Organometallics **2003,** *22,* 3016−3018

A Bis-Carbenealkenyl Copper(I) Complex from a Tripodal Tris-Carbene Ligand

Xile Hu, Ingrid Castro-Rodriguez, and Karsten Meyer*

Department of Chemistry and Biochemistry, University of California, San Diego,
9500 Gilman Drive, MC 0358, La Jolla, California 92093-0358

Received May 28, 2003

Summary: The new tris-carbene ligand [TIME^{t-Bu}] has been synthesized and fully characterized. Reaction of the free carbene with a copper(I) salt provided an unprecedented dinuclear Cu(I)−Cu(I) complex, in which the cuprous ion is coordinated in a trigonal planar ligand environment of three different carbon ligators. Interestingly, one of the three chelating carbon atoms can be formed only via C−H activation of the unsaturated imidazole backbone of the carbene chelator. Accordingly, the title complex is described as a bis-carbenealkenyl copper(I) complex.

Interest in the chemistry of transition metal complexes supported by diamino carbene ligands of the Arduengo−Wanzlick type[1] has arisen from reports of their remarkable activity in C−C bond formation catalysis.[2−5] Much attention is now drawn to chelating and pincer-type bis-carbene ligands to further enhance the thermal robustness of the resulting metal catalysts.[6−8] However, polycarbene ligands are still scarce, and prior to this study only two types of tripodal carbene ligands have been reported: the arene-functionalized tris-carbene ligand 1,3,5-{tris(3-*tert*-butylimidazol-2-ylidene)methyl}-2,4,6-trimethylbenzene[9,10] and the boron-anchored chelators hydrotris(3-alkylimidazol-2-ylidene)-borate (alkyl = Me, Et).[11] While the mesitylene-anchored tris-carbene ligand provides a cavity that fits only exceptionally large metal ions, such as the monovalent thallium(I) ion,[10] the boron-derivatized carbene tripods form saturated homoleptic hexakis-carbene complexes.[11] The development of tris-carbene ligand systems for transition metal coordination and subsequent application in homogeneous catalysis and small molecule activation are current efforts in our laboratory. Inspired by recent developments utilizing tripodal donor ligand supported copper(I) complexes for C−C and C−H bond activation,[12,13] as well as dioxygen-activation[14] chemistry, we sought to prepare the copper(I) complex of a tripodal tris-carbene chelator.

Only recently we reported the synthesis of the precursor of the carbon-anchored tripodal carbene ligand system 1,1,1-[tris-(3-methylimidazol-2-ylidene)methyl]-ethane (TIME^{Me}).[15] The reaction of the imidazolium salt with silver oxide affords its corresponding D_3-symmetrical trinuclear silver complex $[(\mathrm{TIME}^{Me})_2\mathrm{Ag}_3](\mathrm{PF}_6)_3$. Transmetalation reactions of this silver compound with metal halides yielded the corresponding isostructural copper(I) and gold(I) complexes $[(\mathrm{TIME}^{Me})_2\mathrm{M}_3]^{3+}$ (M = Cu, Au) with linear C−M−C entities.[15] The free carbene ligand of this chelating system, however, is not accessible to date and, thus, has greatly limited application for metal complexation. Herein we now report the synthesis and characterization of the free tris-carbene ligand [1,1,1-tris(3-*tert*-butylimidazol-2-ylidene)methyl]-ethane (TIME^{t-Bu}) (**2**) and its corresponding Cu(I) complex, $[(\mathrm{TIME}^{t-Bu})_2\mathrm{Cu}_2](\mathrm{PF}_6)_2$ (**3**), with a hitherto unknown trigonal planar bis-carbenealkenyl coordination environment.

Deprotonation of the imidazolium salt precursor, [1,1,1-tris(3-*tert*-butylimidazolium-1-yl)methyl]ethane hexafluorophosphate, $[\mathrm{TIME}^{t-Bu}](\mathrm{PF}_6)_3$ (**1**),[16] with 3 equiv of potassium *tert*-butoxide in THF at room temperature yields the corresponding free carbene TIME^{t-Bu} (**2**).[16] Single crystals of **2** suitable for X-ray diffraction analysis were grown from a saturated solution of ether at −35 °C. The solid-state molecular structure of **2** is depicted in Figure 1.[17]

The structure of **2** contains three distinct imidazole rings with no appreciable intra- or intermolecular interactions. Each imidazole ring displays structural features similar to those of other reported simple 1,3-disubstituted imidazole-2-ylidenes.[1,2] The average $\mathrm{C_{carbene}}$−N distance is 1.365 Å, and the average N−$\mathrm{C_{carbene}}$−N angle is 102.1°.

---

(1) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(2) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.

(3) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

(4) Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678.

(5) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291−1309.

(6) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340−2341.

(7) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201−202.

(8) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376−1377.

(9) Dias, H. V. R.; Jin, W. C. *Tetrahedron Lett.* **1994**, *35*, 1365−1366.

(10) Nakai, H.; Tang, Y. J.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2003**, 24−25.

(11) Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 310−312.

(12) Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Perez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 896−897.

(13) Diaz-Requejo, M.; Caballero, A.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Perez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 978−983.

(14) Karlin, K. D.; Kaderli, S.; Zuberbuhler, A. D. *Acc. Chem. Res.* **1997**, *30*, 139−147.

(15) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612−614.

(16) See Supporting Information.

(17) Crystallographic data for **2**: $\mathrm{C_{26}H_{42}N_6}$, space group *C*2/*c*, monoclinic, a = 26.317(6) Å, b = 11.992(3) Å, c = 21.092(5) Å, β = 125.531°, V = 5417(2) A^3, Z = 8, ρ_{calcd} = 1.076 mg/m^3, $R(F)$ = 0.0468, $wR(F^2)$ = 0.1154, GOF = 1.009 ($I > 2\sigma(I)$).

10.1021/om0304006 CCC: $25.00
Publication on Web 06/25/2003

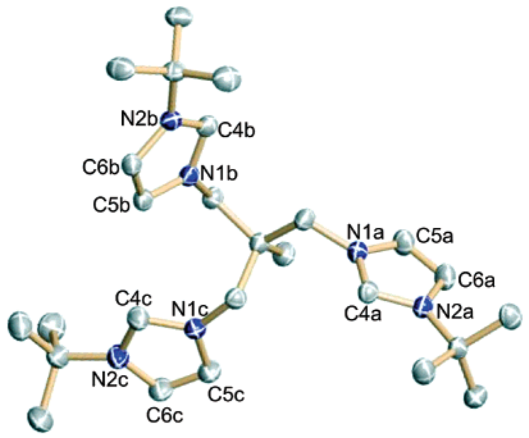
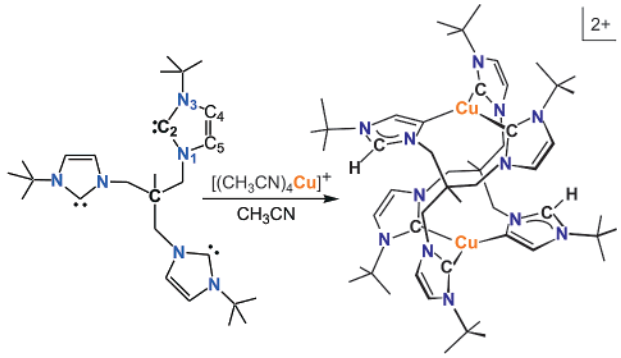


Figure 1. Solid-state molecular structure of carbene ligand TIME$^{t-\mathrm{Bu}}$ (**2**). Hydrogen atoms are omitted for clarity, thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): C4a−N1a 1.3623(16), C4a−N2a 1.3667(16), C5a−C6a 1.3408(18), N1a−C4a−N2a, 102.04(10).

Scheme 1. Synthesis of the Complex [(TIME$^{t-\mathrm{Bu}}$)$_2$Cu$_2$](PF$_6$)$_2$



Isolation of free ligand **2** provides convenient access to a new generation of metal complexes bearing tripodal carbene ligands.

Reaction of 1 equiv of **2** with [(CH$_3$CN)$_4$Cu](PF$_6$) in acetonitrile affords the copper complex **3** as an off-white powder in high yields (~70%) (Scheme 1).[16]

In the molecular structure of [(TIME$^{t-\mathrm{Bu}}$)$_2$Cu$_2$](PF$_6$)$_2$ (**3**) (Figure 2),[18] two copper ions are related by a crystallographically defined inversion center. Each copper ion is three-coordinate in a trigonal planar ligand environment of three carbon centers.

Two carbon ligators stem from one ligand forming an unusual eight-membered ring with the cuprous ion, while a third carbon ligator is provided by a pendent arm of a second ligand, which, with its two remaining pendent arms, coordinates to a symmetry-related copper center. The average Cu−C bond distance is 1.996 Å, consistent with those of other reported Cu(I) carbene complexes.[6,19] At 119.73°, the average C−Cu−C angle is close to 120° for an idealized trigonal planar ligand environment.

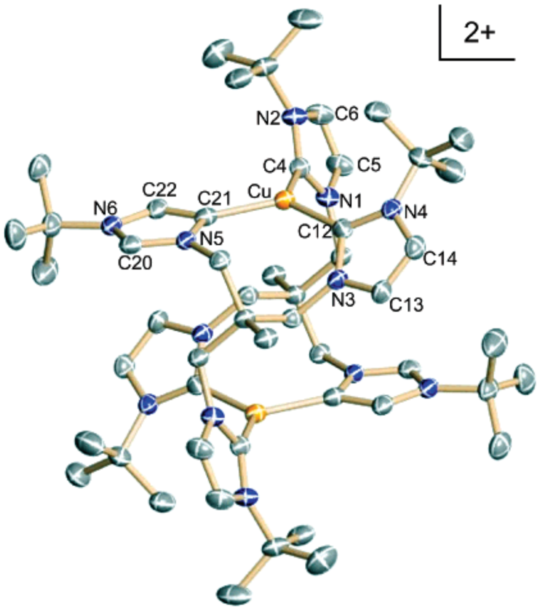


Figure 2. Solid-state molecular structure of complex [(TIME$^{t-\mathrm{Bu}}$)$_2$Cu$_2$](PF$_6$)$_2$·4DMSO (**3**). Hydrogen atoms, anions, and solvent molecules are omitted for clarity, thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): Cu−C4 1.9881(14), Cu−C12 1.9933(13), Cu−C21 1.9938(14), N1−C4−N2 102.84(11), N3−C12−N4 102.60(11), N5−C20−N6 108.52(20), N5−C21−C22 101.51(11), C4−Cu−C12 124.27(5), C12−Cu−C21 116.59(5), C21−Cu−C4 118.34(6).

Remarkably, the structure of **3** reveals the existence of an "alkenyl" binding mode within the Cu−C entity. Two of the three carbon ligands coordinated to the copper ion are "normal" diamino carbene centers corresponding to the carbon centers conventionally labeled as the C2 carbon of the imidazole ring (Scheme 1). The third carbon ligand, however, formally is the C5 backbone atom of the imidazole ring structure. The formation of such a compound clearly involves C−H activation at the C5 position and subsequent protonation of the C2 carbene carbon. The ligand can thus be considered an alkenyl functionality, a formulation that is further supported by NMR spectroscopy (vide infra). While the crystallographically determined N−C−N angles of two of the imidazole rings are 102.94 and 103.01°, resembling angles typically found for imidazole-2-ylidene entities,[2] the C5-metalated imidazole ring exhibits a much larger N−C−N angle of 108.63°. Although this type of metal binding to N-heterocyclic carbene ligands was previously reported for complexes synthesized directly from the corresponding imidazolium salts,[20,21] this is the first example of this binding mode generated by metal coordination to the free carbene starting material.

The ^{1}H and ^{13}C NMR spectra of **3** are consistent with the atom connectivities determined by X-ray crystallography. In the ^{1}H spectrum, the low-field signal of unity intensity (8.41 ppm) was assigned to the imidazole C2 proton, while five signals of unity intensity at higher field (7.33−6.63 ppm) were assigned to the backbone

---

(18) Crystallographic data for **3**: C$_{52}$H$_{84}$Cu$_2$F$_{12}$N$_{12}$P$_2$·4DMSO, space group *P*2(1)/*c*, monoclinic, $a = 10.6501(10)$ Å, $b = 18.1215(17)$ Å, $c = 20.3429(19)$ Å, $\beta = 93.638(2)°$, $V = 3918.2(6)$ A^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.362$ mg/m^3, $R(F) = 0.0342$, $wR(F^2) = 0.0847$, GOF = 0.914 ($I > 2\sigma(I)$).

(19) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027−2031.

(20) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274−2275.

(21) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473−10481.

protons bound to C4 and C5. Three intense signals at 1.71, 1.42, and 1.30 ppm were readily assigned to three nonequivalent *tert*-butyl groups in **3**. In the ^{13}C spectrum, the "normal" carbene carbons give rise to two well-resolved signals at 188.9 and 188.7 ppm, while the alkenyl carbon appears at 168.7 ppm. These NMR spectroscopic characteristics are known to be diagnostic for these two different modes of carbon metal binding.[6,20,21]

In summary, we presented the synthesis and full characterization of a novel tris-carbene ligand system and its corresponding dinuclear copper complex. This unexpected 2:2 complex renders the Cu(I) ion in a coordinatively unsaturated trigonal planar coordination environment. Dinuclear **3** not only provides an open coordination site protected via the *t*-Bu-functionalized imidazole rings but also possesses a flexible and partly shielded inner cavity. The distance between the two Cu(I) ions in the solid-state structure was determined to be approximately 5.2 Å. This void should thus be well suited to host a variety of small molecules. Accordingly, possible applications of **3** in dioxygen-activation and C−C bond formation chemistry are currently under investigation. The neutral, six-electron donor ligand **2** should find a broad range of applications in inorganic and organometallic coordination chemistry.

Acknowledgment. This work was supported by the University of California, San Diego. We thank Dr. Peter Gantzel and Prof. Arnold L. Rheingold for help with the crystallography.

Supporting Information Available: Experimental and spectroscopic details of new compounds, an ORTEP plot of the imidazolium salt $(TIME^{t-Bu})Br_3$ (**1a**), and complete listings of structural parameters for **1a**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0304006