

Synthesis, spectroscopic characterization and electronic structure of some new Cu(I) carbene complexes

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Abstract. Reaction of oligomeric Cu(I) complexes $[\text{Cu}\{\mathit{m}\text{-S-C(=NR)(O-Ar-CH}_3)\}]_n$ with Lewis acids gave Cu(I) carbene complexes, which were characterized by ^1H and ^{13}C NMR spectroscopy. Cu(I) carbene complexes could be directly generated from RNCS, Cu(I)-OAr and Lewis acids; this method can be used to prepare Cu(I) carbene complexes with different substituents on the carbene carbon. The complexes were unreactive towards olefins and do not undergo cyclopropanation. Electronic structure calculations (DFT) show that the charge on the carbene carbon plays an important role in controlling the reactivity of the carbene complex.

Keywords. Copper(I) carbene complex; carbene complex synthesis; Cu(I)-carbene electronic structure.

1. Introduction

Metal carbene complexes are arguably the most versatile organometallic reagents that have been developed for organic synthesis.¹ Different reactions of these complexes have been reported since their discovery and have been reviewed extensively,² and the discovery process continues unabated. Recently, a review by Wolfgang Kirmse brought out the importance of copper (I) carbene complexes in the area of asymmetric synthesis.³ Organic syntheses, particularly with diazo alkanes,^{4,5} insertion reactions of ylides, formation of formamidines from isocyanides in alcohols⁶, thermolysis of alkyl copper compounds⁷ and polymerization of diazoalkanes⁸ have been reported with copper salts. In all the above copper-catalyzed reactions, carbenes are believed to be the intermediates, although they have not been isolated or characterized. The first synthesis of a stable Cu(I) carbene complex was reported by Arduengo *et al*.⁹ Raubenheimer *et al* reported the first solid state molecular structure of a stable Cu(I) carbene complex stabilized by two hetero atoms.¹⁰ Recently Hofmann *et al* identified the intermediacy of a copper(I) carbene complex in a cyclopropanation reaction, and for the first time spectroscopically detected the carbene in

the cyclopropanation reaction.¹¹ Barluenga *et al* synthesized and structurally characterized a typical Fischer carbene complex at 120 K.¹² Apart from the synthetic and spectroscopic studies of copper (I) carbene complexes, studies on systems that display reactivity patterns are very few in the literature.¹³ The title compounds are Cu(I) carbene complexes that have been synthesized from an entirely new type of reaction for which there is no literature precedent. We have developed it into as general a method as possible. The lack of reactivity is attributed to the charge difference on the carbene carbon which has been deduced by electronic structure calculations.

2. Experimental section

2.1 Materials and methods

Dichloromethane and diethylether were purified and dried by conventional methods and distilled under nitrogen. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ was freshly prepared before use. (Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive.*) PhNCS, MeNCS, and *bis*(diphenylphosphino)methane were purchased from Aldrich (USA). Diethylmalonate was purchased from Merck (India). Phenols were purchased from Ranbaxy (India).

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Physical measurements. ^1H NMR spectra were recorded on a Bruker ACF 200 MHz and ^{13}C NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. IR spectra were recorded in the solid state dispersed in KBr pellets.

2.2 General method to prepare copper(I) carbene complexes

RNCS (3 mmol) was added to a suspension of $\text{Cu}(\text{I})\text{-OR}'$ (3 mmol). The resulting suspension was stirred for 8 h and then filtered. The filtrate was dried in vacuo and washed with petroleum ether (3×5 ml). The yellow-orange solid residue was dissolved in CH_2Cl_2 (30 ml) and ZnCl_2 (6 mmol) was added and stirred for one hour till the orange colour disappeared to give a turbid solution. Filtration yielded a colourless solution and an insoluble black mass. The solution was dried *in vacuo* to give an air sensitive copper (I)–carbene complex for which spectroscopic data could be recorded. The complexes proved too air-sensitive for elemental analyses.

2.2a Complex 1 [$\text{Cu}(\text{Cl})(\text{C}(\text{NHPH})(\text{O}-\text{C}_6\text{H}_4-\text{CH}_3))$]: ^1H -NMR (200 MHz, CDCl_3 , 297 K): δ 2.33 (s, 3H, CH_3), 6.7–7.5 (m, 9H, Ph), 10.96 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 297 K): δ 20.6 (s, CH_3), 121.0–131.0 (Ph), 184.94 (Cu=C) ppm. IR (KBr, cm^{-1}): 3054 (C–H), 3566 (N–H).

2.2b Complex 2 [$\text{Cu}(\text{Cl})(\text{C}(\text{NHCH}_3)(\text{O}-\text{C}_6\text{H}_4-\text{CH}_3))$]: ^1H -NMR (200 MHz, CDCl_3 , 297 K): δ 3.14 (NCH₃), 7.1–7.6 (m, 4H, Ph), 11.6 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 297 K): δ 127.0–129.0 (Ph), 239.7 (Cu=C) ppm.

2.2c Complex 3 [$\text{Cu}(\text{Cl})(\text{C}(\text{NHPH})(\text{CH}(\text{COOEt})_2))$]: ^1H -NMR (200 MHz, CDCl_3 , 297 K): δ 1.19–1.3 (6H, CH_3), 4.16–4.3 (4H, CH_2), 7.2–7.4 (m, 5H, Ph), 10.9 (1H CH), 11.4 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 297 K): δ 14.0 (CH_3), 62.0 (CH_2), 120.0–131.0 (Ph), 188.11 (Cu=C) ppm.

2.2d Complex 4 [$\text{Cu}(\text{Cl})(\text{C}(\text{NHPH})(\text{nBu}))$]: ^1H -NMR (200 MHz, CDCl_3 , 297 K): δ 1.2–2.6 (3H, CH_3), 3.4–3.7 (6H, CH_2), 7.06–7.5 (m, 5H, Ph), 9.47 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 297 K): δ 12.0, 22.77, 28.41, 38.3 (nBu), 120.0–127.0 (Ph), 172.1 (Cu=C) ppm.

2.2e Complex 5 [$\text{Cu}(\text{Cl})(\text{C}(\text{NHPH})(\text{OPh}))$]: ^1H -NMR (200 MHz, CDCl_3 , 297 K): δ 2.34 (3H, 4- CH_3), 3.16 (3H, CH_3 , MeNC). 6.98–7.1 (m, 5H, Ph),

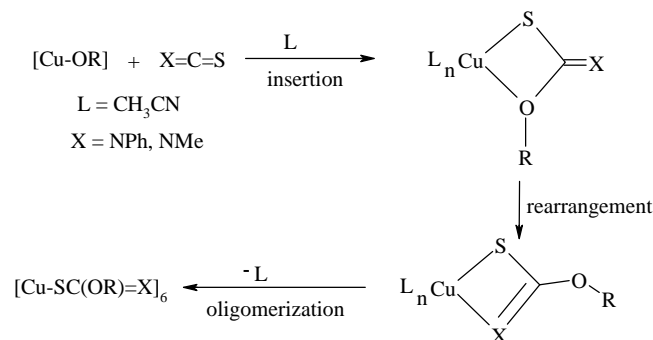
9.75 (br, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 297 K): δ 20.7 (4- CH_3), 30.4 (CH_3N), 121.6–130.1 (Ph), 183.33 (Cu=C) ppm.

Results and discussion

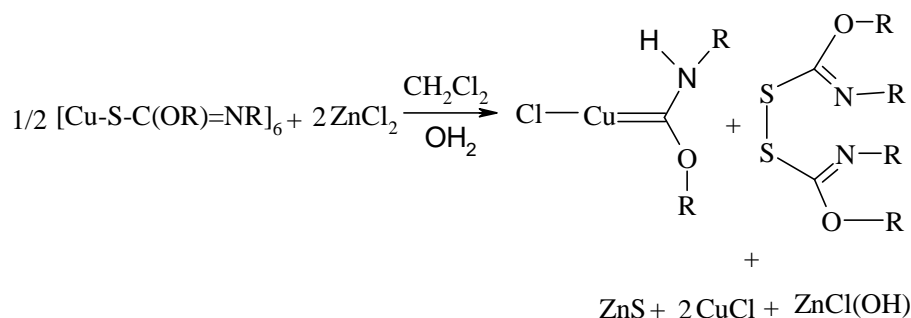
Reaction of copper (I) aryloxide with heterocumulenes such as PhNCS and MeNCS and CS_2 to give oligomeric complexes has been reported in the literature.¹⁴ Primarily, these heterocumulenes undergo insertion into the $\text{Cu}(\text{I})\text{-OAr}$ bond followed by a rearrangement, resulting in the formation of an oligomeric product (scheme 1). Steric and electronic effects have also been studied for this reaction apart from the structural studies of the oligomeric compounds. These oligomeric $\text{Cu}(\text{I})$ complexes also undergo ligand exchange reactions.¹⁵ When an attempt was made to carry out transmetallation with other d^{10} metal ions such as Zn^{2+} and Ag^+ , the formation of a copper (I) carbene complex was observed (scheme 2).¹⁵

The black precipitate formed in this reaction was insoluble in all common solvents and found to contain both copper and zinc. It tests positive for the presence of chloride. Based on the stoichiometry given in scheme 2, it is hypothesized to be a mixture of ZnS and cuprous chloride.

The colourless solution in the reaction mixture was found to contain the air sensitive copper (I) carbene. It could only be characterized by ^{13}C NMR and ^1H NMR spectroscopy. For all complexes, the ^{13}C NMR chemical shift of the carbene carbon appears in the low field region characteristic of copper (I) carbenes. The proposed structure is given in figure 1. Due to their air- and moisture-sensitive nature, elemental analysis could not be obtained. The complexes turn green on exposure to air. However, the synthetic method is quite general and there appears to be no limitation on the phenols and heterocumulenes that can be utilized in this synthesis. Attempts to crystal-



Scheme 1.



Scheme 2.

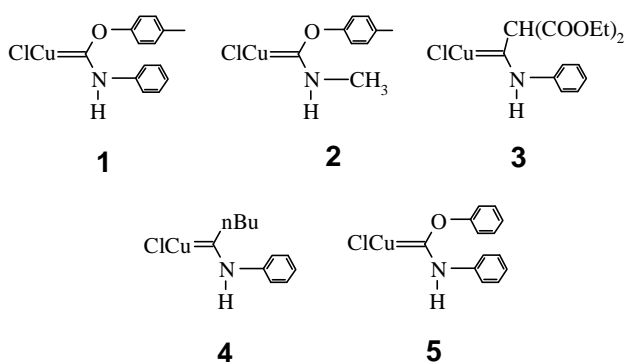
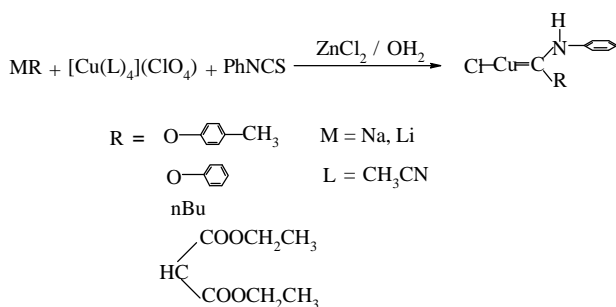


Figure 1. Proposed structure of complexes 1–5.



Scheme 3.

lographically characterize these carbene complexes from the dichloromethane and ether solutions failed.

3.1 One-pot synthesis of Cu(I) carbene complexes

In the above methodology, the appropriate precursor has to be prepared before reacting it with a Lewis acid. The overall time to complete the reaction is nearly eight hours. In order to reduce the reaction time, and extend the possibilities, a one-pot reaction was attempted. The heterocumulene and ZnCl_2 were added to the solution of Cu(I)OR in dichloromethane. The reaction mixture was stirred for 1 h to give the product (scheme 3). The formation of the carbene complex was identified only by ^{13}C and ^1H NMR spectroscopy. Although the carbene is formed in the reaction and

is identical to the corresponding product formed in the multi-step reaction, the major limitation of the one-pot procedure is the difficulty of separating the carbene complex from the unreacted heterocumulene.

4. Reactivity studies

Complex **1** was selected for the reactivity study. Several attempts were made to transfer the carbene fragment from the copper (I) centre to an olefin, aldehyde or a metal centre but the expected product was not isolated. This shows that this copper (I) carbene is very inert towards typical substrates. This behaviour of the copper (I) carbene complex prompted us to examine its electronic structure with the help of DFT calculations.

5. Electronic structure of Cu(I) carbene complexes

5.1 Model systems

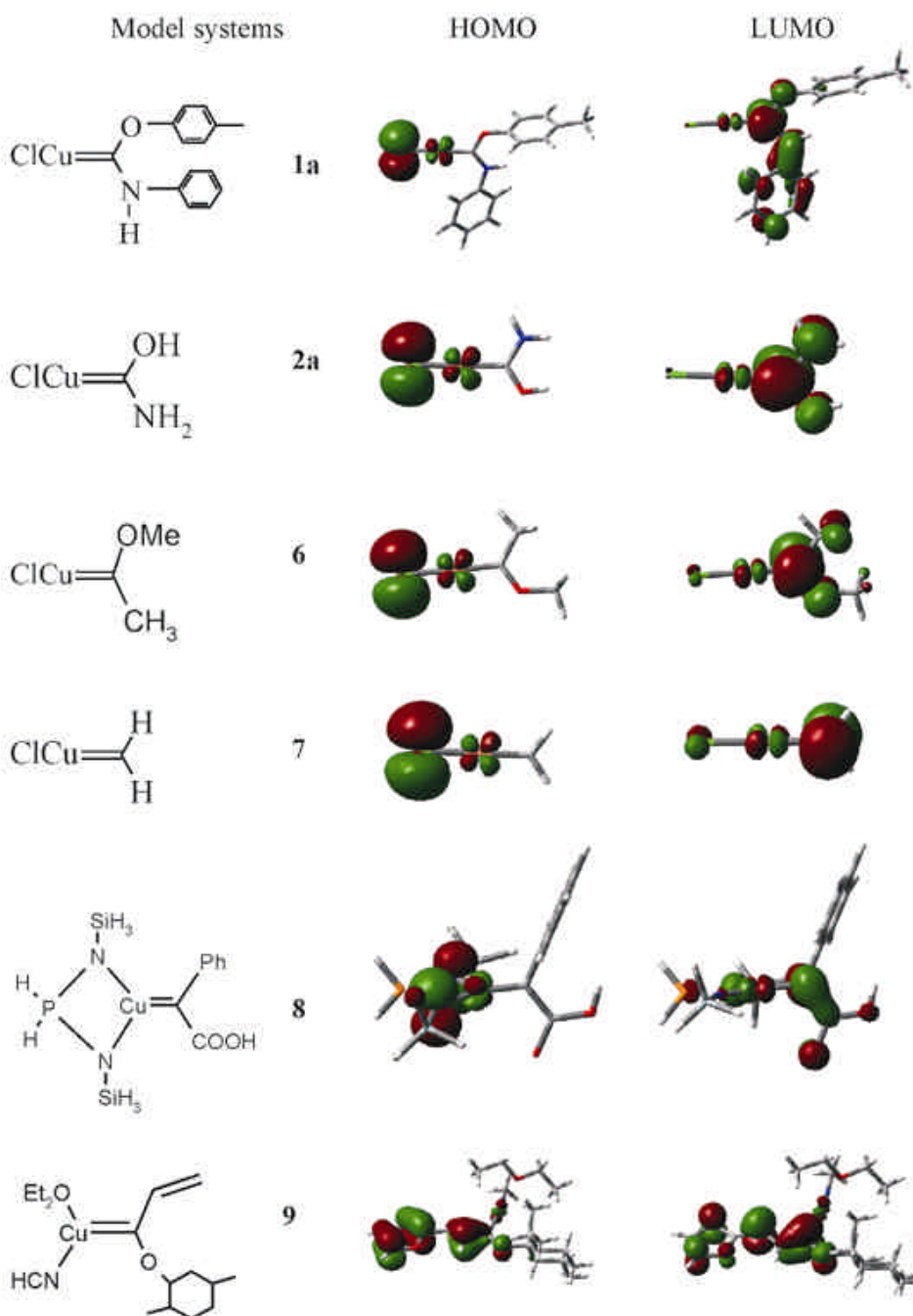
Model systems of copper (I) carbene complexes have been constructed to reflect the different type of Cu(I) carbenes synthesized recently by us and others. The effect of heteroatoms on the reactivity of the carbene complexes was also probed in a systematic fashion (**1a**, **2a**, **6** and **7**). Some of the recently characterized carbene complexes (**8** and **9**) were also examined at the same level of theory.

5.2 Computational details

All calculations were carried out at the DFT level with the 3-parameter fit of exchange and correlation functional introduced by Becke (B3LYP)¹⁶ as implemented in Gaussian 98.¹⁷ The basis set LANL2DZ was used for all atoms as implemented in Gaussian 98. Contour plots of the molecular orbitals of the

Table 1. Selected bond distances, angles and NBO analysis of the model systems **1a**, **2a** and **6–9**.

System	Distances (Å)		Angle (deg) Cl–Cu=C	HOMO-LUMO (eV)	Mulliken charges	
	Cu=C	Cu–Cl			C	Cu
1a	1.927	2.142	178.94	4.25	0.28	0.60
2a	1.923	2.133	176.66	4.68	0.29	0.59
6	1.900	2.135	177.23	3.54	0.20	0.62
7	1.837	2.121	179.96	2.74	–0.45	0.72
8	1.876	–	–	2.71	–0.29	0.90
9	1.900	–	–	3.62	0.06	0.76

**Figure 2.** HOMO and LUMO of the model systems, **1a**, **2a** and **6–9**.

complex calculated at the same level were generated using Gaussview-03. Natural charges were calculated using the NBO method.¹⁸

5.3 Molecular orbital calculations

The geometric structures of model systems [ClCu(C(O-C₆H₄-CH₃)(NH-C₆H₅))] (**1a**), [ClCu(C(OH)(NH₂))] (**2a**), [ClCu(C(CH₃)(OCH₃))] (**6**), ([ClCu(CH₂)] (**7**), were optimized and the important bond distances and bond angles have been tabulated (table 1). In general, chemical reactions are controlled either by the frontier orbitals or the charge on the reacting atoms. If reactions are orbital-controlled, the frontier orbitals would be different for the simple carbene complex and the heteroatom substituted, unreactive carbene complexes.

The HOMO and the LUMO of all the model systems are given in figure 2 including those of the simple carbene complex (model system **7**). The HOMO of all the model systems is centred on the halogen and copper. The maximum contribution comes from the halogen or the ancillary ligand. The LUMO of all the model systems is centred on the carbene carbon. The charge on the carbene carbon and the copper (I) centre are listed in Table 1 for all the model systems. The charge on copper in all the model systems is not very different but the charge on the carbene carbon varies significantly. In the simple ClCu(CH₂) carbene complex, the carbene carbon carries a negative charge (-0.45) but other carbene carbons in the heteroatom-substituted carbene complexes carry a positive charge! Since the LUMO is located on the carbene carbon, this carbene carbon is electrophilic. If the reactivity of carbene complexes were to be controlled by the orbitals, all the four complexes would be expected to display similar reactivity patterns. But this is not true. Complex **7** reacts with olefins but other heteroatom substituted carbene complexes synthesized in this study do not. This reveals that the reactivities of copper(I) carbene complexes are probably not frontier orbital-controlled as much as they are charge-controlled.

The energy difference between HOMO and LUMO is smaller for the simple ClCu(CH₂) carbene complex when compared to other heteroatom-substituted copper(I) carbene complexes, a larger energy difference was calculated for the model system **2a** (table 1). According to the principle of absolute hardness,⁹ model system **7** should be the most reactive among all complexes. This is true because the simple

ClCu(CH₂) reacts with olefins²⁰ but other heteroatom-substituted carbene complexes are not reactive.

Recently, Hofmann *et al* reported the reactive Cu(I) carbene complex which on treatment with the styrene gives an acyclic product.¹¹ The Mulliken charges and molecular orbital calculations were carried out for this complex using a model system (**8**). The electronic structure of this complex is similar to the electronic structure of model system **7**. The carbene carbon of Hofmann's complex carries a negative charge (-0.29) which supports our hypothesis. The HOMO of this complex is centred on the carbene and copper and nitrogen atoms of the NPN ligand, and this complex can be considered a nucleophilic carbene (table 1, figure 2). Similar calculations were also carried out using the CCDC structural data for another fully characterized Cu(I) carbene complex reported by Barluenga *et al*¹². The carbene carbon of this complex carries a positive charge (0.06) and so is electrophilic in nature. This complex may not react with the olefin as **8** or **7** does. The HOMO of the model complex **9** is more stabilized than the HOMO of model system **8** (table 1, figure 2).

6. Conclusion

Reaction of oligomeric Cu(I) complexes [Cu{*m*-S-C(=NR)(O-Ar-CH₃)}]_n with Lewis acids generate carbene complexes. Based on this reaction, a new general method to prepare Cu(I) carbene complexes has been developed. The spectroscopic characterization showed that these complexes have ¹³C signals very similar to the carbenes characterized recently by others. A direct reaction of the alkyl isothiocyanate with the copper(I) aryloxide in the presence of a Lewis acid also gives the carbene complex. The complexes synthesized in this study are inert towards olefins. The electronic structure of Cu(I) carbenes have been studied to understand the inertness of the carbenes that have been isolated. Although the frontier orbitals of reactive and unreactive carbenes are similar, the charge on an unreactive carbene is positive and reactive carbenes have a negative charge. So the reactivity of these carbenes appear to be charge-controlled.

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