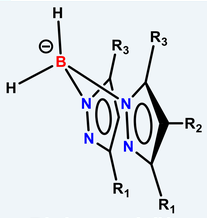
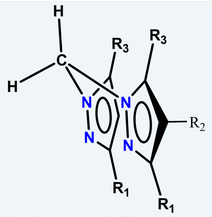
Probing the influence of phenanthroline-based ligands on group 11 metal-ethylene complexes: discoveries and catalytic prospects

Deepika Karade, Vo Quang Huy Phan, H. V. Rasika Dias*
The University of Texas at Arlington, Arlington, Texas

INTRODUCTION

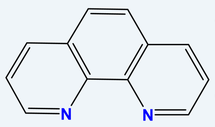


Bis(pyrazolyl)borate "Bp"



Bis(pyrazolyl)methane "Bpm"

- Poly(pyrazolyl)borate systems
- Highly tunable
- Isolable small hydrocarbon complexes
- Ideal for structure and bonding studies
- Catalysis of small unsaturated hydrocarbons



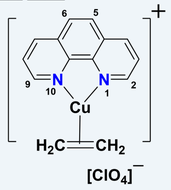
1,10-Phenanthroline "Phen"

- Phenanthroline ligand system
- Planar and rigid backbone
- Entropic advantages over flexible bidentate nitrogen ligands
- luminescent materials, homogeneous catalysis, chemo-sensors, and as agents in DNA intercalation, antibacterial, and anticancer treatments.

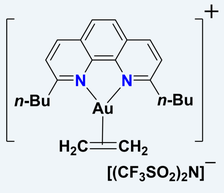
AIM

This study focuses on using two sterically demanding phen ligands, 2,9-bis(2,4,6-triisopropylphenyl)-1,10-phenanthroline (L1) and 2,9-bis(2,4,6-trifluoromethylphenyl)-1,10-phenanthroline (L2), to investigate coinage metal-ethylene complexes.

Previous work

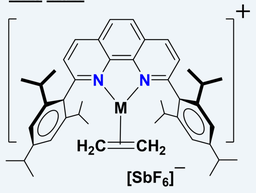


Masuda and co-workers

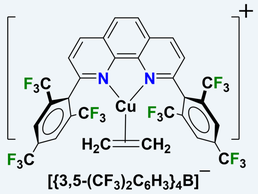


Hashmi and co-workers

This work



M = Cu (1), Ag (2), Au (3)



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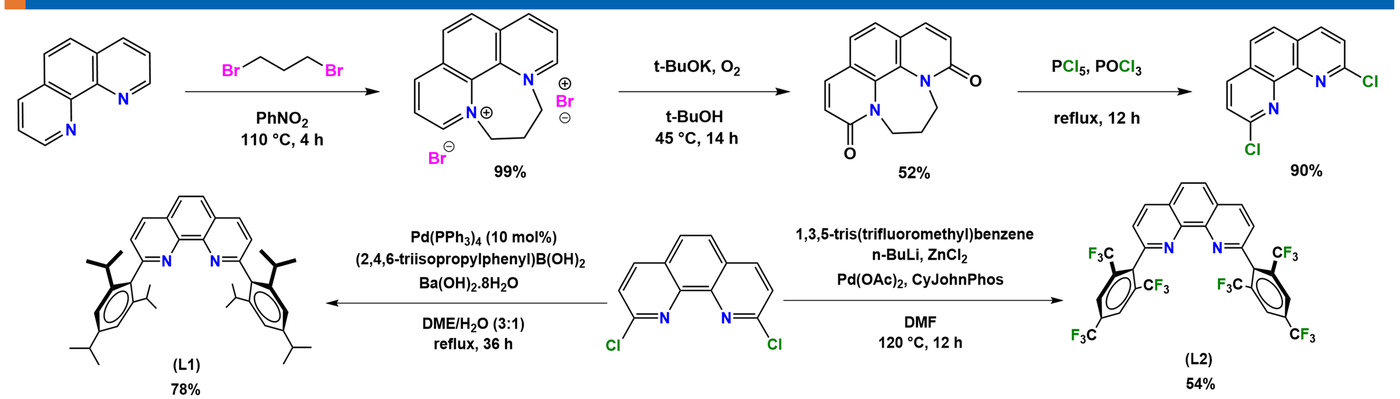
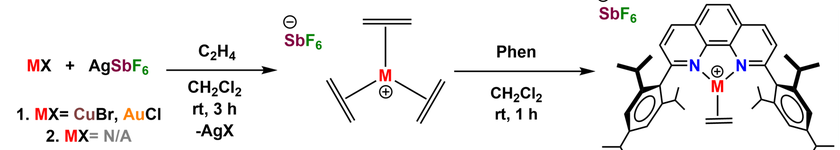
LIGAND SYNTHESIS

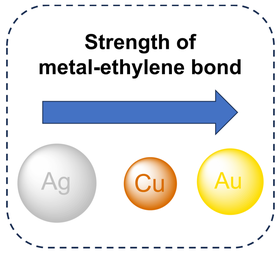


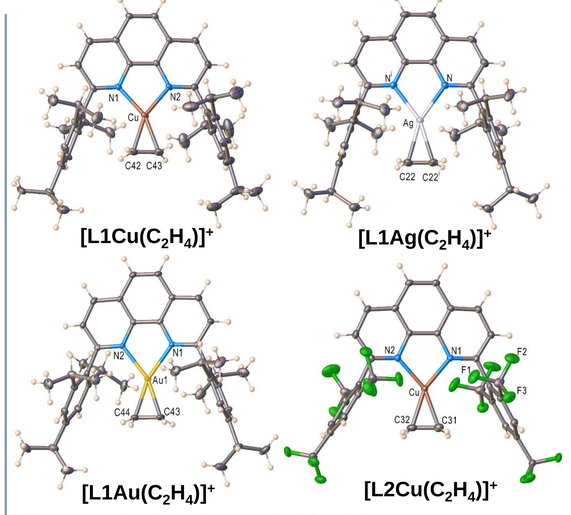
COMPLEX SYNTHESIS AND MOLECULAR STRUCTURES



Compound	δ_H (H_2C=) ($\Delta\delta_H$) (ppm)	δ_C (H_2C=) ($\Delta\delta_C$) (ppm)
Free ethylene	5.40	123.2
$[L1Cu(C_2H_4)][SbF_6]$	3.23 (-2.17)	86.21 (-36.99)
$[L1Ag(C_2H_4)][SbF_6]$	3.50 (-1.9)	101.92 (-21.28)
$[L1Au(C_2H_4)][SbF_6]$	2.34 (-3.04)	61.08 (-62.12)
$[L2Cu(C_2H_4)][BArF]$	3.53 (-1.87)	-

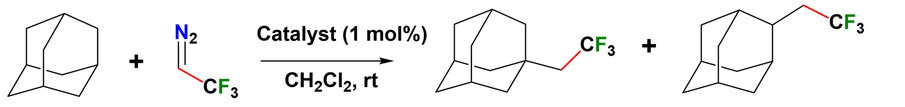
$\Delta\delta$ = δ (free ethylene resonance) - δ (ethylene resonance of the metal complex).





The counter ions have been omitted for clarity.

C-H BOND FUNCTIONALIZATION *VIA* CARBENE INSERTION



catalyst $[L1Cu(C_2H_4)]^+$ (1)	35%	4%	total yield 39%
catalyst $[L2Cu(C_2H_4)]^+$ (4)	65%	19%	total yield 84%

Reaction conditions: Catalyst (1 mol%), adamantane (5.0 equiv), add CF_3CHN_2 (1.0 equiv) in 0.5 hours at rt, stir 3 hour. Yields determined by ^{19}F NMR with internal standard.

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CONCLUSION

- Solid-state structural data was obtained for a rare isoleptic series $[L1M(C_2H_4)]^+$ (M = Cu, Ag, Au).
- First well-authenticated silver(I)-ethylene adduct supported by phenanthroline was reported.
- Structural and NMR data indicate that gold(I) strongly affects the ethylene moiety, while silver(I) forms the weakest bond.
- Preliminary catalytic investigations suggest copper complexes, especially $[L2Cu(C_2H_4)]^+$, are effective for $C(sp^3)$-H functionalization via trifluoromethyl carbene insertion.

CONNECT HERE

karaded1709

dxk2232@mavs.uta.edu

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Dias research group

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