Appendix 1

The Development of a Novel N-Heterocyclic Carbene Ligand Featuring a Chelating Imine Moiety

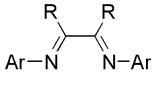
A1.1 Abstract

The previously described chelating N-heterocyclic carbenes (NHCs) were designed as electron-rich analogs to the salicylaldimine (sal) ligands featured on our neutral Ni catalysts for olefin polymerization. As part of our thorough investigation, we decided to target chelating NHCs to serve as analogs to the diimine ligands featured on Brookhart's cationic Ni and Pd catalysts.[1] Pursuant to this goal, a bidentate NHC/imine ligand was synthesized. This compound was demonstrated to be a competent ligand for transition metals in the synthesis of a Ag carbene. Although the attempted ligation to group 10 metals led only to ligand decomposition, the new compounds show promise as ligands.

A1.2 Introduction

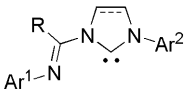
As discussed in Chapter 1, the two major developments in late metal-catalyzed olefin polymerization were the discovery of neutral Ni catalysts by our group[2] and others[3] and cationic Ni and Pd diimine catalysts (**A1.1**) by Brookhart and coworkers.[1] During the course of our development of NHC analogs to sal ligands, we realized that NHC analogs of diimine ligands could be made as well. Just as our NHC sal analogs featured an NHC in place of the imine moiety, we envisioned replacement of a single imine moiety of the diimine ligands with an NHC as well (**A1.2**, Figure A1.1).

Figure A1.1. Proposed imine/carbene ligands **A1.2** as analogs to diimine ligands (**A1.1**).



A1.1

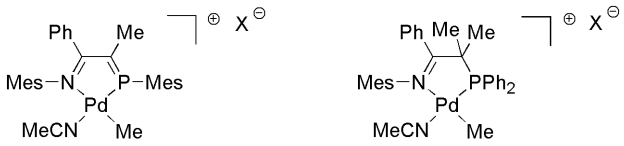
R = H, Me



A1.2

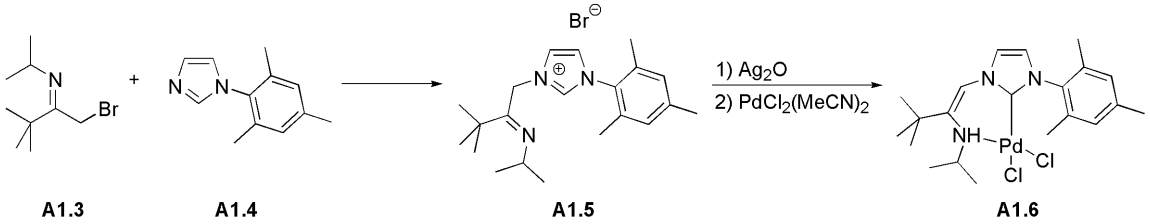
Not surprisingly, given the great deal of interest in group 10 diimine catalysts, this is not the first time that analogs of diimine ligands have been studied.[4] For example, Brookhart and coworkers took an approach somewhat similar to that proposed above: replacement of one of the imine arms of the diimine ligand with a phosphine[5] or phosphinidine moiety.[6] These compounds were ligated to Pd (Figure A1.2) and the resulting complexes were shown to be active catalysts for ethylene polymerization.

Figure A1.2. Phosphine and phosphinidine diimine analogs presented by Brookhart and coworkers.



Additionally, the development of the proposed imine/carbene ligands is not an entirely novel avenue of study. There have been many examples of bidentate ligands featuring an NHC paired with a neutral two-electron donor.[7] Of particular interest is an example from Green and coworkers of an NHC ligand very similar to the one we propose above.[8] Treatment of α-bromo imine (**A1.3**) with 1-mesitylimidazole (**A1.4**) afforded ligand precursor **A1.5** (Scheme A1.1). Generation of the Ag carbene followed by carbene transfer to an appropriate Pd source led to Pd complex **A1.6**.

Scheme A1.1. Synthesis of ligand **A1.5** and Pd complex **A1.6**.



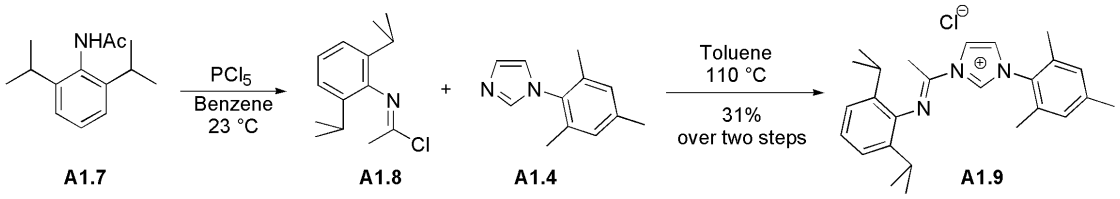
Though ligand **A1.5** features the same coordinating functionalities as our proposed imine/carbene ligand **A1.2**, there are some key differences. Upon ligation of **A1.5** to Pd, the imine functionality tautomerized to the enamine, thus transforming the ligand into a neutral amine/NHC–chelating ligand. Furthermore, ligand **A1.5** is not an exact analog of a diimine, since it forms a six-member ring when coordinated to a metal,

in contrast to the five-member ring formed by coordination of diimine ligands. While this Pd complex was well characterized, its polymerization activity was not determined.

A1.3 Ligand and Complex Synthesis

The key step of the synthesis of the proposed imine/NHC ligand precursors is iminylation of an imidazole to form the precursor salt. The synthesis began with acetylation of 2,6-diisopropylaniline to afford *N*-(2,6-diisopropylphenyl) acetamide (**A1.7**, Scheme A1.2). This intermediate was then treated with PCl_5 in benzene to give the corresponding imidoyl chloride (**A1.8**), which was not isolated.[9] Compound **A1.8** was then mixed with 1-mesitylimidazole (**A1.4**) in refluxing toluene to provide the desired product (**A1.9**) as a white solid.

Scheme A1.2. The synthesis of NHC precursor **A1.9**.

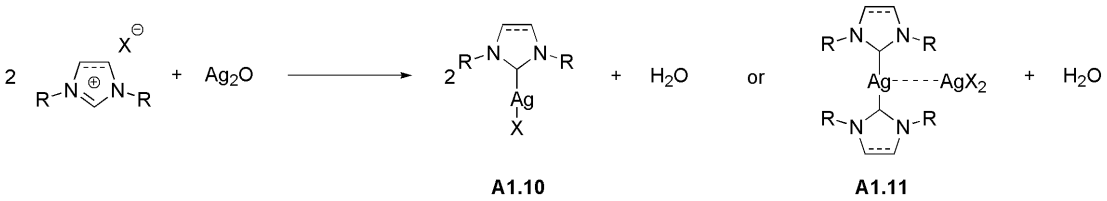


A1.7 A1.8 A1.4 A1.9

Treatment of NHC precursor **A1.9** with KHMDS, in order to activate the heterocycle, provided no characterizable products. Therefore, as an alternative, the Ag carbene of **A1.9** was targeted. Silver carbenes have proven to be excellent NHC transfer agents.[10] They are easy to synthesize – commonly by treatment of an NHC precursor with Ag_2O to yield the Ag carbene and water (Scheme A1.3). Silver NHCs typically take a linear structure with either one (**A1.10**) or two (**A1.11**) NHC ligands on a single metal atom. If two NHC molecules are ligated to a single Ag atom, then that cationic Ag(I)

complex is paired with an anionic AgX_2 anion.[10] Silver carbenes are quite stable and serve as excellent NHC transfer reagents to other metals, a process driven thermodynamically by the loss of an insoluble Ag salt, *e.g.* AgCl.

Scheme A1.3. The synthesis of Ag carbenes.



The Ag carbene (**A1.12**) of compound **A1.9** was formed by NHC precursor **A1.9** with Ag_2O in CH_2Cl_2 (Scheme A1.4). Crystals of **A1.12** suitable for X-ray crystallography were obtained by allowing a solution in pentane/CH_2Cl_2 to stand at 0 °C for an extended period of time.[11] This structure is presented in Figure A1.3.

Scheme A1.4. The synthesis of Ag carbene **A1.12**.

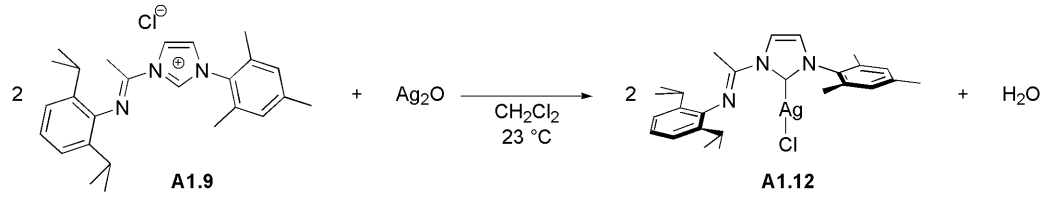
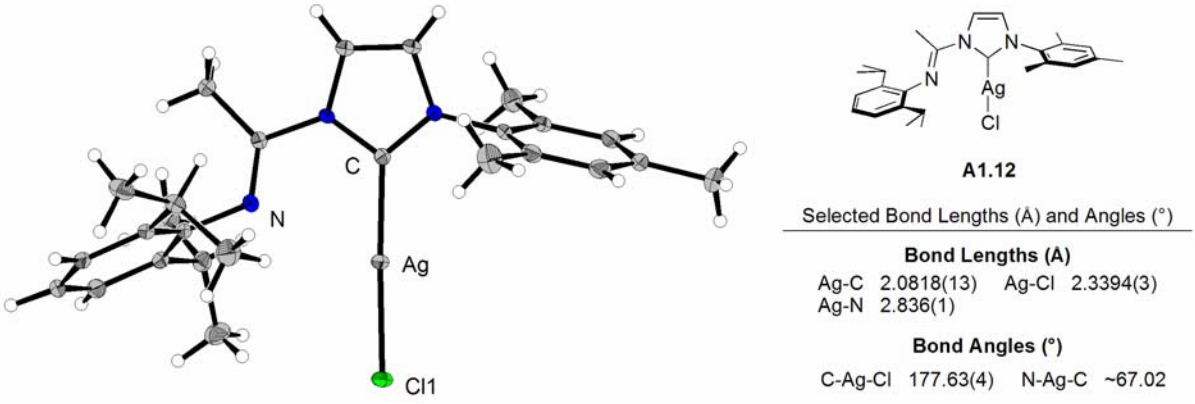


Figure A1.3. Molecular structure of Ag complex **A1.12**. Atoms are represented by thermal ellipsoids at 50% probability.



Based on the crystallographic structure of **A1.12**, the distance between the imine N and Ag atoms is 2.836 Å. Although the imine is oriented such that the lone electron pair on N is directed toward the Ag atom, the two atoms are too far away to have a significant interaction. Silver tends to form linear, low coordinate complexes, and therefore it is not surprising that it is not bound by the imine.[12] Thus, the fact that the imine is oriented toward the metal center is most likely the result of the molecule occupying the lowest energy conformation in the solid state.

With the Ag carbene **A1.12** in hand, the next step was to transfer the NHC onto group 10 metal atoms, with a view toward making catalytically active complexes. (dme)$NiBr_2$ was chosen as a Ni source for the synthesis of compound **A1.13** (Scheme A1.5). The Ag carbene was generated as described above, and then a suspension of (dme)$NiBr_2$ was added to give a light blue solution (Scheme A1.5). This was somewhat promising, as Ni diimine complexes are known to be blue.[1] The ^{1}H NMR was indeterminate, thus we obtained the X-ray crystal structure of the blue compound, which proved to be tetrakis(1-mestiylimidazole)$NiBr_2$ (**A1.14**, Figure A1.4).

Scheme A1.5. Attempted synthesis of Ni-NHC complex **A1.13**.

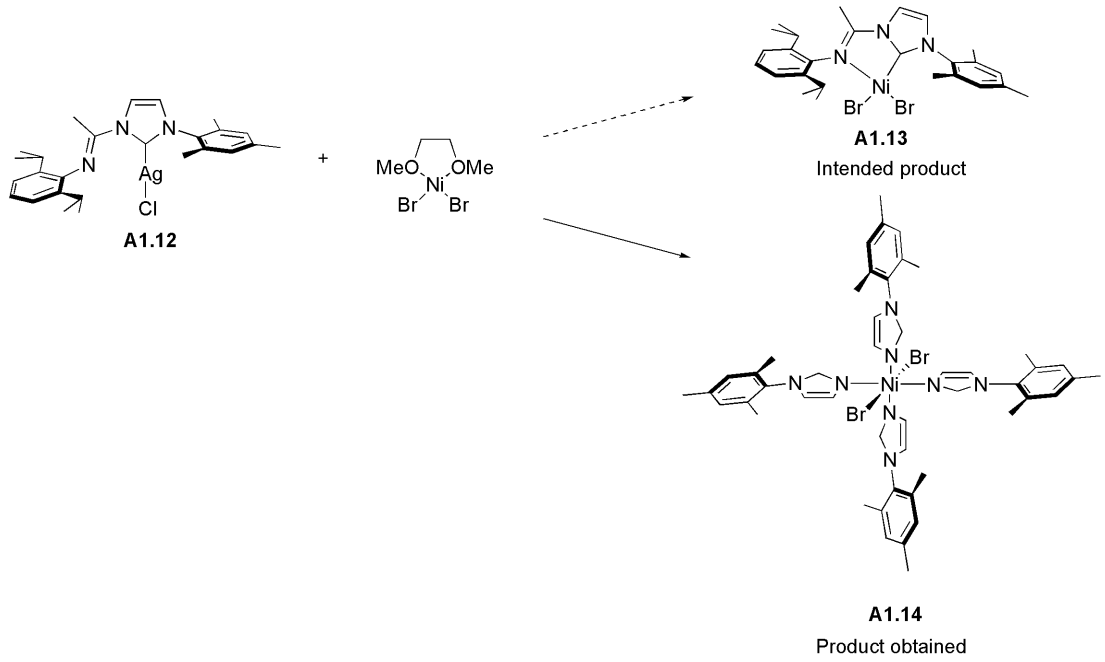
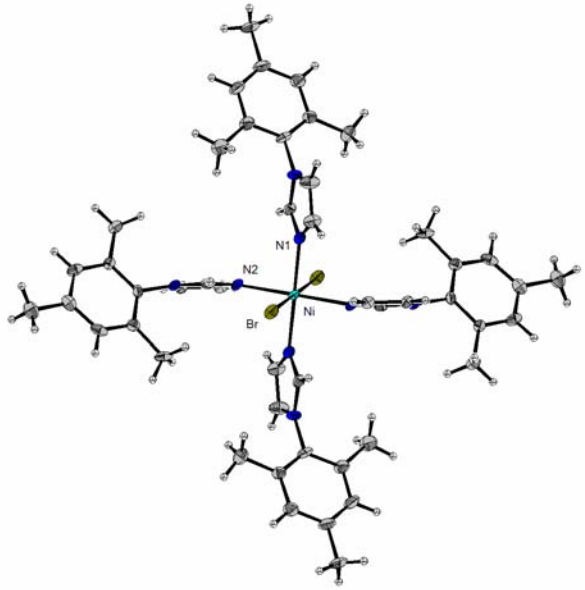
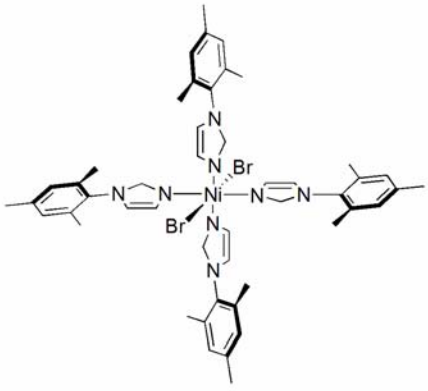


Figure A1.4. Molecular structure of Ni complex **A1.14**. Atoms are represented by thermal ellipsoids at 50% probability.





A1.14

Selected Bond Lengths (Å) and Angles (°)

Bond Lengths (Å)

Ni-N(1)	2.047(4)	Ni-Br	2.6774(6)
Ni-N(2)	2.117(4)		

Bond Angles (°)

N(1)-Ni-N(1)'	180.00(16)	N(1)-Ni-Br	90.15(12)
N(1)-Ni-N(2)	90.20(17)	N(1)'-Ni-Br	89.85(12)
N(1)'-Ni-N(2)	89.80(17)	N(2)-Ni-Br	88.30(12)

Clearly, the mesitylimidazole components of compound **A1.14** are derived from ligand **A1.9**. From the appearance of this compound, however, it is not clear what has happened. It is also unclear what has happened to the imine portion of the ligand. Certainly, based on our previous experience (see Chapter 4), Ni NHC compounds can exhibit strange behavior. Therefore, we decided to target a more well-behaved metal. Staying in group 10, we decided to attempt the synthesis of a Pt complex. Platinum complexes are typically more stable than those of the other group 10 metals, especially Ni. $(PtCl_2(C_2H_4))_2$ was chosen as a Pt source in the targeted synthesis of compound **A1.15**. This Pt source was chosen based on the successful use of chloro-bridged Pd dimers described in Chapter 3. A suspension of this Pt compound was mixed with a solution of Ag carbene **A1.12** to give a yellow product (Scheme A1.6). Again, an indeterminate ^1H NMR spectrum was obtained and X-ray crystallography provided the structure (**A1.16**, Figure A1.5).

Scheme A1.6. Attempted synthesis of Pt-NHC complex **A1.15**.

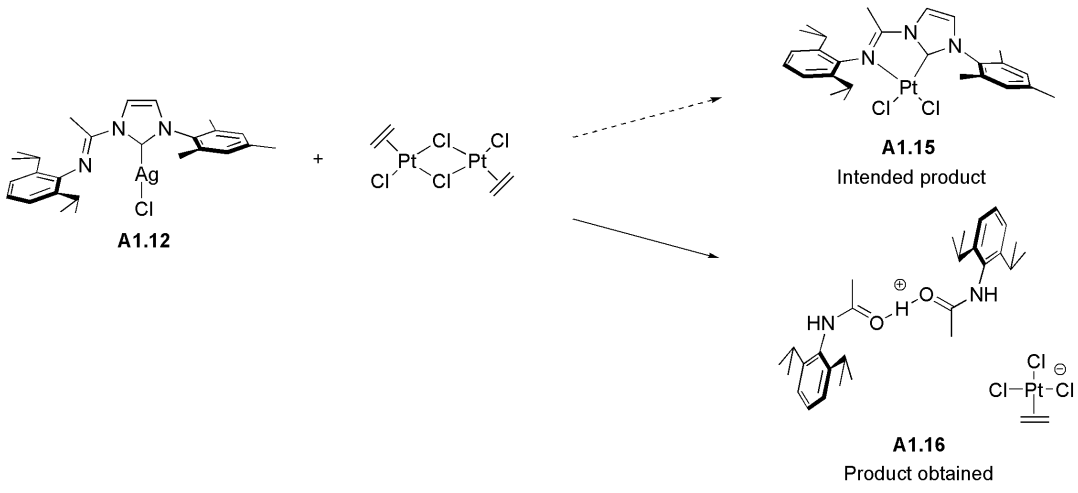
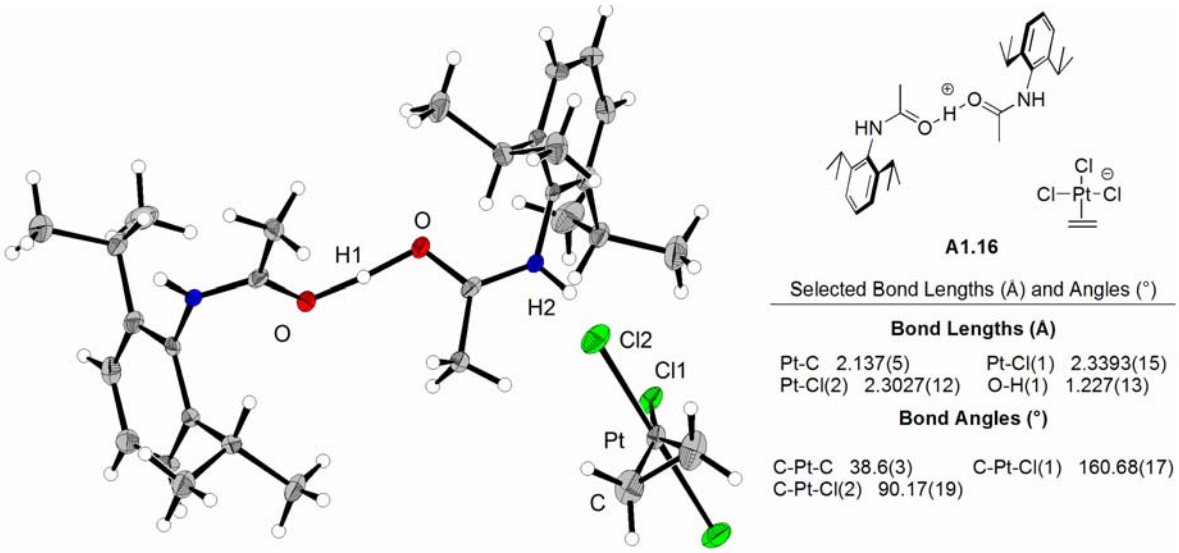


Figure A1.5. Molecular structure of Pt complex **A1.16**. Atoms are represented by thermal ellipsoids at 50% probability.



Compound **A1.16** features an ion pair of the $PtCl_3(C_2H_4)$ anion and two molecules of *N*-(diisopropylphenyl) acetamide bridged by a proton as the cation. While this is an interesting compound, similar structures have been reported. In those cases, the distance between hydrogen-bonded oxygen atoms is nearly identical to the distance observed in **A1.16** (2.431 Å).[13] Comparison of Pt compound **A1.16** with Ni compound **A1.14** reveals that the portion of the ligand lost in the structure of Ni complex **A1.14** has appeared in Pt complex **A1.16**, and therefore, their mechanisms of formation may be related. In both cases the C–N bond between the imine and imidazole functionalities of ligand **A1.9** was cleaved. Closer examination of the structure **A1.16** reveals additional oxygen and hydrogen atoms, most likely arising from water. Whether the source of the water was the solvent (which was collected from a drying column and assumed to be dry) or from the formation of the Ag carbene is unclear. It is also unclear whether C–N cleavage occurs before ligation to the second metal (Ni or Pt), or is metal-mediated.

A1.4 Conclusion

A novel chelating NHC/imine ligand has been synthesized, and its complex with Ag has been characterized. However, during attempted transfer of the NHC ligands to other metal atoms, unexpected metal complexes resulted. Just as before, we encountered difficulty in the synthesis of a targeted NHC complex due to unexpected and undesired rearrangements of the ligand itself. The problems we have encountered en route to complexes of chelating NHCs have demonstrated that, contrary to popular opinion, NHCs are not simply strongly σ-basic and weakly π-acidic analogs of phosphine or any other two-electron donor ligands. NHCs, no matter how stable they may be, are still carbenes, and as such are reactive compounds. However, despite the setbacks described above, the successful synthesis of Ag carbene **A1.12** suggests that these problems can be overcome, and complexes of imine/carbene ligand **A1.9** can be made.

A1.5 Acknowledgments

This work was supported by the Rohm and Haas Corporation. Compound **A1.12** was synthesized and crystallized by Donde Anderson. Larry Henling and Mike Day performed the X-ray crystallographic analyses of compounds **A1.12**, **A1.14** and **A1.16**.

A1.6 Experimental Details

Materials and Methods. All reactions involving metal complexes were conducted in oven-dried glassware under a nitrogen atmosphere using standard glovebox techniques. Solvents were prepared by passage through alumina. All commercially obtained reagents were used as received. Organic reagents were purchased from Sigma-Aldrich and metal salts obtained from Strem. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz, 75 MHz and respectively) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C spectra are reported in terms of chemical shift.

1-(Mesityl)-3-(1-(2,6-diisopropylphenyl)-ethylidene)-imidazolium chloride (A1.9). N-(2,6-Diisopropylphenyl)acetamide[14] (**A1.7**) (1.05 g, 4.77 mmol, 1.00 equiv) was suspended in benzene (~30 mL). To this solution was added phosphorus pentachloride (0.993 g, 4.77 mmol, 1.00 equiv) in portions. The suspended solid went into solution, turning yellow. It was allowed to stir at 23 °C for 1 hr. At this point, a distillation apparatus was attached, and the benzene was removed, leaving a yellow oil. To this was added 1-mesitylimadazole[15] (**A1.4**) (0.888 g, 4.77 mmol, 1.00 equiv). A white precipitate formed immediately. This solid was taken up in CH_2Cl_2, and ether was slowly added to the solution, giving **A1.9** as a white precipitate (0.638 g, 1.50 mmol, 31.4 % yield). ^{1}H

NMR (300 MHz, $CDCl_3$): δ 12.11 (s, 1H), 8.51 (s, 1H), 7.28 (s, 1H), 7.20 (bs, 3H), 7.05 (bs, 2H), 2.78 (s, 3H), 2.67 (septet, *J* = 6 Hz, 2H), 2.34 (s, 3H), 2.25 (s, 6H), 1.16 (dd, *J* = 9, 27 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 226.8, 140.9, 137.2, 134.9, 130.4, 130.1, 126.0, 124.4, 124.1, 123.9, 118.8, 29.0, 23.7, 23.5, 23.2, 21.5, 18.4, 17.7. HRMS: Calc'd. for $C_{26}H_{34}N_3$ (M^+): 388.2753. Found 388.2741.

1-(Mesityl)-3-(1-(2,6-diisopropylphenyl)-ethylidene)-imidazolyl silver (I) chloride (A1.12). 1-(Mesityl)-3-(1-(2,6-diisopropylphenyl)-ethylidene)-imidazolium chloride (**A1.9**) (0.30 g, 0.71 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (~10 mL). To this was added a suspension of silver(I) oxide (0.16 g, 0.71 mmol, 1.0 equiv) in CH_2Cl_2 (~5 mL). The resulting suspension was allowed to stir at 23 °C overnight. The next day, the dark Ag_2O suspension had turned light grey. It was filtered, and the solvent was removed from the filtrate under reduced pressure, leaving a colorless solid. Crystals suitable for X-ray diffraction crystallography were obtained by allowing a concentrated solution of **A.12** in CH_2Cl_2/pentane to stand at 0 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 2.1 Hz, 1H), 7.22-7.12 (m, 3H), 7.06 (d, *J* = 2.1 Hz, 1 H), 7.01 (s, 2H), 2.73 (septet, *J* = 6.9 Hz, 2H) 2.61 (s, 3H), 2.35 (s, 3H), 2.09 (s, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 151.8, 142.1, 140.3, 136.7, 135.8, 134.7, 130.0, 125.1, 123.6, 123.1, 119.4, 28.7, 23.5, 23.1, 21.3, 18.8, 18.2.

Tetrakis(1-mesitylimidazole) nickel (II) bromide (A1.14). A solution of 1-(mesityl)-3-(1-(2,6-diisopropylphenyl)-ethylidene)-imidazolyl silver (I) chloride (**A1.12**) (205 mg, 3.87 mmol, 1.00 equiv), freshly prepared as described above, was mixed with a CH_2Cl_2 (10 mL) suspension of nickel (II) bromide dimethoxyethane adduct (0.12 g, 0.39 mmol,

1.0 equiv). This immediately provided a light blue solution with a heavy precipitate. This was allowed to stir at 23 °C for 1 hr, then filtered through Celite. The filtrate solvent was removed under reduced pressure, leaving a light blue solid. Crystals suitable for X-ray diffraction crystallography were obtained by slow evaporation of a solution of **A1.14** from ethyl acetate.

Bis((2,6-Diisopropylphenyl)acetamide) η^2-(C_2H_4)-chloroplatinic acid (A1.16). A solution of 1-(mesityl)-3-(1-(2,6-diisopropylphenyl)-ethylidene)-imidazolyl silver (I) chloride (**A1.12**) (0.127 g, .240 mmoles, 1.00 equiv), freshly prepared as described above, was mixed with a CH_2Cl_2 (~10 mL) suspension of $(PtCl_2(C_2H_4))_2$ (0.141 g, 0.240 mmol, 1.00 equiv). This immediately provided a light yellow solution with a heavy precipitate. This was allowed to stir at 23 °C for 1 hr, then filtered through Celite. The filtrate solvent was removed under reduced pressure, leaving a light yellow solid. Crystals suitable for X-ray diffraction crystallography were obtained by layering pentane over a concentrated THF solution of **A1.16** and storing the resulting layered solution at –40 °C.

A1.7 References

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[11] The crystallization of **A1.12** was placed in a refrigerator and largely forgotten. Therefore, the "extended period of time" turned out to be around two years, at which point it was rediscovered during a lab cleanup and found to have produced quite nice crystals. If nothing else, this fact is a testament to the role of serendipity in chemical research, as well as the stability of complex **A1.12**.

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