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Ab Initio Study of Structures, Energetics, and Bonding in Formally High-Oxidation-State Copper Organometallics

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Geometry-optimized structures, energies, and harmonic vibrational frequencies of closed-shell states of CuL^+, XCu^IL, and $XCu^{III}L$ fragments ($L = CO$, C_2H_4, C_2H_2; $X = H^-$, F^-, OH^-, O^{2-}, N^{3-}) have been obtained at the MP2 level using valence-DZP-quality basis sets with effective core potentials. Natural population analyses have been used to interpret the nature of metal−ligand interactions. The computed data for all the Cu(I) species are along expected lines. Interestingly, the formally high-oxidation-state species also have effectively d^{10} configurations, with the electron deficiency localized in the ligands. As a result, the Cu−X bonds are long and, in a few cases, the ligand L dissociates during geometry optimization. In the computed minima, the Cu−L interaction energies are fairly large, primarily due to electrostatic interactions. The extent of π-back-donation is generally low in "Cu(III)" systems. However, a strong π-donor group enhances the ability of the metal to engage in $d\pi-p\pi$ bonding with CO, C_2H_4, or C_2H_2, making it comparable to a typical Cu^IL system in all respects. The trends are virtually identical in all three lowest energy closed-shell states of the ethylene and acetylene complexes.

Introduction

High-oxidation-state (HOS) organometallics, which were initially viewed as structural novelties,[1] have been increasingly recognized as chemically useful species.[2] Several catalytic transformations invoke the intermediacy of HOS organometallics.[3] In some cases, as in metathesis reactions, intermediates have been structurally characterized.[4] In other reactions, such as in C−H activation,[5] hydroxylation,[6] or epoxidation,[7] there is very little information regarding the nature of these species. Several HOS species have been generated in the gas phase by Schwarz and co-workers.[8] These fragment ions exhibit interesting reactivity patterns with organic fragments.

Understanding the bonding in these intermediates would greatly enhance our ability to design better catalysts. Ideally, structural characterization of HOS organometallics would enable one to understand the nature of bonding in these complexes. Such results are available in the case of early-transition-metal HOS organometallics.[9] However, structurally characterized late-transition-metal HOS organometallics are rare.[10]

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The d-electron count on the metal would make a significant difference in modulating the metal−ligand π interactions. The well-established bonding principles known in low-oxidation-state organometallics[11] may not be applicable to HOS organometallics.[12] Hence, there is a great need for detailed examination of the nature of bonding in late-transition-metal HOS organometallic systems.

Copper(III) is a typical late-transition-metal HOS species for which several examples of coordination complexes exist.[13] However, organometallic complexes containing Cu(III) are rare.[14] Although the intermediacy of alkyl cuprates has been postulated,[15] there are no examples of well-characterized Cu(III) complexes having metal−carbon bonds. In a few cases in which such bonding had been proposed, e.g., in a CF_3^- complex and in cuprates involved in additions to enones, charge distributions derived through ab initio calculations indicate the involvement of Cu(I) species, with the electron deficiency shared by many ligands.[16,17] The metal−ligand interactions are suggested to be governed by multicenter and not by two-center dative bonds in these systems. These studies raise the question whether a genuine Cu(III) organometallic species can be stabilized.[18] One approach would be to reduce the complement of ligands in the coordination sphere of the metal. This may force the metal to share the electron deficiency to a greater extent. Of particular interest are the copper(III) oxo and nitrido species which have already been generated in the gas phase.[19] These units may serve as suitable building blocks for forming late-transition-metal HOS organometallic species.

In this paper, we report a computational study of a number of Cu(III) units with an ancillary ligand having varying σ- and π-donor characteristics. We consider the ability of these fragments to form complexes with CO, ethylene, or acetylene. The electronic structures have been analyzed in detail. The results are used to interpret interaction energies, geometries, formal charges, bond orders, and vibrational frequencies. The extent to which the metal ion participates in σ-acceptor and π-back-donation interactions as the ancillary ligand is varied is examined. The results are compared with those for related Cu(I) species to understand the effect of the formal oxidation state on bonding.

Theoretical Methods and Systems Studied

We have chosen well-tested theoretical procedures[20] for the present work. Ab initio calculations, including electron correlation with relatively large basis sets, have been carried out. For the metal, effective core potentials (ECPs) proposed by Hay

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and Wadt[21] were employed. As recommended by Frenking and co-workers,[20d] only the 1s, 2s, and 2p orbitals on copper are treated as the core. The contraction scheme corresponding to HW3DZ2P(441/2111/41), in the notation of these authors, was employed.[22] The ligand atoms were described using the 6-31G-(d) basis set. Structures of all the species considered in this study were optimized at the MP2 level.[23] To obtain reliable interaction energies, additional calculations were carried out at the CCSD(T)[24] level (coupled-cluster method with single and double excitations and a perturbative estimate of the triple excitations) with MP2-optimized geometries. Harmonic vibrational frequencies were calculated in all cases at the MP2 level. Natural population analyses[25] were also performed on all the structures. The Gaussian 94[26] suite of programs was used for the calculations. The GAMESS package[27] was used for generating the orbital plots.

Calculations were carried out on complexes of Cu^{3+}, CuH^{2+}, $CuOH^{2+}$, CuF^{2+}, CuO^{+}, and CuN with CO, C_2H_4, and C_2H_2. A second series of calculations was performed on the corresponding copper(I) complexes, involving Cu^{+}, CuH, CuOH, and CuF fragments. The three organic ligands are the most important representatives for probing η^1 and η^2 modes of bonding. The auxiliary groups H^-, OH^-, and F^- have been chosen to model the effects of exclusively or predominantly σ-type interactions with the metal. In addition, the oxo and nitrido units have been employed to probe the consequences of more effective π donation to the metal. Further, introduction of these groups produces large variations in the effective charge on the metal and hence reveals the significance of electrostatic interactions in modulating various properties.

In all the Cu(I) complexes, the lowest energy closed-shell singlet state was considered. A similar choice may not correspond to the ground state for the unsaturated Cu(III) species. Nevertheless, addition of ligands would increasingly stabilize the singlet state in general. Further, due to closed-shell repulsion involving the σ-donor orbitals on the ligands, the d_{z^2} orbital on the metal may be expected to be empty in Cu(III) systems. Therefore, calculations on the Cu(III) complexes were carried out on the configuration in which two electrons are removed from a σ orbital (corresponding to the d_{z^2} orbital of the metal) of the corresponding Cu(I) systems. The results on this singlet state for the various species enable a uniform comparison to be made and may also serve as ideal models of HOS species of direct interest to experimentalists. We therefore first consider structures and energetics with this choice of electronic state.

Alternative possibilities were also considered for d^8 systems with the electrons removed from a $d\pi$ orbital. In the complexes of ethylene and acetylene, electrons can be removed from the *in-plane* or *out-of-plane* π orbitals. Both sets of closed-shell configurations were studied with full geometry optimization at the MP2 level. However, there is a complication in the case of CuX fragments and their carbonyl complexes. Due to degeneracy of π orbitals in these linear systems, open-shell states result. Therefore, we discuss the results obtained for alternative closed-shell states only for the ethylene and acetylene complexes.

Table 1. MP2-Optimized Geometries and Total Energies of Cu−X Fragments

system	energy (−hartree)		Cu−X (Å)
	MP2	CCSD(T)	
Cu^{+}	195.012 25	194.980 54	
Cu^{3+}	192.782 03	192.866 00	
H−Cu	195.837 59	195.808 59	1.526
HO−Cu[a]	270.899 68	270.869 03	1.794
F−Cu	294.902 89	294.868 69	1.749
$H-Cu^{2+}$	194.832 42	194.815 47	1.864
$HO-Cu^{2+}$ [a]	269.883 82	269.901 14	1.745
$F-Cu^{2+}$	293.763 47	293.768 29	1.913
$O-Cu^{+}$	269.799 63	269.806 63	1.613
N−Cu	249.597 99	249.614 41	1.656

[a] Additional parameters for HO−Cu and $HO-Cu^{2+}$, respectively, are O−H = 0.973, 1.012 Å; ∠Cu−O−H = 119.8, 144.6°.

Results

The optimized geometries and energies at the MP2 level for all the fragments considered are given in Table 1. Total energies computed using the CCSD(T) procedure are also included in the table. The Cu−X bond distances are similar to those computed earlier for Cu−OH, Cu−F, and OCu^{+}, for which comparison is available.[28] The $Cu^{III}-X$ distances may be expected to be shorter than $Cu^{I}-X$ lengths. However, this is not borne out by the computed data. The Cu−X distances for the hydrido and fluoro derivatives are substantially longer in the HOS systems, while there is only a minor variation in the hydroxy derivatives. In the latter, the Cu−O−H angle shows a large increase (25°) on going to the Cu(III) species.

The energies of the CO complexes of the various fragments at the MP2 and CCSD(T) levels are provided in Table 2. The interaction energies determined via eq 1 are also included. While the trends are similar at the

$$XCu^{n+} + L \rightarrow XCuL^{n+} \qquad (1)$$

two theoretical levels employed, the CCSD(T) values are generally smaller and are likely to be more reliable.[20,29] At this level, the interaction energies vary over a large

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Table 2. MP2-Optimized Geometries, Total Energies, Interaction Energies, and C−O Stretching Frequencies of Carbon Monoxide Complexes[a]

system	energy		Cu−C	C−O	Cu−X	ΔE		ν_{C-O}
	MP2	CCSD(T)				MP2	CCSD(T)	
CO	113.021 22	113.038 17		1.151				2119
$CuCO^+$	308.080 83	308.059 99	1.974	1.142		−29.73	−25.91	2182
HCuCO	308.902 28	308.878 70	1.858	1.151	1.537	−27.28	−20.04	2115
HOCuCO[b]	383.990 59	383.962 17	1.770	1.156	1.747	−43.73	−34.49	2082
FCuCO	407.995 44	407.964 18	1.774	1.154	1.711	−44.76	−35.97	2097
$HCuCO^{2+}$	307.942 38	307.943 50	2.076	1.139	1.815	−55.69	−56.39	2204
$HOCuCO^{2+}$ [b]	383.022 56	383.041 57	1.998	1.138	1.781	−73.75	−64.17	2220
$FCuCO^{2+}$	406.902 32	406.918 06	2.019	1.141	2.099	−73.82	−70.03	2176
$OCuCO^+$	382.888 94	382.905 66	2.043	1.138	1.582	−53.46	−38.19	2225
NCuCO	362.681 09	362.706 90	1.832	1.154	1.622	−38.84	−34.09	2080

[a] Bond lengths, bond angles, total energies, interaction energies, and frequencies are in Å, deg, −hartrees, kcal mol^{-1}, and cm^{-1}, respectively. [b] Additional parameters for HO−Cu−CO and $HO-Cu-CO^{2+}$ are respectively O−H = 0.969, 1.004, ∠C−Cu−O (OH) = 178.6, 161.8, ∠Cu−C−O(CO) = 178.8, 179.8, and ∠Cu−O−H = 118.2, 153.9.

Table 3. MP2 Total Energies, Optimized Geometries, and Interaction Energies of Ethylene Complexes[a]

system	energy	Cu−C	C−C	C−H	Cu−X	∠HCC	ϕ(HCCCu)	ΔE
C_2H_4	78.285 03		1.336	1.085		121.7		
$CuC_2H_4^+$	273.360 86	2.192	1.370	1.089		121.0	95.0	−39.90
$HCuC_2H_4$	274.163 67	2.135	1.367	1.087	1.540	121.3	94.7	−25.76
$HOCuC_2H_4$[b]	349.246 58	2.021	1.386	1.087	1.768	120.9	97.9	−38.83
		2.019		1.087		120.8	98.0	
$FCuC_2H_4$	373.255 71	2.009	1.389	1.087	1.722	120.8	98.1	−42.54
$OCuC_2H_4^+$	348.176 59	2.238	1.372	1.090	1.589	120.9	94.4	−57.69
$NCuC_2H_4$	327.949 49	2.023	1.404	1.087	1.611	120.3	99.3	−41.71

[a] Bond lengths, bond angles and dihedral angles, total energies, and interaction energies are in Å, deg, −hartrees, and kcal $mole^{-1}$, respectively. [b] Additional parameters for $HO-Cu-C_2H_4$: O−H = 0.968; ∠O−Cu−X1 = 179.9 (X1 is the midpoint of C−C); ∠Cu−O−H = 118.3.

range, from 20 to 70 kcal/mol. Uniformly larger interaction energies are obtained in the dicationic species $HCuCO^{2+}$, $HOCuCO^{2+}$, and $FCuCO^{2+}$. Interestingly, the corresponding values for two other Cu(III) species, $OCuCO^+$ and NCuCO, are quite similar to those obtained for most Cu(I) complexes.

The MP2-optimized geometrical parameters of the complexes are also provided in Table 2. Minimum energy structures could be obtained for all complexes, with the exception of $CuCO^{3+}$, for which the Cu−C distance showed a monotonic increase during geometry optimization. The computed geometries were confirmed to be true minima on the basis of their vibrational frequencies. All optimized structures are linear, with the exception of the hydroxy species, which have C_s symmetry. While the Cu−C−O angles are close to 180° in all the structures, the C−Cu−O angle deviates substantially from linearity in the $HOCuCO^{2+}$ ion. The unusual feature in metal−ligand bond lengths as a function of metal oxidation state noted in Cu−X fragments (Table 1) is found in the carbonyl complexes as well. The Cu−X and Cu−C distances are uniformly larger in the Cu(III) complexes compared to Cu(I) analogues. Correspondingly, the C−O bond length is shorter in the HOS systems. The geometry of NCuCO is exceptional. The Cu−X and Cu−C distances are relatively short, while the C−O distance is long. The values are comparable to those obtained for most Cu(I) systems.

An important finding in the present study is that metal−carbonyl interaction energies do not correlate inversely with the Cu−C distances. The dicationic species have large interaction energies but also have long bonds.

Table 2 includes the MP2 harmonic C−O stretching frequency, a parameter of considerable interest from the experimental and theoretical points of view, for all the complexes. The increase in the C−O frequency on complexation with Cu^+ obtained in the present study (63 cm^{-1}) is in close agreement with experimental[30] and theoretical values in related systems.[31] The frequency is reduced in Cu(I) complexes in the presence of an ancillary ligand. The value is substantially higher in most Cu(III) species. A notable exception is NCuCO, for which the computed CO frequency is the lowest of all systems considered.

The computed total energies, interaction energies, and key geometrical parameters for the ethylene complexes of Cu(I) and Cu(III) fragments are summarized in Table 3. Stable structures of complexes were obtained for all the Cu(I) systems as well as for the complexes involving CuO^+ and CuN fragments. However, similar structures could not be obtained for the ethylene complexes of Cu^{3+}, HCu^{2+}, $HOCu^{2+}$, and FCu^{2+}. In these systems, the C−C bond of the ethylene unit became very long during geometry optimization, indicating fragmentation of the ligand. In the other minimum energy structures, the C−C bond lengths vary from 1.37 to 1.40 Å, significantly longer than in free ethylene.

The metal−carbon bond lengths in the ethylene complexes of Cu(I) fragments and NCu unit are quite similar. The *out-of-plane* bending of the hydrogen atoms is also in the same range. The Cu−C distances are markedly longer in the $OCuC_2H_4^+$ complex. The *out-of-plane* bending in the alkene is correspondingly small. Despite these geometric features, which are indicative of poor bonding, the interaction energy is the largest in this system (57.7 kcal/mol at the MP2 level).

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Table 4. MP2 Total Energies, Optimized Geometries, and Interaction Energies of Acetylene Complexes[a]

system	energy	Cu−C	C−C	C−H	Cu−X	∠H−C−C	Δ*E*
C_2H_2	77.066 79		1.218	1.066		179.7	
						179.8	
$CuC_2H_2^+$	272.136 79	2.156	1.237	1.076		169.9	−36.24
$HCuC_2H_2$	272.944 30	2.058	1.242	1.072	1.538	167.2	−25.05
$HOCuC_2H_2$[b]	348.025 98	1.963	1.256	1.074	1.764	160.8	−37.34
		1.966		1.074		160.7	
$FCuC_2H_2$	372.035 62	1.955	1.258	1.074	1.719	160.3	−41.38
$OCuC_2H_2^+$	346.949 20	2.217	1.235	1.080	1.591	171.3	−51.94
$NCuC_2H_2$	326.725 40	1.975	1.269	1.076	1.618	155.5	−38.04

[a] Bond lengths, bond angles, total energies, and interaction energies are in Å, deg, −hartrees, and kcal mol^{-1}, respectively. [b] Additional parameters for HO−Cu−C_2H_2: O−H = 0.967; ∠O−Cu−X2 = 179.6 (X2 is the midpoint of C−C); ∠Cu−O−H = 119.9.

Table 5. Natural Population Analysis Data for Carbonyl Complexes

system	charge on Cu[a]	charge on X	total charge on CO	Wiberg bond index Cu−C	Wiberg bond index C−O	occupancy of C−O π*
CO			0.00		2.11	0.000
$CuCO^+$	0.95 (1.00)		0.05	0.18	2.31	0.010
HCuCO	0.46 (0.49)	−0.55	0.09	0.34	2.20	0.030
HOCuCO	0.72 (0.81)	−0.78[b]	0.06	0.45	2.18	0.057
FCuCO	0.76 (0.86)	−0.81	0.05	0.43	2.19	0.048
$HCuCO^{2+}$	1.32 (1.29)	0.60	0.07	0.11	2.43	0.002
$HOCuCO^{2+}$	1.52 (1.56)	0.32[c]	0.15	0.22	2.44	0.002
$FCuCO^{2+}$	1.71 (1.81)	0.14	0.15	0.18	2.47	0.002
$OCuCO^+$	1.26 (1.28)	−0.33	0.07	0.17	2.34	0.006
NCuCO	0.86 (0.96)	−0.86	0.00	0.36	2.18	0.059

[a] Values for the corresponding Cu−X fragments are shown in parentheses. [b] Values for the individual atoms: O, −1.24; H, 0.46. [c] Values for the individual atoms: O, −0.31; H, 0.63.

The computed energies, structures, and frequencies for the acetylene complexes are given in Table 4. The fragmentation pattern noted in the ethylene complexes with an overall charge of 2+ or 3+ was found in the acetylene complexes as well. Thus, data are provided only for structures which are true minima at the MP2 level.

The trends in the geometric parameters and interaction energies in the acetylene complexes are the same as those found in the corresponding ethylene derivatives. The Cu−C bond lengths in the NCu complex are quite short. Consistently, the C−C distance is long and the acetylene unit is severely bent. However, the maximum interaction energy is computed for the complex of OCu^+, which has relatively long Cu−C distances, a short C−C bond length, and modest bending of the HCC units.

Discussion

General Trends. In comparison to the Cu(I) ion, the Cu(III) unit is expected to be a better σ acceptor for two reasons. Electrostatic interaction should be more effective in the trication. Further, an additional vacant orbital is available in the Cu(III) species. In Cu^+ complexes, σ-donation to the metal can occur only to the higher energy 4s and 4p orbitals and also has to overcome filled orbital repulsion with the d^{10} core. In contrast, the presence of a vacant d_{z^2} orbital should lead to a strong σ-bond in Cu(III) complexes. Hence, shorter Cu−X distances are expected in the fragments of the Cu(III) ion. Another difference is expected between Cu(I) and Cu(III) species. The magnitude of π-back-donation should be large in the former. More tightly bound d orbitals in Cu(III) species are unlikely to interact strongly with π-acceptor orbitals on the ligand.

The above expectations are not fully borne out in the computed trends of metal−ligand bond lengths, interaction energies, and vibrational frequencies. The interaction energies are indeed higher in Cu(III) species, but the metal−ligand bonds are consistently longer. Unusually long bond distances are found even in the Cu^{III}−X fragments. The extent of π-back-donation, as revealed for example by C−O stretching frequency, is smaller in most Cu(III) complexes. However, a significant exception is found in the complexes of the NCu fragment. Most properties of these complexes resemble those of typical Cu^+ complexes. The extent of π-back-bonding appears to be even stronger in the NCu complexes.

To understand the above features, the electronic structures of all the computed structures were analyzed in detail. Natural population analyses were carried out to obtain charges on all atoms and also Wiberg bond indices.[25] Since atomic charges may not be true reflections of formal oxidation states, we also examined occupancies of individual atomic orbitals on the metal as well as of the π^*-orbital on the organic ligand.

We first discuss the electronic structures of the carbonyl complexes. On the basis of bonding features, the trends in the calculated molecular properties are interpreted. The extent to which the conclusions are valid for the ethylene and acetylene complexes is discussed in the subsequent section.

Carbonyl Complexes. The charge on the metal in Cu(I) carbonyl complexes (Table 5) is along expected lines. In the Cu−H fragment, donation by the hydride ion reduces the metal charge to less than 0.5. The charge is larger with electronegative ancillary ligands, OH^- and F^-. Formation of the carbonyl complex reduces the metal charge marginally. The values are in the range typical for Cu(I) species. The natural charge on the metal in Cu(III) systems is higher, but not by as much as expected. For example, the metal charge in CuH^{2+} is only 1.29, while somewhat larger values are obtained in $CuOH^{2+}$ (1.56) and CuF^{2+} (1.81). The metal charge on the oxo and nitrido fragments is substantially smaller. There is relatively small variation in the metal charge on going to the carbonyl complex in the Cu(III) systems. The metal charge in NCuCO is in the range expected for a Cu(I) system.

The variations in the charge of the ancillary ligand X^- in the carbonyl complexes follow a complementary trend. The values range from −0.55 to −0.81 in the Cu(I) systems, reflecting partial σ-donation from negatively charged ligands. The data for the Cu(III) species are unusual. The ancillary ligand is computed to carry

Table 6. Natural Electron Configuration on Each Atom for Fragments and Carbonyl Complexes

system	electron configuration			
	Cu	C	O	X
$CuCO^+$	3d(9.96)4s(0.09)	2s(1.50)2p(1.97)	2s(1.72)2p(4.68)	
HCu	3d(9.96)4s(0.53)			1s(1.49)
HCu^{2+}	3d(9.68)4s(0.02)			1s(0.29)
HCuCO	3d(9.86)4s(0.68)	2s(1.47)2p(1.86)	2s(1.72)2p(4.77)	1s(1.55)
$HCuCO^{2+}$	3d(9.59)4s(0.08)	2s(1.45)2p(2.10)	2s(1.72)2p(4.57)	1s(0.40)
HOCu	3d(9.93)4s(0.22)			*a*
$HOCu^{2+}$	3d(9.42)4s(0.02)			*b*
HOCuCO	3d(9.77)4s(0.46)	2s(1.45)2p(1.91)	2s(1.72)2p(4.77)	*c*
$HOCuCO^{2+}$	3d(9.33)4s(0.13)	2s(1.40)2p(2.10)	2s(1.72)2p(4.55)	*d*
FCu	3d(9.93)4s(0.15)			2s(1.99)2p(5.86)
FCu^{2+}	3d(9.15)4s(0.03)			2s(2.00)2p(4.81)
FCuCO	3d(9.77)4s(0.42)	2s(1.46)2p(1.91)	2s(1.72)2p(4.76)	2s(1.96)2p(5.84)
$FCuCO^{2+}$	3d(9.20)4s(0.07)	2s(1.38)2p(2.14)	2s(1.72)2p(4.51)	2s(2.00)2p(4.86)
OCu^+	3d(9.70)4s(0.01)			2s(1.99)2p(4.28)
$OCuCO^+$	3d(9.62)4s(0.11)	2s(1.47)2p(1.99)	2s(1.72)2p(4.65)	2s(1.97)2p(4.35)
NCu	3d(9.91)4s(0.03)			2s(1.97)2p(3.98)
NCuCO	3d(9.80)4s(0.25)	2s(1.47)2p(1.95)	2s(1.72)2p(4.76)	2s(1.91)2p(3.94)

[a] O, 2s(1.85)2p(5.40); H, 1s(0.55). [b] O, 2s(1.90)2p(4.30); H, 1s(0.36). [c] O, 2s(1.82)2p(5.41); H, 1s(0.53). [d] O, 2s(1.87)2p(4.42); H, 1s(0.37).

a net *positive* charge in the carbonyl complexes of HCu^{2+}, $HOCu^{2+}$, and FCu^{2+}. The corresponding values in OCu^+ and NCu complexes are negative, but the magnitudes are fairly small. Interestingly, the carbonyl ligand remains virtually neutral in all the complexes. The negligible change in the total charge on the carbonyl group as one goes from Cu(I) complexes to the corresponding Cu(III) species is remarkable.

A detailed analysis of individual atomic orbital occupancies provides greater insights into the origin of the variations in the formal charges. The metal atom has the expected d^{10} configuration in all the Cu(I) fragments and complexes (Table 6). Even with highly electronegative ancillary ligands, as in HOCuCO and FCuCO, the d orbital population is 9.77. Thus, σ-donation to the metal is almost exclusively restricted to the 4s orbital on the metal (the occupancy of the 4*p* orbitals[32] is in the range 0.01−0.05 and hence is not given in the table). On the basis of the 4s orbital population, H^- is a good donor, while OH^- and F^- donate considerably less electron density. The carbonyl ligand does not increase the 4s population to a significant extent in the $CuCO^+$ species. However, in the presence of an ancillary ligand X, σ-donation from the carbonyl group to the 4s orbital is much higher. As a result, the formal charge on the metal lies in a narrow range, 0.46−0.76, in these complexes.

The electronic configurations computed for the Cu(III) fragments and complexes are quite unexpected. In all the systems, the d orbital occupancies are considerably greater than 9. The smallest value obtained is for the FCu^{2+} fragment (9.15). The NCu fragment and the corresponding CO complex have d populations as large as 9.91 and 9.80, respectively. The orbital occupancies in the ancillary ligands confirm that electron depletion has not occurred at the metal site. For example, in the HCu^{2+} fragment, the configuration at the metal is $d^{9.68}$, while the s orbital on H has only 0.29 electron. It is evidently incorrect to view this species as a hydride complex of Cu(III). The electronic structure corresponds to that of a protonated Cu(I) ion, with the metal acting as a σ-donor. Remarkably, the orbital populations of FCu^{2+} are also not consistent with the description that the ion is a complex between between F^- and Cu^{3+}. Similarly, CuO^+ and CuN species correspond to Cu(I) complexes of O and N^-, respectively. The introduction of the carbonyl ligand does not alter the metal electron configurations significantly. Hence, all the structures are effectively Cu(I) species. The electron deficiency is essentially localized on the ligands.

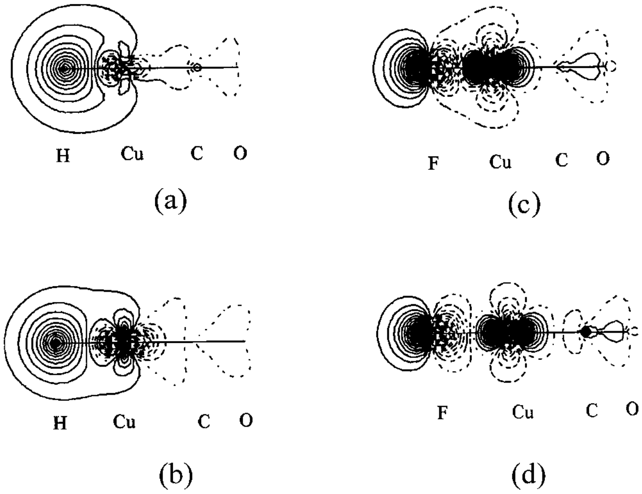

Figure 1. Contour diagrams of (a) the HOMO of HCuCO, (b) the LUMO of $HCuCO^{2+}$, (c) the HOMO of FCuCO, and (d) the LUMO of $FCuCO^{2+}$.

The above interpretations are confirmed by the contour maps of individual molecular orbitals. The HOMO of HCuCO is mainly concentrated on the hydride 1s orbital, with weak bonding interactions with the metal 4s and 4p (σ) orbitals and antibonding overlap with the 3d (σ) orbital (Figure 1a). Therefore, on oxidation, electrons are removed principally from the hydride unit, although there is bound to be some bond reorganization. The region with maximum electron depletion can be recognized from the LUMO of $HCuCO^{2+}$ species (Figure 1b). While the 3d (σ) coefficient is noticeably large, the major contribution is evidently from the hydrogen 1s orbital. Thus, to a good approximation the species may be viewed as a protonated Cu(I) complex. It may appear surprising that electrostatic forces do not push the two positively charged units apart. However, this is not

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(32) The metal 4p orbitals correspond to Rydberg orbitals in the natural population analyses.

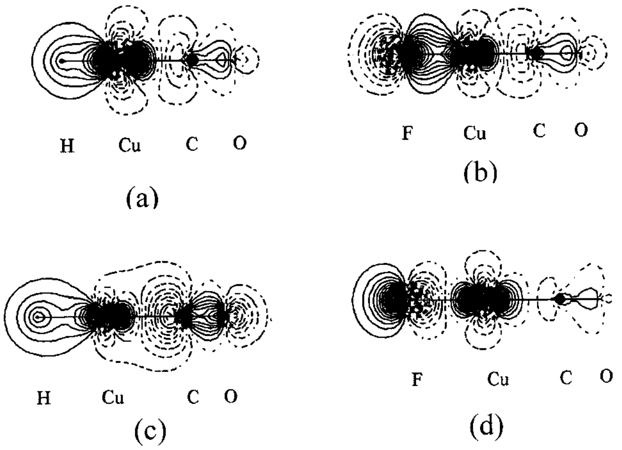

Figure 2. Contour diagrams of the predominantly d_{z^2} orbital of (a) HCuCO, (b) FCuCO, (c) $HCuCO^{2+}$, and (d) $FCuCO^{2+}$.

without precedence. Oxidative addition to positively charged metal complexes are known.[33] Many simple dications have also been suggested to have a large barrier to fragmentation and are known to survive as local minima.[34] The computed energetics (Table 1) show that the bare fragment HCu^{2+} is also a metastable minimum with respect to loss of a proton.

It is of interest to find whether the fluoro derivative has a similar electronic structure. The HOMO of FCuCO is mainly a p (σ) lone pair on fluorine, with bonding interaction with the empty metal σ orbitals. This orbital is higher in energy than the π lone pairs on fluorine because of its strong repulsive interaction with the Cu 3d (σ) orbital (Figure 1c). Ionization of this system leads to considerable electron reorganization. The LUMO of $FCuCO^{2+}$ has a fair amount of 3d (σ) coefficient. However, the coefficient of the fluorine p (σ) orbital is quite substantial (Figure 1d). Therefore, electron deficiency in this system is also shared to a large extent by the ancillary ligand.

Additional support for the above arguments is provided by the presence of a filled orbital with primarily d_{z^2} character in all the systems. In the Cu(I) complexes HCuCO and FCuCO, the corresponding orbitals have bonding interactions with the σ-orbital of the ancillary ligand and antibonding interactions with the 5σ orbital of the carbonyl unit (Figure 2a,b). An orbital with essentially the same characteristics is occupied in the corresponding dicationic derivatives as well (Figure 2c,d). The d_{z^2} contribution is even more pronounced in the filled MO's of $OCuCO^+$ and NCuCO.

The extent of π-back-donation in the various complexes can be inferred by the occupancy value of the CO π^*-orbital obtained by natural population analysis. The values are negligible in all the dicationic species. However, Cu(I) complexes and NCuCO are calculated to have large π^*-occupancy numbers (Table 5).

The exceptionally large π-interaction in NCuCO is partly a consequence of the relatively low charge on the metal. The dπ orbitals are higher in energy, making them more effective as donor orbitals. An additional factor also contributes to the π-donor ability of the metal. Due to interaction with the filled π-orbitals on the nitrido ancillary ligand, the dπ orbital energy is pushed up further. The π-framework of NCuCO effectively corresponds to a push−pull system. The magnitude of π-back-donation is enhanced through the captodative nature of the ligands. A similar description has been used to interpret the variations in C−O stretching frequencies in ruthenium carbonyl complexes with π donor groups in the trans position.[35]

The above analysis of electronic structures clarifies the unusual trends in the computed properties. Since the formal HOS species really correspond to Cu(I) complexes, the relatively low natural charges on the metal atom can now be understood. The variations in the charges result from the differing abilities of the ancillary ligands to accommodate the electron deficiency. The highest metal charge is computed for the $FCuCO^{2+}$ species due to the presence of the strong acceptor, F^+. A proton as an ancillary ligand leads to depletion of electron density from Cu(I) to a lesser degree. In the extreme case of the nitrido complex, the metal charge is in the same range as in “normal” Cu(I) complexes (Table 5).

The variations in the calculated bond orders (Table 5) can also be understood. The metal in the “HOS” systems does not act as a good acceptor, since the d_{z^2} orbital remains nearly filled. The bonding interaction with relatively electron deficient ligands is weak. Therefore, the computed Cu−C bond indices in the HOS systems are fairly low. The only case in which the bond index is moderately high is the nitrido complex. In this system, effective π-back-donation enhances the Cu−C bond order.

The C−O bond orders are primarily determined by electrostatic interaction. A higher metal charge would polarize the 5σ carbonyl lone pair in such a way as to reduce its C−O antibonding character. Consequently, there is a clear correlation between metal charge and the C−O bond order. The largest C−O bond index is computed for $FCuCO^{2+}$. Again, the value in NCuCO is similar to that in typical Cu(I) complexes.

The calculated bond lengths are entirely consistent with the electronic structures of these species. The values show the expected inverse dependence on bond orders. The relatively weak Cu−C bonds in the HOS systems have correspondingly large bond lengths. The C−O bond lengths also reflect the changes expected from electrostatic effects.

The absence of correlation between bond lengths and interaction energies implies that the latter are determined by multiple factors. Data from Tables 2 and 5 indicate that the interaction energies are proportional to the charge on the metal. Therefore, ΔE is not just a measure of Cu−C covalent interactions (σ-donor and π-back-donation). Electrostatic interaction between the metal and the ligand lone pair determines the magnitude of stabilization. There is an additional way by which interaction energy is higher in systems with a large charge on the metal. The C−O bond order

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increases substantially due to polarization in such systems. This contribution from electron reorganization in the C−O bond (and, to some extent, the Cu−X unit) on going from the fragments to the complex enhances the interaction energy. As a result of all these factors, the overall interaction energies show a clear dependence on electrostatic effects.

The carbonyl frequencies are also controlled to a large extent by electrostatics, although the values are modulated by π-back-donation effects. The frequency in $CuCO^+$ is higher than in the free carbonyl ligand (Table 2). This trend of higher frequencies in charged complexes has been demonstrated experimentally[36] and has also been interpreted on the basis of electrostatic effects using model calculations.[37] The value is substantially lower in the “normal” Cu(I) complexes HCuCO, HOCuCO, and FCuCO. The reduction results from the smaller charge on the metal and also includes the effect of π-back-donation to the carbonyl π*-orbital. In the dicationic species and in $OCuCO^+$, the increased charge on the metal, with concomitant absence of π-back-donation, leads to a corresponding increase in the C−O stretching frequency. The value for NCuCO is, remarkably, the lowest of all the species considered in this study. The electrostatic contribution from the reduced effective charge on the metal alone cannot account for this reduction. The presence of strong π-back-donation in this captodative system, as confirmed by the population analysis data and orbital contours, is responsible for the unusual C−O stretching frequency in this system.

Trends in Ethylene and Acetylene Complexes. The extents of σ-donation and π-back-donation interactions of ethylene and acetylene ligands are expected to be different from those of the carbonyl group. Further, the η^2-mode of coordination by ethylene and acetylene ligands reduces the symmetry of the complexes, compared to that of the carbonyl counterparts. Necessarily, *in-plane* and *out-of-plane* π-type interactions would be different in the lower symmetry structures. Despite these effects, many of the key features of the electronic structures of carbonyl complexes are found to be common for the ethylene and acetylene complexes as well.

Most importantly, the electronic configuration at the metal is close to d^{10} in all the complexes. As in the corresponding carbonyl complexes, the electron deficiency is transferred to the ligand in the formally Cu(III) species. However, a subtle difference is noted. In the carbonyl complexes, most of the deficiency was localized in the ancillary ligand, X. In contrast, in the ethylene and acetylene complexes of Cu(III) with H^-, OH^-, and F^- as the ancillary ligand, electrons are effectively removed from the organic fragment. As a consequence, C−C bond cleavage is noted during geometry optimization of these species. Stable structures, retaining the organic ligand intact, could be obtained only for the oxo and nitrido derivatives. In these species, the charge distributions (Table 7) are very similar to those in the carbonyl complexes (Table 5).

Table 7. Natural Population Analysis Data for Ethylene and Acetylene Complexes

	charge		Wiberg bond index		occupancy	
system	Cu	X	Cu−C	C−C	C−C π	C−C π*
C_2H_4				2.03	2.00	0.00
$CuC_2H_4^+$	0.92		0.13	1.90	1.89	0.03
$HCuC_2H_4$	0.51	−0.54	0.12	1.89	1.91	0.06
$HOCuC_2H_4$	0.80	−0.79	0.21	1.81	1.89	0.12
$FCuC_2H_4$	0.84	−0.82	0.21	1.80	1.89	0.13
$OCuC_2H_4^+$	1.24	−0.34	0.12	1.91	1.89	0.02
$NCuC_2H_4$	0.93	−0.86	0.20	1.77	1.89	0.17
C_2H_2				2.99	2.00	0.00
$CuC_2H_2^+$	0.95		0.11	2.88	1.92	0.03
$HCuC_2H_2$	0.53	−0.54	0.15	2.83	1.91	0.07
$HOCuC_2H_2$	0.85	−0.79	0.24	2.74	1.89	0.14
$FCuC_2H_2$	0.88	−0.81	0.24	2.74	1.89	0.15
$OCuC_2H_2^+$	1.27	−0.34	0.10	2.89	1.92	0.02
$NCuC_2H_2$	0.98	−0.83	0.23	2.69	1.89	0.22

In view of the similarity in the electronic structures, the major trends in the calculated charges, bond orders, and interaction energies are the same in the various complexes. The total metal−olefin and metal−acetylene bond orders (twice the Cu−C Wiberg bond index) are quite substantial. Both σ-donation as well as π-back-donation are quite effective. Acetylene, as expected, is computed to be the most efficient π acceptor, among the three ligands considered. These conclusions are clearly borne out by the π- and π*-occupancy values (Tables 5 and 7). The former are less than 1.9 in most of the ethylene and acetylene complexes. The occupancy of the π*-orbital through back-donation is quite significant in formally Cu(I) complexes as well as in the NCu derivatives. In the acetylene complex of NCu, the value is as high as 0.22.

Although the metal−ligand bond orders are larger in the ethylene and acetylene complexes, the interaction energies are not significantly higher than in the carbonyl complexes. One possible reason is that the latter are to a large extent determined by electrostatic effects. Since the charge on the metal does not vary much, the interaction energies are similar. Another factor may also be responsible for the energetic trends. Due to orbital polarization induced by complexation, the σ lone pair of the carbonyl group has reduced C−O antibonding character. The stabilization of the carbonyl unit enhances the metal−ligand interaction energy. In contrast, ligation reduces the C−C bond order in ethylene and acetylene complexes. The metal−ligand bonding interaction has to overcome the destabilization within the ligand. Therefore, the magnitude and trends in interaction energies are similar for the carbonyl, ethylene, and acetylene complexes.

Structures and Energetics in Alternative Closed-Shell States. In the above discussion, all the “Cu(III)” species were calculated with a closed-shell configuration by removing a pair of electrons from a σ orbital of the corresponding Cu(I) system. This is a natural choice, since the d_{z^2} orbital is expected to be unfilled in Cu(III) complexes (d^8 systems) with ligands exclusively along the z axis. The results obtained using this orbital occupancy, which we shall refer to as a “σ-hole” configuration, reveal that the metal retains its full comple-

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Table 8. MP2 Total Energies, Optimized Geometries, Selected Natural Population Analysis Data, and Interaction Energies for Ethylene and Acetylene Complexes of OCu^+ and NCu in Three Closed-Shell Electronic States

system/state	energy[a] MP2	Cu−C	C−C	Cu−X	q(Cu)	q(X)	electron confign on Cu	occupancy on C−C π^*	ΔE^b
$OCuC_2H_4^+$									
σ-hole	−348.176 59 (0.00)	2.238	1.372	1.589	1.24	−0.34	3d(9.60)4s(0.15)	0.017	−57.59
in-plane π-hole	−348.187 68 (−7.0)	2.247	1.366	1.634	0.97	−0.09	3d(9.70)4s(0.31)	0.012	−55.03
out-of-plane π-hole	−348.191 73 (−9.5)	2.198	1.369	1.625	0.97	−0.09	3d(9.69)4s(0.32)	0.019	−57.57
$NCuC_2H_4$									
σ-hole	−327.949 49 (0.00)	2.023	1.404	1.611	0.93	−0.86	3d(9.77)4s(0.22)	0.172	−41.71
in-plane π-hole	−328.008 26 (−36.9)	2.037	1.364	1.804	0.64	−0.69	3d(9.84)4s(0.47)	0.044	−29.43
out-of-plane π-hole	−328.021 01 (−44.9)	2.025	1.388	1.759	0.70	−0.67	3d(9.78)4s(0.47)	0.139	−37.42
$OCuC_2H_2^+$									
σ-hole	−346.949 20 (0.00)	2.217	1.235	1.591	1.27	−0.34	3d(9.61)4s(0.11)	0.015	−51.94
in-plane π-hole	−346.961 17 (−7.5)	2.219	1.232	1.639	0.99	−0.08	3d(9.72)4s(0.28)	0.015	−49.84
out-of-plane π-hole	−346.973 67 (−15.4)	2.010	1.239	1.619	0.99	−0.10	3d(9.68)4s(0.30)	0.024	−57.68
$NCuC_2H_2$									
σ-hole	−326.725 40 (0.00)	1.975	1.269	1.618	0.98	−0.83	3d(9.74)4s(0.22)	0.219	−38.04
in-plane π-hole	−326.785 39 (−37.6)	2.109	1.235	1.810	0.65	−0.69	3d(9.83)4s(0.47)	0.044	−26.52
out-of-plane π-hole	−326.806 37 (−50.8)	1.945	1.264	1.736	0.76	−0.65	3d(9.73)4s(0.47)	0.196	−39.68

[a] Relative energies in kcal mol^{-1} are given in parentheses. [b] Values are in kcal mol^{-1}.

ment of d electrons and the deficiency is localized essentially in the ligands. Can the same behavior be expected if an electron pair is removed from a different d orbital?

We considered the possibility of alternative "π-hole" states by optimizing the structures of ethylene and acetylene complexes of OCu^+ and NCu at the MP2 level with different orbital occupancies. Due to the lower symmetry in these species, *in-plane* and *out-of-plane* π orbitals are distinguishable. Hence, initial guess configurations with electrons removed from d_{xz} and d_{yz} orbitals were independently generated, yielding results for two closed-shell states, in addition to the σ-hole state discussed earlier. A summary of results with the three possible electronic configurations (differing in the dominant determinants in the perturbation expansion) is provided in Table 8.

The π-hole states are lower in energy than the σ-hole counterparts in all the cases considered. The energy differences are very small in the OCu^+ complexes, the three states being bunched together within 15 kcal mol^{-1}. The preference for the π-hole state is greater in the NCu complexes. While the in-plane π-hole state is 38 kcal mol^{-1} lower in energy than the σ-hole state, the out-of-plane π-hole state is even more stable. In the acetylene complex of NCu, the preference is as large as 51 kcal mol^{-1} (Table 8).[38]

Although the ground state of the Cu(III) species is different from the state derived from the σ-hole configuration, the principal conclusions derived in the previous sections are found to be generally valid. The nature of the dominant electronic configuration does not alter the key feature of the electronic structure of these species. In particular, the electronic configuration at the metal remains close to d^{10} in all the states! The electron density on copper is, in fact, slightly higher in the π-hole states, compared to the σ-hole state discussed earlier. Both 3d and 4s orbital occupancies are higher in the former states. Correspondingly, the natural charge on copper is lower (less than 1 in all the systems). These data reinforce the conclusion that the electron deficiency remains mainly in the ancillary ligand, in all the low-energy states of these species. Hence, the structures, bond orders, and energies are best interpreted as resembling those of Cu(I) complexes.

There are a few systematic differences in the computed properties of the various states of the ethylene and acetylene complexes. The Cu−O and Cu−N distances are the shortest in the σ-hole state. The bonds are longer and of similar length in the two π-hole states. Since the electrons are primarily removed from the ancillary ligands, the σ-hole state is characterized by a polarized Cu−X bond involving the electron pair on the d_{z^2} orbital of copper. Similar bonding involving the dπ orbital in the π-hole states is not equally effective. This would account for the calculated variations in the Cu−X lengths as well as the near-constancy of the Cu−C and C−C lengths in the various states.

There is another notable difference among the three possible closed-shell states. In the in-plane π-hole state, the corresponding dπ-orbital cannot effectively interact with the π^*-orbital of the organic ligand. This is because the empty pπ-orbital on the ancillary ligand in this system is involved in a stronger interaction with the dπ-orbital. The lack of π-back-donation to ethylene and acetylene in the in-plane π-hole state is clearly revealed by the low natural occupancy number for the π^*-orbital (Table 8). This is especially evident in the NCu complexes, which show strong π-back-donation in the other electronic states. The absence of back-donation to the organic ligand in the in-plane π-hole state results in longer Cu−C and shorter C−C bonds. The binding energy of the Cu−X fragment to the organic ligand is also the lowest in this state. Remarkably, the interaction energies (with respect to the appropriate states of the fragment)[39] as well as the magnitude of π-back-donation for the σ-hole state and the out-of-plane π-hole state are very close. This implies that the nature

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(38) A preliminary CASSCF study on the ethylene and acetylene complexes of NCu with six electrons distributed over five frontier orbitals confirms that the out-of-plane π-hole closed-shell configuration makes the dominant configuration in each case.

(39) The energies of the π-hole states of the linear fragments were approximately obtained by using configurations in which only one of the π MO's is doubly filled.

of bonding in the most stable closed shell state is quite similar to that in the σ-hole state.

Conclusions

Ab initio calculations at the MP2 level using effective core potentials on the metal and DZP basis functions on the ligands have been carried out on complexes of X−Cu fragments with carbon monoxide, ethylene, and acetylene. The structures and energies of formally Cu(III) species show several unusual features. Not all structures survive as true minima on the potential energy surface. The minima obtained are characterized by long Cu−X and Cu−C bonds. The corresponding bond orders are also low. However, the interaction energies between Cu−X fragments and the ligand are quite large. The computed properties for the NCu complexes are very close to those of typical Cu(I) species.

The above trends are explained on the basis of the electronic structures of these complexes. In all the formally Cu(III) species, the electron deficiency is concentrated in the ligands. While the electrons are removed mainly from the ancillary unit X in the carbonyl complexes, the organic ligand shares the deficiency in the ethylene and acetylene complexes. The electronic configuration on the metal is close to d^{10} in all the systems. Ligand to metal σ-donation is therefore relatively weak, resulting in long Cu−X and Cu−C bonds. The higher interaction energies result mainly from electrostatic effects in these highly charged systems.

The magnitude of π-back-donation is also not significant in these species, with one important exception. In the NCu complexes, the π-lone pair on N raises the energy of the dπ-orbital, enabling it to interact more effectively with the π*-orbital on the organic ligand. Hence, these systems are remarkably similar to typical Cu(I) complexes, in terms of computed bond lengths, bond orders, interaction energies, and vibrational frequencies. The above conclusions are found to be valid for two other closed-shell states of the ethylene and acetylene complexes of OCu^+ and NCu.

The calculated electronic structures for the HOS copper species have considerable significance for their reactivity and catalytic properties. The metal not only provides enhanced electrostatic interaction but also drains away electron density substantially from the ligands. Since the electron deficiency is localized primarily on the ligands, these are likely to be highly activated, especially toward nucleophilic attack.

The present study generalizes the findings of Snyder[16,17] that apparently Cu(III) organometallic complexes do not have a d^8 electronic configuration. The electronic structures are close to those expected of Cu(I) species. This preference is established even with very few ligands. Since a larger number of ligands would be able to share electron deficiency more effectively, claims of generation of genuine isolated Cu(III) species should be evaluated critically. Rigorous experimental criteria such as those used recently by Solomon and co-workers[13a] for coordination complexes have to be employed.

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Supporting Information Available: Tables giving detailed natural population analysis data (6 pages). Ordering information is given on any current masthead page.

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