

Communications

An Unusually Static, Sterically Hindered Silver Bis(N-heterocyclic carbene) Complex and Its Use in Transmetalation

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Summary: A dimeric silver complex of the bulky bis(N-heterocyclic carbene) ligand 1,1'-dimesityl-3,3'-methylenediimidazol-2,2'-diylidene exhibits a surprisingly static structure in solution, due to a favorable chelate ring conformation, yet serves as a convenient transmetalation reagent for the formation of a new κ^2 -bis(NHC) rhodium(I) complex. The latter complex demonstrates a strong influence of N-substituent steric bulk on the bis(NHC) binding mode.

N-heterocyclic carbenes (NHC's) have emerged as a versatile class of ancillary ligands in organometallic chemistry.¹ Following Arduengo's discovery of stable imidazol-2-ylidenes in 1991,² enormous interest has centered on the use of carbene ligands in homogeneous catalysis.³ The increased catalytic activity observed in a number of reactions⁴ has been attributed to a combination of electronic effects, resulting from the higher

σ -donicity of NHC ligands compared with phosphines,⁵ and enhanced thermal stability, which may inhibit catalyst deactivation.⁶

A widely employed synthetic strategy introduced by Wang and Lin⁷ involves the use of silver–NHC complexes as air-stable reagents for carbene transfer to catalytically important transition metals.^{8–11} Most Ag–NHC complexes undergo rapid carbene exchange in solution,¹² and it has been suggested that their efficacy as transmetalation agents correlates with this Ag–C bond lability.¹¹

As part of an effort to design new catalysts containing chelating carbene ligands, we have investigated silver complexes of sterically hindered bis(imidazol-2-ylidenes). Bidentate NHC's have received less attention than their monodentate counterparts in catalysis,^{6,13} and we hy-

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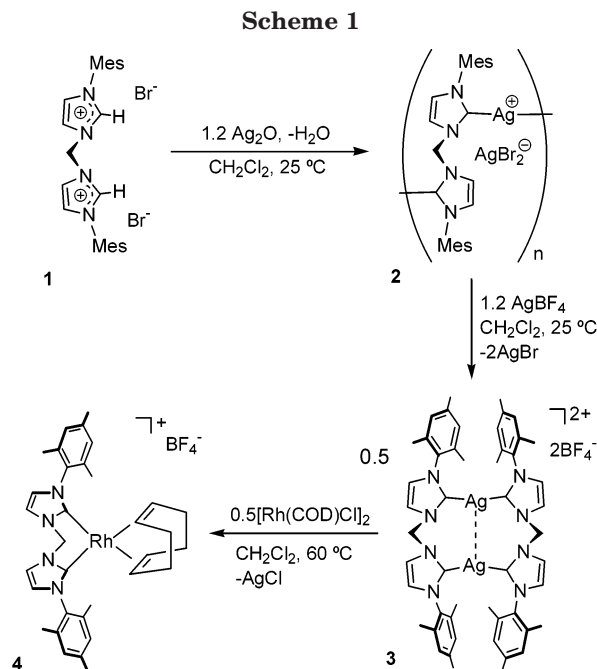
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pothesize that combining the stronger ligand binding arising from the chelate effect with increased steric bulk could improve catalyst activity by preventing decomposition of highly reactive intermediates. Our initial interest focused on the bulky bis(NHC) 1,1'-dimesityl-3,3'-methylenediimidazol-2,2'-diylidene (DIMes^{Me}), a ligand which was first employed by Herrmann and co-workers in a palladium CO/ethylene copolymerization catalyst¹⁴ but has not been widely investigated. Herein we report the synthesis of a silver complex of DIMes^{Me} that has an unusually static dimeric structure in solution. This compound is nevertheless an effective transmetalating agent and promises easy access to sterically hindered bis(NHC) transition-metal complexes with potential catalytic utility.

Treatment of 1,1'-dimesityl-3,3'-methylenediimidazolium dibromide¹⁴ (**1**) with 1.2 equiv of Ag₂O in CH₂Cl₂ for 2 h at 25 °C (Scheme 1), followed by filtration through Celite and removal of solvent, afforded a brown, amorphous solid. The ¹H NMR spectrum of this material (DMSO-*d*₆) was complex and could not be fully interpreted, but no imidazolium N₂C–H resonances (δ 8.5–10) were evident. On the basis of reaction stoichiometry and literature precedent,¹² we formulate this material as $[(\kappa^2, \mu_2\text{-DIMes}^{\text{Me}})\text{Ag}]_n[\text{AgBr}_2]_n$ (**2**), containing a mixture of oligomers with bridging dicarbene ligands. Precursor **2** released AgBr upon reaction with 1.2 equiv of AgBF₄ in hot acetonitrile, and colorless microcrystals were obtained upon crystallization from CH₂Cl₂/Et₂O. X-ray crystallographic analysis¹⁵ revealed a dicarbene-bridged dimer, $[(\kappa^2, \mu_2\text{-DIMes}^{\text{Me}})_2\text{Ag}_2][\text{BF}_4]_2$ (**3**) (Figure 1).¹⁶ This differs from other structurally characterized Ag complexes of hydrocarbon-linked bis(NHC) ligands,

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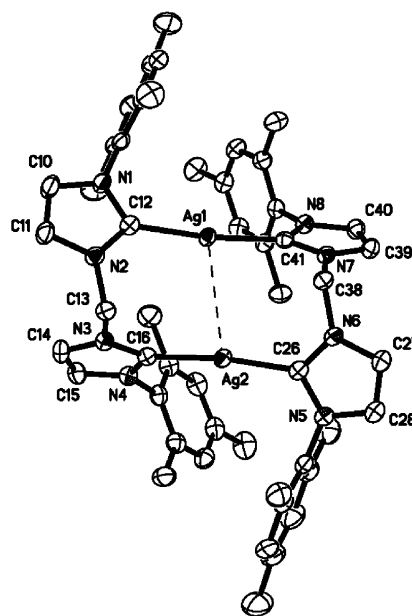


Figure 1. Molecular structure of **3**, with BF₄[−] anions omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected distances (Å) and angles (deg): Ag(1)–C(12) = 2.095, Ag(1)–C(41) = 2.093(2), Ag(2)–C(16) = 2.081(2), Ag(2)–C(26) = 2.086(3), Ag(1)–Ag(2) = 3.2039(3), C(12)–Ag(1)–C(41) = 173.50(9), C(16)–Ag(2)–C(26) = 171.93(10).

which are either monomeric¹⁷ or polymeric¹² with terminal or bridging halide ligands, respectively. However, similar dimeric structures have been observed for silver complexes of chelating CNC pincer^{8,18} and C₂N₂ cyclophane¹⁹ bis(NHC) ligands. The Ag–C bond lengths (2.081(2)–2.095(2) Å) and near-linear C–Ag–C angles (173.50(9), 171.93(10)°) of **3** are within the normal ranges for published silver NHC complexes.

An intriguing feature of **3** not identified in previously reported bis(NHC) silver dimers is the short Ag–Ag contact of 3.2039(3) Å. Strong interactions between closed-shell, d¹⁰ metals are well documented for gold,²⁰

(15) Crystal data for **3**: C₅₀H₅₆B₂F₈N₈Ag₂·3CH₂Cl₂, *M*_r = 1413.17, triclinic, space group *P*1, *a* = 13.7737(13) Å, *b* = 14.1295(14) Å, *c* = 18.4534(18) Å, α = 86.8310(10)°, β = 71.7930(10)°, γ = 68.0620(10)°, *U* = 3156.8(5) Å³, *T* = 103(2) K, *Z* = 2, *D*_c = 1.487 g cm^{−3}, μ (Mo K α) = 0.939 mm^{−1}, 13 348 independent reflections (*R*_{int} = 0.028). Final *R*1(2 σ) = 0.0355, *wR*2(all data) = 0.0986.

(16) Preparation of **3**: Ag₂O (153 mg, 0.659 mmol) and 1,1'-dimesityl-3,3'-methylenediimidazolium dibromide (300 mg, 0.549 mmol) were stirred in CH₂Cl₂ (10 mL) for 2 h at 25 °C. The mixture was filtered, and the solvent was removed in vacuo to yield **2** as a brown solid. The entire sample was stirred for 30 min in hot CH₃CN (60 °C) with AgBF₄ (128 mg, 0.659 mmol), and then the mixture was filtered and solvent was removed in vacuo. The tan solid was dissolved in CH₂Cl₂, filtered, and concentrated to ~1 mL under reduced pressure. Addition of Et₂O afforded colorless microcrystals of **3** (260 mg, 81%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ 8.06 (s, 4H, *CH* im), 7.48 (s, 4H, *CH* im), 7.26 (d, 2H, ²*J*_{HH} = 13.6 Hz, *CH*₂), 7.07 (s, 4H, *m*-H), 6.95 (s, 4H, *m*-H), 6.53 (d, 2H, ²*J*_{HH} = 13.6 Hz, *CH*₂), 2.42 (s, 12H, *p*-CH₃), 1.58 (s, 12H, *o*-CH₃), 1.25 (s, 12H, *o*-CH₃). ¹H NMR (400 MHz, CD₂Cl₂, −90 °C): δ 8.02 (s, 2H, *CH* im), 7.73 (s, 2H, *CH* im), 6.99 (s, 2H, *CH* im), 6.95 (s, 2H, *CH* im), 6.91 (s, 4H, *m*-H), 6.84 (s, 4H, *m*-H), 6.61 (AB, 4H, *J* = 13.4, *C* = 14.1 Hz, *CH*₂), 2.39 (s, 12H, *p*-CH₃), 1.86 (s, 6H, *o*-CH₃), 1.38 (s, 6H, *o*-CH₃), 1.14 (s, 6H, *o*-CH₃), 1.05 (s, 6H, *o*-CH₃). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 180.9 (2 d, ¹*J*_{AgC} = 182, ¹*J*_{109AgC} = 210 Hz, AgC), 138.8 (Mes), 135.0 (Mes), 134.0 (Mes), 133.8 (Mes), 129.2 (im), 129.0 (im), 124.6 (Mes), 122.3 (Mes), 63.5 (*CH*₂), 20.7 (*p*-CH₃), 16.7 (*o*-CH₃), 16.4 (*o*-CH₃). ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ −148.5. Anal. Calcd for C₅₀H₅₆B₂F₈N₈Ag₂·0.16CH₂Cl₂: C, 51.38; H, 4.84; N, 9.55. Found: C, 51.05; H, 4.99; N, 9.48.

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but examples involving silver are relatively rare.²¹ Ag–Ag distances shorter than twice the van der Waals radius (3.40 Å) are considered diagnostic for such “argentophilic” interactions.²² A few examples are known for mixed-ligand Ag complexes with NHC’s combined with other donors,^{7,11,12,23} but to our knowledge there are no other published examples of such interactions with the Ag centers coordinated solely by carbene ligands.²⁴

The structure of the 12-membered bicyclic chelate ring formed by the bridging ligands is unusual, describing a C_2 -symmetric twisted-boat conformation with both CH_2 tethers protruding away from the Ag_2 core in one direction. This contrasts with reported Ag bis(NHC) dimers, which have chairlike^{8,19} or helical¹⁸ structures. An interesting result of this geometry is projection of most of the mesityl steric bulk toward one face of the Ag_2 unit, leaving the other face exposed and capped by a BF_4^- anion ($d(\text{Ag}–\text{F}) = 3.510, 3.461$ Å to one F; Figure S3, Supporting Information). Counterintuitively, molecular mechanics calculations (UFF, Gaussian03) on analogues of **3** with CH_3 N-substituents show the boat form to be favored over the chair by 3.4 kcal/mol. *N*-Mesityl substituents increase this difference to 9.6 kcal/mol due to unfavorable intraligand $\text{CH}_3–\text{CH}_3$ contacts in the chair form and result in a close Ag–Ag approach in the boat form (3.43 Å) that is near the observed distance. Thus, the Ag–Ag interaction of **3** is most likely a fortuitous result of ligand geometry and not a driving force for adoption of the boat conformation.

The ^1H NMR spectrum of **3** supports retention of a rigid-boat conformation in solution, with two methylene C–H and three aryl– CH_3 resonances, the latter indicating hindered rotation of the mesityl rings.¹⁶ At -90 °C, the two *o*- CH_3 resonances separate into two distinct sets of two peaks, consistent with a C_2 -symmetric conformation that is static at low temperature but undergoes a rapid “twist” interconversion between enantiomers at room temperature.

The coordinated carbenes of **3** manifest a sharp pair of doublets at δ 180.9 in the ^{13}C NMR spectrum with well-resolved silver–carbon coupling ($^1J_{\text{AgC}} = 182, ^1J_{\text{AgC}} = 210$ Hz). This implies nonlabile silver–carbene bonds. The majority of reported silver NHC complexes exhibit broad singlets or no carbene ^{13}C NMR signal, generally taken as evidence of fluxionality in solution.¹² In fact, only a few silver NHC complexes with well-resolved silver–carbon couplings have been reported.^{7,10,25} Among these, there is only one structurally character-

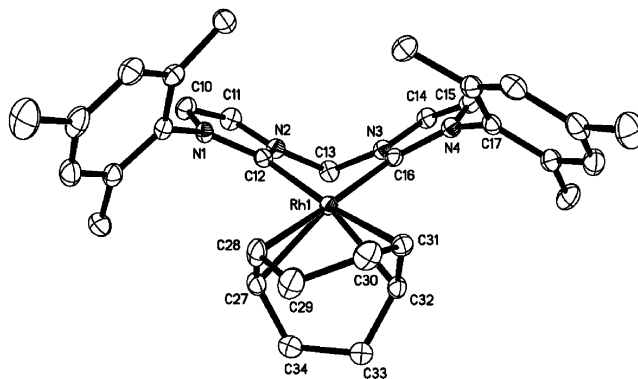


Figure 2. Molecular structure of **4**, with the BF_4^- anion omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected distances (Å) and angles (deg): Rh(1)–C(12) = 2.054(3), Rh(1)–C(16) = 2.058(3), Rh(1)–C(27) = 2.185(3), Rh(1)–C(28) = 2.223(3), Rh(1)–C(31) = 2.216(3), Rh(1)–C(32) = 2.204(3); C(12)–Rh(1)–C(16) = 85.29.

ized example containing a chelating bis(NHC).¹⁸ It is also dimeric, but the helical structure adopted by the bridging CNC “pincer” dicarbenes differs from that of **3**. Further evidence of Ag–C bond nonlability is provided by the surprising thermal stability of **3**, which shows only 16% decomposition on heating in $\text{DMSO}-d_6$ for 5 days at 100 °C. Given the present evidence, we propose that the unusually static solution structure of **3** results from kinetic stabilization of the silver–NHC bonds by a favorable chelate ring conformation that is enforced by steric bulk.

Despite its apparent nonlability in solution, **3** is useful as a carbene transfer agent. Treatment of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) with 1 equiv of **3** in CH_2Cl_2 in a sealed ampule at 60 °C provided $[(\kappa^2\text{-DIMes}^{\text{Me}})\text{Rh}(\eta^2:\eta^2\text{-COD})][\text{BF}_4]$ **4** (Scheme 1) as orange crystals after removal of AgCl and addition of hexane.²⁶ An X-ray crystal structure²⁷ (Figure 2) and solution NMR data²⁶ characterize a rigid κ^2 -bis(NHC) chelate ring. The combination of steric hindrance and strongly donating NHC ligands in **4** could be useful in catalytic reactions such as hydroformylation and hydrogenation, and potential precatalysts could be prepared following literature precedent for replacement of COD with ligands such as CO ²⁸ and MeOH ²⁹ to impart

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(24) As a reviewer has pointed out, one published Ag bis(NHC) dimer has an Ag–Ag distance of 3.158(10) Å that is evident from data in the Cambridge Structural Database (CCDC No. 157858), though this was not reported in the paper.¹⁸

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(26) Preparation of **4**: $[\text{Rh}(\text{COD})\text{Cl}]_2$ (43 mg, 0.086 mmol) and **3** (100 mg, 0.086 mmol) were stirred in CH_2Cl_2 at 60 °C for 2 h in a sealed ampule. The mixture was filtered, the solution was concentrated in vacuo, and hexane was added to afford orange crystals of **4** (90 mg, 77%). See the Supporting Information for analytical data.

(27) Crystal data for **4**: $\text{C}_{33}\text{H}_{40}\text{BF}_4\text{N}_4\text{Rh}\cdot\text{CH}_2\text{Cl}_2$, $M_r = 767.34$, monoclinic, space group $P2_1/c$, $a = 17.605(3)$ Å, $b = 13.365(2)$ Å, $c = 16.052(2)$ Å, $\beta = 115.776(2)^\circ$, $V = 3401.1(9)$ Å³, $T = 103(2)$ K, $Z = 4$, $D_c = 1.499$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.712$ mm⁻¹, 8057 independent reflections ($R_{\text{int}} = 0.027$). Final $R1(2\sigma) = 0.0469$, $wR2(\text{all data}) = 0.1271$.

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greater photolability and thermal lability, respectively. Compound **4** may also be useful in certain reactions in an unmodified form, given that a similar [bis(NHC)Rh(η^2 : η^2 -COD)]⁺ complex is a highly active alkyne hydrosilylation catalyst.³⁰

Interestingly, Crabtree, Faller, and co-workers have proposed that the mode of bis(NHC) coordination in rhodium complexes is determined primarily by tether length, and they concluded that linkers of at least two carbons are required to achieve nonbridging κ^2 coordination to Rh^I based on a study of hydrocarbon-tethered bis(NHC) ligands with ⁿBu N-substituents.²⁸ The formation of **4** with a more sterically demanding bis(NHC) suggests that N-substituent bulk plays at least as

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important a role as linker length in determining the coordination mode of bidentate NHC ligands.

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Supporting Information Available: Text, tables, and figures giving full synthetic procedures for **3** and **4**, crystal structure and refinement data for **3** and **4**, and MM calculation details; crystal data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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