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Audrey Beillard, Xavier Bantreil, Thomas-Xavier Métro, Jean Martinez, Frédéric Lamaty. Unraveling the synthesis of homoleptic [Ag(N,N-diaryl-NHC)₂]Y (Y = BF₄, PF₆) complexes by ball-milling. Dalton Transactions, 2016, 45 (44), pp.17859-17866. 10.1039/C6DT03564G . hal-02364127

HAL Id: hal-02364127

<https://hal.science/hal-02364127>

Submitted on 29 Jan 2021

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Unraveling the synthesis of homoleptic [Ag(*N,N*-diaryl-NHC)₂]Y (Y = BF₄, PF₆) 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(idin)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 organic synthesis,^{1a} catalysis⁶ and organometallic chemistry.⁷

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 [Ag(NHC)₂]Y complexes, featuring *N,N*-

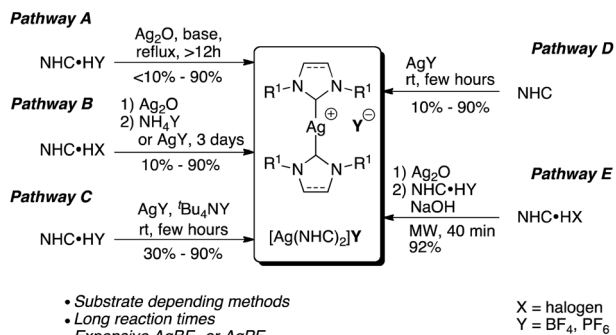
diarylimidazol(idin)ene ligands, a cationic silver center and a non-coordinating counter anion (Y = BF₄, PF₆); we reasoned that solvent-free ball-milling could bring a new paradigm and become the user-friendly and general method for the production of these challenging [Ag(NHC)₂]⁺ complexes. Indeed, only eight structures containing *N,N*-diarylimidazol(idin)ene ligands and BF₄¹⁰ and PF₆¹¹ 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 [Ag(NHC)₂]Y 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,^{10c} 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.

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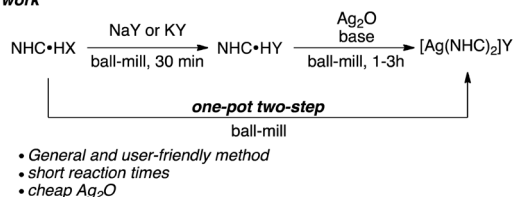
Results and discussion

When **1a**·HBF₄ and **1a**·HPF₆ 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, ¹H NMR analysis of the crude mixture

Previous work



This work



Scheme 1 Synthetic pathways to homoleptic [Ag(NHC)₂]Y (Y = BF₄/PF₆) complexes.

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.¹⁶ 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]BF₄ and

Table 1 Optimization of the mechanosynthesis of cationic silver complexes^a

| Entry | NaOH (equiv.) | Ag ₂ O (equiv.) | NMR conv. (%) | |
|-------|---------------|----------------------------|--|--|
| | | | [Ag(1a) ₂]BF ₄ | [Ag(1a) ₂]PF ₆ |
| 1 | 0 | 0.55 | 4 | 7 |
| 2 | 0.5 | 0.55 | 56 | 46 |
| 3 | 1.1 | 0.55 | 100 (91) ^b | 100 (91) ^b |
| 4 | 1.1 | 0.27 | 91 | 82 |

^a Reactions performed under air, in a vibrating ball-mill (vbm) at 25 Hz, total mass of reactants accounted for 182 mg. ^b Isolated yield is given in brackets.

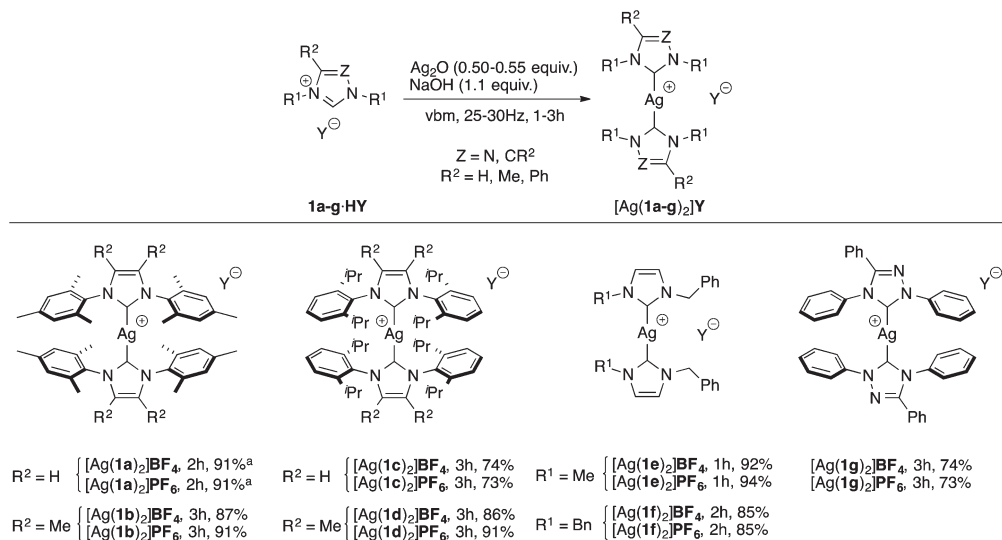
[Ag(**1a**)₂]PF₆ could be readily obtained in 91% yield in solely 2 hours of ball-milling under solvent-free conditions. To compare, their synthesis in solution required inert atmosphere in refluxing acetonitrile with 1.5 equivalent of Ag₂O (Y = BF₄, Scheme 1, pathway A)^{10b,17} and 2 days of reaction through pathway B (Y = PF₆, Scheme 1).^{11a} Of note, utilisation of a pestle and mortar to mix either **1a**•HBF₄ or **1a**•HPF₆ with NaOH (1.1 eq.) and Ag₂O (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–**1g**•HY (Y = BF₄, PF₆), including *N,N*-diaryl and *N,N*-dialkyl imidazolium as well as triazolium salts (Scheme 2). **1b**•HBF₄ and **1b**•HPF₆, although featuring high steric hindrance caused by the presence of the methyl groups on the imidazolium, were efficiently converted into complexes [Ag(**1b**)₂]BF₄ and [Ag(**1b**)₂]PF₆ 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 metalation 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]PF₆ in 70% yield by reacting 1 equivalent of silver(i) oxide in refluxing acetonitrile for 17 h.¹⁸ Finally, ball-milling conditions revealed once more efficient when starting with triazolium salts **1g**•HY, furnishing the unprecedented complexes [Ag(**1g**)₂]BF₄ and [Ag(**1g**)₂]PF₆ in 74% and 73% yield respectively (Scheme 2). It is important to highlight that even though PF₆[−] salts are less reactive than BF₄[−] salts, the use of ball-mill allowed to obtain both families of complexes in similar yields.

To the best of our knowledge, among all the complexes synthesized, only four compounds were previously described in literature.¹⁹ All the complexes were fully characterized by ¹H, ¹³C and ¹⁹F NMR. The cationic structure of [Ag(**1d**)₂]BF₄ and [Ag(**1e**)₂]BF₄ 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]BF₄, featuring *N,N*-dialkyl ligands, as well as [Ag(**1d**)₂]BF₄ and [Ag(**1d**)₂]PF₆, 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 substrates¹⁸ and involving excess of silver(i) oxide in refluxing acetonitrile,



Scheme 2 Mechano-synthesis of various homoleptic 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. ^a Reaction performed at 25 Hz.

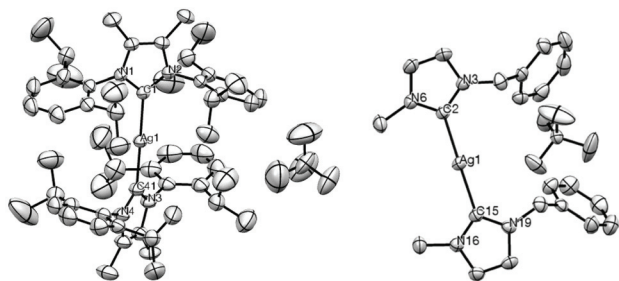


Fig. 1 ORTEPs (probability at 50% level) of silver complexes $[Ag(1d)_2]BF_4$ and $[Ag(1e)_2]BF_4$. H atoms are omitted for clarity.

and conditions B, which are the direct application of milling conditions but in acetonitrile as solvent and under magnetic stirring.¹⁹ 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, ¹H 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**-HPF₆. In solution, using either conditions A or B, less than 7% conversion of **1d**-HPF₆ 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**-HPF₆ 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)

Table 2 Comparative synthesis of $[Ag(1d)_2]BF_4$, $[Ag(1d)_2]PF_6$ and $[Ag(1e)_2]BF_4$ ^a

$Y = BF_4, PF_6$

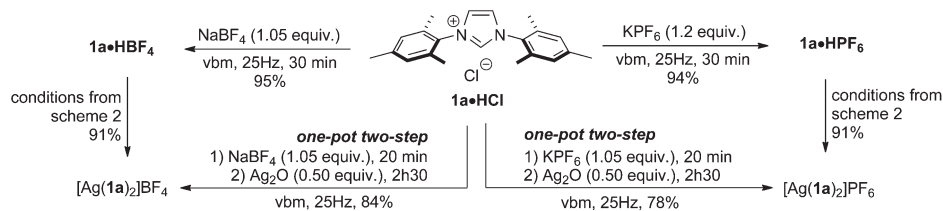
Conditions A: Ag₂O, CH₃CN, reflux, 17h
Conditions B: Ag₂O, NaOH, CH₃CN, rt, 17h
Conditions C: Ag₂O, NaOH, vbm, 1-3h

| Entry | Substrate | Conditions | NMR conv. (%) |
|-------|-----------------------------|------------|-----------------------|
| 1 | 1e -HBF ₄ | A | 75 |
| 2 | | B | 67 |
| 3 | | C | 100 (92) ^b |
| 4 | 1d -HBF ₄ | A | 32 |
| 5 | | B | 86 |
| 6 | | C | 100 (86) ^b |
| 7 | 1d -HPF ₆ | A | 7 |
| 8 | | B | <5 |
| 9 | | C | 100 (91) ^b |

^a Conditions A: Ag₂O (1 equiv.), CH₃CN, reflux, 17 h; conditions B: Ag₂O (0.5–0.55 equiv.), NaOH (1.1 equiv.), CH₃CN, rt, 17 h; conditions C: Ag₂O (0.5–0.55 equiv.), NaOH (1.1 equiv.), vbm, 1–3 h. ^b Isolated yield is given in brackets.

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,²⁰ we envisioned using imidazolium chloride as starting material. To our delight, when **1a**-HCl was reacted with NaBF₄ or KPF₆ in a vibrating ball-mill agitated during 30 min



Scheme 3 One-pot two-step synthesis of cationic silver complexes from **1a-HCl**.

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 *N,N*-diaryl ligands, *N,N*-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. ¹H NMR 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-*d*₆ 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. ¹³C NMR 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-*d*₆ 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.), Ag₂O (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 CH₂Cl₂ and the suspension was filtrated 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 CH₂Cl₂ and filtrated 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. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.67 (d, *J* = 1.4 Hz, 4H), 6.99 (s, 8H), 2.41 (s, 12H), 1.67 (s, 24H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 181.4 (dd, *J* = 192.4, 13.8 Hz), 138.8, 134.9, 134.0, 128.8, 123.63, 123.58, 20.7, 16.7; ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -148.3; HRMS calcd for C₄₂H₄₈N₄Ag [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

bowl was closed and subjected to grinding for 3 × 1 hour 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[[1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazol-2-ylidene]silver tetrafluoroborate (117.8 mg, 0.137 mmol, 86%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.00 (s, 8H), 2.42 (s, 12H), 1.81 (s, 12H), 1.61 (s, 24H); ¹³C NMR (101 MHz, CDCl₃) δ 178.3 (dd, *J* = 190.6, 13.7 Hz), 138.7, 134.4, 133.2, 128.9, 125.94, 125.89, 20.7, 16.6, 8.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -143.6; HRMS calcd for C₄₆H₅₆N₄Ag [M - BF₄⁻]⁺: 771.3536; found: 771.3565.

Bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1c)₂]BF₄. 1,3-Bis-(2,6-diisopropylphenyl)imidazolium tetrafluoroborate (136.2 mg, 0.286 mmol, 1.00 eq.), Ag₂O (33.1 mg, 0.143 mmol, 0.50 eq.) and NaOH (12.6 mg, 0.315 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. The yellow solid was washed with Et₂O and dried under vacuum to afford bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver tetrafluoroborate (126.5 mg, 0.130 mmol, 91%) as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.76 (s, 4H), 7.50 (t, *J* = 7.8 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 8H), 2.27–2.13 (m, 8H), 1.01 (d, *J* = 6.8 Hz, 24H), 0.75 (d, *J* = 6.9 Hz, 24H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 181.4 (dd, *J* = 201.9, 14.4 Hz), 144.7, 134.5, 130.3, 125.71, 125.65, 124.1, 28.1, 24.0, 23.7; ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -148.3; HRMS calcd for C₅₄H₇₂N₄Ag [M - BF₄⁻]⁺: 883.4808; found: 883.4803.

Bis[[1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazol-2-ylidene]silver tetrafluoroborate [Ag(1d)₂]BF₄. [1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate (138.2 mg, 0.274 mmol, 1.00 eq.), Ag₂O (31.7 mg, 0.137 mmol, 0.50 eq.) and NaOH (12.1 mg, 0.301 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[[1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazol-2-ylidene]silver tetrafluoroborate (120.5 mg, 0.117 mmol, 86%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) 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-*d*₆) 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-*d*₆) δ -148.3; HRMS calcd for C₅₈H₈₀N₄Ag [M - BF₄⁻]⁺: 939.5434; found: 939.5429.

Bis[[1-benzyl-3-methyl]imidazol-2-ylidene]silver tetrafluoroborate [Ag(1e)₂]BF₄. 1-Benzyl-3-methylimidazolium tetrafluoroborate (109.7 mg, 0.422 mmol, 1.00 eq.), Ag₂O (53.7 mg, 0.232 mmol, 0.55 eq.) and NaOH (18.6 mg, 0.464 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 1 hour 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 (104.3 mg, 0.193 mmol, 92%) as a white powder. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.56 (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-*d*₆) 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-*d*₆) δ -148.3; HRMS calcd for C₂₂H₂₄N₄Ag [M - BF₄⁻]⁺: 451.1052; found: 451.1050.

Bis[1,3-dibenzylimidazol-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[1,3-dibenzylimidazol-2-ylidene]silver tetrafluoroborate (107.7 mg, 0.156 mmol, 85%) as a white powder. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.57 (s, 4H), 7.31–7.22 (m, 12H), 7.21–7.15 (m, 8H), 5.27 (s, 8H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 137.3, 128.8, 128.1, 127.5, 122.9, 54.3 (the ¹³C of carbene was not observed due to the low concentration of the sample); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -148.3; HRMS calcd for C₃₄H₃₂N₄Ag [M - BF₄⁻]⁺: 603.1678; found: 603.1681.

Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver tetrafluoroborate [Ag(1g)₂]BF₄. 1,3,4-Triphenyl-1,2,4-triazolium tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq.), Ag₂O (38.7 mg, 0.167 mmol, 0.50 eq.) and NaOH (14.7 mg, 0.367 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 × 1 hour 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[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver tetrafluoroborate (97.7 mg, 0.124 mmol, 74%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (d, *J* = 7.4 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.55–7.48 (m, 12H), 7.46–7.37 (m, 12H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 183.0 (d, *J* = 194.2 Hz), 153.8, 138.8, 136.3, 131.2, 130.1, 129.8, 129.6,

129.1, 128.8, 126.8, 124.1, 122.6; ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.3; HRMS calcd for $\text{C}_{40}\text{H}_{30}\text{N}_6\text{Ag}$ [$\text{M} - \text{BF}_4^-$] $^+$: 701.1578; found: 701.1584.

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

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver hexafluorophosphate $[\text{Ag}(\mathbf{1a})_2]\text{PF}_6$. From imidazolium hexafluorophosphate: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate (131.8 mg, 0.293 mmol, 1.00 eq.), Ag_2O (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_2Cl_2 and the suspension was filtrated 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, Ag_2O (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_2Cl_2 and filtrated 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. ^1H NMR (300 MHz, DMSO- d_6) δ 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) δ 181.4 (dd, $J = 192.4, 13.8$ Hz), 138.7, 134.9, 134.0, 128.8, 123.62, 123.55, 20.7, 16.6; ^{31}P NMR (162 MHz, DMSO- d_6) δ -144.2 (sept, $J = 711.4$ Hz); ^{19}F NMR (376 MHz, DMSO- d_6) δ -70.1 (d, $J = 711.4$ Hz).

Bis[1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazol-2-ylidene]silver hexafluorophosphate $[\text{Ag}(\mathbf{1b})_2]\text{PF}_6$. [1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (136.4 mg, 0.285 mmol, 1.00 eq.), Ag_2O (33.0 mg, 0.143 mmol, 0.50 eq.) and NaOH (12.5 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 3×1 hour in the vibrating ball-mill operated at 30 Hz. The black powder was recovered with CH_2Cl_2 and the suspension was filtrated 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. ^1H NMR (400 MHz, DMSO- d_6) δ 6.99 (s, 8H), 2.41 (s, 12H), 1.80

(s, 12H), 1.61 (s, 24H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 178.3 (dd, $J = 190.6, 14.1$ 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) δ -144.2 (hept, $J = 711.4$ Hz); ^{19}F NMR (376 MHz, DMSO- d_6) δ -70.2 (d, $J = 711.4$ Hz) HRMS calcd for $\text{C}_{46}\text{H}_{56}\text{N}_4\text{Ag}$ [$\text{M} - \text{PF}_6^-$] $^+$: 771.3536; found: 771.3545.

Bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver hexafluorophosphate $[\text{Ag}(\mathbf{1c})_2]\text{PF}_6$. 1,3-Bis-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate (140.1 mg, 0.262 mmol, 1.00 eq.) Ag_2O (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_2Cl_2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The white solid was dissolved in a minimum of CH_2Cl_2 , washed three times with water and concentrated under vacuum. The solid was washed with water and Et_2O and dry under vacuum to afford bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] silver hexafluorophosphate (96.9 mg, 94.1 μmol , 72%) as a white solid. ^1H NMR (400 MHz, DMSO- d_6) δ 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) δ 181.4 (dd, $J = 201.6, 14.5$ 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) δ -144.2 (hept, $J = 711.3$ Hz); ^{19}F NMR (376 MHz, DMSO- d_6) δ -70.2 (d, $J = 711.3$ Hz).

Bis[1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]silver hexafluorophosphate $[\text{Ag}(\mathbf{1d})_2]\text{PF}_6$. [1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (141.7 mg, 0.252 mmol, 1.00 eq.) Ag_2O (29.2 mg, 0.126 mmol, 0.50 eq.) and NaOH (11.1 mg, 0.277 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_2Cl_2 and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]silver hexafluorophosphate (124.1 mg, 0.114 mmol, 91%) as a white powder. ^1H NMR (400 MHz, DMSO- d_6) δ 7.53 (t, $J = 7.8$ Hz, 4H), 7.20 (d, $J = 7.8$ Hz, 8H), 2.18-2.05 (m, 8H), 1.69 (s, 12H), 1.01 (d, $J = 6.9$ Hz, 24H), 0.69 (d, $J = 6.9$ Hz, 24H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 145.2, 133.1, 130.9, 127.6, 124.8, 28.4, 25.4, 23.1, 9.7; ^{31}P NMR (162 MHz, DMSO- d_6) δ -133.2 to -157.4 (m). ^{19}F NMR (376 MHz, DMSO- d_6) δ -70.1 (d, $J = 711.2$ Hz); HRMS calcd for $\text{C}_{58}\text{H}_{80}\text{N}_4\text{Ag}$ [$\text{M} - \text{PF}_6^-$] $^+$: 939.5434; found: 939.5433.

Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver hexafluorophosphate $[\text{Ag}(\mathbf{1e})_2]\text{PF}_6$. 1-Benzyl-3-methylimidazolium hexafluorophosphate (126.9 mg, 0.321 mmol, 1.00 eq.), Ag_2O (40.9 mg, 0.177 mmol, 0.55 eq.) and NaOH (14.1 mg, 0.353 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 1 hour 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 hexafluorophosphate (90 mg, 0.151 mmol, 94%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) 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-*d*₆) 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); ³¹P NMR (162 MHz DMSO-*d*₆) δ -144.2 (sept, *J* = 711.3 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -70.2 (d, *J* = 711.4 Hz); HRMS calcd for C₂₂H₂₄N₄Ag [M - PF₆]⁺: 451.1052; found: 451.1052.

Bis[1,3-dibenzylimidazol-2-ylidene]silver hexafluorophosphate [Ag(1f)₂]PF₆. 1,3-Dibenzylimidazolium hexafluorophosphate (129.5 mg, 0.328 mmol, 1.00 eq.), Ag₂O (38.0 mg, 0.164 mmol, 0.50 eq.) and NaOH (14.4 mg, 0.361 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[1,3-dibenzylimidazol-2-ylidene]silver hexafluorophosphate (104.7 mg, 0.140 mmol, 85%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.56 (s, 4H), 7.31–7.23 (m, 12H), 7.21–7.15 (m, 8H), 5.27 (s, 8H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 137.2, 128.7, 128.0, 127.4, 122.8, 54.2 (the ¹³C of carbene was not observed due to the low concentration of the sample); ³¹P NMR (162 MHz, DMSO-*d*₆) δ -144.2 (sept, *J* = 711.2 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -70.1 (d, *J* = 711.2 Hz); HRMS calcd for C₃₄H₃₂N₄Ag [M - PF₆]⁺: 603.1678; found: 603.1680.

Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver hexafluorophosphate [Ag(1g)₂]PF₆. 1,3,4-Triphenyl-1,2,4-triazolium hexafluorophosphate (133.7 mg, 0.302 mmol, 1.00 eq.), Ag₂O (35.0 mg, 0.151 mmol, 0.50 eq.) and NaOH (13.3 mg, 0.332 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 × 1 hour 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[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver hexafluorophosphate (93.8 mg, 0.111 mmol, 73%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.55–7.47 (m, 6H), 7.45–7.37 (m, 6H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 183.1 (d, *J* = 200.0 Hz), 153.8, 138.8, 136.3, 131.2, 130.1, 129.8, 129.5, 129.1, 128.8, 126.8, 124.1, 122.6; ³¹P NMR (162 MHz, DMSO-*d*₆) δ -144.2 (sept, *J* = 711.4 Hz); ¹⁹F NMR

(376 MHz, DMSO-*d*₆) δ -70.2 (d, *J* = 711.4 Hz); HRMS calcd for C₄₀H₃₀N₆Ag [M - PF₆]⁺: 701.1583; found: 701.1584.

Acknowledgements

Université de Montpellier and CNRS are acknowledged for funding. Pascal Retailleau (Institut de Chimie des Substances Naturelles) is gratefully acknowledged for the XRD analysis of [Ag(1d)]BF₄.

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