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Structurally Characterized Coinage-Metal–Ethylene Complexes

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Despite the interest in them, easily isolable and thermally stable Cu^I, Ag^I, and Au^I complexes of ethylene are still limited and get increasingly sparse as one descends the group 11 triad towards gold. Recently, there have been some notable developments in this field, including the isolation of gold–ethylene complexes and coinage-metal adducts with more than one ethylene molecule on a metal center. This article focuses on the chemistry of coinage-metal–ethylene adducts that have been synthesized and characterized by X-ray crystallography. Thus far, bidentate and tridentate donors based on nitrogen appear to be the ligands of choice for stabilizing species with an $M–C_2H_4$ ($M = Cu^I$, Ag^I, and Au^I) moiety. Weakly donating ligands and anions are also commonly used, as they do not interfere with and displace the ethylene from the metal center. The ethylene ^{13}C NMR chemical shift provides useful information about the nature of the metal–ethylene interaction. In some adducts (especially those with relatively weak $M–C_2H_4$ interactions), the change in the C=C bond length upon coordination to the metal site is difficult to discern because it falls within the errors associated with the crystallographically determined C=C bond length value. IR and Raman C=C stretching data would be useful but, probably due to the very weak nature of the IR band and the lack of convenient access to the Raman instruments, are often not reported. In this microreview, results from some computational and gas-phase spectroscopic studies are also provided for comparison.

Introduction

Transition-metal–ethylene complexes are among the most important classes of compounds in chemistry. For example, Zeise's platinum–ethylene complex $K[PtCl_3(C_2H_4)]\cdot H_2O$, commonly known as the Zeise's salt, synthesized in 1827, was the first organometallic compound to be isolated in pure form.[1–3] This seminal discovery marks the beginning of organotransition-metal chemistry. The Dewar–Chatt–Duncanson model of olefin bonding was motivated in large part by a desire to understand the bonding in transition-metal–alkene adducts such as those of silver(I).[4–6] The complexes between coinage metals (Cu, Ag, Au) and alkenes also figure prominently in a number of significant application areas ranging from biochemistry,[7–14] chroma-

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Jiang Wu was born in Changzhou, China, in 1978. He graduated in Chemistry from the Nanjing University of Science and Technology in 2001. Jiang Wu joined the group of Professor Dias in 2005 at the University of Texas at Arlington as a Ph.D. student. His research interests are in the areas of organometallic chemistry and the development of new synthetic methods. He has played a major role in the isolation of the first structurally characterized gold–ethylene complexes.

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tographic separations,[15,16] olefin–paraffin separations,[17–23] computational and spectroscopic and kinetic–thermodynamic studies,[24–69] to modern organic synthesis,[70–73] and in several industrial catalytic processes.[74] For example, copper–ethylene adducts are of interest as models for the ethylene (the smallest plant hormone) receptor site in plants.[12,13] Silver-catalyzed oxidation of ethylene to ethylene oxide is a major industrial process.[74–78] Gold-based materials serve as excellent catalysts for the selective epoxidation of propene and other alkenes.[70,79,80]

Despite the interest in them, isolable Cu^I, Ag^I, and Au^I complexes bearing simple alkene ligands are somewhat limited. This scarcity is most noticeable with ethylene adducts.[8,70,81–85] In fact, structurally characterized coinage-metal–ethylene complexes are not that common and get increasingly sparse as one moves down the group 11 triad towards gold. Furthermore, compounds that feature more than one ethylene moiety on Cu^I, Ag^I, and Au^I are exceedingly rare.[85–88] This is due in large part to the poor thermal stability, and/or light sensitivity, and high lability of the olefin ligand, which create difficulties during the isolation of these complexes. There are, however, some recent notable developments in the field of coinage-metal–ethylene adducts, including the first report containing structural data on a gold(I)–ethylene complex[84] and the isolation of tris(ethylene) complexes $[M(C_2H_4)_3]^+$ (M = Cu, Ag, Au).[85,87,88] This review is aimed at providing an overview of *structurally authenticated ethylene complexes of Cu^I, Ag^I, and Au^I*, and highlighting the key developments resulting from the use of nitrogen-based supporting ligands such as tris(pyrazolyl)borates (scorpionates).[89] Some useful data from computational studies are also presented.

Bonding, Computational, and Gas-Phase Spectroscopic Studies

The bonding in coinage-metal–ethylene complexes can be described by the Dewar–Chatt–Duncanson model as a synergistic combination of σ-donor and π-acceptor interactions between the metal ion and the ethylene π-system (Figure 1).[4,5] Figure 2 (left) shows the limiting bonding schemes in which the ethylene–metal-ion interaction is weak and typically dominated by the ethylene-to-metal-ion σ-donation (leading to the T-shaped structure). At the other extreme [Figure 2 (right)], σ-donation and, more importantly, the metal-ion-to-ethylene π-back-donation is dominant, and it results in a metallacyclopropane ring structure and a C=C bond with a bond order approaching unity. Note that both the σ-donor and π-back-bonding contributions lead to the lengthening of the C=C bond. Thus, metal–ethylene adducts should show C=C distances that are longer than that of free ethylene, although the extent of lengthening depends on a number of factors such as the charge on the metal and the nature of any auxiliary ligands.

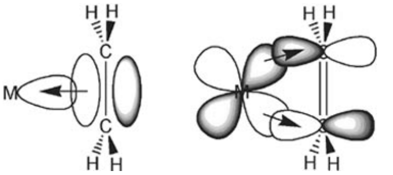

Figure 1. Schematic representation of the metal–ethylene bonding model: donation to a vacant orbital of a metal from the filled π-orbital of ethylene (left); back-donation to the empty antibonding π*-orbital of ethylene from a filled metal d-orbital (right).

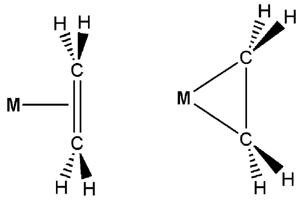

Figure 2. Limiting structures of a metal–ethylene complex: T-shaped structure (left) and metallacyclopropane (right).

The electron affinity (EA) and promotion energy (PE) data of cationic d^{10}-coinage-metal ions {EA [$nd^{10}\rightarrow nd^{10}(n+1)s^1$]: 7.72, 7.59, 9.22 eV (which correlates with the σ-acceptor property), and PE [$nd^{10}\rightarrow nd^9(n+1)p^1$]: 8.25, 9.94, 7.83 eV (which correlates inversely with the π-donor property) for Cu^I, Ag^I, and Au^I, respectively} indicate that the Au^+ cation is the best σ-acceptor and best π-donor among the coinage-metal family members, while the Ag^+ cation has the weakest σ-acceptor and π-donor character.[2] The experimental bond dissociation energy (BDE) values for $M^+–C_2H_4$ (M = Cu, Ag, Au) are available, and for $Ag^+–C_2H_4$, the experimental BDE is 33.7 kcal/mol.[38] The corresponding value for the copper(I) analog is 41.5 kcal/mol,[33] while for gold(I) it is believed to be about 69 kcal/mol or has an upper limit of 82 kcal/mol.[34,36,90] Thus, gold(I) forms the strongest interaction with ethylene while silver(I) forms the weakest bond. These experimental data involve the bonding of ethylene with metal ions with no auxiliary ligands. Obviously, the coinage-metal-ion–ethylene interactions will be further influenced by the secondary donors with varying steric-electronic properties.

Copper, silver, and gold adducts of ethylene have been investigated in detail by several groups by using computational methods.[27,32,34–37,43,47,68,81,85,90] Although there are some differences among the calculated BDE values of the $Cu^+/Ag^+/Au^+$–ethylene interactions and the ideal descriptions of the metal–ligand interaction [e.g., by classifying it as T-shaped, or indicating the extent of its metallacyclopropane character, or the relative importance and magnitude of the electrostatic and covalent (σ-donor and π-back-bonding) components], the results of most of these studies agree well with the experimental BDE data and predict bond energies to vary discontinuously as one descends the group 11 triad, indicating that gold(I) is the cation most strongly bonded to ethylene.[27,35] For example, using a variety of density functional and wavefunction-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^+); CCSD(T) approaches generally predicted the weakest binding energies.[35]

The importance of the electrostatic and covalent character of the coinage-metal-ion–ethylene (M^+–C_2H_4) interaction has been investigated by energy-decomposition techniques.[27,35] These results point to more electrostatic than covalent character in the M^+–C_2H_4 bond of coinage-metal ions. The covalent term, however, is significant according to more recent studies, and it accounts for about 40% of the attractive interaction,[27] and in some cases a percentage even closer to 50%, for Au^+–C_2H_4.[35] Further division of the covalent term into σ- and π-components has also been carried out. In these cationic species, ethylene-to-metal-ion σ-donor bonding is the dominant component. However, there is some disagreement over the relative importance of the π-back-bonding, especially in the silver(I) and gold(I) adducts of the type M^+–C_2H_4 (e.g., predicted to range from 30.5% to a negligible fraction of the covalent term).[27,35,43] Neutral molecules of the type F–M(C_2H_4) (M = Cu, Ag, Au) and cationic $[Au(bpy)(C_2H_4)]^+$ have also been investigated by using computational methods.[28,81] Results show that the secondary ligands affect the M–C and C=C bonds and the extent of the π-back-bonding contribution. Interestingly, in the gold adduct $[Au(bpy)(C_2H_4)]^+$, the π-back-bonding contribution is calculated to be even higher than that of the σ-bonding component.[81]

Coinage-metal adducts containing more than one ethylene ligand have also attracted interest. Guo and Castleman have proposed experimental estimates from gas-phase ion–molecule reactions for the binding enthalpies of a second ethylene to $Ag(C_2H_4)^+$: –32 kcal/mol (298 K).[38] Deubel and co-workers have calculated the binding energies of two ethylene molecules to coinage-metal cations by using both relativistic and nonrelativistic pseudopotentials. Focusing on the former methodology with a "pure" functional (BLYP), these researchers obtained stabilization energies of –103 kcal/mol (Cu^+), –73 kcal/mol (Ag^+) and –114 kcal/mol (Au^+) for the aggregate binding of two ethylene molecules to M^+.[91] Zuilhof, Sudhölter, and co-workers have evaluated (among other things) the binding of three ethylene groups to Ag^+ in an interesting study of silver ion chromatography.[31] These researchers obtained an aggregate binding enthalpy of –92 kcal/mol. A spoke-wheel structure for $[Ag(C_2H_4)_3]^+$ is also predicted to be more stable than the upright conformation.[31,85] Krossing et al. estimated an energy difference of 11 kcal/mol for the two conformers in $[Ag(C_2H_4)_3]^+$.[85] The BP86-calculated aggregate binding enthalpies reported by Dias, Cundari and co-workers for the coordination of three ethylene molecules to Cu^+, Ag^+, and Au^+ ions are –120, –85, and –131 kcal/mol, respectively.[88] They predict the spoke-wheel structure for the tris(ethylene)gold adduct $[Au(C_2H_4)_3]^+$ to be more stable than the upright conformation by about 19 kcal/mol.

Overall, these experimental and computational data show that the coinage-metal-ion–ethylene bond energies are significant and vary in the order Ag < Cu < Au. Coinage-metal complexes containing more than one ethylene ligand are also reasonable synthetic targets. A judicious choice of auxiliary ligands could further enhance both the thermodynamic and kinetic stability of coinage-metal–ethylene adducts, leading to novel and experimentally characterizable examples.

Structurally Characterized Copper(I)–Ethylene Complexes

It has been well known for nearly a century that copper(I) salts, such as cuprous chloride, and ethylene react both in solution and in the solid state to form adducts.[3,92–94] These compounds have limited stability and decompose unless low temperatures and high ethylene pressures are maintained. This reversible adduct formation by Cu^I has been exploited in the separation of olefins like ethylene from paraffins and in important catalytic processes such as the oxychlorination of ethylene.[17,74,95–98] Copper(I)–alkene complexes are involved as catalytically active species and/or resting states in the copper-catalyzed aziridination, cyclopropanation, and conjugate addition of Grignard reagents to α,β-unsaturated carbonyl compounds.[71] Copper(I)–ethylene adducts are also important in nature. Ethylene is involved in many important facets of plant development, such as germination, growth, fruit ripening, aging, and separation of leaves or fruits.[99] It is believed that the ethylene receptor is a copper(I) site in a metalloenzyme (ETR 1).[8,13,100] Copper is also implicated in the metabolism of ethylene to ethylene oxide and other products.[8] Overall, copper–ethylene complexes are of tremendous importance in several fields including biochemistry, organic synthesis, and in industrial applications. Studies also show that most copper(I)–ethylene adducts are fairly labile (and lose ethylene quite easily) presenting difficulties with isolation and structural and spectroscopic studies. However, as it will be evident from the following account, now there are several reports of structurally well-authenticated copper–ethylene adducts in the literature. The key structural and spectroscopic data of these copper(I)–ethylene adducts are given in Table 1.

In 1983, Thompson et al. reported the synthesis of two tris(pyrazolyl)boratocopper–ethylene adducts and their structural information.[8] $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$ (Figure 3) and $\{[HB(Pz)_3]Cu(C_2H_4)CuCl\}_2$ (Figure 4) have been synthesized by treating $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]K$ with CuI and $[HB(Pz)_3]K$ with CuCl in the presence of ethylene, respectively. $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$ features a κ^3-bonded tris(pyrazolyl)borato ligand, while $\{[HB(Pz)_3]Cu(C_2H_4)CuCl\}_2$ has a three-coordinate copper site and a $Cu(C_2H_4)$ moiety bonded to the tris(pyrazolyl)borate group in κ^2-fashion. Crystalline samples of these adducts are stable toward loss of ethylene in a nitrogen atmosphere. However, the ethylene moiety of these adducts can be removed by evacuation. They are also air-sensitive molecules.

The highly fluorinated analog $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$ (Figure 5) reported by Dias and Lovely et al. is a remarkably stable copper–ethylene complex.[82] It is an

Table 1. Selected structural parameters and NMR spectroscopic data for coinage-metal–ethylene complexes: CN = coordination number at the coinage metal; for *d*(M–C) and *d*(C=C), average bond lengths are given if more than one is present; ^{1}H NMR data in $CDCl_3$ unless otherwise noted, the ^{13}C NMR data have been reported in the same solvent.

Compound	CN	*d*(M–C) [Å]	*d*(C=C) [Å]	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]/$^1J_{CH}$[Hz]	Ref.
$[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$	4	2.014(5)	1.329(9)	4.41 (CD_2Cl_2)		[8]
$\{[HB(Pz)_3]Cu(C_2H_4)CuCl\}_2$	3	1.999 (3)	1.347(5)	4.43 (CD_2Cl_2)		[8]
$[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$	4	2.022(6)	1.325(9)	4.96	89.1/161	[82]
$[HB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$	4	2.009(9)	1.34(1)	4.80	85.7/158	[82]
$[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Cu(C_2H_4)$	4	2.012(11)	1.30(1)	4.91	85.7/159	[82]
$[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$	4	2.038(3)	1.334(4)	4.80	85.4/161	[103]
$[Bu^t{}_2P(NSiMe_3)_2]Cu(C_2H_4)$	3	1.987(3)	1.362(6)	3.48 (C_6D_6)	73/158	[104]
$[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$	3	1.989(2)	1.365(3)	2.919 (C_6D_6)	74.7/158	[107]
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$	3	2.014(3)	1.364(4)	3.86	86.1	[109]
$[(tmen)Cu(C_2H_4)]ClO_4$	3	1.97(1)	1.36(1)	4.16 (CD_3COCD_3)		[114]
$[(bpy)Cu(C_2H_4)]ClO_4$	3	1.992(12)	1.353(15)	4.92 (CD_3COCD_3)		[111]
$[(phen)Cu(C_2H_4)]ClO_4$	3	2.010(13)	1.361(22)	5.00 (CD_3COCD_3)		[111]
$[Cu(NH(py)_2)(C_2H_4)]ClO_4$	3	2.019 (3)	1.359 (7)	4.70 (CD_3COCD_3)		[110]
$[Cu(Hhq)_2(C_2H_4)]ClO_4$	3	2.046(6)	1.32(1)	5.22 (CD_3COCD_3)		[113]
$\{[Cu_2(bpm)_2(C_2H_4)(Me_2CO)](ClO_4)_2\}_n$	3	2.022(6)	1.30(1)			[112]
β-$(C_2H_4)CuAlCl_4$	4	2.089	1.34		105 (solid)	[86]
$(C_2H_4)_2CuAlCl_4$	5[a]	2.137	1.34		109 (solid)	[86]
$[Cu(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$	3	2.147(1)	1.331(16)	5.47 (CD_2Cl_2)	110.0	[87]
$[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$	4	2.301(7)	1.298(14)	5.56 (C_6D_{12})	104.9/164	[83]
$[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$	4	2.2822(18)	1.340(4)	5.47	104	[125]
$[MeB\{3\text{-}(C_2F_5)Pz\}_3]Ag(C_2H_4)$	4	2.301(2)	1.314(4)	5.48 (CD_2Cl_2)	105.5/161	[124]
$[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$	4	2.27(3)	1.323(12)	3.42	95.4	[126]
$[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$	3	2.265(4)	1.296(7)	4.72	101.7	[125]
$[HC\{(CF_3)C(3,5\text{-}\{CF_3\}_2C_6H_3)N\}_2]Ag(C_2H_4)$	3	2.22(2)	1.392(19)	3.78 (C_6D_6)		[127]
$[\{Ag(C_2H_4)\}_3\{OC(CF_3)_3\}_2][Al\{OC(CF_3)_3\}_4]$	3	2.289(8)	1.351(15)	5.54 (CD_2Cl_2)	112.2	[128]
$[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$	3	2.396(5)	1.304(10)	5.77 (CD_2Cl_2)	116.4	[85]
$[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$	3	2.102(6)	1.388(8)	3.81	63.7/163	[84]
$[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$	3	2.095(5)	1.378(8)	3.69	59.3/165	[84]
$[Au(C_2H_4)_3][SbF_6]$	3	2.268(5)	1.367(4)	4.94 (CD_2Cl_2)	92.7	[88]
C_2H_4			1.313(1) (X-ray) 1.3369(16) (electr. diff.)	5.40 (CD_2Cl_2)	123.3/156	[82,151,152]

[a] Three-coordinate Cu has two weak Cu···Cl contacts.

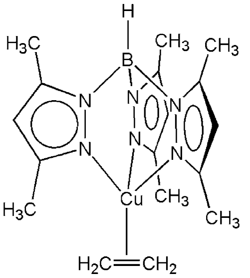

Figure 3. Copper(I)–ethylene adduct $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$.

air-stable solid and does not lose ethylene under reduced pressure. $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$ has been obtained by treating $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Na(thf)$ with CuOTf in the presence of ethylene. Closely related compounds $[HB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ and $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Cu(C_2H_4)$ have also been synthesized and characterized by X-ray crystallography and NMR spectroscopy.[82] The catalytic applications of $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$[101,102] and the fluorinated adducts $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$ and $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Cu(C_2H_4)$ have also been reported.[82] More recently, Dias et al. reported the synthesis of $[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ (Figure 6) containing a *B*-methylated tris(pyrazolyl)borate group.[103] It has been syn-

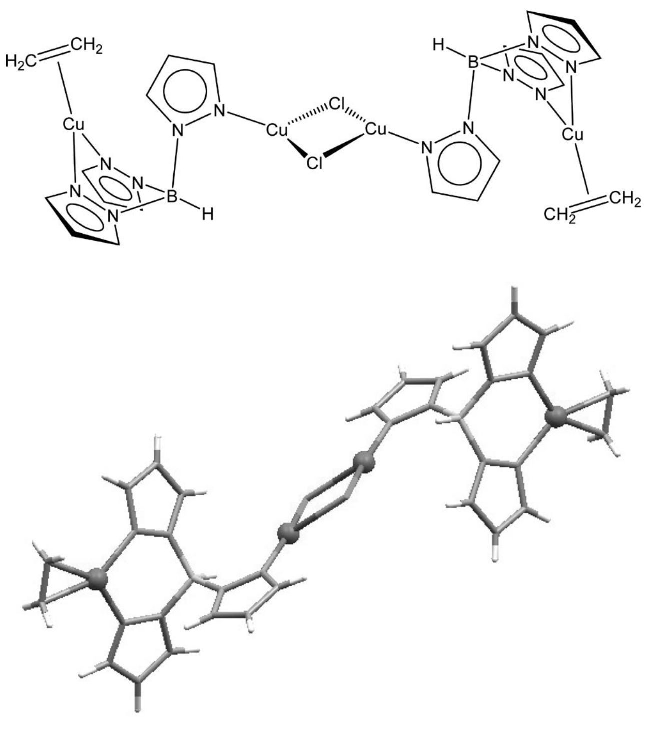

Figure 4. Copper(I)–ethylene complex $\{[HB(Pz)_3]Cu(C_2H_4)CuCl\}_2$ and a view of the crystal structure.

thesized by using a thallium derivative $[MeB\{3\text{-}(CF_3)Pz\}_3]Tl$, CuOTf, and ethylene. These adducts feature κ^3-bonded (albeit somewhat asymmetrically with different Cu–N distances) tris(pyrazolyl)borate donors. Unlike $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(R)Pz\}_3]Cu(C_2H_4)$ (R = CF_3, Ph, H), $[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ contains a non-disordered ethylene moiety on copper. A rare molecule featuring an unsupported Cu^I–Sn^{II} bond has been synthesized by treating $[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ with $[(Bn)_2ATI]SnCl$.[103]

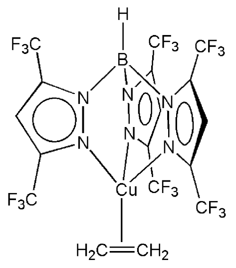

Figure 5. Copper(I)–ethylene complex $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$.

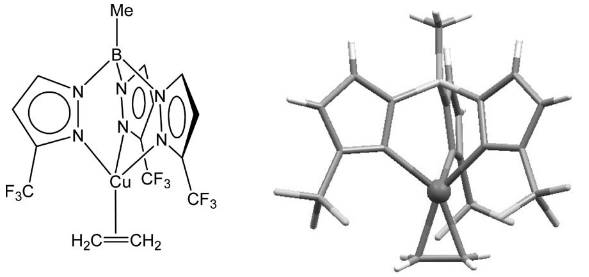

Figure 6. Copper(I)–ethylene complex $[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ and a view of the crystal structure.

Neutral, thermally stable, three-coordinate copper(I)–ethylene complexes have been obtained by using iminophosphanamide, 1,5-diazapentadienyl, and 1,3,5-triazapentadienyl ligands. $[tBu_2P(NSiMe_3)_2]Cu(C_2H_4)$ (Figure 7) reported by Hofmann et al. was obtained by treating $[tBu_2P(NSiMe_3)_2]Li$ with $CuBr(SMe_2)$ under an ethylene atmosphere.[104] $[tBu_2P(NSiMe_3)_2]Cu(C_2H_4)$ shows high stability both in solution and in the solid state. The ^{13}C NMR spectroscopic data and $^1J_{CH}$ coupling constant of the copper(I)-coordinated ethylene have also been reported for this molecule. It also reacts with O_2[105] and catalyzes cyclopropanation of styrene with α-carbonyl diazoalkanes, as well as serving as a precursor for the detection of a copper carbene $[tBu_2P(NSiMe_3)_2]Cu{=}C(Ph)CO_2Et$.[106] The synthesis of $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (Figure 8) and its reactivity towards O_2 were reported by Warren et al.[107] This copper(I)–ethylene adduct has been obtained by using $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Tl$, $CuBr(SMe_2)$, and ethylene. It catalyzes cyclopropanation of styrene with N_2CPh_2, and serves as a precursor for the isolation of an important copper–carbene complex.[108] Dias et al. reported the synthesis of a copper–ethylene adduct featuring a highly fluorinated 1,3,5-triazapentadienyl ligand.[109] $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (Figure 9) has been obtained by a reaction between $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(NCMe)$ and ethylene. Compounds $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$, $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$, and $[tBu_2P(NSiMe_3)_2]Cu(C_2H_4)$ have three-coordinate, trigonal-planar metal sites. Interestingly, despite large differences in steric–electronic properties of the auxiliary ligands, the C=C distances of the bound ethylene in $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$, $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$, and $[tBu_2P(NSiMe_3)_2]Cu(C_2H_4)$ show identical values. Notable differences between the fluorinated and nonfluorinated systems, however, were observed in the ethylene ^{13}C and ^1H NMR chemical shift values.

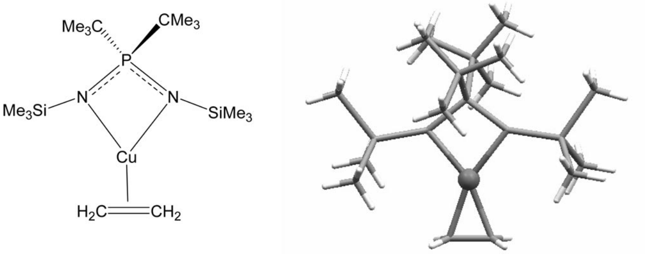

Figure 7. Copper(I)–ethylene complex $[tBu_2P(NSiMe_3)_2]Cu(C_2H_4)$ and a view of the crystal structure.

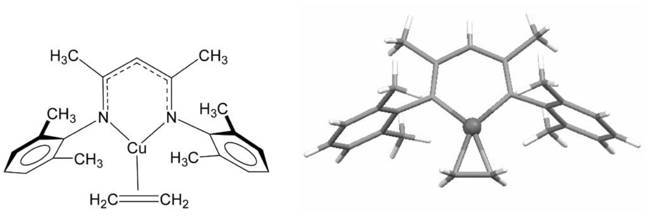

Figure 8. Copper(I)–ethylene complex $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ and a view of the crystal structure.

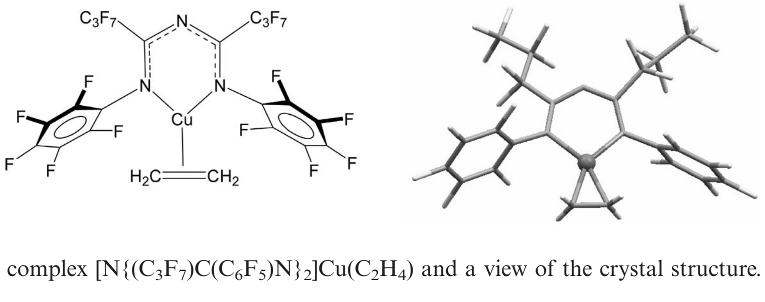

Figure 9. Copper(I)–ethylene complex $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ and a view of the crystal structure.

Several structurally characterized and cationic copper(I)–ethylene adducts are also known. Early examples of this kind were reported by Thompson et al. using di-2-pyridylamine [HN(py)$_2$] auxiliary ligands,[110] and by Masuda et al. using 2,2′-bipyridine and 1,10-phenanthroline supporting ligands.[111] The synthesis of [{HN(py)$_2$}Cu(C$_2$H$_4$)]-ClO$_4$ (Figure 10) has been achieved by treating a mixture of copper(II) perchlorate hexahydrate, ethylene, and copper dust in methanol with HN(py)$_2$. [(bpy)Cu(C$_2$H$_4$)]ClO$_4$ and [(phen)Cu(C$_2$H$_4$)]ClO$_4$ have been synthesized by treating a mixture of [Cu(MeCN)$_4$]ClO$_4$ and C$_2$H$_4$ with 2,2′-bipyridine and 1,10-phenanthroline, respectively. The lack of significant C=C bond lengthening in [(bpy)Cu(C$_2$H$_4$)]ClO$_4$ and [(phen)Cu(C$_2$H$_4$)]ClO$_4$ have been explained by using the involvement of Rydberg orbitals.[111]

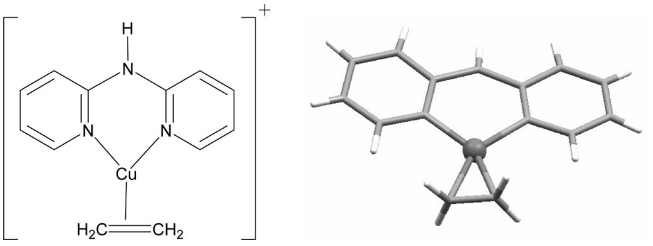

Figure 10. The cationic portion of the copper(I)–ethylene complex [Cu(NH(py)$_2$)(C$_2$H$_4$)]ClO$_4$ and a view of the crystal structure.

The cationic copper(I)–ethylene adduct {[Cu$_2$(bpm)$_2$-(C$_2$H$_4$)(Me$_2$CO)](ClO$_4$)$_2$}$_n$ (Figure 11) obtained by Munakata et al. by using the 5,6-benzopyrimidine supporting ligand has a polymeric structure.[112] It has been synthesized by treating a mixture of copper(II) perchlorate hexahydrate, copper plates, and ethylene in acetone with 5,6-benzopyrimidine (bpm). Munakata et al. also described the synthesis of a cationic copper–ethylene complex obtained by using 2-hydroxyquinoxaline as the supporting ligand.[113] [Cu(Hhq)$_2$-(C$_2$H$_4$)]ClO$_4$ (Figure 12) aggregates in the solid state as a result of intermolecular hydrogen bonds and π–π stacking. Suenaga and Munakata et al.[114] have isolated a fairly simple, cationic copper–ethylene complex by using tetraethylenediamine. The synthesis of [(tmen)Cu(C$_2$H$_4$)]ClO$_4$ involves the use of [Cu(MeCN)$_4$]ClO$_4$, C$_2$H$_4$, and tetraethylenediamine. The complex is a monomeric species. The C=C stretching frequency has been observed at 1525 cm^{-1} (cf. 1623 cm^{-1} for free ethylene). They also point to an interesting relationship between the C=C distance and ^{1}H NMR chemical shift of coordinated ethylene. All the cationic, copper(I)–ethylene adducts described above feature three-coordinate, trigonal-planar copper sites.

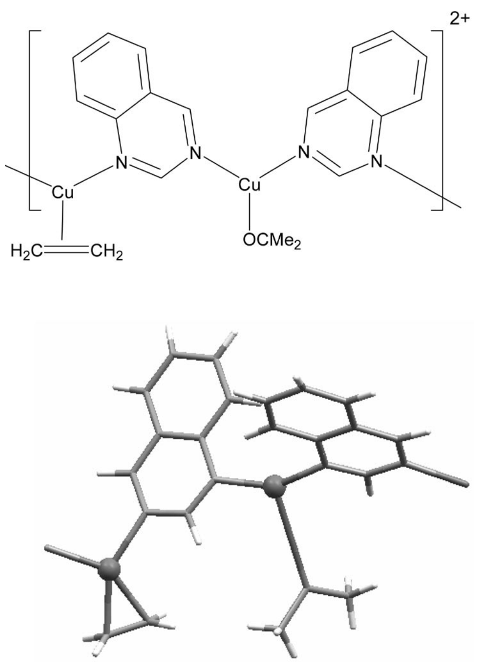

Figure 11. The cationic portion of the copper(I)–ethylene complex {[Cu$_2$(bpm)$_2$(C$_2$H$_4$)(Me$_2$CO)](ClO$_4$)$_2$}$_n$ and a view of the crystal structure.

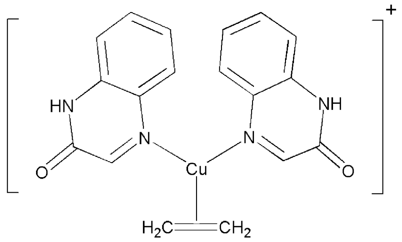

Figure 12. The cationic portion of the copper(I)–ethylene complex [Cu(Hhq)$_2$(C$_2$H$_4$)]ClO$_4$.

The use of Lewis basic ligands such as nitrogen-based donors should enhance the copper–ethylene back-bonding. Obviously, the increase in electron density at the copper(I) depends also on the exact nature of the auxiliary ligand and the substituents present on the auxiliary ligand. Steric effects of the ligands also play a major role in the stability of species containing a copper–ethylene moiety. Highly electron-withdrawing ligands, on the other hand, decrease the π-back-bonding component but increase the σ-acceptor ability (Lewis acidity) at the copper center. Martin et al. has demonstrated the isolation of copper(I)–ethylene adducts by enhancing the reactivity at copper by creating a Lewis acidic environment (e.g., by using CuCl/AlCl$_3$ mixtures).[86,115] It is also noteworthy that CuCl/AlCl$_3$ or CuAlCl$_4$ systems have been used in a variety of catalytic processes and in olefin separation applications. The syntheses of (C$_2$H$_4$)CuAlCl$_4$ and (C$_2$H$_4$)$_2$CuAlCl$_4$ involve a reaction between CuAlCl$_4$ at different ethylene pressures.[86] The bis(ethylene) adduct (C$_2$H$_4$)$_2$CuAlCl$_4$ (Figure 13) is particularly noteworthy, since it is the only structurally characterized bis(ethylene) adduct of copper reported to date, and it represents a very rare coinage-metal complex featuring more than one ethylene moiety on the metal center. The compound (C$_2$H$_4$)$_2$CuAlCl$_4$ is essentially trigonal planar, and inter- and intramolecular Cu–ClAl contacts lead to a 1D chain. The (C$_2$H$_4$)CuAlCl$_4$ adopts a ladder-type chain structure and has pseudo-tetrahedral copper sites. The solid state (MAS) ^{13}C NMR spectroscopic data are available and show ethylene peaks at 109 and 105 ppm, for the bis- and monoethylene adducts, respectively. These signals are shifted by only 14 and 18 ppm upfield from that of free ethylene and point essentially to σ-only interaction between the copper(I) and ethylene.

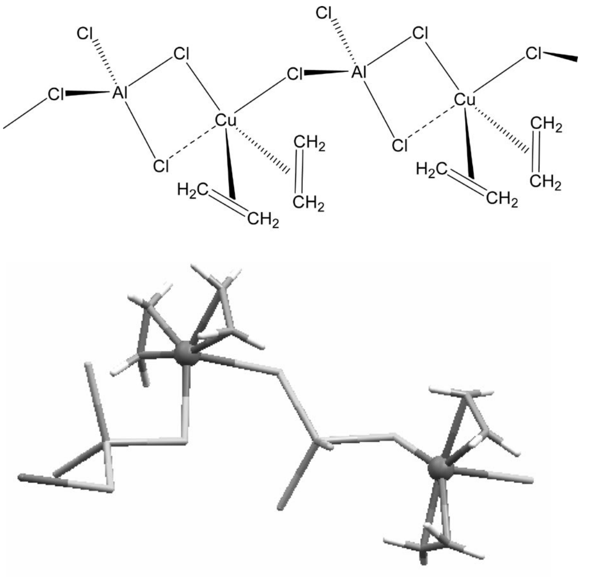

Figure 13. Bis(ethylene)copper(I) adduct $(C_2H_4)_2CuAlCl_4$ and a view of the crystal structure.

In late 2007, Santiso-Quinones, Krossing, and coworkers reported the isolation of a tris(ethylene)copper(I) adduct $[Cu(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ (Figure 14) by using the large, weakly coordinating anion $[Al\{OC(CF_3)_3\}_4]^-$.[87] The Raman C=C stretching band of this molecule has been observed at 1577 cm^{-1} [compared to 1623 cm^{-1} in free ethylene[116,117] and 1516 cm^{-1} for the isoelectronic $Ni(C_2H_4)_3$].[118] The $[Cu(C_2H_4)_3]^+$ adopts a planar spoke-wheel structure. Dias et al. also reported the isolation of a compound containing the $[Cu(C_2H_4)_3]^+$ cation.[88] $[Cu(C_2H_4)_3][SbF_6]$, however, contains a more common anion: $[SbF_6]^-$.

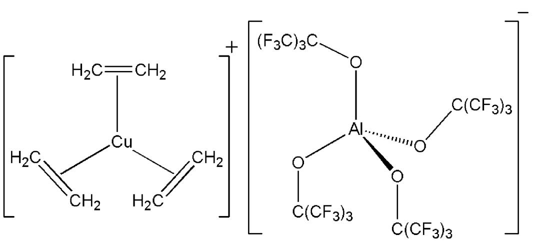

Figure 14. Tris(ethylene)copper(I) complex $[Cu(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$.

Structurally Characterized Silver(I)–Ethylene Complexes

Silver(I) plays an important role in the epoxidation of ethylene and olefin–paraffin separation.[74–76,119] These are processes of huge industrial significance. For instance, current global demand for ethylene oxide (produced by the partial oxidation of ethylene with silver catalysts and oxygen) is approximately 40 billion pounds per year.[77] Silver salts are used in the chromatographic separation of alkenes[15,16,31] and play an interesting role in plant-biology-related areas such as in preventing ethylene-induced wilting of plant products like cut flowers.[7,9,11,14] In addition, there are numerous spectroscopic investigations and computational studies of Ag^I-(C_2H_4) adducts.[22,24,26,31,35,38,43–46,85] Yet, isolable silver(I)–ethylene complexes are rare.[29,40] Silver(I) in general forms very labile ethylene adducts because of its weak σ-acceptor and very poor π-donor nature.[2] The light-sensitivity of silver adducts, the oxidizing nature of silver, and the easy displacement of the coordinated C_2H_4 by other weakly donating species (including common solvents) present further synthetic challenges. Loss of entropy resulting from the "fixing" of gaseous ethylene also plays a detrimental role during the isolation of silver–ethylene adducts.[85]

It has been known for some time that silver(I) salts such as $AgBF_4$, $AgNO_3$, and $AgClO_4$ react with ethylene, but the resulting adducts reversibly lose ethylene at room temperature or in the absence of ethylene pressure.[3,120–123] For example, the synthesis of needlelike crystals believed to be of an ethylene adduct of silver nitrate has been achieved in 1963, but this material is stable only at temperatures below –30 °C or under high ethylene pressure.[122] The first well-authenticated silver(I)–ethylene complex $[HB\{3,5\text{-}(CF_3)_2\text{-}Pz\}_3]Ag(C_2H_4)$ (Figure 15) was reported by Dias et al. in 1997.[83] It is an air-stable, colorless solid. Remarkably, solid samples of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ do not lose ethylene under reduced pressure. The synthesis involves a reaction between $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(thf)$ and ethylene. $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ features a tetrahedral silver(I) site and a κ^3-bonded tris(pyrazolyl)borato ligand. ^{13}C NMR spectroscopic data and the $^1J_{CH}$ coupling constant of the silver(I)-coordinated ethylene have also been reported for this molecule. A few years later, Krossing et al. reported the isolation of $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ (Figure 16).[85] This is an important discovery and represents the first isolable tris(ethylene) complex of a coinage-metal ion. The $[Ag(C_2H_4)_3]^+$ cation adopts a planar spoke-wheel structure (rather than the upright conformation). More recently, Dias et al. showed that it is possible to stabilize the $[Ag(C_2H_4)_3]^+$ cation by using the readily available $[SbF_6]^-$ counterion.[88] Relative to free ethylene, CD_2Cl_2 solutions of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ and $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ show *downfield* shifted ^1H and upfield shifted ^{13}C NMR signals for the silver-coordinated ethylene.

Several tris(pyrazolyl)borato ligands have been utilized successfully in the isolation of silver(I)–ethylene adducts. For example, Dias et al. reported the isolation of $[MeB\{3\text{-}(C_2F_5)Pz\}_3]Ag(C_2H_4)$,[124] $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ (Figure 17),[125] $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ (Figure 18),[125] and $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$ (Figure 19).[126] $[MeB\{3\text{-}(Mes)\text{-}Pz\}_3]Ag(C_2H_4)$ is a rare example of a thermally stable silver–ethylene adduct supported by a nonfluorinated, relatively electron rich supporting ligand. $[MeB\{3\text{-}(C_2F_5)Pz\}_3]$-

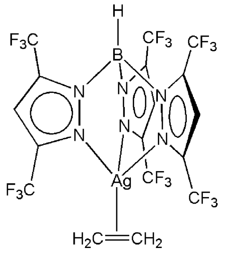

Figure 15. Silver(I)–ethylene complex $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$.

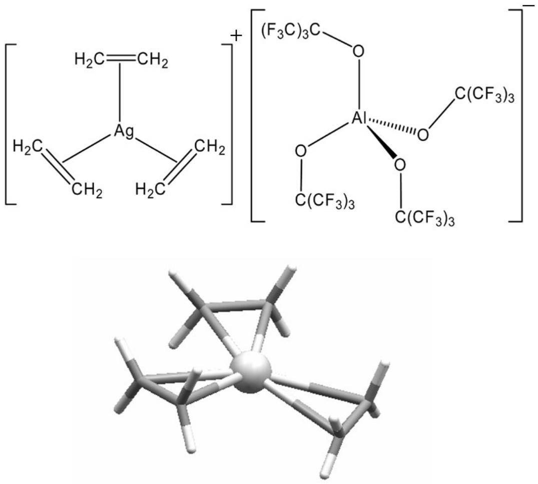

Figure 16. Tris(ethylene)silver(I) complex $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ and a view of the crystal structure of the cation.

$Ag(C_2H_4)$, $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$, and $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ have been synthesized by using the lithium salt of the corresponding ligand, AgOTf, and ethylene. $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$ has been synthesized by treating $[MeB\{3\text{-}(Mes)Pz\}_3]Tl$ with AgOTf under an ethylene atmosphere. Solid $[MeB\{3\text{-}(C_2F_5)Pz\}_3]Ag(C_2H_4)$ and $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$ do not lose ethylene under reduced pressure. $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ and $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$, in contrast, lose ethylene slowly even from solid samples. The higher stability of $[MeB\{3\text{-}(C_2F_5)Pz\}_3]Ag(C_2H_4)$ over $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ points to the importance of steric effects, while the difference in stability between $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ and $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ can be attributed primarily to the electronic effects of the ligand. The polymeric product $\{[PhB\{3\text{-}(CF_3)Pz\}_3]Ag\}_n$ resulting from the loss of ethylene from $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ has been isolated, and it has an interesting helical structure with a hexagonal pore.[125] The ethylene adduct $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ features a three-coordinate silver site and a rare κ^2-bonded tris(pyrazolyl)borato ligand. All the tris(pyrazolyl)boratosilver–ethylene adducts described here have labile ethylene groups in solution. Reaction of $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$ with CO has led to $[MeB\{3\text{-}(Mes)Pz\}_3]AgCO$, which is the first well-characterized classical Ag^I–CO complex.[126]

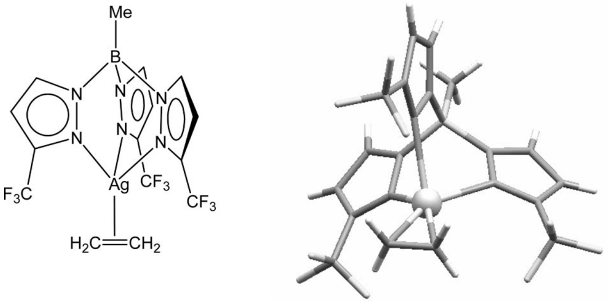

Figure 17. Silver(I)–ethylene adduct $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ and a view of the crystal structure.

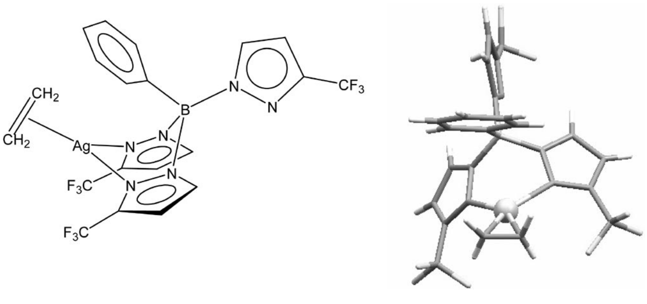

Figure 18. Silver(I)–ethylene adduct $[PhB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ and a view of the crystal structure.

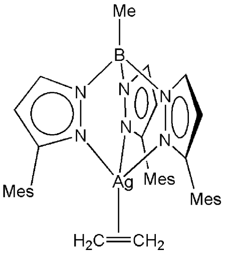

Figure 19. Silver(I)–ethylene adduct $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$.

Daugulis et al. reported the utility of fluorinated 1,5-diazapentadienyl ligands in silver–ethylene chemistry.[127] $[HC\{(CF_3)C(3,5\text{-}\{CF_3\}_2C_6H_3)N\}_2]Ag(C_2H_4)$ (Figure 20) has been obtained by treating $\{[HC\{(CF_3)C(3,5\text{-}\{CF_3\}_2C_6H_3)N\}_2]Ag(NCMe)\}_2$ with ethylene. $[HC\{(CF_3)C(3,5\text{-}\{CF_3\}_2C_6H_3)N\}_2]Ag(C_2H_4)$ is stable at room temperature if stored under ethylene. Recently, Krossing et al. reported a cage cation, $[\{Ag(C_2H_4)\}_3\{OC(CF_3)_3\}_2]^+$ (Figure 21), containing silver–ethylene bonds.[128] The synthesis of $[\{Ag(C_2H_4)\}_3\{OC(CF_3)_3\}_2][Al\{OC(CF_3)_3\}_4]$ involves a reaction between $AgOC(CF_3)_3$, $Ag[Al\{OC(CF_3)_3\}_4]$, and ethylene. The Raman band corresponding to the ethylene C=C stretch was observed at 1572 cm^{-1} (compared to that of gaseous ethylene at 1623 cm^{-1}).[116,117] The related band for $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ has been observed at 1585 cm^{-1}.[128] The crystal structure of an ethylene sorption complex of fully vacuum-dehydrated, Ag^+-exchanged zeolite X has also been reported.[129]

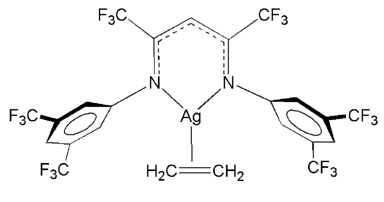

Figure 20. Silver(I)–ethylene complex $[HC\{(CF_3)C(3,5\text{-}\{CF_3\}_2\text{-}C_6H_3)N\}_2]Ag(C_2H_4)$.

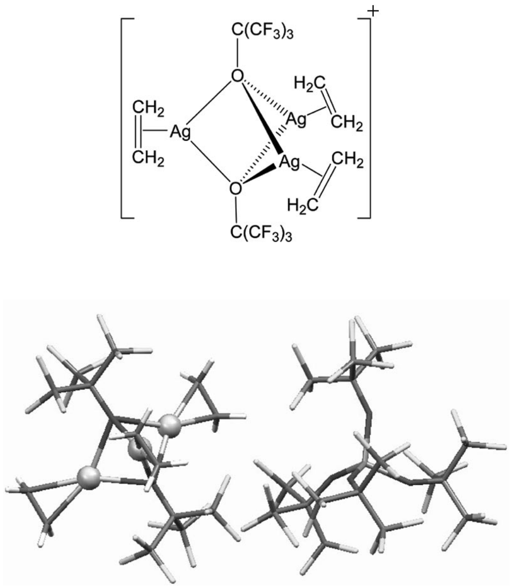

Figure 21. The cationic portion of the $[\{Ag(C_2H_4)\}_3\{OC(CF_3)_3\}_2][Al\{OC(CF_3)_3\}_4]$ and a view of the crystal structure of $[\{Ag(C_2H_4)\}_3\{OC(CF_3)_3\}_2][Al\{OC(CF_3)_3\}_4]$.

Structurally Characterized Gold(I)–Ethylene Complexes

Interestingly, although $(C_2H_4)Au^+$ clearly has the largest bond dissociation energy among $(C_2H_4)M^+$ (M = Cu, Ag, Au), isolable complexes of even substituted olefins are quite limited,[70,81] and only AuCl(*cis*-cyclooctene),[130] $Au_4(MNT)(dppee)_2Cl_2$ [MNT = 1,2-dicyanoethene-1,2-dithiolate-*S*,*S*′; dppee = *cis*-bis(diphenylphosphanylethylene)],[131] [AuCl(*endo*-dicyclopentadiene)]$_2$,[132] $[Au(bpy^{iPr})(CH_2{=}CHPh)][PF_6]$,[133] and $[Au(bpy^{o\text{-}Xyl})(CH_2{=}CHPh)][PF_6]$[81] have been characterized by means of crystal-structure determination prior to 2007. Early work on gold–alkene adducts mainly involves (alkene)AuCl type complexes.[134–143] These adducts tend to have poor thermal and solution stabilities. Recently, Cinellu and co-workers reported NMR spectroscopic data for several cationic gold–ethylene adducts supported by 6-substituted-2,2′-bipyridines.[81]

The first structurally characterized gold(I)–ethylene adducts were reported by Dias et al. in 2007.[84] They reported the synthesis of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$ (Figure 22) and $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$ (Figure 23), which were achieved by treating the sodium salt of the corresponding ligand with AuCl under an ethylene atmosphere. Solid $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$ and $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$ show remarkable stability and do not lose ethylene under reduced pressure. $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$ does not show signs of decomposition even after exposure to air and indoor light for several days. The gold atom in these adducts adopts a rare trigonal-planar geometry. The tris(pyrazolyl)borato ligands coordinate to gold in κ^2-fashion. $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$ and $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$ display significantly upfield shifted ^1H and ^{13}C NMR signals for the gold-coordinated ethylene.

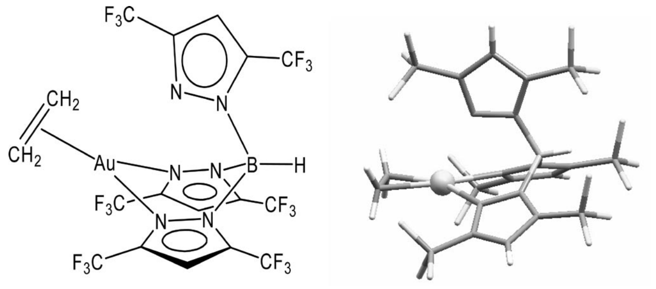

Figure 22. Gold(I)–ethylene complex $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$ and a view of the crystal structure.

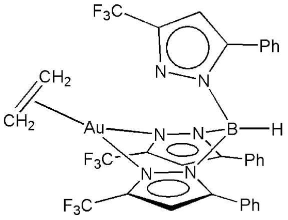

Figure 23. Gold(I)–ethylene complex $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$.

Compounds that feature more than one ethylene moiety on Cu^I, Ag^I, and Au^I are exceedingly rare. As indicated above, $[Cu(C_2H_4)_2ClAlCl_3]$ and $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ were the only well-characterized molecules of this type in the literature prior to 2007. Dias et al. recently reported the isolation of the first tris(ethylene)gold(I) adduct $[Au(C_2H_4)_3][SbF_6]$ (Figure 24).[88] Remarkably, this cationic species has been obtained by a facile process using a commercially available anion, $[SbF_6]^-$. The Raman band corresponding to the ethylene C=C stretch was observed at 1543 cm^{-1} (compared to that of gaseous ethylene at 1623 cm^{-1}).[116,117] As mentioned earlier, they also reported the spectroscopic and other evidence for the existence of the Cu^I and Ag^I analogs, $[Cu(C_2H_4)_3][SbF_6]$ and $[Ag(C_2H_4)_3][SbF_6]$. These adducts show the ethylene C=C stretch in their Raman spectra at 1566 and 1584 cm^{-1}, respectively.[88]

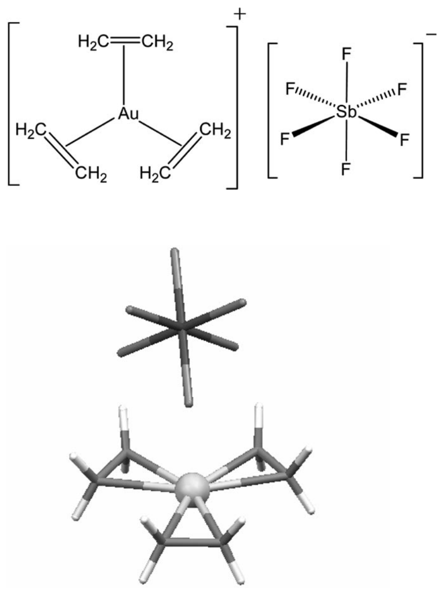

Figure 24. The tris(ethylene)gold(I) complex $[Au(C_2H_4)_3][SbF_6]$ and the view showing the crystal structure of the $[Au(C_2H_4)_3][SbF_6]$.

Spectroscopic and Structural Data and Group Trends

Table 1 contains important bond length and spectroscopic data of coinage-metal–ethylene complexes that have been characterized by X-ray crystallography. The number of well-authenticated examples of M(I)–C_2H_4 (M = Cu, Ag, Au) in the literature goes down dramatically as one moves down the coinage-metal triad. The adducts highlighted in Table 1 feature either three- or four-coordinate metal sites with pseudo-trigonal-planar or tetrahedral coordination geometry. Nitrogen-based donors, and in particular tris(pyrazolyl)borates (commonly known as scorpionates),[89] are by far the most widely used supporting ligands in stabilizing molecules with M(I)–C_2H_4 (M = Cu, Ag, Au). Neutral molecules bearing fluorinated supporting ligands or cationic metal complexes with weakly coordinating counteranions are also commonly found in the structurally characterized coinage-metal–ethylene adducts. Thus, most of the metal adducts highlighted in this review contain relatively electron-poor metal sites with relatively low back-bonding capacity. In the absence of other complicating factors (e.g., shielding due to ring current of aryl substituents), the increased Lewis acidity at the metal is reflected in the ethylene ^1H and ^{13}C NMR chemical shifts. For example, the ethylene ^{13}C NMR signal of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (δ = 86.1 ppm) appears at a much more downfield (higher frequency) region relative to the corresponding signal in $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (δ = 74.4 ppm) or $[t\text{Bu}_2P(NSiMe_3)_2]Cu(C_2H_4)$ (δ = 73.0 ppm). The latter two adducts have relatively electron-rich copper sites. The ethylene ^1H NMR signal of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Cu(C_2H_4)$ appears at δ = 4.96 ppm, while the corresponding peak in $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]Cu(C_2H_4)$ was observed at a relatively upfield (low frequency) region (δ = 4.41 ppm). Relatively large upfield shifts for the ethylene ^1H NMR signal have been observed when the $M(C_2H_4)$ moiety is flanked by aryl substituents. In such molecules, the aryl ring-current effects perhaps also contribute to the upfield shift.

Silver adducts do not show a large upfield shift of the ethylene ^{13}C NMR resonance, which is indicative of the relatively poor back-bonding nature of Ag^I.[81,144] For example, the ethylene ^{13}C NMR signal of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ has been observed at δ = 104.9 ppm. $(C_2H_4)CuAlCl_4$ and $(C_2H_4)_2CuAlCl_4$ represent two rare copper complexes with relatively high values for the ethylene ^{13}C NMR signal. Interestingly, the ethylene ^1H NMR signal of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Ag(C_2H_4)$ appears at δ = 5.56 ppm, which is higher than that observed for free ethylene (δ = 5.40 ppm). Cationic $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ shows some of the highest ^1H and ^{13}C NMR chemical shift values for metal-bonded ethylene. In contrast, $[MeB\{3\text{-}(Mes)Pz\}_3]Ag(C_2H_4)$ exhibits significantly low ^1H and ^{13}C NMR chemical shift values for silver-bound ethylene. This molecule, however, contains a relatively electron-rich tris(pyrazolyl)borato supporting ligand. In addition, ^1H chemical shift values are also likely to be affected by the flanking mesityl rings.

Gold adducts such as $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Au(C_2H_4)$ display clearly some of the lowest ethylene ^{13}C NMR chemical shift values (shifted about 60 ppm upfield from that of free ethylene) in the coinage-metal family pointing to significant Au^I→ethylene back-bonding (despite having highly fluorinated supporting ligands). ^{13}C NMR spectroscopic data of cationic $[Au(bpy^{o\text{-}Xyl})(C_2H_4)][PF_6]$ are available, and its ethylene carbon peak shifts upfield by about 62 ppm from the free ethylene peak position.[81] For comparison, ethylene oxide, ethylene sulfide, and cyclopropane, featuring sp^3-hybridized carbon atoms show ^{13}C NMR signals at 39.7, 18.9, –2.2 ppm,[145] respectively (cf. 123.3 ppm for free ethylene).

$[HB\{3,5\text{-}(CF_3)_2Pz\}_3]M(C_2H_4)$ (M = Cu, Ag, Au) represents a group of isoleptic coinage-metal adducts, and this series offers an opportunity to examine group trends of the group 11 triad. The M–N and M–C bond lengths of these adducts follow the same trend as the covalent radii of M(I) (e.g., Cu–C < Au–C < Ag–C).[146,147] The relative upfield shift of the ethylene ^{13}C NMR resonance relative to that of free ethylene is highest in the gold adduct (δ = 60 ppm) followed by the copper (δ = 34 ppm) and silver (δ = 19 ppm) adducts. The upfield shift of this signal has been attributed to an increased contribution from metal-to-ethylene π-back-donation.[81,144,148,149] Although the ^1J(C–H) coupling constant is commonly taken as a measure of the s-character of the C–H bond,[150] these adducts display essentially identical ^1J(C–H) values for ethylene carbons. Therefore, ^1J(C–H) is not a good indicator of the nature of the M–ethylene interaction in these adducts.

One of the most important parameter for the adducts listed in Table 1 is the C=C bond length. Unfortunately, some of the molecules show disorder in the ethylene moieties or have high esd values associated with C=C distance and are therefore not suitable for probing the effect on the C=C bond upon coordination to the metal ion. Nevertheless, there are several structures with well-behaved ethylene units (e.g., in some cases, even the positions of ethylene hydrogen atoms have been located and refined) and are useful for this purpose. The C=C bond length of three-coordinate adducts $\{[HB(Pz)_3]Cu(C_2H_4)CuCl\}_2$, $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$, $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$, and $[t\text{Bu}_2P(NSiMe_3)_2]Cu(C_2H_4)$ are 1.347(5), 1.364(4), 1.365(3), and 1.362(6) Å, respectively. The corresponding distance in the cationic $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ is 1.359(7) Å. The X-ray structure of *free solid ethylene* is known, and it has a C=C distance of 1.313(1) Å.[151] The C=C bond length of *ethylene gas* obtained from electron diffraction methods is 1.3369(16) Å,[152] which agrees well with computed values.[153] Relative to the 1.313(1) Å (X-ray) value, the coordination of copper clearly lengthens the C=C bond, while the lengthening is insignificant or small as compared to 1.3369(16) Å.

Silver complexes such as $[MeB\{3\text{-}(C_2F_5)Pz\}_3]Ag(C_2H_4)$ and $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ have well-behaved ethylene moieties. Here the C=C bond length changes very little from that of free ethylene. The expected distance change due to the weak $Ag^I–C_2H_4$ interaction is small and often gets overshadowed by experimental errors (esd values) associated with measured bond lengths. In some silver adducts, the C=C distance "appears" to be even shorter than that of the free ethylene C=C bond length, although other structural parameters of these adducts show no apparent signs for concern. Perhaps, neutron diffraction studies on some of these molecules may provide useful information on the real C=C distance change and the level of pyramidalization at the ethylene carbon atoms. Studies by Ibers[154,155] and Guggenberger[156,157] as well as the neutron diffraction study of the Zeise's salt by Koetzle and Bau et al.[158] indeed point to relatively small distortions of ethylene and simple alkenes (in contrast to alkenes with electronegative or delocalizable substituents such as C_2F_4 or $C_2(CN)_4$) upon coordination to even better back-bonding metal ions. Interestingly, $[MeB\{3\text{-}(CF_3)Pz\}_3]Cu(C_2H_4)$ and $[MeB\{3\text{-}(CF_3)Pz\}_3]Ag(C_2H_4)$ have very similar distances but show about 20 ppm difference in the ethylene ^{13}C NMR shift. Overall, the C=C bond length of $M(I)–C_2H_4$ adducts resulting from X-ray studies should be best considered together with other parameters such as ^{13}C NMR and/or vibrational spectroscopic data when used for discussions on metal–ethylene bonding.

Gold adducts such as $[HB\{3\text{-}(CF_3)\text{-}5\text{-}(Ph)Pz\}_3]Au(C_2H_4)$ show relatively long C=C bonds, and taken together with NMR spectroscopic data, point to strong $Au^I–C_2H_4$ interactions (consistent with theoretical data).

IR and Raman C=C bond stretching data would also be useful in the study of these metal–ethylene complexes but are often not reported. The more widely used and accessible technique of the two in most laboratories is IR spectroscopy, but the IR band corresponding to the C=C stretch is very weak and difficult to detect in most of these adducts. Note that for free ethylene, the C=C stretch couples heavily with the CH_2 deformation (scissoring) of the same symmetry, producing modes at 1623 cm^{-1} and 1342 cm^{-1}.[117] This mixing is believed to be even larger in metal–ethylene adducts.[159] The degree of mixing also varies with the metal ion. Thus, the C=C wavenumber shift (from 1623 cm^{-1}) upon coordination of ethylene to a metal ion should be considered with due caution when interpreting bond properties.[159] Nevertheless, Raman spectroscopic data for the $[M(C_2H_4)_3][SbF_6]$ (M = Cu, Ag, Au) series available and the position of the C=C stretching band varies as expected on the basis of the relative σ-acceptor/π-back-bonding ability of the metal ion (i.e., the gold analog shows the largest wavenumber shift, whereas silver shows the smallest change). The gold adduct also shows the largest upfield shift of the ethylene peak in the ^{13}C NMR spectrum.[88] For example, the ethylene ^{13}C NMR peak in $[Cu(C_2H_4)_3][SbF_6]$ appears at δ = 109.6 ppm, whereas the corresponding peaks in the silver and gold analogs were observed at 116.9 and 92.7 ppm, respectively.

Summary and Concluding Remarks

Ethylene complexes of Cu^I, Ag^I, and Au^I are important in a number of areas ranging from fundamental studies to industrial applications. Although the BDE of $M^+–C_2H_4$ (M = Cu, Ag, Au) is relatively high, especially for copper(I) and most certainly for gold(I), and $M(I)–C_2H_4$ adducts are expected to be thermodynamically stable, the labile nature of the coinage-metal(I)–ethylene interaction has plagued the isolation of "bottle-able" coinage-metal–ethylene compounds for many years. Presently, there are a number of well-authenticated copper complexes, and a few silver and only a very few gold adducts in the literature. A vast majority of these adducts have been isolated by using either bidentate or tridentate ligands based on nitrogen donors. Weakly donating ligands and anions are also commonly used, as they do not interfere and displace the ethylene from the metal center (e.g., leading to dimer formation or anion coordination). Steric protection of the metal site further stabilizes the metal–ethylene adduct. Silver(I) and copper(I) complexes containing more than one ethylene molecules are also known. The isolation of tris(ethylene) adducts such as $[Cu(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$, $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$ and $[Au(C_2H_4)_3][SbF_6]$, as well as $[Cu(C_2H_4)_3][SbF_6]$ and $[Ag(C_2H_4)_3][SbF_6]$, are particularly noteworthy. Closely related adducts such as $Ni(C_2H_4)_3$ involving group 10 elements have been known since the early 1970s (however, structurally characterized adducts of this family are also very limited).[118,159]

The ethylene ^{13}C NMR chemical shift provides useful information about the nature of the metal–ethylene interaction. In comparison to those of silver and copper, related gold(I) complexes show large upfield shifts for ethylene carbon atoms relative to free ethylene. Auxiliary ligands also have a significant influence on the structural and spectroscopic parameters of the $M–C_2H_4$ moiety. Errors associated with the crystallographically determined C=C bond length sometimes overshadow the expected lengthening of the C=C bond upon coordination to the metal site.[160] The C=C bond lengthening is expected to be highest for Au^I followed by those for Cu^I and Ag^I. Catalytic properties of some of the coinage-metal–ethylene adducts are known. They show excellent catalytic nitrene- and carbene-transfer chemistry. A few ethylene displacement reactions have also been reported.

Overall, coinage-metal–ethylene adducts are slowly becoming a more familiar class of compounds that can be synthesized conveniently, stored in solid form, and studied by using a variety of routine analytical techniques including X-ray crystallography. However, as it is apparent from the preceding account, much remains to be done in this area, such as the use of different types of supporting ligands to stabilize M(I)–C_2H_4 adducts, synthesis of multiethylene adducts of M(I), exploring their reactivity and catalytic properties, spectroscopic investigations and computational studies of neutral adducts. We will most likely see some of these voids getting filled and even some unforeseen usages for M(I)–C_2H_4 adducts in due course.

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