Organometallic Benzylidene Anilines: Donor-Acceptor Features in NCN-Pincer Pt(II) Complexes with a 4-(E)-[(4-R-phenyl)imino]methyl substituent††

Guido D. Batema,[a] Martin Lutz,[b] † Anthony L. Spek,[b] ‡ Cornelis A. van Walree,[a,c] Gerard P. M. van Klink,[a, d] and Gerard van Koten*[a]

Table S1. UV/Vis data of PtCl[NCN(CH=NC6H4R’-4’)-4] 1–5.[a]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1 (R’ = NMe2)</th>
<th>2 (R’ = Me)</th>
<th>3 (R’ = H)</th>
<th>4 (R’ = Cl)</th>
<th>5 (R’ = CN)</th>
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</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>383 (40)</td>
<td>350 (47)</td>
<td>350</td>
<td>353 (32)</td>
<td>361</td>
</tr>
<tr>
<td></td>
<td>335 (22)</td>
<td>234 (26)</td>
<td>254</td>
<td>293</td>
<td>244</td>
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<tr>
<td></td>
<td>240 (23)</td>
<td>207 (47)</td>
<td>237</td>
<td>236</td>
<td>202</td>
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<tr>
<td></td>
<td>204 (49)</td>
<td></td>
<td>203</td>
<td>205</td>
<td></td>
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<tr>
<td>Dichloromethane</td>
<td>386 (40)</td>
<td>355 (41)</td>
<td>353 (25)</td>
<td>358 (32)</td>
<td>367 (37)</td>
</tr>
<tr>
<td></td>
<td>334 (23)</td>
<td>245 (18)</td>
<td>254 (10)</td>
<td>292 (7)</td>
<td>246 (21)</td>
</tr>
<tr>
<td></td>
<td>243 (24)</td>
<td></td>
<td></td>
<td>252 (12)</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>386 (40)</td>
<td>357 (41)</td>
<td>357 (45)</td>
<td>362 (55)</td>
<td>372 (49)</td>
</tr>
<tr>
<td></td>
<td>339 (22)</td>
<td>292 (11)</td>
<td>292 (11)</td>
<td>294 (15)</td>
<td>294 (18)</td>
</tr>
<tr>
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<td>257 (14)</td>
<td>259 (9)</td>
<td>258 (12)</td>
<td>258 (18)</td>
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<td>Ethyl acetate</td>
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<td>354</td>
<td>354</td>
<td>358</td>
<td>367</td>
</tr>
<tr>
<td></td>
<td>338 (20)</td>
<td>286</td>
<td>287</td>
<td>291</td>
<td>298</td>
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<tr>
<td></td>
<td>280 (17)</td>
<td>254</td>
<td>255</td>
<td>257</td>
<td>265</td>
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<td></td>
<td>257 (20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>384</td>
<td>354</td>
<td>354</td>
<td>360</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>337</td>
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<td>286</td>
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<td></td>
<td>237</td>
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<td>233</td>
<td>254</td>
<td>252</td>
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<tr>
<td>Benzene</td>
<td>392 (37)</td>
<td>359 (41)</td>
<td>357</td>
<td>362 (45)</td>
<td>372</td>
</tr>
<tr>
<td></td>
<td>338 (22)</td>
<td>288 (10)</td>
<td>290</td>
<td>294 (11)</td>
<td>303</td>
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<tr>
<td></td>
<td>283 (11)</td>
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</tbody>
</table>

[a] Absorption wavelength (in nm) at room temperature in air-saturated solutions (c = ×10⁻⁵ M), absorption coefficient between brackets (ε in ×10³ M⁻¹ cm⁻¹).

Table S2. Experimental details for the X-ray crystal structure determinations

<table>
<thead>
<tr>
<th>compound</th>
<th>2</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
</table>
| Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2014
<table>
<thead>
<tr>
<th></th>
<th>C₂₀H₂₆Cl₃N₃Pt</th>
<th>C₁₀H₂₃Cl₂N₃Pt</th>
<th>C₂₀H₂₃ClN₄Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>fw</td>
<td>538.98</td>
<td>559.39</td>
<td>549.96</td>
</tr>
<tr>
<td>crystal colour</td>
<td>orange</td>
<td>orange</td>
<td>yellow</td>
</tr>
<tr>
<td>crystal size [mm³]</td>
<td>0.39 × 0.18 × 0.09</td>
<td>0.27 × 0.27 × 0.09</td>
<td>0.30 × 0.15 × 0.08</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P₂₁/c (no. 14)</td>
<td>P₂₁/c (no. 14)</td>
<td>P₂₁/c (no. 14)</td>
</tr>
<tr>
<td>a [Å]</td>
<td>18.2341(6)</td>
<td>18.1760(4)</td>
<td>18.3716(7)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>8.9441(5)</td>
<td>8.9325(3)</td>
<td>9.1309(4)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>11.9240(6)</td>
<td>11.8834(3)</td>
<td>11.5847(3)</td>
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<td>β [°]</td>
<td>95.965(2)</td>
<td>94.713(3)</td>
<td>94.535(1)</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>1934.13(3)</td>
<td>1922.84(3)</td>
<td>1937.24(12)</td>
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<tr>
<td>Z</td>
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<tr>
<td>Dₓ [g/cm³]</td>
<td>1.851</td>
<td>1.932</td>
<td>1.886</td>
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<tr>
<td>µ [mm⁻¹]</td>
<td>7.400</td>
<td>7.582</td>
<td>7.392</td>
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<td>abs. corr. method</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>analytical</td>
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<tr>
<td>abs. corr. range</td>
<td>0.21 – 0.51</td>
<td>0.18 – 0.51</td>
<td>0.17 – 0.44</td>
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<tr>
<td>refl. (meas./unique)</td>
<td>41054 / 4438</td>
<td>53574 / 4417</td>
<td>23964 / 4433</td>
</tr>
<tr>
<td>param./restraints</td>
<td>233 / 0</td>
<td>230 / 0</td>
<td>276 / 60</td>
</tr>
<tr>
<td>R1/wR2 [I&gt;2σ(I)]</td>
<td>0.0112 / 0.0229</td>
<td>0.0156 / 0.0327</td>
<td>0.0295 / 0.0671</td>
</tr>
<tr>
<td>R1/wR2 [all refl.]</td>
<td>0.0148 / 0.0239</td>
<td>0.0219 / 0.0343</td>
<td>0.0326 / 0.0683</td>
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<tr>
<td>S</td>
<td>1.072</td>
<td>1.055</td>
<td>1.151</td>
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<td>extinction coeff.</td>
<td>0.00097(4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pmin/max [e/A³]</td>
<td>–0.41 / 0.39</td>
<td>–0.99 / 0.45</td>
<td>–1.63 / 1.63</td>
</tr>
</tbody>
</table>

**Table S3.** Selected NMR and IR data of PtCl[NCN(CH=NC₆₅H₄R’-4’)-4] (1–5).[a]

<table>
<thead>
<tr>
<th></th>
<th>δ¹H (HC=N)</th>
<th>δ¹³C (C–Pt)[b]</th>
<th>δ¹³C (HC=N)[b]</th>
<th>δ¹⁹⁵Pt</th>
<th>σp (σF, σR)</th>
<th>Hammett[e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>CD₂Cl₂[b]</td>
<td>C₆D₆[c]</td>
<td>(HC=N)[b]</td>
<td>(Pt)[b,d]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Hammett constants calculated for 1,2- and 1,4-substituted derivatives.
The respective ATR-IR spectra of the organometallic benzylidene anilines 1–5 show C=N stretch vibrations that are all slightly shifted to lower frequencies (around 1611 – 1617 cm⁻¹, Table S3) as compared to those of analogous organic benzylidene anilines (1635 – 1616 cm⁻¹). This common feature points to a small change of the C=N bond order which may be caused by the presence of the electron donating NCN-pincer platinum(II) chloride grouping in each of these compounds. Furthermore, the narrow frequency range of the C=N stretch vibrations in the series 1–5 establishes that the electronic effect of substituent R’ on the azomethine group is small which is a common feature of para-substituted organic benzylidene anilines. No trend was observed between the C=N stretch frequencies and either the Hammett substituent parameter σᵢ of 1–5 or the C=N bond lengths of 2, 4, and 5 (C13-N3, Table 1).

References