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

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

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ABSTRACT: O- and S-heterocyclic carbene (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, 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 alkylaminocarbenes (CAACs, II) and cyclic aminoarylcarbenes (CAArCs). Whereas replacing NR units for oxygen or sulfur atoms should likewise have a substantial effect, it is surprising that the NOHCs (III) and NSHCs (IV) have been explored far more modestly.

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.

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.

Figure 1. HOMO and LUMO energies (in eV, also visualized), singlet–triplet energy gaps (ΔEVT 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.

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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 OHCA, as values of over −50 kcal mol\(^{-1}\) are indicative of reactive carbenes. The calculations imply that OHCs and SHCs complement the range of available heterocyclic carbone ligands.

A number of OHC\(^{13}\) and SHC complexes\(^{13,14}\) 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 (I\(^{O}\)) and SHC (I\(^{S}\)) to the NMe-substituted NHC (I\(^{N}\)) (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 \(\delta^{77}\text{Se}\) NMR chemical shifts; the more deshielded species correspond to the more strongly accepting carbenes.\(^{15}\)

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

![Diagram of Scheme 1](image)

The synthesis of the selones of I\(^{N}\), I\(^{O}\), and I\(^{S}\) is shown in Scheme 1 together with the observed \(\delta^{77}\text{Se}\) NMR chemical shifts. These follow the order I\(^{N}\)-Se < I\(^{O}\)-Se < I\(^{S}\)-Se in accord with their calculated LUMO energies (see the Supporting Information). The chemical shifts for I\(^{N}\)-Se (80 ppm) and I\(^{O}\)-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, I\(^{S}\)-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 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\(_2\)(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 dibenzotetrahexofulvalene (DBTTF) likely due to its larger dimerization energy;\(^{18}\) [IrCl(cod)]\(_{1N}\) (2\(^{N}\)) was prepared via an established procedure\(^{17}\) (93%; see the Supporting Information). The \(13\text{C}\) NMR spectra show a more deshielded carbene carbon for 2\(^{O}\) (δ 209.2 ppm) than for 2\(^{N}\) (δ 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\(^{N}\), consistent with the stronger \(\pi\)-back-bonding of the OHC ligand.

Other Ir complexes are likewise accessible. For example, treating DBTOF with [IrCl\(_2\)Cp*]\(_{1N}\) (Cp* = pentamethylcyclopentadienyl) 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. 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 benzodithiolium tetrafluoroborate and [IrCl\(_2\)Cp*]\(_{2}\) in THF led indeed to 3\(^{S}\) in a remarkably high yield of 80%
(Scheme 3, bottom); slow addition limits the formation of the carbene dimer. All three Ir(III) complexes respectively, are informative, as they ring in an orthogonal arrangement.\(^{24}\)

The molecular structures of the complexes obtained by single-crystal X-ray diffraction measurements show surprisingly different spatial orientations (Figure 4).\(^{23}\) The carbene ligand

![Scheme 3. Synthesis of the Ir(III) Complexes 3N, 3O, and 3S](image)

of 3\(^{O}\) 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 3\(^{N}\), which has a longer Ir–C bond of 2.027(4) Å. These two structures have approximate C\(_2\) geometries, while 3\(^{S}\) 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 3\(^{O}\) to 3\(^{S}\) 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” 3\(^{N}\) to be favored over “orthogonal” 3\(^{S}\) by a significant 12.5 kcal mol\(^{-1}\); the “N” notation reflects the ligand’s orthogonality. The two conformational isomers of both 3\(^{O}\) and 3\(^{S}\) 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\(^{O}\), 1\(^{S}\), and 1\(^{N}\)) with [IrCl\(_2\)Cp*] in the “orthogonal” complexes by using an energy decomposition analysis at the BP86-D3/TZ2P level (C\(_{s}\) symmetry). For comparison, the Ir–carbene bond distances of 3\(^{N}\) and 3\(^{S}\) were fixed to the equilibrium value of 3\(^{O}\) (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 3\(^{N}\) and 3\(^{S}\) than for 3\(^{O}\) (Figure 5 and Table S3). π back-bonding from the metal d\(_{xz}\) orbital into the LUMO of the carbene (p\(_z\) orbital) is instead stronger for 3\(^{O}\) (24%) and 3\(^{S}\) (24%) than for 3\(^{N}\) (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 3\(^{N}\). 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 3\(^{N}\) < 3\(^{O}\) < 3\(^{S}\) population of their carbene fragment orbitals.

In an attempt to quantify the net donation of the 1\(^{N}\), 1\(^{O}\), and 1\(^{S}\) 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.\(^{26}\)

\(^{114.08(14)}\) C, 1114.18(13), C, and 1111.68(13).
We were able to obtain \([\text{IrCl(CO)}_2\text{1}^N]\) (4\(^N\)); Figure 6), but exposure of \([\text{Ir(Cl)}(\text{cod})(2^O)]\) to CO led, unfortunately, to instant decomposition. This observation in itself illustrates the strong acceptor properties of 1\(^O\). Since the TEP of (2040 cm\(^{-1}\)) for 4\(^N\) compares well with the computed value of 2044 cm\(^{-1}\) (BP86-D3/TZ2P geometry), we would have expected a larger TEP for 4\(^O\) on the basis of its calculated value of 2057 cm\(^{-1}\), which is in line with the stronger \(\pi\)-accepting property of 1\(^O\).

Finally, the computed TEP of 2049 cm\(^{-1}\) which is in line with the stronger \(\pi\)-accepting property of 1\(^O\). Its molecular structure, obtained by a single-crystal X-ray structure determination, shows the \(\text{BF}_4^-\) anion to be well separated from the cationic complex (the shortest CH···F contact is 2.366 Å). The Ag\(^+\) complex has approximate \(\sigma\)-donor capacity of \(\sigma\)-acceptor properties of \(\text{IrCl}(\text{cod})\)

Figure 6. Complexes 4\(^N\), 4\(^O\), and 4\(^S\) 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 means of alkene dissociation seemed appealing, the reaction of DBTOF or DBTTF with silver(I) salts invariably led to the unknown silver complexes. Instead, reacting benzo[d]thiophen-7a,7f-diol with a slightly 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 \(\text{BF}_4^-\) anion to be well separated from the cationic complex (the shortest CH···F contact is 2.366 Å). The Ag\(^+\) complex has approximate \(\sigma\)-donor symmetry with two coplanar 1\(^1\) 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-ligated Ag(I) complexes\(^{29}\) 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 the analogy to the Ag-mediated NHC transfer reactions.\(^{30}\) We first pursued iridium complex 2\(^O\), the missing sulfur analogue of 2\(^N\) (see Scheme 2), by transferring one SHC ligand from 5\(^S\) to \([\text{IrCl(cod)}]\); 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 \([\text{IrCl(cod)}]\) did not yield Ir complex 2\(^S\); 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 \([\text{CuBrSMe}_2]\) or \([\text{AuClSMe}_3]\) 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 \(D_{2s}\)-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 transmetalation reagent. The bonding to the d\(^{10}\) group 11 metal cations are governed by electrostatic interactions\(^{32}\) 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 S, S, and S and for the Gold NHC and OHC Complexes [Au(1N)2]+ (8S) and [Au(1O)2]+ (8O)

<table>
<thead>
<tr>
<th>Substance</th>
<th>S8 (Ag)</th>
<th>S8 (Cu)</th>
<th>S8 (Au)</th>
<th>S8 (Au)</th>
<th>S8 (O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE$_{bond}$ (kcal mol$^{-1}$)</td>
<td>2071.0</td>
<td>1869.0</td>
<td>2020.0</td>
<td>2030.0</td>
<td>2011.0</td>
</tr>
<tr>
<td>ΔE$_{del}$ (kcal mol$^{-1}$)</td>
<td>-847.0</td>
<td>-966.0</td>
<td>-1451.0</td>
<td>-1432.0</td>
<td>-1411.0</td>
</tr>
<tr>
<td>ΔE$_{tot}$ (kcal mol$^{-1}$)</td>
<td>-152.2</td>
<td>-193.7</td>
<td>-215.0</td>
<td>-238.9</td>
<td>-205.4</td>
</tr>
</tbody>
</table>

[M(CAAC)$_2$]$_2$⁺ (M = Cu, Ag, Au) complexes, which have been studied by Bertrand and Frenking using the EDA-NOCV scheme and by Weinhold within the NBO model. The main orbital contribution for the SHC complexes (S8, S7, and S6) and for the Gold NHC and OHC complexes [Au(1N)2]+ (8S) and [Au(1O)2]+ (8O) are uncorrected. Solution1H, 13C, 11B, and 1S-Se.)

- **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 S8 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 is and SHC 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-565 Melting Point apparatus and are uncorrected. Solution1H, 13C, 1B, 19F, and 77Se NMR spectra were recorded on Bruker Avance 250 (300 MHz), 400 (H, 13C, 1B, 19F, and 77Se) and 500 (H, 13C) spectrometers at 298 K, unless otherwise stated. Chemical shifts (δ) are expressed with a positive sign, in parts per million. Solution1H and 13C chemical shifts were referenced internally to residual protio (1H) or deuterio (13C) solvent, while 1B, 19F, and 77Se chemical shifts are relative to BF$_3$Et$_2$O, CFCl$_3$, and 0.25 mol/L KSeCN (aqueous, −329 ppm) external references, respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. The 1H and 13C resonance signals and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. The 1H and 13C resonances were attributed by means of 2D HSQC and HMBC experiments when necessary. Infrared spectra were recorded with a Shimadzu FT-IR 8400S spectrometer. Vibrational bands (ν) are expressed in cm$^{-1}$. ElectrospRAY ionization (ESI) mass spectra were recorded on a Bruker Daltonics microTOF apparatus in positive ion mode (capillary potential of 4500 V), Benzo-1,3-dioxole-2-2-seleno (1S-2Se).
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. Mp: 115–117 °C dec. H NMR (400 MHz, CDCl₃): δ 7.57 (m, 2H, H₃ or H₄), 7.40 (m, 2H, H₅ or H₆), 7.35 (m, 2H, H₇), 2.60 (m, 8H, H₆ or H₇). ¹³C({¹H} NMR (100 MHz, CDCl₃) δ 209.2 (s, C₁), 146.7 (s, C₂), 126.5 (s, C₅ or C₆), 111.8 (s, C₄ or C₅), 104.7 (s, C₆), 56.1 (s, C₇), 33.6 (s, C₁ or C₂), 29.4 (s, C₃ or C₄). IR (ATR): ν 3097, 3057, 3018, 2952, 2880, 2833, 1466, 1333, 1194, 1049, 746. HRMS (ESI+): calcld for [M + Cl]⁺ = C₁₁H₁₂ClN₂, 241.0774; found, 241.0785.

3. A solution of bis(1,3-dimethylbenzimidazolidin-2-ylidine) (29.2 mg, 0.10 mmol, 1.0 equiv) in toluene (1 mL) was added to a solution of [IrCl(Cp*)] (79.7 mg, 0.10 mmol, 1.0 equiv) in toluene (1 mL). The reaction mixture was stirred for 4 h at 100 °C and then for 2 days at room temperature in order to ensure full conversion and limit thermal decomposition. The resulting yellow precipitate was isolated by filtration, washed with diethyl ether (3 × 2 mL), and dried under vacuum to give 3. Yield: 95 mg (88%). Crystals suitable for X-ray crystallography were grown at room temperature by vapor diffusion of pentane into a concentrated solution of 3 in dichloromethane. Mp: 334 °C. H NMR (400 MHz, CDCl₃): δ 7.37 (m, 2H, H₃ or H₄), 7.30 (m, 2H, H₅ or H₆), 4.17 (s, 6H, HN or CN) and 1H NMR (400 MHz, CDCl₃): 1.84 (s, 15H, CH₃). IR (ATR): ν 1444, 1375, 1344, 766, 743. HRMS (ESI+): calcld for [M − Cl]⁻ = C₁₀H₁₁ClN₂, 231.0 (s, C₁), 150.1 (s, C₂), 127.5 (s, C₃), 123.3 (s, C₄), 92.8 (s, C₅ or C₆), 87.2 (s, C₇ or C₈). IR (ATR): ν 3061, 2983, 2964, 2918, 1751, 1491, 1435, 1421, 1400, 1373, 1027, 939, 875, 777. HRMS (ESI+): calcld for [M − Cl]⁻ = C₁₀H₁₁ClN₂, 219.0230; found, 219.0250.

4. Iridium NHC(COD) complex 2 (55 mg, 0.11 mmol, 1.0 equiv) was transferred into a Schlenk flask and solubilized in dichloromethane (25 mL). CO gas was bubbled through the solution for 10 min. Volatiles were removed in vacuo. The yellow residue was washed with pentane (3 × 2 mL) and dried under vacuum to give 4. Yield: 43 mg (91%). Mp: 158–159 °C dec. ¹H NMR (500 MHz, CDCl₃): δ 7.49 (m, 2H, H₃ or H₄), 7.43 (m, 2H, H₅ or H₆), 4.10 (s, 6H, HN). ¹³C({¹H} NMR (126 MHz, CDCl₃) δ 183.4 (s, C₁), 182.3 (s, CO₂), 168.5 (s, CO₃), 153.1 (s, C₃), 124.4 (s, C₄ or C₅), 111.1 (s, C₆ or C₇), 35.4 (s, C₈). IR (ATR): ν 2947, 2054, 1969, 1456, 1338, 1130, 1094, 766, 743. HRMS (ESI+): calcld for [M + H⁺] = C₁₀H₁₁IrClN₂O₃, 431.0125; found, 431.129.

5. Benzodithiolium tetrafluoroborate (500 mg, 2.08 mmol, 1.0 equiv) and silver(I) 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 5 as a grey solid. Yield: 473 mg (91%). Crystals of poor but sufficient quality for X-ray crystallography were grown by slow vapor diffusion of hexane 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 dibenzotetrazolofulvalene 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.

6. The iridium dimer complex (67.3 mg, 0.10 mmol, 1.0 equiv) and 5 (100.0 mg, 0.22 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 subsequently rinsed with dichloromethane (20 mL). The clear brown solution was concentrated under vacuum to a volume of ca. 2 mL. Addition of pentane (20 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 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: >70 °C dec. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (m, 4H, H₃ or H₄), 7.82 (m, 4H, H₅ or H₆), 7.36 (m, 4H, H₇ or H₈). ¹³C({¹H} NMR (100 MHz, CDCl₃) δ 150.6 (s, C₁), 129.3 (s, C₂ or C₃), 125.2 (s, C₄ or C₅), C₆ or C₇ not detected. ¹⁹F{¹H} NMR (128 MHz, CDCl₃) δ -1.2 (s, BF₄). ¹⁹F{¹H} NMR (235 MHz, CDCl₃) δ -151.7 (s). IR (ATR): ν 3090, 3055, 1439, 1427, 1088, 1030, 964, 950, 758. HRMS (ESI+): calcld for [M − BF₄]⁻ = C₁₀H₈AgS₂, 410.8554; found, 410.8548.

7. Dichloromethane (10 mL) was slowly added to a copper bromide dimethyl sulfoxide complex (41.2 mg, 0.22 mmol, 1.0 equiv) and 5 (100 mg, 0.20 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 7 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, H₃ or H₄), 7.84–7.82 (m, 4H, H₅ or H₆). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 235.4 (s, C₁), 149.7 (s, C₅), 129.1 (s, C₆ or C₇).
Yield: 52 mg (88%). Mp: 110°.

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°.

The crystal structures were determined on a Bruker D8 Venture detector at 123(2) K using Mo Kα radiation (300, 0.1 mmol, 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°.

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