Stability of Group 11 Carbonyl Complexes Cl−M−CO (M = Cu, Ag, Au)

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The stability of carbonyl complexes of the group 11 chlorides ClMCO (M = Cu, Ag, Au) is investigated at the *ab initio* level using relativistic and nonrelativistic energy adjusted pseudopotentials for the metal atoms. The gold compound ClAuCO is relativistically stabilized resulting in an increase of the ClAu−CO dissociation energy of ca. 120 kJ/mol at the coupled cluster level (CCSD(T)). This explains the unusual stability of this compound compared to its lighter congeners observed by experimental methods. Structural data and vibrational frequencies are predicted. Our calculated results agree well with the few measured molecular properties available. For example, the calculated ClAu−CO dissociation energy of 182 kJ/mol is close to Calderazzo's estimate of 200 kJ/mol. The unusual blue shift of the CO stretching frequency measured in ClAuCO compared to free CO is, however, not due to the effects of relativity as might be expected. A MO analysis shows that both metal-d and metal-p contributions are important in metal−ligand bonding in contrast to the interpretation given from Mössbauer data. Electric field gradients are discussed which are very sensitive to relativistic effects and to CO coordination on the metal center.

I. Introduction

Carbonyl compounds of group 11 metals have not been investigated in great detail.[1−4] Most of the group 11 carbonyl species synthesized are those of copper.[1] The simplest carbonyl species, MCO, have been detected in matrix isolation for M = Cu and Au,[5] but not for M = Ag, which was the subject of two recent theoretical investigations.[6,7] Silver carbonyl compounds are very rare[2] and the carbonyl chemistry of gold seems to be not well developed.[4] Very recently, Strauss et al.[8] succeeded in synthesizing the first stable silver dicarbonyl species, $Ag(CO)_2^+$, isoelectronic to the well-known cyano complex $Ag(CN)_2^-$. Strauss pointed out[8] that the CO ligands in $Ag(CO)_2^+$ are less strongly bound compared to its heavier congener $Au(CO)_2^+$,[9] which was verified and analyzed theoretically by Veldkamp and Frenking.[10] All experimental and theoretical data on group 11 carbonyls[1−3,6,10] so far suggest the following sequence in thermodynamic stability: Au ≈ Cu ≫ Ag.[11] Enhanced metal−ligand stability in gold compounds is well-known[6,12] and often explained in terms of relativistic effects.[13]

The gold carbonyl compound ClAuCO has been known experimentally since 1925.[14] ClAuCO is a crystalline colorless solid, extremely moisture sensitive but stable at room temperature.[14,15] It is used for the synthesis of a variety of LAuCl compounds (L any ligand).[16] A survey of LAuCO compounds has been given recently by Calderazzo.[17] Silver carbonyl species of the form LAgCO are unknown so far.[2] There have been several copper carbonyl species of the form LCuCO (L = Cl, Br, CF_3COO, ...) isolated or at least identified,[1,18] but they seem to react rapidly to CuL and CO.[1,19] There have been many attempts to isolate solid ClCuCO, however, this species exists only in situ under an atmosphere of carbon monoxide[19,20] and has been identified and analyzed only very recently in matrix isolation.[18] Hence, there is experimental evidence for the sequence in stability LAuCO > LCuCO ≫ LAgCO, as

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(1) Bauer, H.; Faust, J.; Flüssel, J. *Gmelin Handbuch der Anorganischen Chemie, Copper, Organocopper Compounds, Part 3,* 8th ed.; Springer Press: Berlin, 1986.

(2) Meyer, R. J.; Pietsch, E. H. E.; Kotowski, A. *Gmelin Handbuch der Anorganischen Chemie, Silber, Teil B5*; Springer Press: Berlin 1975).

(3) Schmidbaur, H. *Gmelin Handbuch der Anorganischen Chemie, Gold, Organogold Compounds,* 8th ed., Springer Press: Berlin, 1980.

(4) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209.

(5) (a) Huber, H.; Kündig, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 2097. (b) McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 51. (c) McIntosh, D.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *98*, 3167. In this paper a frequency of 1966 cm^{-1} has been assigned to the species AgCO, which is doubtful (see refs 6 and 7). (d) McIntosh, D.; Ozin, G. A.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 3640.

(6) Schwerdtfeger, P.; Bowmaker, G. A. *J. Chem. Phys.* **1994**, *100*, 4487.

(7) Marian, C. *Chem. Phys. Lett.* **1993**, *215*, 582.

(8) (a) Hurlburt, P. K.; Rack, J. J.; Dec, S. F.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1993**, *32*, 373. (b) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.

(9) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1975**, *97*, 2097.

(10) Veldkamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613.

(11) $Cu(CO)_x^+$ and $Ag(CO)_x^+$ ($x = 1-4$) have recently been studied by collision-induced dissociation in a mass spectrometer, see: Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 4071.

(12) (a) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D.W. *J. Chem. Phys.* **1989**, *91*, 1762. (b) Schwerdtfeger, P. *Phys. Rev. A* **1991**, *43*, 1644. (c) Schwerdtfeger, P.; Boyd, P. D. W. *Inorg. Chem.* **1992**, *31*, 327.

(13) (a) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (b) Schwarz, W. H. E. Fundamentals of Relativistic Effects in Chemistry. In *Theoretical Models of Chemical Bonding,* Maksic, Z. B., Ed.; Springer: Heidelberg, Germany, 1989; Vol. II, p 593.

(14) Machot, W.; Gall, H. *Chem. Ber.* **1925**, *58*, 2175.

(15) Kharasch, M. S.; Isbell, H. S. *J. Am. Chem. Soc.* **1930**, *52*, 2919.

(16) Fischer, D.; Hönes, G.; Kreuzbichler, I.; Neu-Becker, U.; Schwager, B. In *Gmelin Handbook of Inorganic and Organometallic Chemistry, Gold,* Keim, R., Schwager, B., Eds.; Springer Press: Berlin, 1994; Supplement Vol. B2.

(17) Calderazzo, F., *J. Organometal. Chem.* **1990**, *400*, 303.

(18) Plitt, H. S.; Bär, M. R.; Ahlrichs, R.; Schnöckel, H. *Inorg. Chem.* **1992**, *31*, 463.

(19) (a) Wagner, O. H. *Z. Anorg. Chem.* **1931**, *196*, 364. (b) Hieber, W.; Schulter, H. *Z. Anorg. Chem.* **1939**, *243*, 145. (c) Hieber, W.; Schulter, H. *Z. Anorg. Chem.* **1939**, *243*, 164. (d) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533.

(20) (a) Backen, W.; Vestin, R. *Acta Chem. Scand., Ser. A* **1979**, *33*, 85. (b) Busch, M. A.; Franklin, T. C. *Inorg. Chem.* **1979**, *18*, 521. (c) Hieber, W.; Behrens, H.; Teller, U. *Z. Anorg. Allg. Chem.* **1942**, *249*, 26. (d) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 4.

0020-1669/96/1335-2089$12.00/0

mentioned above. Calderazzo estimated the bonding energy of ClAu−CO to be around 200 kJ/mol.[17]

The fundamental stretching frequency (0 → 1 transition) of free CO is 2138 cm^{-1}.[21] CO binding on transition metals usually results in a metal-d_π to CO π^*-back-bonding and in a subsequent red-shift of the CO stretching frequency.[22] In contrast, the CO stretching frequency in ClAuCO is slightly increased to 2152 cm^{-1} in THF and 2163 cm^{-1} in $SOCl_2$.[23] This is similar to CO bound on gold-surfaces (2174 cm^{-1}).[24] Such blue-shifts are known only for CO interactions with Lewis acids, such as BeO,[25] HCl, or HF.[26] Frenking et al. pointed out that BeO is the strongest diatomic Lewis acid,[27] resulting in a blue-shift of the CO stretching frequency in OBeCO to 2190 cm^{-1}.[25] Note that the calculated OBe−CO binding energy of 170 kJ/mol[28] is similar to the one estimated by Calderazzo for ClAuCO.[17] In contrast, there is experimental evidence that the CO stretching frequency in ClCuCO is downward shifted to 2130 cm^{-1} in H_2O, 2085 cm^{-1} in THF, and 2070 cm^{-1} in MeOH.[29] Note, however, that the CO stretching frequency obtained from a matrix isolation study is 2157 cm^{-1} and larger compared to the free CO value.[21] Hence, the CO stretching frequency is rather sensitive to the environment effects.

In a series of papers we investigated relativistic effects in gold compounds.[6,12,30,31] It is now well-established that many of the unusual features found in gold chemistry are due to relativistic effects.[12,13,32,33] In a recent paper on gold(I) compounds we demonstrated that coordination number two is relativistically stabilized; i.e. the dissociation energy of AuL_2^- → AuL + L^- is relativistically increased for L = halogen.[30] This could explain the unusual high binding energy of CO with AuCl. Very recently, Ziegler et al.[34] and Rösch et al.[35] investigated relativistic effects in carbonyl compounds of the late transition elements. They both concluded that relativistic effects play a crucial role in the chemical properties of the heavier transition element carbonyls, for example, relativistic effects increase the metal-CO bond dissociation energy.[34,35] Rösch also calculated a blue-shift of 56 cm^{-1} in the CO stretching frequency of PtCO when compared to free CO, a result of both relativistic effects (34 cm^{-1}) and coordination (20 cm^{-1} at the nonrelativistic level).[35] Jones noted that the Au−C bond is unusually short which may be ascribed to the effects of libration.[36] However, short gold−ligand bond distances are not unusual and often a result of relativistic effects with some contribution from lanthanide contraction.[12,13] The electronegativity of gold is relativistically increased by ca. 0.5,[33] resulting in a higher charge density around the gold atom and therefore in a smaller dipole moment of AuCl. Hence, the Lewis acidity should be decreased by relativistic effects, and therefore, the blue-shift of the CO stretching frequency in ClAuCO can hardly be rationalized within this simple model. We therefore decided to investigate structure and bonding in group 11 metal carbonyl compounds of the form ClMCO (M = Cu, Ag, Au) in detail by *ab initio* methods.

The computational details are given in the next section. Results and discussion are presented in section III. Conclusions are drawn in section IV.

II. Computational Details

The geometry of all compounds have been optimized at the Hartree-Fock level (HF) and second-order Møller−Plesset level (MP2)[37,38] using energy-adjusted relativistic pseudopotentials for Cu, Ag, and Au.[12,39] The corresponding valence basis sets for Cu, Ag, and Au used are defined as follows: (21111111s/22111p/22111d/11f) for Cu,[39] (2111111s/22111p/31111d/11f) for Ag,[39] and (21111111s/411p/21111d/11f) for nonrelativistic and scalar relativistic Au.[12] For Cl we used a (631111s/52111p/1d) McLean−Chandler basis set with a d-polarization function of exponent 0.75.[40] For C and O we used a simple 6-311G* basis set[41] because this basis set gave excellent results for the CO stretching frequency at the MP2 level.[42] The exponents for the metal f-functions applied are as follows: Cu and Ag, 3.1235, 1.3375; Au, 2.5, 1.1447.[6] In order to test the importance of these f-functions for the correlation of the Au(5d)-core, we repeated all MP2 optimizations leaving out these metal f-functions (MP2(−f)). The Hessian matrix was calculated analytically (if f-functions were excluded from our calculations) or numerically in order to obtain the harmonic frequencies for all compounds. Single-point coupled cluster CCSD(T) calculations have been carried out at the MP2 optimized geometries in order to obtain more accurate estimates for the Au−CO bond dissociation energy. Basis set superposition errors are neglected since we expect that errors arising from basis set and electron correlation incompleteness are at least of similar size. All structures are kept in the linear arrangement ($C_{\infty v}$). The results of our calculations are listed in Tables 1−7.

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(21) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(22) (a) Chatt, J.; Duncanson, L. *J. Chem. Soc.* **1933**, *8*, 2939. (b) Dewar, M. T. S. *Bull. Soc. Chim. Fr.* **1950**, *18*, C71. (c) Bagus, P. S.; Müller, W. *Chem. Phys. Lett.* **1985**, *115*, 535; **1985**, *115*, 540.

(23) (a) Dell'Amico, D. B.; Calderazzo, F. *Gazz. Chim. Acta* **1973**, *103*, 1099. (b) Dell'Amico, D. B.; Calderazzo, F.; Dell'Amico, G. *Gazz. Chim. Acta* **1977**, *107*, 101.

(24) Kautaradze, N. N. *Zh. Fiz. Khim.* **1968**, *42*, 1286.

(25) Andrews, L.; Tague, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 6856.

(26) Andrews, L.; Arlinghaus, R. T.; Johnson, G. L. *J. Chem. Phys.* **1983**, *78*, 6347.

(27) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007.

(28) Frenking, G.; Koch, W. *J. Chem. Soc., Chem. Commun.* **1988**, 1147.

(29) (a) Rucci, G.; Zanzottera, C.; Lachi, M. P.; Camia, M. *J. Chem. Soc., Chem. Commun.* **1971**, 652. (b) Mason, R., Rucci, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1132. (c) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* **1976**, *15*, 968. (d) Bigorgne, M. *J. Organomet. Chem.* **1978**, *160*, 345. (e) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1981**, *20*, 3382.

(30) (a) Schwerdtfeger, P. *J. Am. Chem. Soc.* **1989**, *111*, 7261. (b) Schwerdtfeger, P.; Boyd, P. D. W.; Brienne, S.; Burrell, A. K. *Inorg. Chem.* **1992**, *31*, 3411.

(31) Schwerdtfeger, P.; Boyd, P. D. W.; Burrell, A. K.; Robinson, W. T.; Taylor, M. J. *Inorg. Chem.* **1990**, *29*, 3593.

(32) (a) Pyykkö, P.; Zhao, Y. *Chem. Phys. Lett.* **1991**, *177*, 103. (b) Pyykkö, P.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133. (c) Häberlen, O. D.; Rösch, N. *J. Phys. Chem.* **1993**, *97*, 4970. (d) Häberlen, O. D.; Schmidbaur, H.; Rösch, N. *J. Am. Chem. Soc.* **1994**, *116*, 8241. (e) Görling, A.; Rösch, N.; Ellis, D. E.; Schmidbaur, H. *Inorg. Chem.* **1991**, *30*, 3986. (f) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (g) Ziegler, T.; Snijders, J. G.; Baerends, E. J. *Chem. Phys. Lett.* **1980**, *75*, 1. (h) Ziegler, T.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1981**, *74*, 1271.

(33) Schwerdtfeger, P. *Chem. Phys. Lett.* **1991**, *183*, 457.

(34) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(35) Chung, S.-C.; Krüger, S.; Pacchioni, G.; Rösch, N. *J. Chem. Phys.* **1995**, *102*, 3695.

(36) Jones, P. G. *Z. Naturforsch., B* **1982**, *37*, 823.

(37) (a) Møller, C.; Plesset, M. S. *J. Chem. Phys.* **1934**, *46*, 618. (b) As implemented in GAUSSIAN92/DFT (ref 38).

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, J. B.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Program GAUSSIAN92/DFT, Revision F.3. Gaussian Inc., Pittsburgh, PA, 1993.

(39) (a) Andrea, D.; Häussermann, U; Dolg, M.; Stoll, H. *Theoret. Chim. Acta* **1990**, *77*, 123. (b) Dolg, M. Stoll, H. *Theor. Chim. Acta* **1989**, *75*, 369.

(40) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980** *72*, 5639.

(41) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980** *72*, 650. (b) As implemented in GAUSSIAN92/DFT (ref 38).

(42) Schwerdtfeger, P.; McFeaters, J. S.; Moore, J. J.; McPherson, D. M.; Cooney, R.; Bowmaker, G. A.; Dolg, M.; Andrae, D., *Langmuir* **1991**, *7*, 116.

(43) (a) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rottray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061. (b) Goggin, P. L.; Mink, J. *Inorg. Chim. Acta* **1979**, *34*, 225.

Table 1. Molecular Properties for Group 11 Carbonyl Compounds ClMCO (M = Cu, Ag, Au) at the Relativistic Level[a]

property	method	ClCuCO	ClAgCO	ClAuCO
r_e(MCl)	HF	2.146	2.372	2.323(2.530)
	MP2(−f)	2.055(2.072)	2.292(2.353)	2.293(2.452)
	MP2	2.033	2.254	2.266(2.400)
	exptl[b]			2.261
r_e(MC)	HF	2.032	2.302	2.038(2.638)
	MP2(−f)	1.749(1.783)	2.013(2.157)	1.901(2.290)
	MP2	1.725	1.947	1.872(2.165)
	exptl[b]			1.93
r_e(CO)	HF	1.097	1.098	1.098(1.099)
	MP2(−f)	1.143(1.143)	1.136(1.134)	1.140(1.133)
	MP2	1.143	1.137	1.141(1.135)
	exptl[b]			1.11
D_e	HF	60.5	36.4	94.2(21.8)
	MP2(−f)	188.1(163.5)	102.5(69.2)	191.1(58.4)
	MP2	208.8	129.1	220.0(77.6)
	MP3[c]	59.8	80.0	162.7(50.7)
	MP4SDQ[c]	258.8	104.9	164.7(58.5)
	CCSD[c]	124.5	88.4	167.1(53.7)
	CCSD(T)[c]	152.1	103.0	182.2(62.5)
k_e(MCl)	HF	1.87	1.48	2.08(1.21)
	MP2(−f)	2.71	1.94	2.40(1.90)
	MP2	3.28	2.14	3.14(1.74)
k_e(MC)	HF	0.71	0.37	1.36(0.17)
	MP2(−f)	2.88	1.32	2.64(1.03)
	MP2	2.89	1.83	2.52(0.85)
k_e(CO)	HF	25.26	25.10	24.99(24.97)
	MP2(−f)	17.63	18.55	18.06(18.72)
	MP2	17.59	18.41	18.04(18.72)
μ_e	HF	7.556	8.652	6.794(9.674)
	MP2(−f)	4.862(5.390)	7.188(8.363)	5.354(8.327)

[a] Bond distances r_e in Å, diagonal force constants k_e in mdyn/Å, dissociation energies D_e in kJ/mol ($\mathrm{ClMCO} \rightarrow \mathrm{MCl} + \mathrm{CO}$), and dipole moments μ_e in Debye. Nonrelativistic values are derived from nonrelativistic pseudopotentials and basis sets and are set in parentheses. The MP2 geometries without inclusion of metal f-functions are listed as MP2(−f). [b] Experimental bond distances for ClAuCO from X-ray diffraction.[36] [c] Energies calculated at the optimized MP2 structures.

Table 2. Molecular Properties for Group 11 Chlorides MCl (M = Cu, Ag, Au) and CO[a]

property	method	CuCl	AgCl	AuCl	CO
r_e	HF	2.163	2.391	2.345(2.539)	1.105
	MP2(−f)	2.069(2.095)	2.325(2.383)	2.292(2.481)	1.138
	MP2	2.041	2.279	2.250(2.434)	1.138
	exptl[b]	2.051	2.281		1.128
k_e	HF	1.77	1.41	1.79(1.22)	24.07
	MP2(−f)	2.30	1.64	2.11(1.41)	18.49
	MP2	2.50	1.84	2.32(1.56)	18.49
μ_e	HF	6.903	7.989	6.323(8.975)	−0.15
	MP2(−f)	5.465(5.781)	6.863(7.625)	5.028(7.997)	−0.32

[a] Bond distances r_e in Å, force constants k_e in mdyn/Å, and dipole moments μ_e in Debye. NR denotes the nonrelativistic calculation using the nonrelativistic pseudopotential and basis set for gold. Diatomic gas phase structures from ref 21. The MP2 geometries without inclusion of metal f-functions are listed as MP2(−f). The nonrelativistic results at the MP2(−f) level are set in parentheses.

III. Results and Discussion

Bond Distances. Accurate gas phase structures are only available for the diatomics CO, CuCl, and AgCl, and these agree nicely with our calculated MP2 results, Table 2. Recently, large scale relativistic coupled cluster calculations for AuCl have been carried out resulting in a bond distance of 2.248 Å[44] in excellent agreement with our MP2 value of 2.250 Å. The coupled-pair functional (CPF) CuCl bond distance of 2.078 Å recently obtained by Ahlrichs et al.[18] agrees well with our MP2 value of 2.041 Å (experimental 2.051 Å[21]). The solid state structure of ClAuCO has been determined from X-ray diffraction measurements by Jones,[36] the experimentally derived bond distances are also listed in Table 1. A comparison with our calculated MP2 values shows that they are in reasonably good agreement with the data published by Jones. Errors are less than 0.005 Å except for the AuC bond distance which deviates by 0.06 Å from the distance given for the crystal structure. This relatively large difference is probably due to solid state effects (Au−Au internuclear distances in the solid state are 3.38 Å indicating a weak aurophilic interaction). Moreover, the Au−CO bond is the weakest bond of all three bonds (Au−C, Au−Cl, and C−O) and therefore more sensitive to the size of the basis set and the electron correlation procedure applied. The all-electron ab-initio results of Ahlrichs et al. for ClCuCO[18] (for CPF; r_e(CuCl) = 2.070 Å, r_e(CuC) = 1.807 Å, and r_e(CO) = 1.128 Å; for MP2, r_e(CuCl) = 2.047 Å, and r_e(CuC) = 1.750 Å, and r_e(CO) = 1.137 Å) suggest that the CuC bond distance is very sensitive to the electron correlation procedure applied, indicating a relatively weak bond. Their MP2 results are in good agreement with our MP2 values, Table 1.

The data in Tables 1 and 2 demonstrate that metal f-functions generally improve the results and are therefore important for an accurate structure prediction. Hartree-Fock (HF) typically overestimates bond distances. In particular, the Ag−C bond distance in ClAgCO changes significantly due to electron correlation effects indicating a very weak silver−carbonyl bond at the HF level. Similar large effects are calculated for the Cu−C bond in ClCuCO and for the nonrelativistically derived Au−C bond in ClAuCO. Electron correlation effects are, however, less significant for the relativistically calculated Au−C bond in ClAuCO, indicating relativistic effects are important for the stability of the gold−carbonyl bond.

The metal−ligand bond distances for all ClMCO species are depicted in Figure 1. The graphs demonstrate the importance of electron correlation contributions, especially for the Ag−C bond. However, they also show the typical anomaly often observed in group 11 metal−ligand bond distances,[21] r_e(Cu−L) < r_e(Au−L) < r_e(Ag−L); i.e, the longest bond distances are usually measured for the silver compound and not for the gold compound, as one would expect. This is due to relativistic effects (with a lesser contribution from lanthanide contraction);[12,13] i.e. a comparison with the nonrelativistic Au−L bond distances shows that these lie well above the Ag−L bond lengths. Moreover, a geometry optimization using nonrelativistic pseudopotentials and basis sets shows the normal monotonic increase in bond distances from copper to gold (at the MP2(−f) level, Table 1): r_e^{NR}(CuCl) < r_e^{NR}(AgCl) < r_e^{NR}(AuCl); r_e^{NR}(CuC) < r_e^{NR}(AgC) < r_e^{NR}(AuC). Relativistic contributions exceed correlation effects for the Au−C and Au−Cl bond distances, which can be contributed to the unusually large relativistic effects found for the group 11 compounds ("group 11 anomaly").[13] We should also mention that relativistic and correlation effects are in general not additive (compare the data in Tables 1−4), as this has been discussed recently for a series of gold compounds.[45]

The Metal-Carbonyl Bond Stability. Calderazzo estimated the $\mathrm{ClAuCO} \rightarrow \mathrm{AuCl} + \mathrm{CO}$ dissociation energy at around 200 kJ/mol which is in excellent agreement with our calculated MP2 value (220 kJ/mol, Table 1) or our single-point CCSD(T) result (ca. 180 kJ/mol). We did not correct for zero-point vibrational

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(44) (a) Baker, L. J.; Bowmaker, G. A.; Bott, R.; Healy, P. C.; Skelton, B. W.; Schwerdtfeger, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 1341. (b) Schwerdtfeger, P. *Mol. Phys.* **1995**, *86*, 359.

(45) Hrusak, J.; Hertwig, R. H.; Schröder, D.; Schwerdtfeger, P.; Koch, W.; Schwarz, H. *Organometallics* **1995**, *14*, 1284.

Table 3. Harmonic Frequencies and Infrared Itensities for the Carbonyl Compounds ClMCO (M = Cu, Ag, Au)[a]

molecule	method	Σ^+ CO str	Σ^+ MC str	Π MCO def	Σ^+ MCl str	Π ClMC def
ClCuCO	HF	2511.3	394.1	287.3	223.0	54.7
	MP2(−f)	2100.1(534.2)	547.2(4.1)	421.6(0.6)	388.0(68.3)	80.7(3.9)
	MP2	2104.4	572.9	437.0	407.0	92.4
	MP2[b]	2144	580	442	389	103
	exptl[c]	2157		362		
	exptl[d]	2100±30				
ClAgCO	HF	2502.2	316.9	235.2	157.3	47.1
	MP2(−f)	2149.2(238.1)	382.0(5.4)	301.8(0.1)	285.1(50.3)	63.2(4.2)
	MP2	2145.5	413.5	328.1	324.7	67.9
ClAuCO	HF	2495.8	352.4	364.6	295.9	78.9
	MP2(−f)	2130.3(452.7)	425.7(13.6)	407.1(2.9)	364.3(47.0)	80.7(1.5)
	MP2	2138.2	459.5	420.2	375.1	81.4
	exptl	2162	443	416	371	95
	NRHF	2494.1	265.6	176.3	105.5	26.6
	NRMP2(−f)	2161.5(152.4)	341.6(17.5)	230.2(0.02)	252.8(29.8)	28.3(4.5)
	NRMP2	2158.4	325.1	246.5	231.1	48.5

[a] Frequencies in cm^{-1}, intensities in km/mol (set in parentheses). MP2(−f) denotes calculations without applying metal f-functions (see also Table 1). The following isotopes have been used: ^{63}Cu, ^{107}Ag, ^{197}Au, ^{35}Cl, ^{12}C, and ^{16}O. The experimental frequencies ν_e for ClAuCO[43] contain anharmonicity effects. NR denotes the nonrelativistic calculation using the nonrelativistic pseudopotential and basis set for gold. [b] MP2 calculations of Ahlrichs et al.[18] [c] Matrix isolation infrared values[18] [d] The CO stretching frequency in ClCuCO is strongly dependent on the solvent chosen.[29]

Table 4. Harmonic Frequencies and Infrared Intensities for the Chlorides MCl (M = Cu, Ag, Au) and CO[a]

method	CuCl	AgCl	AuCl	AuCl/NR[b]	CO
HF	365.9	301.4	320.2	263.8	2441.2(148.1)
MP2(−f)	417.0(32.3)	325.4(32.1)	347.3(20.5)	283.4(31.7)	2139.4(39.2)
MP2	434.0	344.3	364.5	298.7	2139.4(39.2)
exptl	415.3	343.5	382.8		2170, *2138*[c]

[a] Frequencies in cm^{-1}, intensities in km/mol (set in parentheses). MP2(−f) denotes calculations without applying metal f-functions (see also Table 2). The following isotopes have been used: ^{63}Cu, ^{107}Ag, ^{197}Au, ^{35}Cl, ^{12}C, and ^{16}O. Experimentally determined ω_e values for the diatomic compounds from ref. 21. [b] NR denotes the nonrelativistic calculation using the nonrelativistic pseudopotential and basis set for gold. [c] 2170 cm^{-1} is the CO harmonic stretching frequency, ω_e. In comparison, 2138 cm^{-1} denotes the measured (anharmonic) 0→1 fundamental transition.[21]

Table 5. MP2 Mulliken Orbital Populations *n* and Gross Atomic Charges *q* for the MCl, CO and ClMCO compounds (M = Cu, Ag, Au)[a]

	ClCuCO	CuCl + CO	ClAgCO	ClAg + CO	ClAuCO	ClAu + CO	NR ClAuCO	NR ClAu + CO
q^{Cl}	−0.36	−0.37	−0.52	−0.55	−0.28	−0.31	−0.60	−0.64
n_s^{Cl}	1.99	1.96	1.98	1.98	1.94	1.96	1.98	1.98
$n_{p\sigma}^{Cl}$	1.57	1.54	1.64	1.65	1.45	1.39	1.71	1.73
$n_{p\pi}^{Cl}$	3.75	3.81	3.83	3.86	3.83	3.89	3.86	3.87
q^{M}	0.31	0.37	0.50	0.55	0.04	0.31	0.60	0.64
n_s^{M}	0.58	0.44	0.60	0.32	1.12	0.65	0.40	0.24
$n_{p\sigma}^{M}$	0.29	0.11	0.04	0.07	0.21	0.09	0.06	0.05
$n_{p\pi}^{M}$	0.17	0.13	0.11	0.09	0.12	0.08	0.08	0.08
$n_{d\sigma}^{M}$	1.82	1.93	1.85	1.96	1.74	1.88	1.89	1.97
$n_{d\pi}^{M}$	3.83	4.02	3.90	4.01	3.77	3.99	3.97	4.02
$n_{d\delta}^{M}$	4.00	4.00	4.01	4.00	4.00	4.00	4.00	4.00
q^{C}	0.12	0.05	0.04	0.05	0.31	0.05	0.00	0.05
n_s^{C}	1.48	1.81	1.62	1.81	1.34	1.81	1.68	1.81
$n_{p\sigma}^{C}$	0.91	0.91	0.92	0.91	0.84	0.91	0.94	0.91
$n_{p\pi}^{C}$	1.36	1.13	1.29	1.13	1.37	1.13	1.25	1.13
q^{O}	−0.07	−0.05	−0.02	−0.05	−0.06	−0.05	−0.01	−0.05
n_s^{O}	1.89	1.81	1.87	1.81	1.88	1.81	1.85	1.81
$n_{p\sigma}^{O}$	1.37	1.41	1.37	1.41	1.37	1.37	1.38	1.37
$n_{p\pi}^{O}$	2.77	2.80	2.74	2.80	2.78	2.80	2.73	2.80

[a] MCl+CO denotes the separated species MCl and CO. NR denotes the nonrelativistic calculation using the nonrelativistic pseudopotential and basis set for gold. The d-populations of the non-metal elements are more or less constant for all the compounds considered: chlorine, 0.05−0.06; carbon, 0.11−0.14; oxygen, 0.04.

energy contributions (ZPVE) because they are usually small compared to the error inherent in the correlation method used; i.e., taking the MP2 values from Tables 3 and 4, we obtain the following ZPVE corrections (in kJ/mol): 9.4 for ClCuCO, 7.1 for ClAgCO and 8.8 for ClAuCO (the anomaly in the ZPVE corrections is due to relativistic effects). The smallest dissociation energy is calculated for ClAgCO (ca. 100 kJ/mol at the CCSD(T) level) in agreement with the fact that this compound has not been isolated yet. We note the large sensitivity of the ClCu−CO dissociation energy upon the electron correlation

Table 6. Results of the Charge Decomposition Analysis for the Three Carbonyl Compounds at the MP2 Level

	donation	back-donation	repulsion
ClCuCO	+0.321	+0.196	−0.118
ClAgCO	+0.099	+0.100	−0.200
ClAuCO	+0.254	+0.232	−0.255

Table 7. MP2 Cl, O, and C Electric Field Gradients (EFG) for the MCl, CO and ClMCO Compounds (M = Cu, Ag, Au)[a]

	ClCuCO	CuCl + CO	ClAgCO	ClAg + CO	ClAuCO	ClAu + CO
Cl	−1.111	−1.603	−1.386	−1.657	−1.827	−2.804
	−1.075	*−1.482*	*−1.225*	*−1.347*	*−1.335*	*−1.417*
C	0.699	0.882	0.739	0.882	0.653	0.882
	0.718	*0.882*	*0.771*	*0.882*	*0.777*	*0.882*
O	0.491	0.732	0.626	0.732	0.448	0.732
	0.535	*0.732*	*0.691*	*0.732*	*0.708*	*0.732*

[a] In atomic units. f-functions at the metal center are omitted. MCl + CO denotes the separated species MCl and CO. Results from nonrelativistic calculations using nonrelativistic pseudopotentials and basis sets for copper, silver, and gold are set in italics.

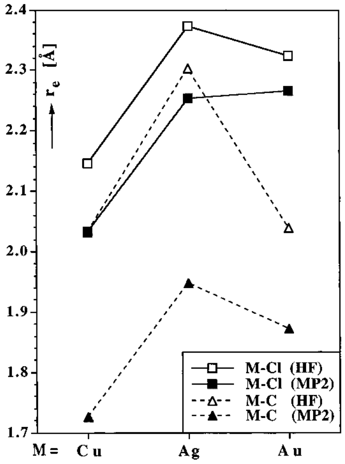

Figure 1. Hartree−Fock (HF) and second-order Møller−Plesset (MP2) metal−ligand bond distances for the ClMCO compounds (M= Cu, Ag, Au).

procedure applied, Table 1. The MP series does not converge smoothly for all ClMCO compounds (see also ref 46). This is in agreement with the results obtained by Ahlrichs et al. for ClCuCO (ClCu−CO dissociation energy: MP2 196 kJ/mol, CPF 155 kJ/mol, ZPVE corrections not included).[18] The CPF dissociation energy of Ahlrichs and co-workers is in excellent agreement with our CCSD(T) result of 152 kJ/mol. We also note that triple contributions to the dissociation energy in the coupled cluster calculations are substantial for all compounds, which is more typical for weakly interacting systems.

Figure 2 shows the ClMCO → MCl + CO dissociation energies along the group 11 series of compounds. We also include the nonrelativistic values for ClMCO dissociation energies at the MP2(−f) level of theory. The graphs all show the same trend, a decrease from ClCuCO to ClAgCO followed by a steep increase from ClAgCO to ClAuCO. This is clearly due to relativistic effects, i.e. relativity seems to stabilize the gold−carbonyl bond (as this is the case for other transition element carbonyl species).[34,35] This is also supported from results obtained from a geometry optimization using nonrelativistic pseudopotentials and basis sets which show a monotonic decrease in metal-CO bond stability from copper to gold (at the MP2(−f) level, in kJ/mol): D_e^{NR}(Cu−CO) > D_e^{NR}(Ag−CO) > D_e^{NR}(Au−CO). A similar relativistic stabilization has been found recently in a van der Waals complex of gold with CO.[6]

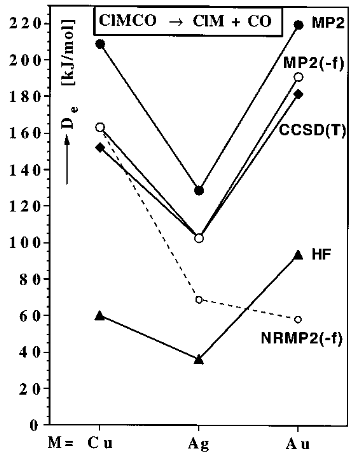

Figure 2. Hartree-Fock (HF), second-order Møller−Plesset (MP2), and coupled cluster CCSD(T) dissociation energies D_e for the decomposition reaction ClMCO → MCl + CO (M= Cu, Ag, Au). The CCSD(T) results are calculated using the MP2 optimized geometries. MP2(−f) denotes MP2 without inclusion of metal f-functions. For MP2(−f) the nonrelativistic (NR) results are also shown.

We briefly mention that BrAuCO has been prepared only very recently; however, attempts to isolate the solid product failed due to rapid decomposition into AuBr and CO. This suggests the stability sequence Cl > Br > I. Indeed, dipole moments calculated for the diatomic gold halides shows a decreasing trend from AuF to AuI,[12] and thus a weaker AuL(dipole)−CO(induced dipole) inductive interaction.

Vibrational Frequencies. The vibrational spectrum of the group 11 chlorides has been determined by experiment[21] and the derived harmonic frequencies are in very good agreement with our MP2 results, Tables 3 and 4. For ClCuCO only the CO stretching frequency is known from experiment which, however, is critically dependent on the solvent chosen.[29] Nevertheless, the mean value for the stretching frequency of 2100 cm^{-1} is in good agreement with our calculated (harmonic) frequency of 2104 cm^{-1} (from microwave data for gas phase CO[21] it is known that anharmonicity effects lower the stretching frequency by ca. 30 cm^{-1}). For ClAuCO the vibrational spectrum has been analyzed in more detail by IR spectroscopy. Again, the agreement with our calculated MP2 values is very good.

The infrared intensities are also listed in Tables 3 and 4. These show that the most intensive band is the CO stretching mode. A comparison with the calculation for free CO shows that the intensity of the CO stretching mode is substantially enhanced due to coordination on the group 11 metal. Part of this significant enhancement in ClAuCO is due to relativistic effects. We should also mention that the M−C and M−Cl modes mix significantly due to the fact that the corresponding modes are of the same symmetry and lie in the same frequencies range. An analysis of the potential energy distribution within Wilson's GF-matrix method[47] shows the following M−Cl/M−C mixing (in %): 32/66 for the 573 cm^{-1} and 71/29 for the 407 cm^{-1} mode in ClCuCO; 49/50 for the 414 cm^{-1} and 52/48 for the 325 cm^{-1} mode in ClAgCO; 4/93 for the 460 cm^{-1} and 99/1 for the 375 cm^{-1} mode in ClAuCO.

The HF frequency for the CO stretching mode is overestimated, a fact which is well-known and can be found in general

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(46) Böhme, M.; Frenking, G. *Chem. Phys. Lett.* **1994**, *224*, 195.

(47) Schwerdtfeger, P.; Bowmaker, G. A.; Boyd, P. D. W.; Earp, C. D.; Hannon, S. F. Program VIB, Version 7.1. Department of Chemistry, University of Auckland, Auckland, New Zealand, 1991.

for all carbon−ligand main group bonding. However, the metal ligand stretches and the bending modes are underestimated at the HF level. Comparing the MP2 frequencies down the group 11 series of compounds for both the MCl and ClMCO compounds we again observe an anomaly as mentioned before, i.e. $\omega_e(\mathrm{Cu{-}L}) > \omega_e(\mathrm{Au{-}L}) > \omega_e(\mathrm{Ag{-}L})$. This is due to the relativistic increase in the metal−ligand M-L stretching force constants (Table 1) which overcompensates the decrease in the reduced mass from M = Cu to M = Au. In fact the relativistic change in the MP2 Au−Cl and Au−C force constants is much larger than the contribution from electron correlation. Substantial relativistic effects can be found in the whole vibrational spectrum of ClAuCO. Even the CO stretching frequency is slightly diminished by ca. 20 cm^{-1} due to relativistic effects. Hence, the observed increase in the CO stretching frequency due to coordination on AuCl is *not* a relativistic effect, at least not at the level of approximation used here. This is in contrast to the findings of Rösch et al. for the PtCO molecule.[35]

Mulliken Population Analysis and Molecular Orbital Interactions. A Mulliken population analysis shows that the oxygen population is largely unaffected by coordination of CO on the metal center, Table 5. Metal d_σ-donation to the ligands is important, and in addition relativistically enhanced in ClAuCO (see also the discussion in ref 12c). Metal d_π-participation is negligible for the diatomic group 11 halides but becomes important when coordination of CO on the metal center occurs. Moreover, the p_π-population at carbon in all ClMCO compounds is increased (and relativistically enhanced in ClAuCO) due to coordination of CO on MCl, hence we conclude that there is gold d_π to carbon p_π*-back-donation. This back-donation can be seen in the MO coefficients of the π^*(CO) virtual orbital, which consists of a mixture of Cl(p_π), M(p_π,d_π), and CO(π^*) orbitals with the main contribution coming, however, from the M(p_π) orbital. Also Ahlrichs et al. postulated a small metal-d_π to CO-π^* back-bonding of 0.2 e for ClCuCO.[18] This does, of course, not explain why there is virtually no decrease or even a small increase in the CO stretching frequency and it would be difficult to explain qualitatively the slight blue-shift in the CO stretching frequency due to coordination. Moreover, previous Mössbauer studies gave no evidence for π-bonding in Au(I) compounds contrary to our results.[48] It is interesting that metal p-participation is more significant for the copper and gold compound than for the silver species partly due to larger chlorine to metal p_σ- and p_π-back-donation.

In order to examine the question of CO → metal charge donation and metal → CO back-donation in more detail we used the recently introduced CDA method (charge decomposition analysis).[49] The CDA expresses the orbitals of a complex in terms of the fragment molecular orbitals of properly chosen fragments. In the present case the molecular orbitals of ClMCO are formed by the linear combination of the fragment orbitals of MCl and CO. Mixing of the occupied and unoccupied fragment orbitals gives the amount of donation and back-donation, respectively, while the mixing of the occupied orbitals indicates the repulsive polarization.[50] It has been shown that the results of the CDA method for various transition metal complexes are in agreement with the standard classification of the ligands.[50]

Table 6 compares the CDA results for the ClMCO complexes. There is significant OC → MCl charge donation for the copper and gold complexes, but the ClM → CO back-donation is also very large, in particular for ClAuCO. Charge donation and back-donation is clearly smaller for the silver complex, which is in agreement with the weaker ClAg−CO bond. It should be noted, however, that there is no direct correlation between the size of the charge donation/back-donation and the strength of the bond.[49] It follows that the CDA method suggests also that there is significant M → CO back-donation in these complexes. We want to point out that the observed blue-shift of the CO stretching frequency by 24 cm^{-1} for ClAuCO[23,43] is not necessarily in disagreement with the calculated sizable OC ← AuCl back-donation. Other factors such as electrostatic interactions and solvent effects could be responsible for the change in the vibrational frequency. It should be noted that ν(CO) of free CO rises if the molecule is placed in an electric field with the carbon atom facing the direction of increasing positive charge.[51]

The effect of the relativistic increase of the gold electronegativity from ca. 1.9 to 2.4 can be clearly seen in the gold atomic charge which is significantly increased in AuCl and ClAuCO. This leads to a significant decrease in the partial charge at the metal atom and the dipole moment for both compounds and therefore again to an anomaly in the dipole moments down the group 11 series of compounds, Tables 1 and 2 (compare also to the dipole moments derived from nonrelativistic MP2(−f) calculations: $\mu_e^{\mathrm{NR}}(\mathrm{ClCuCO}) < \mu_e^{\mathrm{NR}}(\mathrm{ClAgCO}) \approx \mu_e^{\mathrm{NR}}(\mathrm{ClAuCO})$).

There are two different orbital interaction schemes in use for the discussion of the bonding behavior in Au(I) complexes, both starting from a positively charged Au^+ ion.[52] The first scheme involves L → Au(6s6p_z) donation, the second the involvement of the Au(5d_{z^2}) orbital through 6s-d_{z^2} hybridization. Jones et al. pointed out[48] that these two schemes will predict different quadrupole splittings for gold in the Mössbauer spectrum. Mössbauer data suggest that binding through 5d_{z^2} orbitals is negligible compared to the 6p_z model for a number of gold(I) compounds including ClAuCO. However, the Mulliken population analysis shows that both contributions are important as this was pointed out earlier for a series of gold(I) halide complexes.[31] Moreover, the MO-coefficients show substantial mixing between the Au(5d_σ,6s,6p_σ) and CO(2s2p_σ) orbitals in the Au−C σ-bond and the Au(5d_σ,6s) and Cl(3s3p_σ) orbitals in the Au−Cl σ-bond. Hence, one has to be careful in interpreting orbital interactions from Mössbauer data.

Figure 3 compares relativistic and nonrelativistic MO interactions between AuCl and CO. The graph nicely shows the relativistic destabilization of the gold 5d level. The Au 6s orbital is missing in this diagram because it can be identified as the first virtual σ-orbital in AuCl, demonstrating the ionic behavior of Au-Cl bonding. This is also reflected in the Mulliken Au and Cl charges and the large dipole moments for both AuCl and ClAuCO. Perhaps the most significant effect is that the CO levels are shifted downward in energy due to the AuCl electrostatic field. Notable is that the binding CO σ-orbital is more stabilized at the relativistic level compared to the nonrelativistic one rationalizing the increased stability of the ClAuCO complex.[53] We also mention that the CO π^*-level is stabilized due to CO addition on AuCl, but equally at the relativistic and nonrelativistic level.

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(48) Jones, P. G.; Maddock, M. J.; Mays, M. J.; Muir, M. M.; Williams, A. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1434.

(49) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.

(50) (a) Frenking, G.; Dapprich, S.; Ehlers, A. W.; Vyboishchikov, S. F., *Proceedings of the II. International Symposium "Stereoselective Reactions of Metal-Activated Molecules", Sonderforschungsbereich 347, Universität Würzburg*; Werner, H., Sundermeyer, J., Eds.; Vieweg: Braunschweig, Germany, 1995; p 207. (b) Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics*, in press.

(51) Hush, N. S.; Williams, M. L. *J. Mol. Spectrosc.* **1974**, *50*, 349.

(52) (a) Orgel, L. E.; Dunitz, J. D. *Adv. Inorg. Chem. Radiochem.* **1970**, *2*, 1. (b) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.

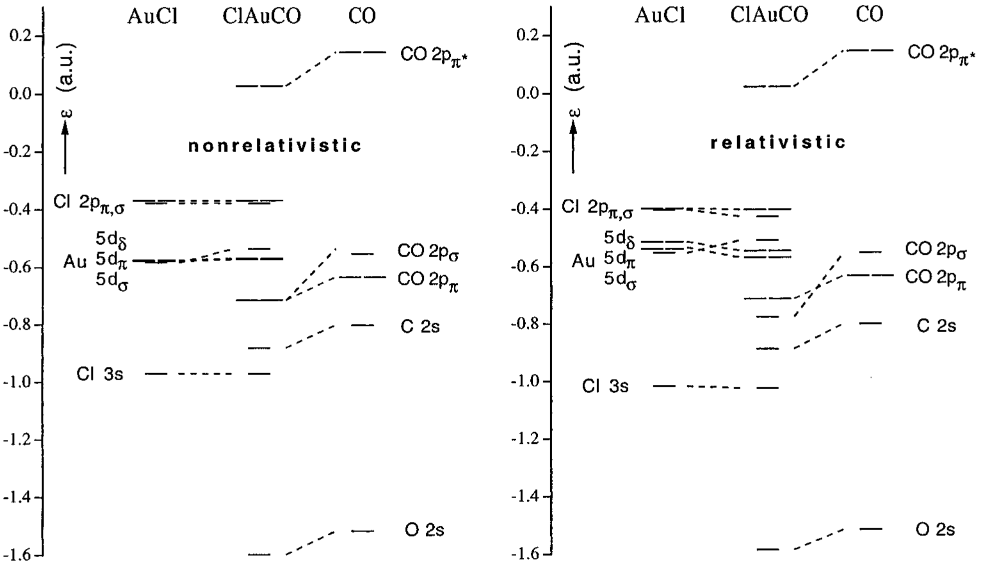

Figure 3. MO-orbital energies ϵ for the AuCl−CO interaction at the relativistic and nonrelativistic levels of theory. For ClAuCO only the major contributions from AuCl and CO are shown by dashed lines (see text for more details). The empty π* orbitals of CO are also included.

Electric Field Gradients. Jones et al. also measured nuclear quadrupole coupling constants NQCC for ^{35}Cl for a variety of compounds, which generally lie in the range from 28 to 36 MHz.[54] However, ClAuCO was not included in his analysis and it may be useful to compare the electric field gradients (EFG) of the different carbonyl compounds, Table 7. Using the ^{35}Cl nuclear quadrupole moment[55] of $-0.08165eQ/10^{-24}$ cm^2 we obtain −35.0 MHz for ClAuCO which lies in the usual range discussed above. One has, however, to be careful with the data given in Table 7, since EFGs are very sensitive to the size of the basis set applied, especially in the core region.[56] For CuCl and AgCl experimental gas phase NQCCs for ^{35}Cl are available (−32.25 and −36.50 MHz, respectively),[57] which are in reasonable agreement with our calculated MP2 results (−30.74 and −31.78 MHz, respectively).

The strength of the CO binding on MCl can be seen as to be proportional to the perturbation in the electron density of both moieties and may therefore be reflected in the change of the Cl, M, C, or O electric field gradients, ΔEFG(M) = EFG(ClMCO) − EFG(MCl+CO). This is indeed the case, i.e. we get for the Cl, C or O field gradients (Table 7) the sequence ΔEFG(Au) > ΔEFG(Cu) > ΔEFG(Ag), similar to the trend calculated for the dissociation energies, Figure 2. As it is well-known, the EFGs are sensitive to the atom p-population. Using the formula given by Townes and Dailey[58] for the unbalanced p-electron population $u_p = 0.5n_{p\pi} - n_{p\sigma}$, one can explain the decrease of the chlorine EFG upon CO coordination, but not the relatively large change calculated. Nevertheless, we conclude that the chlorine EFG is most sensitive to changes in the molecular environment and even predicts correctly the trend in the metal−carbonyl bond stability.

It was pointed out before that relativistic effects are important for chlorine electric field gradients due to the large relativistic change in the molecular electron density.[31] For chlorine, however, this is an indirect effect arising mainly from the relativistically increased electronegativity of the gold atom, thus distorting substantially the chlorine p-orbitals. Table 7 shows that the chlorine EFGs for nonrelativistic ClCuCO, ClAgCO, and ClAuCO are quite similar, and relativistic effects decrease the Cl EFG by 37% in ClAuCO. Significant relativistic changes are also calculated for the C and O EFGs. The relativistic increase in the chlorine EFG can be explained by the ionic model of Townes and Dailey[58] which predicts an increase in the EFG with decreasing ionicity or increasing covalency in the metal−chlorine bond. Due to the relativistic increase of the metal electronegativity, the ionicity of the M−Cl bond decreases thus increasing the chlorine EFG.

IV. Conclusions

We investigated the effects of relativity and electron correlation for the CO coordination on the group 11 halides. The least stable molecule is ClAgCO and we conclude that it would be rather difficult to synthesize this compound. ClAuCO is stabilized by relativistic effects and the calculated dissociation energy agrees nicely with the best estimate of Calderazzo.[17] The calculated frequencies for ClAuCO are in good agreement with experimental data, however, we have not been able to explain the slight blue-shift in CO by theoretical methods, i.e. we obtain a slight decrease of ca. 1 cm^{-1} due to CO coordination on AuCl. Differences are due to solvent effects, the neglect of anharmonicity corrections and limitations in the basis sets and electron correlation procedure used. Both metal-d and metal-p contributions to the metal−ligand bonds are important. Electric field

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(53) At the Hartree-Fock level the total electronic energy is a sum of the orbital energies plus Coulomb and exchange contributions. Thus, a relativistic increase in the bond dissociation energy may therefore be traced back to a relativistic stabilization of one or more of the molecular orbitals.

(54) (a) Jones, P. G.; Williams, A. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1431. (b) Bowmaker, G. A. In *Spectroscopy of Inorganic-based Materials*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: New York, 1987; p 1.

(55) Pyykkö, P.; Li, J. *1992 Nuclear Quadrupole Moments*, Report HUKI 1−92, ISSN 0784−0365; Department of Chemistry, University of Helsinki: Helsinki, 1992. For the conversion of the electric field gradients *eq* from au in MHz we used the equation: (e^2qQ/h) [MHz] = 234.9 (eq [au]) ($eQ/10^{-24}$ cm^2).

(56) Schwerdtfeger, P.; Aldridge, L. P.; Boyd, P. D. W.; Bowmaker, G. A. *Struct. Chem.* **1990**, *1*, 405.

(57) Hoeft, J.; Lovas, F. T.; Tiemann, E.; Törring, T. *Z. Naturforsch., A* **1970**, *25*, 35. (b) Nair, K. P. R.; Tiemann, E.; Hoeft, J. *Z. Naturforsch., A* **1977**, *32*, 1053. (c) Tiemann, E.; Hoeft, J. *Z. Naturforsch., A* **1977**, *32*, 1477. (d) Hoeft, J. Nair, K. P. R., *Z. Naturforsch. A* **1979**, *34*, 1290. (e) Hoeft, J.; Lovas, F. T.; Tiemann, E.; Törring, T., *Z. Naturforsch. A* **1971**, *26*, 240.

(58) (a) Townes, C. H.; Dailey, B. P. *J. Chem. Phys.* **1949** *17*, 782. (b) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants;* Academic Press: London, 1969.

gradients are found to be sensitive upon relativistic effects and CO coordination on MCl. We like to mention that the CO ligand is readily replaceable by other ligands.[15,59] Since there is no gold(I) fluorine compound known so far,[31] we suggest that a possible route of obtaining gold−fluorine bonds is by replacing the CO ligand with fluorine (AuClCO +MF → M[AuClF], M bulky cation).

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(59) (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 728; *Angew. Chem.* **1976**, *88*, 830. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299; *Angew. Chem.* **1977**, *89*, 305.