

Review

Carbonyl and Olefin Adducts of Coinage Metals Supported by Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Ligands and Silver Mediated Atom Transfer Reactions

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1. Introduction

Tris(pyrazolyl)borates, first reported about 40 years ago, are a very useful class of monoanionic, nitrogen-based, auxiliary ligands in coordination and organometallic and bioinorganic chemistry.^{1,2} They readily coordinate, usually as face-capping tridentate ligands ($\kappa^3\text{-}N,N',N''$), to a wide variety of metal ions affording thermally stable metal complexes. Furthermore, it is possible to modify the steric and electronic properties of these ligands quite easily by varying the number and nature of substituents on the pyrazolyl rings and on the boron atom, thereby providing a convenient avenue to fine-tune the properties at the tris(pyrazolyl)borate ligand bound metal center. More than 100 tris(pyrazolyl)borate ligand varieties have been synthesized including the parent $[\text{HB}(\text{Pz})_3]^-$ and the closely related pyrazolyl ring alkylated or arylated systems (e.g., $[\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{Pz})_3]^-$, $[\text{HB}(3\text{-}(t\text{-Bu})\text{Pz})_3]^-$, $[\text{HB}(3,5\text{-}(\text{Ph})_2\text{Pz})_3]^-$), polyhalogenated ligands (e.g., $[\text{HB}(3,5\text{-}(\text{CF}_3)_2\text{Pz})_3]^-$, $[\text{HB}(3,4,5\text{-}(\text{Br})_3\text{Pz})_3]^-$), and B-substituted ligand varieties (e.g., $[\text{MeB}(3\text{-}(t\text{-Bu})\text{Pz})_3]^-$, $[\text{MeB}(3\text{-}(\text{CF}_3)\text{Pz})_3]^-$, $[\text{PhB}(3\text{-}(t\text{-Bu})\text{Pz})_3]^-$).^{1–3} A few of these molecules are illustrated in Figure 1. Several excellent reviews and chapters dealing with various aspects of

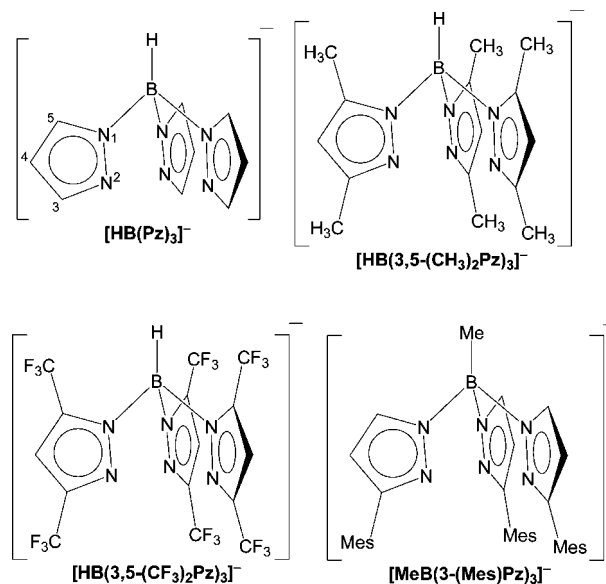


Figure 1. A few examples of tris(pyrazolyl)borate ligands.

tris(pyrazolyl)borates and the more general and related ligand classes, poly(pyrazolyl)borates and poly(pyrazolyl)alkanes are also available.^{1,2,4}

Tris(pyrazolyl)borates and to a lesser degree related ligands like bis(pyrazolyl)borates and poly(pyrazolyl)alkanes have played an important role in several key areas of coinage metal (Cu, Ag, Au) chemistry.^{2,3,5} They have been immensely useful in the stabilization of group 11 metal complexes of small carbon-based ligands, in the synthesis of metalloenzyme models relevant to biochemistry, and in the development of homogeneous catalysts. For example, tris(pyrazolyl)borate ligands have led to significant discoveries in the chemistry of *coinage metal complexes of carbon monoxide and ethylene*, and *silver-mediated carbene transfer processes*. A description of these developments and the related molecules stabilized by poly(pyrazolyl)borates and poly(pyrazolyl)alkanes and processes catalyzed by other silver salts/adducts will be the focus of this review.

2. Coinage Metal Complexes of Carbon Monoxide and Olefins

Transition metal complexes of small molecules like carbon monoxide and ethylene are historically and chemically some of the most important classes of compounds in organometallic chemistry. For example, Zeise's salt $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$, synthesized in 1827, was the first organo-transition metal compound to be isolated in pure form.^{6–8} The first metal carbonyl complexes (like $\text{PtCl}_2(\text{CO})_2$ and $\text{Pt}_2\text{Cl}_4(\text{CO})_2$) were discovered a few decades later (in 1868) by Schützenberger.^{7,9,10}

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Rasika Dias was born in Colombo, Sri Lanka. He completed his undergraduate studies in chemistry at the University of Peradeniya and obtained a B.Sc. Honours (First Class) degree in 1983. He then moved to the US (1984) to pursue his graduate work in Chemistry at University of California, Davis, under the direction of Professor Philip Power and received his Ph.D. in 1988. His graduate research was mainly focused on the low-valent and low-coordinate compounds of group 13–15 elements. After this, he spent close to three years at DuPont Central Research & Development, Delaware, as a Visiting Research Scientist, working with Dr. Anthony Arduengo, and played a major role in the development of “stable” carbenes (NHC) and their main-group element adducts. Rasika joined the University of Texas at Arlington faculty in 1992, where he is presently a Full Professor in the Department of Chemistry and Biochemistry. Rasika is also a Visiting Research Professor at the Institute of Fundamental Studies in Kandy, Sri Lanka. His current research activities concern homogeneous catalysis, photoluminescent materials, coordination chemistry of fluorinated ligands, synthesis of isolable models for reaction intermediates, development of greener routes to conducting polymers, and the study of bonding in metal adducts.

Many transition metal catalyzed industrial processes employ CO or ethylene as a reagent and involve metal–carbonyl or metal–ethylene intermediates.¹¹ The Dewar–Chatt–Duncanson model of metal–olefin bonding was motivated in large part by a desire to understand the bonding in adducts such as that between silver and ethylene.^{12–14}

The coinage metal (Cu, Ag, Au) complexes of carbon monoxide and olefins are also very important, and figure prominently or have been implicated in a number of significant applications ranging from separation or removal of gases from mixtures and biochemistry to modern organic synthesis and several industrial catalytic processes.^{15–25} For example, Cu(I)/ZnO catalyzes the synthesis of methanol from carbon monoxide and hydrogen (syngas).²⁶ Copper salts (e.g., CuCl/AlCl₃ in aromatic solvents like toluene) have been used for the selective removal of CO from gas mixtures.²⁰ Copper(I) salts also carry out an important function in the oxychlorination of ethylene.²⁷ Copper–ethylene adducts are of interest as models for ethylene (the smallest plant hormone) receptor site in plants.^{28–31} Silver-mediated ethylene epoxidation and olefin–paraffin separation are industrial processes of significant importance.^{32–36} Gold-based materials serve as excellent catalysts for the low-temperature oxidation of carbon monoxide and selective epoxidation of propene and other alkenes.^{17,23,37–40} Copper(I), silver(I), and gold(I) carbonyl cation catalyzed carbonylation reactions of olefins and alcohols have also been reported.^{18,24,41,42}

Unlike Cu(I), the number of easily isolable and thermally stable (at room temperature) Ag(I) and Au(I) complexes of carbon monoxide and ethylene are fairly limited.^{19,21,22,24,43,44} As evident from the following account, they also become increasingly sparse as one moves down the group 11 triad toward gold. Nitrogen-based supporting ligands and, in



particular, tris(pyrazolyl)borates have played a major role in stabilizing and enabling convenient study of such species.^{1,3,22} The first part of this review is aimed at highlighting the chemistry of Cu(I), Ag(I), and Au(I) complexes of carbon monoxide and olefins supported by tris(pyrazolyl)borates and the related ligands like bis(pyrazolyl)borates and poly(pyrazolyl)alkanes.

Carl Lovely is a native of the U.K. and grew up in the small brewery town of Burton-on-Trent, in central England. He attended The University of Birmingham where he obtained a B.Sc. (Hons) in Chemistry in 1987 and remained there to conduct Ph.D. studies with Professor W. Brian Jennings on oxaziridine chemistry (1990). After a postdoctoral fellowship at the Organisches-Chemisches Institut der Universität Heidelberg with Prof. Klaus Weinges (1991), he then moved to the US, where he did postdoctoral work with Prof. Leo Paquette (1992–1993, Department of Chemistry) and then Prof. Robert Brueggemeier (1993–1996, College of Pharmacy), both at The Ohio State University. He then moved to the University of Texas at Arlington as an assistant professor and was subsequently promoted to associate professor in 2002, and full professor in 2008. His research interests include the development of synthetic methods for heterocycle synthesis, transition metal-mediated and -catalyzed reactions, and natural products total synthesis.

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2.1. Tris(pyrazolyl)borato Coinage Metal Complexes of Carbon Monoxide

Cationic coinage metal–carbonyl complexes have been investigated using computational and mass spectrometric methods. For example, CCSD(T)/B3LYP predicted bond dissociation energies for Cu⁺–CO, Ag⁺–CO, and Au⁺–CO are 36.7, 22.3, and 42.9 kcal/mol, respectively.⁴⁵ They agree well with the experimental BDEs for Cu⁺–CO (36(2) kcal/mol), Ag⁺–CO (21(1) kcal/mol), and Au⁺–CO (estimated to be about 48 kcal/mol).^{46–48} Note that these data concern bonding of CO with metal ions in the gas phase and with no auxiliary ligands (coordination number at metal = 1). Calculated (CCSD(T)) M(I)–CO bond dissociation energies for CIMCO adducts are 36.3, 24.6, and 43.5 kcal/mol for M = Cu, Ag, and Au, respectively.⁴⁹ Based on experimental data, Calderazzo estimated the Au(I)–CO BDE value for ClAuCO at about 47.8 kcal/mol (200 kJ/mol).⁵⁰ Overall, among coinage metal monocarbonyl species mentioned above, gold(I) forms the strongest interaction with CO, while silver(I) forms the weakest bond in the coinage metal ion series. Computational data on [M(CO)_n]⁺ (where n > 1) are also available.^{51,52} Interestingly, Au⁺ has stronger M–CO bonds than the copper and silver analogs when n = 1 or 2, but they become weaker than those of Cu and Ag when n = 3 and 4.⁵¹ Bonding in these adducts (σ -donor/ π -back-bonding interactions, electrostatic effects, etc.) have also been examined computationally.^{19,52}

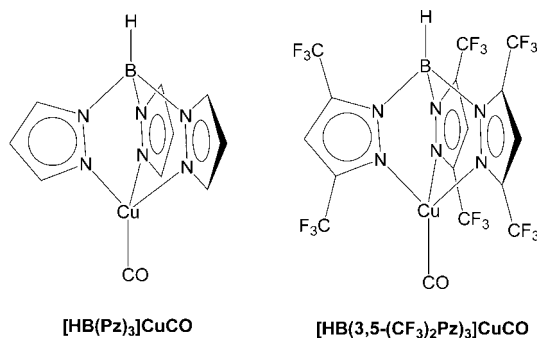
Table 1. Selected Structural Parameters and IR and NMR Spectroscopic Data of Coinage Metal Carbonyl Complexes Supported by Tris(pyrazolyl)borate and Related Tris(pyrazolyl)methane Ligands

compound	$\bar{\nu}_{\text{CO}}$ (cm ⁻¹)	M–C (Å)	C–O (Å)	¹³ C (ppm)	ref
[HB(3,5-(<i>i</i> -Pr) ₂ Pz ₃)]CuCO	2056	1.769(8)	1.118(10)	176.4	66, 72
[HB(3-(<i>t</i> -Bu),5-(<i>i</i> -Pr)Pz ₃)]CuCO	2057	1.76(1)	1.14(1)	174.0	68, 72, 74
	2054				
[HB(3-(<i>t</i> -Bu),5-(CH ₃)Pz ₃)]CuCO	2059	1.797(6)	1.109(6)		68, 74
	2061	1.794(14)	1.117(14)		
[HB(3,5-(CH ₃) ₂ Pz ₃)]CuCO	2066	1.785 (4)	1.125 (4)		58, 82, 129
	2060				
[HB(3-(<i>t</i> -Bu)Pz ₃)]CuCO	2069				63
[HB(3-(Ph),5-(<i>i</i> -Pr)Pz ₃)]CuCO	2075				74
[HB(3-(<i>p</i> - <i>t</i> -BuPh),5-(CH ₃)Pz ₃)]CuCO	2078	1.752(10)	1.120(10)		61
[HB(3-(Mes)Pz ₃)]CuCO	2079				62
[MeB(3-(Mes)Pz ₃)]CuCO	2075				43
[HB(3,5-(Ph) ₂ Pz ₃)]CuCO	2080	1.78(1)	1.08(1)	173.8	63, 66, 72, 74
	2086				
[HB(Pz ₃)]CuCO	2083	1.765(14)	1.120(6)		58–60
[HB(3-(CF ₃)Pz ₃)]CuCO	2100	1.790(4)	1.126(5)		70
[HB(3-(C ₃ F ₇)Pz ₃)]CuCO	2102	1.799(10)	1.119(13)		73
[HB(3-(CF ₃),5-(Ph)Pz ₃)]CuCO	2103	1.773(5)	1.113(5)		44
[HB(3-(CF ₃),5-(CH ₃)Pz ₃)]CuCO	2109				62
[HB(3-(C ₂ F ₅)Pz ₃)]CuCO	2110	1.804(4)	1.115(5)		73
[HB(3,4,5-(Br) ₃ Pz ₃)]CuCO	2110				77
[HB(3,5-(CF ₃) ₂ Pz ₃)]CuCO	2137	1.808(4)	1.110(5)		69
[MeB(3-(Mes)Pz ₃)]AgCO	2125	1.994(3)	1.111(4)		43
[HB(3-(CF ₃),5-(Ph)Pz ₃)]AgCO	2149				44
[MeB(3-(C ₂ F ₅)Pz ₃)]AgCO	2153	2.030(4)	1.117(4)	176.1	21
[HB(3,4,5-(Br) ₃ Pz ₃)]AgCO	2153				85
[HB(3,5-(CF ₃) ₂ Pz ₃)]AgCO	2178	2.037(5)	1.116(7)	175.5	84, 124
[HB(3,5-(CF ₃) ₂ Pz ₃)]AuCO	2144	1.862(9)	1.113(11)	173	88
[MeB(3-(Mes)Pz ₃)]AuCO	2083				43
{[HC(3,5-(CH ₃) ₂ Pz ₃)]CuCO}PF ₆	2113				93
{[HC(3-(Ph)Pz ₃)]CuCO}PF ₆	2104				93
{[HC(3-(<i>t</i> -Bu)Pz ₃)]CuCO}PF ₆	2100	1.778(10)	1.133(9)		93
{[HC(3,5-(<i>i</i> -Pr) ₂ Pz ₃)]CuCO}PF ₆	2109	1.783(7)	1.118(9)	174.0	72
{[HC(3,5-(<i>i</i> -Pr) ₂ Pz ₃)]CuCO}ClO ₄	2107	1.777(5)	1.127(6)	173.7	72
{[HC(3,5-(Ph) ₂ Pz ₃)]CuCO}ClO ₄	2108				76
[O ₃ SC(Pz ₃)]CuCO	2101				95
[O ₃ SC(3-(<i>t</i> -Bu)Pz ₃)]CuCO	2093				95
	2088				
CO	2143		1.12822(7)	184	19

Copper salts like CuCl are well-known to bind CO,^{53,54} but the resulting products like Cu(CO)Cl are difficult to isolate.⁵⁵ They are often unstable toward oxidation or loss of the coordinated CO. For example, compounds like Cu(CF₃CO₂)CO that can be synthesized and dried under reduced pressure to obtain an analytically pure Cu(I)–CO containing species were not common prior to the 1970s.^{56,57} The first Cu(I)–CO complex involving a tris(pyrazolyl)borate ligand was isolated by Bruce and co-workers in 1972. This compound, [HB(Pz₃)]CuCO, has been synthesized by treating [HB(Pz₃)]K with CuCl under a CO atmosphere.⁵⁸ The X-ray crystal structure of [HB(Pz₃)]CuCO has also been reported and represents the first structurally characterized copper(I)–carbonyl adduct.⁵⁹ It features a pseudo-tetrahedral copper site with a linear Cu–CO moiety. The CO displacement chemistry of [HB(Pz₃)]CuCO (primarily by phosphines) has also been examined.^{58,60}

Since the discovery of [HB(Pz₃)]CuCO, a fair number of well-authenticated tris(pyrazolyl)boratocopper(I)–carbonyl adducts have been reported by various groups (see Table 1). They perhaps constitute the largest group of well-characterized and closely related copper(I)–CO adducts in the literature. These molecules contain various alkyl or aryl substituents on the pyrazolyl rings and on the boron. Most of these copper(I)–CO adducts have been synthesized by using an alkali metal complex of the tris(pyrazolyl)borate ligand, a copper(I) salt, and CO. A few other routes to Cu(I)–CO adducts, such as the displacement of acetonitrile,^{61,62}

NO,^{63,64} THF,⁶² and O₂ from isolable copper complexes by CO^{65,66} or a reaction between a tris(pyrazolyl)boratocopper dimer and CO, have also been reported.^{67,68}



[HB(3,5-(CF₃)₂Pz₃)]CuCO represents a Cu(I)–CO adduct with six highly electron-withdrawing CF₃ groups on the tris(pyrazolyl)borate ligand.⁶⁹ It is an air-stable solid. This molecule shows the highest CO stretching frequency value (2137 cm⁻¹) in the IR among currently known tris(pyrazolyl)boratocopper(I)–carbonyl adducts. For example, the carbonyl stretching frequency of [HB(3,5-(CF₃)₂Pz₃)]CuCO is about 71 cm⁻¹ higher than that of nonfluorinated analog [HB(3,5-(CH₃)₂Pz₃)]CuCO.⁶⁰ Copper complexes of the [HB(3,5-(CF₃)₂Pz₃)]⁻ ligand show relatively high oxidation potentials.⁷⁰ Some of the tris(pyrazolyl)boratocopper(I)–carbonyl

adducts have been investigated using computational methods.^{70–72} DFT calculations point to the presence of a relatively acidic copper center in $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{CuCO}$.⁷⁰ The ν_{CO} values of the tris(pyrazolyl)boratocopper(I)–carbonyl adducts have been used as an indirect measure of estimating the relative electron density at copper and the donor properties of the tris(pyrazolyl)borate ligands.^{44,69,70,72–74} IR and computational data indicate that the substituents like CF_3 at the pyrazolyl ring 5-position (see Figure 1 for numbering scheme) also exert a significant effect on the electronic properties of the metal center (e.g., $[\text{HB}(3\text{-(CF}_3)\text{Pz})_3]\text{CuCO}$ ($\bar{\nu}_{\text{CO}} = 2100\text{ cm}^{-1}$) and $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{CuCO}$ ($\bar{\nu}_{\text{CO}} = 2137\text{ cm}^{-1}$)). Substituents like methyl on boron do not appear to have a significant effect in altering the electronic properties of these ligands. For example, the carbonyl stretching bands of $[\text{HB}(3\text{-(Mes)Pz})_3]\text{CuCO}$ ($\bar{\nu}_{\text{CO}} = 2079\text{ cm}^{-1}$) and $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{CuCO}$ ($\bar{\nu}_{\text{CO}} = 2075\text{ cm}^{-1}$) appear at a very similar position.⁷⁵ ^{63}Cu NMR chemical shifts of some tris(pyrazolyl)boratocopper(I)–carbonyl complexes have been reported.^{74,76} In general, ^{63}Cu NMR signals of copper(I) adducts with alkyl groups on tris(pyrazolyl)borate ligands are observed at lower fields (downfield region) than those containing phenyl substituents (e.g., $[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]\text{CuCO}$ ($\delta(^{63}\text{Cu}) = 716\text{ ppm}$) and $[\text{HB}(3,5\text{-(Ph)}_2\text{Pz})_3]\text{CuCO}$ ($\delta(^{63}\text{Cu}) = 585\text{ ppm}$)). These studies also show that there is a good correlation between the $\delta(^{63}\text{Cu})$ value and the CO stretching frequency value. The ^{63}Cu NMR chemical shift is a sensitive measure of the electron donor ability of the ligand on a $\text{Cu(I)}\text{--CO}$ moiety. The ^{13}C NMR shifts of copper bound CO, on the other hand, do not correlate with the ν_{CO} values. Some of the tris(pyrazolyl)boratocopper(I)–carbonyl adducts show ν_{CO} values very close to the values of $\text{Cu(I)}\text{--CO}$ adducts based on copper(I)-containing proteins.^{67,72} IR data of copper(I)–carbonyl adducts have also been related to the catalytic properties of tris(pyrazolyl)boratocopper adducts because they reflect the acidity at the metal center and correlate to the electrophilicity of the reactive intermediates.⁷⁷

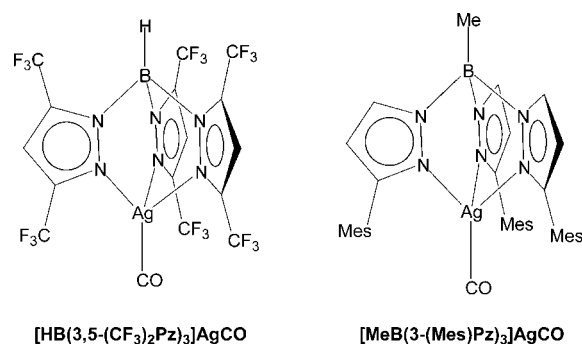
Some reactivity studies of tris(pyrazolyl)boratocopper(I)–carbonyl adducts are also available. Most of these involve substitution reactions with phosphines. For example, $[\text{HB}(3,5\text{-(Ph)}_2\text{Pz})_3]\text{CuCO}$ reacts with PMe_3 forming $[\text{HB}(3,5\text{-(Ph)}_2\text{Pz})_3]\text{CuPMe}_3$ while, perhaps due to steric reasons, PPh_3 does not displace CO from this molecule.⁶⁷ The PPh_3 , on the other hand, reacts with $[\text{HB}(\text{Pz})_3]\text{CuCO}$, $[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]\text{CuCO}$, and $[\text{HB}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_3]\text{CuCO}$ and displaces CO affording the corresponding $\text{Cu(I)}\text{--PPh}_3$ adduct.^{60,67,78} Norbornadiene also replaces CO from $[\text{HB}(\text{Pz})_3]\text{CuCO}$.⁷⁹ The photochemistry of the resulting $[\text{HB}(\text{Pz})_3]\text{Cu}(\text{NBD})$ has been investigated. The treatment of $[\text{HB}(3\text{-(CF}_3)\text{Pz})_3]\text{CuCO}$ with olefins like 1,5-COD has not resulted in CO displacement products.⁸⁰ The reaction between $[\text{HB}(\text{Pz})_3]\text{CuCO}$ and Cp_2MoH_2 has afforded an interesting $\text{Cu}\text{--Mo}$ bonded adduct.⁸¹ Unlike $[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]\text{CuCO}$, the loss of CO from $[\text{HB}(\text{Pz})_3]\text{CuCO}$ in solution is facile leading to $\{[\text{HB}(\text{Pz})_3]\text{Cu}\}_2$.⁸²

Tris(pyrazolyl)borate ligands have played a prominent role in the development of isolable silver(I)–carbonyl adducts.³ Fluorinated ligands are particularly important in this regard. This is because compared with the common nonfluorinated tris(pyrazolyl)borates such as $[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]^-$, the fluorinated systems have weakly coordinating donor (nitrogen) sites.⁷⁰ Thus, silver complexes supported by fluorinated tris(pyrazolyl)borates are less likely to aggregate (e.g., to form nitrogen-bridged dimers)⁸³ by displacing other second-

ary ligands. This feature is particularly important for the isolation of silver adducts containing fairly labile ligands. Furthermore, silver adducts of fluorinated hydrotris(pyrazolyl)borates show lower tendency to decompose via a redox process forming silver metal because they have relatively less-reducing B–H moieties. More recently, B–H-free tris(pyrazolyl)borate ligands have been used in this field.^{21,43} Overall, fluorinated systems like $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ are excellent supporting ligands for the stabilization of thermally stable silver(I) tris(pyrazolyl)borates featuring carbon monoxide.

The first tris(pyrazolyl)boratosilver(I)–carbonyl adduct was reported by Dias and co-workers in 1995.⁸⁴ $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{AgCO}$ has been synthesized by bubbling CO into a hexane solution of $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Ag}(\eta^2\text{-toluene})$. The silver(I)–CO adduct $[\text{MeB}(3\text{-(C}_2\text{F}_5)\text{Pz})_3]\text{AgCO}$ based on a B-methylated ligand appeared more recently.²¹ It has been obtained by treating $[\text{MeB}(3\text{-(C}_2\text{F}_5)\text{Pz})_3]\text{Li}$ with AgOTf under a carbon monoxide atmosphere. $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{AgCO}$ ($\bar{\nu}_{\text{CO}} = 2178\text{ cm}^{-1}$ in Nujol or 2162 cm^{-1} in CH_2Cl_2) and $[\text{MeB}(3\text{-(C}_2\text{F}_5)\text{Pz})_3]\text{AgCO}$ ($\bar{\nu}_{\text{CO}} = 2153\text{ cm}^{-1}$ in KBr) display ν_{CO} values higher than that of free CO ($\bar{\nu}_{\text{CO}} = 2143\text{ cm}^{-1}$).²¹ The solution IR data indicating the formation of $[\text{HB}(3\text{-(CF}_3)_2\text{Pz})_3]\text{AgCO}$ ($\bar{\nu}_{\text{CO}} = 2149\text{ cm}^{-1}$ in hexane)⁴⁴ and $[\text{HB}(3,4,5\text{-(Br)}_3\text{Pz})_3]\text{AgCO}$ ($\bar{\nu}_{\text{CO}} = 2153\text{ cm}^{-1}$ in THF) have also been reported.⁸⁵ The IR and ^{13}C NMR data suggest that these silver carbonyl adducts belong to nonclassical metal carbonyl family and show very little, if any, $\text{Ag}\text{--CO}$ π -back-bonding.¹⁹ Computational studies on species like $\text{Ag}^+\text{--CO}$ indicate that charge interactions (which change the polarization of the π -orbital of CO) have a significant influence on the C–O stretching frequency.^{19,52} The π -back-bonding is also highly sensitive to the M–C distance. $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{AgCO}$ is a rare $\text{Ag(I)}\text{--CO}$ complex featuring a relatively electron-rich (and nonfluorinated) tris(pyrazolyl)borate.⁴³ The ν_{CO} band of this adduct has been observed at 2125 cm^{-1} , which is lower than that of the free CO ($\bar{\nu}_{\text{CO}} = 2143\text{ cm}^{-1}$). $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{AgCO}$ belongs to the classical metal carbonyl family. This has been synthesized by replacing ethylene from $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ by CO. Interestingly, computational data involving free silver(I) ion show that $\text{Ag}^+\text{--C}_2\text{H}_4$ and $\text{Ag}^+\text{--toluene}$ bonds are stronger compared with the $\text{Ag}^+\text{--CO}$ bond.⁸⁶

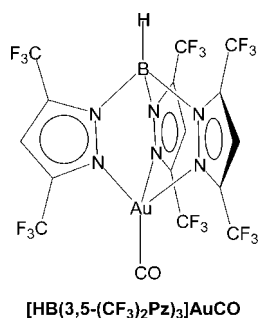
Although, the gold adduct $\text{Au}(\text{CO})\text{Cl}$ has been known



since 1925,⁸⁷ the first tris(pyrazolyl)boratogold(I)–carbonyl complex appeared in the literature only in 1996.⁸⁸ $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{AuCO}$ has been synthesized by treating the corresponding silver(I) adduct $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{AgCO}$ with ClAuCO . X-ray crystallographic data show that $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{AuCO}$ features a somewhat rare tetrahedral gold

center. Solution IR data of $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{AuCO}$ ($\bar{\nu}_{\text{CO}} = 2083 \text{ cm}^{-1}$) have also been reported.⁴³

Group trends of carbonyl adducts of group 11 metal have



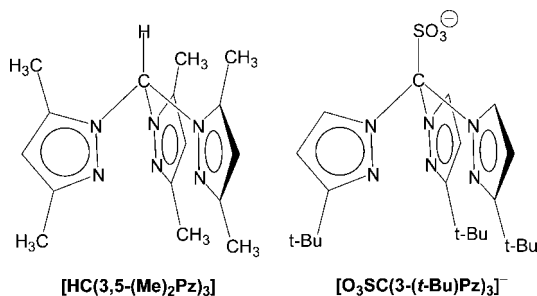
been investigated.^{43,88} Metal–CO distances and the CO stretching frequencies of the $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{MCO}$ ($\text{M} = \text{Cu, Ag, Au}$) series follow the order $\text{Ag} > \text{Au} > \text{Cu}$ and $\text{Ag} > \text{Au} \geq \text{Cu}$, respectively.^{19,88} The observed trend in the M–C bond distance agrees well with the experimental data from microwave spectroscopic studies on XMCO ($\text{X} = \text{F, Cl, I; M} = \text{Cu, Ag, Au}$)⁸⁹ and follows the size of covalent radii of M(I) ions (i.e., $\text{Ag} > \text{Au} > \text{Cu}$) as supported by computational work and structural studies on isoleptic coinage metal adducts.^{19,49,90–92}

2.2. Related Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Coinage Metal Complexes of Carbon Monoxide

Neutral tris(pyrazolyl)methane ligands like $[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]$ are closely related to the anionic tris(pyrazolyl)borates like $[\text{HB}(3,5\text{-(Me)}_2\text{Pz})_3]^-$.² These ligands, albeit to a lesser extent, have also been used successfully in the isolation of copper–carbonyl complexes (Table 1). For example, $\{[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}\}\text{PF}_6$ has been obtained by treating the corresponding acetonitrile adduct $\{[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuNCMe}\}\text{PF}_6$ with carbon monoxide.⁹³ The CO stretching frequency of the cationic $\{[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}\}^+$ is higher than that of the closely related but neutral $[\text{HB}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}$, indicating weaker back-bonding in the former with the CO ligand. $\{[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}\}^+$ and the related $[\text{HB}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}$ have also been investigated using DFT.⁷² Results show that tris(pyrazolyl)methane ligands are weaker donors to copper(I) than the corresponding borate ligands. ⁶³Cu NMR chemical shifts of the $\{[\text{HC}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}\}\text{ClO}_4$, $\{[\text{HC}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_3]\text{CuCO}\}\text{ClO}_4$, and $\{[\text{HC}(3,5\text{-(Ph)}_2\text{Pz})_3]\text{CuCO}\}\text{ClO}_4$ have been reported and show good correlation to the ν_{CO} values.⁷⁶ They have also been compared with the ⁶³Cu NMR chemical shifts of the related tris(pyrazolyl)borates. For example, $\{[\text{HC}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_3]\text{CuCO}\}^+$, $\{[\text{HC}(3,5\text{-(Ph)}_2\text{Pz})_3]\text{CuCO}\}^+$, $[\text{HB}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_3]\text{CuCO}$, and $[\text{HB}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_3]\text{CuCO}$ display ⁶³Cu NMR signals at 449, 440, 730, and 585 ppm, respectively.⁷⁶

Copper–carbonyl complexes of anionic tris(pyrazolyl)methanesulfonate ligands have also been reported.^{94,95} A comparison of ν_{CO} data of $[\text{O}_3\text{SC}(\text{Pz})_3]\text{CuCO}$ and $[\text{O}_3\text{SC}(3\text{-(}t\text{-Bu)Pz})_3]\text{CuCO}$ to the related tris(pyrazolyl)methane and tris(pyrazolyl)borate analogs (e.g., $[\text{O}_3\text{SC}(3\text{-(}t\text{-Bu)Pz})_3]\text{CuCO}$ to $\{[\text{HC}(3\text{-(}t\text{-Bu)Pz})_3]\text{CuCO}\}^+$ and $[\text{HB}(3\text{-(}t\text{-Bu)Pz})_3]\text{CuCO}$) suggests that anionic tris(pyrazolyl)methanesulfonate ligands are weaker donors than the anionic tris(pyrazolyl)borates but are stronger donors than the neutral tris(pyrazolyl)methane

ligands.⁹⁵ Tris(pyrazolyl)methanesulfonate ligands display N,N,N- and N,N,O-coordination modes with copper(I).



Compounds $[\text{H}_2\text{C}(3,5\text{-(Me)}_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OCIO}_3$,^{96a} $\{[\text{H}_2\text{C}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_2]\text{Cu}(\text{CO})\}_2(\mu\text{-ClO}_4)(\text{ClO}_4)$,^{96b} $[\text{H}_2\text{C}(3\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OSO}_2\text{CF}_3$,⁹⁷ $[\text{H}_2\text{C}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OSO}_2\text{CF}_3$,⁹⁷ and $[\text{PhCH}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OSO}_2\text{CF}_3$ ⁹⁷ represent isolable copper(I)–carbonyl complexes featuring bis(pyrazolyl)alkane supporting ligands. They display ν_{CO} values at 2108, 2104, 2120, 2127, and 2117 cm^{-1} , respectively. X-ray crystal structures show the presence of four-coordinate copper sites in adducts like $[\text{H}_2\text{C}(3\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OSO}_2\text{CF}_3$ and $[\text{H}_2\text{C}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OSO}_2\text{CF}_3$ due to CF_3SO_3^- ion coordination to copper⁹⁷ or in $[\text{H}_2\text{C}(3,5\text{-(Me)}_2\text{Pz})_2]\text{Cu}(\text{CO})\text{OCIO}_3$ and $\{[\text{H}_2\text{C}(3,5\text{-(}i\text{-Pr)}_2\text{Pz})_2]\text{Cu}(\text{CO})\}_2(\mu\text{-ClO}_4)(\text{ClO}_4)$ due to copper–perchlorate ion interaction. Copper carbonyl complexes of bis(pyrazolyl)borate or tetrakis(pyrazolyl)borate complexes are rare. The bis(pyrazolyl)borate adduct $[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{CuCO}$ has been observed in solution ($\bar{\nu}_{\text{CO}} = 2127 \text{ cm}^{-1}$ in toluene)⁹⁷ but has not been isolated. The CO/olefin (e.g., cyclooctene, 4-vinylanisole) exchange studies indicate that the copper–carbonyl complexes supported by $[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]^-$ and $[\text{H}_2\text{C}(3,5\text{-(Me)}_2\text{Pz})_2]$ ligands are more stable than the corresponding olefin derivative.⁹⁸ Copper–carbonyl complexes supported by tetrakis(pyrazolyl)borate ligands are also known.^{99–102} $[\text{B}(\text{Pz})_4]\text{CuCO}$ ($\bar{\nu}_{\text{CO}} = 2083 \text{ cm}^{-1}$) represents the first such species.¹⁰² $[\text{B}(\text{Pz})_4]\text{CuCO}$ is reported to be less stable than $[\text{HB}(\text{Pz})_3]\text{CuCO}$ or $[\text{HB}(3,5\text{-(Me)}_2\text{Pz})_3]\text{CuCO}$.⁹⁹ $[\text{B}(\text{camphp})_4]\text{CuCO}$, has been used as a catalyst in cyclopropanation chemistry.¹⁰³ In contrast to tris(pyrazolyl)borates, bis- and tetrakis(pyrazolyl)borates or poly(pyrazolyl)alkanes have not been used successfully so far in the isolation of silver or gold carbon monoxide complexes.²

There are several poly(pyrazolyl)borato and poly(pyrazolyl)alkane complexes of tungsten and molybdenum featuring bridging carbonyl moieties between the group 6 element and either copper or gold.^{104–109} These adducts will not be discussed in this review because they are not poly(pyrazolyl)borate or -alkane adducts of group 11 metal ions.

2.3. Tris(pyrazolyl)borato Coinage Metal Complexes of Ethylene

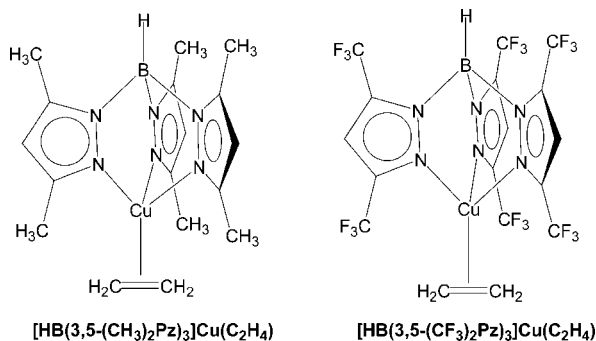
It has been known for a long time that ethylene forms adducts with coinage metal ions.²² However, the isolation of coinage metal–ethylene adducts that are stable at room temperature and do not lose ethylene is challenging because most of them are fairly labile.^{22,110–112} The experimental bond dissociation energy (BDE) values for $\text{M}^+ - \text{C}_2\text{H}_4$ ($\text{M} = \text{Cu, Ag, Au}$) are available. It is 33.7 kcal/mol for

Table 2. Selected Structural Parameters and ^1H and ^{13}C NMR Spectroscopic Data of Coinage Metal Ethylene Complexes Supported by Tris(pyrazolyl)borate Ligands

compound	CN ^a	M–C (Å) ^b	C=C (Å) ^b	^1H (ppm) ^c	^{13}C (ppm)/ $^1\text{J}_{\text{CH}}$ (Hz)/solvent	ref
[HB(3,5-(CH ₃) ₂ Pz) ₃]Cu(C ₂ H ₄)	4	2.014(5)	1.329(9)	4.41 (CD ₂ Cl ₂)		30
{[HB(Pz) ₃]Cu(C ₂ H ₄)CuCl} ₂	3	1.999 (3)	1.347(5)	4.43 (CD ₂ Cl ₂)		30
[HB(3,5-(CF ₃) ₂ Pz) ₃]Cu(C ₂ H ₄)	4	2.022(6)	1.325(9)	4.96 (CDCl ₃)	89.5/161 (C ₆ D ₁₂)	122
[HB(3-(CF ₃)Pz) ₃]Cu(C ₂ H ₄)	4	2.009(9)	1.34(1)	4.80 (CDCl ₃)	85.8/158 (C ₆ D ₆)	122
[HB(3-(CF ₃),5-(Ph)Pz) ₃]Cu(C ₂ H ₄)	4	2.012(11)	1.30(1)	4.91 (CDCl ₃)	85.7/159 (C ₆ D ₆)	122
[MeB(3-(CF ₃)Pz) ₃]Cu(C ₂ H ₄)	4	2.038(3)	1.334(4)	4.80 (CDCl ₃)	85.4/161 (CDCl ₃)	123
[HB(3,5-(CF ₃) ₂ Pz) ₃]Ag(C ₂ H ₄)	4	2.301(7)	1.298(14)	5.56 (C ₆ D ₁₂)	104.9/164 (C ₆ D ₁₂)	124
[MeB(3-(CF ₃)Pz) ₃]Ag(C ₂ H ₄)	4	2.2822(18)	1.340(4)	5.47 (CDCl ₃)	104.0 (CDCl ₃)	126
[MeB(3-(C ₂ F ₅)Pz) ₃]Ag(C ₂ H ₄)	4	2.301(2)	1.314(4)	5.48 (CD ₂ Cl ₂)	105.5/161 (CDCl ₃)	21
[MeB(3-(Mes)Pz) ₃]Ag(C ₂ H ₄)	4	2.27(3)	1.323(12)	3.42 (CDCl ₃)	95.4 (CDCl ₃)	43
[PhB(3-(CF ₃)Pz) ₃]Ag(C ₂ H ₄)	3	2.265(4)	1.296(7)	4.72 (CDCl ₃)	101.7 (CDCl ₃)	126
[HB(3,5-(CF ₃) ₂ Pz) ₃]Au(C ₂ H ₄)	3	2.102(6)	1.380(10)	3.81 (CDCl ₃)	63.7/165 (CDCl ₃)	127
[HB(3-(CF ₃),5-(Ph)Pz) ₃]Au(C ₂ H ₄)	3	2.095(5)	1.387(9)	3.69 (CDCl ₃)	59.3/165 (CDCl ₃)	127
C ₂ H ₄			1.313(1)	5.40 (CD ₂ Cl ₂)	123.3/156	122,130–132
		(X-ray)				
		1.3369(16)				
		(Elec. Diff.)				
		1.338				
		(calculated)				

^a CN = coordination number at the coinage metal. ^b Average M–C and C=C distances are given if more than one is present. ^c Solvent given in parentheses.

$\text{Ag}^+-\text{C}_2\text{H}_4$.¹¹³ The corresponding value for the copper(I) analog is 41.5 kcal/mol¹¹⁴ while for $\text{Au}^+-\text{C}_2\text{H}_4$, it is believed to be about 69 or has an upper limit of 82 kcal/mol.^{48,115,116} Copper, silver, and gold adducts of ethylene have also been investigated in detail by computational methods. For example, using a variety of density functional and wave function based (i.e., MP2 and CCSD(T)) methods, Koch et al. calculated ethylene binding energies within the following ranges: –47 to –58 kcal/mol (Cu^+), –33 to –37 kcal/mol (Ag^+) and –64 to –73 kcal/mol (Au^+) with CCSD(T) approaches generally predicting the weakest binding energies.¹¹⁷ Overall, gold(I) forms the strongest interaction with ethylene, while silver(I) forms the weakest bond. Note that these data concern bonding of ethylene with metal ions in the gas phase and with no auxiliary ligands.



Thompson et al. reported the synthesis of first isolable tris(pyrazolyl)borate copper–ethylene adducts [HB(3,5-(CH₃)₂Pz)₃]Cu(C₂H₄) and {[HB(Pz)₃]Cu(C₂H₄)CuCl}₂ and their structural information.³⁰ These molecules are of interest as models for ethylene (the smallest plant hormone) receptor site in plants.^{28,29} Synthesis of [HB(3,5-(CH₃)₂Pz)₃]Cu(C₂H₄) and {[HB(Pz)₃]Cu(C₂H₄)CuCl}₂ involves the treatment of [HB(3,5-(CH₃)₂Pz)₃]K with CuI or [HB(Pz)₃]K with CuCl in the presence of ethylene, respectively. The key structural and spectroscopic data of these and other tris(pyrazolyl)boratocopper(I)–ethylene adducts are given in Table 2. The tris(pyrazolyl)borate ligand in [HB(3,5-(CH₃)₂Pz)₃]Cu(C₂H₄) coordinates to copper in κ^3 -fashion, while {[HB(Pz)₃]Cu(C₂H₄)–

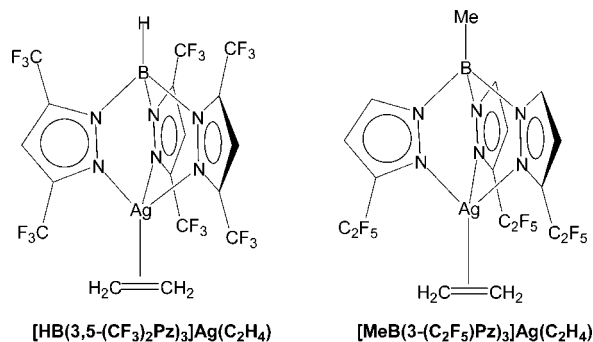
CuCl)₂ features a copper(I)–ethylene moiety supported by a κ^2 -bonded tris(pyrazolyl)borate. These adducts lose ethylene under reduced pressure. They are also air-sensitive molecules. Reaction of O₂ with [HB(3,5-(CH₃)₂Pz)₃]Cu(C₂H₄) leads to a copper–peroxo complex {[HB(3,5-(CH₃)₂Pz)₃]Cu}₂(μ -O₂),^{118,119} but the bound O₂ can be displaced by molecules such as CO and ethylene. Catalytic properties of [HB(3,5-(CH₃)₂Pz)₃]Cu(C₂H₄) have been investigated. It catalyzes the carbene transfer (from ethyl diazoacetate) to form cyclopropanes, cyclopropenes, and nitrene transfer (from PhI=NTs) to yield aziridines.^{120,121} These reactions are believed to involve electrophilic copper–carbene and paramagnetic copper–nitrene (behaves as an electrophilic nitrogen-centered radical) intermediates, respectively.¹²¹

[HB(3,5-(CF₃)₂Pz)₃]Cu(C₂H₄), which features a highly fluorinated tris(pyrazolyl)borate reported by Dias et al., is an air-stable solid and does not lose ethylene under reduced pressure.¹²² Closely related [HB(3-(CF₃)Pz)₃]Cu(C₂H₄) and [HB(3-(CF₃),5-(Ph)Pz)₃]Cu(C₂H₄), as well as the B-methylated analog [MeB(3-(CF₃)Pz)₃]Cu(C₂H₄), have been reported and characterized by X-ray crystallography.^{122,123} [HB(3,5-(CF₃)₂Pz)₃]Cu(C₂H₄) and [HB(3-(CF₃),5-(Ph)Pz)₃]Cu(C₂H₄) serve as competent aziridination catalysts.¹²² Reaction of [MeB(3-(CF₃)Pz)₃]Cu(C₂H₄) with [(Bn)₂ATI]SnCl has afforded [MeB(3-(CF₃)Pz)₃]Cu–Sn(Cl)[(Bn)₂ATI] featuring an unsupported Cu(I)–Sn(II) bond.¹²³

Silver(I)–ethylene complexes represent yet another very important class of compounds stabilized by tris(pyrazolyl)borate ligands.³ Fluorinated tris(pyrazolyl)borates have served an important role in silver chemistry since they have weakly donating nitrogen atoms and show less propensity to displace ethylene from the silver atom leading to aggregates. Fluorinated hydrotris(pyrazolyl)borates also have less reducing B–H moieties. [HB(3,5-(CF₃)₂Pz)₃]Ag(C₂H₄), reported in 1997 by Dias et al., represents the first well-authenticated silver(I)–ethylene complex.¹²⁴ It has been synthesized by treating [HB(3,5-(CF₃)₂Pz)₃]Ag(THF) with ethylene. Solid samples of [HB(3,5-(CF₃)₂Pz)₃]Ag(C₂H₄) are air-stable and do not lose ethylene under reduced pressure. Compared with free ethylene, CD₂Cl₂ solutions of [HB(3,5-(CF₃)₂Pz)₃]Ag(C₂H₄) show *downfield* shifted ^1H and *upfield* shifted ^{13}C NMR signals for the silver-coordinated ethylene (see Table

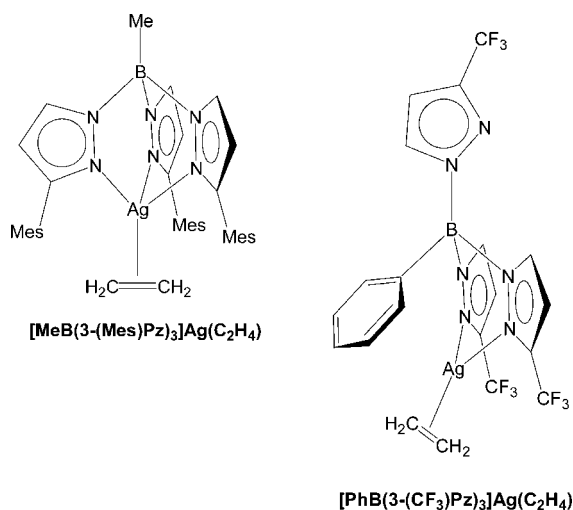
2). As indicated earlier, silver-catalyzed ethylene epoxidation is an important industrial process. Silver adducts like $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ are believed to be useful models for possible intermediates in this process. The fluorinated $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ ligand has also enabled the isolation of a rare silver–ethylene oxide adduct, $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Ag}(\text{OC}_2\text{H}_4)$.¹²⁵

The silver ethylene adducts $[\text{MeB}(3\text{-(C}_2\text{F}_5)\text{Pz})_3]\text{Ag}$ –



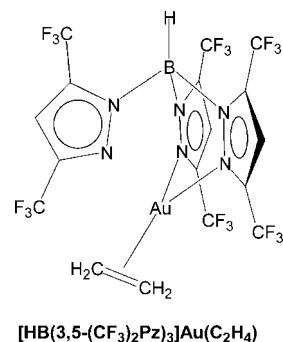
(C_2H_4) ,²¹ $[\text{MeB}(3\text{-(CF}_3)\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$,¹²⁶ and $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ ⁴³ containing B-methylated tris(pyrazolyl)borates, as well as the B-phenyl-substituted $[\text{PhB}(3\text{-(CF}_3)\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$,¹²⁶ have also been synthesized and isolated as thermally stable solids. $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ is a rare silver–ethylene adduct supported by a relatively electron-rich tris(pyrazolyl)borate ligand. All the tris(pyrazolyl)boratosilver–ethylene adducts described above, with the exception of $[\text{PhB}(3\text{-(CF}_3)\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$, feature pseudo-tetrahedral silver sites and κ^3 -bonded tris(pyrazolyl)borate ligands. $[\text{PhB}(3\text{-(CF}_3)\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$, in contrast, has a trigonal planar silver atom and a κ^2 -bonded tris(pyrazolyl)borate ligand.¹²⁶ The product resulting from the loss of ethylene from $[\text{PhB}(3\text{-(CF}_3)\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ has been isolated and characterized. It is a polymer with a very interesting helical structure and a hexagonal pore.¹²⁶

Interestingly with gold(I), isolable ethylene complexes are



rare regardless of the supporting ligand.²² The first tris(pyrazolyl)boratogold(I)–ethylene adducts appeared in the literature only in 2007.¹²⁷ $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ and $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ have been synthesized by reacting $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Na}$ and $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Na}$ with AuCl under an ethylene atmosphere.¹²⁷ They do not lose ethylene under reduced pressure. The

tris(pyrazolyl)borate ligands in these gold adducts show somewhat uncommon κ^2 -bonding. They also feature rare three-coordinate, trigonal planar gold atoms. $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ and $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ display significantly upfield shifted ^1H and ^{13}C NMR signals for the gold-coordinated ethylene. For example, the ethylene ^{13}C NMR signal of $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ shows about a 60 ppm upfield shift from the free ethylene. This points to significant $\text{Au}(\text{I}) \rightarrow$ ethylene back-bonding (despite having highly fluorinated supporting ligands).²² The closely related $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Cu}(\text{C}_2\text{H}_4)$ and $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Ag}(\text{C}_2\text{H}_4)$ show much smaller upfield shifts from the free ethylene (34 and 18 ppm, respectively).



2.4. Related Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Coinage Metal Complexes of Olefins

A few coinage metal complexes of olefins larger than ethylene supported by various poly(pyrazolyl)borate and poly(pyrazolyl)alkane ligands are also known. $[\text{HB}(\text{Pz})_3]\text{Cu}(\text{propylene}) \cdot \text{CuCl}$ and $[\text{HB}(\text{Pz})_3]\text{Cu}(\text{cyclohexene}) \cdot \text{CuCl}$ reported by Thompson and co-workers are the first examples of this type.³⁰ Although these two contain tris(pyrazolyl)borate ligands, due to steric reasons, tris(pyrazolyl)borates or -alkanes (especially those with substituents on the pyrazolyl ring 3-positions) are in general not very useful for stabilizing coinage metal ion moieties bearing alkenes larger than ethylene.⁸⁰ Dias et al. described the use of a fluorinated bis(pyrazolyl)borate to isolate copper complexes of styrene and 1,5-cyclooctadiene (1,5-COD).¹²⁸ X-ray crystal structures of $[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{styrene})$ and $\{[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}\}_2(1,5\text{-COD})$ have been reported. These copper(I)–olefin adducts feature three-coordinate, trigonal planar copper sites. $[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Cu}(\text{L})$ (L = cyclooctene, 4-vinylisole, 4-chlorostyrene, triethylvinylsilane) are also known, and their carbonylation reactions have been investigated.⁸⁰

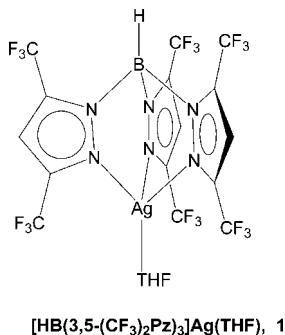
Neutral bis(pyrazolyl)alkanes like $[\text{H}_2\text{C}(3,5\text{-(Me)}_2\text{Pz})_2]$, $[\text{H}_2\text{C}(3\text{-(CF}_3)\text{Pz})_2]$, $[\text{H}_2\text{C}(3,5\text{-(CF}_3)_2\text{Pz})_2]$, and $[\text{PhCH}(3,5\text{-(CF}_3)_2\text{Pz})_2]$ have also been used as supporting ligands to isolate copper(I) complexes of substituted alkenes (e.g., cyclooctene, 4-vinylisole, triethylvinylsilane).^{97,98} The X-ray crystal structure of $\{[\text{H}_2\text{C}(3,5\text{-(Me)}_2\text{Pz})_2]\text{Cu}(\text{cyclooctene})\}[\text{CF}_3\text{SO}_3]$ has been reported.⁹⁸

A silver adduct of a substituted alkene has also been reported.⁹⁷ $\{[\text{H}_2\text{C}(3,5\text{-(CF}_3)_2\text{Pz})_2]\text{Ag}(\text{cyclooctene})\}\text{BF}_4$ has been obtained from a mixture of $[\text{H}_2\text{C}(3,5\text{-(CF}_3)_2\text{Pz})_2]$, AgBF_4 , and cyclooctene.

3. Silver-Mediated Atom Transfer Reactions

As described in the first part of this review, we and others have extensively used tris(pyrazolyl)borate and to a lesser degree other bis(pyrazolyl)borate and poly(pyrazolyl)alkane ligands for the isolation of reactive or labile coinage metal adducts and to examine their structures, bonding, and properties.^{1,2,4} Some of these complexes represent possible models of intermediates in catalytic processes and may indeed serve as useful catalysts for a number of organic transformations.

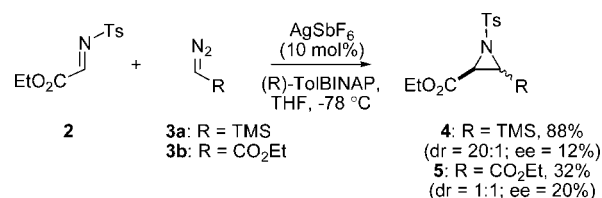
The silver chemistry is particularly noteworthy because the use of *homogeneous* silver catalysts in organic synthesis is quite rare.^{133,134} The use of silver salts has a long history in organic chemistry, but generally they have been used stoichiometrically, and until quite recently their uses were broadly limited to oxidation reactions and as halogen scavengers. Silver acetylides have begun to emerge as useful compliments to main group or copper analogs,¹³⁵ and silver complexes have been used quite extensively as Lewis acids;¹³⁶ however their use in atom transfer reactions is less common.^{133,134} Recent investigations from our own^{137–141} and other laboratories have demonstrated that various silver salts and complexes (e.g., [HB(3,5-(CF₃)₂Pz)₃]Ag(THF), **1**) can function in this capacity,^{133,134} in some cases leading to the observation of some unusual reactivity. A description of this chemistry, in particular the use of silver complexes to activate diazo compounds, will be the focus of the second part of this review.



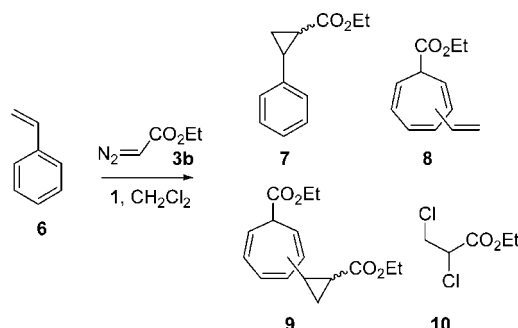
The largest group of transfer reactions catalyzed by silver(I) complexes is undoubtedly reactions involving diazo compounds, which have appeared over the last ten years or so. It is worth noting that prior to these reports, silver compounds have been used for many years to catalyze the Wolff rearrangement, the conversion of α -diazoketones to ketenes, although the precise role of the metal is not clear.^{142,143} This reaction has been reviewed elsewhere and will not be discussed here.¹⁴³

One of the earliest reports of the use of silver catalysis in carbene transfer¹⁴⁴ was by Jørgensen and co-workers who reported the preparation of aziridines by net carbene addition (via a diazo compound) to *N*-tosyl iminoesters.¹⁴⁵ Generally, the copper catalysts were superior, although a catalyst derived from AgSbF₆ and (*R*)-Tol-BINAP provided the corresponding aziridine **4** from **2** and trimethylsilyl diazomethane **3a** (R = TMS) in excellent chemical yield with high levels of diastereoselectivity; unfortunately the enantioselectivity was poor (Scheme 1). Attempts to extend this reaction with ethyl diazoacetate (EDA, **3b**, R = CO₂Et) were less successful, with reduced yield and reduced diastereoselectivity obtained but interestingly a slight improvement in the enantioselectivity for the chiral trans isomer (the cis isomer is *meso*).

Scheme 1



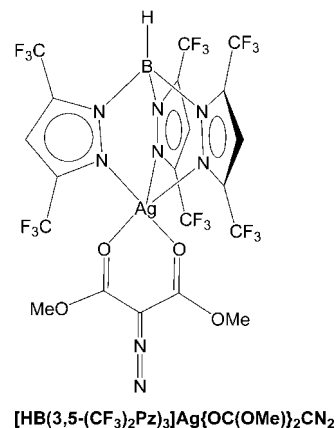
Scheme 2



whereas it was observed with copper catalysts, leading them to speculate that the reaction did not involve a metallacarbene with silver but was in fact Lewis acid catalyzed.

3.1. Cyclopropanation

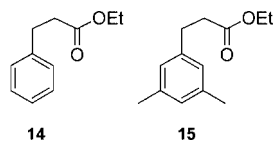
Our early experience with the Ag(I)–diazomalonate complex [HB(3,5-(CF₃)₂Pz)₃]Ag{OC(OMe)₂CN₂},¹⁴⁶ which was quite stable, led us to attempt the preparation of the corresponding complex with the more reactive EDA; however no characterizable silver complex was obtained. Interestingly, the evolution of a gas, presumably nitrogen, was observed indicating that a reaction occurred, possibly the formation of a reactive silver–carbene. Based on these observations, the experiment was repeated in the presence of a carbene trap to intercept the putative silver carbene.



The first attempt at cyclopropanation with styrene **6** was not successful in the formation of the corresponding cyclopropane cleanly; rather a complex mixture of products containing the expected cyclopropane **7** (Scheme 2), the ring expanded product **8**, the solvent insertion product **10**, and

other products (possibly **9**) was formed.¹³⁸ This is in contrast to the corresponding copper complex, which smoothly cyclopropanates a variety of olefins.¹⁴⁷ Subsequently it was determined by conducting the reaction with benzene in CH₂Cl₂ or in neat benzene, the ring expansion product **13a**, via the norcaradiene **12a** (Büchner reaction), was obtained in good yield (Scheme 3, Table 3).¹³⁸ Evaluation of the substrate scope revealed that other aromatic derivatives **11b–f** participate in the rearrangement, but generally the yields of the ring-expanded products **12b–f** were lower than with benzene. In some cases (**11b** and **11f**) competitive benzylic C–H insertion was observed, providing **14** and **15**, respectively.

Perez and co-workers have observed similar Büchner



chemistry, as well as cyclopropanation with styrene with the polybrominated tris(pyrazolyl)borato–silver complex [HB(3,4,5-(Br)₃Pz)₃Ag], although no chemical yields were provided in either case.⁸⁵ The corresponding copper tris(pyrazolyl)borate complexes served as excellent cyclopropanation catalysts,^{147–150} unusually leading to the formation of the *cis* isomer as the major product in most cases.^{147–150}

Recently, Davies and Thompson have demonstrated that several donor–acceptor compounds **17** and **19** undergo very selective silver-catalyzed (as AgSbF₆) cyclopropanation of a variety of olefins, which in the presence of Rh₂(OAc)₄ predominantly undergo C–H insertion.¹⁵¹ Generally, very high levels of chemoselectivity were observed, with cyclopropanation typically favored $\geq 15:1$ over C–H insertion (Schemes 4 and 5, Tables 4 and 5); only with the styryl diazoacetate and cyclohexadiene is lower selectivity observed (Table 5, entry 2). In addition to high levels of chemoselectivity, excellent diastereoselectivities are observed, with additional isomers undetected by ¹H NMR spectroscopy.¹⁵¹

3.2. C–Halogen Addition–Rearrangement Reactions

The reaction of carbenes with haloalkanes and allyl halides has been described previously in the literature; generally speaking these processes are quite unselective.^{152–157} In the course of our investigation of cyclopropanation of olefins, we noticed the formation of a byproduct, ethyl 2,3-dichloropropanoate (**10**, Scheme 2) when the reaction was conducted in dichloromethane, resulting from the net insertion of the carbene into the C–Cl bond. Subsequently, when the reaction was repeated using dichloromethane as the substrate, the insertion product was obtained in 26% yield (Scheme 6, Table 6).¹⁴⁰ An investigation of the scope and limitations of this reaction was performed, and it was found that similar products were obtained with a number of polychloromethane and polybromomethane derivatives (Table 6, entries 1–3). Attempts to extend this reaction to other haloalkanes was not successful, providing instead the α -haloacetate derivative (net 1,1-hydrohalogenation) and the olefin (Table 6, entries 4–7).¹⁴⁰ Based on these results, a mechanism (Scheme 7) involving the intermediacy of a silver carbene **31** was proposed in which the insertion product arises from the

Scheme 3

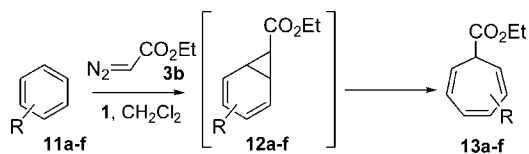


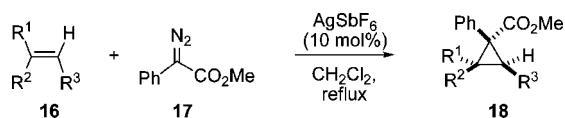
Table 3. Yields and Isomer Ratios of the Silver-Catalyzed Büchner Reaction of Benzene Derivatives with EDA

Substrate	Product	Yield (%) ^{a,b}	Isomer Ratio (2:3:4)
		74	n/a
11a	13a	75 ^c	n/a
		64 ^d	1:1.8:2.4
11b	13b	62 ^e	
		40	1:0:19
11c	13c		
		49 ^f	1:8.5:18
11d	13d		
		14 ^f	0:1:1
11e	13e		
		35 ^g	N/A
11f	13f		

^a The yields are the average of at least two runs, refer to isolated material and, unless noted, were conducted in CH₂Cl₂. ^b In the reactions conducted in CH₂Cl₂, there was 15–25% of the C–Cl insertion product **10** observed in the ¹H NMR spectrum of the crude reaction mixture. ^c These reactions were conducted in the neat arene. ^d 4% of the C–H insertion product was observed in the ¹H NMR spectrum of the crude reaction mixture. ^e 5% of the C–H insertion product was observed in the ¹H NMR spectrum of the crude reaction mixture. ^f The purified material was contaminated with ca. 5% of the C–Cl insertion product. ^g 28% of the C–H insertion product **15** was observed in the ¹H NMR spectrum of the crude reaction mixture.

formation of the halonium ylide **32** and 1,2-shift **32** \rightarrow **10**, **28**, and **29**. Alternatively, if the substrate and thus the

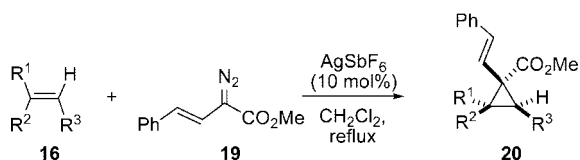
Scheme 4

Table 4. Silver-Catalyzed Cyclopropanation with 17^a

entry	R ¹	R ²	R ³	yield (%)
1	H	-(CH ₂) ₄ -		88
2	H	-(CH=CHCH ₂ CH ₂)-		79
3	H			80
4	H	H	Ph	96
5	Ph	Ph	H	82
6	Me	H	Ph	80
7	H	Me	Ph	86
8	Ph	H	Ph	84
9	H	Ph	Ph	54

^a Five to ten equivalents of the olefin was employed.

Scheme 5

Table 5. Silver-Catalyzed Cyclopropanation with 19^a

entry	R ¹	R ²	R ³	yield (%)
1	H	-(CH ₂) ₄ -		43
2	H	-(CH=CHCH ₂ CH ₂)-		67 ^b
3	H			
4	H	H	Ph	82
5	Ph	Ph	H	56 ^c
6	Me	H	Ph	65
7	Ph	H	Ph	34

^a Five to ten equivalents of the olefin was employed. ^b Includes 15% of insertion product. ^c Reaction conducted at room temperature

halonium ylide **32** contain a β -hydrogen, this can be removed by an intramolecular deprotonation with concomitant loss of halide resulting in formation of the olefin **34** and the α -haloacetate **30**. No independent evidence has been obtained to support this pathway; thus at this point, this mechanism is purely speculative (see below).

The interception of metallacarbenes (Cu or Rh) with allylic-substituted amines, ethers, thioethers, and selenides and their subsequent [2,3]-rearrangement is well-documented;¹⁵⁸ on the other hand few reports exist of the corresponding process with allylic halides.^{159–161} Very recently it has been reported that the tris(pyrazolyl)borosilver complex **1** does in fact catalyze this reaction in excellent efficiencies, although the diastereoselectivities are very low at this point (Table 7, Schemes 8 and 9).¹³⁷ In this case, allylic halides **34–38** are reacted with ethyl or *t*-butyl diazoacetate (BDA) in the presence of **1** (Scheme 8), which leads to the formation of homoallylic haloacetates **40a,b–44a,b** (Table 7, entries 1–5). Similar rearrangement products were obtained from the propargylic substrates **45** and **46**, although in this case allenes **48b** and **49a,b** were obtained (Scheme 9). A mechanism involving the formation and rearrangement of the halonium ylide (**39** or **47**) was proposed, again via the intermediacy of a silver carbene.¹³⁷

Most of the substrates evaluated in this reaction were primary halides; however one example of a secondary

Scheme 6

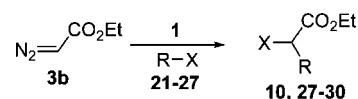
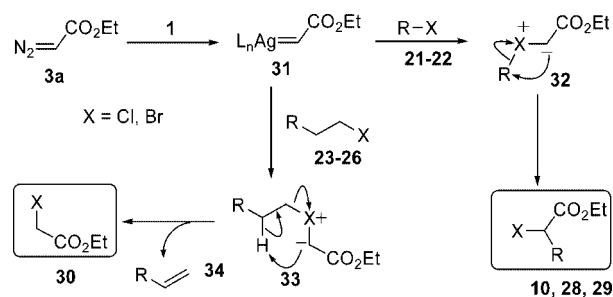


Table 6. Products and Yields of the Carbene Insertion into Haloalkanes

Entry	Substrate	Product	Yield (X =	
			Cl)	Br)
(a = Cl, b = Br)				
(% ^{a,b})				
	CH ₂ X ₂			
1	21	10	26	65
	CHX ₃			
2	22	28	60	29 ^{c,d}
	CX ₄			
3	23	29	62	48 ^{c,e}
4	24	30	39	78
5	25	30a	70	-
6	26	30	63 ^{f,g}	60 ^h
7	27	30a	73	-

^a These isolated yields are based on the average of at least two experiments and on the amount of EDA used. ^b The material balance is accounted for by dimerization of EDA (fumarate and maleate). ^c Reaction performed in CH₂Cl₂. ^d 9% of **10a** formed. ^e 3% of **10a** formed. ^f Yield determined by GC. ^g 47% (GC yield) of cyclohexene was formed. ^h 7% (GC yield) of cyclohexene formed.

Scheme 7



substrate, **50**, was reported to successfully engage in this rearrangement (Scheme 10, **50** → **51**).¹³⁷

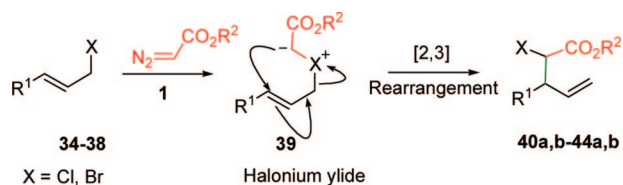
Of note is that in both the C–halogen insertion and C–halogen rearrangement reactions, new carbon–carbon bonds are formed as a result of the participation of the halogen, but it is also retained in the product. This is quite unusual as in most cases, metal-catalyzed reactions involving halogens result in the consumption of the halogen.

Table 7. Products and Yields from the Rearrangement^a

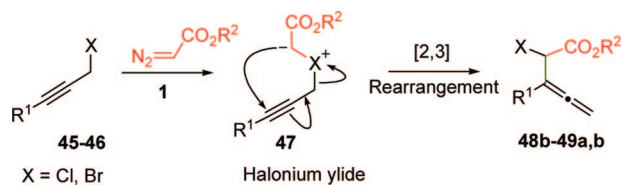
Entry	Substrate	Product	R/Yield (%)	
			Et (a)	<i>t</i> -Bu (b)
1			75	65
	34	40		
2			86 (1:1) ^b	96 (1:1) ^b
	35	41		
3			59	84
	36	42		
4			57	89
	37	43		
5			70 (1:1) ^b	80 (1:1) ^b
	38	44		
6			-	66
	45	48		
7			71	74
	46	49		

^a The reactions are conducted in neat halide with the exception of entry 5, in which the substrate is dissolved in CH₂Cl₂. ^b *Syn/anti* ratio, determined by ¹H NMR spectroscopy.

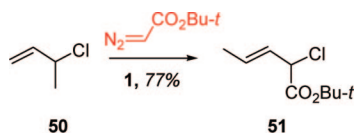
Scheme 8



Scheme 9



Scheme 10



Scheme 11

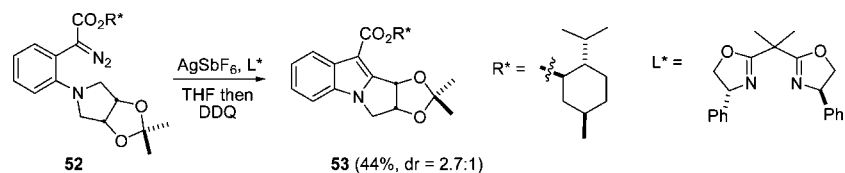



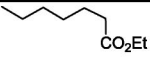
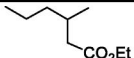
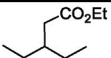

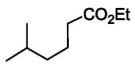
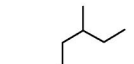


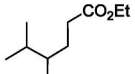
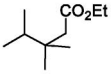

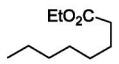
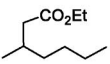
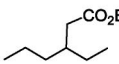
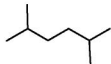
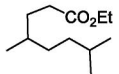
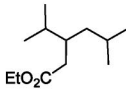
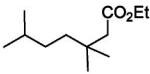

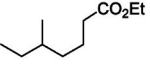
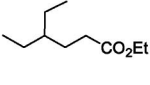
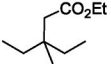

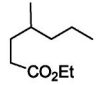
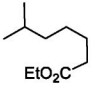
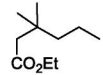

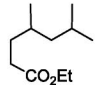
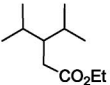
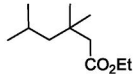
Table 8. C–H Insertion into Cyclic Substrates Catalyzed by Tris(pyrazolyl)borato–Silver and –Copper Complexes 1 and 54

Entry	Substrate	Products	Catalyst	
			1	54
1	56	62	88	60
2	57	63	88	58
3	58	64	24	73
4	59	65	41	73
5	60	66	0	-
6	61	67	0	-

3.3. C–H Insertion

Several silver complexes have been investigated in C–H insertion reactions of carbenes. One of the earliest reports by Sulikowski and Burgess describes an intramolecular C–H insertion of a chiral aryl diazoacetate **52** as part of study toward the total synthesis of the mitomycin family of natural products (Scheme 11).¹⁶² Among several catalysts that were screened was AgSbF₆ in the presence of bis(isoxazoline)-type ligands, which led to the formation of the desired insertion product in moderate yield and modest diastereoselectivity. More recently, both our group and Perez's group have demonstrated that silver complexes derived from tris(pyrazolyl)borate ligands are effective for C–H insertion with diazoacetates.^{85,139,141} Complex **1** efficiently effects insertion of EDA into cycloalkanes **56** and **57** (Table 8, entries 1 and 2), but in the case of oxygen-containing substrates **58–61**, the C–H insertion yields were rather modest (Table 8, entries 3–6).¹³⁹ Some of the same substrates were evaluated with the corresponding tris(pyrazolyl)boratocopper catalyst **54**, and in this case, the oxygen-containing substrates appear to react more efficiently (Table 8, entries 1–4). Two related silver complexes, **1** and **55**, were examined in C–H insertion reactions with several

Table 9. C–H Insertions into Acyclic Alkanes Catalyzed by Tris(pyrazolyl)borato–Silver Complexes 1 and 55^a

Cat	Substrate	Primary site/%	Secondary site/%	Tertiary site/%
				
1		41	47	12
55^a		29	57	14
				
1		59 (both)	27	14
55^a		42 (both)	37	21
				
1		80		20
55^a		60		40
				
55^a		22	56	21
				
55^a		46	17	37
				
55^a		18	48	33
				
55^a		50	39	21
				
55^a		81	6	13

^a These values have been normalized to account for C–H insertion products only.

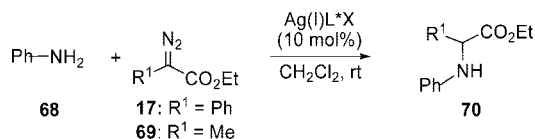
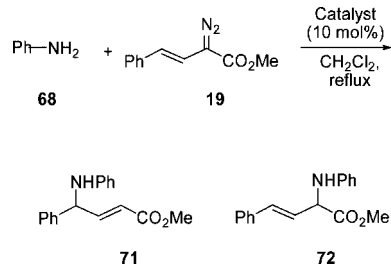
acyclic alkanes;^{85,139,141} the chemical yields were excellent, and interestingly, both complexes exhibited relatively high proportions of C–H insertion at the primary carbon (Table 9). Perez and co-workers speculated that this increased selectivity for primary insertion was due to increased electrophilic character at the metal center rather than steric factors.^{85,163}

3.4. N–H Insertion

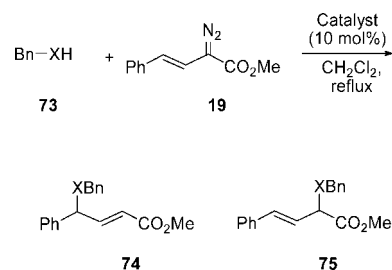
Both copper and rhodium complexes have been shown to catalyze carbene insertion into N–H bonds providing a convenient method for amino acid synthesis;¹⁶⁴ accordingly the corresponding silver-catalyzed process has attracted attention. Jørgensen and co-workers reported the reaction of aniline with substituted diazoacetate derivatives and several

Table 10. Silver(I)-Catalyzed N–H Insertion

Entry	Ag-salt	Ligand	R ¹	Yield (%)	ee (%)
1	AgSbF ₅		Me	8	25
2	AgOTf		Me	5	48
3	AgOTf		Me	4	20
4	AgClO ₄		Me	5	48
5	AgSbF ₅		Ph	33	13
6	AgOTf		Ph	49	9
7	AgOTf		Ph	58	9
8	AgOTf		Ph	58	(±)

Scheme 12**Scheme 13**

simple silver salts admixed with bisoxazoline ligands (Scheme 12).¹⁶⁵ Generally the yields were quite moderate, as were the enantioselectivities (Table 10). Parallel investigations with copper-based catalysts showed improved chemical yields, but the enantioselectivities were still poor. The authors suggest that the silver-mediated reactions proceed via a Lewis acid catalyzed pathway, rather than the expected carbene

Scheme 14**Table 11. Metal-Catalyzed NH Insertion**

entry	catalyst	yield (71 + 72, %)	71/72
1	Rh ₂ (OAc) ₄ ^a	79	<2:98
2	Cu(OTf) ₂	72	85:15
3	AgBF ₄	67	73:27
4	AgClO ₄	64	67:33
5	AgOTf	66	65:35

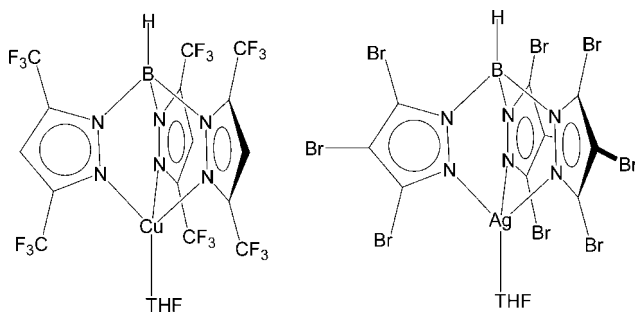
^a Catalyst at 1 mol % was used in this case.

Table 12. Metal-Catalyzed O–H and S–H Insertion

entry	X	catalyst	yield (74 + 75, %)	74/75
1	O	Rh ₂ (OAc) ₄ ^a	78	<2:98
2	O	Cu(OTf) ₂	53	72:28
3	O	AgBF ₄	67	>98:2
4	O	AgClO ₄	71	>98:2
5	O	AgOTf	63	>98:2
6	S	Cu(OTf) ₂	68	78:22
7	S	AgBF ₄	69	69:31
8	S	AgClO ₄	71	68:32
9	S	AgOTf	59	72:28

^a Catalyst at 1 mol % was used in this case.

transfer mechanism, which was thought to be operating in the case of the copper catalysts.¹⁶⁵

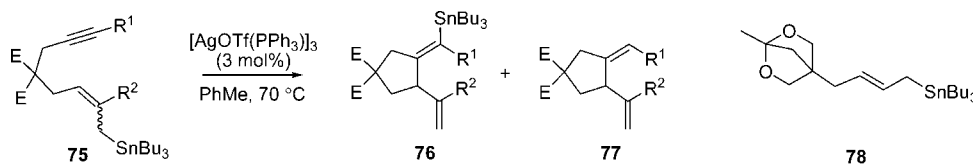
**[HB(3,5-(CF₃)₂Pz)₃]Cu(THF), 54****[HB(3,4,5-(Br)₃Pz)₃]Ag(THF), 55**

Hu and co-workers have examined N–H (and O–H and S–H) insertions in the presence of silver salts, as well as with copper or rhodium catalysts, with styryl diazoacetates.¹⁶⁶ Two possible products, 71 and 72, were obtained, which are derived from either direct insertion or insertion with net transposition (Schemes 13 and 14). Silver and copper salts tended to favor transposition (Table 11, entries 2–5; Table 12, entries 2–9), whereas rhodium favored direct insertion (Table 11, entry 1; Table 12, entry 1). The selectivity differences between the two products were again rationalized in terms of two mechanistic pathways. In the case of rhodium-based catalysts, it was proposed that the reaction occurs via a metallacarbene, whereas with copper and silver catalysts, the reaction was interpreted as proceeding by Lewis acid activation.

Table 13. Silver-Catalyzed Cyclocarbostannylation

entry	substrate	time/h	yield (%)	yield (%)	
1	(<i>E</i>)- 75a	E = CO ₂ Me, R ¹ = H, R ² = Me	0.5	76a (87)	77a (3)
2	(<i>E</i>)- 75b	E = CO ₂ Me, R ¹ = R ² = H	5.0	76b (71)	77b (6)
3	(<i>Z</i>)- 75c	E = SO ₂ Ph, R ¹ = R ² = H	3.5	76c (72)	77b (9)
4	(<i>E</i>)- 75d	E = SO ₂ Ph, R ¹ = H, R ² = Me	0.5	76d (90)	
5	(<i>Z</i>)- 75d	E = SO ₂ Ph, R ¹ = H, R ² = Me	0.5	76d (91)	
6	(<i>E</i>)- 75e	E = CH ₂ OAc, R ¹ = R ² = H	2.5	76e (69)	77e (12)
7	(<i>E</i>)- 75f	E = CH ₂ OTBDPS, R ¹ = R ² = H	2.0	76f (93)	
8	(<i>E</i>)- 75g	E = CH ₂ OH, R ¹ = R ² = H	0.2 ^a	76g (31)	77g (11)

^a Compound **78** was obtained in 30% yield in addition to the expected products **76g** and **77g**.

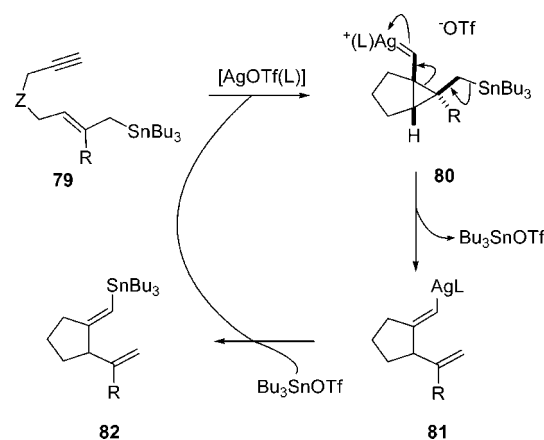
Scheme 15

3.5. Intermediacy of Silver Carbenes

While at this point, there is no independent evidence for the formation of silver carbenes in the reactions described above, the overall behavior of the intermediate in many of these transformations is *consistent* with the formation of a silver carbene. In addition, Perez and co-workers have reported a DFT study on the mechanism of Ag-catalyzed C–H insertion of diazoesters, and this investigation details the role of silver carbenes as intermediates.¹⁶³ All of the examples described above involved the reaction of diazoacetate derivatives with silver salts to initiate the formation of a putative silver carbene, or in some cases Lewis acid type of activation has been proposed. However, very recently Porcel and Echavarren have reported an intramolecular cyclization of an allylstannane to a pendant alkyne (Scheme 15).¹⁶⁷ As can be seen in Table 13, the reactions proceed in moderate to excellent yield, providing the dienyl stannane, and in some cases, some reductive destannylation occurs. Several asymmetric reactions were reported with substrate, leading to the formation of the expected adduct in reasonable enantioselectivities (ee = 73–78%) in a preliminary screen with several ligands. Mechanistically, most alkyne cyclizations of this type have been interpreted in terms of the catalyst serving as a Lewis acid, activating the π -bond to nucleophilic attack,^{168–172} and while this pathway is feasible, the authors prefer one involving the intermediacy of a silver carbene.¹⁶⁷ Control studies ruled out a pathway involving transmetalation, along with the participation of silver acetylides; therefore the pathway depicted in Scheme 16 is offered as a possibility. It is proposed that the silver complex selectively activates the alkyne to form the cyclopropyl carbene–silver(I) complex **80**. Fragmentation leads to the formation of alkenyl silver complex **81**; reaction with Bu₃SnOTf then leads to the formation of the final cyclization product and regeneration of the silver catalyst.

4. Summary

We have attempted to provide an overview of a growing area of investigation of the use of modified tris(pyrazolyl)borates and related pyrazole-based ligands, which confer not only useful stabilities on a range of complexes including coinage metal adducts of carbon monoxide and olefins, which permits their isolation and even structural characterization, but also lead to some unusual reactivity profiles. In particular,

Scheme 16

we have highlighted the chemistry of some silver complexes in carbene transfer reactions, putting their chemistry in context with earlier work. To date, only limited descriptions have appeared in the literature, but it is anticipated that the chemistry described herein will provide the inspiration for other applications of these and related complexes in synthesis.

5. Acknowledgments

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6. References

- (1) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999.
- (2) Pettinari, C.; Santini, C. *Comp. Coord. Chem. II* **2004**, *1*, 159.
- (3) Dias, H. V. R.; Fianchini, M. *Comments Inorg. Chem.* **2007**, *28*, 73.
- (4) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
- (5) Pettinari, C.; Cingolani, A.; Lobbia, G. G.; Marchetti, F.; Martini, D.; Pellei, M.; Pettinari, R.; Santini, C. *Polyhedron* **2004**, *23*, 451.
- (6) Hunt, L. B. *Platinum Met. Rev.* **1984**, *28*, 76.
- (7) Elschenbroich, C. *Organometallics*, 3rd ed.; VCH: Weinheim, Germany, 2006.
- (8) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653.
- (9) Schutzenberger, P. C. R. *Hebd. Seances Acad. Sci.* **1870**, *70*, 1134.

- (10) Bagnoli, F.; Dell'Amico, D. B.; Calderazzo, F.; Englert, U.; Marchetti, F.; Herberich, G. E.; Pasqualetti, N.; Ramello, S. *J. Chem. Soc., Dalton Trans.* **1996**, 4317.
- (11) Crabtree, R.; Mingos, M., Eds. *Comprehensive Organometallic Chemistry III*; Elsevier: Amsterdam, 2007.
- (12) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, C71.
- (13) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
- (14) Winstein, S.; Lucas, H. J. *J. Am. Chem. Soc.* **1938**, 60, 836.
- (15) Perez, P. J.; Diaz-Requejo, M. M. Copper Organometallics. In *Comprehensive Organometallic Chemistry III*; Crabtree, R., Mingos, M., Eds. Elsevier: Amsterdam, 2007.
- (16) Yam, V. W. W.; Cheng, E. C. C. Silver Organometallics. In *Comprehensive Organometallic Chemistry III*; Crabtree, R., Mingos, M., Eds. Elsevier: Amsterdam, 2007.
- (17) Schmidbaur, H.; Schier, A. Gold Organometallics. In *Comprehensive Organometallic Chemistry III*; Crabtree, R., Mingos, M., Eds. Elsevier: Amsterdam, 2007.
- (18) Tsumori, N.; Xu, Q.; Hirahara, M.; Tanihata, S.; Souma, Y.; Nishimura, Y.; Kuriyama, N.; Tsubota, S. *Bull. Chem. Soc. Jpn.* **2002**, 75, 2257.
- (19) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, 49, 1.
- (20) Capracotta, M. D.; Sullivan, R. M.; Martin, J. D. *J. Am. Chem. Soc.* **2006**, 128, 13463, and references therein.
- (21) Dias, H. V. R.; Wang, X. *Dalton Trans.* **2005**, 2985, and references therein.
- (22) (a) Dias, H. V. R.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, 509. (b) Dias, H. V. R.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, 2113.
- (23) Kung, M. C.; Davis, R. J.; Kung, H. H. *J. Phys. Chem. C* **2007**, 111, 11767.
- (24) Xu, Q. *Coord. Chem. Rev.* **2002**, 231, 83, and references therein.
- (25) Fry, H. C.; Lucas, H. R.; Sarjeant, A. A. N.; Karlin, K. D.; Meyer, G. *J. Inorg. Chem.* **2008**, 47, 241, and references therein.
- (26) Lee, S. *Methanol Synthesis Technology*; CRC Press: Boca Raton, FL, 1990.
- (27) Neurock, M.; Zhang, X.; Olken, M.; Jones, M.; Hickman, D.; Calverley, T.; Gulotty, R. *J. Phys. Chem. B* **2001**, 105, 1562.
- (28) Schaller, G. E.; Bleecker, A. B. *Science* **1995**, 270, 1809.
- (29) Rodriguez, F. I.; Esch, J. J.; Hall, A. E.; Binder, B. M.; Schaller, G. E.; Bleeckert, A. B. *Science* **1999**, 283, 996.
- (30) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, 105, 3522, and references therein.
- (31) Binder, B. M.; Rodriguez, F. I.; Bleecker, A. B.; Patterson, S. E. *FEBS Lett.* **2007**, 581, 5105.
- (32) Serafin, J. G.; Liu, A. C.; Seyedmonir, S. R. *J. Mol. Catal. A* **1998**, 131, 157.
- (33) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, 35, 265.
- (34) Linic, S.; Piao, H.; Adib, K.; Barteau, M. A. *Angew. Chem., Int. Ed.* **2004**, 43, 2918.
- (35) Torres, D.; Lopez, N.; Illas, F.; Lambert, R. M. *J. Am. Chem. Soc.* **2005**, 127, 10774.
- (36) Joergensen, K. A. *Chem. Rev.* **1989**, 89, 431.
- (37) Min, B. K.; Friend, C. M. *Chem. Rev.* **2007**, 107, 2709.
- (38) Hashmi, A. S. K. *Chem. Rev.* **2007**, 107, 3180.
- (39) Ishida, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2007**, 46, 7154.
- (40) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, 115, 301.
- (41) Xu, Q.; Souma, Y. *Studies Surf. Sci. Catal.* **2003**, 145, 215.
- (42) Xu, Q.; Souma, Y. *Top. Catal.* **1998**, 6, 17.
- (43) Dias, H. V. R.; Fianchini, M. *Angew. Chem., Int. Ed.* **2007**, 46, 2188.
- (44) Dias, H. V. R.; Goh, T. K. H. *Polyhedron* **2004**, 23, 273.
- (45) Mogi, K.; Sakai, Y.; Sonoda, T.; Xu, Q.; Souma, Y. *J. Phys. Chem. A* **2003**, 107, 3812.
- (46) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, 117, 4071.
- (47) Schwarz, H. *Angew. Chem., Int. Ed.* **2003**, 42, 4442.
- (48) Schroeder, D.; Schwarz, H.; Hrusak, J.; Pyykkö, P. *Inorg. Chem.* **1998**, 37, 624.
- (49) Antes, I.; Dapprich, S.; Frenking, G.; Schwerdtfeger, P. *Inorg. Chem.* **1996**, 35, 2089.
- (50) Calderazzo, F. *J. Organomet. Chem.* **1990**, 400, 303.
- (51) Lupinetti, A. J.; Jonas, V.; Thiel, W.; Strauss, S. H.; Frenking, G. *Chem.—Eur. J.* **1999**, 5, 2573.
- (52) Frenking, G.; Froehlich, N. *Chem. Rev.* **2000**, 100, 717.
- (53) Manchot, W.; Brandt, W. *Justus Leibigs Ann. Chem.* **1910**, 370, 286.
- (54) Manchot, W.; Friend, J. N. *Justus Leibigs Ann. Chem.* **1908**, 359, 100.
- (55) Haakansson, M.; Jagner, S. *Inorg. Chem.* **1990**, 29, 5241.
- (56) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, 8, 2533.
- (57) Dell'Amico, D. B.; Alessio, R.; Calderazzo, F.; Della Pina, F.; Englert, U.; Pampaloni, G.; Passarelli, V. *Dalton* **2000**, 2067.
- (58) Bruce, M. I.; Ostazewski, A. P. *J. Chem. Soc., Chem. Commun.* **1972**, 1124.
- (59) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, 14, 2051.
- (60) Bruce, M. I.; Ostazewski, A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.
- (61) Conry, R. R.; Ji, G.; Tipton, A. A. *Inorg. Chem.* **1999**, 38, 906.
- (62) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, 120, 11408.
- (63) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, 115, 11285.
- (64) Carrier, S. M.; Ruggiero, C. E.; Tolman, W. B.; Jameson, G. B. *J. Am. Chem. Soc.* **1992**, 114, 4407.
- (65) Kitajima, N.; Koda, T.; Iwata, Y.; Morooka, Y. *J. Am. Chem. Soc.* **1990**, 112, 8833.
- (66) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Morooka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, 114, 1277.
- (67) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Morooka, Y. *Chem. Lett.* **1989**, 421.
- (68) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, 263, 357.
- (69) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **1995**, 34, 5380.
- (70) Dias, H. V. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1996**, 15, 2994.
- (71) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, 362, 511.
- (72) Fujisawa, K.; Ono, T.; Ishikawa, Y.; Amir, N.; Miyashita, Y.; Okamoto, K.-I.; Lehnert, N. *Inorg. Chem.* **2006**, 45, 1698.
- (73) Dias, H. V. R.; Kim, H.-J. *Organometallics* **1996**, 15, 5374.
- (74) Imai, S.; Fujisawa, K.; Kobayashi, T.; Shirasawa, N.; Fujii, H.; Yoshimura, T.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, 37, 3066.
- (75) Dias, H. V. R.; Wang, X. *Polyhedron* **2004**, 23, 2533.
- (76) Kujime, M.; Kurahashi, T.; Tomura, M.; Fujii, H. *Inorg. Chem.* **2007**, 46, 541.
- (77) Caballero, A.; Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Perez, P. J. *J. Am. Chem. Soc.* **2003**, 125, 1446.
- (78) Kitajima, N.; Koda, T.; Moro-Oka, Y. *Stud. Org. Chem. (Amsterdam)* **1988**, 33, 273.
- (79) Sterling, R. F.; Kutal, C. *Inorg. Chem.* **1980**, 19, 1502.
- (80) Pampaloni, G.; Peloso, R.; Graiff, C.; Tiripicchio, A. *Dalton Trans.* **2006**, 3576.
- (81) Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* **1977**, 30, 2293.
- (82) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, 98, 711.
- (83) Effendy; Lobbia, G. G.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2000**, 308, 65.
- (84) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1995**, 117, 11381.
- (85) Urbano, J.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Diaz-Requejo, M. M.; Perez, P. J. *Organometallics* **2005**, 24, 1528.
- (86) Ma, N. L. *Chem. Phys. Lett.* **1998**, 297, 230.
- (87) Manchot, W.; Gall, H. *Ber. Dtsch. Chem. Ges.* **1925**, 58B, 2175.
- (88) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, 35, 3687.
- (89) Walker, N. R.; Gerry, M. C. L. *Inorg. Chem.* **2002**, 41, 1236.
- (90) Pyykkö, P. *Chem. Rev.* **1988**, 88, 563.
- (91) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjairami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Gamage, C. S. P.; Dias, H. V. R. *Inorg. Chem.* **2005**, 44, 8200.
- (92) Bayler, A.; Schier, A.; Bowmaker, G. A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, 118, 7006.
- (93) Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1996**, 15, 2029.
- (94) Chenskaya, T. B.; Berghahn, M.; Kunz, P. C.; Frank, W.; Kläui, W. *J. Mol. Struct.* **2007**, 829, 135.
- (95) Kläui, W.; Berghahn, M.; Frank, W.; Reiss, G. J.; Schonherr, T.; Rheinwald, G.; Lang, H. *Eur. J. Inorg. Chem.* **2003**, 2059.
- (96) (a) Chou, C.-C.; Su, C.-C.; Yeh, A. *Inorg. Chem.* **2005**, 44, 6122. (b) Fujisawa, K.; Noguchi, Y.; Miyashita, Y.; Okamoto, K.; Lehnert, N. *Inorg. Chem.* **2007**, 46, 10607.
- (97) Pampaloni, G.; Peloso, R.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, 26, 4278.
- (98) Boni, A.; Pampaloni, G.; Peloso, R.; Belletti, D.; Graiff, C.; Tiripicchio, A. *J. Organomet. Chem.* **2006**, 691, 5602.
- (99) Abu Salah, O. M.; Bruce, M. I.; Hameister, C. *Inorg. Syntheses* **1982**, 21, 107.
- (100) Abu Salah, O. M.; Bruce, M. I.; Walsh, J. D. *Aust. J. Chem.* **1979**, 32, 1209.
- (101) Brunner, H.; Singh, U. P.; Boeck, T.; Altmann, S.; Scheck, T.; Wrackmeyer, B. *J. Organomet. Chem.* **1993**, 443, C16.
- (102) Abu Salah, O. M.; Bruce, M. I. *J. Organomet. Chem.* **1975**, 87, C15.
- (103) Singh, U. P.; Babbar, P.; Hassler, B.; Nishiyama, H.; Brunner, H. *J. Mol. Catal. A* **2002**, 185, 33.
- (104) Byers, P. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 93.

- (105) Byers, P. K.; Carr, N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3701.
- (106) Sargent, A. L.; Hall, M. B. *Polyhedron* **1990**, *9*, 1799.
- (107) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988**, *66*, 2194.
- (108) Liu, Y. Y.; Mar, A.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988**, *66*, 1997.
- (109) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 5154.
- (110) Straub, B. F.; Eisentrager, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507.
- (111) Masuda, H.; Yamamoto, N.; Taga, T.; Machida, K.; Kitagawa, S.; Munakata, M. *J. Organomet. Chem.* **1987**, *322*, 121.
- (112) Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. *Inorg. Chem.* **1986**, *25*, 2622.
- (113) Guo, B. C.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1991**, *181*, 16.
- (114) Sievers, M. R.; Jarvis, L. M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 1891.
- (115) Schroeder, D.; Hrusak, J.; Hertwig, R. H.; Koch, W.; Schwerdtfeger, P.; Schwarz, H. *Organometallics* **1995**, *14*, 312.
- (116) Stringer, K. L.; Citir, M.; Metz, R. B. *J. Phys. Chem. A* **2004**, *108*, 6996.
- (117) Hertwig, R. H.; Koch, W.; Schroeder, D.; Schwarz, H.; Hrusak, J.; Schwerdtfeger, P. *J. Phys. Chem.* **1996**, *100*, 12253.
- (118) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057.
- (119) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079.
- (120) Perez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1993**, *12*, 261.
- (121) Diaz-Requejo, M. M.; Perez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1997**, *16*, 4399.
- (122) Dias, H. V. R.; Lu, H.-L.; Kim, H.-J.; Polach, S. A.; Goh, T. K. H. H.; Browning, R. G.; Lovely, C. J. *Organometallics* **2002**, *21*, 1466.
- (123) Dias, H. V. R.; Wang, X.; Diyabalanage, H. V. K. *Inorg. Chem.* **2005**, *44*, 7322.
- (124) Dias, H. V. R.; Wang, Z.; Jin, W. *Inorg. Chem.* **1997**, *36*, 6205.
- (125) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724.
- (126) Dias, H. V. R.; Wu, J.; Wang, X.; Rangan, K. *Inorg. Chem.* **2007**, *46*, 1960.
- (127) Dias, H. V. R.; Wu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7814.
- (128) Dias, H. V. R.; Richey, S. A.; Diyabalanage, H. V. K.; Thankamani, J. *J. Organomet. Chem.* **2005**, *690*, 1913.
- (129) Blake, A. J.; Carling, D. A.; George, M. W.; Hubberstey, P.; Lopez Garcia, R.; Wilson, C. *Acta Crystallogr.* **2002**, *E58*, m41.
- (130) Van Nes, G. J. H.; Vos, A. *Acta Crystallogr.* **1979**, *B35*, 2593.
- (131) Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitsu, K.; Young, J. E., Jr. *J. Chem. Phys.* **1965**, *42*, 2683.
- (132) Dias, H. V. R.; Fianchini, M.; Cundari, T. R.; Campana, C. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 556.
- (133) Li, Z.; He, C. *Eur. J. Org. Chem.* **2006**, 4313.
- (134) Diaz-Requejo, M. M.; Perez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441.
- (135) Halbes-Letinois, U.; Weibel, J.-M.; Pale, P. *Chem. Soc. Rev.* **2007**, *36*, 259.
- (136) Yanagisawa, A.; Arai, T. *Chem. Commun.* **2008**, 1165.
- (137) Krishnamoorthy, P.; Browning, R. G.; Singh, S.; Sivappa, R.; Lovely, C. J.; Dias, H. V. R. *Chem. Commun.* **2007**, 731.
- (138) Lovely, C. J.; Browning, R. G.; Badarinarayana, V.; Dias, H. V. R. *Tetrahedron Lett.* **2005**, *46*, 2453.
- (139) Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2004**, *23*, 1200.
- (140) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9270.
- (141) Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2005**, *24*, 5784.
- (142) Julian, R. R.; May, J. A.; Stoltz, B. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 4478.
- (143) Kirmse, W. *Eur. J. Org. Chem.* **2002**, 2193.
- (144) We use the term carbene transfer to represent the net chemical transformation and not necessarily to imply that this is a reactive intermediate (either a free carbene or a metallacarbene).
- (145) Juhl, K.; Hazell, K. A.; Jorgensen, K. A. *J. Chem. Soc., Perkin Trans. I* **1999**, 2293.
- (146) Dias, H. V. R.; Polach, S. A. *Inorg. Chem.* **2000**, *39*, 4676.
- (147) Browning, R. G., Ph.D. Dissertation, The University of Texas at Arlington, 2003.
- (148) Morilla, M. E.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *Organometallics* **2004**, *23*, 293.
- (149) Díaz-Requejo, M. M.; Caballero, A.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 978.
- (150) Díaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 3167.
- (151) Thompson, J. L.; Davies, H. M. L. *J. Am. Chem. Soc.* **2007**, *129*, 6090.
- (152) Migita, T.; Ando, W.; Kondo, S.; Matsuyama, H.; Kosugi, M. *Nippon Kagaku Zasshi* **1970**, *91*, 374.
- (153) Urry, W. H.; Bilow, N. *J. Am. Chem. Soc.* **1964**, *86*, 1815.
- (154) Urry, W. H.; Eiszner, J. R.; Wilt, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 918.
- (155) Urry, W. H.; Wilt, J. H. *J. Am. Chem. Soc.* **1954**, *76*, 2594.
- (156) Urry, W. H.; Eiszner, J. R. *J. Am. Chem. Soc.* **1952**, *74*, 5822.
- (157) Urry, W. H.; Eiszner, J. R. *J. Am. Chem. Soc.* **1951**, *73*, 2977.
- (158) Hodgson, D. M.; Pierard, F. Y. T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2003**, *30*, 50.
- (159) Simonneaux, G.; Galardon, E.; Paul-Roth, C.; Gulea, M. M., S. J. *Organomet. Chem.* **2001**, *617–618*, 360.
- (160) Doyle, M. P.; Forbes, D. C.; Vasbinder, M. M.; Peterson, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 7653.
- (161) Doyle, M. P.; Tamblin, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094.
- (162) Burgess, K.; Lim, H.-J.; Porte, A. M.; Sulikowski, G. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 220.
- (163) Braga, A. A. C.; Maseras, F.; Urbano, J.; Caballero, A.; Mar Diaz-Requejo, M.; Perez, P. J. *Organometallics* **2006**, *25*, 5292.
- (164) Moody, C. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 9148.
- (165) Bachmann, S.; Fielenbach, D.; Jorgensen, K. A. *Org. Biomol. Chem.* **2004**, *2*, 3044.
- (166) Yue, Y.; Wang, Y.; Hu, W. *Tetrahedron Lett.* **2007**, *48*, 3975.
- (167) Porcel, S.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2672.
- (168) Zhao, J.; Hughes, C. O.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 7436.
- (169) Sun, J.; Kozmin, S. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4991.
- (170) Harrison, T. J.; Kozak, J. A.; Corbella-Pané, M.; Dake, G. R. *J. Org. Chem.* **2006**, *71*, 4525.
- (171) Sweis, R. F.; Schramm, M. P.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7442.
- (172) Harrison, T. J.; Dake, G. R. *Org. Lett.* **2004**, *6*, 5023.

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