

Mechanochemistry for facilitated access to *N,N*-diaryl NHC metal complexes†

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A user-friendly and solvent-free mechanosynthetic strategy allowed light-sensitive silver(I) complexes featuring *N,N*-diaryl N-heterocyclic carbenes (NHC), including challenging and sterically hindered ligands, to be yielded efficiently. The first transmetalations using ball-milling to obtain palladium and copper NHC complexes were performed. A convenient one-pot two-step metalation/transmetalation procedure was also realized.

Introduction

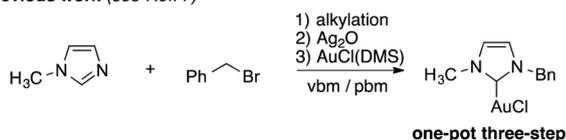
Mechanochemistry and, more specifically, ball-milling is becoming an increasingly valuable technique for solvent-free and environmentally friendly synthesis of organometallic complexes.¹ Among the advantages of ball-milling, the lowering of solvent use² along with excellent agitation generally induced enhanced reaction rates while working without external heating. Additionally, ball-milling provides user-friendly procedures with a simplified set-up of reactions and recovery of products, and applications in various domains can be found in the literature.³ Organometallic synthesis has been demonstrated to be efficient using solid-state protocols (by grinding reagents using a mortar and pestle) to give generally better and faster reactions than those obtained by solution chemistry.⁴ With ball-milling technology, along with more controlled and homogeneous agitation, the same advantages have been found for the synthesis of organometallic complexes featuring a wide variety of metals and ligands.⁵ For example, solvent-free ball-milling could supersede solution chemistry in the multicomponent synthesis of rhenium species.^{5d} Similarly, a one-pot two-step mechanosynthesis of analytically pure salen–zinc complexes is possible within only 1 h of milling.^{5c} As a demonstration that mechanochemistry can lead to enhanced reactivity, a relevant example is the reaction of asymmetrically substituted azobenzene with palladium(II) acetate. Just as in solution,

initially a cyclopalladated compound can be obtained, but further milling with additional Pd(OAc)₂ yields quantitatively the double-palladated complex, which cannot be obtained under classical solution conditions.^{5f}

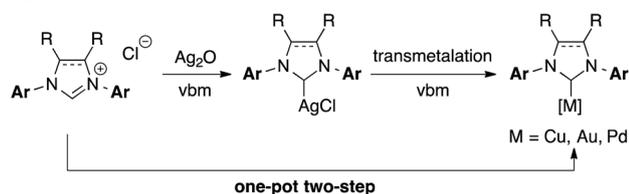
In this context, recently we built on our expertise in mechanochemistry⁶ to demonstrate that the synthesis of *N,N*-dialkyl-imidazolium salts and corresponding N-heterocyclic carbene (NHC) silver complexes in a ball-mill are extremely efficient.⁷ Moreover, the first and only mechano-transmetalation to date yielded a NHC gold complex, which could also be obtained through a one-pot three-step procedure without isolating intermediates. This report was, nevertheless, limited to *N,N*-dialkyl ligands, whereas organometallic complexes featuring *N,N*-diaryl-NHC are widely described in the literature.⁸ In addition, reports involving modification or synthesis of NHC–metal complexes using grinding or ball-milling are limited. Nolan *et al.* described the modification of [AuCl(NHC)] complexes into the corresponding [Au(OR)(NHC)] complexes using a mortar and pestle.^{4h} In 2015, Adams *et al.* demonstrated that the synthesis of PEPPSI-type compounds could be performed efficiently in a ball-mill from the imidazolium salt, pyridinium precursor, potassium hydroxide and the appropriate metal source.⁹ More challenging due to their generally lower nucleophilicity and higher steric hindrance,¹⁰ the metalation in solution of *N,N*-diaryl imidazolium salts in the presence of silver(I) oxide often require longer reaction times (24 h) than their *N,N*-dialkyl analogues.¹¹ In addition, working in refluxing solvent was sometimes necessary. Thus, we wanted to assess if ball-milling could facilitate this transformation and yield *N,N*-diaryl-NHC silver complexes (Scheme 1), thereby opening a synthetic route to other *N,N*-diaryl-NHC metal complexes. It is noteworthy that, in addition to their importance as NHC transfer reagents, several *N,N*-diaryl-NHCs silver complexes have shown high cytotoxicity against cancer cell lines.¹²

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Previous work (see Ref. 7)



This work



Scheme 1 Synthetic strategy for NHC-transition metal mechanosynthesis.

Results and discussion

Classical conditions for solvent-free milling, using a stainless-steel ball and jar agitated with a vibratory ball-mill (vbm) at a frequency of 25 Hz, were first applied. To our delight, the reaction of IMes-HCl (1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, Fig. 1) with Ag₂O yielded 82% of the corresponding [AgCl(IMes)] complex in only 1 h 40 min (Table 1, entry 1). As a comparison,

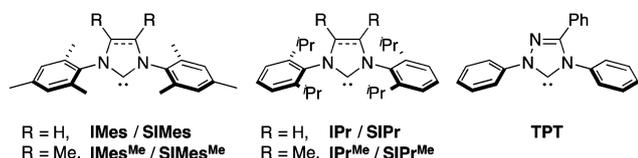


Fig. 1 Structure of the NHC used in this study.

the use of a planetary ball-mill (pbm) at 450 rpm allowed [AgCl(IMes)] to be obtained in a similar manner,¹³ thus allowing envisioning of a facilitated scale-up. An important feature is that silver(I) complexes are sensitive to light, and reactions in solution must be protected from light. Stainless-steel milling jars are not transparent to light, and decomposition of the complexes was not observed which, in addition to a short reaction time, renders the grinding method even more user-friendly. To support the robustness of the method, a prolonged synthesis of [AgCl(IMes)] for 10 h in the vbm gave the pure complex in 79% yield, and degradation was not observed.

In all cases, before the work-up on the whole reaction mixture, a sample was deposited on cotton and CDCl₃ was added to quickly solubilize and filter the mixture. Conversions were then calculated by ¹H NMR. To ensure that the conversion measured was obtained by mixing solid reagents together, and that the reaction was not occurring during this work-up, a control experiment was performed. IMes-HCl and Ag₂O were gently mixed together for <1 min to obtain a homogeneous mixture. A sample was directly taken and the work-up described above was applied. ¹H NMR spectra showed 0% conversion, indicating that no reaction had occurred during the work-up. In addition, the same reaction was performed again and stopped after 15 min of milling. ¹H NMR spectra were recorded before and after work-up of the whole reaction mixture. In both cases, ≈30% conversion was measured, indicating that no reaction had occurred during treatment of the reaction using solvent.

When SIMes-HCl (1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride) was used, milling at 25 Hz did not give reasonable conversions. However, increasing the frequency to 30 Hz, thus transferring more energy to the reaction mixture, allowed

Table 1 Mechanosynthesis of silver complexes^a

Entry	Product	%V _{bur} ^b	t (h)	Yield (%)	Conditions from lit.
1	[AgCl(IMes)]	35.1	1.7	82 ^c	Ag ₂ O (1.15 eq.), CH ₂ Cl ₂ , 7 h, reflux, 73% ¹⁴ Ag ₂ O (0.65 eq.), H ₂ O, 24 h, reflux, 92% ¹⁵
2	[AgCl(SIMes)]	34.5	1.5	89	Ag ₂ O (0.65 eq.), toluene, 30 min, 110 °C, MW, 83% ¹⁶ Ag ₂ O (1.5 eq.), CH ₂ Cl ₂ , 24 h, r.t., 95% ¹⁷ Ag ₂ O (0.65 eq.), H ₂ O, 24 h, reflux, 88% ¹⁵
3	[AgCl(IPr)]	42.9	3	89	Ag ₂ O (0.65 eq.), THF, 30 min, 110 °C, MW, 90% ¹⁶ Ag ₂ O (0.5 eq.), CH ₂ Cl ₂ , 6 h, reflux, 94% ¹⁸ Ag ₂ O (0.65 eq.), H ₂ O, 24 h, reflux, 87% ¹⁵
4	[AgCl(SIPr)]	44.0	3	73	Ag ₂ O (0.65 eq.), toluene, 30 min, 110 °C, MW, 85% ¹⁶ Ag ₂ O (0.5 eq.), CH ₂ Cl ₂ , 24 h, r.t., 92% ¹⁷ Ag ₂ O (0.65 eq.), H ₂ O, 24 h, reflux, 74% ¹⁵
5	[AgCl(IMes ^{Me})]	n.a.	3	81	Ag ₂ O (0.65 eq.), THF, 30 min, 110 °C, MW, 92% ¹⁶
6	[AgCl(SIMes ^{Me-cis})]	n.a.	3	86	Unprecedented
7	[AgCl(SIMes ^{Me-trans})]	n.a.	3	86	Ag ₂ O (1.0 eq.), CH ₂ Cl ₂ , 24 h, 82% ¹⁹
8	[AgCl(IPr ^{Me})]	44.9	3	82	Ag ₂ O (0.65 eq.), CH ₂ Cl ₂ , 3 h, r.t., 82% ²⁰
9	[AgCl(SIPr ^{Me})]	n.a.	3	77	Unprecedented
10	[AgCl(TPT)]	n.a.	3	89	Unprecedented

^a Total mass of reactants: 182 mg, vbm = vibratory ball-mill. ^b Data from lit.²⁰ n.a. = not available. ^c Reaction performed at 25 Hz.

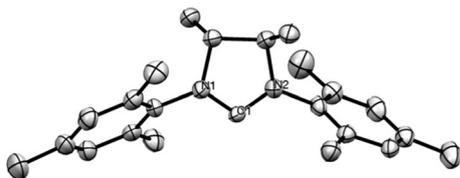
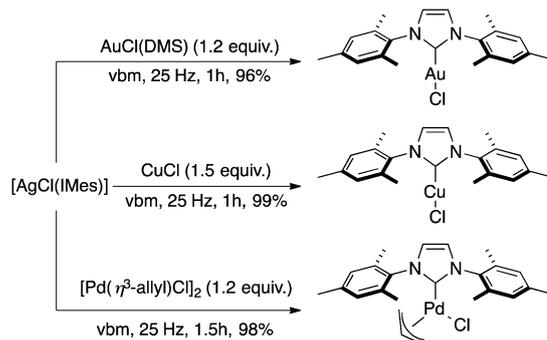


Fig. 2 ORTEPs (probability at 50% level) of $\text{SIMes}^{\text{Me-trans}}$. H and Cl atoms have been omitted for clarity.

$[\text{AgCl}(\text{SIMes})]$ to be obtained in 89% yield after 1 h 30 min (Table 1, entry 2). $\text{IPr}\cdot\text{HCl}$ and $\text{SIPr}\cdot\text{HCl}$ (1,3-bis(2,6-diisopropylphenyl)-imidazolium and imidazolidinium chlorides), which are known to be more sterically hindered, as witnessed by the $\%V_{\text{bur}}^{21}$ of the ligand from literature data,²⁰ induced a lowered reactivity. Nevertheless, the milling method again proved to be highly efficient when a slightly prolonged reaction time of 3 h was applied. Under these conditions, $[\text{AgCl}(\text{IPr})]$ and $[\text{AgCl}(\text{SIPr})]$ were obtained in 89% and 73% yield, respectively (Table 1, entries 3 and 4). Having these results in hand with the most classical NHC ligands used for organometallic synthesis, we decided to extend this methodology to less common and even more sterically hindered NHC bearing methyl groups on the imidazole ring backbone. To ensure full conversion in each case, reaction conditions were kept at 30 Hz for 3 h. Satisfyingly, $[\text{AgCl}(\text{IMes}^{\text{Me}})]$ and its saturated congeners, $[\text{AgCl}(\text{SIMes}^{\text{Me-cis}})]$ and $[\text{AgCl}(\text{SIMes}^{\text{Me-trans}})]$, could be isolated in 81–86% yield (Table 1, entries 5–7). It is important to note that the two isomers, $\text{SIMes}^{\text{Me-cis}}\cdot\text{HCl}$ and $\text{SIMes}^{\text{Me-trans}}\cdot\text{HCl}$, were separated during their synthesis, characterized and assigned thanks to X-ray diffraction of the *trans* isomer (Fig. 2). To the best of our knowledge, it is the first time that they were reacted separately to furnish the two diastereomeric silver(i) complexes.

Similarly, $[\text{AgCl}(\text{IPr}^{\text{Me}})]$ and unprecedented $[\text{AgCl}(\text{SIPr}^{\text{Me}})]$, which was obtained as a mixture of isomers, could be produced in 82% and 77% yield, respectively (Table 1, entries 8 and 9). Finally, the methodology was also extended to the triazolium salt $\text{TPT}\cdot\text{HCl}$ (1,3,4-triphenyl-1,2,4-triazolium chloride, Fig. 1), which was converted to the corresponding silver complex in 89% yield (Table 1, entry 10). The mechanochemical method appeared to be quite general and allowed to access previously described as well as unprecedented NHC–silver(i) complexes in good-to-excellent yields and in short reaction times. For comparison, conditions from the literature to obtain the complexes have been added to Table 1. The mechanochemical method was, in general, found to be more efficient than classical solution conditions, either with dichloromethane or water, yielding the desired complexes in similar yields than those described in the literature, but in reduced reaction times and without the need to protect the reaction mixture from light. Conditions using microwave activation were found to be faster because the metalation occurred in 30 min, but heating at 110 °C in toxic toluene or THF was necessary. The mechanochemical method is, therefore, one of the most efficient ways to produce NHC silver complexes.

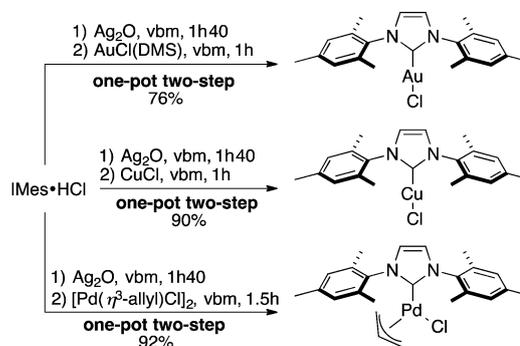
We were pleased to find that the mechanosynthesis of $[\text{AgCl}(\text{NHC})]$ complexes was highly practical. We questioned if transmetalation involving *N,N*-diaryl NHC could be feasible in



Scheme 2 Transmetalation of $[\text{AgCl}(\text{IMes})]$ using mechanochemistry.

the ball-mill. In particular, transmetalation leading to gold, copper and palladium complexes was envisioned. Indeed, such complexes are widely used in catalysis and $[\text{AuCl}(\text{IMes})]$ and $[\text{CuCl}(\text{IMes})]$ have also been reported to display higher cytotoxicity than cisplatin in various cancer cell lines.^{12b,22} Gratifyingly, mechanical agitation allowed an almost quantitative $[\text{AuCl}(\text{IMes})]$, $[\text{CuCl}(\text{IMes})]$ and $[\text{PdCl}(\eta^3\text{-allyl})(\text{IMes})]$ yield starting from $[\text{AgCl}(\text{IMes})]$ in only 1 h to 1.5 h of reaction, using a stainless-steel ball and jar agitated with a vbm at a frequency of 25 Hz (Scheme 2). Importantly, the last two examples represent the first transmetalations in a ball-mill leading to copper and palladium complexes. Conditions for the synthesis of the gold complex were directly applied from our previous report involving *N,N*-dialkyl NHC ligands.⁷ A rapid optimization of the stoichiometry and reaction time allowed a full conversion to be reached, as confirmed by ^1H NMR, when copper and palladium reagents were used in slight excess.

In order to increase the usefulness of this methodology, we attempted to perform both metalation and transmetalation in a one-pot two-step process, starting directly from $\text{IMes}\cdot\text{HCl}$ without isolating the $[\text{AgCl}(\text{IMes})]$ intermediate (Scheme 3). Using this procedure, both the use of a solvent for isolating the intermediate and the light-exposure issue of the silver complexes could be avoided. Satisfyingly, this one-pot two-step strategy allowed the isolation of $[\text{AuCl}(\text{IMes})]$ in 76% yield, in only 2 h 40 min of reaction time in the ball-mill. Similarly, $[\text{CuCl}(\text{IMes})]$ and $[\text{PdCl}(\eta^3\text{-allyl})(\text{IMes})]$ could be synthesized in higher yield



Scheme 3 One-pot two-step synthesis of organometallic complexes from $\text{IMes}\cdot\text{HCl}$.

than with the procedure involving isolation of the intermediate silver complex (90% and 92% yield vs. 81% and 80% yield, respectively).

Conclusion

Silver complexes featuring *N,N*-diaryl *N*-heterocyclic carbenes could be obtained in < 3 h at room temperature under solvent-free ball-milling. This user-friendly and highly efficient method allowed transmetalation with copper, gold and palladium without observable decomposition of the silver complex. Ultimately, a highly practical one-pot two-step metalation/transmetalation procedure allowed copper, gold and palladium complexes to be yielded directly in short reaction times and without isolation of the silver intermediates.

Experimental

General remarks

All reagents were purchased from Sigma-Aldrich, Fluka and Alfa Aesar and used without further purification. The milling treatments were carried out either in a vibrating Retsch Mixer Mill 200 (vbm) or in a Retsch PM100 Planetary Mill (pbm). "Milling load" is defined as the sum of the mass of the reactants per free volume in the jar. ¹H NMR spectra were recorded on Bruker Avance DPX 300 MHz, 400 MHz or Bruker Avance III 600 MHz spectrometers. They are reported in ppm using deuterated solvent used 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, m = multiplet, sept = septuplet; coupling constant in Hz; integration. ¹³C NMR spectra were recorded on Bruker Avance AM 75 MHz or 101 MHz spectrometers and are reported in ppm using deuterated solvent used for calibration (CDCl₃ at 77.2 ppm or DMSO-*d*₆ at 39.5 ppm). HRMS analysis was performed on a Q-ToF (Waters, ESI,† 2001) spectrometer.

All of reaction mixtures were recovered with a solvent and filtrated over celite to remove metallic particles lost by the reactor during ball-milling.

All of the reactions using a vbm were made at 25 Hz or 30 Hz under air with no interruption of the milling.

Syntheses

General procedure for the synthesis of [AgCl(IMes)] in a vbm.

1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (132.4 mg, 0.389 mmol, 1.00 eq.) and silver oxide (49.5 mg, 0.214 mmol, 0.55 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h and 40 min in a vbm operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]silver chloride (142.3 mg, 0.318 mmol, 82%) as a pale-brown solid.

Synthesis of [AgCl(IMes)] in a pbm. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (122.0 mg, 0.358 mmol, 1.00 eq.)

and silver oxide (45.6 mg, 0.197 mmol, 0.55 eq.) were introduced in a 12 mL stainless-steel grinding bowl with 50 stainless-steel balls (diameter, 5 mm). Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 2 h in a pbm operated at 450 rpm. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]silver chloride (140.3 mg, 0.313 mmol, 88%) as a pale-brown solid.

[AgCl(IMes)]. ¹H NMR (300 MHz, CDCl₃) δ 7.14 (d, *J* = 1.5 Hz, 2H), 7.00 (s, 4H), 2.36 (s, 6H), 2.08 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 183.1 (dd, *J* = 256.0, 18.3 Hz), 139.9, 135.3, 134.7, 129.7, 122.9, 122.8, 21.2, 17.8. Data in agreement with the literature.²³

[AgCl(SIMes)]. White solid, 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.96 (s, 4H), 4.01 (s, 4H), 2.31 (s, 6H), 2.30 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 164.2, 138.9, 135.4, 135.1, 129.9, 51.2, 51.1, 21.0, 17.9. Data in agreement with the literature.²³

[AgCl(IPr)]. White powder, 89% yield. A mixture of [AgCl(IPr)] and [Ag(IPr)₂]Cl were obtained in 95:5 ratio. Peaks for [AgCl(IPr)] (major product) are reported: ¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.22 (d, *J* = 1.8 Hz, 2H), 2.62–2.47 (m, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 184.6 (dd, *J* = 258.5, 21.4 Hz), 145.7, 134.6, 130.9, 124.5, 123.8, 123.7, 28.8, 24.8, 24.1. Data in agreement with the literature.²³

[AgCl(SIPr)]. White solid, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 4H), 4.06 (s, 4H), 3.05 (hept, *J* = 6.9 Hz, 4H), 1.342 (d, *J* = 6.9 Hz, 12H), 1.337 (d, *J* = 6.9 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ ¹³C of carbene was not observed, 146.7, 134.6, 130.2, 124.9, 54.1, 54.0, 29.0, 25.6, 24.2. Data in agreement with the literature.²³

[AgCl(IMes^{Me})]. Pale-brown solid, 81% yield. A mixture of [AgCl(IMes^{Me})] and [Ag(IMes^{Me})₂]Cl was obtained in 90:10 ratio. Peaks for [AgCl(IMes^{Me})] (major product) are reported: ¹H NMR (300 MHz, CDCl₃) δ 6.99 (s, 4H), 2.35 (s, 6H), 2.01 (s, 12H), 1.91 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 178.8 (dd, *J* = 258.4, 18.4 Hz), 139.5, 135.0, 134.0, 129.7, 126.13, 126.07, 21.2, 17.8, 9.3. HRMS calcd for C₂₃H₂₈N₂Ag [M – Cl]⁺: 439.1303; found: 439.1308.

[AgCl(SIMes^{Me-cis})]. White solid, 86% yield. ¹H NMR (300 MHz, CDCl₃) δ 6.96 (s, 2H), 6.94 (s, 2H), 4.47 (s, 2H), 2.36 (s, 6H), 2.30 (s, 6H), 2.27 (s, 6H), 1.19 (d, *J* = 5.5 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 206.1 (dd, *J* = 242.4, 17.4 Hz), 138.5, 136.3, 135.5, 134.1, 130.1, 130.0, 61.4, 61.3, 21.0, 19.1, 18.1, 13.0; HRMS calcd for C₄₆H₆₀N₄Ag [M – Cl]⁺: 775.3869; found: 775.3879.

[AgCl(SIMes^{Me-trans})]. White solid, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.94 (s, 2H), 6.91 (s, 34H), 4.07–3.91 (m, 2H), 2.32 (s, 6H), 2.28 (s, 6H), 2.26 (s, 6H), 1.28 (d, *J* = 5.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 207.64 (dd, *J* = 242.0, 17.4 Hz), 138.6, 136.6, 135.3, 134.0, 130.1, 130.0, 66.64, 66.54, 21.0, 19.1, 18.4, 18.0; HRMS calcd for C₄₆H₆₀N₄Ag [M – Cl]⁺: 775.3869; found: 775.3870.

[AgCl(IPr^{Me})]. Pale-brown solid, 82% yield. After purification, a mixture of [AgCl(IPr^{Me})] and [Ag(IPr^{Me})₂]Cl was obtained in 97:3 ratio. Peaks for [AgCl(IPr^{Me})] (major product) are reported: ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.60–7.53 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 4H), 2.39 (sept, *J* = 6.8 Hz, 4H), 1.95 (s, 6H), 1.22 (d, *J* = 6.8 Hz, 12H), 1.18 (d, *J* = 6.8 Hz, 12H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 178.9 (dd, *J* = 253.1, 18.1 Hz), 146.0, 133.2, 131.1, 127.3, 127.2, 124.9, 28.6, 25.5, 23.4, 9.6. Data in agreement with the literature.²⁰

[AgCl(SIPr^{Me})]. White solid, 77% yield. Mixture of diastereoisomers (57:43) ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 6.7 Hz, 4H), 4.57 (s, 2H, 43%), 4.01 (s, 2H, 57%), 3.26 (sept, *J* = 6.8 Hz, 2H, 57%), 3.15 (sept, *J* = 6.9 Hz, 2H, 43%), 3.06 (sept, *J* = 6.9 Hz, 2H, 43%), 2.95 (sept, *J* = 6.8 Hz, 2H, 57%), 1.35–1.26 (m, 18H), 1.23 (d, *J* = 6.7 Hz, 12H, 57%), 1.19 (d, *J* = 6.7 Hz, 6H, 43%), 1.14 (d, *J* = 4.8 Hz, 6H, 43%); major diastereoisomer: ¹³C NMR (101 MHz, DMSO-*d*₆) δ 206.3 (dd, *J* = 201.0, 17.2 Hz), 147.5, 146.8, 132.9, 129.8, 124.7, 124.4, 68.3, 68.2, 28.2, 28.1, 25.9, 25.1, 23.6, 22.8, 17.4; minor diastereoisomer: ¹³C NMR (101 MHz, DMSO-*d*₆) δ 203.9 (dd, *J* = 201.2, 17.8 Hz), 147.4, 146.8, 133.2, 129.6, 124.5, 63.0, 62.9, 28.3, 28.0, 25.9, 25.2, 23.4, 23.1, 12.8; HRMS calcd for C₂₉H₄₂N₂Ag [M – Cl]⁺: 525.2399; found: 525.2404.

[AgCl(TPT)]. Brown crystallized powder, 89% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.08–8.00 (m, 2H), 7.64–7.48 (m, 9H), 7.46–7.41 (m, 4H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 183.5, 154.1, 139.5, 137.0, 131.6, 130.6, 130.3, 130.0, 129.6, 129.2, 127.5, 124.7, 123.3; HRMS calcd for C₂₀H₁₅N₃Ag [M – Cl]⁺: 404.0317; found: 404.0317.

Preparation of [CuCl(IMes)] from [AgCl(IMes)]. [1,3-Bismesitylimidazol-2-ylidene]silver chloride (136.6 mg, 0.305 mmol, 1.00 eq.) and copper(I) chloride (45.3 mg, 0.458 mmol, 1.50 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h in a vbm operated at 25 Hz. The white powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]copper chloride (122.7 mg, 0.304 mmol, 100%) as a white powder.

One-pot two-step preparation of [CuCl(IMes)] from IMes-HCl. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (100.6 mg, 0.295 mmol, 1.00 eq.) and silver oxide (37.6 mg, 0.162 mmol, 0.55 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). The bowl was closed and subjected to grinding for 1 h and 40 min in a vbm operated at 25 Hz. The bowls were opened and copper(I) chloride (43.8 mg, 0.442 mmol, 1.50 eq.) added. Total mass of the reagents was calculated so that milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h in a vbm operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford

[1,3-bismesitylimidazol-2-ylidene]copper chloride (107.2 mg, 0.266 mmol, 90%) as a white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.07 (s, 2H), 7.01 (s, 4H), 2.36 (s, 6H), 2.11 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 179.9, 139.6, 135.5, 134.5, 129.6, 129.2, 122.6, 121.9, 21.2, 17.8. Data in agreement with the literature.²⁴

Preparation of [AuCl(IMes)] from [AgCl(IMes)]. [1,3-Bismesitylimidazol-2-ylidene]silver chloride (101.7 mg, 0.227 mmol, 1.00 eq.) and chloro(dimethylsulfide)gold (80.3 mg, 0.273 mmol, 1.20 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h in a vbm operated at 25 Hz. The yellow powder was recovered with dichloromethane and the suspension was filtrated over silica. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]gold chloride (117.5 mg, 0.219 mmol, 96%) as a pale-yellow powder.

One-pot two-step preparation of [AuCl(IMes)] from IMes-HCl. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (75.5 mg, 0.221 mmol, 1.00) and silver oxide (28.2 mg, 0.122 mmol, 0.55 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). The bowl was closed and subjected to grinding for 1 h and 40 min in a vbm operated at 25 Hz. Afterwards, chloro(dimethylsulfide)gold (78.3 mg, 0.266 mmol, 1.20 eq.) were added. Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h and 30 min in a vbm operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over silica. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]gold chloride (90.2 mg, 0.168 mmol, 76%) as a pale-yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 7.10 (s, 1H), 6.99 (s, 2H), 2.35 (s, 3H), 2.11 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 173.5, 139.8, 134.71, 134.68, 129.5, 122.4, 21.2, 17.8. Data in agreement with the literature.²⁵

Preparation of [PdCl(η³-allyl)(IMes)] from [AgCl(IMes)]. [1,3-Bismesitylimidazol-2-ylidene]silver chloride (118.8 mg, 0.265 mmol, 1.00 eq.) and allylpalladium chloride dimer (63.1 mg, 0.173 mmol, 0.65 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h and 30 min in a vbm operated at 25 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum and the resulting solid was put on silica, filtrated with cyclohexane to remove excesses of allylpalladium chloride dimer and ethyl acetate to collect the desired product. Ethyl acetate was evaporated to afford [1,3-bismesitylimidazol-2-ylidene](η³-2-propen-1-yl)palladium chloride (122.0 mg, 0.250 mmol, 94%) as a pale-yellow powder.

One-pot two-step preparation of [PdCl(η³-allyl)(IMes)] from IMes-HCl. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (87.8 mg, 0.258 mmol, 1.00) and silver oxide (32.8 mg, 0.142 mmol, 0.55 eq.) were introduced in a 10 mL stainless-steel grinding bowl with one stainless-steel ball (diameter, 10 mm). The bowl was

closed and subjected to grinding for 1 h and 40 min in a vbm operated at 25 Hz. Afterwards, allylpalladium chloride dimer (61.3 mg, 0.167 mmol, 0.65 eq.) was added. Total mass of the reagents was calculated so that the milling load was 19.2 mg mL⁻¹. The bowl was closed and subjected to grinding for 1 h and 30 min in a vbm operated at 25 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum and the resulting solid was put on silica, filtrated with cyclohexane to remove excesses of allylpalladium chloride dimer and ethyl acetate to collect the desired product. Ethyl acetate was evaporated to afford [1,3-bismesitylimidazol-2-ylidene](η^3 -2-propen-1-yl)palladium chloride (110.8 mg, 0.227 mmol, 88%) as a pale-yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H), 6.97 (s, 4H), 4.93–4.77 (m, 1H), 3.94–3.83 (m, 1H), 3.39 (d, J = 6.1 Hz, 1H, 25%), 3.20 (d, J = 6.1 Hz, 1H, 75%), 2.81 (d, J = 13.5 Hz, 1H, 75%), 2.76 (d, J = 13.4 Hz, 1H, 25%), 2.33 (s, 6H), 2.23 (s, 6H), 2.20 (s, 6H), 1.87 (d, J = 12.1 Hz, 1H, 25%), 1.80 (d, J = 11.8 Hz, 1H, 75%); major diastereoisomer: ¹³C NMR (101 MHz, CDCl₃) δ 183.8, 139.0, 136.0, 135.6, 129.2, 129.1, 123.1, 114.4, 72.5, 49.3, 21.3, 18.43, 18.37; minor diastereoisomer: ¹³C NMR (101 MHz, CDCl₃) δ 183.3, 139.0, 136.0, 135.5, 129.3, 129.2, 123.2, 113.9, 71.7, 52.5, 21.3, 18.71, 18.66. Data in agreement with the literature.²⁶

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