Electronic Supporting Information

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

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Supplementary Computational Details


1.0.1 Frontier Orbitals of $1^N$, $1^O$ and $1^S$

Table S1. Energy levels and plots of HOMO and LUMO for $1^N$, $1^O$ and $1^S$. Contour value: 0.1 a.u. Computed at B3LYP/TZVP.

<table>
<thead>
<tr>
<th></th>
<th>$1^N$</th>
<th>$1^O$</th>
<th>$1^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LUMO</strong></td>
<td>-0.74 eV</td>
<td>-1.56 eV</td>
<td>-1.89 eV</td>
</tr>
<tr>
<td><strong>HOMO</strong></td>
<td>-6.05 eV</td>
<td>-7.36 eV</td>
<td>-6.79 eV</td>
</tr>
</tbody>
</table>
### Determination of TEPs for $2^N$, $2^O$ and $2^S$

**Table S2.** Calculated and experimental CO stretching frequencies (in cm$^{-1}$) for the [IrCl(CO)$_2$(L)] complexes with $L=L^N$ and $L^O$ and corresponding TEPs.

<table>
<thead>
<tr>
<th></th>
<th>$2^N$: [IrCl(CO)$_2$(1$^N$)]</th>
<th>$2^O$: [IrCl(CO)$_2$(1$^O$)]</th>
<th>$2^S$: [IrCl(CO)$_2$(1$^S$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_s$ (calc.) / $v_{as}$ (calc.)</td>
<td>2052 / 1980</td>
<td>2069 / 1997</td>
<td>2058 / 1987</td>
</tr>
<tr>
<td>$v_{mean}$ (calc.)</td>
<td>2016</td>
<td>2033</td>
<td>2023</td>
</tr>
<tr>
<td>TEP (calc.)*</td>
<td>2044</td>
<td>2057</td>
<td>2049</td>
</tr>
<tr>
<td>$v_s$ (exp.) / $v_{as}$ (exp.)</td>
<td>2054 / 1980</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>$v_{mean}$ (exp.)</td>
<td>2012</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>TEP (exp.)*</td>
<td>2040</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*obtained via the following relationship, as established by Nolan et al.:[1]

$y = 0.847 \times + 336$ cm$^{-1}$

with $y$ corresponding to the TEP and $x$ to $v_{mean}$ of the Ir carbonyl complex.
1.0.3 Energy Decomposition Analysis of $3^N$, $3^O$ and $3^S$

The complexes $3^N$, $3^O$ and $3^S$ were optimized in their “orthogonal” conformations in $C_s$ symmetry (with the carbene coplanar with the mirror plane bisecting the $[\text{IrCl}_2\text{Cp}^*]$ fragment); the bonding was studied by means of EDA calculations. The $C_s$-optimized structures allowed symmetry partitioning between $\sigma$- and $\pi$-contributions to the orbital interaction energy $\Delta E_{oi}$. The $\sigma$-contribution (coplanar with the mirror plane) corresponds then to the irreproducible representation $a'$, while the $\pi$-contribution (perpendicular to the symmetry plane) is described by $a''$.

Table S3. Energy decomposition analyses and calculated bond dissociation energies (BDEs) for $3^N$ (at the equilibrium Ir-$\text{C}_\text{carbene}$ bond distance and at the equilibrium bond distance of the OHC in $3^O$), $3^O$ and $3^S$ (at the equilibrium Ir-$\text{C}_\text{carbene}$ bond distance and at the equilibrium bond distance of the OHC in $3^O$). Energies are given in kcal/mol.

<table>
<thead>
<tr>
<th></th>
<th>$3^N$</th>
<th>$3^N$</th>
<th>$3^O$</th>
<th>$3^O$</th>
<th>$3^S$</th>
<th>$3^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{Ir-carbene}}$</td>
<td>2.053 Å</td>
<td>1.906 Å</td>
<td>1.906 Å</td>
<td>1.962 Å</td>
<td>1.906 Å</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{prep}}$</td>
<td>62.48</td>
<td>58.41</td>
<td>66.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{a'}$</td>
<td>-88.46</td>
<td>-112.13</td>
<td>-108.39</td>
<td>-102.68</td>
<td>-113.33</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{a''}$</td>
<td>-15.48</td>
<td>-24.40</td>
<td>-33.98</td>
<td>-30.36</td>
<td>-35.46</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{orb}}$</td>
<td>-103.94</td>
<td>-136.54</td>
<td>-142.37</td>
<td>-133.04</td>
<td>-148.80</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{elstat}}$</td>
<td>-215.39</td>
<td>-312.36</td>
<td>-250.03</td>
<td>-231.50</td>
<td>-268.08</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{Pauli}}$</td>
<td>262.33</td>
<td>398.28</td>
<td>323.36</td>
<td>295.94</td>
<td>348.97</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{disp}}$</td>
<td>-15.21</td>
<td>-15.60</td>
<td>-8.45</td>
<td>-10.36</td>
<td>-10.33</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{\text{bond}}$</td>
<td>-72.21</td>
<td>-66.22</td>
<td>-77.49</td>
<td>-78.96</td>
<td>-78.24</td>
<td></td>
</tr>
<tr>
<td>BDE</td>
<td>9.73</td>
<td>19.08</td>
<td>12.76</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The influence of sterics on the Ir-carbene bond in case of the NHC ligand is furthermore exemplified by replacing the Cp* ligand by less bulky Cp, resulting in a shortening of the Ir-C bond and a simultaneous increase of the σ-donation contribution to the bonding interaction. For a discussion on the strength of metal-NHC bonds depending on the steric properties of NHC ligands, see also ref. [24] and references therein.

**Table S4.** Energy decomposition analyses for [IrCl2CpNHC], [IrCl2CpOHC] and [IrCl2CpSHC]. Energies are given in kcal/mol.

<table>
<thead>
<tr>
<th></th>
<th>[IrCl2CpNHC]</th>
<th>[IrCl2CpOHC]</th>
<th>[IrCl2CpSHC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Ir-C\text{carbene})=2.036 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE_{a'}</td>
<td>-97.66</td>
<td>-108.53</td>
<td>-108.68</td>
</tr>
<tr>
<td>ΔE_{a''}</td>
<td>-15.58</td>
<td>-28.67</td>
<td>-26.51</td>
</tr>
<tr>
<td>ΔE_{orb}</td>
<td>-113.24</td>
<td>-137.20</td>
<td>-135.16</td>
</tr>
<tr>
<td>ΔE_{elstat}</td>
<td>-226.67</td>
<td>-245.79</td>
<td>-244.85</td>
</tr>
<tr>
<td>ΔE_{Pauli}</td>
<td>276.99</td>
<td>321.06</td>
<td>318.12</td>
</tr>
<tr>
<td>ΔE_{disp}</td>
<td>-12.78</td>
<td>-6.69</td>
<td>-8.58</td>
</tr>
<tr>
<td>ΔE_{bond}</td>
<td>-75.70</td>
<td>-68.62</td>
<td>-70.48</td>
</tr>
</tbody>
</table>
1.0.1 Bond Analysis of Coinage Metal Bis(carbene) Complexes

The cations of the coinage metal complexes $^7\text{S}$ (Cu), $^5\text{S}$ (Ag) and $^8\text{S}$ (Au) were optimized in D$_{2h}$ symmetry; the bonding was studied by means of EDA calculations. The C$_s$-optimized structures allowed symmetry partitioning between $\sigma$- and $\pi$-contributions to the orbital interaction energy $\Delta E^{oi}$. The $\sigma$-contribution corresponds then to the irreproducible representation a$_g$ (and b$_{1u}$), while the $\pi$-contribution is described by b$_{2g}$ (and b$_{3u}$).

Table S5. Energy decomposition analyses and computed bond distances for the cations of $^7\text{N}$, $^7\text{O}$ and $^7\text{S}$. Energies are given in kcal/mol, distances in Å.

<table>
<thead>
<tr>
<th></th>
<th>[Cu($^7\text{N}$)$_2$]$^+$</th>
<th>[Cu($^7\text{O}$)$_2$]$^+$</th>
<th>[Cu($^7\text{S}$)$_2$]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{bond}}$</td>
<td>-214.06</td>
<td>-183.20</td>
<td>-193.69</td>
</tr>
<tr>
<td>$\Delta E_{\text{orb}}$</td>
<td>-143.23</td>
<td>-138.08</td>
<td>-149.10</td>
</tr>
<tr>
<td>$\Delta E_{\sigma}$</td>
<td>-93.56</td>
<td>90.93</td>
<td>-96.57</td>
</tr>
<tr>
<td>$\Delta E_{\pi}$</td>
<td>-31.63</td>
<td>32.50</td>
<td>-34.07</td>
</tr>
<tr>
<td>$\Delta E_{\text{elstat}}$</td>
<td>-282.93</td>
<td>-252.15</td>
<td>-258.61</td>
</tr>
<tr>
<td>$\Delta E_{\text{Pauli}}$</td>
<td>221.37</td>
<td>209.38</td>
<td>-218.57</td>
</tr>
<tr>
<td>$\Delta E_{\text{disp}}$</td>
<td>-9.32</td>
<td>-2.38</td>
<td>-4.56</td>
</tr>
<tr>
<td>$\Delta E_{\sigma} / \Delta E_{\pi}$</td>
<td>3.0</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Distance Cu-C</td>
<td>1.888</td>
<td>1.873</td>
<td>1.869</td>
</tr>
</tbody>
</table>
Table S6. Energy decomposition analyses and computed bond distances for the cations of 5N, 5O and 5S. Energies are given in kcal/mol, distances in Å.

<table>
<thead>
<tr>
<th></th>
<th>[Ag(1N)2]^+</th>
<th>[Ag(1O)2]^+</th>
<th>[Ag(1S)2]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_{bond}</td>
<td>-172.80</td>
<td>-144.09</td>
<td>-152.20</td>
</tr>
<tr>
<td>ΔE_{orb}</td>
<td>-123.44</td>
<td>-114.83</td>
<td>-122.94</td>
</tr>
<tr>
<td>ΔE_{σ}</td>
<td>-85.08</td>
<td>80.54</td>
<td>-84.73</td>
</tr>
<tr>
<td>=ΔE_{ag^+}ΔE_{b1u}</td>
<td>-68.61-16.47</td>
<td>-63.85-16.69</td>
<td>-66.85-17.88</td>
</tr>
<tr>
<td>ΔE_{π}</td>
<td>-23.28</td>
<td>22.06</td>
<td>-23.09</td>
</tr>
<tr>
<td>=ΔE_{b2g^+}ΔE_{b3u}</td>
<td>-12.96-10.32</td>
<td>-13.90-8.16</td>
<td>-13.08-10.01</td>
</tr>
<tr>
<td>ΔE_{elstat}</td>
<td>-276.75</td>
<td>-236.77</td>
<td>-242.52</td>
</tr>
<tr>
<td>ΔE_{Pauli}</td>
<td>236.54</td>
<td>212.75</td>
<td>220.10</td>
</tr>
<tr>
<td>ΔE_{disp}</td>
<td>-9.16</td>
<td>-5.22</td>
<td>-6.82</td>
</tr>
<tr>
<td>ΔE_{σ} / ΔE_{π}</td>
<td>3.7</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Distance Ag-C</td>
<td>2.076</td>
<td>2.070</td>
<td>2.071</td>
</tr>
</tbody>
</table>
Table S7. Energy decomposition analyses and computed bond distances for the cations of 8N, 8O and 8S. Energies are given in kcal/mol, distances in Å.

<table>
<thead>
<tr>
<th></th>
<th>[Au(1N)₂]⁺</th>
<th>[Au(1O)₂]⁺</th>
<th>[Au(1S)₂]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE(_{\text{bond}})</td>
<td>-238.88</td>
<td>-205.39</td>
<td>-215.02</td>
</tr>
<tr>
<td>ΔE(_{\text{orb}})</td>
<td>-193.16</td>
<td>-190.11</td>
<td>-197.49</td>
</tr>
<tr>
<td>ΔE(_{\sigma})</td>
<td>-143.15</td>
<td>-141.10</td>
<td>-145.09</td>
</tr>
<tr>
<td>=ΔE(<em>{\text{ag}})+ΔE(</em>{\text{b1u}})</td>
<td>-123.38-19.77</td>
<td>-120.71-20.39</td>
<td>-123.24-21.85</td>
</tr>
<tr>
<td>ΔE(_{\pi})</td>
<td>-31.13</td>
<td>-32.02</td>
<td>-32.32</td>
</tr>
<tr>
<td>ΔE(_{\text{elstat}})</td>
<td>-388.12</td>
<td>-347.79</td>
<td>350.30</td>
</tr>
<tr>
<td>ΔE(_{\text{Pauli}})</td>
<td>354.17</td>
<td>338.26</td>
<td>340.34</td>
</tr>
<tr>
<td>ΔE(_{\text{disp}})</td>
<td>-11.11</td>
<td>-5.74</td>
<td>-7.54</td>
</tr>
<tr>
<td>ΔE(<em>{\sigma}/ΔE</em>{\pi})</td>
<td>4.6</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>Distance Au-C</td>
<td>2.030</td>
<td>2.011</td>
<td>2.020</td>
</tr>
</tbody>
</table>
Optimized Structures
Coordinate are given in the xyz file. Only transition metal complexes are displayed.

1.1.1 [IrCl(cod)L] Complexes

\[
\begin{align*}
\text{[IrCl(CO)\textsubscript{2}NHC] (2\textsuperscript{N})} & \quad E: -9.585209011778973 \text{ a.u.} \\
\text{[IrCl(CO)\textsubscript{2}OHC] (2\textsuperscript{O})} & \quad E: -7.947041970035843 \text{ a.u.}
\end{align*}
\]

1.1.2 [IrCl(CO)\textsubscript{2}L] Complexes

\[
\begin{align*}
\text{[IrCl(CO)\textsubscript{2}NHC] (4\textsuperscript{N})} & \quad E: -6.520127907299566 \text{ a.u.} \\
\text{[IrCl(CO)\textsubscript{2}OHC] (4\textsuperscript{O})} & \quad E: -4.871662382774268 \text{ a.u.} \\
\text{[IrCl(CO)\textsubscript{2}S\textsubscript{HC}] (4\textsuperscript{S})} & \quad E: -4.694431724551164 \text{ a.u.}
\end{align*}
\]
1.1.3 $[\text{IrCl}_2\text{Cp}^*\text{L}]$ Complexes

$[\text{IrCl}_2\text{Cp}^*\text{NHC}]$ “parallel” / “horizontal”

E: -10.79186795 a.u.

$[\text{IrCl}_2\text{Cp}^*\text{NHC}]$ “orthogonal” / “vertical”

E: -10.77076204 a.u.

$[\text{IrCl}_2\text{Cp}^*\text{OHC}]$ “parallel” / “horizontal”

E: -9.15032400 a.u.

$[\text{IrCl}_2\text{Cp}^*\text{OHC}]$ “orthogonal” / “vertical”

E: -9.15417340 a.u.

$[\text{IrCl}_2\text{Cp}^*\text{SHC}]$ “parallel” / “horizontal”

E: -8.97566707 a.u.

$[\text{IrCl}_2\text{Cp}^*\text{SHC}]$ “orthogonal” / “vertical”

E: -8.93568192 a.u.
1.1.4 [IrCl$_2$CpL] Complexes

[IrCl$_2$CpNHC] “parallel” / “horizontal”

E: -7.7170697 a.u.

[IrCl$_2$CpOHC] “parallel” / “horizontal”

E: -6.08876171 a.u.

[IrCl$_2$CpSHC] “parallel” / “horizontal”

E: -5.91056130 a.u.
1.1.5 Coinage Metal Bis(carbene) Complexes

\[
\begin{align*}
[Cu(SHC)_2]^+ & \quad (7^S) \\
E: & \quad -8.97566707 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Ag(SHC)_2]^+ & \quad (5^S) \\
E: & \quad -8.93568192 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Au(SHC)_2]^+ & \quad (8^S) \\
E: & \quad -8.97566707 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Cu(NHC)_2]^+ & \quad (7^N) \\
E: & \quad -8.93568192 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Ag(NHC)_2]^+ & \quad (5^N) \\
E: & \quad -8.97566707 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Au(NHC)_2]^+ & \quad (8^N) \\
E: & \quad -8.93568192 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Cu(OHC)_2]^+ & \quad (7^O) \\
E: & \quad -8.97566707 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Ag(OHC)_2]^+ & \quad (5^O) \\
E: & \quad -8.93568192 \text{ a.u.}
\end{align*}
\]

\[
\begin{align*}
[Au(OHC)_2]^+ & \quad (8^O) \\
E: & \quad -8.97566707 \text{ a.u.}
\end{align*}
\]
**Figure S1.** $^1$H NMR spectrum of 1$^N$-Se. The signal of residual CHCl$_3$ overlaps with the signal corresponding to the aromatic protons of 1$^N$-Se.
Figure S2. J-modulated $^{13}$C{$^{1}$H} NMR spectrum of $^{1}$N-Se.
Figure S3. $^{77}$Se$^{1\text{H}}$ NMR spectrum of $1^\text{N}$-Se.

Figure S4. $^1\text{H}$ NMR spectrum of $1^\text{O}$-Se.
Figure S5. J-modulated $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $^{1}\text{O}_{\text{Se}}$.

Figure S6. $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of $^{1}\text{O}_{\text{Se}}$. 
Figure S7. $^{1}$H NMR spectrum of 1$^8$-Se.

Figure S8. J-modulated $^{13}$C$^{1}$H NMR spectrum of 1$^8$-Se.
Figure S9. $^{77}$Se\{H\} NMR spectrum of $^{1}$Se-Se.

Figure S9. $^{1}$H NMR spectrum of $^{2}$N.
Figure S10. J-modulated $^{13}$C{1H} NMR spectrum of $2^N$.

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Figure S10. $^1$H NMR spectrum of $2^O$. Traces of cod are present.
Figure S11. J-modulated $^{13}$C{\textsuperscript{1}H} NMR spectrum of $2^0$.

Figure S12. $^1$H NMR spectrum of $3^N$. 
Figure S13. J-modulated $^{13}$C/$^1$H NMR spectrum of $3^N$.

Figure S14. $^1$H NMR spectrum of $3^O$. 
Figure S15. J-modulated $^{13}$C{$^1$H} NMR spectrum of $3^0$.

Figure S16. $^1$H NMR spectrum of $3^8$. 
Figure S17. J-modulated $^{13}$C{$^1$H} NMR spectrum of 3$^S$.

Figure S18. $^1$H NMR spectrum of 4$^N$. 

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Figure S19. J-modulated $^{13}C\{^1H\}$ NMR spectrum of $4^N$.

Figure S19. $^1H$ NMR spectrum of $5^S$.
Figure S20. J-modulated $^{13}$C{$^1$H} NMR spectrum of 5$.\textsuperscript{8}$

Figure S21. $^1$H NMR spectrum of 6$.\textsuperscript{8}$. 
Figure S22. J-modulated $^{13}$C{${}^1$H} NMR spectrum of 6S.

Figure S23. $^1$H NMR spectrum of 7S.
Figure S24. J-modulated $^{13}$C{${}^1$H} NMR spectrum of 7$^8$.

Figure S25. $^1$H NMR spectrum of 8$^8$. 

S27
Figure S26. J-modulated $^{13}$C{¹H} NMR spectrum of $8^S$.

Figure S27. Stacked $^1$H NMR spectra of $7^S$, $5^S$ and $8^S$ in CD$_2$Cl$_2$. 
Selected Crystallographic Data

2O: red crystals, C15H16ClIrO2, Mr = 455.93, crystal size 0.20 × 0.08 × 0.04 mm, monoclinic, space group P21/c (No. 14), a = 10.1091(5) Å, b = 12.2077(7) Å, c = 10.8064(7) Å, β = 99.320(2)°, V = 1316.00(13) Å3, Z = 4, ρ = 2.301 Mg/m³, μ(Mo-Kα) = 10.342 mm⁻¹, F(000) = 864, 2θmax = 55.0°, 26417 reflections, of which 3018 were independent (Rint = 0.040), 173 parameters, R1 = 0.018 (for 2742 I > 2σ(I)), wR2 = 0.044 (all data), S = 1.07, largest diff. peak / hole = 1.899 / -1.300 e Å⁻³.

2N: yellow crystals, C17H22ClIrN2 ∙ CH₂Cl₂, Mr = 566.94, crystal size 0.18 × 0.10 × 0.04 mm, orthorhombic, space group Pbca (No. 61), a = 15.3074(7) Å, b = 15.3703(7) Å, c = 16.2915(8) Å, V = 3833.1(3) Å³, Z = 8, ρ = 1.965 Mg/m³, μ(Mo-Kα) = 7.387 mm⁻¹, F(000) = 2192, 2θmax = 55.2°, 148517 reflections, of which 4414 were independent (Rint = 0.034), 220 parameters, R1 = 0.014 (for 4011 I > 2σ(I)), wR2 = 0.030 (all data), S = 1.06, largest diff. peak / hole = 0.726 / -0.596 e Å⁻³.

3N: yellow crystals, C19H25Cl2IrN2, Mr = 544.51, crystal size 0.20 × 0.04 × 0.04 mm, orthorhombic, space group P2₁2₁2₁ (No. 19), a = 8.6776(3) Å, b = 13.5060(5) Å, c = 16.6034(6) Å, V = 1945.91(12) Å³, Z = 4, ρ = 1.859 Mg/m³, μ(Mo-Kα) = 7.139 mm⁻¹, F(000) = 1056, 2θmax = 55.0°, 16635 reflections, of which 4456 were independent (Rint = 0.025), 226 parameters, R1 = 0.017 (for 4330 I > 2σ(I)), wR2 = 0.034 (all data), S = 1.11, largest diff. peak / hole = 1.042 / -0.846 e Å⁻³.

3O: orange crystals, C17H19Cl2IrO2, Mr = 518.42, crystal size 0.16 × 0.12 × 0.04 mm, monoclinic, space group P21/c (No. 14), a = 7.7486(5) Å, b = 20.3828(13) Å, c = 11.1329(8) Å, β = 99.343(2)°, V = 1735.0(2) Å³, Z = 4, ρ = 1.985 Mg/m³, μ(Mo-Kα) = 8.007 mm⁻¹, F(000) = 992, 2θmax = 55.2°, 98402 reflections, of which 3990 were independent (Rint = 0.023), 205 parameters, R1 = 0.012 (for 3911 I > 2σ(I)), wR2 = 0.026 (all data), S = 1.23, largest diff. peak / hole = 0.572 / -0.478 e Å⁻³.

3S: orange crystals, C17H17Cl2IrS2, Mr = 550.54, crystal size 0.36 × 0.27 × 0.18 mm, orthorhombic, space group Pbca (No. 61), a = 14.1248(8) Å, b = 15.8887(8) Å, c = 16.1578(8) Å, V = 3626.2(3) Å³, Z = 8, ρ = 2.017 Mg/m³, μ(Mo-Kα) = 7.882 mm⁻¹, F(000) = 2112, 2θmax = 55.2°, 40129 reflections, of which 4184 were independent (Rint = 0.039), 205 parameters, R1 = 0.018 (for 3852 I > 2σ(I)), wR2 = 0.041 (all data), S = 1.13, largest diff. peak / hole = 0.989 / -0.971 e Å⁻³.
5S: [C₁₄H₈AgS₄](BF₄), Fw = 499.12, yellow needle, 0.33 × 0.08 × 0.06 mm³, monoclinic, P2₁/c (no. 14), a = 14.6784(13), b = 14.2406(11), c = 7.7488(5) Å, β = 91.219(4) °, V = 1619.4(2) Å³, Z = 4, Dₓ = 2.047 g/cm³, µ = 1.80 mm⁻¹. The crystal appeared to be twinned with a twofold rotation about hkl=(1,0,0) as twin operation. Consequently, two orientation matrices were used for the integration with the Eval15 software.³ 33861 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹. Multiscan absorption correction and scaling was performed with TWINABS³ (correction range 0.33-0.43). 3717 Reflections were unique (Rint = 0.048), of which 3151 were observed [I>2σ(I)]. The structure was solved with Patterson overlay methods using SHELXT.⁴ Least-squares refinement was performed with SHELXL-2014 against F² of all reflections using a HKLF-5 reflection file.⁵ Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 218 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0611 / 0.1845. R1/wR2 [all refl.]: 0.0710 / 0.1983. S = 1.111. Batch scale factor of the second twin fragment BASF = 0.314(3). Residual electron density between -0.82 and 2.66 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.⁶

Notable are the C-Ag bond distances of 2.115(7) and 2.103(6) Å in the upper range of comparable bis-NHC ligated Ag(I) complexes. The bond distances of the NHC complexes are however influenced by repulsive steric interactions between the two ligands, absent in case of the SHC complexes. (A CCDC database search revealed that C-Ag bond bond distances of structurally characterized linear Ag bis(NHC) complexes span ca. from 2.017 Å to 2.161 Å.)

6S: orange crystals, C₂₂H₂₀IrS₄ · BF₄ · 1.5 C₆H₅F, Mr = 835.78, crystal size 0.20 × 0.12 × 0.06 mm, orthorhombic, space group Pbcm (No. 57), a = 8.5330(4) Å, b = 18.6546(10) Å, c = 38.1239(5) Å, V = 6068.6(5) Å³, Z = 8, ρ = 1.830 Mg/m³, µ(Mo-Kα) = 4.731 mm⁻¹, F(000) = 3272, 2θmax = 55.2°, 43575 reflections, of which 7094 were independent (Rint = 0.036), 405 parameters, 56 restraints, R1 = 0.045 (for 6485 I > 2σ(I)), wR2 = 0.083 (all data), S = 1.24, largest diff. peak / hole = 3.303 / -4.664e Å⁻³ (bad quality of the data, see cif-file for details).
Fig. X-Ray1. Molecular structure of $2^0$ (displacement parameters are drawn at 50% probability level).
**Fig. X-Ray2.** Molecular structure of $2^N$ (displacement parameters are drawn at 50% probability level).

**Fig. X-Ray3.** Molecular structure of $3^N$ (displacement parameters are drawn at 50% probability level).

**Fig. X-Ray4.** Molecular structure of $3^O$ (displacement parameters are drawn at 50% probability level).
**Fig. X-Ray5.** Molecular structure of $3^S$ (displacement parameters are drawn at 50 % probability level).

**Fig. X-Ray6.** Molecular structure of $5^S$ (displacement parameters are drawn at 50 % probability level).
Fig. X-Ray7. Molecular structure of $6^5$ (displacement parameters are drawn at 50% probability level).
References


