Synthesis, Structures, and Electronic Properties of O- and S-Heterocyclic Carbene Complexes of Iridium, Copper, Silver, and Gold

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ABSTRACT: O- and S-heterocyclic carbenes (OHCs, SHCs) are shown experimentally and computationally to be stronger π acceptors than NHCs and lack, of course, substituents at the heteroatoms. These different electronic and steric characteristics make OHCs and SHCs interesting ligands for coordination chemistry. Convenient synthetic routes are presented to access their iridium(I), iridium(III), and coinage-metal(I) (Cu, Ag, Au) complexes in good yields by means of dissociation of olefins, deprotonation of precursor salts, and transmetalation from a silver carbene complex. Molecular structures and detailed bonding analyses of these complexes are presented.

N-heterocyclic carbenes (NHCs, I, Figure 1) have had a profound impact on organic synthesis,6 catalysis,3 and materials research.4 The strong σ-donor and π-acceptor properties of the NHCs underline the stability of their transition-metal (TM) complexes.5 These Fischer-type carbene complexes have been heavily explored for catalysis by electronic and steric tuning of the ligands,6 such as modifying the backbone to cyclic diamidocarbenes (VII), which are strongly π back-bonding, but also by replacing an NR for a CR2 unit as in cyclic alkylaminocarbenes (CAACs, II)7 and cyclic aminoarylcarbenes (CAArCs).8 Whereas replacing NR units for oxygen or sulfur atoms should likewise have a substantial effect, it is surprising that the NOHCs (III)9 and NSHCs (IV)10 have been explored far more modestly.11

This study focuses on O- and S-heterocyclic carbenes (OHCs (V) and SHCs (VI)) in which both NR units of the NHC are exchanged for O or S atoms. The coordination of these carbenes is, a priori, determined by electronic stabilization only, which is in contrast with any of the NHCs (I–IV), where the fanlike behavior of the N substituents contributes to steric shielding of the transition metal.6a

The electronic donor/acceptor properties of the OHC and SHC carbenes can be inferred from the relative energies of the frontier orbitals, which are compared in Figure 1 with those of the more familiar NHCs (I–IV), where the fanlike behavior of the N substituents contributes to steric shielding of the transition metal.6a

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stability of a carbene, is a significant 69.7 kcal mol$^{-1}$ for OHC and similar in magnitude to that of NHC I, while the smaller value for SHCs (43.3 kcal mol$^{-1}$) resembles that of diamidocarbene VII. The large difference in dimerization energies ($\Delta$G$^{dimer}$) of OHCs (−26.7 kcal mol$^{-1}$) and SHCs (−55.6 kcal mol$^{-1}$) also suggests a higher stability for OHCa, as values of over −50 kcal mol$^{-1}$ are indicative of reactive carbones.15 The calculations imply that OHCs and SHCs complement the range of available heterocyclic carbene ligands. A number of OHCs and SHC complexes13,14 have been reported in the literature. To enhance their general accessibility and possibly boost their applicability, we present here three synthetic routes, akin to those developed for NHCs, to access OHC and SHC TM complexes, report on their molecular structures, and quantify their electronic characteristics.

We decided to compare the benzannulated derivatives of OHC (1$^O$) and SHC (1$^S$) to the NMe-substituted NHC (1$^N$) (Figure 2). Their $\pi$-acceptor abilities can be estimated with the help of selenium adducts (Scheme 1), the electronic properties of which correlate with the $^{77}$Se NMR chemical shifts; the more deshielded species correspond to the more strongly accepting carbones.15

**Scheme 1. Synthesis of Selones 1$^N$-Se, 1$^O$-Se, and 1$^S$-Se with $^{77}$Se NMR Shifts**

![Figure 2. Benzannulated NHC, OHC, and SHC heterocyclic carbones 1 with their respective superscript notations N, O, and S.](https://dx.doi.org/10.1021/acs.organomet.0c00066)

The synthesis of the selones of 1$^N$, 1$^O$, and 1$^S$ is shown in Scheme 1 together with the observed $^{77}$Se NMR chemical shifts. These follow the order 1$^N$-Se < 1$^O$-Se < 1$^S$-Se in accord with their calculated LUMO energies (see the Supporting Information). The chemical shifts for 1$^N$-Se (80 ppm) and 1$^O$. Se (317 ppm) are well within the −20 to 800 ppm range for known carbene–Se adducts and reflect OHC to be the stronger $\pi$ acceptor. To the best of our knowledge, 1$^S$-Se has the most deshielded shift of 1017 ppm (1), suggesting this carbene to be by far the strongest $\pi$ acceptor.

Carbene TM complexes are commonly generated by dissociating an alkene, deprotonating a precursor salt, or transmetalating a carbene from a silver complex.16 For OHCs the instability of the dioxonium salts adversely affects the deprotonation route and the access to Ag complexes. Therefore, the splitting of an olefin was chosen as the starting point for the Ir complexes.

**Ir COMPLEXES**

Treating a solution of dibenzotetraoxofulvalene (DBTOF)17 in toluene with [IrCl$_2$(cod)]$_2$ (cod = 1,5-cyclooctadiene) for 4 days at room temperature gave the red Ir(I) OHC complex 2$^O$ in 58% yield (Scheme 2), but SHC complex 2$^S$ could not be obtained in this manner from dibenzotetraoxofulvalene (DBTTF) likely due to its larger dimerization energy;18 [IrCl(cod)]$^N$ (2$^N$) was prepared via an established procedure19 (93%; see the Supporting Information). The $^{13}$C NMR spectra show a more deshielded carbene carbon for 2$^O$ ($\delta$ 209.2 ppm) than for 2$^N$ ($\delta$ 192.0 ppm), in accordance with the stronger $\pi$-accepting ability of the OHC ligand.20 The molecular structures, determined by single-crystal X-ray structure determinations, confirmed the formation of the Ir(Cl)(cod) OHC complex 2$^O$ and its NHC analogue 2$^N$ (Figure 3). The observed Ir–carbene bond distance of 1.940(3) Å in 2$^O$ is shorter than the 2.0226(19) Å in 2$^N$ (1.925 versus 1.994 Å at the BP86-D3/TZ2P level), which is consistent with the stronger $\pi$ back-bonding of the OHC ligand.

[17]}

**Scheme 2. Synthesis of the Ir(I) Complex 2$^O$**

![Figure 3. Structures of 2$^O$ (left) and 2$^N$ (right) in the crystal form. Ellipsoids are set at 50% probability; H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): 2$^O$, Ir1–C2 1.940(3), Ir1–C10 2.112(3), Ir1–C11 2.131(2), C14–C15 1.379(4), C10–C11 1.426(4), Ir1–C14 2.226(3), Ir1–C15 2.276(3), Ir1–C12 2.3531(6), O1–C2 1.349(3), C2–O3 1.346(3), C2–Ir–C11 91.67(7), O3–C2–O1 108.7(2); 2$^N$, Ir1–C1 2.0226(19), Ir1–C10 2.106(2), Ir1–C11 2.1120(19), C14–Cl5 1.383(3), C10–Cl11 1.413(3), Ir1–C14 2.1860(19), Ir1–Cl5 2.2061(19), Ir1–Cl1 2.3585(5), N1–C1 1.359(2), C1–N2 1.357(2), C1–Ir1–Cl1 88.76(5), N1–C1–N2105.66(16).](https://dx.doi.org/10.1021/acs.organomet.0c00066)
of 3° is orthogonal to the Cp* ligand and has a rather short Ir–C bond of 1.9535(17) Å, whereas both ligands are aligned ("parallel") in 3N°, which has a longer Ir–C bond of 2.027(4) Å. These two structures have approximate C₃ symmetry, while 3° has a "skewed" conformation with a 24° angle bisecting the planes of the ligands and an Ir–C bond length of 1.999(2) Å that is intermediate to those of the others. We conclude that the rotation of the carbene by 90° from 1° to 1N° is sterically driven, as the N-methyl groups would interfere with the Cp* ring in an orthogonal arrangement.24

BP86-3D/TZ2P calculations corroborated this hypothesis, showing "parallel" 3N° to be favored over "orthogonal" 3° by a significant 12.5 kcal mol⁻¹; the N° notation reflects the ligand's orthogonality. The two conformational isomers of both 3° and 3 are indeed found to be approximately isoelectronic (see the Supporting Information). At this juncture it seemed relevant to examine the nature of the interaction of the carbene ligands (1°, 1N°, and 1S°) with [IrCl₂(Cp*)] in the "orthogonal" complexes by using an energy decomposition analysis at the BP86-D3/TZ2P level (C₃ symmetry). For comparison, the Ir–carbene bond distances of 3°, 3N°, and 3S° were fixed to the equilibrium value of 3° (1.906 Å) to eliminate the effect of steric interactions with the Cp* ligand. σ donation from the carbene lone pair into the empty metal d orbital dominates the bonding in all three complexes and is stronger for 3N° and 3S° than for 3° (Figure 5 and Table S3). π back-bonding from the metal dₐ orbital into the LUMO of the carbene (pₓ orbital) is instead stronger for 3° (24%) and 3S° (24%) than for 3N° (18%) due to the smaller energy gap and better overlap between the fragment orbitals (Figure 5). It appears that NHC π back-bonding is too modest to compensate the steric interaction in the orthogonal complex,²⁵ in concurrence with the experimentally observed and computationally favored parallel conformation of 3N°. The energy decomposition analysis further confirms the strong π-accepting property of both the OHC and SHC ligands, which is evident from the relative energy differences Δε and the 3N° < 3° < 3S° population of their carbene fragment orbitals.

In an attempt to quantify the net donation of the 1N°, 1°, and 1S° ligands to the Ir(1) center, we turned to the Tolman electronic parameter, which reflects the ligand donor properties in the CO stretching frequencies of the metal carbonyl group. There are ample such parameters known for NHC TM complexes with excellent linear correlations. The difficulty is, of course, that a CO ligand is required at the Ir center.²⁶
We were able to obtain \([\text{IrCl(CO)}]_2(\text{cod})\) ([4]S; Figure 6), but exposure of \([\text{IrCl}](\text{cod})(\text{2})\) to CO led, unfortunately, to instant decomposition. This observation in itself illustrates the strong acceptor properties of \([1]S\). Since the TEP of (2040 cm\(^{-1}\)) for \([4]S\) compares well with the computed value of 2044 cm\(^{-1}\) (BP86-D3/TZ2P geometry), we had expected a larger TEP for \([4]S\) on the basis of its calculated value of 2057 cm\(^{-1}\), which is in line with the stronger \(\pi\)-accepting property of \([1]S\). Finally, the computed TEP of 2049 cm\(^{-1}\) for \([4]S\) indicates that the net donation of the SHC ligand lies between those of NHC and OHC, which agrees with the noted good \(\pi\)-acceptor and intermediate \(\sigma\)-donor capacity of \([1]S\) (see the Supporting Information).

### Cu, Ag, AND Au COMPLEXES

For the synthesis of the OHC and SHC coinage metal(I) complexes, we explored transmetalation, which required access to the unknown silver complexes. Whereas their synthesis by means of alkene dissociation seemed appealing, the reaction of DBTOF or DBTTF with silver(I) salts invariably led to elemental silver, probably due to olefin oxidation akin to tetra-N-alkenes and in line with electrochemical studies.\(^{18,27}\) Instead, reacting benzothiolium tetrafluoroborate with a slight excess of silver acetate afforded SHC silver complex \([5]S\) in high (91\%) yield (Scheme 4).\(^{28}\) \([5]S\) was fully characterized by NMR spectroscopy (see the Supporting Information). Its molecular structure, obtained by a single-crystal X-ray structure determination, shows the BF\(_4^-\) anion to be well separated from the cationic complex (the closest CH···F contact is 2.366 Å). The Ag\(^+\) complex has approximate \(D_{4h}\) symmetry with two coplanar \([1]S\) ligands and a C—Ag—C angle of 176.8(2)° (Figure 7, left). The Ag—carbene bond lengths of 2.115(7) and 2.103(6) Å are in the upper range of comparable bis-NHC-bridged Ag(I) complexes\(^{37}\) and reflect weak metal—carbene interactions that are attributed to electronic factors, as the carbene ligands exercise no steric repulsion.

With \([5]S\) in hand, its potential as a carbene transfer agent could be examined in analogy to the Ag-mediated NHC transfer reactions.\(^{30}\) We first pursued iridium complex \([5]S\), the missing sulfur analogue of \([2]S\) (see Scheme 2), by transferring one SHC ligand from \([5]S\) to \([\text{IrCl(cod)}]_2\), but instead obtained bis-SHC complex \([6]S\) (Scheme 4, top right) together with an equimolar amount of the unreacted Ir complex; employing 2 equiv of \([5]S\) gave \([6]S\) in 73\% yield. The \(^{1}H\) and \(^{13}C\) NMR spectra reveal a highly symmetrical cod ligand and indicate the presence of two SHC ligands, which was confirmed by the molecular structure obtained from a single-crystal X-ray analysis (Figure 7, right). Whereas the reaction of the Ag complex \([5]S\) with \([\text{IrCl(cod)}]_2\) did not yield Ir complex \([2]S\) but instead Ir complex \([6]S\), the important conclusion is that the Ag\(^+\) complex can serve as an SHC transmetallating complex.

To further validate the ability of \([5]S\) to transfer its SHC carbene, we examined its exposure to Cu(I) and Au(I) salts. Reacting \([5]S\) with an equimolar amount of [CuBr(SMe\(_2\))] or [AuCl(SMe\(_2\))] led to the coinage-metal bis-SHC complexes \([7]S\) and \([8]S\) in 74\% and 88\% yields, respectively (Scheme 4, right). Both complexes were characterized spectroscopically (see the Supporting Information), as no suitable crystals could be obtained for X-ray crystal structure determinations. The \(^{13}C\) NMR chemical shifts of the carbene carbon atoms of \([7]S\) and \([8]S\) at \(\delta\) 235.4 and 232.0 ppm, respectively, compare well with \(\delta\) 231.1 for the Ir complex \([3]S\) and reflect the strong \(\pi\)-acceptor ability of the SHC carbene ligand.

The bonding nature of the coinage metal complexes \([5]S\), \([7]S\), and \([8]S\) was assessed at the BP86/TZ2P level using \(D_{2a}\) optimized geometries. The lengths of the metal—carbene bonds (\([5]S\), 2.071 Å; \([7]S\), 1.869 Å; \([8]S\), 2.020 Å) and their strengths (Ag < Cu < Au), as deduced from an energy decomposition analysis (Table 1), follow the commonly observed trends.\(^{31}\) Silver complexes have the weakest bond, which concurs with their use as a transmetallation reagent. The bonding to the d\(^{10}\) group 11 metal cations is governed by electrostatic interactions and is comparable to those of the

![Figure 6. Complexes \([4]S\), \([5]S\), and \([6]S\) together with their calculated and observed TEPs.](image-url)

![Figure 7. Structures of \([5]S\) (left) and \([6]S\) (right); only one of two independent molecules in the asymmetric unit is shown.)](image-url)
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Table 1. Energy Decomposition Analyses and Bond Dissociation Energies (in kcal mol−1) for the Coinage-Metal (SHC) Complexes S, S′, and S″ and for the Gold NHC and OHC Complexes [Au(N(1))2]+ (S′) and [Au(1)]2+ (S″)

<table>
<thead>
<tr>
<th>ΔE_bond (kcal mol−1)</th>
<th>[M(CAAC)2]+ (M = Cu, Ag, Au)</th>
<th>ΔE_bond (kcal mol−1)</th>
<th>[M(CAAC)2]+ (M = Cu, Ag, Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s (Ag) s′ (Cu) s″ (Au)</td>
<td>2.071 1.869 2.020 2.030 2.011</td>
<td>ΔE_bond (kcal mol−1)</td>
<td>[M(CAAC)2]+ (M = Cu, Ag, Au)</td>
</tr>
<tr>
<td>s (Ag) s′ (Cu) s″ (Au)</td>
<td>1.847 2.020 2.030 2.011</td>
<td>ΔE_bond (kcal mol−1)</td>
<td>[M(CAAC)2]+ (M = Cu, Ag, Au)</td>
</tr>
<tr>
<td>s (Ag) s′ (Cu) s″ (Au)</td>
<td>1.837 2.020 2.030 2.011</td>
<td>ΔE_bond (kcal mol−1)</td>
<td>[M(CAAC)2]+ (M = Cu, Ag, Au)</td>
</tr>
<tr>
<td>s (Ag) s′ (Cu) s″ (Au)</td>
<td>1.827 2.020 2.030 2.011</td>
<td>ΔE_bond (kcal mol−1)</td>
<td>[M(CAAC)2]+ (M = Cu, Ag, Au)</td>
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IN CONCLUSIONS

In summary, we report on the convenient syntheses of new OHC and SHC transition-metal complexes by (1) dissociation of a suitable olefin, (2) deprotonation of a precursor salt, or (3) transmetalation from a precursor Ag complex. The hitherto neglected OHCs and SHCs differ both electronically and sterically from the classical NHCs and thereby extend the panoply of available carbene ligands. Their strong π-accepting properties can be beneficial in synthetic and catalytic applications. Especially notable is the capability of S to transfer the SHC ligand, allowing for facile access to a much wider range of carbene complexes. The applicability of the new benzannulated heterocyclic carbenes OHC S and SHC S is a target for further study.

EXPERIMENTAL SECTION

Materials and Methods. All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox, unless otherwise stated. Dry, oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-filled, sealed capillaries using a Büchi M-S65 Melting Point apparatus and are uncorrected. Solution 1H, 13C, 11B, orbital contribution for the SHC complexes (1 for the Au(I) complexes and the Supporting Information for comparison to the NHC ligand, the SHC and OHC ligands transfer the SHC ligand, allowing for facile access to a much larger panoply of available carbene ligands. Their strong π-accepting properties can be beneficial in synthetic and catalytic applications. Especially notable is the capability of S to transfer the SHC ligand, allowing for facile access to a much wider range of carbene complexes. The applicability of the new benzannulated heterocyclic carbenes OHC S and SHC S is a target for further study.

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days. Over time, the media changed gradually from orange to brown. Volatiles were removed in vacuo, and the residue was washed with diethyl ether (8 × 5 mL) to remove starting material and byproducts; the product is also slightly soluble in diethyl ether. The remaining red-orange solid was dried under vacuum to give 2. Yield: 280 mg (58%). Crystals suitable for X-ray crystallography were grown at room temperature by vapor diffusion of diethyl ether into a solution of 2 in dichloromethane. The compound decomposes under nitrogen and only slowly (over days) in solution, as indicated by formation of a black insoluble residue. Mp: 115–117 °C dec. 1H NMR (400 MHz, CDCl3): δ 7.55 (m, 2H, H2 or H3), 7.40 (m, 2H, H4 or H5), 5.53 (m, 2H, H6 or H7), 5.32 (m, 2H, H8), 2.62 (m, 8H, H9 and H10). 13C{1H} NMR (100 MHz, CDCl3): δ 209.2 (s, C1), 183.4 (s, C2), 182.3 (s, C3), 168.5 (s, COtrans), 153.1 (s, C4), 124.4 (s, C5 or C6), 111.1 (s, C7 or C8), 35.4 (s, C9). IR (ATR): ν 2947, 2054, 1569, 1456, 1333, 1130, 1094, 766, 743. HRMS (ESI+): calcd for [M + H]− = C19H25ClN2Ir+, 509.1328; found, 509.1330.

5. Benzodithiolium tetrafluoroborate (500 mg, 2.08 mmol, 1.0 equiv) and silver(1) acetate (695.3 mg, 4.17 mmol, 2.0 equiv) were suspended in THF (30 mL) and heated to reflux for 20 min. After it was cooled to room temperature, the green reaction mixture was filtered by cannula filtration. The remaining dark gray residue was washed with THF (2 × 5 mL) and extracted into acetonitrile (6 × 5 mL). During the extraction, the receiving flask was cooled to −78 °C in order to freeze the acetonitrile solution and avoid decomposition. Volatiles were removed under vacuum at room temperature to give 5s as a green solid. Yield: 473 mg (91%). Crystals of poor but sufficient quality for X-ray crystallography were grown by vapor diffusion of hexanes into a concentrated solution of 5s in dichloromethane. Slightly longer reflux times (e.g., 40 min) during the synthesis resulted in complete decomposition. The compound was moderately stable in chlorinated solvents but decomposed rapidly (mostly to dibenzotetraphiofulvalene and an unknown insoluble residue) in the presence of coordinating solvents such as acetonitrile or THF and was best stored in the solid state at −20 °C in the dark.

Mp: >70 °C dec. 1H NMR (400 MHz, CDCl3): δ 8.85 (m, 4H, H1 or H2), 7.82 (m, 4H, H3 or H4). 13C{1H} NMR (100 MHz, CDCl3): δ 150.6 (s, C1), 129.3 (s, C2 or C3), 125.2 (s, C4 or C5), Cn or C6, C7, or C8 not detected. 1H{1H} NMR (128 MHz, CDCl3): δ −1.2 (s, BF4). 19F{1H} NMR (235 MHz, CD3CN): δ −151.7 (s). IR (ATR): ν 3090, 3055, 1439, 1427, 1088, 1030, 964, 950, 758. HRMS (ESI+): calcd for [M − BF4]− = C19H16Ag3F4+, 410.8554; found, 410.8548.

6. The iridium dimer complex (67.3 mg, 0.1 mmol, 1.0 equiv) and 5 (100.0 mg, 0.2 mmol, 2.0 equiv) were suspended in dichloromethane (8 mL) and stirred at ambient temperature for 30 min. The brown reaction mixture was filtered over a pad of Celite which was washed with dichloromethane (8 mL) and dried under vacuum to give 6 as a dark brown solid. Yield: 100 mg (73%). Crystals suitable for X-ray crystallography were grown at 4 °C by layering a concentrated solution of 6 in fluorobenzene/dichloromethane (1:1) with fluorobenzene. Mp: >120 °C dec. 1H NMR (400 MHz, CDCl3): δ 8.21–8.16 (m, 4H, H1 or H2), 7.56–7.51 (m, 4H, H3 or H4), 4.26–4.20 (m, 4H, H5 or H6). 1C{1H} NMR (100 MHz, CDCl3): δ 240.6 (s, C1), 147.1 (s, C2), 128.0 (s, C3 or C4), 123.9 (s, C5 or C6), 90.7 (s, C7), 31.8 (s, C8). 19F{1H} NMR (235 MHz, CD3CN): δ −152.8. IR (ATR): ν 3090, 3055, 2955, 2881, 2837, 1435, 1026, 926, 847, 752. HRMS (ESI+): calcd for [M − BF4]− = C19H14F8Ir2+, 433.0314; found, 433.0310.

7. Dichloromethane (10 mL) was slowly added to a copper bromide dimethyl sulfoxide complex (41.2 mg, 0.2 mmol, 1.0 equiv) and stirred at ambient temperature for 30 min. The green reaction mixture was filtered over a pad of Celite. The clear dark green solution was evaporated to dryness. The brown residue was washed with diethyl ether (3 × 2 mL) and dried under vacuum to give 7s as a brown solid. Yield: 67 mg (74%). Mp: >85–120 °C dec. 1H NMR (400 MHz, CDCl3): δ 8.49–8.47 (m, 4H, H1 or H2), 7.84–7.82 (m, 4H, H3 or H4). 1C{1H} NMR (100 MHz, CDCl3): δ 235.4 (s, C1), 149.7 (s, C2), 129.1 (s, C3 or C4).
124.5 (s, C1, or C2), 1.0 equiv) and 8 (50 mg, 0.1 mmol, 1.0 equiv) were suspended in dichloromethane and stirred at ambient temperature for 30 min. The green reaction mixture was filtered via cannula. The clear dark green solution was concentrated under vacuum to a volume of ca. 1 mL. Addition of pentane (10 mL) led to the precipitation of a solid which was isolated by cannula filtration, washed with diethyl ether (3 × 3 mL), and dried under vacuum to give 8 as a gray-greenish solid. Yield: 52 mg (88%). Mp: 110 °C. 

The bonding interactions of the transition-metal to ligand bonds were analyzed with the ADF implemented energy decomposition50 on the two fragments plus an electrostatic interaction energy part (ΔE_elec) and an orbital interaction energy (charge transfer, polarization) part (ΔE_orb). The energy necessary to convert fragments from their ground-state equilibrium geometries to the geometry and electronic state they acquire in the complex is represented by a preparation energy term (ΔE_prep). The overall bond energy (ΔE_tot) is formulated as

ΔE_tot = ΔE_prep + ΔE_elec + ΔE_orb + ΔE_int

Note that ΔE_prep is defined as the negative of the bond dissociation energy (BDE), i.e. ΔE_prep = E(molecule) – ΣE(fragment), thereby resulting in negative values for stable bonds. The orbital interaction term ΔE_orb accounts for interactions between occupied orbitals on one fragment with unoccupied orbitals on the other fragment, including HOMO–LUMO interactions and polarization (empty/occupied orbital mixing on the same fragment). The charge transfer part is the result of both σ donation from the ligand to the metal and π back-donation from the metal into the unoccupied orbitals of the ligand. Instead of separating the charge transfer and polarization parts, we used the extended transition state (ETS) method developed by Ziegler and Rauk to decompose ΔE_orb into contributions from each irreducible representation of the interaction system.51

X-ray Structure Determination. The crystal structures were determined on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo Kr radiation (2θ, 3θ, 4θ, 5θ, 6θ) (0.71073 Å). Direct methods (2θ, 3θ, 6θ) or Patterson methods (2θ, 3θ) were used for structure solution (SHELXS-97).51 Refinement was carried out using SHELXL-2014 (full-matrix least-squares on F²).52 Hydrogen atoms were localized by difference Fourier synthesis and refined using a riding model. Semiempirical absorption corrections were applied for the compounds. For 2θ, 3θ, 3θ, and 4θ extinction corrections were applied.53 3θ was refined as a two-component inversion twin (BASF = 0.277(7)). In 6θ one solvent molecule is disordered about a 2-fold axis (see cif file for details). CCDC 1451141 (2θ), CCDC 1451142 (3θ), CCDC 1451143 (3θ), CCDC 1451144 (3θ), CCDC 1451145 (3θ), CCDC 1451203 (5θ), and 145116 (6θ) contain the supplementary crystallographic data for this paper. Additional crystallographic information is available in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00066.

NMR spectra, additional computational details and crystallographic data, geometries of computed structures (PDF)

Computed Cartesian coordinates (XYZ)

Accession Codes

CCDC 1451141−1451146 and 1451203 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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