Dalton Transactions

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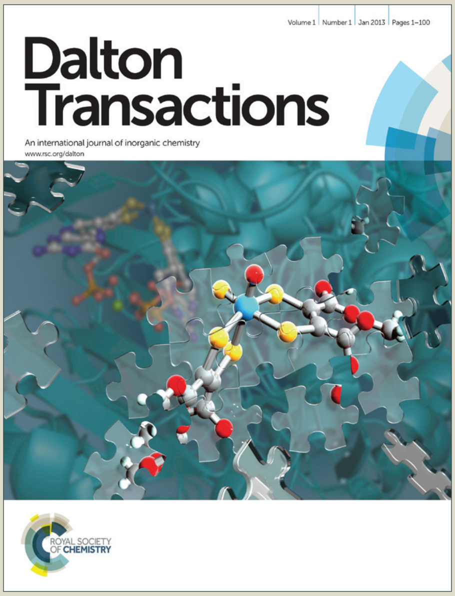

View Article Online
DOI: 10.1039/C5DT03018H

Transition Metal-mediated Donor-acceptor Coordination of Low-oxidation State Group 14 Element Halides

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
www.rsc.org/

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The reactivity of tungsten carbonyl adducts of Group 14 element (Ge, Sn and Pb) dihalides towards the metal-based donors (η^5-C_5H_5)Rh(PMe_2Ph)$_2$ and Pt(PCy_3)$_2$ was examined. When (η^5-C_5H_5)Rh(PMe_2Ph)$_2$ was treated with the Lewis acid supported Ge(II) complex, THF•$GeCl_2$•W(CO)$_5$, cyclopentadienyl ring activation occured, whereas the analogous Lewis acidic units $SnCl_2$•W(CO)$_5$ and $PbCl_2$ form direct adducts with the Rh complex to yield Rh-Sn and Rh-Pb dative bonds. Attempts to prepare metal coordinated element (II) hydrides by adding hydride sources to the above mentioned rhodium-E(II) halide complexes were unsuccesful; in each case insoluble products were formed along with regeneration of free (η^5-C_5H_5)Rh(PMe_2Ph)$_2$. In a parallel study, ECl_2•W(CO)$_5$ (E = Ge or Sn) groups were shown to participtate in E-Cl oxidation addition chemistry with (Cy_3P)$_2$Pt to give the formal Pt(II) complexes ClPt(PCy_3)$_2$ECl•W(CO)$_5$.

Introduction

A central concept in synthetic inorganic chemistry is the use of electron-donating ligands to bind/stabilize reactive inorganic species with unusual bonding environments. In this regard *N*-heterocyclic carbenes (NHCs) such as IPr ([(HCNDipp)$_2$C:]; Dipp = 2,6-$^{i}Pr_2C_6H_3$) and their structural analogues have been used to intercept novel main group species such as B_2 and the homologous ditetrelene series :E=E: (E = Si, Ge and Sn).[1,2] Also of relevance to this paper is our use of NHCs in conjunction with various Lewis acidic capping units to coordinate the inorganic methylene analogues :EH_2 (E = Si, Ge, and Sn) via a general donor-acceptor approach (*e.g.* IPr•GeH_2•BH_3).[3] In addition, we have extended this protocol to include EH_2 complexes supported by the *N*-heterocyclic olefin (NHO) IPr=CH_2 and the Wittig reagent Ph_3P=CMe_2.[4] Interest in these complexes stems from the formation of EH_2 as intermediates en route to bulk semi-conductors and metals via tetrelane (EH_4) degradation.[5] Moreover we have recently demonstrated that luminescent Ge nanoparticles could be prepared from the mild, one pot, decomposition of the donor-acceptor GeH_2 complex Ph_3PCMe_2•GeH_2•BH_3.[6]

Metal centered Lewis bases (MLBs), wherein an electron rich metal center acts as a formal two-electron donor, are being increasingly investigated within the context of supporting low-oxidation state main group element chemistry.[7] A possible advantage of MLBs over traditional organic-based donors is the ability to dramatically alter the coordination properties of a MLB via co-ligand modification and/or by changing the metal entirely. Since Nowell and Russell's synthesis of [(η^5-C_5H_5)(CO)$_2$Co$\rightarrow$$HgCl_2$] in 1964,[8] various late metal MLBs based on Ir, Pt and Rh have been developed.[9] Moreover metal centered Lewis bases can readily form stable coordinative interactions with electron deficient Group 13 (B, Al and Ga)[10] and Group 14 (Ge, Sn and Pb)[11] compounds. Herein we explore the ability of the half sandwich complex CpRh(PMe_2Ph)$_2$ (Cp = η^5-C_5H_5)[12] and the nucleophilic Pt(0) donor Pt(PCy_3)$_2$ to interact with divalent Group 14 species. An ultimate goal of this program would be to generate mixed metal donor-acceptor complexes of EH_2 units (E = Ge, Sn and Pb) for the later preparation of binary E_xM_y (M = metal) bulk or nanomaterials.[13]

Results and discussion

We began our study with an attempt to synthesize a $GeCl_2$ donor-acceptor complex using CpRh(PMe_2Ph)$_2$ as a Lewis base and W(CO)$_5$ as a capping Lewis acid. However when THF•$GeCl_2$•W(CO)$_5$ was combined with CpRh(PMe_2Ph)$_2$ in toluene for 12 hrs, the resulting deep yellow solid gave spectroscopic signatures consistent with C-H bond activation of the cyclopentadienyl ligand. Specifically, a highly upfield positioned doublet of triplet resonance was found at -11.98 ppm in the ^{1}H NMR spectrum in CD_2Cl_2 ($^2J_{H\text{-}P}$ = 29.9 Hz and $^1J_{H\text{-}Rh}$ = 19.9 Hz), indicating that hydrogen migration to yield a terminal Rh-H group transpired. Moreover two distinct Cp-H resonances of equal intensity were noted at 5.40 and 5.75 ppm, respectively, consistent with a mono-functionalized Cp unit. X-ray crystallography later confirmed that hydrogen migration/Cp ring activation did occur to form the Rh(III) product [(CO)$_5$W•$GeCl_2$(η^5-C_5H_4)]RhH(PMe_2Ph)$_2$ (**1**) (eqn. (1), Fig. 1). A related hydride migration/Cp activation process was noted when CpRh(PMe_3)$_2$ was treated with the bulky alkyl halides ^{t}BuI or ^{i}PrI, affording the alkylated-cyclopentadienyl rhodium salts [(η^5-C_5H_4R)RhH(PMe_3)$_2$]I (R = ^{t}Bu or ^{i}Pr).[14] It is likely that the high electrophilicity of the $GeCl_2$•W(CO)$_5$ unit promotes attack at the Cp ring in CpRh(PMe_2Ph)$_2$, followed by

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†*Electronic supplementary information (ESI) available: Tables of crystallographic data for compounds **1-6**. CCDC 1416191-1416196. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXX.*

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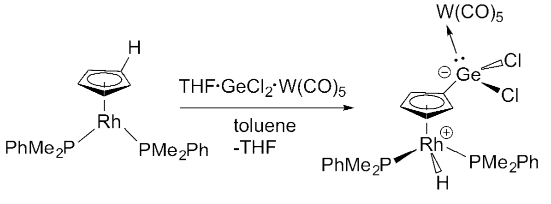
proton transfer to the basic Rh center. As shown in Fig. 1, $[(CO)_5W\bullet GeCl_2(\eta^5\text{-}C_5H_4)]RhH(PMe_2Ph)_2$ (**1**) has a $GeCl_2\bullet W(CO)_5$ group directly attached to a Cp ring with a Ge-C bond distance of 1.9709(19) Å; this value is similar to the covalent Ge-C bond length found within Power's aryl(halo)digermene $Ar^{Mes}Ge(Cl)Ge(Cl)Ar^{Mes}$ [2.000(6) Å] (Ar^{Mes} = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$).[15] The Ge-W interaction in **1** is 2.5820(2) Å and is the same within experimental error as the average Ge-W distance of 2.5833(16) Å in $IPr\bullet GeCl_2\bullet W(CO)_5$.[16] The hydride bound to the Rh center in **1** could be located in the electron difference map and the refined Rh-H bond length [1.51(3) Å] is of similar value as in $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ [1.51(4) Å].[17]



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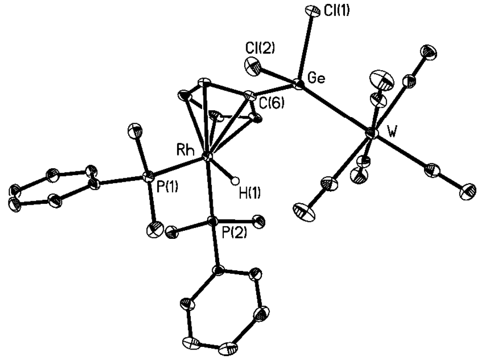
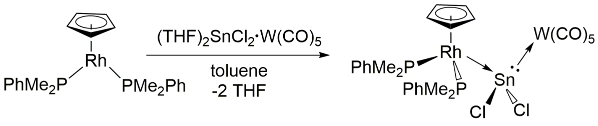


Fig. 1. Molecular structure of $[(CO)_5W\bullet GeCl_2(\eta^5\text{-}C_5H_4)]RhH(PMe_2Ph)_2$ (**1**) with thermal ellipsoids presented at a 30 % probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-H(1) 1.51(3), Ge-C(6) 1.9709(19), Ge-Cl(1) 2.2464(5), Ge-Cl(2) 2.2324(5), Ge-W 2.5820(2); Cl(1)-Ge-Cl(2) 96.62(2), C(6)-Ge-W 129.52(6), Ge-C(6)-Rh 123.82(9), Ge-C(6)-Rh 123.82(9).

A different reactivity profile was noted when $CpRh(PMe_2Ph)_2$ was combined with the Sn(II) dihalide adduct $(THF)_2SnCl_2\bullet W(CO)_5$. In this case the resulting yellow-orange solid did not yield any spectroscopic evidence for Rh-H bond formation. The ^1H NMR spectrum of the product in $CDCl_3$ contained two virtual triplet resonances assigned to two diastereotropic methyl groups within the phosphine ligands (at 1.92 and 2.08 ppm), while one Cp environment was present, as evidenced by a singlet resonance at 5.25 ppm. Crystals of suitable quality for X-ray analysis were subsequently obtained and conclusively identified the product as the expected Lewis acid-base adduct $CpRh(PMe_2Ph)_2\bullet SnCl_2\bullet W(CO)_5$ (**2**) (eqn. (2)). The molecular structure of **2** (Fig. 2) shows a Rh-Sn single bond distance of 2.6152(5) Å, which is comparable to the terminal Rh-Sn linkage reported within *mer*-$[\{Rh(CNC_8H_9)_3(SnCl_3)(\mu\text{-}SnCl_2)\}_2]$ [2.606(1) Å].[18] The Rh-Sn bond in **2** is however elongated compared to the Rh-Sn bonds within Marder's Sn(II) bis-adduct $Cl_2Sn[Rh(PMe_3)_3Cl]_2$ [2.712(1) Å].[11a]

Following a related protocol as what was just discussed, the clean formation of the metal only Lewis pair $CpRh(PMe_2Ph)_2\bullet PbCl_2$ (**3**) was accomplished by combining an equimolar amount of $PbCl_2$ with $CpRh(PMe_2Ph)_2$ in toluene (eqn. (3)). Two broad methyl resonances from the PMe_2Ph ligands were located at 1.42 and 1.62 ppm in the ^1H NMR spectrum of **3** in CD_2Cl_2, while the corresponding $^{31}P\{^1H\}$ NMR spectrum afforded a doublet signal at 8.2 ppm with a $^1J_{Rh\text{-}P}$ constant of 170 Hz.



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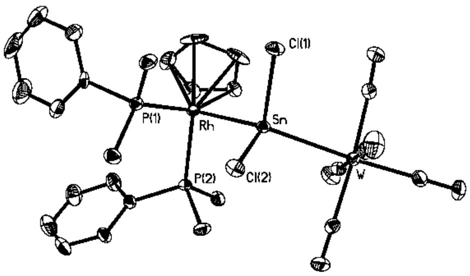

Fig. 2. Molecular structure of $CpRh(PMe_2Ph)_2\bullet SnCl_2\bullet W(CO)_5$ (**2**) with thermal ellipsoids presented at a 30 % probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-Sn 2.6152(5), Sn-Cl(1) 2.4544(14), Sn-Cl(2) 2.4685(15), Sn-W 2.7736(4); Rh-Sn-W 134.438(17), Cl(1)-Sn-Cl(2) 91.60(6).

The crystallographically determined structure of compound **3** is shown in Fig. 3. and displays a highly pyramidalized lead center [Σ° at Pb (*avg.*) = 296.7°] with a Rh-Pb bond length of 2.7561(7) Å; this is, to our knowledge, the first structural characterization of such a bond.

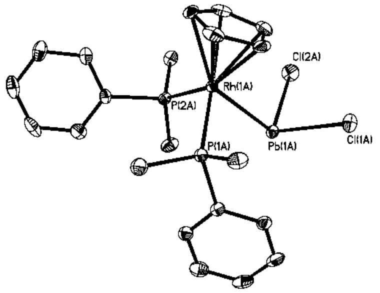

Figure 3. Molecular structure of $CpRh(PMe_2Ph)_2\bullet PbCl_2$ (**3**) with thermal ellipsoids presented at a 30 % probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with parameters associated with a second molecule in the asymmetric unit listed in square brackets: Rh(1A)-Pb(1A) 2.7561(7) [2.7530(7)], Pb(1A)-Cl(1A) 2.6314(16) [2.6540(16)], Pb(1A)-Cl(2A) 2.6515(16) [2.6489(16)]; Cl(1A)-Pb(1A)-Cl(2A) 95.65(6) [98.91(6)], Rh(1A)-Pb(1A)-Cl(1A) 99.78(4) [111.8(2)], Rh(1A)-Pb(1A)-Cl(2A) 101.25(4) [97.48(4)].

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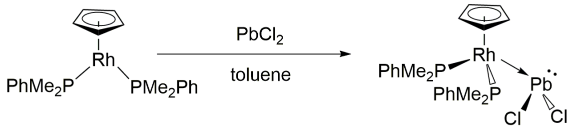

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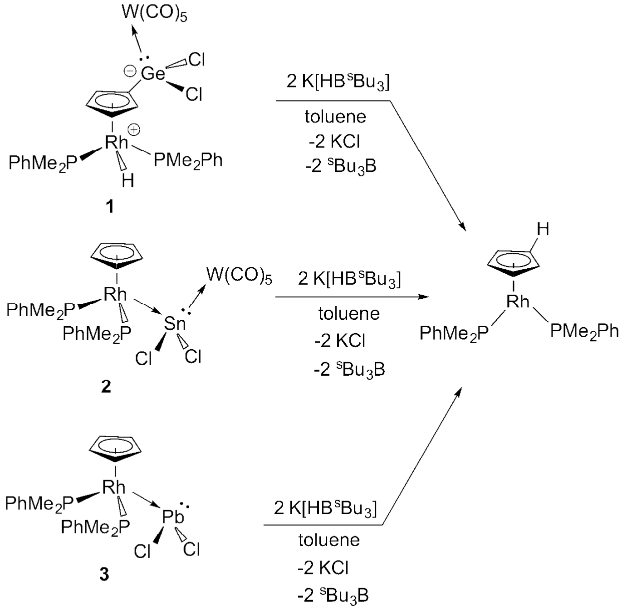
We decided to react compounds **1**-**3** with various hydride sources to gain access to new metal-supported EH_2 complexes (E = Ge, Sn or Pb). Motivated by our prior successes with using $Li[BH_4]$ to generate donor-acceptor complexes of Group 14 dihydrides (*e.g.* IPr•SnH_2•$W(CO)_5$),[3a,4a] we first treated $CpRh(PMe_2Ph)_2$•$SnCl_2$•$W(CO)_5$ (**2**) with two equivalents of $Li[BH_4]$ in Et_2O. The resulting reaction proceeds with the immediate formation of an insoluble black precipitate, presumably consisting of metallic tin and/or tin-tungsten clusters; the only product found in the colorless supernatant was the known phosphine-borane adduct, $PhMe_2P$•BH_3.[19] The formation of $PhMe_2P$•BH_3 likely occurs via $PhMe_2P$ decomplexation from rhodium and coordination to the Lewis acidic by-product BH_3 that is generated from $Li[BH_4]$ during Cl^-/H^- exchange. As a result, we chose not to explore $Li[BH_4]$ as a hydride source for the related adducts **1** and **3**. In order to obviate phosphine dissociation from Rh, the alkylated borate salt $K[HB^{s}Bu_3]$ was selected as a hydride delivery agent as after H^-/Cl^- exchange, the resulting by-product, $^{s}Bu_3B$, is a hindered borane of low Lewis acidity.[20] However when compounds **1**-**3** were separately treated with two equivalents of $K[HB^{s}Bu_3]$, the regeneration of free $CpRh(PMe_2Ph)_2$ occurred in all cases (Scheme 1). Of note, when $[(CO)_5W$•$GeCl_2(\eta^5$-$C_5H_4)]RhH(PMe_2Ph)_2$ (**1**) was treated with $K[HB^{s}Bu_3]$, the formal hydrogen transfer from Rh back to the Cp ring was noted, along with the cleavage of C(Cp)-Ge bond, leading to $CpRh(PMe_2Ph)_2$ formation.



Scheme 1. Reactivity of compounds **1**-**3** with $K[HB^{s}Bu_3]$. The fate of the $W(CO)_5$ units and tetrel elements (Ge and Sn) in these reactions is unknown.

Positing that the soft-soft coordinative Rh-Pb interactions in **3** might still support the formation of a Pb(II) hydride complex at a later stage, $CpRh(PMe_2Ph)_2$•$PbCl_2$ (**3**) was treated with different Lewis acids in an attempt to form the Pb(II) dihalide precursors $CpRh(PMe_2Ph)_2$•$PbCl_2$•LA (LA = Lewis acid). We initially reacted compound **3** with an equimolar amount of THF•$GeCl_2$•$W(CO)_5$ with the goal of producing the formal tetrahalodimetallene complex $CpRh(PMe_2Ph)_2$•Cl-$_2PbGeCl_2$•$W(CO)_5$. However, when **3** was treated with one equivalent of THF•$GeCl_2$•$W(CO)_5$, the clean formation of the previously synthesized Cp-ring activation product $[(CO)_5W$•$GeCl_2(\eta^5$-$C_5H_4)]RhH(PMe_2Ph)_2$ (**1**) transpired along with the expulsion of $PbCl_2$ from the coordination sphere of rhodium (Scheme 2). In another effort to obtain a donor-acceptor complex of $PbCl_2$, the bulky fluorinated arylborane ($BAr^F{}_3$) (Ar^F = 3,5-$(F_3C)_2C_6H_3$) was combined with compound **3**. Interestingly, this reaction afforded a new product with a Rh-H ^{1}H NMR resonance at -11.58 ppm in C_6D_6 (doublet of triplet pattern), consistent with a related C-H bond activation occurring as in the formation of **1**. Furthermore, the presence of two distinct Cp resonances in the ^{1}H NMR spectrum and an accompanying ^{11}B NMR signal in the region expected for four-coordinate boron (-10.1 ppm), suggested that electrophilic attack at Cp by $BAr^F{}_3$ happened. Fortunately colorless crystals of the product could be obtained and X-ray crystallography confirmed the formation of the Cp ring-activated Rh(III) complex $[\eta^5$-$C_5H_4BAr^F{}_3]RhH(PMe_2Ph)_2$ (**4**) (Scheme 2, Fig. 4). An independent synthesis of **4** was also accomplished by combining an equimolar mixture of $CpRh(PMe_2Ph)_2$ and $BAr^F{}_3$ in toluene. The noted inability of the Pb center in **3** to bind to $W(CO)_5$ is likely due to the lower nucleophilicity of Pb(II) centers in relation to Sn(II) (*i.e.* the inert pair effect).[3e]

The molecular structure (Fig. 4) of compound **4** shows a Rh-H bond distance of 1.50(3) Å, which is of similar value as the Rh-H bond length in compound **1**. The C(Cp)-B bond distance in **4** was found to be 1.636(3) Å which is elongated in comparison to the C(Cp)-B interaction of 1.545(3) Å in $[(C_6F_5)_2B(\eta^5$-$C_5H_4)]TiCl_3$.[21]

We also briefly explored the chemistry of another metal centered Lewis base $Pt(PCy_3)_2$[22] towards Group 14 dihalide complexes. First, $Pt(PCy_3)_2$ was treated with THF•$GeCl_2$•$W(CO)_5$ in toluene. In place of 1:1 adduct formation, oxidative addition of the Ge-Cl bond at Pt occurs affording $ClPt(PCy_3)_2Ge(Cl)$•$W(CO)_5$ (**5**) as a yellow, moisture-sensitive solid. Recently Braunschweig, Jones and coworkers reported the formation of the Lewis acid-base adduct, $(Cy_3P)_2Pt$•$GeCl_2$ from the direct interaction of $Pt(PCy_3)_2$ with Cl_2Ge•dioxane.[11d] However the presence of a Lewis acidic $W(CO)_5$ unit at the Ge(II) center facilitates Ge-Cl bond oxidative addition to form **5** (eqn. (4)). Similar oxidative additions involving electron deficient BX_3 (X = Cl, Br or I),[23] GaX_3 (X = Br or I),[24] and $BiCl_3$[25] to Pt(0) complexes are known. The crystal structure of **5** is presented in Fig. 5 and shows a Pt-Ge bond distance of 2.3526(5) Å, which is somewhat contracted in length in comparison to the Pt-Ge distance in $(PCy_3)_2Pt$•$GeCl_2$ [2.397(1) Å].[11d] The overall geometry at Pt is square planar, consistent with a Pt(II) formal oxidation state, while the proximal Ge center adopts a distorted T-shaped geometry with a stereochemically active lone pair (*e.g.* Pt-Ge-Cl(2) angle = 104.87(2)°). The ^{31}P{^{1}H} NMR spectrum of **5** in C_6D_6 yields a resonance at 16.9 ppm with resolvable platinum satellites ($^1J_{P\text{-}Pt}$ = 2412 Hz).

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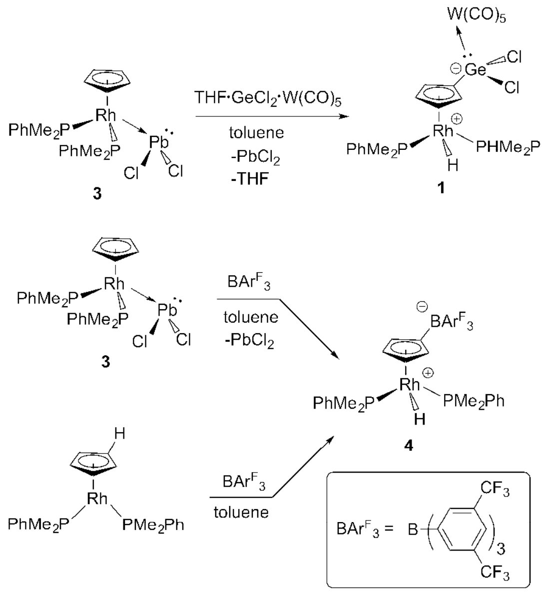
Compound **5** was also combined with two equivalents of hydride source, K[HB^{s}Bu$_3$] with the intention of yielding a stable Ge(II) hydride complex. However upon hydride addition, the only species identified in the ^{31}P{^{1}H} NMR spectrum of the resulting product mixture was free PCy$_3$; the formation of ^{s}Bu$_3$B was also confirmed by ^{11}B NMR spectroscopy.



Scheme 2. Reactivity of **3** with different Lewis acids, leading to C-H bond activation.

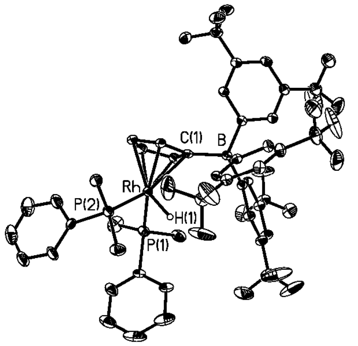
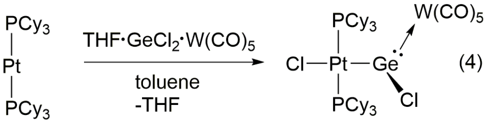


Fig. 4. Molecular structure of [η^5-C$_5$H$_4$BAr$^F_3$]RhH(PMe$_2$Ph)$_2$ (**4**) with thermal ellipsoids presented at a 30 % probability level; all carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B-C(1) 1.636(3), Rh-H 1.50(3); B-C(1)-Rh 132.18(13), average C(1)-B-C(Ar^F) = 109.5 (3).

The bis(phosphine) complex Pt(PCy$_3$)$_2$ was then mixed with one equivalent of (THF)$_2$SnCl$_2$•W(CO)$_5$, resulting in the formation of two different Pt(PCy$_3$)$_2$-containing products by ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectroscopy. Specifically, the ^{31}P{^{1}H} NMR spectrum of the product mixture afforded two resonances in a 7:3 ratio with resolvable ^{195}Pt satellites at 26.1 ($^{1}J_{\text{P-Pt}}$ = 2392 Hz) and 47.4 ($^{1}J_{\text{P-Pt}}$ = 3063 Hz) ppm. Whereas the ^{195}Pt{^{1}H} NMR spectrum gave two different triplets at -3725 ($^{1}J_{\text{P-Pt}}$ = 2395 Hz) and -4543 ($^{1}J_{\text{P-Pt}}$ = 3056 Hz) ppm. Unfortunately we were not able effectively separate these two products from each other, a crystal of one of the products, ClPt(PCy$_3$)$_2$Sn(Cl)•W(CO)$_5$ (**6**), was selected from the product mixture and identified by X-crystallography (Fig. 6). Compound **6** likely forms via the oxidative addition of a Sn-Cl bond to a Pt(0) center, in similar fashion as for the Ge congener **5**. The molecular structure of **6** shows a square planar Pt environment with a Pt-Sn bond distance of 2.5061(3) Å, which is shorter than the reported dative Pt-Sn bond in (Cy$_3$P)$_2$Pt•SnCl$_2$ [2.599(1) Å].[11d] It is likely that the other species present in the abovementioned reaction mixture is the non-activated adduct (Cy$_3$P)$_2$Pt•SnCl$_2$•W(CO)$_5$. To see if one species could be converted into the other, the product mixture was heated in C$_6$D$_6$ at 50 °C for 5 hours, however no change in the relative ratio of intensities of two signals in the resulting ^{31}P{^{1}H} NMR spectrum was found. At higher temperatures (> 80 °C) both species decompose to yield multiple new species (*ca.* 10) from which no clean product could be isolated.



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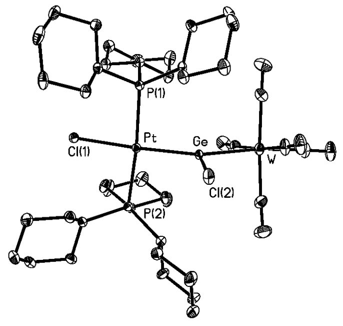

Figure 5. Molecular structure of ClPt(PCy$_3$)$_2$Ge(Cl)•W(CO)$_5$ (**5**) with thermal ellipsoids presented at a 30 % probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt-Ge 2.3526(5), Ge-Cl(2) 2.2489(9), Pt-Cl(1) 2.4176(8), Ge-W 2.5745(5); Cl(1)-Pt-Ge 176.20(2), Pt-Ge-Cl(2) 104.87(2), Pt-Ge-W 147.463(10).

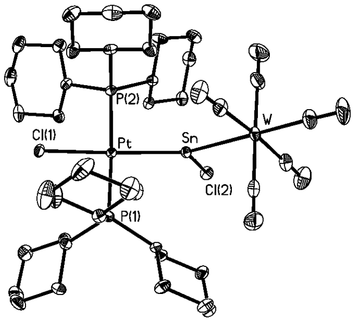

Fig. 6 Molecular structure of ClPt(PCy$_3$)$_2$Sn(Cl)•W(CO)$_5$ (**6**) with thermal ellipsoids presented at a 30 % probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt-Sn 2.5061(3), Sn-Cl(2) 2.4149(11), Pt-Cl(1) 2.4110(11), Sn-W 2.7309(3); Cl(1)-Pt-Sn 172.63(3), Pt-Sn-Cl(2) 107.89(3), Pt-Sn-W 144.019(13).

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Conclusions

In conclusion, the reactivity of the metal centered Lewis basic complexes $CpRh(PMe_2Ph)_2$ and $Pt(PCy_3)_2$ towards various electron deficient E(II) dihalide units (E = Ge, Sn and Pb) was explored. When strong Lewis acids were combined with the Rh complex $CpRh(PMe_2Ph)_2$ the formation of Cp-activated products and Rh-H bonds occurred in place of direct Rh-E bond formation. In the case of $Pt(PCy_3)_2$, the formal oxidation addition of Ge-Cl and Sn-Cl bonds transpired to give the products $ClPt(PCy_3)_2E(Cl)\bullet W(CO)_5$ (E = Ge and Sn). Attempts to form the corresponding Group 14 hydrides via H^- addition to E-Cl residues were unsuccessful, and in each case hydride addition to the Rh complexes **1**-**3** afforded free $CpRh(PMe_2Ph)_2$. Future work will involve tailoring the nature of the metal centered Lewis bases and Lewis acidic partner to obtain viable EH_2 precursor complexes for mixed element deposition processes.

Experimental Details

Materials and Instrumentation.

All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[26] manufactured by Innovative Technology, Inc., degassed (freeze–pump–thaw method), and stored under an atmosphere of nitrogen prior to use. $Li[BH_4]$, $K[HB^sBu_3]$ (1.0 M solution in THF), and $PbCl_2$ were purchased from Aldrich and used as received. $(THF)_2SnCl_2\bullet W(CO)_5$,[27] $THF\bullet GeCl_2\bullet W(CO)_5$,[16] $CpRh(PMe_2Ph)_2$,[12] BAr^F_3 (Ar^F = 3,5-$(F_3C)_2C_6H_3$),[28] and $(Cy_3P)_2Pt$[22] were prepared according to literature procedures. ^1H, ^{11}B, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, ^{119}Sn and ^{195}Pt NMR spectra were recorded on a Varian iNova- 400 spectrometer and referenced externally to $SiMe_4$ (^1H and $^{13}C\{^1H\}$), 85 % H_3PO_4 ($^{31}P\{^1H\}$), $F_3B\bullet OEt_2$ (^{11}B), $CFCl_3$ ($^{19}F\{^1H\}$), $SnMe_4$ (^{119}Sn), and $Na_2[PtCl_6]$ in D_2O (^{195}Pt) respectively. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as Nujol mulls between NaCl plates. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray Crystallography. Crystals of suitable quality for X-ray diffraction studies were removed from a vial in a glovebox and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on an X-ray diffractometer.[29] All data were collected at the University of Alberta using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα, $[(CO)_5W\bullet GeCl_2(\eta^5\text{-}C_5H_4)]RhH(PMe_2Ph)_2$ (**1**), $CpRh(PMe_2Ph)_2\bullet PbCl_2$ (**3**), $ClPt(PCy_3)_2GeCl\bullet W(CO)_5$ (**5**), $ClPt(PCy_3)_2SnCl\bullet W(CO)_5$ (**6**)) or Cu Kα ($CpRh(PMe_2Ph)_2\bullet SnCl_2\bullet W(CO)_5$ (**2**), $[\eta^5\text{-}C_5H_4BAr^F_3]RhH(PMe_2Ph)_2$ (**4**)) radiation with the crystals cooled to −100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces.[30] Structures were solved using intrinsic phasing SHELXT[31] ($CpRh(PMe_2Ph)_2\bullet PbCl_2$ (**3**), $[\eta^5\text{-}C_5H_4BAr^F_3]RhH(PMe_2Ph)_2$ (**4**), $ClPt(PCy_3)_2GeCl\bullet W(CO)_5$ (**5**), and $ClPt(PCy_3)_2SnCl\bullet W(CO)_5$ (**6**)), or Patterson search/ structure expansion facilities within the DIRDIF-2008 program suite[32] ($[(CO)_5W\bullet GeCl_2(\eta^5\text{-}C_5H_4)]RhH(PMe_2Ph)_2$ (**1**), $(CpRh(PMe_2Ph)_2\bullet SnCl_2\bullet W(CO)_5$ (**2**)), structure refinement was accomplished using either SHELXL-97 or SHELXL-2013.[31] All carbon-bound hydrogen atoms were assigned positions on the basis of the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms. For compounds **1**, and **4**, all hydrogen atoms attached to heteroatoms (Rh) were located from difference Fourier maps, and their coordinates and isotropic displacement parameters were allowed to refine freely.

Synthetic details.

Synthesis of $[(CO)_5W\bullet GeCl_2(\eta^5C_5H_4)]RhH(PMe_2Ph)_2$ *(**1**).* A 3 mL toluene solution of $CpRh(PMe_2Ph)_2$ (33 mg, 0.074 mmol) was added dropwise to a 3 mL toluene solution of $(THF)\bullet GeCl_2\bullet W(CO)_5$ (40 mg, 0.074 mmol), and the mixture was stirred overnight. The resulting dark yellow precipitate was separated from the mother liquor, washed with 5 mL of hexanes and dried under vacuum. Pure product was obtained by crystallization from hexanes/CH_2Cl_2 at -35 °C. Yield: 30 mg (45 %). ^1H NMR (500 MHz, CD_2Cl_2): δ = 7.42-7.48 (m, 2H, Ar*H*), 7.34-7.42 (br, 4H, Ar*H*), 7.18-7.27 (m, 4H, Ar*H*), 5.75 (s, 2H, Cp), 5.40 (s, 2H, Cp), 1.65 (vt, $N = |^2J_{H\text{-}P} + {}^4J_{H\text{-}P}|$ = 8.4 Hz, 6H, CH_3), 1.54 (vt, $N = |^2J_{H\text{-}P} + {}^4J_{H\text{-}P}|$ = 8.4 Hz, 6H, CH_3), -11.98 (dt, $^2J_{H\text{-}P}$ = 29.9 Hz, $^1J_{H\text{-}Rh}$ = 19.9 Hz, 1H, Rh-*H*). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 202.6 (s, CO_{ax}), 199.1 (s, CO_{eq}, satellite: $^1J_{C\text{-}W}$ = 124 Hz), 135.0 (vt, $N = |^1J_{C\text{-}P} + {}^3J_{C\text{-}P}|$ = 53.6 Hz, Ar*C*), 130.8 (s, Ar*C*), 130.2 (s, Ar*C*), 128.8 (s, Ar*C*), 94.4 (s, Cp), 90.1 (s, Cp), 22.1 (vt, *N* = 34.1 Hz, CH_3), 21.0 (vt, *N* = 37.9 Hz, CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ = 14.6 (d, $^1J_{P\text{-}Rh}$ = 139 Hz). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41-7.49 (m, 2H, Ar*H*), 7.33-7.41 (m, 4H, Ar*H*), 7.14-7.28 (m, 4H, Ar*H*), 5.66 (s, 2H, Cp), 5.43 (s, 2H, Cp), 1.65 (vt, $N = |^2J_{H\text{-}P} + {}^4J_{H\text{-}P}|$ = 10 Hz, 6H, CH_3), 1.56 (vt, $N = |^2J_{H\text{-}P} + {}^4J_{H\text{-}P}|$ = 10 Hz, 6H, CH_3), -11.92 (dt, Rh-*H*, $^2J_{H\text{-}P}$ = 29.9 Hz, $^1J_{H\text{-}Rh}$ = 19.9 Hz, 1H, Rh-*H*). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 14.1 (d, $^1J_{P\text{-}Rh}$ = 139.1 Hz). IR (Nujol, cm^{-1}): 1901 (br, υ_{CO}), 1970 (s, υ_{CO}), 2059 (s, υ_{CO}). Anal. Calcd. for $C_{26}H_{27}Cl_2GeO_5P_2RhW$: C, 34.25; H, 2.98. Found: C, 34.25; H, 3.14. Mp (°C): 132-135 (decomposes).

Synthesis of $CpRh(PMe_2Ph)_2\bullet SnCl_2\bullet W(CO)_5$ *(**2**).* A 3 mL toluene solution of $CpRh(PMe_2Ph)_2$ (18 mg, 0.041 mmol) was added dropwise to a 3 mL toluene solution of $(THF)_2SnCl_2\bullet W(CO)_5$ (36 mg, 0.045 mmol), and the mixture was stirred overnight. The resulting orange yellow precipitate was separated from the mother liquor, washed with 5 mL of hexanes and dried under vacuum. Yield: 38 mg (94 %). Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/hexanes at -35 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44-7.50 (m, 2H, Ar*H*), 7.36-7.44 (m, 4H, Ar*H*), 7.14-7.22 (m, 4H, Ar*H*), 5.25 (s, 5H, Cp), 2.08 (vt, *N* = 10 Hz, 6H, CH_3), 1.92 (vt, *N* = 10 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 203.0 (s, CO_{ax}), 200.7 (s, CO_{eq}), 139.6 (vt, *N* = 48.6 Hz, Ar*C*), 130.7 (s, Ar*C*), 129.5 (s, Ar*C*), 129.1 (s, Ar*C*), 95.1 (s, Cp), 22.9 (vt, *N* = 35.9 Hz, CH_3), 15.6 (vt, *N* = 35.8 Hz, CH_3). $^{31}P\{^1H\}$ NMR (201 MHz, $CDCl_3$): δ = 4.6 (d, $^1J_{Rh\text{-}P}$ = 153 Hz, satellites: $^3J_{P\text{-}W}$ = 77 Hz). IR (Nujol, cm^{-1}): 1892 (br, υ_{CO}), 1965 (s, υ_{CO}), 2054 (s, υ_{CO}). Anal. Calcd. for $C_{26}H_{27}Cl_2O_5P_2RhSnW$: C, 32.60; H, 2.84. Found: C, 32.42; H, 2.92. Mp (°C): 150-153 (decomposes).

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DOI: 10.1039/C5DT03018H

Synthesis of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ *(**3**).* A 3 mL toluene solution of $CpRh(PMe_2Ph)_2$ (68 mg, 0.15 mmol) was added dropwise to a 3 mL toluene suspension of $PbCl_2$ (51 mg, 0.18 mmol), and the mixture was stirred overnight. The solvent was removed under vacuum and the remaining red powder was washed twice with 5 mL portions of hexanes and dried. The red solid was then dissolved in 10 mL of CH_2Cl_2 and the resulting solution was filtered. The solvent was removed from the filtrate and the product was dried under vacuum. Yield: 65 mg (60 %). Crystals suitable for X-ray crystallography were grown from hexanes/THF at -35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.41-7.58 (m, 6H, Ar*H*), 7.22-7.38 (m, 4H, Ar*H*), 5.11 (s, 5H, Cp), 1.62 (br, 6H, CH_3), 1.42 (br, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2): δ = 136.7 (vt, *N* = 46.9 Hz, Ar*C*), 130.6 (s, Ar*C*), 129.9 (s, Ar*C*), 129.3 (s, Ar*C*), 94.0 (s, Cp), 22.1 (vt, *N* = 33.7 Hz, *C*H$_3$), 15.4 (vt, *N* = 33.4 Hz, *C*H$_3$). $^{31}P\{^{1}H\}$ NMR (201 MHz, CD_2Cl_2): δ = 8.2 (d, $^{1}J_{Rh\text{-}P}$ = 170 Hz). Anal. Calcd. for $C_{21}H_{27}Cl_2P_2PbRh$: C, 34.92; H, 3.77. Found: C, 35.07; H, 3.76. Mp (°C): 185-188 (decomposes).

Synthesis of $[\eta^5\text{-}C_5H_4BAr^F{}_3]RhH(PMe_2Ph)_2$ *(**4**).* A 3 mL toluene solution of $CpRh(PMe_2Ph)_2$ (83 mg, 0.19 mmol) was added dropwise to a 3 mL toluene solution of $BAr^F{}_3$ (136 mg, 0.19 mmol) and the mixture was stirred overnight to give a red solution. The solvent was removed from the mixture under vacuum to afford a deep yellow-orange oil. The oil was re-dissolved in 3 mL of Et_2O and the solvent was removed anew to yield an orange powder. This product was then washed with a mixture of Et_2O/hexanes (1 mL + 3 mL) to give **4** as a white powder. Yield: 100 mg (48 %). Crystals suitable for X-ray were grown from hexanes/Et_2O at -35 °C C. ^{1}H NMR (500 MHz, C_6D_6): δ = 8.27 (s, 6H, *o*-$C_6H_3(CF_3)_2$), 7.80 (s, 3H, *p*-$C_6H_3(CF_3)_2$), 6.89-6.92 (m, 6H, Ar*H*), 6.55-6.75 (m, 4H, Ar*H*), 4.70 (s, 2H, Cp), 4.30 (s, 2H, Cp), 0.67 (vt, *N* = 10 Hz, 6H, CH_3), 0.58 (vt, *N* = 10 Hz, 6H, CH_3), -11.58 (dt, $^{2}J_{H\text{-}P}$ = 31.6 Hz, $^{1}J_{H\text{-}Rh}$ = 21.6 Hz, 1H, Rh-*H*). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6): δ = 162.0 (q, $^{1}J_{B\text{-}C}$ = 51.2 Hz, *ipso*-$C_6H_3(CF_3)_2$), 135.8 (vt, *N* = 50.6 Hz, Ar*C*), 135.2 (s, *o*-$C_6H_3(CF_3)_2$), 130.7 (s, Ar*C*), 130.0 (br, Ar*C*), 129.9 (q, $^{2}J_{C\text{-}F}$ = 31.4 Hz, *m*-$C_6H_3(CF_3)_2$), 128.6 (s, Ar*C*), 125.8 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz, CF_3), 118.6 (s, *p*-$C_6H_3(CF_3)_2$), 92.8 (s, Cp), 89.2 (s, Cp), 21.6 (vt, *N* = 33.0 Hz, *C*H$_3$), 20.5 (vt, *N* = 37.0 Hz, *C*H$_3$). $^{31}P\{^{1}H\}$ NMR (161 MHz, C_6D_6): δ = 13.6 (d, $^{1}J_{P\text{-}Rh}$ = 133.3 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6): δ = -10.1 (s, -*B*Ar$^F{}_3$). $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6): δ = -62.0 (s, CF_3). Anal. Calcd. for $C_{45}H_{36}BF_{18}P_2Rh$: C, 49.39; H, 3.32. C, 49.31; H, 3.62. Mp (°C): 152-155.

Reaction of $[(CO)_5W{\bullet}GeCl_2(\eta^5\text{-}C_5H_4)]RhH(PMe_2Ph)_2$ *(**1**) with* $K[HB^{s}Bu_3]$*.* To a 5 mL toluene solution of **1** (110 mg, 0.12 mmol) was added $K[HB^{s}Bu_3]$ (254 µL, 1.0 M solution in THF, 0.25 mmol), and the mixture was stirred overnight. The mother liquor was separated from the black precipitate by filtration and the solvent was removed from the filtrate to yield an orange oil containing a mixture of $CpRh(PMe_2Ph)_2$ and $^{s}Bu_3B$ (as determined by ^{1}H, ^{11}B and $^{31}P\{^{1}H\}$ NMR spectroscopy in C_6D_6).[33]

Reaction of $CpRh(PMe_2Ph)_2{\bullet}SnCl_2{\bullet}W(CO)_5$ *(**2**) with* $K[HB^{s}Bu_3]$*.* To a 5 mL toluene solution of **2** (96 mg, 0.10 mmol), was added $K[HB^{s}Bu_3]$ (210 µL, 1.0 M solution in THF, 0.21 mmol), and the mixture was stirred overnight. The mother liquor was separated from the black precipitate by filtration and the solvent was removed from the filtrate to yield an orange oil containing a mixture of $CpRh(PMe_2Ph)_2$ and $^{s}Bu_3B$.

Reaction of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ *(**3**) with* $K[HB^{s}Bu_3]$*.* To a 5 mL toluene solution of **3** (56 mg, 0.077 mmol) was added $K[HB^{s}Bu_3]$ (178 µL, 1.0 M solution in THF, 0.18 mmol), and the mixture was stirred overnight. The mother liquor was separated from the grey precipitate by filtration and the solvent was removed from the filtrate to yield an orange oil consisting of a mixture of $CpRh(PMe_2Ph)_2$ and $^{s}Bu_3B$.

Reaction of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ *(**3**) with* $THF{\bullet}GeCl_2{\bullet}W(CO)_5$*.* A 3 mL toluene solution of $THF{\bullet}GeCl_2{\bullet}W(CO)_5$ (25 mg, 0.043 mmol) was added dropwise to a 3 mL toluene suspension of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ (31 mg, 0.043 mmol) and the mixture was stirred overnight. The solvent was removed under vacuum from the black suspension to give a black powder. The only soluble product identified by ^{1}H and $^{31}P\{^{1}H\}$ NMR was $[\eta^5\text{-}C_5H_4GeCl_2{\bullet}W(CO)_5]RhH(PMe_2Ph)_2$ (**1**).

Reaction of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ *(**3**) with* $BAr^F{}_3$*.* A 3 mL toluene solution of $BAr^F{}_3$ (40 mg, 0.062 mmol) was added dropwise to a 3 mL toluene suspension of $CpRh(PMe_2Ph)_2{\bullet}PbCl_2$ (45 mg, 0.062 mmol) and the mixture was stirred overnight. The solvent was removed under vacuum from the black suspension to obtain a black powder. The only NMR identified product was $[\eta^5\text{-}C_5H_4BAr^F{}_3]RhH(PMe_2Ph)_2$ (**4**).

Synthesis of $ClPt(PCy_3)_2GeCl{\bullet}W(CO)_5$ *(**5**).* A solution of $Pt(PCy_3)_2$ (180 mg, 0.24 mmol) in 3 mL of toluene was added dropwise to a 3 mL toluene solution of $THF{\bullet}GeCl_2{\bullet}W(CO)_5$ (130 mg, 0.24 mmol). The reaction mixture was stirred for 24 hrs and the solvent was removed under vacuum. Then 5 mL of hexanes was added to the oily product followed by stirring for one hour. The precipitate was separated from the mother liquor and dried under vacuum to give a yellow powder. Yield: 210 mg (72%). Crystals suitable for X-ray were obtained from a concentrated hexanes solution at -35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 2.40-2.62 (br, 6H, Cy), 2.10-2.30 (br, 12H, Cy), 1.14-1.90 (m, 48H, Cy). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6): δ = 200.9 (s, *C*O$_{ax}$), 198.8 (s, *C*O$_{eq}$), 35.6 (br, C^1, Cy), 31.9 (s, $C^{3,5}$, Cy), 30.7 (s, $C^{3,5}$, Cy), 27.9 (br s, $C^{2,6}$, Cy), 27.5 (br s, $C^{2,6}$, Cy), 26.7 (s, C^4, Cy). $^{31}P\{^{1}H\}$ NMR (201 MHz, C_6D_6): δ = 16.9 (s, satellites: $^{1}J_{P\text{-}Pt}$ = 2412 Hz). $^{195}Pt\{^{1}H\}$ NMR (85.5 MHz, C_6D_6): δ = -3645 (t, $^{1}J_{P\text{-}pt}$ = 2447 Hz). IR (Nujol, cm^{-1}): 1932 (br, υ_{CO}), 1984 (s, υ_{CO}), 2065 (s, υ_{CO}). Anal. Calcd. for: $C_{41}H_{66}Cl_2GeO_5P_2PtW$: C, 40.25; H, 5.44. Found: C, 41.05; H, 5.51. Mp (°C): 120-123 (decomposes).

Reaction of $ClPt(PCy_3)_2GeCl{\bullet}W(CO)_5$ *(**5**) with* $K[HB^{s}Bu_3]$*.* To a 5 mL THF solution of **5** (20 mg, 0.016 mmol), was added $K[HB^{s}Bu_3]$ (34 µL, 1.0 M solution in THF, 0.034 mmol), and the mixture was stirred overnight. The solvent was removed from the mixture to yield an dark orange oil containing a mixture of PCy_3 and $^{s}Bu_3B$ as soluble products.[33]

Synthesis of $ClPt(PCy_3)_2SnCl{\bullet}W(CO)_5$ *(**6**).* A 3 mL toluene solution of $Pt(PCy_3)_2$ (180 mg, 0.24 mmol) was added dropwise to a 3 mL toluene solution of $(THF)_2SnCl_2{\bullet}W(CO)_5$ (130 mg, 0.24 mmol). The reaction mixture was stirred for 24 hrs and the volatiles were removed under vacuum. 5 mL of hexanes was then added to the oily product followed by stirring for one hour. The precipitate was separated from the mother liquor and dried under vacuum to give a red powder. A few crystals suitable for X-ray crystallography were grown from the mixture in hexanes at -35 °C. The crystallographic data identified one of the products as $ClPt(PCy_3)_2SnCl{\bullet}W(CO)_5$, whereas the ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectroscopy on the product indicated the presence of two products with the following NMR data: ^{31}P{^{1}H} NMR (201 MHz, C_6D_6): δ = 26.1 (s, satellites: $^{1}J_{\text{P-Pt}}$ = 2392 Hz), 47.4 (s, satellites: $^{1}J_{\text{P-Pt}}$ = 3063 Hz). ^{195}Pt{^{1}H} NMR (85.5 MHz, C_6D_6): δ = -3725 (t, $^{1}J_{\text{P-pt}}$ = 2395 Hz), -4543 (t, $^{1}J_{\text{P-pt}}$ = 3056 Hz).

Acknowledgements

This work was supported by the Natural Science and Engineering Research Council of Canada (Discovery Grant for E.R.) and the Canada Foundation for Innovation (CFI). The authors also acknowledge Dr. Tapas Purkait for experimental assistance. The authors also thank Dr. Christian Hering-Junghans for helpful suggestions.

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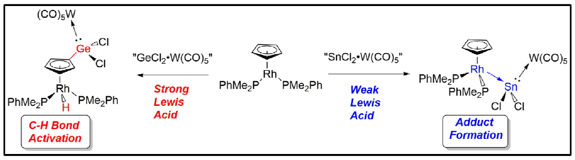
TOC Graphic



The main group element triggered C-H bond activation of a Rh-bound Cp ligand is reported. The key aspect of this transformation is the presence of a highly Lewis acidic Group 14 element site.

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Supporting Information

Transition Metal-mediated Donor-acceptor Coordination of Low-oxidation State Group 14 Element Halides

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<ins>Contents</ins>

DOI: 10.1039/C5DT03018H

Table S1. Crystallographic data for compound **1**

A. Crystal Data

formula	$C_{26}H_{27}Cl_2GeO_5P_2RhW$
formula weight	911.66
crystal dimensions (mm)	0.27×0.14×0.11
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	8.9888 (3)
b (Å)	24.3719 (7)
c (Å)	14.4140 (4)
β (deg)	104.3064 (3)
V (Å^3)	3059.81 (16)
Z	4
ρ_{calcd} (g cm^{-3})	1.979
μ (mm^{-1})	5.572

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	56.65
total data collected	28051 ($-11 \leq h \leq 11$, $-32 \leq k \leq 31$, $-19 \leq l \leq 19$)
independent reflections	7477 ($R_{\text{int}} = 0.0162$)
number of observed reflections (*NO*)	7036 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6400–0.3265
data/restraints/parameters	7477 / 0 / 351
goodness-of-fit (S)[e] [all data]	1.058
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0160
wR_2 [all data]	0.0379
largest difference peak and hole	1.032 and –0.480 e Å^{-3}

[a] Obtained from least-squares refinement of 9932 reflections with $4.44° < 2\theta < 56.48°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. Gould,

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O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen,

[d] G. M. Sheldrick, *Acta Crystallogr.*2008, **A64**, 112–122.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0187P)^2 + 1.4453P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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Table S2. Crystallographic data for compound **2**

A. Crystal Data

formula	$C_{26.25}H_{27.5}Cl_{2.5}O_5P_2RhSnW$
formula weight	979.00
crystal dimensions (mm)	0.27 × 0.02 × 0.02
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	15.3972 (2)
b (Å)	9.0453 (1)
c (Å)	23.3877 (3)
β (deg)	90.5374 (12)
V (Å^3)	3257.12 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.996
μ (mm^{-1})	19.58

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	145.17
total data collected	21691 ($-19 \leq h \leq 18$, $-11 \leq k \leq 11$, $-28 \leq l \leq 28$)
independent reflections	6344 (R_{int} = 0.0781)
number of observed reflections (*NO*)	5092 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[d,e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8514–0.1190
data/restraints/parameters	6344 / 0 / 347
goodness-of-fit (*S*)[f] [all data]	1.031
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0345
wR_2 [all data]	0.0868
largest difference peak and hole	1.130 and –1.373 e Å^{-3}

[a] Obtained from least-squares refinement of 9963 reflections with 6.84° < 2θ < 143.88°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. Gould,

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O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen,

[d] G. M. Sheldrick, *Acta Crystallogr.*2008, **A64**, 112–122.

[e] Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent dichloromethane chlorine or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure (P. van der Sluis and A. L. Spek, *Acta Crystallogr.*1990, **A46**, 194–201) as implemented in *PLATON* (A.L. Spek, *Acta Crystallogr.*1990, **A46,** C34; A. L. Spek, *J. Appl. Cryst.*2003, **36**, 7–13. *PLATON* - a multipurpose crystallographic tool. UtrechtUniversity, Utrecht, The Netherlands). A total solvent-accessible void volume of 225.6Å^3 with a total electron count of 43 (consistent with one molecule of solvent CH_2Cl_2, or 0.25 molecule per formula unit of the metal complex molecule) was found in the unit cell.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0403P)^2 + 0.9612P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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Table S3. Crystallographic data for compound **3**

A. Crystal Data

formula	$C_{21}H_{27}Cl_2P_2PbRh$
formula weight	722.36
crystal dimensions (mm)	0.09 × 0.08 × 0.07
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	17.346 (5)
b (Å)	15.351 (4)
c (Å)	18.164 (5)
β (deg)	95.470 (3)
V (Å^3)	4814 (2)
Z	8
ρ_{calcd} (g cm^{-3})	1.993
μ (mm^{-1})	8.030

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.52
total data collected	41795 ($-22 \leq h \leq 22$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$)
independent reflections	11064 ($R_{int} = 0.0573$)
number of observed reflections (*NO*)	8280 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7619–0.5292
data/restraints/parameters	11064 / 0 / 495
goodness-of-fit (S)[d] [all data]	1.120
final$R$ indices[e]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0364
wR_2 [all data]	0.0816
largest difference peak and hole	1.992 and –1.824 e Å^{-3}

[a] Obtained from least-squares refinement of 9990 reflections with $4.50° < 2\theta < 53.30°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[d] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.

[d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; w =

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$[\sigma^2(F_o{}^2) + (0.0316P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2]/3)$.

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^4)]^{1/2}$.

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Table S4. Crystallographic data for compound **4**

A. Crystal Data	
formula	$C_{48}H_{43}BF_{18}P_2Rh$
formula weight	1137.48
crystal dimensions (mm)	0.26×0.20×0.16
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	12.2135 (3)
b (Å)	12.5991 (3)
c (Å)	17.0103 (4)
α (deg)	80.6961 (10)
β (deg)	81.3382 (8)
γ (deg)	75.2500 (8)
V (Å^3)	2481.49 (10)
Z	2
ρ_{calcd} (g cm^{-3})	1.522
μ (mm^{-1})	4.305
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.46
total data collected	17405 ($-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-21 \leq l \leq 20$)
independent reflections	9416 ($R_{\text{int}} = 0.0129$)
number of observed reflections (*NO*)	9241 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d,e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6786–0.4912
data/restraints/parameters	9416 / 0 / 716
goodness-of-fit (S)[f] [all data]	1.026
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0319
wR_2 [all data]	0.0860
largest difference peak and hole	1.112 and –0.806 e Å^{-3}

[a] Obtained from least-squares refinement of 9844 reflections with $8.46° < 2\theta < 144.24°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT-2014*)

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[d] G. M. Sheldrick, G. M. *Acta Crystallogr.*2015, **C71**, 3–8. (*SHELXL-2014*)

[e] Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedureas implemented in *PLATON* (A. L. Spek,. *Acta Crystallogr.*2015, **C71**, 9–18. *PLATON* - a multipurpose crystallographic tool. UtrechtUniversity, Utrecht, The Netherlands). A total solvent-accessible void volume of 221Å^3 with a total electron count of 50 (consistent with 1 molecule of solvent hexane, or 0.5 molecules per formula unit of the rhodium complex) was found in the unit cell.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0493P)^2 + 2.1386P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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Table S5. Crystallographic data for compound **5**

A. Crystal Data	
formula	$C_{44}H_{73}Cl_2GeO_5P_2PtW$
formula weight	1266.39
crystal dimensions (mm)	0.29×0.09×0.06
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	10.172 (2)
b (Å)	12.807 (3)
c (Å)	20.478 (4)
α (deg)	105.848 (2)
β (deg)	103.959 (2)
γ (deg)	93.004 (3)
V (Å^3)	2470.6 (8)
Z	2
ρ_{calcd} (g cm^{-3})	1.702
μ (mm^{-1})	5.964
B. Data Collection and Refinement Conditions	
diffractometer	BrukerD8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.18
total data collected	22384 ($-13 \le h \le 13$, $-16 \le k \le 16$, $-26 \le l \le 26$)
independent reflections	11338 ($R_{\text{int}} = 0.0148$)
number of observed reflections (*NO*)	9930 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7960–0.3812
data/restraints/parameters	11338 / 3[d] / 534
goodness-of-fit (S)[e] [all data]	1.117
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0212
wR_2 [all data]	0.0603
largest difference peak and hole	1.248 and –1.042 e Å^{-3}

[a] Obtained from least-squares refinement of 9783 reflections with $4.46° < 2\theta < 55.04°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

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[c] G. M. Sheldrick, *ActaCrystallogr.*2008, **A64**, 112–122.

[d] The C–C distances within the minor component of the disordered solvent hexane molecule were restrained to be approximately equal by use of the *SHELXL***SADI** instruction.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0333P)^2 + 0.5140P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S6. Crystallographic data for compound **6**

A. Crystal Data

formula	$C_{41}H_{66}Cl_2O_5P_2PtSnW$
formula weight	1355.58
crystal dimensions (mm)	0.23×0.18×0.09
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	14.8910 (4)
b (Å)	16.3240 (4)
c (Å)	22.1599 (6)
V (Å^3)	5386.6 (2)
Z	4
ρ_{calcd} (g cm^{-3})	1.672
μ (mm^{-1})	5.379

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.98
total data collected	47820 ($-19 \leq h \leq 19$, $-21 \leq k \leq 21$, $-28 \leq l \leq 28$)
independent reflections	12339 ($R_{int} = 0.0289$)
number of observed reflections (*NO*)	11780 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6982–0.4584
data/restraints/parameters	12339 / 18[d] / 512
Flack absolute structure parameter[e]	0.0093(19)
goodness-of-fit (S)[f] [all data]	1.005
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0176
wR_2 [all data]	0.0404
largest difference peak and hole	0.737 and –0.323 e Å^{-3}

[a] Obtained from least-squares refinement of 9906 reflections with $4.44° < 2\theta < 51.62°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.

[d] Distances within the disordered solvent n-hexane molecule were restrained to idealized target

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DOI: 10.1039/C5DT03018H

distances during refinement: d(C1SA–C2SA) = d(C2SA–C3SA) = d(C3SA–C4SA) = d(C4SA–C5SA) = d(C5SA–C6SA) = d(C1SB–C2SB) = d(C2SB–C3SB) = d(C3SB–C4SB) = d(C4SA–C5SB) = d(C5SB–C6SB) = 1.50(1) Å; d(C1SA···C3SA) = d(C2SA···C4SA) = d(C3SA···C5SA) = d(C4SA···C6SA) = d(C1SB···C3SB) = d(C2SB···C4SB) = d(C3SB···C5SB) = d(C4SB···C6SB) = 2.45(1) Å.

[e] H. D. Flack, *Acta Crystallogr.*1983, **A39**, 876–881; H. D. Flack, G. Bernardinelli, *Acta Crystallogr.*1999, **A55**, 908–915; H.D. Flack, G. Bernardinelli, *J. Appl. Cryst.*2000, **33**, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0115P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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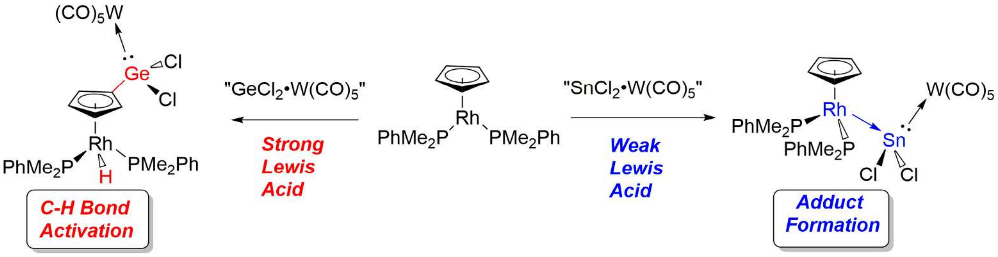
DOI: 10.1039/C5DT03018H



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