Unraveling the synthesis of homoleptic \([\text{Ag(N,N-diaryl-NHC)}]_2\text{Y} \ (Y = \text{BF}_4, \text{PF}_6)\) complexes by ball-milling

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Unraveling the synthesis of homoleptic 
\[ \text{[Ag(N,N-diaryl-NHC)_2]Y (Y = BF}_4, \text{ PF}_6) \] complexes by ball-milling†

Audrey Beillard, Xavier Bantreil,* Thomas-Xavier Métro,* Jean Martinez and Frédéric Lamaty*

A user-friendly and general mechanochemical method was developed to access rarely described NHC (N-heterocyclic carbene) silver(I) complexes featuring \( N,N \)-diarylimidazol(izin)ene ligands and non-coordinating tetrafluoroborate or hexafluorophosphate counter anions. Comparison with syntheses in solution clearly demonstrated the superiority of the ball-milling conditions.

Introduction

Solvent-free mechanochemistry showed numerous advantages over traditional solution chemistry.\(^1\) In a number of cases, molecules that are otherwise inaccessible by traditional synthesis in solution could be synthesized by using a ball-mill.\(^2\) An impressive example of the superiority of ball-milling over solution chemistry was the reaction of unsymmetrical azobenzene derivatives with palladium(II) acetate that allowed to obtain a doubly cyclopalladated complex that could not be formed in solution.\(^3\) Besides, working under solvent-free or under Liquid-Assisted Grinding (LAG)\(^4\) conditions generally leads to reduced environmental impact and enhanced reaction rates. Simplified set-up of reactions and recovery of products are additional advantages provided by ball-mills. Many areas of chemistry have benefited from these aspects: inorganic chemistry,\(^5\) synthetic organic chemistry,\(^6\) catalysis\(^7\) and organometallic chemistry.\(^8\)

Pursuing our quest to disclose advantages of ball-milling in synthetic chemistry,\(^8\) we recently demonstrated that mechanochemistry could supersede solution chemistry in the synthesis of \( N,N \)-dialkylimidazolium halides and their corresponding NHC (N-heterocyclic carbene) silver(I) halide complexes.\(^9\) We next turned our attention to the synthesis of the rarely described homoleptic \( \text{[Ag(NHC)_2]Y} \) complexes, featuring \( N,N \)-diarylimidazol(izin)ene ligands, a cationic silver center and a non-coordinating counter anion \( \text{[Ag(NHC)_2]Y} \); we reasoned that solvent-free ball-milling could bring a new paradigm and become the user-friendly and general method for the production of these challenging \( [\text{Ag(NHC)}]_2 \) complexes. Indeed, only eight structures containing \( N,N \)-dialkylimidazol(izin)ene ligands and BF\(_4\)\(^10\) and PF\(_6\)\(^11\) counter anions were reported over the years, highlighting the difficulty to obtain such complexes. Their relative scarcity could be explained by the rather laborious approaches described in literature to access \( [\text{Ag(NHC)}]_2 \) complexes. For instance, direct metalation with silver(I) oxide required the use of toxic solvent at reflux (Scheme 1, pathway A).\(^12\) Metalation of imidazolium halides followed with anion exchange required prolonged reaction times (up to 3 days, pathway B).\(^13\) Direct metalation could also be performed using silver tetrafluoroborate or hexafluorophosphate, but these reactants are highly expensive compared to silver(I) oxide (pathway C).\(^14\) These silver salts could also be reacted with free NHC, which needs prior isolation and rigorous manipulation due to high moisture sensitivity (pathway D).\(^15\) The most convenient method so far was reported by the group of Cazin,\(^16\) and involved the intermediate synthesis of a NHC silver(I) chloride, which was then reacted under microwave irradiation with an imidazolium tetrafluoroborate in the presence of an excess of sodium hydroxide (pathway E). Nevertheless, this technique was limited to one example of homoleptic complex.

Results and discussion

When 1a-HBF\(_4\) and 1a-HPF\(_6\) were reacted with silver(I) oxide (0.55 equiv.) in a stainless steel bowl in a vibrating ball-mill (vbm) at 25 Hz for 2 h, \(^1\)H NMR analysis of the crude mixture...
indicated 4% and 7% conversion, respectively (Table 1, entry 1). The presence of a non-coordinating counter anion, in comparison with more coordinating chloride anion, might slightly increase the pK_a of the imidazolium, thus limiting its reactivity with silver oxide. Thus, sodium hydroxide was added to enable the deprotonation of the imidazolium precursor. To our delight, the addition of 1.1 equivalent of sodium hydroxide provided full conversion regardless of the counter anion (Table 1, entry 3). Reducing the amount of silver to a stoichiometric amount was detrimental to the conversion (Table 1, entry 4). In fine, homoleptic complexes [Ag(1a)_2]BF_4 and [Ag(1a)_2]PF_6 could be readily obtained in 91% yield in solely 2 hours of ball-milling under solvent-free conditions. To compare, their synthesis in solution required inert atmosphere in refluxing acetonitrile with 1.5 equivalent of Ag_2O (Y = BF_4, Scheme 1, pathway A) and 2 days of reaction through pathway B (Y = PF_6, Scheme 1). Of note, utilisation of a pestle and mortar to mix either 1a-HBF_4 or 1a-HPF_6 with NaOH (1.1 eq.) and Ag_2O (0.55 eq.) for 1 minute every 20 minutes during 2 hours led to very low conversion of the substrates (≤5% conversion), indicating that continuous agitation is required to reach complete conversion in a reasonable amount of time.

The optimized milling conditions were then applied to a wide array of imidazolium salts 1a-HY-ig-HY (Y = BF_4, PF_6), including N,N-diaryl and N,N-dialkyl imidazolium as well as triazolium salts (Scheme 2). 1b-HBF_4 and 1b-HPF_6, although featuring high steric hindrance caused by the presence of the methyl groups on the imidazolium, were efficiently converted into complexes [Ag(1b)_2]BF_4 and [Ag(1b)_2]PF_6 in 87% and 91% yield, respectively. Similarly, highly encumbered N,N-(2,6-diisopropylphenyl)imidazolium derivatives 1c-HY and 1d-HY were transformed to [Ag(1c)_2]Y in 73–74% yield and to [Ag(1d)_2]Y in 86–91% yield after 3 h milling at 30 Hz (Scheme 2).

The generality of the conditions were confirmed by the successful metatation of N,N-dialkylimidazolium salts 1e-HY and 1f-HY. Corresponding homoleptic silver complexes could be isolated in excellent yield and in only 1–2 h of reaction. In comparison, previous literature described the synthesis of [Ag(1e)_2]PF_6 in 70% yield by reacting 1 equivalent of silver(i) oxide in refluxing acetonitrile for 17 h. Finally, ball-milling conditions revealed once more excellent conversion chemistry for the synthesis of these complexes, we can be stored for months in a freezer without observable degradation.

To the best of our knowledge, among all the complexes synthesized, only four compounds were previously described in literature. All the complexes were fully characterized by ^1H, ^13C and ^19F NMR. The cationic structure of [Ag(1d)_2]BF_4 and [Ag(1e)_2]BF_4 were confirmed by X-ray diffraction on single crystals obtained by slow diffusion of diethyl ether in a dichloromethane solution of each complex (Fig. 1). These complexes are stable provided they are protected from light, and can be stored for months in a freezer without observable degradation.

To clearly establish the superiority of ball-milling over solution chemistry for the synthesis of these complexes, we attempted the synthesis in solution of unprecedented complexes [Ag(1e)_2]BF_4, featuring N,N-dialkyl ligands, as well as [Ag(1d)_2]BF_4 and [Ag(1d)_2]PF_6 featuring highly sterically demanding N,N-diaryl ligands (Table 2). Imidazolium salts were submitted to two sets of conditions: conditions A, which were found to be efficient in literature for other substrates and involving excess of silver(i) oxide in refluxing acetonitrile,
and conditions B, which are the direct application of milling conditions but in acetonitrile as solvent and under magnetic stirring. For the sake of comparison, conditions C, which are solvent-free ball-milling conditions (cf. Scheme 2), were included in Table 2. After 17 h reaction, \(^1\)H NMR analysis of the crude mixtures indicated that full conversion of the imidazolium salts were not reached in solution. In comparison, the ball-mill permitted to fully convert the imidazoliums in less than 3 h, thus enabling the isolation of the complexes after filtration of the crude mixture on celite (Table 2, entries 3, 6 and 9). The benefits of the ball-mill were unambiguously demonstrated with the use of N,N-diarylimidazolium salt 1d·HPF\(_6\). In solution, using either conditions A or B, less than 7% conversion of 1d·HPF\(_6\) into [Ag(1d)\(_2\)]PF\(_6\) were observed after 17 h of reaction while the complex could be isolated in 91% yield after 3 h of milling treatment. Of note, complete conversion of 1d·HPF\(_6\) was not reached after 48 h of reaction both in conditions A and B. In these conditions, the corresponding complex [Ag(1d)\(_2\)]PF\(_6\) was formed in very small quantities (7% and <5% under conditions A and B respectively) along with an unidentified compound preventing isolation of pure [Ag(1d)\(_2\)]PF\(_6\). These results are clearly indicating that this ball-milling method enabled the synthesis of a complex for which solvent-based conditions were unsuccessful.

As multistep sequences were previously described with success,\(^2\) we envisioned using imidazolium chloride as starting material. To our delight, when 1a·HCl was reacted with NaBF\(_4\) or KPF\(_6\) in a vibrating ball-mill agitated during 30 min

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**Scheme 2**  Mechanosynthesis of various homoletic cationic silver complexes. Reaction conditions: reactions performed under air, in a vibrating ball-mill (vbm) at 30 Hz, with 1.1 eq. of NaOH. Total mass of reactants accounted for 182 mg. *Reaction performed at 25 Hz.*

**Table 2** Comparative synthesis of [Ag(1d)\(_2\)]BF\(_4\), [Ag(1d)\(_2\)]PF\(_6\) and [Ag(1e)\(_2\)]BF\(_4\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conditions</th>
<th>NMR conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1e·HBF(_4)</td>
<td>A</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>B</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>C</td>
<td>100 (92)(^b)</td>
</tr>
<tr>
<td>4</td>
<td>1d·HBF(_4)</td>
<td>A</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>B</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>C</td>
<td>100 (86)(^b)</td>
</tr>
<tr>
<td>7</td>
<td>1d·HPF(_6)</td>
<td>A</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>B</td>
<td>&lt;5</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>C</td>
<td>100 (91)(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions A: Ag\(_2\)O (1 equiv.), CH\(_3\)CN, reflux, 17 h; conditions B: Ag\(_2\)O (0.5–0.55 equiv.), NaOH (1.1 equiv.), CH\(_3\)CN, rt, 17 h; conditions C: Ag\(_2\)O (0.5–0.55 equiv.), NaOH (1.1 equiv.), vbm, 1–3 h. \(^b\) Isolated yield is given in brackets.
at 25 Hz, corresponding 1a-HBF₄ and 1a-HPF₆ salts were isolated in 95% and 94% yield, respectively (Scheme 3). A one-pot two-step procedure to obtain the NHC silver(i) complexes directly from 1a-HCl was then realized. Thus, homoleptic [Ag(1a)₂]BF₄ and [Ag(1a)₂]PF₆ complexes were isolated in less than 3 h in 84% and 78% yield, respectively, without isolation of the intermediate (Scheme 3).

Conclusion

In summary, a general and user-friendly method that clearly outclasses solution conditions was developed thanks to ball-milling. Access to a wide panel of homoleptic cationic silver(i) complexes, featuring sterically hindered N₅N-diaryl ligands, N₅N-dialkyl ligands as well as triazolylidene ligands, was demonstrated. Of note, this strategy enabled the synthesis of a large number of unprecedented compounds, including the complex [Ag(1d)₂]PF₆ that was inaccessible through classical solution conditions. In addition, a highly convenient and environmentally friendly one-pot two-step procedure allowed to yield homoleptic silver complexes directly from corresponding imidazolium chloride, without isolation of intermediates.

Experimental

General information

All reagents were purchased from Aldrich Chemical Co., Fluka and Alfa Aesar and used without further purification. The milling treatments were carried out either in a Retsch MM200 or MM400 vibrating ball-mill operated at 25 Hz or 30 Hz. Milling load is defined as the sum of the mass of the reactants per free volume in the bowl. ¹HNMR spectra were recorded on a Bruker Avance DPX 200 MHz, 300 MHz or 400 MHz spectrometer and are reported in ppm using deuterated solvent for calibration (CDCl₃ at 7.26 ppm or DMSO-d₆ at 2.50 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ¹³CNMR spectra were recorded on Bruker Avance AM 50 MHz, 75 MHz or 101 MHz spectrometers and are reported in ppm using deuterated solvent for calibration (CDCl₃ at 77.2 ppm or DMSO-d₆ at 39.5 ppm). HRMS analysis were performed on a Q-Tof (Waters, ESI, 2001) spectrometer.

Synthesis of [Ag(NHC)₂]BF₄

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1a)₂]BF₄. From imidazolium tetrafluoroborate: 1,3-bis(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (126.6 mg, 0.323 mmol, 1.00 eq.), AgO (41.1 mg, 0.178 mmol, 0.55 eq.) and NaOH (14.2 mg, 0.355 mmol, 1.1 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 2 hours in the vibrating ball-mill operated at 25 Hz. The black powder was recovered with CH₃Cl and the suspension was filtered over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver tetrafluoroborate (117.6 mg, 0.146 mmol, 91%) as a white solid.

From imidazolium chloride: 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (100.7 mg, 0.295 mmol, 1.00 eq.) and NaBF₄ (34.1 mg, 0.310 mmol, 1.05 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). The bowl was closed and subjected to grinding for 20 minutes in the vibrating ball-mill operated at 25 Hz. Afterwards, Ag₂O (39.2 mg, 0.148 mmol, 0.50 eq.) and NaOH (13.0 mg, 0.325 mmol, 1.10 eq.) were added. Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 2 hours and 30 minutes. The black powder was recovered with CH₃Cl and filtered over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver tetrafluoroborate (100.0 mg, 0.124 mmol, 84%) as a white solid. ¹HNMR (300 MHz, DMSO-d₆) δ 7.67 (d, J = 1.4 Hz, 4H), 6.99 (s, 8H), 2.41 (s, 12H), 1.67 (s, 24H); ¹³CNMR (101 MHz, DMSO-d₆) δ 181.4 (dd, J = 192.4, 13.8 Hz), 138.8, 134.9, 134.0, 128.8, 123.68, 123.58, 20.7, 16.7; ¹⁹FNMR (376 MHz, DMSO-d₆) δ −148.3; HRMS calcd for C_{48}H_{48}N_{18}Ag [M − BF₄⁻]⁺: 715.2930; found: 715.2932.

Bis[1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazol-2-ylidene]silver tetrafluoroborate [Ag(1b)₂]BF₄. [1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate (131.8 mg, 0.314 mmol, 1.00 eq.), Ag₂O (36.3 mg, 0.157 mmol, 0.50 eq.) and NaOH (13.8 mg, 0.345 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The
Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1f)2]BF4. 1,3-Dibenzylimidazolium tetrafluoroborate (123.3 mg, 0.367 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 2 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 3 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 2 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 3 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). 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The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 3 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag2O (42.5 mg, 0.183 mmol, 0.50 eq.) and NaOH (16.1 mg, 0.404 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The black powder was recovered with CH2Cl2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver tetrafluoroborate (104.3 mg, 0.193 mmol, 92%) as a white powder. ¹H NMR (300 MHz, DMSO-d₆) δ 7.57 (s, 2H), 7.47 (s, 2H), 7.41–7.15 (m, 10H), 5.32 (s, 4H), 3.77 (s, 6H); ¹³C NMR (101 MHz, DMSO-d₆) δ 137.5, 128.9, 128.1, 127.6, 123.4, 122.5, 54.1, 38.3 (the ¹³C of carbene was not observed due to the low concentration of the sample); ¹⁹F NMR (376 MHz, DMSO-d₆) δ −148.3; HRMS calcd for C₄₅H₃₄N₄Ag [M − BF₄⁻]: 451.1052; found: 451.1050.

Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1g)₂]BF₄. 1,3,4-Triphenyl-1,2,4-triazol-2-ylidene silver tetrafluoroborate (178.3 mg, 0.124 mmol, 74%) as a white solid. ¹H NMR (300 MHz, DMSO-d₆) δ 7.53 (t, J = 7.8 Hz, 4H), 7.21 (d, J = 7.8 Hz, 8H), 2.13 (sept, J = 6.9 Hz, 8H), 1.69 (s, 12H), 1.02 (d, J = 6.9 Hz, 24H), 0.69 (d, J = 6.9 Hz, 24H); ¹³C NMR (101 MHz, DMSO-d₆) δ 178.4 (dd, J = 204.3, 14.7 Hz), 144.7, 132.7, 130.5, 127.2, 127.1, 124.4, 27.9, 25.0, 22.6, 9.2; ¹⁹F NMR (376 MHz, DMSO-d₆) δ −148.3; HRMS calcd for C₅₈H₄₆N₄Ag [M − BF₄⁻]: 939.5429; found: 939.5429.
129.1, 128.8, 126.8, 124.1, 122.6; \(^{19}F\) NMR (376 MHz, DMSO-
\(d_6\)) \(\delta -148.3;\) HRMS calc’d for \(\text{C}_{46}\text{H}_{50}\text{N}_4\text{Ag}[\text{M} - \text{BF}_4^-]\): 701.1578; found: 701.1584.

**Synthesis of \([\text{Ag(NHC)}_2]\)PF\(_6\)**

\[\text{Bis[1,3-bis[2,4,6-trimethylphenyl]imidazol-2-ylidene]silver hexafluorophosphate \([\text{Ag(1a)}_2]\)PF\(_6\).}\] From imidazolium hexafluorophosphate: 1,3-bis[2,4,6-trimethylphenyl]imidazolium hexafluorophosphate (131.8 mg, 0.293 mmol, 1.00 eq.), AgO (37.3 mg, 0.761 mmol, 0.55 eq.) and NaOH (12.9 mg, 0.322 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL\(^{-1}\). The bowl was closed and subjected to grinding for 2 hours in the vibrating ball-mill operated at 25 Hz. The black powder was recovered with CH\(_2\)Cl\(_2\) and the suspension was filtered over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis[2,4,6-trimethylphenyl]imidazol-2-ylidene]silver hexafluorophosphate (115.3 mg, 0.144 mmol, 91%) as a white solid.

From imidazolium chloride: 1,3-bis[2,4,6-trimethylphenyl]imidazolium chloride (89.3 mg, 0.262 mmol, 1.00 eq.) and KPF\(_6\) (50.8 mg, 0.275 mmol, 1.05 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). The bowl was closed and subjected to grinding for 20 minutes in the vibrating ball-mill operated at 25 Hz. Afterwards, AgO (30.3 mg, 0.131 mmol, 0.50 eq.) and NaOH (11.5 mg, 0.288 mmol, 1.10 eq.) were added. Total mass of the reagents was calculated so that milling load equals 19.2 mg mL\(^{-1}\). The bowl was closed and subjected to grinding for 2 hours and 30 minutes. The black powder was recovered with CH\(_2\)Cl\(_2\) and recovered over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis[2,4,6-trimethylphenyl]imidazol-2-ylidene]silver hexafluorophosphate (83 mg, 0.0963 mmol, 78%) as a white solid. \(^1\)H NMR (300 MHz, DMSO-
\(d_6\)) \(\delta 7.67 (d, J = 1.2 Hz, 1H), 7.00 (s, 2H), 2.41 (s, 3H), 1.68 (s, 6H);\) \(^{13}C\) NMR (101 MHz, DMSO-
\(d_6\)) \(\delta 181.4 (d, J = 192.4, 13.8 Hz), 138.7, 134.9, 134.0, 128.8, 126.3, 123.5, 120.7, 16.6;\) \(^{31}P\) NMR (162 MHz, DMSO-
\(d_6\)) \(\delta -144.2 (\text{sept}, J = 711.4 Hz);\) \(^{19}F\) NMR (376 MHz, DMSO-
\(d_6\)) \(\delta -70.1 (d, J = 711.4 Hz).\)

**Bis[1,3-bis[2,4,6-trimethylphenyl]-4,5-dimethyl]imidazol-2-ylidene]silver hexafluorophosphate \([\text{Ag(1b)}_2]\)PF\(_6\).** 1,3-Bis[2,4,6-trimethylphenyl]-4,5-dimethylimidazolium hexafluorophosphate (136.4 mg, 0.285 mmol, 1.00 eq.), AgO (33.0 mg, 0.143 mmol, 0.50 eq.) and NaOH (125 mg, 0.314 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL\(^{-1}\). The bowl was closed and subjected to grinding for 3 \times 1 hour in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH\(_2\)Cl\(_2\) and the suspension was filtered over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis[2,4,6-trimethylphenyl]-4,5-dimethyl]imidazol-2-ylidene]silver hexafluorophosphate (119.0 mg, 0.130 mmol, 91%) as a beige solid. \(^1\)H NMR (400 MHz, DMSO-
\(d_6\)) \(\delta 6.99 (s, 8H), 2.41 (s, 12H), 1.80 (s, 12H), 1.61 (s, 24H);\) \(^{13}C\) NMR (101 MHz, DMSO-
\(d_6\)) \(\delta 178.3 (d, J = 190.6, 14.1 Hz), 138.7, 134.4, 133.2, 128.9, 126.0, 20.8, 16.6, 8.6;\) \(^{31}P\) NMR (162 MHz, DMSO-
\(d_6\)) \(\delta -144.2 (\text{hept}, J = 711.4 Hz);\) \(^{19}F\) NMR (376 MHz, DMSO-
\(d_6\)) \(\delta -70.2 (d, J = 711.4 Hz)\) HRMS calc’d for \(\text{C}_{46}\text{H}_{50}\text{N}_4\text{Ag}[\text{M} - \text{PF}_6^-]\): 771.3536; found: 771.3545.

**Bis[1,3-bis[2,4,6-diisopropylphenyl]imidazol-2-ylidene]silver hexafluorophosphate \([\text{Ag(1c)}_2]\)PF\(_6\).** 1,3-Bis[2,4,6-diisopropylphenyl]imidazolium hexafluorophosphate (141.0 mg, 0.262 mmol, 1.00 eq.) AgO (30.3 mg, 0.131 mmol, 0.50 eq.) and NaOH (11.5 mg, 0.288 mmol, 1.10 eq.) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL\(^{-1}\). The bowl was closed and subjected to grinding for 3 hours in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH\(_2\)Cl\(_2\) and the suspension was filtered over celite. The filtrate was concentrated under vacuum. The white solid was dissolved in a minimum of CH\(_2\)Cl\(_2\), washed three times with water and concentrated under vacuum. The solid was washed with water and Et\(_2\)O and dry under vacuum to afford bis[1,3-bis[2,6-diisopropylphenyl]imidazol-2-ylidene]silver hexafluorophosphate (96.9 mg, 94.1 \mu mol, 72%) as a white solid.

\(^1\)H NMR (400 MHz, DMSO-
\(d_6\)) \(\delta 7.77 (d, J = 0.9 Hz, 4H), 7.51 (t, J = 7.8 Hz, 4H), 7.18 (d, J = 7.8 Hz, 8H), 2.20 (sept, J = 6.9 Hz, 8H), 1.01 (d, J = 6.9 Hz, 24H), 0.75 (d, J = 6.9 Hz, 24H);\) \(^{13}C\) NMR (101 MHz, DMSO-
\(d_6\)) \(\delta 181.4 (d, J_{df} = 201.6, 14.5 Hz), 144.6, 134.5, 130.3, 125.7, 125.6, 124.0, 28.1, 24.0, 23.7;\) \(^{31}P\) NMR (162 MHz, DMSO-
\(d_6\)) \(\delta -144.2 (\text{hept}, J = 711.3 Hz);\) \(^{19}F\) NMR (376 MHz, DMSO-
\(d_6\)) \(\delta -70.2 (d, J = 711.3 Hz).\)
steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 hour in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH₂Cl₂ and the suspension was filtered over celite. The filtrate was concentrated under vacuum to afford bis[1-benzyl-3-methyl]imidazol-2-ylidene]silver hexafluorophosphate (90 mg, 0.151 mmol, 94%) as a white powder. 

H NMR (400 MHz, DMSO-d₆) δ 7.55 (d, J = 1.7 Hz, 2H), 7.46 (d, J = 1.7 Hz, 2H), 7.34–7.24 (m, 10H), 5.32 (s, 4H), 3.77 (s, 6H); 

13C NMR (101 MHz, DMSO-d₆) δ 137.4, 128.8, 128.0, 127.5, 123.3, 122.4, 54.0, 38.2 (the 13C of carbene was not observed due to the low concentration of the sample); 

19F NMR (376 MHz, DMSO-d₆) δ −70.2 (d, J = 711.4 Hz); HRMS calcld for C₄₀H₃₆N₆Ag [M – PF₆]⁻: 701.1583; found: 701.1584.

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Notes and references


19 See ESI† for details.