

it seems that only one other report of rapid intramolecular long-range positive hole transfer in cation radicals has been published.¹⁵ This situation may be contrasted to the relatively large number of published reports of very rapid long-range intramolecular electron-transfer processes in anion radicals.^{16a-c,17} This work provides yet another convincing demonstration that saturated groups are not "insulators" but can, in fact, be very efficient mediators in electron-transfer processes.¹⁶ In this context, we believe that electron-transfer processes in general, not just positive hole transfer, can be strongly accelerated by laticyclic hyperconjugative interactions. The work described herein also indicates that perhaps there is something, after all, in the suggestion^{3d,16e} that the very rapid electron-transfer steps in the photosynthetic reaction center could be mediated by the isoprenoid phytol side chains of the special chlorophyll pair, bacteriopheophytin, and menaquinone, via a process similar to laticyclic hyperconjugation! The observation of long-range photoinduced electron transfer in molecular monolayers might also be a consequence of a type of laticyclic hyperconjugative interaction between adjacent alkyl chains.¹⁸

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Relativistic Effects in Gold Chemistry. 2. The Stability of Complex Halides of Gold(III)

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The stability of the +III oxidation state in gold is unique within the group 11 elements. The halogen chemistry of copper and silver is restricted mostly to the oxidation state +I and +II. In contrast, the Au(I) compounds AuF and AuF₂⁻ have not been isolated although both AuF₃ and AuF₄⁻ exist.¹ There have been many attempts to rationalize these observations.¹⁻³ It has been shown in the first paper of this series³ that relativistic effects are significant in determining the chemical and physical properties of gold. This communication demonstrates that the stability of the

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Table I. Molecular Properties for the Square-Planar Gold(III) Halide Complexes AuX₄⁻ (X = F, Cl, Br, I)^a

molecule	method	r _e	D _e	ΔU ₀	D _e ^{SO}	ΔU ₀ ^{SO}	Δ _R ΔU ₀ ^{SO}
F	NR	1.980	329.4	-81.3			
	R	1.930	523.5	116.6	519.1	113.7	195.0
Cl	NR	2.424	327.9	-100.1			
	R	2.344	496.4	80.3	485.9	73.3	173.4
Br	NR	2.549	292.4	-110.6			
	R	2.492	396.0	-13.3	352.9	-42.1	68.5
I	NR	2.830	220.3	-151.5			
	R	2.716	308.2	-38.9	217.2	-99.6	51.9

^a Au-X bond distance r_e in Å, dissociation energy D_e(AuX₄⁻ → Au + 3X + X⁻) in kJ mol⁻¹. ΔU₀ is given in eq 1. D_e^{SO} and ΔU₀^{SO} are the spin-orbit corrected D_e and ΔU₀ values using the Dirac-Fock atomic values calculated with program MCFD and the experimental spin-orbit splittings given in Moore's tables.¹²

Table II. Molecular Properties for the Linear Gold(I) Halide Complexes AuX₂⁻ (X = F, Cl, Br, I)^a

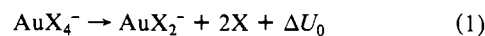
molecule	method	r _e	D _e	D _e ¹	D _e ²	D _e ^{SO}	D _e ^{2SO}
F	NR	2.236	410.7	247.6	163.1		
	NR/CISD ^b	2.215	460.4	207.7	252.7		
	NR/CISDSC	2.210	569.0	274.3	294.7		
	R	2.017	406.9	318.3	88.6	405.4	87.4
	R/CISD	2.028	483.2	316.5	166.7	481.6	165.1
	R/CISDSC	2.032	600.8	385.3	215.5	599.2	213.9
Cl	NR	2.630	428.0	210.1	217.9		
	R	2.398	416.1	255.4	160.7	412.6	157.2
Br	NR	2.750	403.0	200.3	202.7		
	R	2.526	382.2	228.1	157.2	367.8	142.8
I	NR	2.934	371.8	180.4	191.4		
	R	2.710	347.1	194.7	152.4	316.8	122.1

^a Au-X bond distance r_e in Å, dissociation energy D_e(AuX₂⁻ → Au + X + X⁻) in kJ mol⁻¹. D_e¹: dissociation energy for AuX₂⁻ → AuX + X⁻. D_e²: AuX → Au + X. D_e = D_e¹ + D_e². D_e^{SO} is the spin-orbit corrected D_e using the Dirac-Fock atomic values calculated with program MCFD and the experimental spin-orbit splittings given in Moore's tables.¹² ^b r_e(AuF) = 2.160 Å at the CISD level.³

gold halide complexes in the +III oxidation state is mainly due to relativistic effects, as suggested as early as in 1978 by Pekka Pyykkö.⁴

Gold(III) compounds have a tendency to add a fourth ligand L to form stable four-coordinate AuX₃L complexes or to oligomerize to form gold(III) halogen-bridged compounds. The monomers AuX₃ (X = F, Cl, Br, I) have never been detected in the gas phase, indicating that the coordination number three is less favorable. This is supported by relativistic Hartree-Fock (HF) calculations showing that dimerization of the monomer AuF₃ would be favored by more than 160 kJ mol⁻¹.⁵ Hence, the Au(III) halide complexes AuX₄⁻ (X = F, Cl, Br, I) have been chosen to discuss the stability of gold(III) species.

Nonrelativistic (NR) and relativistic (R) HF calculations using accurate pseudopotentials with a small core definition for gold, i.e., a [Xe4f¹⁴] core,³ have been performed for the Au(III) and Au(I) halide complexes in order to examine their relative stability according to eq 1. A modified version of GAUSSIAN86⁶ has been



used. The geometries are optimized by a Fletcher-Powell procedure.⁶ The basis sets and pseudopotentials are given in the first paper of this series.³ The calculated molecular properties for both series of complexes AuX₄⁻ and AuX₂⁻ (X = F, Cl, Br, I) are listed in Tables I and II, respectively.⁷

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In only a few cases are structural data of gold halide complexes in the solid state available.¹ In all cases they compare favorably with our calculated HF values: e.g., the Au-F bond distance in KAuF_4 is 1.95 Å,¹ which is in excellent agreement with our value (Table I). The relativistic bond contractions ($\Delta r_{\text{re}} = r_{\text{e}}(\text{NR}) - r_{\text{e}}(\text{R})$) are much smaller for the Au(III) halide complexes ($\Delta r_{\text{re}} < 0.12$ Å) compared to the Au(I) species ($\Delta r_{\text{re}} < 0.23$ Å).³ This is probably due to the larger 5d contributions in the Au(III)-X bond relative to the Au(I)-X bond quenching the effect of the relativistic bond contraction originating from the 6s orbital.⁸ In contrast to Au(I) halides³ a relativistic bond stabilization ($\Delta_{\text{R}}D_{\text{e}} = D_{\text{e}}(\text{NR}) - D_{\text{e}}(\text{R}) < 0$) is found for Au(III) halides. The dissociation energies (Tables I and II) show that the size of this effect is dependent on the nature of the ligand as well as on the magnitude of the 5d participation in the Au-X bond (at the HF level $\Delta_{\text{R}}D_{\text{e}}$ is 74.5 kJ mol⁻¹ for AuF_3 , 3.8 kJ mol⁻¹ for AuF_2^- , and -94.1 kJ mol⁻¹ for AuF_4^- , and this trend compares with the gross 5d population⁸). Comparing the dissociation energies for both AuX_2^- and AuX_4^- , we obtain the differences in the HF energies ΔU_0 in eq 1. In all cases the nonrelativistic value of ΔU_0 falls in the range -80 to -150 kJ mol⁻¹, indicating that the oxidation state +I is preferred (a negative ΔU_0 favors the right-hand side of eq 1 if entropy effects are neglected). This does not change if we add the HF dissociation energies for the diatomic halides,⁹ $D_{\text{e}}(\text{X}_2)$. In contrast, the relativistic values of ΔU_0 are positive for fluorine but slightly negative for bromine and iodine (-13 and -39 kJ mol⁻¹, respectively). Furthermore, experimentally AuI_4^- and AuI_2^- were observed to be in equilibrium,¹⁰ which is consistent with the relatively small calculated relativistic value of ΔU_0 shown in Table I. Hence, the nonrelativistic results clearly show a preference for the oxidation state +I in gold. The unusual high thermodynamic stability of the Au(III) halide complexes is therefore a relativistic effect.

Correcting for spin-orbit coupling does not modify this conclusion. The spin-orbit-corrected dissociation energies D_{e} and the ΔU_0^{SO} values (Table I and II) have been derived from atomic Dirac-Fock calculations¹¹ by using program MCDP.¹² Also electron correlation is not expected to modify the HF trends because correlation effects in $D_{\text{e}}(\text{NR})$ and $D_{\text{e}}(\text{R})$ would be similar, and the difference $\Delta_{\text{R}}\Delta U_0^{\text{SO}} = \Delta U_0^{\text{SO}}(\text{NR}) - \Delta U_0^{\text{SO}}(\text{R})$ is very large at the HF level (195 kJ mol⁻¹ for AuF_4^-). To support this, configuration interaction (CI) calculations with single and double substitutions (CISD) for AuF_2^- and AuF_4^- at the relativistic as well as the nonrelativistic level of the theory have been carried out, the latter only at the calculated HF bond distances given in Table I.¹⁴ At the CISD and the size-consistency corrected level (CISDSC)⁶ both the nonrelativistic and relativistic D_{e} values for AuF_2^- were comparable to the calculated HF values. At the given HF bond distances for AuF_4^- $\Delta_{\text{R}}\Delta U_0 = 137.2$ kJ mol⁻¹ at the

CISDSC level, which is still significantly large (cf. Table I).

The preference of coordination number two in Au(I) halides is seen if we compare the two dissociation energies D_{e}^1 and D_{e}^2 given in Table II. Relativistic and spin-orbit effects increase the preference for this coordination number. Furthermore, the value of D_{e} for AuF_2^- suggests that this compound, the only example of the AuX_2^- series not currently known, should be a stable species if a suitable synthetic route can be developed.¹⁵ The Au(III) fluorine complex is the most stable found along the halide series. This is consistent with the fact that the only isolated Cu(III) and Ag(III) complexes are the fluorine complexes of the alkali metals, e.g., CsCuF_4 and CsAgF_4 ,¹⁶ both of which are more reactive than CsAuF_4 .¹⁶ Also, AuI_4^- has never been isolated¹ consistent with the negative ΔU_0^{SO} value calculated on the nonrelativistic and relativistic level of the theory. A detailed analyses will be the subject of a further paper in this series.

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Registry No. AuF_4^- , 43739-91-9; AuCl_4^- , 14337-12-3; AuBr_4^- , 14337-14-5; AuI_4^- , 14349-64-5; AuF_2^- , 55031-54-4; AuCl_2^- , 21534-24-7; AuBr_2^- , 23000-74-0; AuI_2^- , 23000-72-8.

(15) The counterion M^+ in MAuF_2 should not have a large M-F dissociation energy to avoid the disproportionation $3\text{MAuF}_2 \rightarrow \text{MAuF}_4 + 2\text{MF} + 2\text{Au}$.

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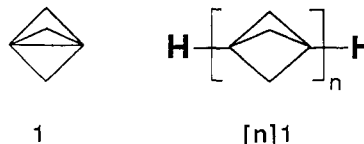
[n]Staffanes: The Parent Hydrocarbons

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Doubly end-functionalized [n]staffanes, the oligomers of [1.1.1]propellane (**1**), have been proposed for use as elements of a molecular-size "Tinkertoy" construction set.¹ The unsubstituted hydrocarbons [n]**1** represent important model compounds for investigations of the structure, vibrations, and electronic properties of these building elements, but only the first two, [1]**1**² and [2]**1**,³ have been known. We report the preparation and characterization of the individual oligomeric hydrocarbons up to $n = 6$ and of a mixture of higher polymers.



[n]Staffanes carrying groups X and Y at the bridgehead positions result from radical-induced addition of **1** across single X-Y bonds.^{1,3-5} The parent hydrocarbons have now been pre-

(7) For AuCl_4^- a basis set of 260 primitive Gaussians contracted to 157 basis functions was used producing a total number of 28 million two-electron integrals. A HF geometry optimization required about 40 h CPU time on an IBM3081 computer.

(8) Mulliken population analyses show that the gross orbital population of the Au(5d) orbital at the relativistic level in AuF is 9.92, in AuF_2^- 9.67, and in AuF_4^- 8.80.

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