl}_2\text{E}(\mu\text{-PyS})_2\text{M}$ core. IM NCs denotes intermetallic nanocrystals.

RESULTS AND DISCUSSION

M-PR₃ binding energy calculations. A previous study of [SnPd]PR₃ complexes bearing different phosphorous-based ligands—P(OPh)₃, PPh₃, and PBu₃—showed thermolysis resulted in the formation of different intermetallic nanocrystal phases—Pd₂₀Sn₃, Pd₃Sn₂, and Pd₂Sn, respectively (“IM NCs” in Figure 1).³⁶ To better understand the effect of the exact phosphine or phosphite ligand binding on the chemistry and reactivity of the heterobimetallic complexes, we computationally calculated their binding energies—formally, heterolytic bond dissociation energies (BDEs)—and enthalpies from their from the [EM]PR₃ complexes (E = Ge or Sn, M = Pd or Pt), according to Scheme 1.

Calculations were performed using density functional theory (DFT) with the popular B₃LYP functional and, for comparison, with restricted Hartree-Fock (RHF) utilizing the MIDI basis set (see Methods). We started by optimizing the geometry of the [EPd]PR₃ complex, followed by breaking the coordination (dative) M-P bond to create two separate fragments, [EM] and free PR₃. Bond energetics were calculated after geometry optimization. In each case, the M-P bond enthalpy (ΔH) and Gibbs free energy (ΔG) were calculated as the difference between the two fragments and the initial complex (Table 1).

Scheme 1. Hypothetical ligand dissociation reaction used to calculate PR₃ binding affinities in heterobimetallic [EM]PR₃ complexes (see SI).

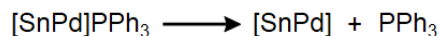


Table 1. Calculated PR₃ binding affinity energies (ΔG) and enthalpies (ΔH) for heterobimetallic complexes.

Complex ^a	ΔG (kcal/mol) ^b	ΔH (kcal/mol) ^c
<i>Restricted Hartree Fock with MIDI basis set</i>		
[GePd]P(OPh) ₃	13.57	25.11
[GePd]PPh ₃	14.87	27.59
[GePd]PBu ₃	21.13	32.99
[SnPd]P(OPh) ₃	9.57	20.57
[SnPd]PPh ₃	10.10	22.82
[SnPd]PBu ₃	15.81	27.46
[SnPt]PPh ₃	11.19	24.16
<i>DFT with B₃LYP, SBKJC basis set</i>		
[GePd]P(OPh) ₃	7.83	21.93
[GePd]PPh ₃	12.51	26.75
[GePd]PBu ₃	19.55	31.82
[SnPd]P(OPh) ₃	7.00	20.55
[SnPd]PPh ₃	10.47	25.39
[SnPd]PBu ₃	16.47	31.43
[SnPt]PPh ₃	1.66	15.31

^a[EM] denotes $\text{Cl}_2\text{E}(\mu\text{-PyS})_2\text{M}$ core (E = Ge or Sn, M = Pd or Pt). ^b $\Delta\text{G} = (\text{G}_{[\text{EM}]} + \text{G}_{\text{PR}_3}) - \text{G}_{[\text{EM}]\text{PR}_3}$. ^c $\Delta\text{H} = (\text{H}_{[\text{EM}]} + \text{H}_{\text{PR}_3}) - \text{H}_{[\text{EM}]\text{PR}_3}$.

Both DFT (B₃LYP) and RHF (MIDI) computational methods afford similar trends. For each EPd series—GePd or SnPd—the BDE’s (ΔG or ΔH) increase in the order: P(OPh)₃ < PPh₃ < PBu₃. In other words, PR₃ ligand binding is weakest for the best π -acceptor, P(OPh)₃, and strongest for the best σ -donor, PBu₃. In both cases, the values are consistently larger—by ca. 5 kcal/mol—for the GePd complexes than for the SnPd complexes, indicating that PR₃ ligand binding may be stronger for Ge- than for analogous Sn-based complexes. This difference is hard to rationalize solely based on the small electronegativity differences (χ_{P} 2.01 for Ge vs. 1.96 for Sn) or the higher Lewis acidity of tin- vs. germanium-chlorides (see LMO analysis below).³⁹ Overall, individual PR₃ binding enthalpies (ΔH) range from 20.6–33.0 kcal/mol and free energies (ΔG) range from 7.0–21.1 kcal/mol.

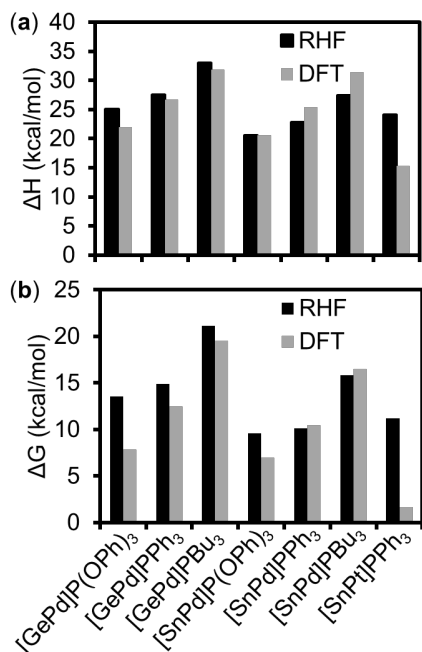


Figure 2. Calculated PR_3 binding affinity enthalpies (ΔH , a) and energies (ΔG , b) in $[\text{EM}]\text{PR}_3$ complexes using two different computational levels of theory (see Methods).

E-M Bonding and orbital calculations. A frontier orbital analysis using the computationally less expensive, restricted Hartree-Fock (RHF) method was used to draw the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) in $[\text{EPd}]$ complexes containing the three phosphorous-based ligands—see Supporting Information (SI) available. In all complexes, the HOMOs are localized along the S–Pd–S axis, with contributions from the Pd d_{xz} and $S p_z$ orbitals. The HOMOs also extend onto the pyridine ring arms of the pincer ligands, with each ring displaying a node on its π -electron density. Interestingly, the HOMOs lack contributions from the group 14 element or the PR_3 ligand. In contrast, the LUMO orbitals extend through the whole $[\text{EPd}]$ framework, across both S–Pd–S and Ge–Pd–P axes (see SI).

Localized molecular orbital (LMO) analysis was carried out with GAMESS by the RHF/MIDI and Edmiston and Ruedenberg method to reveal E–Pd bonding features of $[\text{EPd}]\text{PR}_3$ (see Methods). The heterobimetallic Sn–Pd bond in $[\text{SnPd}]\text{PPh}_3$ possesses a main contribution from the p orbital of Sn and a small contribution from the s orbital of Pd (Figure 3 and Table 2). Similar features are observed for the heterobimetallic E–Pd bond across different $[\text{SnPd}]$ complexes containing a variety of PR_3 ligands (R = OPh, Ph, Bu), as well as in $[\text{GePd}]\text{PPh}_3$ (see Table 2 and SI). Interestingly, $[\text{GePd}]\text{PPh}_3$ shows a small p-orbital contribution from Pd to Ge–Pd bonding. Based on these results, we conclude that the E atom (Ge or Sn) in the heteropincer ligands acts as an L-type ligand toward Pd. Based on the exact orbital contributions, the L-type character is only slightly smaller—and the X-type character slightly higher—for Ge compared to Sn (Table 2). These observations are generally

consistent with prior natural bonding orbital (NBO) analysis of similar heterobimetallic complexes.²²

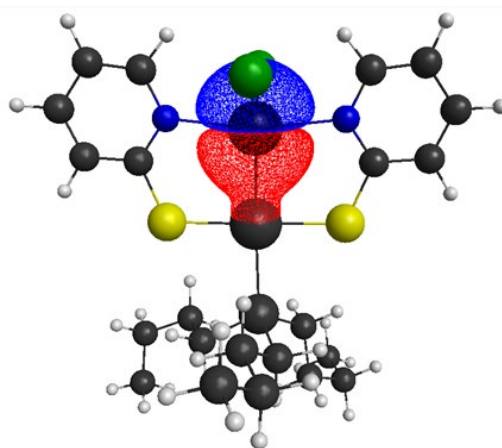


Figure 3. Localized molecular orbital (LMO) analysis for the Sn–Pd bond in $[\text{SnPd}]\text{PBu}_3$ (additional examples in SI).

Complex / LMO	Orbital vector (coefficient)	Pd bonding contribution ^b
$[\text{GePd}]\text{PPh}_3$	0.006, (s, Pd)	0.57 (s, Pd)
	0.024 (p, Pd)	2.26 (p, Pd)
	1.061 (s, Ge)	
$[\text{SnPd}]\text{P(OPh)}_3$	0.005 (s, Pd)	0.46 (s, Pd)
	1.081 (p, Sn)	
$[\text{SnPd}]\text{PPh}_3$	0.005 (s, Pd)	0.44 (s, Pd)
	1.144 (p, Sn)	
$[\text{SnPd}]\text{PBu}_3$	0.005 (s, Pd)	0.50 (s, Pd)
	0.991 (p, Sn)	

^aSee Methods and SI. ^bRatio $\times 100$.

Correlating calculations with experiments: NMR spectroscopy. The ^{31}P chemical shift (δ / ppm) of the PR_3 ligand when bound to a $[\text{SnPd}]\text{PR}_3$ pincer complex shifts upfield—to lower values—as the M–P binding enthalpy increases (ΔH); it decreases from 128.0 ppm for R = OPh, to 24.9 ppm for R = Ph, and 6.85 ppm for R = Bu. Similarly, the change in ^{31}P chemical shift (δ / ppm) between $[\text{SnPd}]$ -bound and free PR_3 ligand increases with the M–P binding enthalpy (ΔH); this difference goes from being almost negligible at -0.1 ppm for R = OPh, to much larger, 30.4 ppm for R = Ph, and 38.2 ppm for R = Bu (Figure 4 and SI). In other words, the weaker the Pd–P bond is, the more the PR_3 ligand in the complex appears to behave as if it was free (unbound). Relevant correlations with Tolman cone angles were reported in other systems.⁴⁰

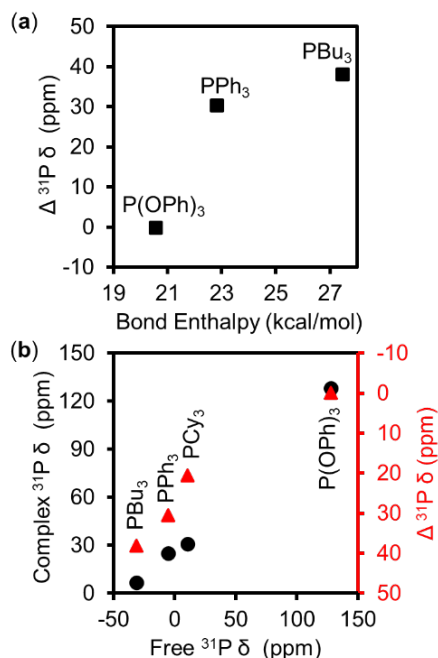


Figure 4. (a) ^{31}P NMR chemical shift difference between $[\text{SnPd}]PR_3$ complexes and free PR_3 ligand (Δ) vs. calculated Pd-P bond enthalpy (ΔH). (b) Relationship between ^{31}P NMR shift of free PR_3 ligands, $[\text{SnPd}]PR_3$ complexes, and Δ (see above).

The Pd-P bond length is slightly longer when E = Sn than when E = Ge, a trend that seems to correlate with the bond energetics calculations as the PR_3 ligands bind more strongly to the heterobimetallic $[\text{GePd}]$ cores. However, we observe a general lack of correlation between M-P bond length and PR_3 ligand binding affinity (ΔH or ΔG) for either germanium or tin. In the $[\text{GePd}]PR_3$ and $[\text{SnPd}]PR_3$ complexes, the Pd-P bond length increases in the order $R = \text{P(OPh)}_3 < \text{PBu}_3 < \text{PPh}_3$ (see SI).

To further probe the bonding in these complexes we used ^{31}P and ^{195}Pt solid-state NMR spectroscopy (ssNMR). ^{195}Pt is an abundant (33.8%) spin-1/2 nucleus. The ^{195}Pt isotropic chemical shift range and chemical shift anisotropy (CSA) can be on the order of several thousand ppm.^{41,42,43} Hence, ^{195}Pt is a highly sensitive probe of the chemical environment. By looking at the ^{195}Pt chemical shift, ^{195}Pt - ^{31}P J-coupling, and ^{195}Pt - $^{119/117}\text{Sn}$ J-coupling for $[\text{SnPt}]PPh_3$, we can assess the chemical environment in these complexes.

Rotor-synchronized $^{31}\text{P}\{^{195}\text{Pt}\}$ J-HMQC was used to analyze and determine a ^{195}Pt isotropic chemical shift of -5293 ppm for $[\text{SnPt}]PPh_3$ (Figure 5, see Methods). This ^{195}Pt chemical shift is in agreement with literature values for complexes with similar Pt environments.^{25,36,44,45,46,47,48} We also observe a ^{31}P - ^{195}Pt J coupling constant of 3.3 kHz and a ^{31}P - $^{119/117}\text{Sn}$ J coupling constant of ca. 4.0 kHz, which correlate well with literature J-coupling values.^{49,50} The ^{31}P spectrum of $[\text{GePt}]PPh_3$ shows a ^{31}P - ^{195}Pt J constant of 2.9 kHz (see Supporting Information), which is very similar to that of the Sn analog.²² A wide-line ^{195}Pt MAS NMR spectrum was also recorded using a constant-time J-HMQC pulse se-

quence that allows for arbitrary indirect dimension spectral widths (see SI).⁵¹ A fit of the ^{195}Pt MAS spectrum reveals that the span (Ω) of the ^{195}Pt chemical shift tensor is 1640 ppm and that the chemical shift (CS) tensor lacks axial symmetry (skew, $\kappa = 0$). Both of these observations are somewhat surprising for a square planar Pt compound, as they often possess axially symmetric CS tensors with spans in the range of 2000 ppm-10000 ppm.^{41,52,53} The low span likely arises because sulfide and phosphine are strong field ligands that form highly covalent bonds to Pt, resulting in sizeable HOMO-LUMO gaps and minimal paramagnetic deshielding.⁵⁴ The lack of axial CS tensor symmetry likely reflects the fact that the strength of covalent bonding interactions differs for the phosphine and sulfide ligands.

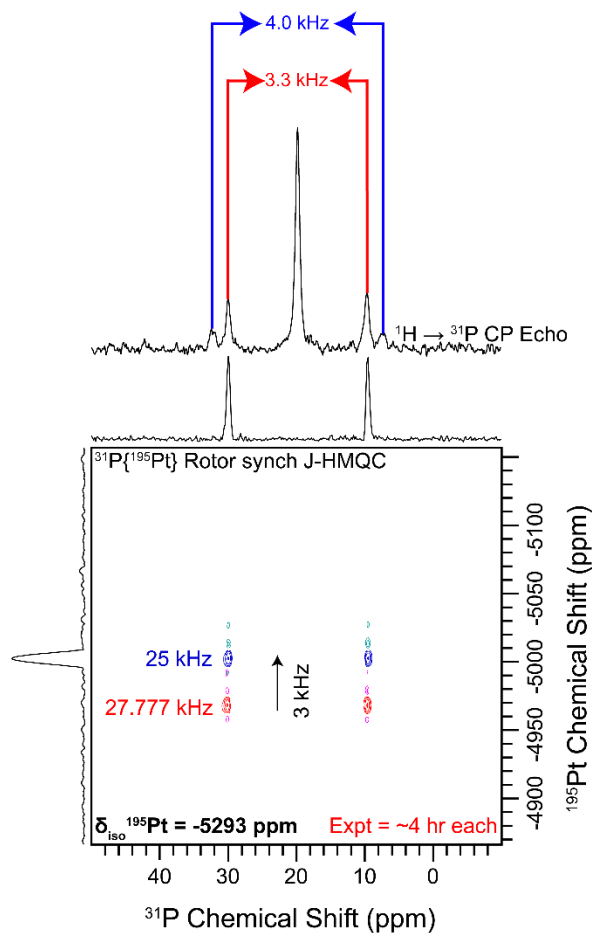


Figure 5. (Top) 1D $^1\text{H} \rightarrow ^{31}\text{P}$ CPMAS spectrum showing satellites arising from J-coupling to ^{195}Pt and ^{119}Sn (25 kHz). (Lower) 2D rotor-synchronized $^{31}\text{P}\{^{195}\text{Pt}\}$ J-HMQC spectra of $[\text{SnPt}]PPh_3$ (27.777 kHz). An isotropic ^{195}Pt chemical shift of -5293 ppm was determined based on the shift of the peak position with the change in MAS frequency.

Ligand exchange experiments. To probe the PR_3 ligand binding affinities experimentally, we monitored solution-phase, ligand exchange experiments by solution ^{31}P NMR spectroscopy. In each experiment, a starting complex $[\text{EPd}]PR_3$ was mixed with one equivalent of a different phosphorous-based ligand (phosphine or phosphite, PR'_3) (Scheme 2, Table 3). When the new added PR'_3 ligand binds

more strongly to [EPd] than the original PR₃ ligand, exchange occurs, and this is easily identifiable by ³¹P NMR. When the new added PR'₃ ligand binds more weakly, this results in the same original ³¹P NMR spectrum.

Scheme 2. Phosphorous-based ligand exchange reactions monitored by ³¹P NMR spectroscopy.

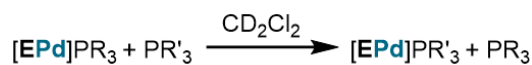


Table 3. Ligand exchange experiments followed by solution-phase ³¹P NMR (³¹P δ / ppm).^a

#	Starting compd.	Added PR' ₃	Products ^b
1	[GePd]PPh ₃ (21.4)	P(OPh) ₃ (128.1)	[GePd]PPh ₃ (21.4), P(OPh) ₃ (128.2) (N.R.)
2	[GePd]PPh ₃ (21.4)	PBu ₃ (-31.3)	[GePd]PBu ₃ (5.54), PPh ₃ (-5.55)
3	[SnPd]PPh ₃ (24.9, br)	P(OPh) ₃ (128.1)	[SnPd]PPh ₃ (24.9, br), P(OPh) ₃ (128.1) (N.R.)
4	[SnPd]PPh ₃ (24.9, br)	PBu ₃ (-31.3)	[SnPd]PBu ₃ (9.81), PPh ₃ (-5.55)
5	[SnPd]P(OPh) ₃ (128, br)	PPh ₃ (-5.52)	[SnPd]PPh ₃ (23.5, br), P(OPh) ₃ (128.1)
6	[SnPd]P(OPh) ₃ (128, br)	PBu ₃ (-31.3)	[SnPd]PBu ₃ (8.81), P(OPh) ₃ (128.1)

7	[SnPd]PBu ₃ (6.85)	PPh ₃ (-5.52)	[SnPd]PBu ₃ (6.86), PPh ₃ (-5.55) (N.R.)
8	[SnPd]PBu ₃ (6.85)	P(OPh) ₃ (128.1)	[SnPd]PBu ₃ , (6.86) P(OPh) ₃ (128.1) (N.R.)

^aSee Methods. ^bN.R. = No reaction.

Interestingly, we find that the square planar *d*⁸ heterobimetallic complexes readily exchange phosphorous-based ligands. An example is shown in Figure 6. When the starting complex is [SnPd]P(OPh)₃, there is a broad resonance at 128 ppm attributed to P(OPh)₃ weakly bound to Pd. When free PPh₃ is added, the new spectrum shows a sharp resonance at 128.1 ppm, corresponding to the now released, free P(OPh)₃, and a broad resonance around 23.5 ppm, which is reminiscent of [SnPd]PPh₃. Also of note is the absence of a free PPh₃ resonance that occurs around -5.52 ppm, indicating that ligand exchange did occur. These results are expected based on our aforementioned calculations, which show that PPh₃ binds more strongly to [SnPd] than P(OPh)₃. The opposite is the case when the reverse reaction is attempted. Mixing [SnPd]PPh₃, which shows a broad resonance at 24.9 ppm, with P(OPh)₃ results in the same spectrum as the forward reaction, *i.e.*, a sharp resonance at 128.1 corresponding to free P(OPh)₃, a broad resonance at 24.9 ppm corresponding to the starting [SnPd]PPh₃ complex, and the absence of a resonance at -5.52 ppm that could indicate any release of PPh₃.

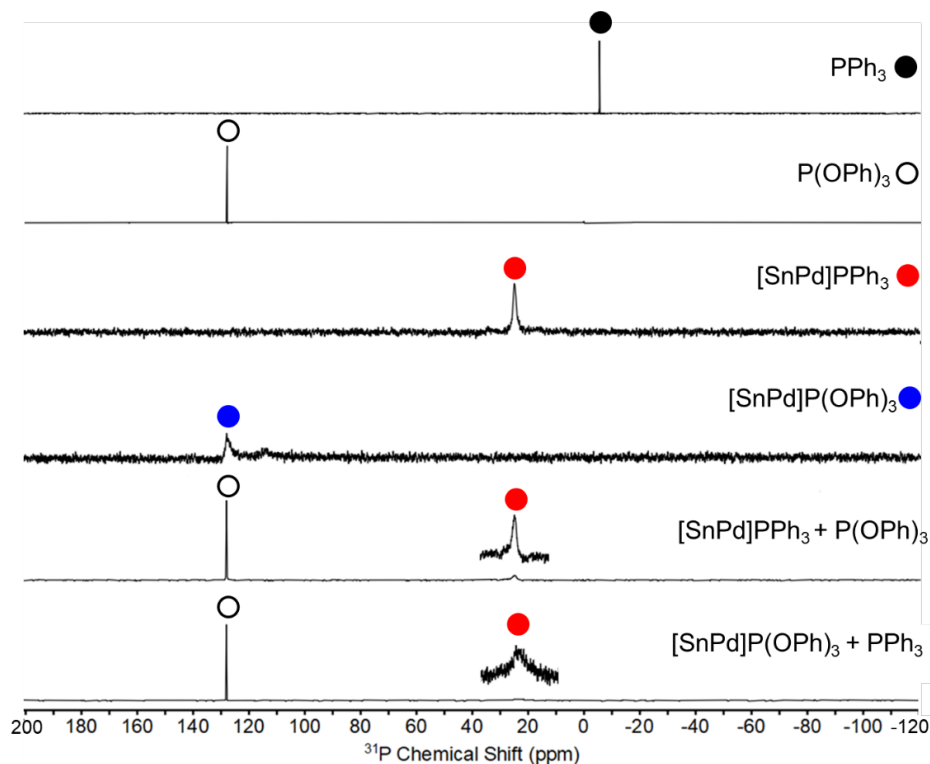


Figure 6. Ligand exchange reaction between [SnPd]PPh₃ and P(OPh)₃ (see also Supporting Information available).

These ligand exchange reactions are also accompanied by a visible color change. For example, the addition of one

equivalent of PBu₃ to a solution of [SnPd]PPh₃ in methylene chloride results in a change in color from orange to yellow (Figure 7). These changes are associated with small

but easily measurable shifts in the UV-Vis absorption spectrum. A first, very intense band at approximately 300 nm ($\epsilon = 40000\text{--}60000\text{ M}^{-1}\text{cm}^{-1}$) may be assigned as a charge transfer band. Replacing PPh_3 with the more electron donating PBU_3 blue shifts the band maximum slightly, from 302 nm to 299 nm. Future studies including time-dependent TD-DFT or similar methods will be required to specifically assign these bands as either LM- or ML-CT transitions. A less intense visible band ($\epsilon = 200\text{--}400\text{ M}^{-1}\text{cm}^{-1}$) also blue shifts from 488 nm to 465 nm. This may be assigned to a Laporte-allowed d-d transition, as these complexes lack centrosymmetry.⁵⁵

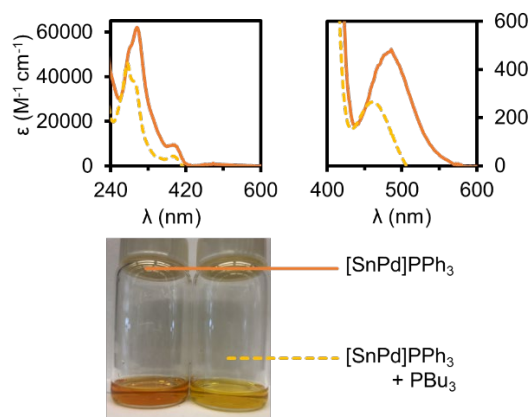


Figure 7. UV-VIS absorption spectra and optical image of [SnPd]PPh₃ in CH_2Cl_2 before and after the addition of one equivalent of PBU₃.

Heterobimetallic 10-14 complexes as catalysts. Pincer complexes are of great interest as catalysts for cross-coupling reactions, as the pincer ligand can help enhance the reactivity and selectivity of the transition metal. Here, we specifically find that heterobimetallic bis(pyridine-2-thiolato)dichloro-germanium and tin complexes of palladium(II) are active catalysts in the Negishi cross-coupling reaction between ethyl-*o*-iodobenzoate (**1**) and cyclohexyl zinc chloride (**2**) (Scheme 3). In the presence of the [EPd] pincer catalysts, full conversion to ethyl 2-cyclohexylbenzoate (**3**) is achieved within 20 min at room temperature (25 °C), with only small amounts of by-products ethylbenzoate (**4**), iodocyclohexane (**5**) and bicyclohexyl (**6**). This is comparable to the results obtained when the catalyst is a monometallic SNS complexes of Pd,^{56,57} and significantly better than those obtained with commercially available $\text{Pd}(\text{PPh}_3)_4$ (Figure 8 and Table 4).

Table 4. Negishi coupling of ethyl-*o*-iodobenzoate (**1**) and cyclohexyl zinc chloride (**2**) catalyzed by heterobimetallic complexes (see Scheme 3).^a

Catalyst	Conv. ^b (%)	TON ^c (TOF, h ⁻¹)	Selectivity ^b			
			3	4	5	6
None	0.434	-	0	56	26	18
[GePd]PPh ₃	100	200 (600)	90	8	1	1
[SnPd]PPh ₃	100	200 (600)	87	7	5	1
[SnPd]P(OPh) ₃	99.5	199 (597)	90	7	1	2
[SnPd]PPh ₃ + PBU ₃ (1 equiv)	1.56	3.12 (9.36)	37	32	26	5

[SnPd]PPh ₃ + PPh ₃ (1 equiv)	63.1	126 (378)	60	20	15	5
[SnPt]PPh ₃	12.7	25.4 (76.2)	4	51	25	20
$\text{Pd}(\text{PPh}_3)_4$	87.1	174 (523)	42	21	31	7

^aReaction conditions: 0.005 mmol catalyst (0.5 mol %), 1 mmol (**1**), 2 mmol (**2**), in 4 mL THF, 25 °C, 20 min (see Methods). ^bDetermined by GC-MS using naphthalene as an internal standard. ^cTON = moles of (**1**) consumed / moles of catalyst; TOF = TON / time.

Scheme 3. Negishi coupling of ethyl-*o*-iodobenzoate (**1**) and cyclohexyl zinc chloride (**2**).

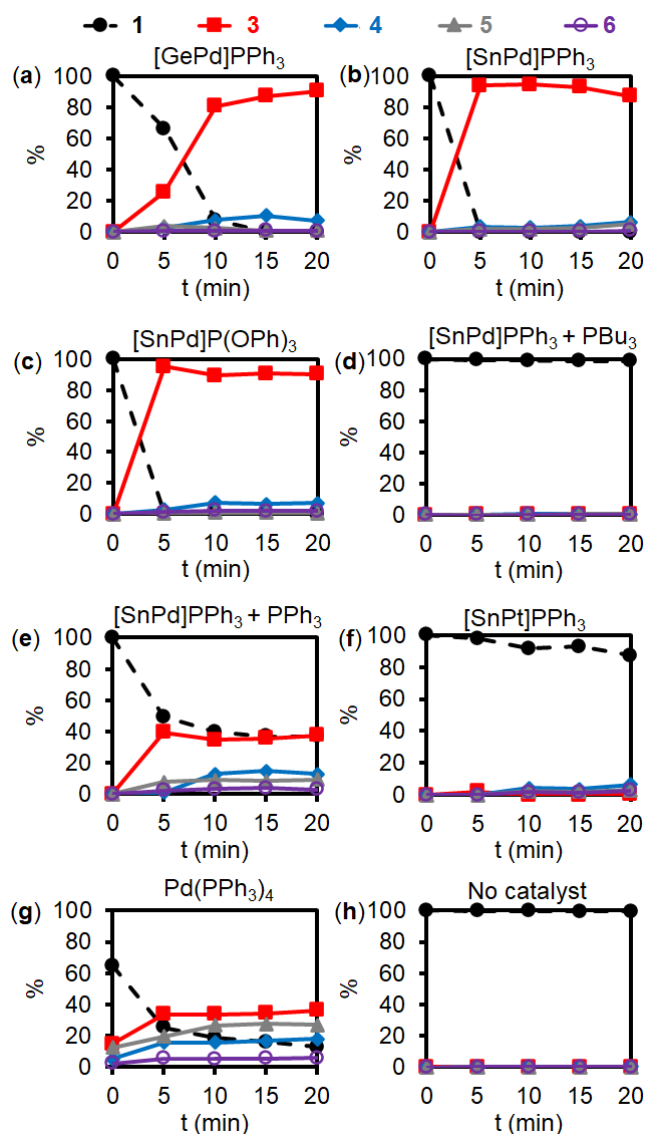
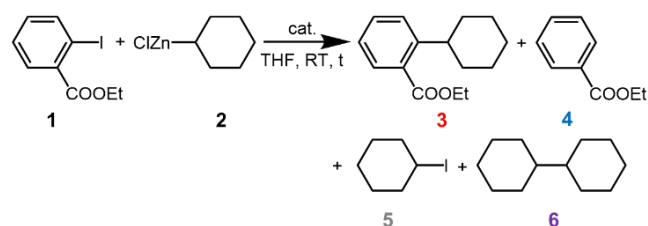


Figure 8. Negishi coupling between ethyl-2-iodobenzoate (**1**) and cyclohexylzinc chloride (**2**)—see Scheme 3—catalyzed by (a) [GePd]PPh₃, (b) [SnPd]PPh₃, (c) [SnPd]P(OPh)₃, (d) [SnPd]PPh₃ + 1 equiv. PBu₃, (e) [SnPd]PPh₃ + 1 equiv PPh₃, (f) [SnPt]PPh₃, (g) Pd(PPh₃)₄, and (h) no catalyst (see Methods).

To examine the effects of heterobimetallic complex structure and composition on catalytic properties, we compared the complexes [GePd]PPh₃ and [SnPd]PPh₃, which only differ in group 14 element. When [GePd]PPh₃ is used as catalyst, the Negishi reaction is complete after 15 min, with the coupling target (**3**) being the major product (90%) (Figure 8a and Table 4). Furthermore, only 8% of the dehalogenated side product (**4**) and minimal amounts of (**5**) and (**6**) are present (see Scheme 3). Notably, the reaction proceeds more quickly with [SnPd]PPh₃, reaching completion in as little as 5 min (Figure 8b and Table 4). Because PPh₃ binds more weakly to Pd in the more active [SnPd]PPh₃ complex, this suggests that the catalyst becomes more readily available when PR₃ ligand dissociation is easier, perhaps due to the opening of an active coordination site at the metal.

To further probe the effect of PR₃ ligand binding affinity on the catalytic activity of the heterobimetallic complexes, we tested the [SnPd]PBu₃ complex as a catalyst. Because PBu₃ binds stronger to Pd than PPh₃—as evidenced by our aforementioned calculations and ligand exchange experiments—we hypothesized that in this case, the catalytic reaction should proceed more slowly. To test this idea, we generated the [SnPd]PBu₃ complex *in-situ* through the addition of one equivalent of PBu₃ to [SnPd]PPh₃. (Note: To date, [SnPd]PBu₃ has been difficult to isolate as crystals,³⁶ hence the advantage of generating it through this method.) As expected, the *in-situ* generated [SnPd]PBu₃ displays minimal activity, with less than 2% conversion after 20 min (Figure 8d and Table 4). This shows that the reaction is severely inhibited by the presence of the strongly binding PBu₃ ligand. Because the presence of the displaced PPh₃ in the reaction solution could also hinder catalysis, we repeated the reaction with a mixture of [SnPd]PPh₃ and one added equivalent of PPh₃. In the presence of the excess PPh₃, only a fraction of the original conversion, 63.1% is observed after 20 min, with a lower selectivity for the coupling product (60%) (Figure 8e and Table 4). Therefore, while excess PPh₃ can also hinder access to the active site, it is the more strongly binding PBu₃ that most significantly inhibits catalyst performance, supporting our hypothesis.

Finally, we looked at the effect of the transition metal on catalyst performance by testing [SnPt]PPh₃ in the coupling reaction. When Pt is used instead of Pd, the reaction displays drastically different behavior. Only 12.7 % conversion and 4 % selectivity to the coupling product (**3**) are achieved after 20 min. The major product is the dehalogenated compound (**4**) (Scheme 3). Because our calculations suggest that PR₃ ligand binding is much weaker for Pt than for Pd, this lack of activity cannot be attributed to being able to access a coordination site at the metal. Instead, this is consistent with C-C coupling reactions occurring much more easily in Pd than in Pt complexes, because the Pd-R bonds

are weaker—and easier to cycle through—than the analogous Pt-R bonds.^{58,59}

Overall, like their monometallic analogs,^{56,57} heterobimetallic 10–14 E-M complexes are active catalysts in Negishi cross coupling reactions. Unlike the monometallic versions, however, the reactivity of the heterobimetallic complexes can also be tuned by changing the group 14 element, in addition to the transition metal, and the phosphine ligand. Furthermore, future studies will be directed at exploring what effect the E-Cl bonds may have during the catalytic cycle. This feature is unique to the heteropincer ligand backbone and is expected to offer unique reactivity: For example, activation of related Si-F bonds was recently used to develop an unprecedented Sila-Negishi cross-coupling reaction.⁶⁰

CONCLUSIONS

In summary, we have examined the binding affinity of phosphorous-based ligands to heterobimetallic 10–14 complexes both theoretically and experimentally. First, using two different computational methods, we calculated the bond dissociation energies and enthalpies for these complexes and observed that the M-P binding affinity decreases in the order PBu₃ > PPh₃ > P(OPh)₃ for both Ge and Sn based complexes. Experimentally, using a series of ³¹P solution NMR exchange reactions, we observe the same order of binding affinities. Additionally, we found that the ³¹P NMR chemical shifts of [SnPd]PR₃ complexes and free PR₃ ligands correlate to the binding strength between these ligands and the heterobimetallic [EM] core.

To further determine the utility of heterobimetallic 10–14 complexes, we demonstrated that the [EPd]PR₃ complexes as active catalysts for the Negishi coupling between ethyl-2-iodobenzoate and cyclohexyl zinc chloride. Our findings show that the group 14 or “tetrel” element, the exact phosphine ligand, and the transition metal all play determinant roles on the catalytic activity: tin complexes are a more active than germanium ones, palladium complexes are active while platinum complexes are not, and the more strongly the phosphine ligand binds to the [EM] core, the less active the catalyst is. We believe these findings will aid in future studies aimed at designing and optimizing heterobimetallic pincer complexes for different applications.

METHODS

Materials. Triphenylphosphine (PPh₃, 99%), triphenylphosphite (P(OPh)₃, 97%), tri-*n*-butylphosphine (P*n*Bu₃, 99%), zinc chloride (ZnCl₂, anhydrous, 97%), and tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄, 99%) were purchased from Strem. Cyclohexylmagnesium chloride (1 M in MeTHF) and ethyl *o*-iodobenzoate (98%) were purchased from Alfa Aesar. Methylene dichloride-*d*₂ (CD₂Cl₂) was purchased from Cambridge Isotope Laboratories, degassed, and dried over activated molecular sieves. Tetrahydrofuran (THF, inhibitor-free, >99.9%) was dried and deoxygenated using an IT PureSolv system. The heterobimetallic pincer complexes [GePd]PPh₃, [SnPd]PPh₃,

[SnPd]P(OPh)₃, [SnPd]PBu₃, and [SnPt]PPh₃ were synthesized using previously reported, available methods.^{21,22,36}

Calculations. All calculations were carried out using GAMESS (2014 R1).^{61,62} The calculations at the DFT level of theory were done using the B3LYP functional^{63,64,65} with the Stevens/Basch/Krauss/Jasien/Cundari (SBKJJC) basis set with effective core potentials (ECPs) for Pd, Pt, Sn, and Ge⁶⁶ and the 6-31G(d,p) basis set for all other elements.^{67,68,69,70} Restricted Hartree-Fock (RHF) calculations (ran without DFT) used the MIDI basis set for all elements.⁷¹ The calculations done as a lower level of theory provided similar results as those with DFT and were less computationally expensive. The starting geometry for each structural optimization was taken from single crystal data available in the Cambridge Structural Database (CSD),⁷² where applicable. Hessian calculations were performed to verify that each optimized geometry had no imaginary vibrational frequencies. The thermodynamic parameters ΔH and ΔG , and zero-point energy corrections were calculated at 298.15 K and 1 atm. Results were visualized using MacMolPlt.⁷³ Localized molecular orbital (LMO) analysis was carried out with GAMESS by RHF/MIDI and the Edmiston and Ruedenberg method.^{74,75}

NMR Spectroscopy. *Exchange experiments in solution.* were performed on a Bruker Avance III 600 spectrometer at room temperature. ³¹P NMR shifts (243.04 MHz) are given in ppm and referenced to the ¹H spectrum (600.39 MHz) residual solvent peaks using indirect referencing methods.⁷⁶ For each exchange reaction, approximately 0.02 mmol of starting complex [EPd]PR₃ was dissolved in 0.5 mL of CD₂Cl₂, followed by an initial spectrum collection. Next, 1 eq (0.02 mmol) of a different phosphorous based ligand, PR'₃, was added directly to the NMR tube and mixed well before obtaining the new spectrum. In the cases where PBu₃ was the added ligand, the ligand exchange process was done in a glovebox and a J Young tube was used.

Solid state NMR experiments were performed on a 9.4 T ($\nu_0(^1\text{H}) = 400$ MHz) Bruker wide-bore magnet spectrometer equipped with a Bruker Avance III HD console. Experiments were performed with a Bruker 2.5 mm HXY MAS probe in triple resonance mode. All samples were packed into 2.5 mm zirconia rotors in air. N₂ gas was used to spin the rotor for MAS experiments. Before the NMR experiments, the magic angle was precisely set by narrowing the second-order spinning sideband peak width of potassium bromide. The ¹H RF powers were calibrated directly on each sample by using a $\pi/2$ -spin-lock pulse sequence to determine the second-order rotary resonance recoupling condition, ($\nu_1 = 2 \times \nu_{rot}$). A 100 kHz RF field was used for all ¹H pulses. Most experiments were performed with a 25 kHz MAS frequency, with a second MAS frequency of 27.777 kHz used for some *J*-HMQC experiments. ¹H longitudinal relaxation (*T*₁) measurements were performed on each sample using a saturation recovery experiment. All experiments were recorded with longitudinal relaxation delays of $1.3 \times T_1$ corresponding to delays of 42.9 s for [SnPt]PPh₃ and 32.5 s for [GePt]PPh₃). Cross-polarization (CP) was directly optimized on each sample by monitoring the signal intensity of a ¹H → ³¹P CPMAS spectrum while varying ¹H spin-lock RF fields and holding the ³¹P spin-lock

RF field constant. ¹H-³¹P cross-polarization (CP) echo experiments used 16 scans with an echo delay of one rotor cycle. The ³¹P{¹⁹⁵Pt} *J*-HMQC experiments used 8 scans with a 160 μ s or 144 μ s *J*-evolution time (half-echo duration) that approximately corresponds to the optimal duration for ³¹P-¹⁹⁵Pt *J* values of ca. 3200 Hz. The rotor-synchronized *J*-HMQC spectra were obtained with 40 and 44 hyper-complex indirect dimension points for 25 kHz and 27.777 kHz MAS, respectively. ¹H chemical shifts were referenced to a 1% solution of tetramethylsilane in CDCl₃ ($\delta_{iso} = 0$ ppm) with a secondary standard of solid adamantane ($\delta_{iso} = 1.76$ ppm). ¹⁹⁵Pt chemical shifts were indirectly referenced to a 1.2 M solution of Na₂PtCl₆ in D₂O ($\delta_{iso} = 0$ ppm) using the IUPAC recommended Larmor frequency ratio of 21.496784% for ¹⁹⁵Pt as compared to ¹H.⁷⁶ ³¹P chemical shifts were indirectly referenced to a 85% solution of H₃PO₄ in H₂O ($\delta_{iso} = 0$ ppm) using the IUPAC recommended Larmor frequency ratio of 40.480742% for ³¹P as compared to ¹H.⁷⁶ All NMR spectra were processed in Bruker Topspin 3.6.2.

UV-Vis Spectroscopy. UV-Vis absorbance spectra were measured on a photodiode array Agilent 8453 spectrophotometer with solvent (dichloromethane) subtracted from all spectra.

Negishi Coupling Reactions. Catalysis experiments were run following similar procedures in the literature.^{56,57} For each reaction, 2 mmol of ZnCl₂ was dissolved in 1 mL of dry THF in a small round bottom flask in a glovebox. The flask was then taken out and attached to a Schlenk line, where it was evacuated and flushed with Ar. Next, 2 mL of cyclohexylmagnesium chloride (1 M in MeTHF) was added to the flask dropwise and the solution was allowed to stir for 1 h at RT. Approximately 0.005 mmol of the catalyst was dissolved in 1 mL of THF and injected into the reaction flask, followed by 1 mmol (~0.1 mL) of ethyl *o*-iodobenzoate. The reaction was allowed to proceed for 20 min, with small aliquots taken at 5 min intervals and prepared for analysis by GCMS. GCMS analysis was performed on an Agilent 7250 GC QTOF instrument using naphthalene as an internal standard.

ASSOCIATED CONTENT

Supporting Information. Additional calculations, including bond lengths, HOMO/LUMO diagrams, and LMO analyses, ³¹P NMR and bond enthalpy data, and exchange experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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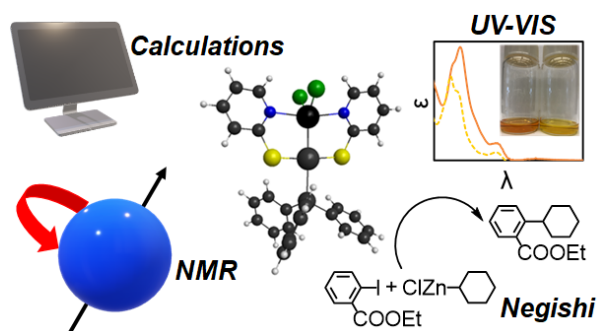
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TOC Synopsis. The structure and reactivity of bis(pyridine-2-thiolato)dichloro-germanium and tin complexes of palladium or platinum is studied theoretically through calculations and experimentally through solution and solid state NMR and UV-Vis spectroscopy. The binding affinity of a terminal PR₃ ligand is shown to determine the activity of these heterobimetallic complexes as cross-coupling catalysts, as demonstrated with the Negishi coupling reaction.