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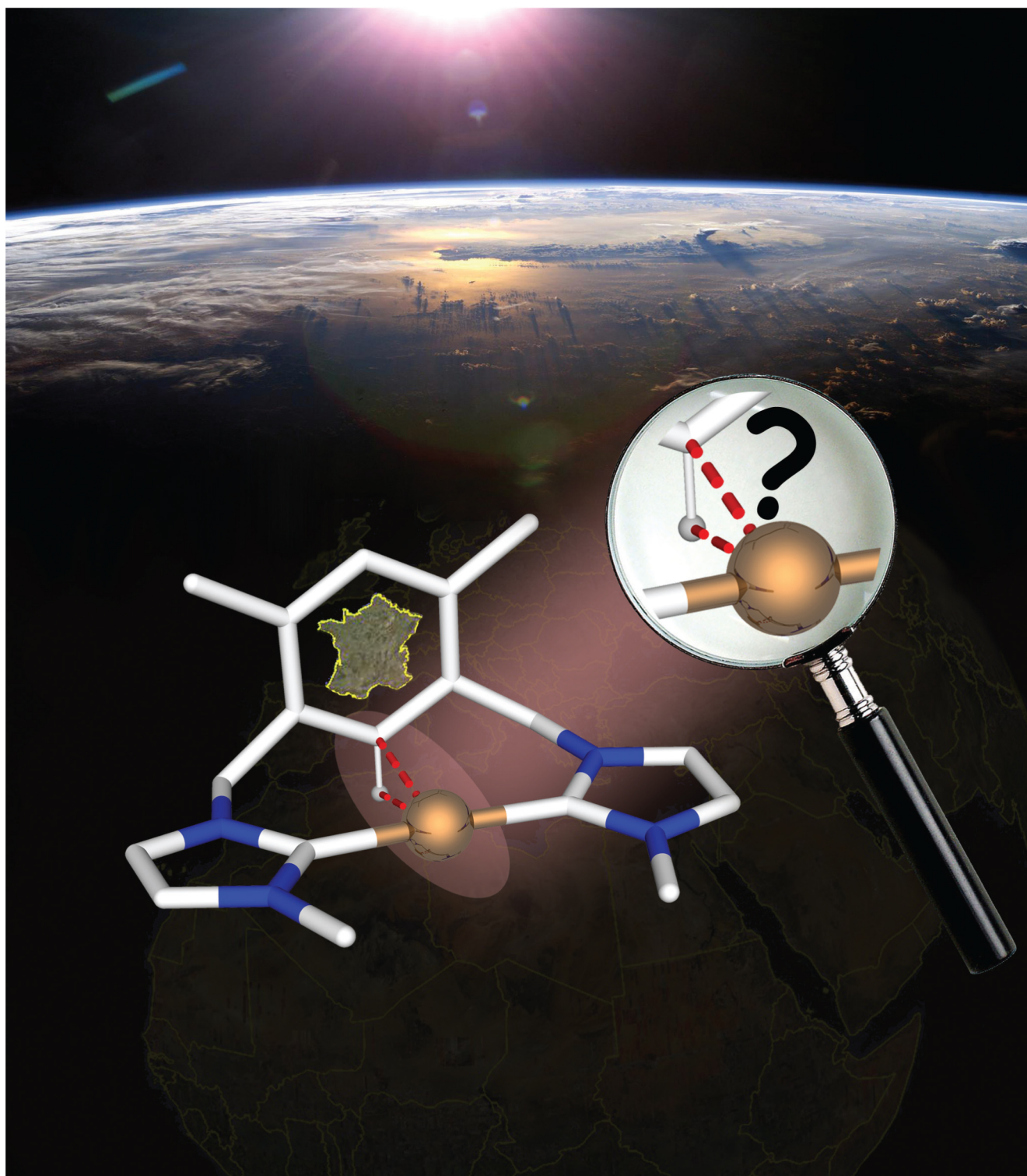**33** PUBLICATIONS **1,038** CITATIONS

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Do Short C−H−M (M = Cu(I), Ag(I)) Distances Represent Agostic Interactions in Pincer-Type Complexes? Unusual NHC Transmetalation from Cu(I) to Ag(I)

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Ⓢ *Supporting Information*

ABSTRACT: New Cu(I) and Ag(I) complexes containing a chelating bis(N-heterocyclic carbene) ligand, in which an aryl group acts as a spacer between the NHC donor groups, have been prepared by deprotonation of the bis-imidazolium salt 1,1′-((4,6-dimethyl-1,3-phenylene)bis(methylene))bis(3-methyl-1*H*-imidazol-3-ium) bis(hexafluorophosphate) ((H₂L)(PF₆)₂). Their structures, determined by X-ray diffraction, reveal a short separation (2.611(4) Å (Cu) and 2.747(7) Å (Ag), respectively) between the metal center and the C2 arene carbon of the ligand, whose metalation would result in pincer-type complexes. However, DFT calculations indicate that these distances do not correspond to C−H−M bonding interactions. Furthermore, whereas Ag(I) NHC complexes are typically used as transmetalation reagents, we report here an unusual example of the reverse situation consisting of a Cu(I) to Ag(I) transfer of NHC ligands.
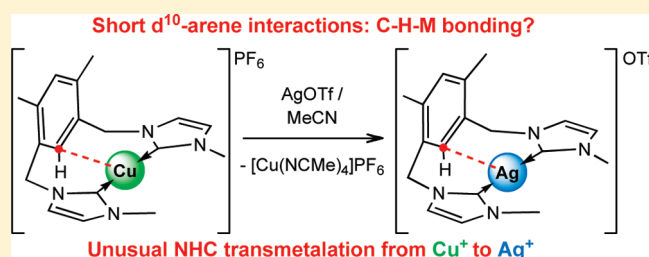
INTRODUCTION

According to Linus Pauling in his book *The Nature of the Chemical Bond*, "a chemical bond between two atoms or groups of atoms occurs in the case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species".[1] Recent studies on metallophilic interactions involving closed-shell d¹⁰ ions such as Cu(I), Ag(I), and Au(I) or pseudo-closed-shell d⁸ ions have emphasized the difficulty to correlate the values of the metal−metal distances with the energies involved.[2−7] According to the van der Waals radii of carbon (1.7 Å) and of such closed-shell metal ions (e.g., Cu(I) 1.40 Å, Ag(I) 1.72 Å),[1,8−10] metal−carbon distances below 3 Å could give rise to attractive interactions or to Pauli repulsion. In the structurally characterized examples of contacts between d⁸ or d¹⁰ metal ions and the CH moiety of an arene ((a) in Scheme 1), the presence of attractive interactions is generally recognized on the basis of the C···M distance. In the case of Cu−CHarene interactions where the C−M distance is below 2.4 Å, the metal coordination sphere tends to adopt a tetrahedral geometry,[11−15] while linear or planar coordination geometry is observed when this distance ranges from 2.4 to 3.0 Å.[16−23] Cu(I) and Ag(I) complexes are known to easily adopt various coordination geometries, and this versatility may complicate clear-cut descriptions of their coordination sphere.

Structurally characterized molecules containing a subunit of type (a) include those involving nonassisted, short metal−arene interactions with, for example, solvent molecules ((b) in

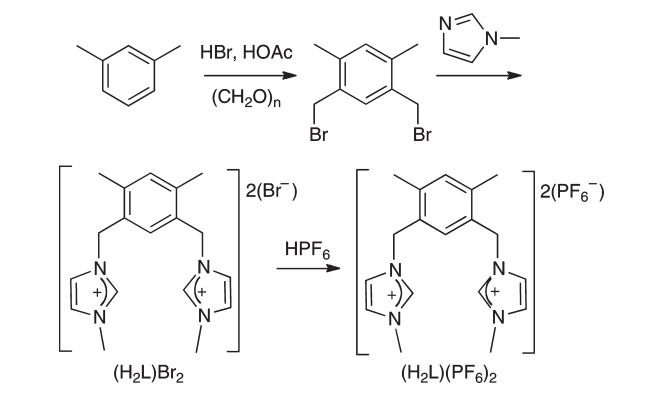**Scheme 1. Types of Short Contacts between Closed-Shell or Pseudo-Closed-Shell Metal Ions and Arenes**

Y = C, O...
Z = C, N, P...
M = Co(I), Rh(I), Cu(I), Ag(I),
Ni(II), Pd(II), Cd(II) ...
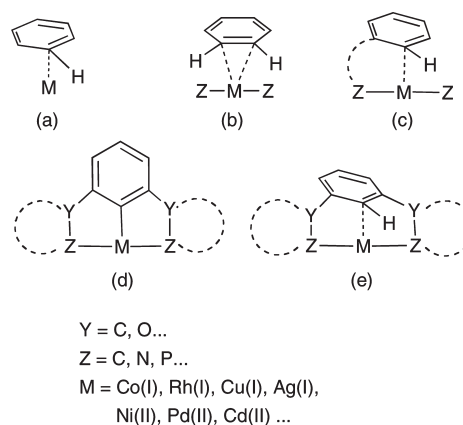
Scheme 1)[21,24−34] and those where an arene C−H bond is brought in close proximity to the metal center owing to the chelate effect of an additional donor function ((c) in Scheme 1c).[35−40] 3c−2e M−C−H interactions are generally considered to be attractive and to be responsible, at least to some extent, for the structure adopted by the complex. The proximity between the metal and the C−H bond may lower the activation
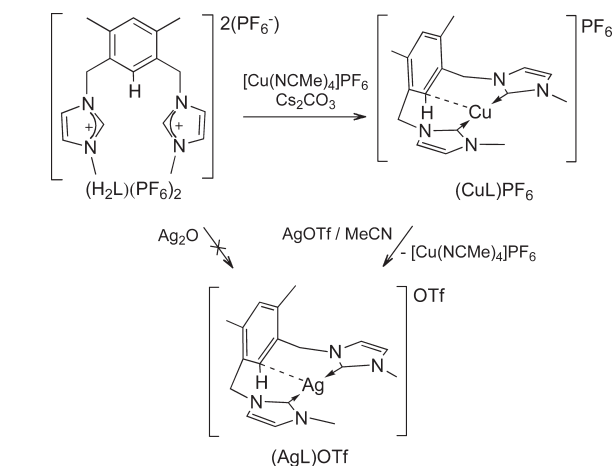
Scheme 2. Synthesis of 1,1′-((4,6-Dimethyl-1,3-phenylene)bis(methylene))bis(3-methyl-1H-imidazol-3-ium) Bis(hexafluorophosphate) ((H₂L)(PF₆)₂)

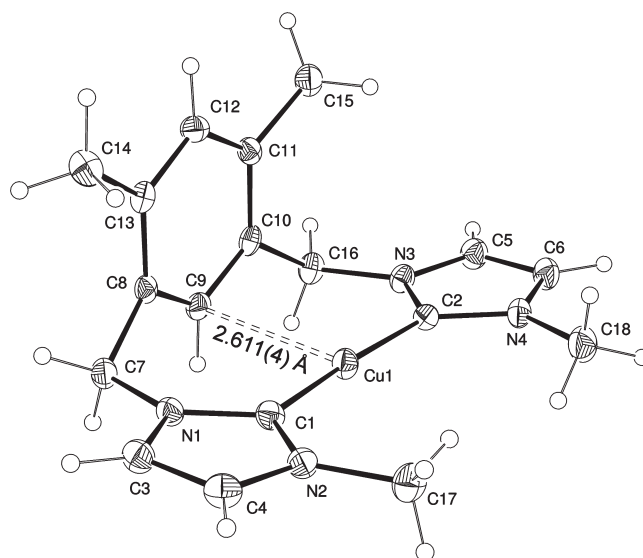**Scheme 3. Synthesis of the [CuL]PF₆ and [AgL]OTf Complexes**

Figure 1. ORTEP of the molecular structure of CuL$^+$ in [CuL]PF₆ with 30% probability thermal ellipsoids. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined *riding* on the corresponding parent atoms. Selected bond lengths (Å) and angles (deg): Cu1−C1 = 1.919(4), Cu1−C2 = 1.914(4), Cu1···C9 = 2.611(4), C1−N1 = 1.377(5), C1−N2 = 1.355(5), C2−N4 = 1.371(5), C2−N3 = 1.367(5), C8−C9 = 1.383(6), C9−C10 = 1.393(5), C11−C12 = 1.388(6), C12−C13 = 1.407(5), C8−C13 = 1.394(7); C1−Cu1−C2 = 173.7(2), C1−Cu1···C9 = 91.8(2), C2−Cu1···C9 = 94.2(2), N1−C1−N2 = 103.1(3), N3−C2−N4 = 102.8(3), C8−C9−C10 = 122.5(4).

energy of a subsequent C−H bond-breaking step with formation of a covalent C−M bond, as observed for example in pincer-type complexes ((d) in Scheme 1d). Consequently, it may not be possible to observe the M−C−H interaction and "arrested" intermediates ((e) in Scheme 1). Examples in which this latter situation corresponds to a local minimum along the reaction coordinates are thus particularly interesting to analyze.[41,42] However, does the proximity between the metal center and the C−H bond always correspond to an attractive interaction and to chemical bonding?

Herein we report new bis(N-heterocyclic carbene) complexes of Cu(I) and Ag(I) obtained from 1,1′-((4,6-dimethyl-1,3-phenylene)bis(methylene))bis(3-methyl-1H-imidazol-3-ium) bis(hexafluorophosphate) ((H₂L)(PF₆)₂) which display a similar and rare conformation. Spectral and structural characterizations of these complexes are examined along with theoretical DFT calculations performed to probe the nature of the bonding between the ligand and the d^{10} ion.

■ RESULTS AND DISCUSSION

The bis(imidazolium) salt (H₂L)(PF₆)₂ was prepared according to Scheme 2 and reacted with [Cu(NCMe)₄]PF₆ in the

presence of the inorganic base Cs₂CO₃ to give [CuL]PF₆ in good yields, in which the doubly deprotonated, bidentate ligand L acts as a trans-chelating N-heterocyclic carbene (NHC).

Although the direct reaction between (H₂L)(PF₆)₂ and Ag₂O failed to give the analogous cationic Ag(I) complex [AgL]PF₆, the latter was successfully obtained by a transmetalation reaction between [CuL]PF₆ and AgOTF in MeCN, which afforded [AgL]OTf (Scheme 3). This reaction is particularly noteworthy since, to the best of our knowledge, carbene transmetalation reactions always feature the opposite direction (from Ag to Cu),[43−46] although transmetalation from Cu to Ru,[47] Au, and Pd[48] has recently been reported. The X-ray molecular structures of [CuL]PF₆ and [AgL]OTf are shown in Figures 1 and 2, respectively. The metal center is coordinated by the N−C−N carbon atoms (C1 and C2; atom labels refer to the ORTEP drawings) of the dicarbene ligand, with an almost linear C1−M−C2 arrangement (C1−Cu1−C2 = 173.7(2)°, C1−Ag1−C2 = 178.3(3)°). The two NHC rings are almost coplanar (angle between their mean planes: 8.1(2)° for CuL$^+$ and 4.2(3)° for AgL$^+$), and the structural constraints lead the aryl ring to be almost perpendicular to the C1, C2, Cu1, C9 plane (angle between the two mean planes: 96.5(1) for CuL$^+$ and 98.3(2)° for AgL$^+$). Both structures show a close contact between the metal center and the arene C9 carbon (Cu1−C9 = 2.611(4) Å, Ag1−C9 = 2.747(7) Å). These relatively short M···C9 separations may suggest an η^1-C interaction between the aryl carbon atom (via its p$_z$ orbital) and the metal center[49] or a three-center, two-electron interaction between the metal and the aromatic C−H bond.[50] For comparison, metal−CH interactions with an aryl group have been observed in macrocyclic Cu(I) and Ag(I) complexes at 2.381(5) and 2.402(5) Å and at

2.565(4) and 2.664(1) Å, respectively, and described as η^1 complexation or two-electron donation from the C—H bond.[17] It is interesting to contrast the behavior of the bis-NHC ligand present in CuL^+ and AgL^+ with that of very similar ligands in a Au(I) complex ((a) in Scheme 4a), where the ligand acted as a bridge rather than a chelate,[51] or in an Ir(I) complex ((b) in Scheme 4b) where no C—H—M interaction was observed.[52] This clearly shows that the proximity between the aryl C9 atom and the coinage metal observed here does not solely result from the chelating nature of the bis-NHC ligand but also depends on the metal fragment being chelated.

Information about the structure of these complexes in solution can be gained from ^1H NMR spectroscopy. The structures of the CuL^+ and AgL^+ cations are likely to be retained in solution, since the ^1H NMR resonance for H9 (attached to C9) displays a downfield shift with respect to the precursor ligand (δ 7.11, 7.95, 7.85 ppm for $(H_2L)(PF_6)_2$, $[CuL]PF_6$, and $[AgL]OTf$, respectively).
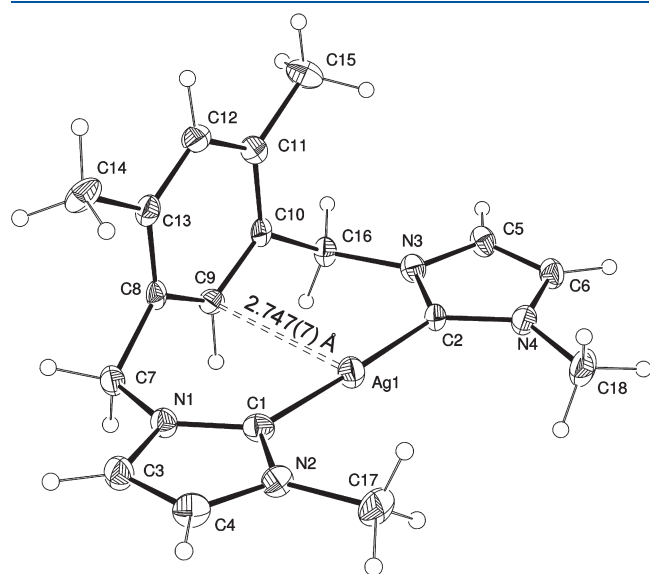

Figure 2. ORTEP of the molecular structure of AgL^+ in $[AgL]OTf$ with 30% probability thermal ellipsoids. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined *riding* on the corresponding parent atoms. Selected bond lengths (Å) and angles (deg): Ag1—C1 = 2.094(7), Ag1—C2 = 2.086(7), Ag1···C9 = 2.747(7), C1—N1 = 1.351(9), C1—N2 = 1.358(9), C2—N4 = 1.352(9), C2—N3 = 1.349(9), C8—C9 = 1.39(1), C9—C10 = 1.39(1), C10—C11 = 1.39(1), C11—C12 = 1.38(1), C12—C13 = 1.40(1), C8—C13 = 1.40(1); C1—Ag1—C2 = 178.3(3), C1—Ag1···C9 = 90.2(2), C2—Ag1···C9 = 88.8(2), N1—C1—N2 = 105.0(6), N3—C2—N4 = 103.6(6), C8—C9—C10 = 122.2(7).

This pronounced deshielding is due to the proximity between C9 and the metal center.

A somewhat related bonding situation was observed in Rh(III) complexes with a trans-spanning bis(oxazoline) ligand obtained by hydrogenolysis of NCN-pincer complexes.[53] An aryl ring, connected to the two oxazolines in mutual meta positions, was found in close enough proximity to the Rh center to allow the proximal proton to couple with the metal in the ^1H NMR spectrum and the corresponding aryl carbon was at a distance between 2.608(7) and 2.632(6) Å from the metal. In this rhodium complex, the ^1H NMR $\Delta\delta$ of the proximal proton between the complex and the free ligand is 1.78 ppm, larger than in CuL^+ and AgL^+ (0.85 and 0.74 ppm, respectively). The unusual structures of CuL^+ and AgL^+ led us to examine whether the d^{10} metal centers are better described as T-/Y-shaped tricoordinated or linearly dicoordinated,[54,55] and the results of detailed DFT calculations are described below.

Quantum Chemical Studies. *Structural Parameters.* A comparison between different computational methods was performed which can give first hints on the interactions between the ligand and the metal. Thus, two different density functionals were tried, each of them without and with Grimme's dispersion correction (see Experimental Section).

There are some differences in the $M-C_{NHC}$ distances depending on the DFT methods used, but all methods agree within 2% (Table 1). Upon going from the Cu(I) to the Ag(I) complex, this

Table 1. Comparison between Computed and Experimental Structural Parameters for the Cations in $[CuL]PF_6$ and $[AgL]OTf$

	d (Å)				
bond	B3LYP	B3LYP-D	BP86	BP86-D	exptl
Chelating Cu^+ Complex					
Cu—C9	2.648	2.673	2.552	2.592	2.611(4)
Cu—C_{NHC}	1.966	1.956	1.937	1.928	1.919(4)
					1.914(4)
Cu—H9	2.711	2.805	2.630	2.751	
C9—H9	1.086	1.085	1.095	1.094	
C12—H12	1.084	1.084	1.093	1.093	
Chelating Ag^+ Complex					
Ag—C9	2.824	2.854	2.768	2.809	2.747(7)
Ag—C_{NHC}	2.147	2.133	2.114	2.103	2.094(7)
					2.086(7)
Ag—H9	2.881	3.000	2.842	2.980	
C9—H9	1.085	1.085	1.094	1.093	
C12—H12	1.084	1.084	1.093	1.093	

Scheme 4. Examples of Complexes Involving Bis-NHC Ligands Similar to L
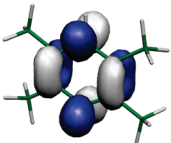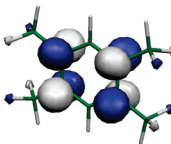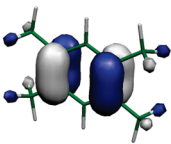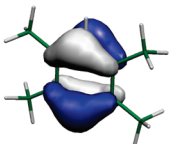

(a)

(b)
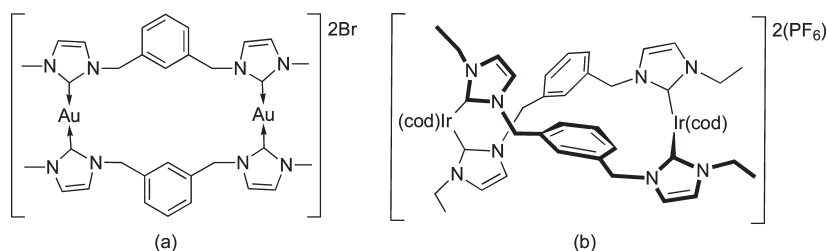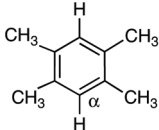
Table 2. Computed Orbital Energies for a Model of the Central Aromatic Ring as Found in the Chelating Ligand in [CuL]PF$_6$ and [AgL]OTf

	orbital energy [eV]
LUMO+1	+0.09
LUMO	+0.07
HOMO	-6.04
HOMO-1	-6.45

Table 3. Computed Orbital Energies for a Model Cationic Cu(I) Center with Two Strongly Bound NHC Ligands as found in [CuL]PF$_6$

	orbital energy [eV]
LUMO+1	-3.16
LUMO	-3.91
HOMO	-9.63
HOMO-1	-9.70
HOMO-2	-10.12
HOMO-3	-10.55
HOMO-4	-10.56
HOMO-5	-10.72
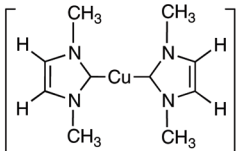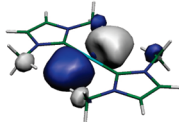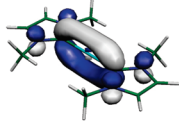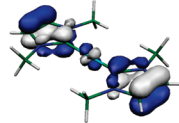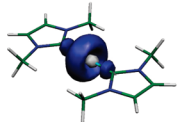
bond length increases independently of the method (as well as experimentally) by 9%. However, when the distances between M and C9 are considered, the four methods result in a scattering of predicted structural parameters of almost 5% (not to mention the distance from M to H9, where this scattering is much higher). A general increase in bond lengths when going from the Cu(I) to the Ag(I) complex is noted, which ranges from 5 to 8%. This strongly suggests that the interaction energy between M and C9 and the H atom attached to it is rather small, so that subtle differences of methods with respect to the preferred bond and torsional angles enforce markedly different distances between M and the ring.

The fact that the C—H distances for the C9 and C12 positions are almost identical also indicates that there is no strong interaction between the occupied bonding or the virtual antibonding C9—H9 orbital and the metal center.

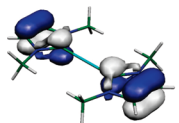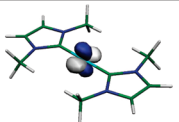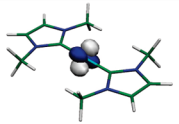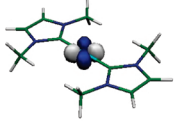*Orbital Interactions.* To identify which orbitals within the above complexes might be able to lead to chemically bonding interactions, frontier orbitals of representative ligand models were studied first and are presented in this section.

(a). (Tetramethyl)benzene. An electron-donating interaction from C$_\alpha$ to Cu is possible from HOMO-1 but not from the HOMO itself (Table 2). Potentially electron accepting ligand orbitals are rather high in energy, which is also not surprising for an aromatic ring without electron-withdrawing substituents. LUMO+1, which is energetically close to the LUMO itself, would in principle be able to interact with occupied orbitals of

Cu. Also, an antibonding σ^* C$_\alpha$—H orbital is even higher in energy and thus even more out of reach for a significant interaction, which agrees well with the fact that the C$_\alpha$—H bond is not elongated in the chelated complex.

(b). Bis(NHC)Cu(I) Complex. An electron-accepting interaction from C$_\alpha$ to Cu is only possible for LUMO+1, which means that the aromatic ring in the chelated complex is not located at

Scheme 5. Reactions Considered for a Comparison between the Chelating and Nonchelating Complexation Energetics for Cu(I), Ag(I), and Au(I) with NHC Ligands as Well as for a RhHCl₂ Moiety with a Chelating or Nonchelating Bis(oxazoline) System
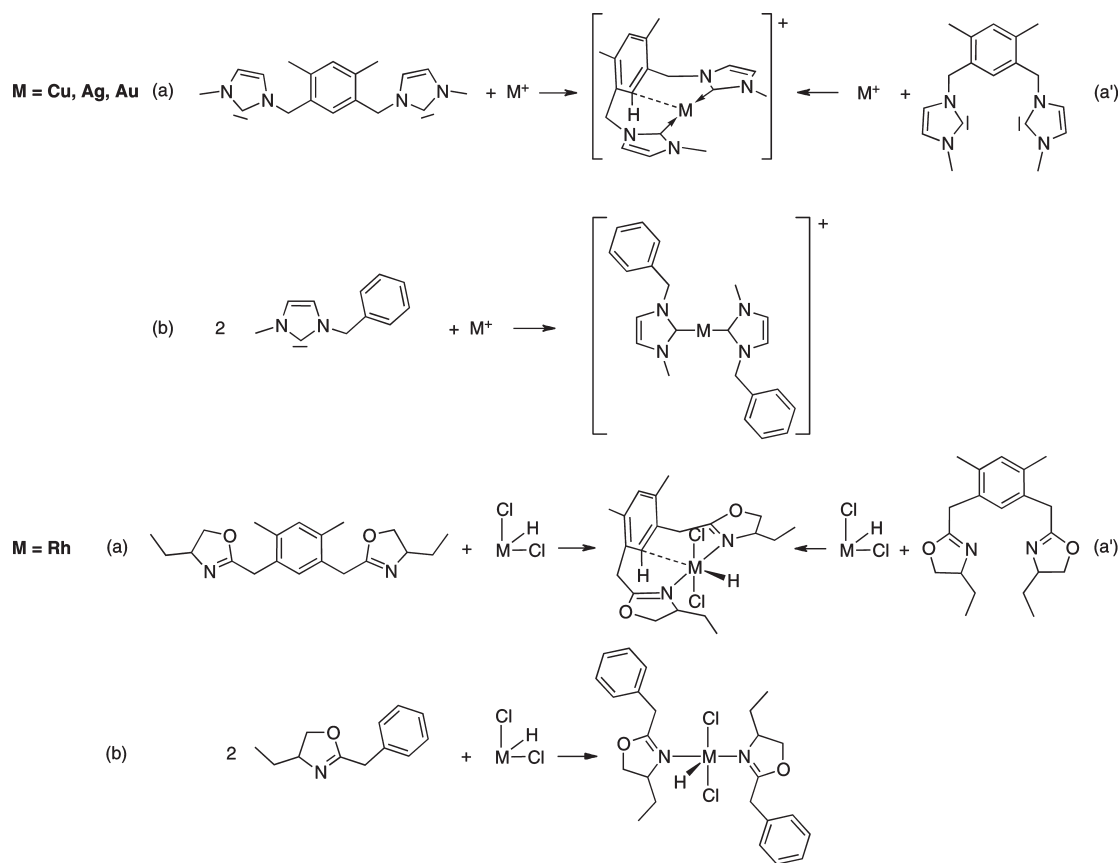
the optimal position for a bonding interaction with the metal (Table 3). The situation is clearer for a potential back-donation from Cu(I) (HOMO-1 would exhibit a suitable symmetry) to the aromatic ring (LUMO+1), which will not be too strong, with an orbital energy difference of almost 10 eV, even when taking into account the typical shift for the cationic L_2Cu^+ fragment toward lower orbital energies.

Complexation Energetics. Complexation of Cu^+, Ag^+, and Au^+ with the chelating ligand under investigation was compared to a complexation by two chemically similar monodentate ligands. An analogous comparison was also made for the Rh(III) complex of ref 53 (Scheme 5).

As can be seen from Table 4, binding by two monodentate ligands is clearly more favorable from an energetic point of view for Cu^+, Ag^+, and Au^+ than chelate formation. The difference in complexation energy between chelating and nonchelating coordination modes (reactions (a) and (b) in Scheme 5, respectively) is predicted to be between 35 and 40 kJ/mol for Cu^+ and Ag^+ when the best conformer of the chelating ligand is assumed as the reactant.

As the lowest energy conformer of the free ligand resembles the structure shown in the above scheme, part of the energetic difference between chelating and nonchelating coordination results from unfavorable rotations of the bidentate ligand to assume a conformation suitable for chelate formation. To gain an idea about the importance of this effect, Table 4 also contains an entry for complexation energetics with a chelating ligand in a

Table 4. Comparison of Chelating and Nonchelating Complexation Energetics for Cu(I), Ag(I), and Au(I) with NHC Ligands as Well as for a RhHCl₂ Moiety with a Bis(oxazoline) Chelating or Nonchelating System at the B3LYP-D Level of Theory

	$\Delta E_{ZPE\text{-corrected}}$ (kJ/mol)			
	(a)	(a′)	(b)	$\Delta\Delta E((a)-(b))$ (kJ/mol)
Cu^+	−734.3	−758.0	−771.4	+37.1
Ag^+	−642.1	−665.8	−681.4	+39.3
Au^+	−782.5	−806.2	−833.7	+51.2
$RhHCl_2$	−397.2	−400.5	−427.5	+30.2

preoriented conformation (reaction (a′); however, also here the ligand was structurally relaxed, i.e. represents a local minimum on the potential energy surface), which is around 24 kJ/mol less stable than the lowest energy conformer. This means that also the complexation of M^+ by the preoriented chelating ligand remains energetically less favorable than complexation by two monodentate ligands.

For Au^+, the destabilization of the chelate is even somewhat higher, i.e. more than 50 kJ/mol (assuming the best conformer of the chelating ligand); this stronger energetic separation might be responsible for the fact that with Au^+ the dinuclear complex shown in (a) in Scheme 4 is formed instead of a mononuclear chelate.

Scheme 6. Model Approach of a Non Sterically Hindered Aromatic Ring (Benzene) to a Simplified Model of the $[Cu(NHC)_2]^+$ Fragment
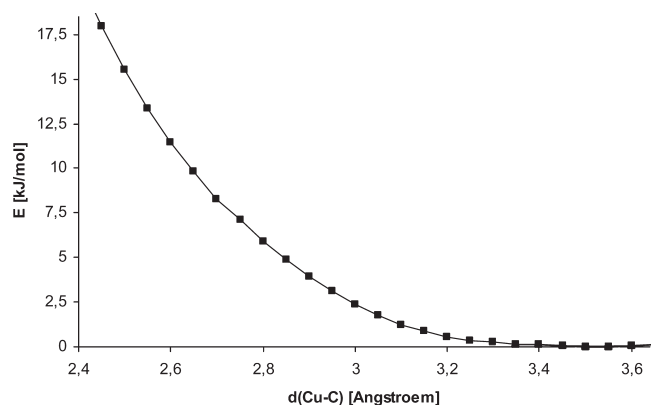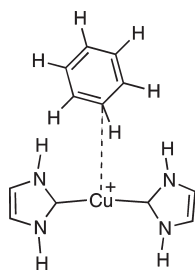

Figure 3. Potential curve for the model approach of a non sterically hindered aromatic ring (benzene) to a model $[Cu(NHC)_2]^+$ fragment at the B3LYP-D/TZVP level of theory.

As mentioned before, a similar formal complexation reaction was also considered for the RhHCl$_2$ fragment (for which in the most stable singlet isomer the three anionic ligands assume a *fac* arrangement, which of course changes to *mer* upon coordination of a trans-chelating ligand) to yield the complex of ref 53 or a nonchelating analogue. Also here, the nonchelating coordination is predicted to be 30 kJ/mol more favorable, which hints that also the bis(oxazoline) chelate complex should be considered as a 16-electron Rh(III) species without a bonding interaction with the aromatic C or the C—H bond.

To make sure that the chosen DFT method yields reliable results, a computational benchmark for a model system was performed at a coupled cluster level of theory. This benchmarking (see Supporting Information) suggests that B3LYP-D does in fact an excellent job in describing weak interactions (as e.g. between the aromatic ring and M) and is clearly more accurate than pure density functionals.

Aromatic Ligand Binding to [ML$_2$]$^+$ and L—M$^+$—L Bending Potential Curves. Potential curves were recorded for the B3LYP-D method, as pure density functionals are well-known not to cover dispersive interactions, which become more and more important when distances between fragments increase. The interaction of an aromatic ring with a $[CuL_2]^+$ fragment was studied for the simplified model system shown in Scheme 6.

Models for the carbene ligands and the aromatic ring were simplified as much as possible in order to focus on the interactions between Cu and the aromatic ring. The computed potential

Scheme 7. $[Cu(NHC)_2]^+$ Model System Used To Record a Bending Potential around Cu(I)

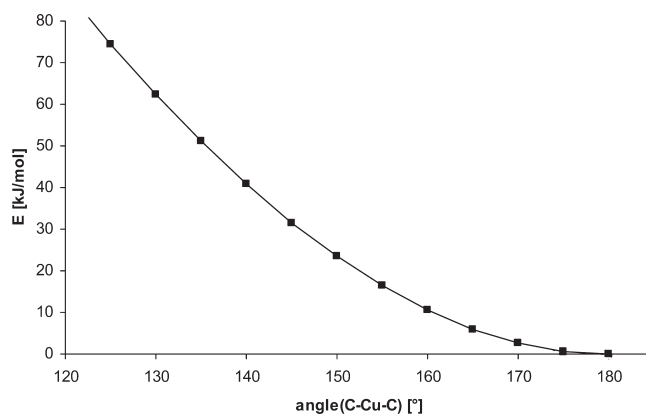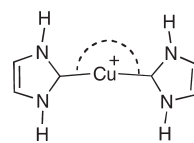**Figure 4.** Potential curve for the model approach of a non sterically hindered aromatic ring (benzene) to a model $[Cu(NHC)_2]^+$ fragment at the B3LYP-D level of theory.

curves suggest a repulsive energy in the order of 10 kJ/mol at distances around 2.6 Å, which is not much compared to usual chemical bonds (far more than 100 kJ/mol): there is definitely no bonding interaction, but potential curves are still rather "flat" in this region (Figure 3).

For Ag$^+$, potential curves were found to behave similarly; the repulsive energy for a distance of 2.8 Å between the Ag(I) center and benzene is computed to be 11.3 kJ/mol at the B3LYP-D level of theory.

The proximity between the aromatic ring and M might influence the maximum C$_{NHC}$—M—C$_{NHC}$ angle that can be assumed within the chelate complex. Therefore, also the energy dependence from this angle was recorded with the same $[Cu(NHC)_2]^+$ model (Scheme 7).

A C_{2v} structure was assumed for this investigation. As for angles as small as e.g. 140° the distance between the two closest H atoms is still larger than 3 Å and thus rather high, computed energies for these and larger angles should reflect primarily the stability of the ligand arrangement around the metal center and not repulsion between two NHC cycles (Figure 4).

It is thus concluded that the observed slight deviations of this angle from the optimum 180° will not be energetically costly. Furthermore, coordination modes of the real chelate complex without the weakly repulsive interactions between the substituted benzene ring and copper cannot occur, as they would require very unfavorable C$_{NHC}$—Cu—C$_{NHC}$ bond angles.

■ **CONCLUSION**

The different investigations presented above all agree with the absence of a chemical bond between the Cu(I) or Ag(I) centers and parts of the aromatic ring. The proximity observed

experimentally between the aromatic carbon and the metal centers results from the combined effects of a chelating ligand structure and the metal preferred coordination geometry: i.e., around a two-coordinate M^+ center, angles of $180°$ are preferred and the repulsion between the metal center and the aromatic ring is still rather small at distances around 2.6 Å (Cu) and 2.8 Å (Ag). The present complexes therefore nicely probe Pauli repulsion between a d^{10} metal center and an aromatic ring that could not be experimentally realized and studied otherwise than by an incorporation of the aromatic ring into the ligand system present in these metal complexes. Whereas an η^1-arene structure was reported for a Rh(III) complex displaying a Rh–aryl carbon distance between 2.608(7) and 2.632(6) Å, we have found here that similarly close metal–carbon separations may actually result from steric rather than electronic effects.[53] From a coordination bond enthalpy point of view, the formation of linear coordination polymers instead of chelate complexes would be more favorable; however, in solution at finite temperature, chelate complexes will profit from their higher entropy compared to a coordination polymer.

Finally, the transmetalation reaction of a NHC ligand from Cu(I) to Ag(I) reported here is of synthetic value and appears unprecedented. It extends the very recently reported examples of NHC transmetalation reactions from Cu to Ru,[47] Au, and Pd.[48]

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. Unless otherwise stated, the ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Bruker Avance 300 instrument at 300.13 and 75.47 MHz, respectively, using TMS as external standard, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC, and ^{13}C-HSQC experiments. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas. Elemental C, H, and N analyses were performed by the Service de microanalyses, Université de Strasbourg, Strasbourg, France. [Cu(NCMe)$_4$]PF$_6$, AgOTf and other chemicals were commercially available and were used as received. The labeling in Figure 1 is used for the NMR signal assignments.

1,1′-((4,6-Dimethyl-1,3-phenylene)bis(methylene))bis(3-methyl-1H-imidazol-3-ium) Dibromide ((H$_2$L)Br$_2$). (H$_2$L)Br$_2$ was synthesized following a procedure similar to that reported for a similar compound.[56] Liquid N-methylimidazole (5.00 mL, 63 mmol) was added to a flask containing solid 1,3-bis(bromomethyl)-4,6-dimethylbenzene (2.92 g, 10 mmol). The resulting suspension was stirred at room temperature for 3 h until the solid turned light yellow. The solid was collected by filtration and washed with diethyl ether (3 × 30 mL), giving a highly hygroscopic off-white solid. Yield, based on 1,3-bis(bromomethyl)-4,6-dimethylbenzene: 4.09 g, 89%. ^{1}H NMR (d_6-DMSO): δ 9.22 (2H, s, NCHN), 7.78 (2H, s, imid), 7.76 (2H, s, imid), 7.29 (1H, s, HC12), 7.19 (1H, s, HC9), 5.43 (4H, s, CH$_2$), 3.88 (6H, s, NCH$_3$), 2.25 (6H, s, CCH$_3$). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 137.6 (C8/C10 C$_{arom}$), 136.6 (NCHN), 133.1 (C12 C$_{arom}$), 130.8 (C9 C$_{arom}$), 130.5 (C11/C13 C$_{arom}$), 123.8 (C$_{imid}$), 122.4 (C$_{imid}$), 49.7 (CH$_2$), 35.9 (NCH$_3$), 18.2 (CCH$_3$) ppm. ESI-MS: m/z 375.1 ([M − Br]$^+$, 39%), 295.2 ([M − 2Br − H]$^+$, 61%). The high hygroscopicity of this compound prevented the recording of satisfactory elemental analyses.

1,1′-((4,6-Dimethyl-1,3-phenylene)bis(methylene))bis(3-methyl-1H-imidazol-3-ium) Bis(hexafluorophosphate) ((H$_2$L)-(PF$_6$)$_2$). (H$_2$L)(PF$_6$)$_2$ was synthesized following a procedure similar to

that reported for a similar compound.[56] A 65% aqueous solution of HPF$_6$ (0.77 mL, 5.67 mmol) was added to a solution of (H$_2$L)Br$_2$ (1.00 g, 2.19 mmol) in water (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h, and the precipitate was collected by filtration. This solid was washed with water (2 × 10 mL) and dried under vacuum for 3 h to give (H$_2$L)(PF$_6$)$_2$ as a white solid. Yield, based on (H$_2$L)Br$_2$: 1.14 g, 89%. ^{1}H NMR (CD$_3$CN): δ 8.32 (2H, br t, ^4J(HH) = 1.6 Hz, NCHN), 7.37 and 7.31 (4H, ABM spin system: ^3J(HH) = ^4J(HH) = 1.6 Hz, imid), 7.23 (1H, s, HC12), 7.11 (1H, s, HC9), 5.30 (4H, s, CH$_2$), 3.83 (6H, s, NCH$_3$), 2.26 (6H, s, CCH$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 139.9 (C8/C10 C$_{arom}$), 137.1 (NCHN), 134.8 (C12 C$_{arom}$), 132.2 (C9 C$_{arom}$), 130.9 (C11/C13 C$_{arom}$), 125.0 (C$_{imid}$), 123.4 (C$_{imid}$), 51.6 (CH$_2$), 37.0 (NCH$_3$), 18.7 (CCH$_3$) ppm. ESI-MS: m/z 441.2 ([M − PF$_6$]$^+$, 96%), 295.2 ([M − 2PF$_6$ − H]$^+$, 4%). Anal. Calcd for C$_{18}$H$_{24}$F$_{12}$N$_4$P$_2$ (586.34): C, 36.87; H, 4.13; N, 9.56. Found: C, 36.62; H, 4.15; N, 9.59.

Synthesis of [CuL]PF$_6$. A suspension of solid (H$_2$L)(PF$_6$)$_2$ (0.294 g, 0.50 mmol), [Cu(NCMe)$_4$]PF$_6$ (0.186 g, 0.50 mmol), and Cs$_2$CO$_3$ (0.488 g, 1.50 mmol) in acetonitrile (10 mL) was stirred at 60 °C for 15 h under an inert atmosphere. The suspension was then cooled to room temperature, and the solvent was removed under vacuum. The resulting colorless solid was then treated with CH$_2$Cl$_2$ (10 mL), and the solution was filtered. The latter was concentrated to 5 mL, and diethyl ether was added to precipitate a white solid. Recrystallization was carried out by layering Et$_2$O onto a MeCN solution, affording colorless crystals of [CuL]PF$_6$ (0.230 g, 92%). Single crystals suitable for X-ray diffraction studies were obtained by slow vapor diffusion of diethyl ether in a saturated acetonitrile solution of the complex. ^{1}H NMR (CD$_3$CN): δ 7.95 (1H, s, HC9), 7.31 (2H, d, ^3J(HH) = 1.7 Hz, imid), 7.20 (1H, s, HC12), 7.11 (2H, d, ^3J(HH) = 1.7 Hz, imid), 5.34 and 5.00 (4H, m, AB spin system, simulated, ^2J(HH) = 12.3 Hz, CH$_2$), 3.77 (6H, s, NCH$_3$), 2.17 (6H, s, CCH$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 138.9 (C8/C10 C$_{arom}$), 135.3 (C12 C$_{arom}$), 134.0 (C11/C13 C$_{arom}$), 133.1 (C9 C$_{arom}$), 123.5 (C$_{imid}$), 122.8 (C$_{imid}$), 52.3 (CH$_2$), 40.1 (NCH$_3$), 18.4 (CCH$_3$) ppm. The resonance of the coordinated NHC carbon could not be observed, probably due to the poor solubility of the complex in CD$_3$CN. ESI-MS: m/z 357.1 ([M − PF$_6$]$^+$, 100%). Anal. Calcd for C$_{18}$H$_{22}$CuF$_6$N$_4$P (502.90): C, 42.99; H, 4.41; N, 11.14. Found: C, 42.57; H, 4.33; N, 11.13.

Synthesis of [AgL]OTf. The direct synthesis of [AgL]PF$_6$ from (H$_2$L)(PF$_6$)$_2$ and Ag$_2$O was unsuccessful (no reaction occurred). However, transmetalation from the Cu(I) complex was achieved by adding AgOTf (0.129 g, 0.50 mmol) to a solution of [CuL]PF$_6$ (0.251 g, 0.50 mmol) in MeCN (10 mL) in a Schlenk tube protected against light. The solution was stirred at room temperature overnight, during which time a white solid precipitated. The solid was collected by filtration, washed with diethyl ether (10 mL), and dried under reduced pressure, affording [AgL]OTf (0.183 g, 67%) as a colorless powder. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of toluene into a saturated acetonitrile solution of the complex. ^{1}H NMR (CD$_3$CN): δ 7.85 (1H, s, HC9), 7.36 (2H, s, imid), 7.16−7.14 (3H, overlapped, HC12 + imid), 5.37 and 5.04 (4H, br, AB spin system, CH$_2$), 3.73 (6H, s, NCH$_3$), 2.11 (6H, s, CCH$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 139.5 (C8/C10 C$_{arom}$), 135.5 (C9 C$_{arom}$), 135.0 (C12 C$_{arom}$), 133.2 (C11/C13 C$_{arom}$), 124.5 (C$_{imid}$), 122.5 (C$_{imid}$), 53.3 (CH$_2$), 40.5 (NCH$_3$), 18.4 (CCH$_3$) ppm. The resonance of the coordinated NHC carbon could not be observed, probably due to the poor solubility of the complex in CD$_3$CN. ESI-MS: m/z 401.1 ([M − OTf]$^+$, 100%). Anal. Calcd for C$_{19}$H$_{22}$AgF$_3$N$_4$O$_3$S (551.33): C, 41.39; H, 4.02; N, 10.16. Found: C, 41.22; H, 4.09; N, 10.09.

X-ray Data Collection and Structure Refinement. Suitable crystals for the X-ray analysis were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[57] (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures

Table 5. X-ray Data Collection and Structure Refinement Parameters

	[CuL]PF$_6$	[AgL]OTf
chem formula	C$_{18}$H$_{22}$CuF$_6$N$_4$P	C$_{19}$H$_{22}$AgF$_3$N$_4$O$_3$S
formula mass	502.91	551.34
cryst syst	triclinic	monoclinic
a/Å	8.553(2)	8.507(2)
b/Å	11.092(3)	19.316(3)
c/Å	11.628(3)	13.392(2)
α/deg	69.90(1)	90.00
β/deg	81.25(2)	91.27(3)
γ/deg	79.82(2)	90.00
unit cell vol/Å^3	1014.7(5)	2200.0(7)
temp/K	173(2)	173(2)
space group	$P\bar{1}$	$P2_1/c$
no. of formula units per unit cell, Z	2	4
abs coeff, μ/mm^{-1}	1.222	1.064
no. of rflns measd	5948	7748
no. of indep rflns	3942	4522
no. of obsd rflns ($I > 2\sigma(I)$)	2819	3656
no. of params	277	284
R_{int}	0.034	0.031
final R1 values ($I > 2\sigma(I)$)	0.058	0.074
final wR2(F^2) values ($I > 2\sigma(I)$)	0.150	0.157
final R1 values (all data)	0.090	0.093
final wR2(F^2) values (all data)	0.165	0.162
goodness of fit on F^2	1.051	1.274
CCDC no.	796850	796851

are summarized in Table 5. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[58] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms.

CCDC 796850 and 796851 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All DFT-calculations were performed using the program package TURBOMOLE.[59] If not mentioned otherwise, the Becke-3-Lee-Yang-Parr hybrid functional (B3LYP)[60] was employed using a TZVP basis set.[61] Apart from B3LYP, additional structure optimizations were also performed with the Becke-Perdew-86 functional (BP86).[62]

At distances well below the sum of van der Waals radii, pure density functionals should yield a reasonable description of the bonding situation: i.e., chemically attractive interactions or Pauli repulsion will be more important than dispersive interactions. However, as this might not be the case, a number of calculations was also performed in which dispersive interactions were taken into account via Grimme's correction.[63]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. CIF files giving X-ray data collection and structure refinement parameters for [CuL]PF$_6$ and [AgL]OTf and text and tables giving details of the various DFT calculations and Cartesian coordinates of the optimized models. This material is available free of charge via the Internet at http://pubs.acs.org.

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