Rhodium and Iridium Complexes of Anionic Thione and Selone Ligands Derived from Anionic N-Heterocyclic Carbenes

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Abstract: The lithium salts of anionic N-heterocyclic thiones and selones \(((\text{WCA-IDipp})E)\text{Li(toluene)}\) (1: E = S; 2: E = Se; WCA = B(C₆F₅)₃) \(\text{IDipp} = 1,3\text{-bis}(2,6\text{-disopropylphenyl})\text{imidazolin-2-ylidene})\), which contain a weakly coordinating anionic (WCA) borate moiety in the imidazole backbone were reacted with Me₃SiCl, to furnish the silylated adducts \((\text{WCA-IDipp})\text{ESiMe}_3\) (3: E = S; 4: E = Se). The reaction of the latter with \([(\eta^5\text{-C}_5\text{Me}_5)\text{MCl(\eta^5\text{-C}_5\text{Me}_5)}] \) (M = Rh, Ir) afforded the rhodium(III) and iridium(III) half-sandwich complexes \(((\text{WCA-IDipp})E)\text{MCl(\eta^5\text{-C}_5\text{Me}_5)}] \) (5–8). The direct reaction of the lithium salts 1 and 2 with a half or a full equivalent of \([\text{M(COD)}\text{Cl}_2] \) (M = Rh, Ir) afforded the monometallic complexes \(((\text{WCA-IDipp})E)\text{M(COD)}\) (9–12) or the bimetallic complexes \([\mu_2-((\text{WCA-IDipp})E)\text{M(COD)})_2(\mu_2-\text{Cl})] \) (13–16), respectively. The bonding situation in these complexes has been investigated by means of density functional theory (DFT) calculations, revealing thiolate or selenolate ligand character with negligible metal-chalcogen \(\pi\)-interaction.

Introduction

Immediately after the isolation and structural characterization of the first stable and “bottleable” N-heterocyclic carbene (NHC),[1] the synthesis of NHC main group element adducts has become an area of extensive research.[2] NHC-phosphinidene species (NHC)PR have been among the earliest examples,[3] and their versatile chemistry has again attracted great interest in recent years,[4] not least because of their use as ligands in transition metal chemistry.[5] In this context, the reaction of the trimethylsilyl-substituted phosphinidene derivative \((\text{IDipp})\text{PSiMe}_3\) \(\text{I} \) \((\text{IDipp} = 1,3\text{-bis}(2,6\text{-disopropylphenyl})\text{imidazolin-2-ylidene}, \text{Figure 1})\) with transition metal halides proved to be particularly useful to enable the transfer of the monoanionic NHC-phosphinidenide moiety II into the coordination sphere of transition metals via M–P bond formation accompanied by trimethylsilyl chloride elimination.[6] Following this approach, half-sandwich complexes such as \(((\text{IDipp})\text{P})\text{MCl(\eta^5\text{-cymene})} \) (M = Ru, Os) and \(((\text{IDipp})\text{P})\text{MCl(\eta^5\text{-C}_5\text{Me}_5)}] \) (M = Rh, Ir) as well as related cationic species were prepared,[6] which have structural and spectroscopic properties very similar to prototypic nucleophilic phosphinidenide complexes of the type \([\text{RP}=\text{ML}] \), for example, low-field \(^{13}\text{P}\) NMR resonances and short metal-phosphorus double bonds.[6] These characteristics can be ascribed to a strong polarization of the \((\text{IDipp})\text{P}^-\) ligand upon metal complexation as described by the mesomeric forms II [and IIIB], with the latter revealing its ability to act as a 2\(\sigma\),2\(\pi\)-electron donor. Compound I has also been used to synthesize NHC-stabilized element-phosphorus species (EP = PP, AsP, GeP,

![Image](https://www.chemeurj.org)

This work:

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\text{Dipp} & \quad \text{Dipp} \\
\text{Dipp} & \quad \text{Dipp}
\end{align*}\]

Figure 1. NHC-phosphinidenide and NHC-chalcogenide ligands.

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SnP),[6] while several other phosphinidene and also arsinidene derivatives such as (IMes)PSiMe₃ and (IMes)AsSiMe₃ have recently become available for future application in transition metal and main group element chemistry. (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).[18]

Replacement of the pnictogen element in (NHC)P- and (NHC)As- systems by the neighboring chalcogen atoms affords neutral (valence) isoelectronic imidazolin-2-thiones and -selones (NHC)E (E = S, Se), which are well-established and important ligands in transition metal chemistry,[5] including the species (IDipp)S and (IDipp)Se analogous to II.[11] (NHC)Se species have also found considerable interest, since their ⁷²Se NMR chemical shifts are frequently used as an indicator for the π-accepting properties of the corresponding NHCs.[14,12] Anionic N-heterocyclic carbenes represent another important variation of classical NHC ligands,[13] and our group introduced carbenes that contain a weakly coordinating anionic (WCA) fluoroborate moiety, for example, B(C₆F₅)₃ at the C4 position of the imidazole ring.[19] These carbenes were termed WCA-NHCs and successfully introduced as ancillary ligands in transition metal chemistry and homogenous catalysis.[14,15] More recently, these carbenes have also found application in main group element chemistry,[6,16] including the preparation of the complete series of lithium chalcogenides [[(WCA-NHC)E]Li(solv.)] (E = O, S, Se, Te).[17] Furthermore, the ⁷²Se NMR spectra of the selenides [[(WCA-NHC)Se]Li(toluen)] were studied to determine the π-accepting properties of the WCA-NHCs, revealing that the counter cation does not exert any significant influence, if it is fully separated from the selenium atom by solvation, for example, in THF-d₈.[18]

In this context, we envisaged that the lithium salts [[(WCA-IDipp)E]Li(toluen)] (1: E = S; 2: E = Se) or, similarly to 1, the trimethylsilyl derivatives (WCA-IDipp)ESiMe₃ (3: E = S; 4: E = Se) might serve as suitable reagents for the transfer of the anionic (WCA-IDipp)E ligand (III, Figure 1). The resulting metal complexes of the type [[(WCA-IDipp)M]Cl] (E = S, Se) will have an identical total charge as the corresponding NHC-phosphinidene complexes [[(IDipp)P]Cl] and therefore allow the comparison of the phosphorus-metal and chalcogen-metal bonds, while preserving the overall structural and electronic properties. Since previous studies with the ligand II included rhodium and iridium complexes,[6,7] we aimed at the synthesis and investigation of related systems with the ligands III, which are reported in this contribution.

Results and Discussion

Synthesis and characterization of rhodium(III) and iridium(III) complexes

The lithium salts 1 and 2 were prepared as toluene solvates following the published procedures.[17,18] Their reactions with trimethylsilyl chloride (Me₃SiCl) in toluene afforded the silanes (WCA-IDipp)ESiMe₃ (3: E = S; 4: E = Se) as off-white solids in 57% and 34% yield, respectively, after separation of LiCl by filtration

and recrystallization from toluene/n-hexane solution (Scheme 1). The ¹H NMR spectra of 3 and 4 (in C₆D₆) indicate a loss of symmetry due to the presence of the B(C₆F₅)₃ moiety in the backbone, and a splitting of the signals corresponding to the Dip groups into two sets is observed. The characteristic signals for the hydrogen atom in the imidazole backbone are observed at 6.67 ppm (3) and 6.73 ppm (4). In the ¹³C NMR spectra, low-field resonances at 141.7 and 136.6 ppm can be assigned to the CS and CSe carbon atoms, respectively. The ¹⁹F resonances for both compounds are found at ca. −15 ppm, and the ⁷²Se NMR spectra show three signals for the ortho-, meta- and para-fluorine atoms. For the selenium compound 4, the ⁷²Se NMR chemical shift is 79 ppm, which is at higher field compared to 114 ppm reported for [[[(WCA-IDipp)Se]Li(toluen)] (2)]¹⁸ and 147 ppm reported for (WCA-IDipp)SeH (both in THF-d₈). Similar chemical shifts have been reported for trimethylsilyl aryl selenides such as 1,4-C₆H₄(SiMe₃)₂ (78 ppm in C₆D₆).[19] NMR data of all compounds are assembled in Table 1.

Table 1. NMR Chemical Shifts (ppm) of the complexes 1–16.

| E    | ML₃   | δ [¹³C (CE)] | δ [⁷²Se] |
|------|-------|-------------|---------|
| ¹H   | S     | Li(tolu.)    | 167.8   | –       |
| ₂H   | Se    | Li(tolu.)    | 161.7   | 114     |
| 3    | S     | SiMe₃       | 141.7   | –       |
| 4    | Se    | SiMe₃       | 136.6   | 79      |
| 5    | S     | RhCl(C₆F₅-C₆H₄) | 153.9 | –       |
| 6    | S     | IrCl(C₆F₅-C₆H₄) | 155.0 | –       |
| 7    | Se    | RhCl(C₆F₅-C₆H₄) | 149.2 | 117     |
| 8    | Se    | IrCl(C₆F₅-C₆H₄) | 146.7 | 122     |
| 9    | S     | Rh(COD)     | 163.0   | –       |
| 10   | S     | Ir(COD)     | 169.0   | –       |
| 11   | Se    | Rh(COD)     | 141.3   | 38      |
| 12   | Se    | Ir(COD)     | 140.8   | 53      |
| 13   | S     | Rh(COD)Cl   | 164.3   | –       |
| 14   | S     | Ir(COD)Cl   | 169.0   | –       |
| 15   | Se    | Rh(COD)Cl   | 141.3   | 39      |
| 16   | Se    | Ir(COD)Cl   | 140.2   | 50      |

(a) ref. [17]. [b] ref. [18].
Single crystals were obtained from toluene/n-hexane solutions of 3 and 4 at –30°C and subjected to X-ray diffraction analysis. The molecular structure of 4 is presented in Figure 2, whereas the molecular structure of 3 is shown in the Supporting Information (Figure S1). Pertinent structural data are summarized in Table 2. As expected, the C1–S1 bond length of 1.7358(11) Å as well as the C1–Se1 bond length of 1.890(2) Å are elongated, when compared to the distances found in the lithiated species 1 (1.685(2) Å) and 2 (1.845(2) Å).\(^{[17,18]}\) The N1–C1–N2 angles increase from 105.23(13)° in 1 to 107.22(9)° in 3 and from 106.03(17)° in 2 to 107.55(19)° in 4, respectively, in agreement with an increase of imidazolium character. Overall, these structural parameters are similar to those established for the protonated species (WCA-IDipp)EH (E = S, Se).\(^{[17]}\) The E–Si bond lengths are 2.2116(5) Å (E = S) and 2.3333(9) Å (E = Se), which is slightly longer compared to trimethylsilyl aryl sulfides\(^{[20]}\) and selenides,\(^{[19]}\) whereas the C1–E–Si angles of 107.97(3)° and 110.20(4)° correspond to the C1–P–Si and C1–As–Si angles of 110.71(4)/106.40(4)° and 108.68(5)/104.10(5)° established each for two independent molecules of the phosphorus and arsenic analogues (IDipp)ESiMe\(_3\) (E = P, As).\(^{[15,16]}\)

It is noteworthy that recrystallization of the selenium compound 4 from THF afforded crystals of the trimethylsilyl ether (WCA-IDipp)Se(CH\(_3\))\(_3\)OSiMe\(_3\), which must have formed by activation and insertion of ring-opened THF into the Se–Si bond; see the Supporting Information for analytical and crystallographic data. This reactivity is reminiscent of frustrated trimethylsilyl-NHC adducts\(^{[21]}\) and suggests an intrinsic lability of the chalcogen-silicon bonds in 3 and 4, which could be exploited for the transfer of the (WCA-IDipp)E upon reaction with transition metal halides. To investigate this reactivity, 3 and 4 were each reacted with half an equivalent of the binuclear rhodium(III) and iridium(III) complexes ([(η\(^5\)-C\(_5\)Me\(_5\))MCl\(_2\)]\(_2\) (M = Rh, Ir) in toluene. After stirring for 15 min at room temperature, the solutions were evaporated, and the 16 valence electron complexes ([(WCA-IDipp)EMCl(η\(^5\)-C\(_5\)Me\(_5\))] (E = S, Se, As)) were isolated as dark brown (S/Se) or dark orange (6/8) solids in moderate yields after washing with diethyl ether and extraction with THF. The \(^{77}\)Se NMR spectra for the selenides 7 and 8 were recorded in THF-\(d_8\) and reveal a high-field shift of the selenium signal to 117 ppm (7) and 122 ppm (8), compared to 79 ppm in the silylated adduct 4.

Single crystals suitable for X-ray diffraction analysis were obtained by layering C\(_6\)D\(_6\) solutions of 5 and 7 or CH\(_2\)Cl\(_2\) solutions of 6 and 8 with n-hexane. Pertinent structural data for the compounds 1–16 are presented in Table 2.

### Table 2. Selected Bond Lengths [Å] and Angles [°] of Compounds 1–16.

| Compound | E | ML\(_n\) | E–C | M–E | M–C\(_{meta}\) | M–E–C1 | E–M–Cl | N–C–N |
|----------|---|--------|-----|-----|------------|--------|--------|-------|
| 1\(^{[a]}\) | S | Li(thf)\(_2\) | 1.685(2) | – | – | – | – | 105.23(13) |
| 2\(^{[b]}\) | Se | Li(tol) | 1.845(2) | 2.543(5) | – | – | – | 106.03(17) |
| 3 | S | SiMe\(_3\) | 1.7358(11) | 2.2116(5) | – | 107.87(4) | – | 107.22(9) |
| 4 | Se | SiMe\(_3\) | 1.890(2) | 2.3333(9) | – | 110.82(7) | – | 107.55(19) |
| 5 | S | RhCl(η\(^5\)-C\(_5\)Me\(_5\)) | 1.730(3) | 2.3001(7) | – | 111.44(8) | 95.00(3) | 107.02(10) |
| 6 | Se | IrCl(η\(^5\)-C\(_5\)Me\(_5\)) | 1.736(3) | 2.2827(10) | – | 111.00(11) | 94.16(3) | 107.0(2) |
| 7 | S | RhCl(η\(^5\)-C\(_5\)Me\(_5\)) | 1.8413(15) | 2.4014(5) | – | 109.19(6) | 97.990(18) | 106.99(12) |
| 8 | Se | IrCl(η\(^5\)-C\(_5\)Me\(_5\)) | 1.897(2) | 2.3970(4) | – | 106.93(7) | 94.47(2) | 107.64(19) |
| 9 | S | Rh(COD) | 1.702(4) | 2.3073(9) | 2.579(2) | 104.11(10) | – | 108.03(3) |
| 10\(^{[c]}\) | Se | Ir(COD) | 1.703(3) | 2.3165(9) | 2.381(3) | 102.48(10) | – | 107.82(9) |
| 11 | S | Rh(COD) | 1.861(2) | 2.4328(4) | 2.587(2) | 100.45(7) | – | 108.18(18) |
| 12 | Se | Ir(COD) | 1.8544(19) | 2.4323(4) | 2.3990(19) | 98.66(6) | – | 108.14(16) |
| 13 | S | Rh\(_2\)(COD)Cl | 1.7487(7) | 2.4288(18) | 2.4540(16) | – | 115.81(3) | 86.39(6) | 107.46(6) |
| 14 | Se | Ir\(_2\)(COD)Cl | 1.760(4) | 2.4104(10) | – | 112.94(12) | 85.50(4) | 107.14(4) |
| 15 | S | Rh\(_2\)(COD)Cl | 1.907(5) | 2.5163(7) | – | 113.37(15) | 86.55(4) | 108.14(4) |
| 16 | Se | Ir\(_2\)(COD)Cl | 1.913(6) | 2.5439(7) | – | 112.39(17) | 86.40(4) | 107.85(4) |

[a] From ref. \([17]\). [b] From ref. \([18]\). [c] Two independent molecules in the asymmetric unit.
solutions of 6 and 8 with n-hexane. The molecular structure of 8 is shown in Figure 3, whereas presentations of 5–7 can be found in the Supporting Information (Figures S4–S6). Relevant structural data are compiled in Table 2. The metal atoms in complexes 5–8 all display a pseudo trigonal-planar environment (two-legged piano stool geometry) with small E–M–Cl angles of 94°–98° (E=S, Se; M=Rh, Ir). In all cases, the imidazole moiety adopts a Z orientation facing the chlorido ligand, and together with small M–E–C1 angles in the range 107°–111°, the overall structural features are very similar to those established for the analogous NHC-phosphinidenide complexes \([(\text{IDipp})\text{P}M\text{Cl}(\text{COD})]\). However, the metal-sulfur bond lengths in complexes bearing chelating imidazolin-2-selone ligands. Slightly shorter metal-sulfur bonds of 2.2694(7) Å (Rh) and 2.2827(10) Å (Ir) were found in structurally closely related 2,6-dimesitylbenzenethiolate (TerS) complexes \([(\text{TerS})M\text{Cl}(\text{COD})]\) (M = Rh, Ir), which also undergo interesting chloride abstraction and ligand addition reactions. As expected, the metal-selenium bonds in 7 and 8 are longer than the metal-sulfur bonds in 5 and 6; with 2.4014(5) Å (7) and 2.3970(4) Å (8), however, they are significantly shorter than found in a few coordinatively saturated half-sandwich rhodium and iridium complexes bearing chelating imidazolin-2-selone ligands.

Synthesis and characterization of rhodium(I) and iridium(I) complexes

We have previously studied the reactions of the N-heterocyclic carbene-trimethylsilyl phosphinidene adduct \((\text{IDipp})\text{PSiMe}_3\) (I) with the binuclear rhodium(I) and iridium(I) 1,5-cyclooctadiene (COD) complexes \([\text{M(COD)}\text{Cl}]_2\) (M = Rh, Ir), which independently of the stoichiometry afforded a bimetallic rhodium complex \([\text{IrCl}(\text{COD})\text{PSiMe}_3\text{Rh}]_2\). In contrast, no elimination of \(\text{Me}_3\text{SiCl}\) was observed with iridium, but instead the monometallic complex \([\text{IrCl}(\text{COD})\text{PSiMe}_3\text{Rh}]\) was isolated. Therefore, the reactions of the silylated sulfur congeners \(3\) with \([\text{M(COD)}\text{Cl}]_2\) were initially studied by NMR spectroscopy, which, depending on the stoichiometry, resulted in a clean formation of the corresponding mono- and bimetallic complexes 9 and 13. However, since the preparation of the silylated educts 3 and 4 proceeded via the lithium species 1 and 2 with a significant loss of yield, they were also directly employed for the synthesis of the corresponding rhodium and iridium COD complexes 9–12 and 13–16 (Scheme 2). Thus, the reactions of 1 or 2 with 0.5 equiv. of \([\text{M(COD)}\text{Cl}]_2\) in toluene furnished the desired compounds \([(\text{WCA-IDipp})\text{E}M\text{(COD)}]\) (9: E = S, M = Rh; 10: E = S, M = Ir; 11: E = Se, M = Rh; 12: E = Se, M = Ir) as orange crystalline solids in satisfactory yields (45%–74%) after filtration and recrystallization from toluene/n-hexane solution. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of complexes 9–12 indicate the formation of C₅ symmetric complexes, e.g., by observation of four well separated doublets and two septets for the isopropyl methyl and methine hydrogen atoms, respectively. In addition, two different sets of CH and CH₂ signals are found for the COD ligand. The \(^{77}\text{Se}\) NMR spectra (in THF-d₈) of the two selenides 11 and 12 exhibit signals at 38 ppm (11) and 53 ppm (12), respectively, indicating less deshielded selenium nuclei compared to the corresponding rhodium(III) and iridium(III) complexes 7 (117 ppm) and 8 (122 ppm, see above).

The molecular structures of 9–12 were determined by single-crystal X-ray diffraction analysis; see Figure 4 for 12 and the Supporting Information for 9–11 (Figures S8–S10). Pertinent structural parameters are assembled in Table 2. In all four

![Figure 3](image3.png)  
**Figure 3.** Molecular structure of 8 in \(\text{8-CH}_2\text{Cl}_2\) with thermal displacement parameters drawn at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity; pertinent structural data for the compounds 1–16 are assembled in Table 2.

![Scheme 2](image2.png)  
**Scheme 2.** Preparation of rhodium and iridium complexes. a) 0.5 equiv. [\(\text{M(COD)}\text{Cl}_2\)] toluene; b) 1 equiv. [\(\text{M(COD)}\text{Cl}_2\)] toluene (M = Rh, Ir).
complexes, the metal resides in square-planar environments. In addition to binding of the $\eta^1$-COD ligand and the selenium atom, the coordination sphere is completed by an arene-metal interaction ($\pi$-face donation)\(^{[26]}\) that largely involves the ipso-carbon atom of the Dipp substituent facing away from the borate moiety. Significantly longer, albeit distinctly different metal-carbon distances are found for the adjacent ortho-carbon atoms, which indicates a situation intermediate between $\eta^1$- and $\eta^2$-coordination modes.\(^{[27]}\) Surprisingly, the Rh–C,\(\text{ipso}\) distances of 2.579(2) Å (9) and 2.587(2) Å (11) are significant longer than the Ir–C,\(\text{ipso}\) distances of 2.381(3) Å (10) and 2.3990(19) Å (12); in view of similar Rh and Ir atomic radii,\(^{[28]}\) this finding indicates a significantly stronger arene-iridium interaction. It is also surprising that $\pi$-face donation in complexes 9–12 does not involve the borate-flanking Dipp substituent, which was consistently found in WCA-NHC complexes, including related rhodium(I) and iridium(I) complexes of the type\([\{\text{WCA-NHC}\} \text{M(COD)}]\) (M = Rh, Ir).\(^{[15a,b,g,h]}\) Theoretical calculations performed for the iridium complexes 10 and 12 (see details below, Table 3) indicate similar energies of the isomeric complexes in which the metal atom is bound to either one of the Dipp substituents, with a slight preference for the experimentally observed anti-isomer versus the syn-isomer (10: $\Delta H_{298K} = -1.5$ kcal mol\(^{-1}\); 12: $\Delta H_{298K} = -2.5$ kcal mol\(^{-1}\)). Moreover, the intramolecular $\pi$-face donation in 9–12 enforces a coplanar orientation of the imidazole ring towards the M–E–C plane with significantly smaller M–E–C angles of 99°–104° compared to the perpendicular arrangement found in the rhodium(II) and iridium(III) half-sandwich complexes 5–8. Perpendicular orientations are also found in related Rh(I) and Ir(I) imidazolin-2-thione complexes such as neutral \([\{\text{ImMe}_2\text{S}\} \text{Rh(COD)Cl}_2]\)\(^{[29]}\) and cationic \([\{\text{ImMe}_2\text{P}\} \text{S} \text{M(COD)}]\) (M = Rh, Ir)\(^{[30]}\) for NHC acronyms see ref\(^{[30]}\). These complexes exhibit longer metal-sulfur bonds compared to 2.3073(2) Å in 9 and 2.3165(9)/2.3148(9) Å in 10 (for two independent molecules). As observed for the Rh/Ir pair 9/10, the metal-selenium bonds in 11/12 (2.4328(4)/2.4323(4) Å) are almost identical; to the best of our knowledge, however, no related imidazolin-2-selone complexes have been reported for comparison.

The stoichiometry of [M(COD)Cl]\(_2\) in the reaction with the lithium salts 1 or 2 can be increased to 1 equiv. to furnish the bimetallic complexes \([\mu_2-(\text{WCA-IDipp})\text{EM}_4\text{COD}]\) (13: E = S, M = Rh; 14: E = S, M = Ir; 15 = E = Se, M = Rh; 16 = E = Se, M = Ir; Scheme 2). The reactions were performed in toluene, and after separation of LiCl and recrystallization, the rhodium complexes 13 and 15 were obtained as dark orange crystals in 83% and 33% yield and the iridium complexes 14 and 16 as dark purple crystals in 64% and 37% yield. The recrystallization of 13 and 15 was performed from a saturated toluene solution layered with n-hexane, whereas for the recrystallization of 14 and 16, a solution in THF was layered with n-hexane. The \(^1\)H and \(^13\)C NMR spectra of the WCA-NHC unit as the monometallic complexes 9–12, revealing time-averaged C, symmetry in solution through fast rotation around the E–C bonds. Because of the bimetallic nature, however, the number of COD signals doubles compared to 9–12. The \(^75\)Se NMR chemical shifts for the WCA-NHC unit as the monometallic complexes 13–15 exhibit the same number of signals for the WCA-NHC unit as the monometallic complexes 9–12, revealing time-averaged C, symmetry in solution through fast rotation around the E–C bonds.

The molecular structures of all four bimetallic complexes could be established by single-crystal X-ray diffraction analysis; see Figure 5 for the representation of 16 and Figures S12–S14 in the Supporting Information for the molecular structures of 13–15. Overall, the structures resemble that of the bridged NHC-phosphinidenide complex \([\mu_2-(\text{IDipp})\text{PRh(COD)S}2\text{M(COD)}]\)\(^{[10]}\) with the bridging chalcogen atoms residing in trigonal-

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**Table 3.** Relative enthalpies ($\Delta H_{298K}$), Natural Bond Orbital (NBO) charges (q), Wiberg Bond Indices (WBI) and selected bond lengths of III, 6, 8, 10 and 12.

| Compound | $\Delta H_{298K}$ [kcal/mol] | q(E) | q(Ir) | WBI(E–C,\(\text{ipso}\)) | WBI(Ir–E) | d(E–C,\(\text{ipso}\)) [Å] | d(Ir–E) [Å] | d(Ir–C,\(\text{ipso}\)) [Å] |
|----------|-----------------------------|------|-------|--------------------------|----------|---------------------------|-----------|--------------------------|
| III (E = S) | –                           | –0.31| –1.44 | 1.688                    | –        | –                         | –         | –                        |
| III (E = Se) | –                           | –0.29| 1.30  | 1.869                    | –        | –                         | –         | –                        |
| 6 (E = S)   | –                           | 0.09 | –0.06 | 1.13                     | 0.88     | 1.740                     | 2.311     | –                        |
| 8 (E = Se)  | 0.20                        | –0.10| 1.04  | 0.90                     | 1.915    | 2.453                     | –         | –                        |
| 10 (E = S)  | –1.5\(^{[4]}\)              | 0.08 | –0.08 | 1.19                     | 0.75     | 1.726                     | 2.383     | 2.368                    |
| 12 (E = Se) | –2.5\(^{[4]}\)              | 0.19 | –0.13 | 1.10                     | 0.79     | 1.892                     | 2.531     | 2.358                    |

[a] $\Delta H_{298K} = H_{298K}(\text{anth}) – H_{298K}(\text{syn})$
pyramidal environments. Z configurations can be assigned to the carbene moieties, which are facing the chlorine atoms, while the imidazole planes adopt approximately horizontal orientations with respect to the metal-metal axes; this renders the complexes C₇ symmetric in the solid state. The four-membered M₁–E–Cl–M₂ rings are puckered and display butterfly-like conformations. As expected, the metal-chalcogen bonds in the bimetallic complexes 13–15 are significantly elongated compared to the monometallic congeners 9–12, with a different degree of asymmetry in the M₁–E and M₂–E bond lengths. Likewise, a pronounced increase of the E–C bond lengths can be observed (Table 2).

**Computational studies**

In order to assess the bonding situation in the thione and selone complexes described above, the structures of the iridium derivatives 6, 8, 10, and 12 were optimized using the density functional theory (DFT) method B97-D, followed by natural bond orbital (NBO) analysis. The computational details are summarized in the Supporting Information, and contour plots of selected NBOs are presented in Tables S16–S19. The calculated structural parameters are in good agreement with the solid-state structures, with the optimized gas-phase geometries consistently showing slightly longer bond lengths (Tables 2 and 3). The Wiberg bond index (WBI) associated with the iridium-consistently showing slightly longer bond lengths (Tables 2 and 3). The Wiberg bond index (WBI) associated with the iridium-atomic orbitals has similar energies and are available for coordination

significantly smaller charge transfer towards the metal atom as indicated by comparatively small NBO charges \( q_{Ir} \). Accordingly, two lone pairs can be assigned each to the sulfur and selenium atoms, which show the expected pure \( p \) or high \( s \) orbital character, respectively. This bonding situation can be best described by polarization of the (WCA-IDipp)E⁻ ligands III (E = S, Se) upon metal coordination as illustrated by the mesomeric form IIIIB in Figure 1, in line with WBI(\( E−C_{Ir} \)) values close to 1.

For complexes 10 and 12, the geometries of both isomers with syn- or anti-orientations of the borate moiety with respect to the iridium atom were optimized, and as mentioned above, the experimentally observed anti-isomer is energetically slightly favored (Table 3). Somewhat weaker iridium-chalcogen bonds can be assigned to these iridium(I) complexes based on the WBI values of 0.75 (10) and 0.79 (12) compared to the iridium(III) species 6 and 8. Again, two lone pairs are located at the chalcogen atoms with high \( s \) and pure \( p \) orbital character; the latter is perpendicular to the imidazole ring, which is coplanar with the Ir–E–Cl plane to enable \( \pi \)-face donation through the ipso-carbon atom. This bonding scheme agrees with the NBO analyses of the anionic thione and selone ligands III (Figure 1), which reveal three lone pairs located at the chalcogen atoms, one with high \( s \) orbital character, while the other two pure \( p \) orbitals have similar energies and are available for coordination to the metal atom in either 6/8 or 10/12 (see the Supporting Information).

**Conclusion**

Half-sandwich complexes of the type \([\{(WCA-IDipp)E\}M(\eta^1-C_6Me_5)](5–8)\) have been synthesized, which are structurally closely related to NHC-phosphinidenide complexes \([\{(Dipp)P\}MCl(\eta^1-C_6Me_5)]\) (M = Rh, Ir). Furthermore, we have demonstrated the ability of these chalcogen ligands to form rhodium(I) and iridium(I) cyclooctadiene complexes \([\{(WCA-IDipp)E\}M(COD)](9–12)\) or complexes \([\mu_2-(WCA-IDipp)E\}M(COD)\] \( (13–16) \), depending on the stoichiometry of the starting materials. Interestingly, the monometallic COD species 9–12 display a \( \pi \)-face donation of one Dipp substituent towards the Rh or Ir atoms in order to saturate their coordination sphere. The bonding schemes of the ligands III were further assessed by computational studies, revealing in all cases distinct metal-chalcogen single bonds and two lone pairs located at the chalcogen atoms. This contrasts with the related NHC-phosphinidenide complexes, where substantial metal-phosphorus \( \pi \) bond character was found.

With the lithium complexes 1/2 and the silyl derivatives 3/4, suitable reagents are available for the transfer of the anionic sulfur and selenium ligands III, which we regard as important new additions to the large family of chalcogenenolate ligands. The coordination chemistry of these systems with main group elements and transition metals has been extensively studied, with considerable implications for the preparation of complexes that mimic the active sites in metalloproteins. We envisage that the anionic charge will significantly expand the scope of
heterocyclic thione and selone ligands in coordination chemistry and homogeneous catalysis,\textsuperscript{(14,15a)} which follows the same concept developed for neutral NHCs with the introduction of their anionic WCA-NHC congeners.\textsuperscript{(14,15a)}

**Experimental Section**

**Materials and Methods:** Unless otherwise indicated, all starting materials were obtained from commercial sources (Sigma-Aldrich, Alfa-Aesar, Roth, TCI, VWR or Fisher Chemical) and were used without further purification. Elemental analyses were carried out on a Vario Micro Cube System. All operations with air- and moisture-sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 2008) or on a high vacuum line using Schlenk techniques. The $^1H$, $^13C$ NMR and $^31P$ NMR spectra were recorded on Bruker AVIII300 (300 MHz), Bruker AVIII400 (400 MHz), Bruker AVIII500 (500 MHz) and Bruker AVIII600 (600 MHz). All spectra were recorded at 298 K. The chemical shifts are expressed in parts per million (ppm) with the residual solvent signal as internal standard for $^1H$ and $^13C$ NMR spectra. All other spectra were calibrated using external references ($^1H$: BF$_3$·Et$_2$O; $^13C$: CFCl$_3$; $^31P$: Me$_2$Se). Coupling constants ($J$) are reported in Hertz ($Hz$) and splitting patterns are indicated as $s$ (singlet), $d$ (doublet), $t$ (triplet), $q$ (quartet), $m$ (multiplet) and $b$ (broad). $^1H$, $^13C$, $^31P$ and $^35Cl$ NMR spectra were measured broadband proton decoupled. Signal assignments were performed based on 2D NMR analysis.

Presentations of all NMR spectra can be found in the Supporting Information. $n$-hexane, tetrahydrofuran (THF), diethyl ether (EtO)$_2$, and toluene were purified by distillation over sodium/benzophenone. Chlorobenzene was purified by distillation over CaH$_2$. Deuterated solvents were purified by stirring the degassed solvents with Na/K alloy overnight. Subsequently, the solvents were filtered and then distilled under reduced pressure. All solvents were stored over molecular sieves (4 Å) in argon atmosphere prior to use. All yields were calculated based on the WCA-IDP containing substrate. $[\text{Rh}($COD$)Cl]_2$, $[\text{Ir}($COD$)Cl]$ and $[\text{Ir}($COD$)Cl]$ were prepared according to literature procedures.

For full crystallographic details, see the Supporting Information.

Deposition Number(s): 2122410-2122424 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Synthesis of (WCA-IDP)SSiMe$_5$ (3): (WCA-IDP)[SiLi(toluene)] (250 mg, 0.243 mmol, 1 equiv.) was suspended in 5 mL toluene and Me$_3$SiCl (40 mg, 0.364 mmol, 1.5 equiv.) diluted in 2 mL toluene was added dropwise, resulting in a pale-yellow and slightly cloudy solution. The mixture was stirred for 3 h at room temperature and subsequently filtered, giving a clear pale-yellow solution. The solvent was evaporated, and the yellow residue was washed with $3 \times 2$ mL $n$-hexane. The yellow washings were discarded and residual solvent in the solid was removed in vacuo, yielding the product as an off-white solid (138 mg, 0.137 mmol, 57\%). $^1H$ NMR (600 MHz, CD$_2$Cl$_2$) $\delta$ = 7.01 (t, $^3J(1H,H) = 7.8$ Hz, 1H, p-Dipp), 6.85 (d, $^3J(1H,H) = 7.8$ Hz, 4H, m-Dipp), 6.67 (s, 1H, CH=C=CH$_2$), 2.73–2.69 (m, 2H, C$_2$H$_4$(CH$_2$)$_2$), 1.13–1.07 (m, 3J$^\text{CH}(CH)=7.8$ Hz, 18H, (CH$_2$)$_3$)$_3$, 0.87–0.83 (m, $^3J(3H,H)=4.8$ Hz, 6H, CH$_2$(CH$_2$)$_2$), $-0.46$ (s, 9H, Si(CH$_3$)$_3$). $^13C$ NMR (96 MHz, CD$_2$Cl$_2$) $\delta$ = 15.18 (s). $^31P$ NMR (151 MHz, CD$_2$Cl$_2$) $\delta$ = 150.50–150.10 (m, Ar$_3$), 148.96–148.35 (m, Ar$_3$), 146.92 (s, O-Dipp), 146.01 (s, O-Dipp), 141.66 (s, N–C–N), 140.75–140.34 (m, Ar$_3$), 139.00–138.72 (m, Ar$_3$), 138.44–138.05 (m, Ar$_3$), 136.85–136.42 (m, Ar$_3$), 133.01 (s, H$_2$C=CB), 132.31 (s, ipso-

$^1H$ NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ = 7.19 (t, $^3J(H,H)=7.8$ Hz, 1H, p-Dipp), 7.03 (t, $^3J(H,H)=7.8$ Hz, 1H, p-Dipp), 6.87 (d, $^3J(H,H)=7.8$ Hz, 4H, m-Dipp), 6.73 (s, 1H, CH=C=CB), 2.79–2.72 (m, 2H, CH$_2$(CH$_2$)$_2$), 2.67–2.54 (m, 2H, CH$_2$(CH$_2$)$_2$), 1.17–1.04 (m, 18H, CH$_2$(CH$_2$)$_2$), 0.91–0.87 (m, $^3J(H,H)=6.8$ Hz, 6H, CH$_2$(CH$_2$)$_2$), $-0.40$ (s, 9H, Si(CH$_3$)$_3$). $^31P$ NMR (161 MHz, CD$_2$Cl$_2$) $\delta$ = 15.09 (s). $^7F$ NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ = 155.89 (d, $^3J(F,F)=53$ Hz, H$_2$C=CB), 150.74–149.47 (m, Ar$_3$), 148.90–148.17 (m, Ar$_3$), 146.85 (s, O-Dipp), 145.96 (s, O-Dipp), 140.89–140.33 (m, Ar$_3$), 139.07–138.58 (m, Ar$_3$), 138.58–138.23 (m, Ar$_3$), 136.63 (s, N–C–N), 136.55–136.06 (m, Ar$_3$), 133.95 (s, H$_2$C=CB), 134.31 (s, ipso-

Synthesis of [(WCA-IDP)SiR$_3$] (5): [(WCA-IDP)SiMe$_5$ (20 mg, 0.020 mmol, 1 equiv.) and $[\text{Ir}($COD$)Cl]_2$] (6.15 mg, 0.010 mmol, 0.5 equiv.) were mixed and dissolved in 2 mL toluene. The mixture turns dark brown within 2 min and was stirred for a total of 15 min at room temperature. The solvent was removed in vacuo and the resulting dark brown solid was washed with 2×1 mL EtO and subsequently extracted with 0.2 mL THF, giving a dark brown clear solution. The solvent was removed in vacuo and the residual THF was removed by co-evaporation with n-hexane, yielding the product as an orange-brown solid (14 mg, 0.0116 mmol, 58\%). $^1H$ NMR (500 MHz, THF-$d_8$) $\delta$ = 7.30 (t, $^3J(H,H)=7.7$ Hz, 1H, p-Dipp), 7.22–7.16 (m, 3H, p-Dipp & m-Dipp), 6.91 (d, $^3J(H,H)=7.5$ Hz, 2H, m-Dipp), 6.61 (s, 1H, H$_2$C=CB), 2.79–2.68 (m, 4H, 2xCH$_2$(CH$_2$)$_2$), 1.31 (d, $^3J(H,H)=6.4$ Hz, 6H, 2xCH$_2$(CH$_2$)$_2$), 1.25 (s, 15H, $^{13}C$P), 0.96 (d, $^3J(H,H)=6.0$ Hz, 6H, CH$_2$(CH$_2$)$_2$), 0.82 (d, $^3J(H,H)=5.9$ Hz, 6H, CH$_2$(CH$_2$)$_2$), 0.72 (d, $^3J(H,H)=6.4$ Hz, 6H, CH$_2$(CH$_2$)$_2$). $^13C$ NMR (126 MHz, THF-$d_8$) $\delta$ = 153.93 (s, N–C–N), 150.92–150.32 (m, Ar$_3$), 148.87 (s, O-Dipp), 148.85–148.48 (m, Ar$_3$), 147.32 (s, O-Dipp), 140.92–140.44 (m, Ar$_3$), 138.93–138.10 (m, 2xAr$_3$), 136.75–136.12 (m, Ar$_3$), 134.28 (s, ipso-

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Synthesis of [{(WCA-IDipp)Se}IrCl3] (8): (WCA-IDipp)SeI (20 mg, 0.0199 mmol, 1 equiv.) and [{(−1-C6Me3)Cl}2] (7.55 mg, 0.0095 mmol, 0.5 equiv.) were mixed and dissolved in 2 mL toluene. The mixture turns dark brown within 2 min and was stirred for a total of 15 min at room temperature. The solvent was removed in vacuo and the resulting dark-orange-brown solid was washed with 2 × 1 mL Et2O and subsequently extracted with 0.2 mL THF, giving a dark brown clear solution. The solvent was removed in vacuo and the residual THF was removed co-evaporation with n-hexane, yielding the product as a dark orange solid (17 mg, 0.0131 mmol, 66%). \(^1^H\) NMR (500 MHz, THF-d6) δ = 7.33–7.29 (1H, p-Dipp), 7.22–7.18 (3H, m, 1H, p-Dipp & m-Dipp), 6.93 (d, (J(1H,1H)) = 7.8 Hz, 2H, m-Dipp), 6.69 (s, 1H, HC=C), 2.78–2.68 (4H, m, 2 × CH2(COD)), 1.29 (d, J(1H,1H)) = 6.6 Hz, 6H, CH2(COD)), 1.25 (s, 15H, Cp∗), 0.95 (d, J(1H,1H)) = 6.5 Hz, 6H, CH2(COD)), 0.83 (d, J(1H,1H)) = 6.3 Hz, 6H, CH2(COD)), 0.73 (d, J(1H,1H)) = 6.7 Hz, 6H, CH2(COD)). \(^1^B\) NMR (161 MHz, THF-d6) δ = −15.05 (s). \(^1^C\) NMR (126 MHz, THF-d6) δ = 151.11–150.34 (m, Ar¹), 149.00–148.48 (m, Ar¹), 147.41 (s, o-Dipp), 146.98 (s, o-Dipp), 146.74 (s, N–C–N), 140.98–140.42 (m, Ar¹), 138.91–138.20 (m, 2 × Ar¹), 137.66–136.17 (m, Ar¹), 134.97 (s, i-Dipp), 134.60 (s, i-Dipp), 134.02 (s, H₃C = CB), 131.04 (s, p-Dipp), 130.85 (s, m-Dipp), 124.61 (s, m-Dipp), 91.19 (s, C=C(p-Cp)), 29.84 (s, CH₂(COD)), 28.64 (s, CH₂(COD)), 26.37 (s, CH₂(COD)), 23.97 (s, CH₂(COD)), 22.22 (s, CH₂(COD)). A signal corresponding to H = CB was not observed. \(^1^F\) NMR (471 MHz, THF-d6) δ = −163.22 (s), −160.85 (s). One CF signal was too broad and could not be resolved. EA – Anal. Calc. for C₄₆H₃₂BCF₃₀N₉R₇S: C, 54.81; H, 4.18; N, 2.32. Found: C, 54.68; H, 4.36; N, 2.22.

Synthesis of [{(WCA-IDipp)SeRhCl₃}] (9): (WCA-IDipp)SeI (toluene) (100 mg, 0.097 mmol, 1 equiv.) was suspended in 3 mL toluene and [Rh(COD)Cl] (24 mg, 0.049 mmol, 0.5 equiv.) was added as one solid portion. The orange mixture was stirred for 5 h at room temperature and subsequently filtered, giving an orange solution. This solution was layered with n-hexane at room temperature, forming orange crystals within 7 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as an orange crystalline solid (79 mg, 0.069 mmol, 71%). \(^1^H\) NMR (400 MHz, CD₂Cl₂) δ = 7.21 (t, J(1H,1H) = 7.8 Hz, 1H, p-Dipp), 6.99 (d, J(1H,1H) = 7.8 Hz, 2H, m-Dipp), 6.72–6.63 (m, 3H, 1H, p-Dipp & m-Dipp), 5.96 (s, 1H, H–CB), 3.88–3.72 (m, 2H, H–CH(COD)), 3.16–3.08 (m, 4H, H–CH(COD) & C=C(p-Cp)), 2.80–2.71 (m, 2H, C=C(p-Cp)), 1.65–1.52 (m, 10H, H–C(COD)), 1.50–1.43 (m, 2H, C=C(p-Cp)), 1.31 (d, J(1H,1H) = 6.8 Hz, 6H, CH₂(COD)), 1.13 (d, J(1H,1H) = 6.6 Hz, 6H, CH₂(COD)), 1.04 (d, J(1H,1H) = 6.8 Hz, 6H, CH₂(COD)), 0.96–0.89 (m, 4H, H–CH(COD)). \(^1^B\) NMR (128 MHz, CD₂Cl₂) δ = −15.30 (s). \(^1^C\) NMR (151 MHz, CD₂Cl₂) δ = 162.98 (s, N–C–N), 150.24–149.45 (m, 1H, p-Dipp), 147.02 (s, 1H, H–CB), 138.46–138.67 (m, Ar¹), 138.50–138.12 (m, Ar¹), 138.12–137.51 (m, Ar¹), 136.42–135.94 (m, Ar¹), 132.84 (s, i-Dipp), 131.31 (s, p-Dipp), 130.63 (s, p-Dipp), 129.87 (s, m-Dipp), 126.00 (s, i-Dipp), 124.15 (s, i-Dipp), 80.80 (s, C=C(COD)), 76.09 (s, C=C(COD)), 29.47 (s, CH₃(CH₂)), 28.88 (s, C=C(COD)), 28.35 (s, CH₃(CH₂)), 27.15 (s, C=C(COD)), 25.71 (s, CH₃(CH₂)), 24.95 (s, C=C(CH₃)), 23.50 (s, CH₂(CH₃)), 22.50 (s, CH₂(CH₃)). A signal corresponding to H = CB was not observed. A signal corresponding to H = CB is overlaid with the residual solvent signal of the CD₂Cl₂. \(^1^F\) NMR (372 MHz, CD₂Cl₂) δ = −127.20–−123.31 (m, 2 × Me–Cp). A signal corresponding to H = CB was not observed. A signal corresponding to H = CB was not observed. A signal corresponding to H = CB was not observed. A signal corresponding to H = CB was not observed. A signal corresponding to H = CB was not observed.
stored at −30 °C, forming orange crystals within 3 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as an orange crystalline solid (88 mg, 0.017 mmol, 74%). 1H NMR (400 MHz, THF-d8) δ = 7.57–7.51 (m, 3H, p-Dipp & m-Dipp), 7.30 (t, J(h,H) = 7.8 Hz, 1H, p-Dipp), 7.03 (d, J(h,H) = 7.8 Hz, 2H, m-Dipp), 6.10 (s, 1H, H-CB), 3.95 (s, 2H, HC-CH(COD)), 2.83 (sept, J(h,H) = 6.8 Hz, 2H, CH(CH3)2), 2.42 (sept, J(h,H) = 6.8 Hz, 2H, CH(CH3)2), 2.11–1.93 (m, 6H, HC-CH(COD) & H-CH(COD)), 1.59 (t, J(h,H) = 6.9 Hz, 6H, CH(C2H5)), 1.31 (d, J(h,H) = 9.8 Hz, 4H, H-CH2(CH3)), 1.15 (d, J(h,H) = 6.8 Hz, 6H, CH(C2H5)), 1.10 (d, J(h,H) = 6.8 Hz, 6H, CH(C2H5)), 0.84 (d, J(h,H) = 6.6 Hz, 6H, CH(CH3)2), 2.48 ppm. 13C NMR (161 MHz, THF-d8) δ = 168.96 (s, C–N–C–N), 150.98–150.38 (m, Ar), 148.92–148.48 (m, Ar), 148.15 (s, O-Dipp), 147.00 (s, O-Dipp), 141.01–140.30 (m, Ar), 139.06–138.09 (m, Ar), 2.0×Ar, 137.67–137.20 (m, Ar), 134.89 (s, p-Dipp), 133.64 (s, ipso-Dipp), 131.35 (s, p-Dipp), 130.36 (m, m-Dipp), 128.33 (s, H-CH2-CB), 124.75 (s, m-Dipp), 122.41 (s, ipso-Dipp), 80.37 (s, C(CH2)), 62.65 (s, C(CH2)), 32.86 (s, C(C=C)), 31.46 (s, CH(CH3)), 28.29 (s, C(C=C)), 26.04 (s, CH(CH3)), 23.89 (s, CH(CH3)), 22.97 (s, CH(CH3)). A signal corresponding to CH2(C2H5) is overlaid with the residual solvent signal of the THF-d8. 19F NMR (377 MHz, THF-d8) δ = −126.36–131.30 (m), −162.06 (t, J(19F,19F) = 20.1 Hz), −166.67 (br s). EA – Anal. Calc. for C29H19BF6N5Se: C, 56.82; H, 4.48; N, 1.98. Found: C, 56.31; H, 4.66; N, 1.84.

Synthesis of [(WCA-IDipp)SeRh(COD)] (11): [(WCA-IDipp)Se]l-toluene (150 mg, 0.193 mmol, 1 equiv) was suspended in 3 mL toluene and [Rh(COD)]Cl2 (34 mg, 0.070 mmol, 0.5 equiv) was added as one solid portion. The orange mixture was stirred for 5 h at room temperature and subsequently filtered, giving a orange solution. This solution was layered with n-hexane and stored at −30 °C, forming orange crystals within 7 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as an orange crystalline solid (112 mg, 0.081 mmol, 83%). 1H NMR (500 MHz, THF-d8) δ = 7.32 (t, J(h,H) = 7.8 Hz, 1H, p-Dipp), 7.12 (t, J(h,H) = 7.8 Hz, 1H, p-Dipp), 6.90 (d, J(h,H) = 7.7 Hz, 2H, m-Dipp), 6.66 (d, J(h,H) = 7.8 Hz, 2H, m-Dipp), 6.19 (s, 1H, H-CB), 4.24–4.12 (m, 2H, HC-CH(COD)), 3.88–3.79 (m, 2H, HC-CH(COD)), 3.65–3.58 (m, 2H, HC-CH(COD)), 2.52–2.44 (m, 2H, CH(CH3)2), 2.36–2.31 (m, 2H, CH(CH3)2), 2.28–2.20 (m, 2H, HC-CH(COD)), 2.16–2.17 (m, 4H, H-CH2(CH2)), 1.49 (m, 3H, CH(CH3)2), 1.45 (m, 3H, CH(CH3)2), 0.88 (s, 3H, CH(CH3)3), 0.83 (d, J(h,H) = 5.8 Hz, 6H, CH(C2H5)), 0.38 ppm. 13C NMR (161 MHz, THF-d8) δ = 14.77 (s). 13C NMR (162 MHz, THF-d8) δ = 153.39 (s, 13C(IDipp) = 59 Hz, H-CB), 151.13–150.51 (m, Ar), 147.55 (m, Ar), 147.22 (m, Ar), 146.12 (s, N–C–N), 140.09–140.56 (m, Ar), 139.02–138.23 (m, 2m, Ar), 136.84–136.54 (m, Ar), 136.46 (s, ipso-Dipp), 135.46 (s, ipso-Dipp), 134.83 (s, H-CH2-CB), 132.22 (s, O-Dipp), 131.50 (s, p-Dipp), 131.16 (s, 2m, p-Dipp), 78.87 (s, C(C=C)), 75.09 (s, C=C)), 31.30 (s, CH(CH3)), 30.91 (s, C=C)), 29.66 (s, CH(CH3)), 29.34 (s, C=C)), 27.75 (s, CH(CH3)), 26.36 (s, CH(CH3)), 23.22 (s, 2CH2CH3)), 2.48 ppm. 19F NMR (377 MHz, THF-d8) δ = −133.03–134.70 (m), −161.70 (br s), −166.31 (br s). 19Se NMR (95 MHz, THF-d8) δ = 37.57 (s). The 19Se/19Rh coupling could not be resolved.

Synthesis of [(WCA-IDipp)SeIr(COD)] (12): [(WCA-IDipp)Se]l-toluene (150 mg, 0.193 mmol, 1 equiv) was suspended in 3 mL toluene and [Ir(COD)]Cl2 (46 mg, 0.070 mmol, 0.5 equiv) was added as one solid portion. The red mixture was stirred for overnight at room temperature and subsequently filtered, giving a red orange solution. This solution was layered with n-hexane and stored at −30 °C, forming red orange crystals within 7 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as a red orange crystalline solid (94 mg, 0.073 mmol, 53%). 1H NMR (500 MHz, THF-d8) δ = 7.53–7.44 (m, 3H, p-Dipp & m-Dipp), 7.30 (t, J(h,H) = 7.8 Hz, 2H, p-Dipp), 7.04 (d, J(h,H) = 7.8 Hz, 2H, m-Dipp), 6.15 (s, 1H, H-CB), 3.84–3.75 (m, 2H, HC-CH(COD)), 2.79 (sept, J(h,H) = 6.6 Hz, 2H, CH(CH3)2), 2.60–2.52 (m, 2H, H-CCH(COD)), 2.35 (sept, J(h,H) = 6.7 Hz, 2H, CH2(COD)), 2.02–2.19 (m, 4H, H-C(CH2)), 1.55 (d, J(h,H) = 6.9 Hz, 6H, CH(CH3)2), 1.24–1.18 (m, 4H, H-CH2(CH2)), 1.15 (d, J(h>H) = 6.7 Hz, 6H, CH(C2H5)), 0.97 (d, J(h,H) = 6.8 Hz, 6H, CH(CH3)2), 0.80 (d, J(h,H) = 6.5 Hz, 6H, CH(C2H5)). 19F NMR (161 MHz, THF-d8) δ = −15.16 (s). 13C NMR (126 MHz, THF-d8) δ = 150.96–150.26 (m, Ar), 148.96–148.61 (m, Ar), 146.48 (s, Ar), 145.67 (s, O-Dipp), 141.13–140.26 (m, Ar), 140.81 (s, N–C–N), 139.24–137.77 (m, 2m, Ar), 136.92–136.05 (m, Ar), 134.59 (s, ipso-Dipp), 134.48 (s, p-Dipp), 134.10 (s, H-CH2-CB), 130.54 (m, p-Dipp), 128.10 (s, m-Dipp), 124.57 (s, O-Dipp), 113.47 (s, m-Dipp), 103.18 (s).
added as one solid portion. The red mixture was stirred overnight at room temperature and subsequently filtered, giving a red purple solution. This solution was layered with n-hexane at room temperature, forming purple crystals within 7 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as a purple crystalline solid (98 mg, 0.063 mmol, 64%). 1H NMR (500 MHz, THF-d8) δ = 7.52 (d, J1H,H = 7.8 Hz, 2H, m-Dipp), 7.49 (t, J1H,H = 7.7 Hz, 1H, p-Dipp), 7.28 (t, J1H,H = 7.8 Hz, 2H, H, m-Dipp), 7.02 (d, J1H,H = 7.8 Hz, 2H, m-Dipp), 6.09 (s, 1H, HC=C), 4.11–0.06 (2m, 2H, H-C=CH(COD)), 3.97–3.89 (m, 2H, H-C=CH(COD)), 2.85–2.77 (2m, 2H, CH2(CH3)), 2.44–2.35 (2m, 2H, CH2(CH3)), 1.91–1.92 (m, 10H, 2 × H-C(CH3)), 1.40–1.24 (m, 10H, 5 × H-C=CH(COD)), 1.13 (t, J1H,H = 6.8 Hz, 6H, CH3(COD)), 0.98 (d, J1H,H = 6.8 Hz, 6H, CH3(COD)), 0.82 (d, J1H,H = 6.6 Hz, 6H, CH3(COD)). 11C NMR (161 MHz, THF-d8) δ = −15.20 (s). 13C NMR (126 MHz, THF-d8) δ = 168.96 (s, N = C–N), 150.90–150.46 (m, Ar), 149.07–148.56 (m, Ar), 148.14 (s, ipso-Dipp), 146.99 (s, ipso-Dipp), 140.94–140.43 (m, Ar), 138.97–138.23 (2m, 2 × Ar), 136.77–136.20 (m, Ar), 134.89 (s, p-Dipp), 133.63 (s, ipso-Dipp), 131.35 (s, p-Dipp), 130.38 (s, Dipp), 128.31 (s, H = C = B), 124.75 (s, m-Dipp), 122.40 (s, ipso-Dipp (95 MHz, THF-d8) δ = 80.35 (s, C = C–COD)), 32.65 (s, 2 × H-C(CH3)), 29.05 (s, CH(CH3)), 28.27 (s, 2 × C=C–C=COD), 26.04 (s, CH(CH3)), 23.88 (s, CH(CH3)), 22.97 (s, CH(CH3)), 22.97 (s, CH(CH3)), A signal corresponding to H = C = B was not observed and the signals corresponding to 2 × C=C–C=COD and CH3(CH3) tert-butyl groups were overlaid with the residual solvent signal of the THF-d8.

13C NMR (471 MHz, THF-d8) δ = −131.74–133.91 (m), −163.06 (s), −167.73 (s). EA Anal. Calc. for C47H31BF6C6F4N4Ir3S·(C2H5): C 49.20; H 4.07; N 1.69. Found: C 49.22; H, 4.05; N, 1.91.

Synthesis of [[WCA-Dipp]SeIr(COD)]2 (15): [[WCA-Dipp]SeLi-toluene] (100 mg, 0.093 mmol, 1 equiv.) was suspended in 3 mL toluene and [Ir(COD)]2 (62 mg, 0.093 mmol, 1 equiv.) was added as one solid portion. The red purple mixture was stirred overnight at room temperature and subsequently filtered, giving a purple solution. This solution was layered with n-hexane and stored at −30 °C, forming purple crystals within 5 d, which were collected by decantation of the supernatant solution. Residual solvent was removed in vacuo, yielding the product as a purple crystalline solid (55 mg, 0.034 mmol, 37%). 1H NMR (500 MHz, THF-d8) δ = 7.60 (t, J1H,H = 7.8 Hz, 1H, p-Dipp), 7.47 (t, J1H,H = 7.8 Hz, 2H, m-Dipp), 7.43 (d, J1H,H = 7.8 Hz, 2H, m-Dipp), 7.21 (d, J1H,H = 7.7 Hz, 2H, m-Dipp), 6.79 (s, 1H, H = C = B), 4.26–4.16 (m, 2H, H-C=CH(COD)), 4.14–4.07 (m, 2H, H-C=CH(COD)), 3.51–3.46 (2m, 2H, H-C=CH(COD)), 2.98–2.82 (2m, 4H, H-C=CH(COD) & CH2(CH3)), 2.42–2.32 (m, 2H, CH2(CH3)), 2.08–1.96 (m, 4H, 2 × H-C=CH(COD)), 1.86–1.75 (2m, 2H, H-C=C(COD)), 1.71–1.64 (m, 2H, H-C=CH(COD)), 1.60–1.52 (2m, 2H, H-C=CH(COD)), 1.42–1.32 (m, 8H, CH(2 × C) & H2 C=C(COD)), 1.28 (d, J1H,H = 6.7 Hz, 6H, CH3(CH3)), 1.23–1.12 (2m, 2H, H-C=C(COD)), 1.09–1.01 (2m, 2H, H-C=C(COD)), 0.88 (d, J1H,H = 6.3 Hz, 6H, CH3(CH3)), 0.83–0.75 (m, 6H, CH3(CH3)). 13B NMR (161 MHz, THF-d8) δ = −14.70 (s). 13C NMR (126 MHz, THF-d8) δ = −154.20 (q, J1B1,C1 = 58.0 Hz, H = C = B), 151.02–150.20 (m, Ar), 149.19–148.40 (m, Ar), 147.33 (s, ipso-Dipp), 147.16 (s, o-Dipp), 140.93–140.55 (m, Ar), 140.18 (s, N = C–N), 139.07–138.21 (2m, 2 × Ar), 137.07–136.31 (m, Ar), 136.22 (s, ipso-Dipp), 135.17 (s, ipso-Dipp & H = C = B), 132.40 (s, p-Dipp), 131.70 (s, p-Dipp), 126.48 (s, m-Dipp), 126.16 (s, m-Dipp), 74.01 (s, C=C(COD)), 71.10 (s, C=C(COD)), 62.06 (s, C=C(COD)), 60.25 (s, C=C(COD)), 35.09 (s, 2 × C=C(COD)), 32.30 (s, 2 × C=C(COD)), 31.83 (s, 2 × C=C(COD)), 30.54 (s, 2 × C=C(COD)), 29.98 (s, CH2(CH3)), 29.40 (s, CH2(CH3)), 27.93 (s, CH2(CH3)), 26.46 (s, CH2(CH3)), 23.63 (s, CH2(CH3)), 23.01 (s, CH2(CH3)). 19F NMR (471 MHz, THF-d8) δ = −133.26–−134.42 (m), −161.51 (br s), −165.81–−166.89 (m).

19Se NMR (95 MHz, THF-d8) δ = 50.48 (s). EA Anal. Calc. for C50H32BCl6C6F4Ir3Se·C, C 45.37; H, 3.68; N, 1.73. Found: C 45.43; H, 3.98; N, 1.43.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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a) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, Chem. Eur. J. 2013, Elsevier, pp. 457-484; b) N. Kuhn, A. Alsheikh, Coord. Chem. Rev. 2005, 249, 829-857; c) M. N. Hopkins, C. Richter, M. Schiedler, F. Glorius, Natuure 2014, 510, 485-495; d) A. Igarashi, E. L. Kolychev, M. Tamm, K. Nomura, Organometallics 2020, 39, 1719–1729.

[1] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[2] A. Liske, D. Verlinden, H. Buhl, K. Schaper, C. Ganter, Angew. Chem. Int. Ed. 2010, 49, 2102–2113; Angew. Chem. 2010, 122, 2184–2189.
[3] A. Liske, D. Verlinden, H. Buhl, K. Schaper, C. Ganter, Angew. Chem. Int. Ed. 2010, 49, 3640–3645; h) J. H. Hering, S. M. J. Mezbori, M. A. Wiebe, J. S. Ritch, Dalton Trans. 2018, 47, 1471–1478; f) F. Naha, K. van Hecke, A. R. Kennedy, D. J. Nelson, Dalton Trans. 2018, 47, 10671–10684.

[4] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[5] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[6] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[7] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[8] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[9] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[10] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[11] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[12] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[13] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[14] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[15] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[16] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[17] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[18] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[19] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[20] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[21] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[22] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[23] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[24] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[25] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[26] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[27] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[28] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[29] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[30] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[31] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[32] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[33] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[34] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[35] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
[36] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.