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# Diferrocenylmercury-Bridged Diphosphine: A Unique Chiral, Ambiphilic, and Redox-active Bidentate Ligand

Alain C. Tagne Kuate,[a],[b] Roger A. Lalancette,[a] Thomas Bannenberg,[c] and Frieder Jäkle*[a]

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 70th birthday

**Abstract:** A novel diphosphine chelate ligand with a wide and flexible bite angle, a unique stereochemical environment, as well as redox-active and ambiphilic character is reported. Initially generated as its $HgCl_2$ complex by reaction of 1,2-fc($PPh_2$)($SnMe_3$) (fc = ferrocenediyl) with $HgCl_2$ in acetone, treatment with [*n*-$Bu_4$N]CN readily liberates the free chiral bidentate ligand. An intermolecular ClHg-Cl → $Hgfc_2$ (2.9929(13) Å) interaction that is unprecedented in ambiphilic ligand chemistry is seen in the solid structure of Hg($fcPPh_2$)$_2$·$HgCl_2$ where the bridging mercury atom acts as a σ-acceptor. In addition, a bis-[Rh(COD)Cl] complex is introduced, which displays relatively short Rh···Hg contacts of 3.4765(5) and 3.4013(1) Å. Wiberg indices of 0.12 are determined for these Rh···Hg interactions and an AIM analysis reveals bond paths with an electron density *ρ*(r) of $1.2 \times 10^{-2}$ and $1.4 \times 10^{-2}$ e/$a_0^3$ at the bond critical points.

The attachment of both Lewis acid and base entities to the same molecular framework gives rise to bifunctional $L_nZ$-type (n = 1-3) ligand systems that exhibit $L_nM \rightarrow Z$ or $L_nM{-}X \rightarrow Z$ coordination toward transition metals with the base (L) acting as a σ-donor and the acid (Z) as a σ-acceptor.[1] Such compounds are referred to as ambiphilic ligands and, for Group 13 Lewis acids, their initial development can be traced back to the works of Hill and coworkers on the "scorpionate" ligand $HB(mt)_3$ (mt = N-methylthioimidazolyl). They demonstrated an intramolecular activation of the B−H bond with formation of an unprecedented direct Ru-B interaction.[2] The strategy was subsequently extended to a range of so-called metallaboratranes involving various other transition metals.[3]

Bourissou further exploited this principle using systems, in which the Z sites are predisposed to directly interact with transition metals without the need for *in situ* generation of the Lewis acid. The *o*-phenylene-linked phosphine-boranes (**I**), diphosphine-boranes (**II**) and triphosphine-boranes (**III**) in Figure 1 (E = B) proved suitable to access a range of complexes with M−X→B or M→B interactions (M = Au, Pt, Ni, Pd, Rh, Ag, Ir, Fe).[4] Replacement of boron in these ligand architectures by other Lewis acidic metals/elements led to further variations in the M→Z interactions.[1d,1e,5] A similar strategy was more recently adopted by Emslie, who introduced the ferrocene-supported diphosphine-borane (**IV**) as a rare example of a chiral ambiphilic ligand.[6] However, **IV** was only isolated as a racemate.

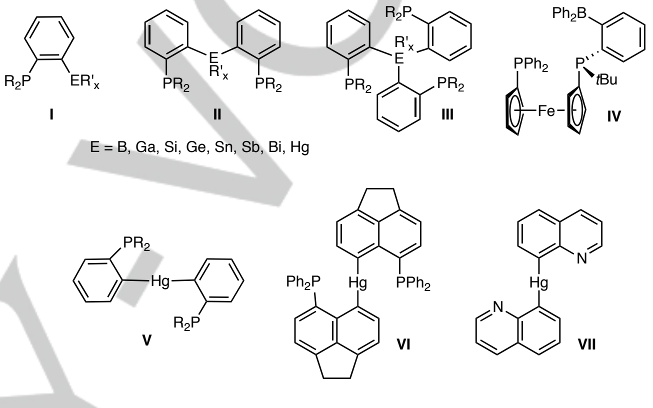

**Figure 1.** Examples of ambiphilic ligands.

Although their coordinating ability is generally not as strong as that of the Group 13 elements, diarylmercury species are known to interact with anionic and neutral guests,[7] showing that they exhibit appreciable Lewis acidity. However, there are relatively few reports of inter- or intramolecular M···Hg contacts with transition metals, although the study of such metallophilic interactions is of fundamental interest to gain a better understanding of the nature of the bonding. When incorporating the Hg atom in the diphosphine framework (**V**), Bennet found evidence for short M···Hg contacts with Hg(II), Ni(II), Pd(II) and Pt(II).[8] More recently, López-de-Luzuriaga extended the use of **V** to systems with group 11 elements [Cu(I), Ag(I), Au(I), Au(III)],[9] while Beckmann observed closed-shell interactions for acenaphthyl-based diphosphine mercury species (**VI**) with Hg(II), Ag(I) and Au(I).[10] On the other hand, the Lewis acidic mercury and the Lewis basic phosphines in **V** and **VI** showed no or only very weak intramolecular P···Hg interactions as indicated by small coupling constants *J*(HgP) in **V** (212 Hz) and **VI** (631 Hz), and a P···Hg distance of 3.001(2) Å in the solid state structure of **VI**.[8,10] Hoefelmeyer observed a similar behavior with bis(8-quinolyl)mercury(II) (**VII**), in which weak intramolecular N···Hg contacts are present in both a linear (3.095 / 3.038 Å) and a bent (3.066 Å) polymorph.[11] However, the Lewis acid properties of these Hg-based ambiphilic ligands are not well established.

The rigidity and stability of the ferrocene moiety make it an excellent backbone for attachment of Lewis acids and Lewis pairs at its edge.[12-15] In addition to the redox properties, the possibility to fine tune the Lewis acidity and to achieve chirality are attractive. Our research group has a long-standing interest in planar chiral Lewis acids and Lewis pair systems.[13-15] Most recently, we

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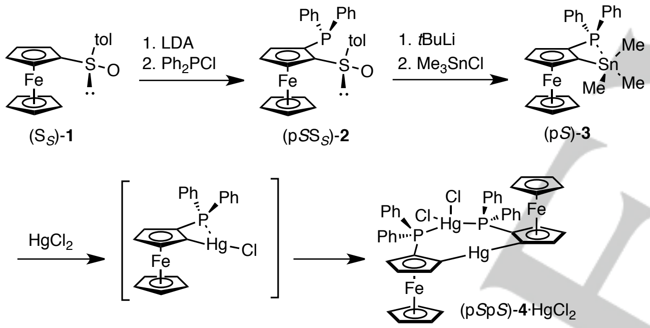
discovered a new class of "Janus-type" biferrocene ligands, in which two ferrocenes are linked together by Lewis acidic (boron) and basic (phosphorus) bridges.[14] They exhibit intriguing anion-responsive ligand properties. Here we introduce a novel diphosphine chelate ligand, $Hg(fcPPh_2)_2$, which displays a unique stereochemical environment with a wide and flexible bite angle, as well as redox-active and ambiphilic character. In the corresponding $HgCl_2$ complex, the diorganomercury moiety behaves as a σ-acceptor as evidenced by an intermolecular $ClHg{-}Cl \rightarrow HgR_2$ interaction that leads to an unusual polymeric structure. To our knowledge, this type of $M{-}X \rightarrow Hg$ interaction (M = transition metal, X = halogen) with a diorganomercury species acting as a σ-acceptor has never been observed. In addition, a bis-[Rh(COD)Cl] complex has been prepared, which displays short $Rh(I) \cdots Hg(II)R_2$ contacts, again an unprecedented structural feature.

The sulfinate group in the previously reported planar chiral ferrocenylphosphine (p*S*,*S*S)-**2**[12g] was replaced with a trimethylstannyl group by treatment with *t*-BuLi and subsequent addition of trimethyltin chloride at low temperature (Scheme 1). Purification by flash column chromatography and subsequent recrystallization from hexanes afforded (p*S*)-**3** as an orange crystalline solid in 60% yield.



**Scheme 1.** Synthesis of complex (p*S*p*S*)-**4**·$HgCl_2$ via mercuriodestannylation.

The $^{31}P$-NMR spectrum of (p*S*)-**3** in $CDCl_3$ displays a signal at −16.2 ppm that is shifted to lower field compared with that of (p*S*,*S*S)-**2** (−24.9 ppm), possibly suggesting a weak P–Sn interaction. The $^{119}Sn$ NMR spectrum exhibits a doublet at −7.2 ppm with a coupling constant of $^1J_{Sn,P}$ = 8.9 Hz, which is close to that found for a related ferrocene-fused phosphine-tin heterocycle.[14a] The structure of (p*S*)-**3** was verified by an X-ray analysis (Figure S1). The tin atom resides in a distorted monocapped tetrahedral configuration (sum of the equatorial angles $\Sigma_{eq}$ 332.2°) with the capping P1 atom approaching Sn1 via the C1, C24 and C25 tetrahedral face. The P1⋯Sn1 distance of 3.798(1) Å is slightly shorter than the sum of the van der Waals radii of P (1.80 Å) and Sn (2.17 Å).[16a] The X-ray structure also offers evidence that a single enantiomer is obtained with the expected (p*S*) stereochemistry according to the Cahn-Ingold-Prelog[17] protocol. In $CHCl_3$ solution a specific rotation of $[\alpha]^{20}_D$ = +184° (*c* = 0.53) is measured for (p*S*)-**3** while that of the precursor (p*S*)-**2** is +142° (*c* = 0.53).[18]

Stirring a mixture of (p*S*)-**3** and $HgCl_2$ in acetone over a period of one hour afforded a yellow precipitate. The mixture was poured into water and the product collected by filtration, washed with hexanes and dried in vacuum. Recrystallization from acetone at –27 °C gave a yellow crystalline solid. Surprisingly, analysis of the product by X-ray diffraction (*vide infra*) revealed the formation of (p*S*p*S*)-**4**·$HgCl_2$ (21% yield), which corresponds to the $HgCl_2$ complex of the chiral chelate ligand $Hg(fcPPh_2)_2$. The formation of diarylmercury species from arylmercury halides in the presence of tertiary phosphines is well known.[19] However, the spontaneous disproportionation of the presumed 1,2-fc($PPh_2$)(HgCl) intermediate to give (p*S*p*S*)-**4**·$HgCl_2$ is unexpected considering that isolated $[HgCl(o\text{-}C_6H_4PPh_2)]_n$ only rearranges into the diphenylmercury species (**V**) on heating in an aqueous solution of potassium cyanide.[9] This poses fundamental questions in regards to the mechanism for the formation of (p*S*p*S*)-**4**·$HgCl_2$ and further studies in this regard are currently under way.

The formation of the $HgCl_2$ complex was substantiated by multinuclear NMR analysis. The $^{31}P$ NMR spectrum of (p*S*p*S*)-**4**·$HgCl_2$ in $CDCl_3$ exhibits a singlet at +28.0 ppm with Hg satellites ($^1J_{P,Hg}$ = 5020 Hz), which is comparable to the values reported for **V**·$HgCl_2$ [+30.5 ppm (in DMSO), $^1J_{P,Hg}$ = 4840 Hz] and **VI**·$HgCl_2$ [+23.5 ppm (in $CD_2Cl_2$), $^1J_{P,Hg}$ = 4850 Hz].[8b,9] Coordination of the phosphine moieties to Hg renders the Ph groups on P inequivalent, resulting in two sets of signals in the $^1H$-NMR spectrum. The expected ligand stereochemistry was verified by refinement of the Flack parameter (0.027) in the crystal structure analysis (*vide infra*), which is close to 0, while measurement of the optical rotation of the bulk material in $CHCl_3$ gave a value of $[\alpha]^{20}_D$ = +112° (*c* = 0.12).

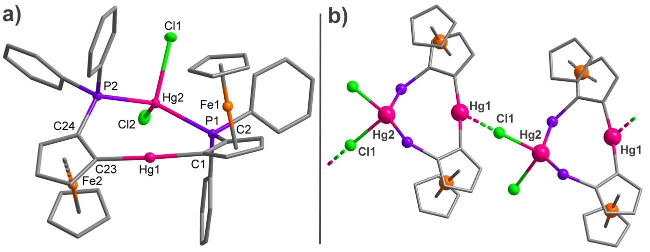


**Figure 2.** a) Molecular structure of (p*S*,p*S*)-**4**·$HgCl_2$·2acetone (50% thermal ellipsoids, hydrogen atoms and solvent molecules omitted); b) illustration of the intermolecular $Hg{-}Cl \rightarrow Hg$ contacts that give rise to a polymeric chain structure (Ph groups omitted for clarity). Selected interatomic distances (Å) and angles (°): Hg1−C1 2.059(6), Hg1−C23 2.070(5), Hg2−P1 2.4886(14), Hg2−P2 2.4918(15), Hg2−Cl1 2.5915(13), Hg2−Cl2 2.5809(14), P1−C2 1.793(6), P2-C24 1.789(6), Hg1⋯Hg2 3.6737(3), Hg1⋯Cl1A 2.9929(13), C1−Hg1−C23 173.3(2), P1−Hg2−P2 138.36(5), Hg2−Cl1⋯Hg1A 164.59(6).

The structure of (p*S*p*S*)-**4**·$HgCl_2$, illustrated in Figure 2, shows a non-centrosymmetric molecule with a distorted tetrahedral configuration at Hg2, which is surrounded by two phosphine and two chloro ligands. The P1–Hg1–P2 bite angle of 138.36(5)° is rather large, rendering the P–Hg1–Cl and Cl–Hg1–Cl angles smaller than expected in a tetrahedral geometry. The Hg1–P bond lengths (2.4886(14)) and 2.4918(15) Å) are slightly longer than the corresponding bond distances in $[Hg(o\text{-}C_6H_4PPh_2)\cdot HgBr_2]$ (2.461(3) and 2.462(3) Å),[8] but close to the

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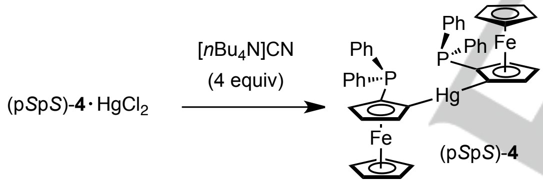
value found for **VI**·$HgCl_2$ (2.491(2) Å).[10] The 8-membered $C_4Hg_2P_2$ heterocycle is strongly puckered and, as a result, the ferrocene units adopt a twisted conformation with an interplanar angle of 37.7(2)° between the substituted Cp-rings. Slight distortions of the individual ferrocene moieties are also evident from dihedral angles between the Cp-rings of 5.0 and 3.0° respectively. The relatively short intra-annular Hg1···Hg2 contact of 3.674(1) Å ($\Sigma_{VdW}$ = 4.10 Å)[16] might suggest a weak $d^{10}$–$d^{10}$ closed-shell interaction, but this is less likely given the tetrahedral geometry at Hg2.[20]

A closer look at the extended structure of (p*S*,p*S*)-**4**·$HgCl_2$·2acetone shows that Hg2 is involved in an intermolecular contact with a chloride atom of a neighbouring $P_2HgCl_2$ fragment, leading to a unique polymeric chain structure (Figure 2). The intermolecular Hg1···Cl1A distance of 2.9929(13) Å (Hg2···Cl1A–Hg1A 164.59(6)°) is significantly shorter than the sum of the van der Waals radii[16] of Cl (1.75 Å) and Hg (2.05 Å). Likely as a result of this interaction, the Hg1−Cl1 distance (2.5915(13) Å) is slightly elongated relative to the Hg1–Cl2 distance (2.5809(14) Å). In addition, the C29−Hg2−C35 angle of 173.3(2)° deviates from the expected perfectly linear geometry, where the Hg2 atom appears to be slightly pulled towards the adjacent Cl and away from Hg1, thereby increasing the intramolecular Hg1···Hg2 distance. The intermolecular ClHg–Cl→Hg interaction observed in (p*S*,p*S*)-**4**·$HgCl_2$ is intriguing as to the best of our knowledge, a diorganomercury species acting as the σ-acceptor for M–X bonds in the context of ambiphilic Lewis acid – Lewis base ligands is unprecedented. It is reminiscent of the M−X→B interactions discussed *vide supra*.



**Scheme 2.** Decomplexation of (p*S*p*S*)-**4**·$HgCl_2$ to give the ambiphilic diphosphine ligand (p*S*p*S*)-**4**.

Having the $HgCl_2$ complex in hand, we pursued the isolation of the corresponding enantiomerically pure free ligand (p*S*p*S*)-**4**, which we anticipate to act as a versatile new chiral ambiphilic ligand with great potential in catalysis applications. Removal of $HgCl_2$ from (p*S*p*S*)-**4**·$HgCl_2$ was accomplished using cyanide as a strongly coordinating anion that is known to form very stable complexes with mercury (Scheme 2). Addition of an excess of [*n*$Bu_4N$]CN to an NMR tube containing (p*S*p*S*)-**4**·$HgCl_2$ in $CDCl_3$ led to the complete disappearance of the $^{31}P$ NMR resonance of (p*S*p*S*)-**4**·$HgCl_2$ (+28.0 ppm) and the appearance of a new upfield signal at –13.4 ppm for the $HgCl_2$-free product. The spectroscopically pure ligand (p*S*p*S*)-**4** was isolated in 78% yield after extraction and recrystallization from hexanes. All attempts to obtain single crystals of enantiomerically pure (p*S*p*S*)-**4** for X-ray diffraction analysis were unsuccessful, but the chirality of the bulk material could be verified by optical rotation measurements in $CHCl_3$ ($[\alpha]^{20}_D$ = +369, *c* = 0.1).

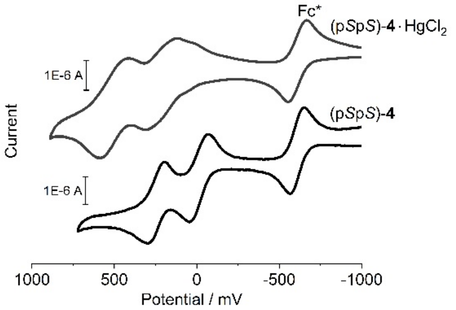
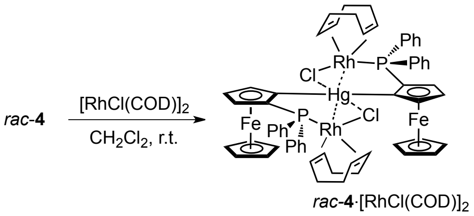


**Figure 3.** Cyclic voltammograms for (p*S*p*S*)-**4** and (p*S*p*S*)-**4**·$HgCl_2$ (100 mV/s, 0.05 M $Bu_4N[B(C_6H_3(CF_3)_2)_4]$ in $CH_2Cl_2$ as electrolyte, reported vs Fc/$Fc^+$).

The photophysical and redox properties of the free ligand (p*S*p*S*)-**4** and its $HgCl_2$ complex were investigated by UV-Vis spectroscopy (Figure S3), cyclic and square-wave voltammetry (Figures 3 and S4). Both compounds show relatively intense dd-transitions in the visible spectral region ((p*S*p*S*)-**4**, $\lambda_{max}$ = 450 nm, ε = 440 $M^{-1}$ $cm^{-1}$; (p*S*p*S*)-**4**·$HgCl_2$, $\lambda_{max}$ = 440 nm, *ε* = 330 $M^{-1}$ $cm^{-1}$), which are slightly blue-shifted when compared with the absorption band of biferrocene ($\lambda_{max}$ = 460 nm).[21] The cyclic voltammogram of (p*S*p*S*)-**4** reveals two successive, well-separated and reversible redox waves for the ferrocene units at $E_{1/2}$ = -38 mV and +207 mV. The redox splitting of $\Delta E$ = 245 mV is indicative of moderate interaction between the two ferrocene units; it is smaller than that for biferrocene[21] (375 / 590 mV, 0.1 M [*n*$Bu_4N$][$PF_6$] / [*n*$Bu_4N$][$BAr_4^F$]) or a thiophosphino-substituted diferrocenyl ethylene derivative[22] (495 mV, 0.1 M [*n*$Bu_4N$][$BAr_4^F$]). While the electrolyte used can considerably influence the measured potentials, the closer proximity of the ferrocene moieties in biferrocene and the π-conjugated bridge in diferrocenylethylene likely promote electronic communication more effectively than the mercury atom bridge in (p*S*p*S*)-**4**. It should be noted that further chemical processes were not observed for (p*S*p*S*)-**4** in contrast to other unprotected ferrocenyl phosphines, such as $FcPPh_2$ or dppf, where the occurrence of redox reactions involving dppf$H^+$, dppf$H^{2+}$, dppfO or dppf$O_2$ is evidenced.[23] The binding of $HgCl_2$ to the phosphorus atoms induces notable changes in the redox behavior of complex (p*S*p*S*)-**4**·$HgCl_2$. Two independent redox waves for the ferrocene units are visible at significantly higher potential ($E_{1/2}$ = 219, 534 mV) with a larger separation of $\Delta E$ = 315 mV, suggesting stronger electronic communication between the ferrocene moieties in (p*S*p*S*)-**4**·$HgCl_2$ than in (p*S*p*S*)-**4**. Importantly, (p*S*p*S*)-**4**·$HgCl_2$ appears to be quite robust as it does not undergo decomposition during electrochemical cycling. In contrast, essentially irreversible electrochemical behavior has been reported upon anodic oxidation of [$MCl_2$(dppf)] (M = Co, Ni, Zn, Cd Hg) and assigned to the instability of the oxidized species [(dppf)$MCl_2$]$^+$, which leads to ligand dissociation and subsequent decomposition of [dppf]$^+$.[24]



**Scheme 3.** Synthesis of complex *rac*-**4**·[Rh(COD)Cl]$_2$.

To further demonstrate the ability of ligand **4** to serve as an ambiphilic ligand to transition metal complexes, and to verify the role of the Lewis acidic Hg, we prepared a Rh(I) complex by treatment of *rac*-**4** with [Rh(COD)Cl]$_2$ (Scheme 3). After recrystallization from CH$_2$Cl$_2$/hexanes, the dirhodium complex *rac*-**4**·[Rh(COD)Cl]$_2$ was isolated as a yellow crystalline solid in 61% yield. The $^{31}$P NMR spectrum shows a doublet at δ = 30.8 ppm ($^1J_{\mathrm{Rh,P}}$ = 149.5 Hz). One of the protons for the substituted Cp ring (δ = 5.50 ppm) is largely shifted to higher field than the others (δ = 4.59 and 4.38 ppm); conversely, two of the cyclooctadiene vinylic protons appear far upfield (δ = 3.10, 2.90 *vs.* 5.75, 5.91 ppm). The molecular structure (Figure 4a,b) comprises two discrete RhCl(COD) moieties each coordinated by a phosphine in a trans arrangement with respect to the Fc–Hg–Fc axis. A slightly distorted linear configuration at the mercury atom is observed (C1–Hg1–C31 = 172.46(19)°). Most importantly, the structure reveals relatively short Rh(I)···Hg(II) contacts of 3.4765(5) and 3.4013(1) Å, which are well below the sum of the van der Waals radii of Rh (2.04)[16c] and Hg (2.05)[16b]. The Hg···Cl contacts are also quite short, in effect resulting in what amounts to a side-on coordination of two Rh-Cl moieties to Hg. Such interactions between Rh(I) and diorganomercury acceptors have never been reported, whereas Au···HgR$_2$,[9,10,25] Pd···HgR$_2$,[8,26] and Pt···HgR$_2$[8,27] interactions are relatively well documented.[28] The P–Rh (2.301(3)/2.303(3) Å) and Rh–Cl (2.374(2)/2.361(2) Å) bonds are slightly elongated when compared with those of the rhodium complex [RhCl(ndb)(PBCy$_2$)] (PBCy$_2$ = *i*Pr$_2$P-*o*-(C$_6$H$_4$)-BCy$_2$, nbd = norbornadiene),[29] in which cooperative binding of the ambiphilic PB ligand to the rhodium center is enabled solely by Rh–Cl→B interactions, with no direct involvement of Rh.

The Rh···Hg interactions in *rac*-**4**·[Rh(COD)Cl]$_2$ were further examined by computational methods. The optimized geometry (B97-D, basis set: Stuttgart RSC 1997 ECP for Fe and Rh; Stuttgart-Koeln MCDHF RSC ECP for Hg, and 6-311g** for C, H, Cl and P) indicated interatomic distances Rh···Hg of 3.4656 and 3.3996 Å, which are very close to those found experimentally (3.4765(5) and 3.4013(1) Å). A Wiberg Bond Index (WBI) of 0.12 was calculated for both Rh···Hg interactions, similar to that reported for a Pd···Hg species (bond index 0.12)[26c] exhibiting metallophilic interaction. Atom in Molecules (AIM) analysis of the optimized geometry reveals bond paths between the Hg and both Rh atoms with electron densities $\rho$(r) at the bond critical points of $1.2 \times 10^{-2}$ and $1.4 \times 10^{-2}$ e/a$_0^3$ (Figure 4c), again similar to those reported for complexes with Pd···Hg interactions[26b,c] ($1.0 \times 10^{-2}$, $1.3 \times 10^{-2}$ and $1.7 \times 10^{-2}$ e/a$_0^3$). The Laplacien of the electron density at the BCP for Rh···Hg was found to be $2.5 \times 10^{-2}$ and $2.8 \times 10^{-2}$ e/a$_0^5$.

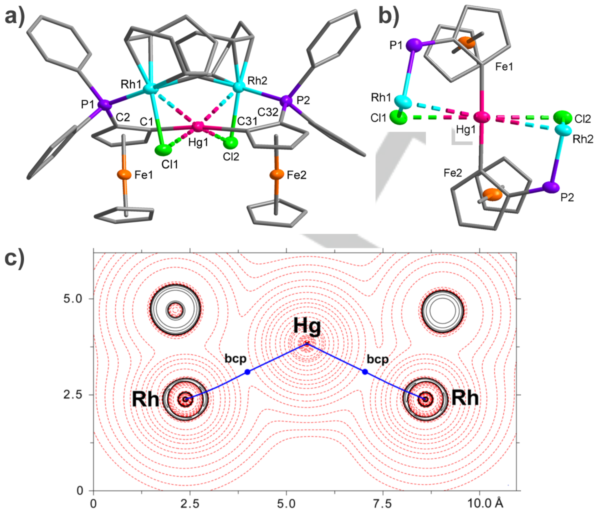


**Figure 4.** a) Molecular structure and b) simplified view of *rac*-**4**·[Rh(COD)Cl]$_2$ (50% ellipsoids, H atoms are omitted for clarity). Selected interatomic distances (Å) and angles (°): Rh1–P1 2.4(14), Rh2–P2 2.3008(14), Rh1–Cl1 2.3734(13), Rh2–Cl2 2.3613(13), Hg1–C1 2.080(5), Hg1–C31 2.081(5), P1–C2 1.799(6), P2–C32 1.790(6), Rh1···Hg1 3.4765(5), Rh2···Hg1 3.4013(1), Hg1···Cl1 3.3064(1), Hg1···Cl2 3.3265(1), C1–Hg1–C31 172.46(19), P1–Rh1–Cl1 88.32(5), P2–Rh2–Cl2 88.67(5), Rh1···Hg1···Rh2 127.074(1), Cl1···Hg1···Cl2 153.227(1), substituted Cp//Cp 43.5. c) AIM contour plot of the electron density and calculated Laplacien for *rac*-**4**·[Rh(COD)Cl]$_2$ showing the bond paths (blue line) and the BCPs (blue circle) between Rh and Hg.

In conclusion, an unexpected redistribution in the reaction of ferrocenylstannane (p*S*)-**3** with HgCl$_2$ resulted in formation of the chelate complex (p*S*,p*S*)-**4**·HgCl$_2$. According to an X-ray structure analysis, the diphosphine ligand exhibits a large bite angle, leading to a distorted tetrahedral geometry about the Hg atom. Inspection of the extended structure revealed the formation of intermolecular Hg–Cl→HgR$_2$ Lewis acid–base interactions, resulting in formation of a unique coordination polymer. Thus, (p*S*p*S*)-**4** may be viewed as an ambiphilic diphosphine-mercury ligand with the mercury atom acting as a σ-acceptor Lewis acid for the M–X bond. The ligand (p*S*,p*S*)-**4** itself can be released by treatment with an excess of [*n*-Bu$_4$N]CN. Considering the unusually large bite angle and unprecedented stereochemical environment, (p*S*,p*S*)-**4** shows great promise as a new chiral bidentate ligand for transition metal complexes. In a first foray, a bis-[Rh(COD)Cl] complex of (p*S*p*S*)-**4** was isolated. Its solid-state structure revealed relatively short Rh···Hg contacts and the presence of bond critical points was verified by an AIM analysis. Intriguingly, in future studies, the redox-active nature of the ligand may lend itself to further tuning of these interactions by redox chemistry.

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**Keywords:** ambiphilic ligand • planar chirality • ferrocene • mercury • phosphine

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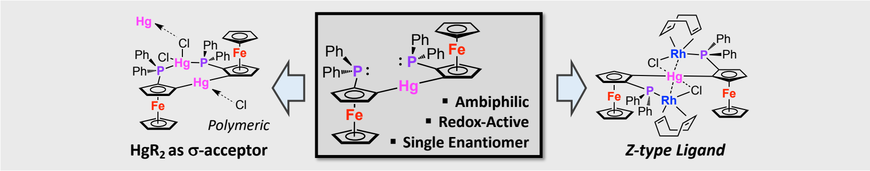
## Entry for the Table of Contents

## COMMUNICATION



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**Diferrocenylmercury-Bridged Diphosphine: A Unique Chiral, Ambiphilic, and Redox-active Bidentate Ligand**

Reaction between 1,2-Fc($PPh_2$)($SnMe_3$) and $HgCl_2$ is accompanied by spontaneous disproportionation to give a novel diphosphine chelate ligand with a wide and flexible bite angle and unique stereochemical environment. Its $HgCl_2$ complex shows unprecedented Hg-Cl→$HgR_2$ interactions that give rise to a polymeric structure, whereas ambiphilic behavior with short Rh⋯Hg contacts is found for a Rh(I) complex by X-ray analysis and further examined by theoretical calculations.