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Synthesis, Structures, and Electronic Properties of O- and S-Heterocyclic Carbine 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, Figure 1) have had a profound impact on organic synthesis, catalysis, and materials research. The strong σ-donor and π-acceptor properties of the NHCs underlie the stability of their transition-metal (TM) complexes. These Fischer-type carbene complexes have been heavily explored for catalysis by electronic and steric tuning of the ligands, 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 alkyamidocarbenes (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

Figure 1. HOMO and LUMO energies (in eV, also visualized), singlet–triplet energy gaps (ΔE^ST in kcal mol⁻¹), and Gibbs free energies of dimerization (in kcal mol⁻¹) for carbenes I–VII with R = Me at the B3LYP/TZVP level.

ΔE^ST

ΔG^ST

I

II

III

IV

V

VI

VII

0.73

-5.63

72.2

-4.4

-55.8

0.03

-5.35

49.1

-5.35

-71.9

-17.9

0.41

-6.08

71.4

-6.08

-28.0

-28.0

-0.18

-6.04

59.6

-6.04

-28.7

-28.7

-0.30

-6.84

69.7

-6.84

-55.6

-55.6

-1.74

-6.60

43.3

-6.60

-37.2

-3.25

-6.79

34.8

-6.79

-37.2

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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 (\(\Delta G^{\text{dimer}}\)) of OHCs (26.7 kcal mol\(^{-1}\)) and SHCs (55.6 kcal mol\(^{-1}\)) also suggests a higher stability for OHCs, as values of over 50 kcal mol\(^{-1}\) are indicative of reactive carbenes.13 The calculations imply that OHCs and SHCs complement the range of available heterocyclic carbene ligands.

A number of OHC\(^{13}\) and SHC complexes\(^{13c,14}\) 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\(^{0}\)) and SHC (1\(^{5}\)) to the NMe-substituted NHC (1\(^{8}\)) (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 carbenes.15

![Figure 2: Benzannulated NHC, OHC, and SHC heterocyclic carbenes 1 with their respective superscript notations N, O, and S.](https://example.com/figure2)

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

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 (!), 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 dioxolium 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\((cod)\)]\(_2\) (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 dibenzotetrathiofulvalene (DBTTF) likely due to its larger dimerization energy;\(^{18}\) [IrCl\((cod)\)]\(_2\) \((2^{N})\) was prepared via an established procedure\(^{19}\) (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\(^{N}\) is shorter than the 2.0226(19) Å in 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.](https://example.com/figure3)

The synthesis of 1\(^{O}\)-Se and 1\(^{S}\)-Se was performed similarly using 1\(^{O}\)-Cl and 1\(^{S}\)-Cl precursors (Scheme 3). The 1\(^{O}\)-Cl complex 3\(^{O}\) was isolated by transmetalation with DBTOF in refluxing toluene for 3 days, while 3\(^{N}\) was obtained quantitatively (Scheme 3, top). NHC complex 3\(^{N}\) was obtained analogously in 88% yield, but SHC complex 3\(^{S}\), like 2\(^{S}\), could not be obtained, as DBTTF would not dissociate even after prolonged heating at 110 °C. To access 3\(^{S}\), we turned to the deprotonation route using the dithiolium salt.21 Slow addition of the strong base potassium hexamethyldisilazide (KHMDS) to a mixture of commercially available benzothiolium tetrafluoroborate and [IrCl\((P^*\_P\_P\_P)\)] in THF led indeed to 3\(^{S}\) in a remarkably high yield of 80%.

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**Scheme 2. Synthesis of the Ir(I) Complex 2\(^{O}\)**

![Scheme 2](https://example.com/scheme2)

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.

Other Ir complexes are likewise accessible. For example, treating DBTOF with [IrCl\((P^*\_P\_P\_P)\)] in refluxing toluene for 3 days gave orange OHC Ir(III) complex 3\(^{O}\) quantitatively (Scheme 3, top). NHC complex 3\(^{N}\) was obtained analogously in 88% yield, but SHC complex 3\(^{S}\), like 2\(^{S}\), could not be obtained, as DBTTF would not dissociate even after prolonged heating at 110 °C.
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 C4 symmetries, while 3S 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 1° notation reflects the ligand’s orthogonality. The two conformational isomers of both 3O and 3S were instead found to be approximately isoenergetic (see the Supporting Information). At this juncture it seemed relevant to examine the nature of the interaction of the carbene ligands (1°, 1S, and 1N) with [IrCl2Cp*] in the “orthogonal” complexes by using an energy decomposition analysis at the BP86-D3/TZ2P level (C5 symmetry). For comparison, the Ir−carbene bond distances of 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 3O (Figure S and Table S3). π back-bonding from the metal dσ orbital into the LUMO of the carbene (pπ orbital) is instead stronger for 3O (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, 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 ΔE and the 3N° < 3O < 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.5c,26

Figure 5. Principal fragment orbitals establishing the back-bonding contribution of the Ir−carbene bond for 3N°, 3S°, and 3° in the orthogonal conformation (calculated with a Ir−C distance of 1.906 Å). Below the table are the LUMOs of 3N° (left), 3O° (middle), and 3S° (right) with isovorlues of 0.07 au. Table columns: ΔE° (symmetrical σ′) and ΔEπ° (antisymmetrical σ′′) are the orbital interaction energy contributions in kcal mol−1; % π is the relative π contribution, ΔEπ° is the HOMO (metal d)−LUMO (carbene p) energy gap of the fragments in eV, S is the orbital overlap, and the population of the carbene LUMO e (see the Supporting Information for details).
We were able to obtain [IrCl(CO),1N] (4N, Figure 6), but exposure of [Ir(Cl)(cod)(2O)] to CO led, unfortunately, to instant decomposition. This observation in itself illustrates the strong acceptor properties of 1N. Since the TEP of (2040 cm⁻¹) for 4N compares well with the computed value of 2044 cm⁻¹ (BP86-D3/TZ2P geometry), we would have expected a larger TEP for 4O on the basis of its calculated value of 2057 cm⁻¹, which is in line with the stronger π-accepting property 1O. Finally, the computed TEP of 2049 cm⁻¹ for 4S indicates that the net donation of the SHC ligand lies between those of NHC and OHC, which agrees with the noted good π-acceptor and intermediate σ-donor capacity of 1S (see the Supporting Information).

Figure 6. Complexes 4N, 4O, and 4S together with their calculated and observed TEPs.

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 elemental silver, probably due to olefin decomposition analysis (Table 1), follow the commonly observed trends. Silver complexes have the weakest bond, decomposition strengths (Ag < Cu < Au), as deduced from an energy transfer reactions. We first pursued iridium complex 2S, the missing sulfur analogue of 5S [IrCl(cod)], but instead obtained bis-SHC complex 6S (Scheme 4, top right) together with an equimolar amount of the unreacted Ir complex; employing 2 equiv of 5S gave 6S in 73% yield. The 1H and 13C 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 5S with [IrCl(cod)] did not yield Ir complex 2S but instead Ir complex 6S, the important conclusion is that the Ag complex can serve as an SHC transmetallating complex.

To further validate the ability of 5S to transfer its SHC carbene, we examined its exposure to Cu(I) and Au(I) salts. Reacting 5S with an equimolar amount of [CuBr(SMe2)] or [AuCl·SMe2] led to the coinage-metal bis-SHC complexes 7S and 8S 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 13C NMR chemical shifts of the carbene carbon atoms of 7S and 8S at δ 235.4 and 232.0 ppm, respectively, compare well with δ 231.1 for the Ir complex 6S and reflect the strong π-acceptor ability of the SHC carbene ligand.

The bonding nature of the coinage metal complexes 5S, 7S, and 8S was assessed at the BP86/TZ2P level using D26-optimized geometries. The lengths of the metal–carbene bonds (5S, 2.071 Å; 7S, 1.869 Å; 8S, 2.020 Å) and their strengths (Ag < Cu < Au), as deduced from an energy decomposition analysis (Table 1), follow the commonly observed trends. Silver complexes have the weakest bond, which concurs with their use as a transmetallation reagent. The bonding to the d10 group 11 metal cations are governed by electrostatic interactions and are comparable to those of the
Table 1. Energy Decomposition Analyses and Bond Dissociation Energies (in kcal mol⁻¹) for the Coinage-Metal (SHC), Complexes S₅, S₇, and S₈ and for the Gold NHC and OHC Complexes [Au(1N)]⁺ (S₈) and [Au(1P)]⁺ (S₈)

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<th></th>
<th>S₅ (Au)</th>
<th>S₅ (Cu)</th>
<th>S₇ (Au)</th>
<th>S₇ (Cu)</th>
<th>S₈ (Au)</th>
<th>S₈ (Cu)</th>
<th>S₈ (Au)</th>
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<tr>
<td>dₛ-ₚₜₑ חו</td>
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<td>1.869</td>
<td>2.020</td>
<td>2.030</td>
<td>2.011</td>
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<tr>
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<td>-34.1</td>
<td>-32.3</td>
<td>-31.1</td>
<td>-32.0</td>
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<tr>
<td>ΔEₑ₉ₐ₅ (kcal mol⁻¹)</td>
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<td>-215.0</td>
<td>-238.9</td>
<td>-205.4</td>
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**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 S₅ 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 and SHC is a target for further study.

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**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-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. Melting points were determined with samples in nitrogen-oxygen-free solvents were employed. 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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 at room temperature, as indicated by formation of a black insoluble residue. 

\[ \text{H NMR (400 MHz, CDCl}_3): \delta 7.55 - 7.37 (m, 2H, H4 or H5), 7.30 \text{ (m, 2H, H2 or H3), 4.17 \text{ (s, 6H, H2).} \]

\[ \text{13C{H} NMR (100 MHz, CDCl}_3): \delta 168.6 (s, C1), 147.1 (s, C2), 126.7 (s, C4), 111.9 (s, C3), 95.8 (s, C6 or C7), 92.2 (s, C6 or C7).} \]

IR (ATR): \nu 2983, 2918, 1702, 1383, 1130, 1094, 777. HRMS (ESI+): [M - Cl]^+ = C_{16}H_{30}ClIrClO_4^−, 645.0314; found, 645.0310.

**5**. Benzodithiolium tetrafluoroborate (500 mg, 2.08 mmol, 1.0 equiv) was 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 5 as a gray solid. Yield: 473 mg (91%). Crystals of poor but sufficient quality for X-ray crystallography were grown by slow vapor diffusion of hexanes into a concentrated solution of 5 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 dibenzotetraoxafulvalene 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.

\[ \text{H NMR (400 MHz, CDCl}_3): \delta 8.55 (m, 4H, H3 or H4), 7.82 (m, 4H, H3 or H4).} \]

\[ \text{13C{H} NMR (100 MHz, CDCl}_3): \delta 125.2 (s, C5 or C6), 125.2 (s, C5 or C6), 129.3 (s, C7 or C8), 90.7 (s, C5 or C6).} \]

IR (ATR): \nu 2831, 1437, 1088, 1300, 960, 758. HRMS (ESI+): [M - BF_4]^+ = C_{16}H_{16}AgS_4BF_4, 995.0205; found, 994.9780.

**6**. The iridium dimer complex (67.3 mg, 0.1 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 6 as a gray solid. Yield: 473 mg (91%). Crystals of poor but sufficient quality for X-ray crystallography were grown by slow vapor diffusion of hexanes into a concentrated solution of 5 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 dibenzotetraoxafulvalene 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.

\[ \text{H NMR (400 MHz, CDCl}_3): \delta 8.55 (m, 4H, H3 or H4), 7.82 (m, 4H, H3 or H4).} \]

\[ \text{13C{H} NMR (100 MHz, CDCl}_3): \delta 125.2 (s, C5 or C6), 125.2 (s, C5 or C6), 129.3 (s, C7 or C8), 90.7 (s, C5 or C6).} \]

IR (ATR): \nu 2831, 1437, 1088, 1300, 960, 758. HRMS (ESI+): [M - BF_4]^+ = C_{16}H_{16}AgS_4BF_4, 995.0205; found, 994.9780.
12.5 (s, C1 or C6). 1B{1H} NMR (128 MHz, CD2Cl2): δ = −0.83 (s).

1F{1H} NMR (235 MHz, CD2Cl2): δ = −150.5 (s). IR (ATR): ν: 3069, 3056, 1549, 1433, 1326, 1312, 1286, 1259, 1232 (s, C6 or C6). 19F{1H} NMR (235 MHz, CD2Cl2): δ = −0.83 (s).

The bonding interactions of the transition-metal to ligand bonds were analyzed with the ADF implemented energy decomposition analysis (EDA) to decompose the total interaction energy into contributions from each orbital interaction energy (charge transfer, back-donation, polarization) part (empty/occupied orbitals on the two fragments plus an electrostatic interaction energy part). The overall bond energy (ΔE_total) is represented by a preparation energy term (ΔE_prep). The overall bond energy (ΔE_total) is formulated as

$$\Delta E_{\text{total}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{prep}}$$

Note that ΔE_prep is defined as the negative of the bond dissociation energy (BDE), i.e. ΔE_prep = E(molecule) − ΣE(fragments), 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.25

X-ray Structure Determination. The crystal structures were determined on a Bruker D8 Venture diffractometer with Phenix100 detector at 123(2) K using Mo Kα radiation (0.71073 Å). Direct methods (SHELXS-97)25 and Patterson methods (SHELX-2014) were used for structure solution (SHELXLS-97).25 Refinement was carried out using SHELXL-2014 (full-matrix least-squares on F2).25 Hydrogen atoms were localized by difference Fourier synthesis and refined using a riding model. Semiempirical absorption corrections were applied for the compounds. For 2°, 3°, 4°, and 5° extinction corrections were applied.36 3° was refined as a two-component inversion twin (BASF = 0.277(7)). In 6° one solvent molecule is disordered about a 2-fold axis (see cif file for details). CCDC 1451141 (2°), CCDC 1451142 (3°), CCDC 1451143 (3°), CCDC 1451144 (4°), CCDC 1451145 (4°), CCDC 1451203 (5°), and CCDC 145166 (6°) 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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