

Combined use of DFT based Reactivity Indices and the Non- covalent Interactions Index in the Study of Intermolecular Interactions

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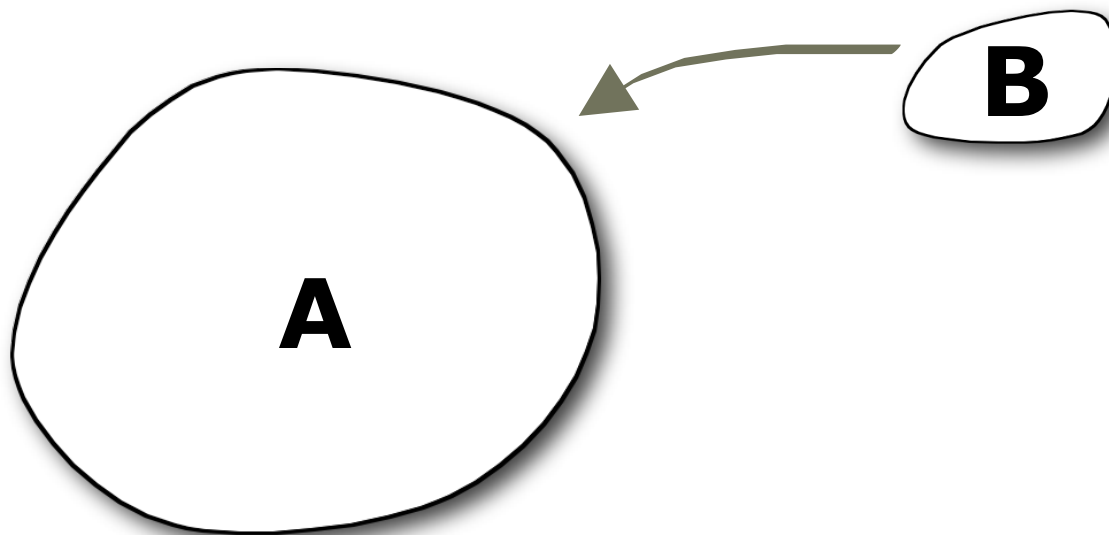
Vrije Universiteit Brussel

Outline

1. Introduction: Chemical Concepts from DFT
2. Divalent Compounds of Sn (Stannylenes): σ - and π -complexation
3. Halogen bonding: Hard and Soft Acids and Bases Perspective
4. Metallophilic Interactions in Dimers of N-Heterocyclic Carbene Copper, Silver and Gold Halides
5. Conclusions

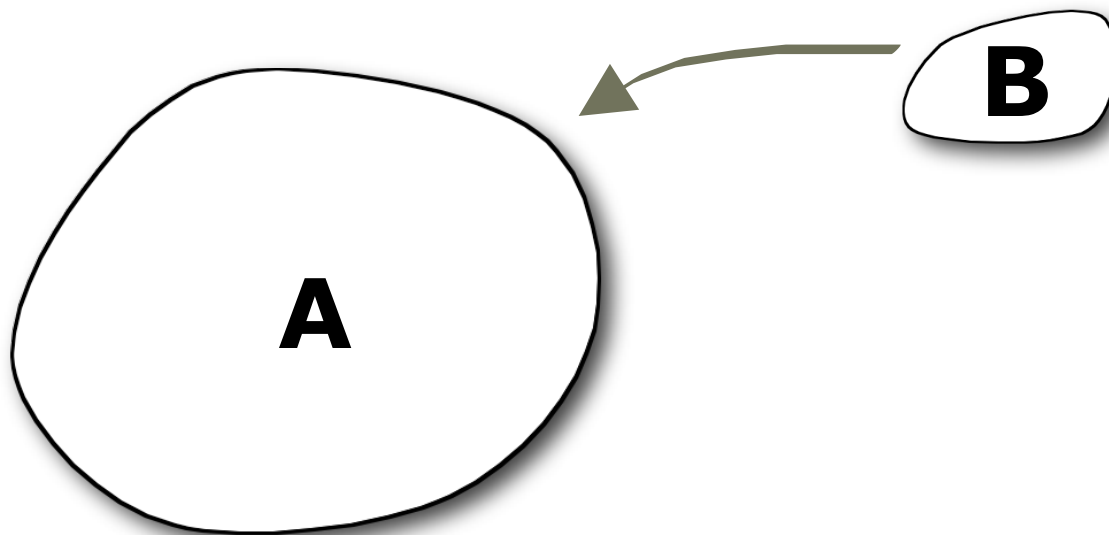
1. Introduction: Chemical Concepts from DFT

Chemical reactivity: Effects of attacking molecule B on molecule A



1. Introduction: Chemical Concepts from DFT

Chemical reactivity: Effects of attacking molecule B on molecule A



$$\begin{cases} N_A^0 \\ v_A^0 \end{cases} \longrightarrow \begin{cases} N_A^0 + \Delta N_A \\ v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r}) \end{cases}$$

Change of number of electrons and external potential of A

» Perturbations on the isolated molecule A: Modeling through Taylor series

- Initial stages of the chemical reaction (onset)

- Weak interactions

» Derivatives (response functions): interesting chemical quantities

$$\begin{aligned}
& E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] - E_A[N_A^0, v_A^0(\mathbf{r})] \\
&= \left(\frac{\partial E_A}{\partial N_A} \right)_{v_A} \Delta N_A + \frac{1}{2} \left(\frac{\partial^2 E_A}{\partial N_A^2} \right)_{v_A} (\Delta N_A)^2 + \dots \\
&+ \int \left[\frac{\delta E_A}{\delta v_A(\mathbf{r})} \right]_{N_A} \Delta v_A(\mathbf{r}) d\mathbf{r} + \int \left[\frac{\delta \partial E_A}{\delta v_A(\mathbf{r}) \partial N_A} \right] \Delta N_A \Delta v_A(\mathbf{r}) d\mathbf{r} + \dots \\
&+ \frac{1}{2} \int \int \left[\frac{\delta^2 E_A}{\delta v_A(\mathbf{r}) \delta v_A(\mathbf{r}')} \right]_{N_A} \Delta v_A(\mathbf{r}) \Delta v_A(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots
\end{aligned}$$

$$E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] - E_A[N_A^0, v_A^0(\mathbf{r})]$$

$$= \left(\frac{\partial E_A}{\partial N_A} \right)_{v_A} \Delta N_A + \frac{1}{2} \left(\frac{\partial^2 E_A}{\partial N_A^2} \right)_{v_A} (\Delta N_A)^2 + \dots$$

Electronic chemical potential $\mu_A = -$ electronegativity

$$+ \int \left[\frac{\delta E_A}{\delta v_A(\mathbf{r})} \right]_{N_A} \Delta v_A(\mathbf{r}) d\mathbf{r} + \int \left[\frac{\delta \partial E_A}{\delta v_A(\mathbf{r}) \partial N_A} \right] \Delta N_A \Delta v_A(\mathbf{r}) d\mathbf{r} + \dots$$

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\end{aligned}$$

$$E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] - E_A[N_A^0, v_A^0(\mathbf{r})]$$

$$= \left(\frac{\partial E_A}{\partial N_A} \right)_{v_A} \Delta N_A + \frac{1}{2} \left(\frac{\partial^2 E_A}{\partial N_A^2} \right)_{v_A} (\Delta N_A)^2 + \dots$$

chemical hardness η_A

$$+ \int \left[\frac{\delta E_A}{\delta v_A(\mathbf{r})} \right]_{N_A} \Delta v_A(\mathbf{r}) d\mathbf{r} + \int \left[\frac{\delta \partial E_A}{\delta v_A(\mathbf{r}) \partial N_A} \right] \Delta N_A \Delta v_A(\mathbf{r}) d\mathbf{r} + \dots$$

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&\quad \text{electron density } \rho_A(\mathbf{r}) \\
&+ \frac{1}{2} \int \int \left[\frac{\delta^2 E_A}{\delta v_A(\mathbf{r}) \delta v_A(\mathbf{r}')} \right]_{N_A} \Delta v_A(\mathbf{r}) \Delta v_A(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots
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Fukui function $f_A^\pm(\mathbf{r})$: electrophilic/nucleophilic reactivity

$$+ \frac{1}{2} \int \int \left[\frac{\delta^2 E_A}{\delta v_A(\mathbf{r}) \delta v_A(\mathbf{r}')} \right]_{N_A} \Delta v_A(\mathbf{r}) \Delta v_A(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots$$

$$\begin{aligned}
& E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] - E_A[N_A^0, v_A^0(\mathbf{r})] \\
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&+ \frac{1}{2} \int \int \left[\frac{\delta^2 E_A}{\delta v_A(\mathbf{r}) \delta v_A(\mathbf{r}')} \right]_{N_A} \Delta v_A(\mathbf{r}) \Delta v_A(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots
\end{aligned}$$

linear response function $\chi_A(\mathbf{r}, \mathbf{r}')$

$$\begin{aligned}
& E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] - E_A[N_A^0, v_A^0(\mathbf{r})] \\
&= \left(\frac{\partial E_A}{\partial N_A} \right)_{v_A} \Delta N_A + \frac{1}{2} \left(\frac{\partial^2 E_A}{\partial N_A^2} \right)_{v_A} (\Delta N_A)^2 + \dots \\
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\end{aligned}$$

Perturbational perspective on chemical reactivity

Ayers, P. W. ; Anderson, J. S. M. Bartolotti, L. J. *Int.J.Quantum Chem.* **2005**, 101, 520.

» Perturbation series : commonly truncated at second order :

$$\begin{aligned} E_A[N_A^0 + \Delta N_A, v_A^0(\mathbf{r}) + \Delta v_A(\mathbf{r})] &= E_A[N_A^0, v_A^0(\mathbf{r})] + \mu_A \Delta N_A + \eta_A (\Delta N_A)^2 \\ &+ \int \rho_A(\mathbf{r}) \Delta v_A(\mathbf{r}) d\mathbf{r} + \int f_A(\mathbf{r}) \Delta N_A \Delta v_A(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \chi_A(\mathbf{r}, \mathbf{r}') \Delta v_A(\mathbf{r}) \Delta v_A(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \end{aligned}$$

» However: sometimes also third order properties important:

$$f_A^2(\mathbf{r}) = \left(\frac{\partial f_A(\mathbf{r})}{\partial N_A} \right)_{v_A} = \left(\frac{\delta \eta_A}{\delta v_A(\mathbf{r})} \right)_{N_A}$$

- Dual descriptor

(Morell, C.; Grand, A.; Toro-Labbé, A *J. Phys. Chem. A* **2005**, *109*, 205.)

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(Morell, C.; Grand, A.; Toro-Labbé, A *J. Phys. Chem. A* **2005**, *109*, 205.)

- Rationalization of Woodward-Hoffmann rules for pericyclic reactions in DFT context

- De Proft, F.; Ayers, P.W.; Fias, S.; Geerlings, P. *J.Chem.Phys.* **2006**, *125*, 214101.
- Ayers, P.W.; C. Morell, C.; De Proft, F.; Geerlings, P. *Chem. Eur. J.* **2007**, *13*, 8240.
- De Proft, F.; Chattaraj, P. K.; Ayers, P. W.; Torrent-Sucarrat, M.; Elango, E.; Subramanian, V.; Giri, S.; Geerlings, P. *J.Chem. Theor. Comput.* **2008**, *4*, 595 (2008)
- Sablon, N.; De Proft, F.; Geerlings P. *Croat. Chem. Acta* **2009**, *82*, 157.
- Jaque, P.; Correa, J. V.; De Proft, F.; Toro-Labbé, A.; Geerlings, P. *Can. J. Chem.* **2010**, *88*, 858.
- Geerlings, P.; Ayers, P. W.; Toro-Labbé, A.; Chattaraj, P. K.; De Proft, F. *Acc. Chem. Res.* **2012**, *55*, 683.

Also : justification for a series of chemical principles :

- » Electronegativity Equalization Principle (Sanderson)
- » Hard and Soft Acids and Bases (HSAB) Principle (Pearson)
- » Maximum Hardness Principle (Pearson)

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Conceptual Density Functional Theory (R. G. Parr)

- (a) Parr, R. G. ; Yang, W. *Ann. Rev. Phys. Chem.* **1995**, 46, 701.
- (b) Kohn, W. ; Becke, A. D. ; Parr, R. G. *J. Phys. Chem.* **1996**, 100, 12974.
- (c) Geerlings, P. ; De Proft, F. ; Langenaeker, W. *Adv. Quant. Chem.* **1999**, 33, 303.
- (d) Chermette, H. *J. Comput. Chem.* **1999**, 20, 129.
- (e) Geerlings, P.; De Proft, F. ; Langenaeker, W. *Chem. Rev.* **2003**, 103, 1793.
- (f) Ayers, P. W. ; Anderson, J. S. M. ; Bartolotti, L. J. *Int. J. Quantum Chem.* **2005**, 101, 520.
- (g) Geerlings, P. ; De Proft, F. *Phys. Chem. Chem. Phys.* **2008**, 10, 3028
- (h) Liu, S. B. *Acta Phys. Chim. Sin.* **2009**, 25, 590.
- (i) Gazquez, J. L. *J. Mexican Chemical Soc.* **2008**, 52, 3.

» This talk: use of DFT reactivity concepts and complementary quantities to study intermolecular interactions

» **Charge transfer component (orbital interaction):**

- Global quantities: chemical potential, chemical hardness

$$\text{electrophilicity: } \omega = \frac{\mu^2}{2\eta}$$

- Local quantities: Fukui function, dual descriptor, local electrophilicity

$$\text{local softness: } s(\mathbf{r}) = Sf(\mathbf{r})$$

$$\text{Global softness: } S = \frac{1}{\eta}$$

(intermolecular comparison)

- Natural Orbitals for Chemical Valence (NOCV)

Natural Orbitals for Chemical Valence (NOCV)

» Constructed by diagonalization of deformation density matrix

» In the NOCV representation, the deformation density $\Delta\rho(\mathbf{r})$ can be expressed as:

$$\Delta\rho(\mathbf{r}) = \sum_{k=1}^{N/2} \nu_k [\Psi_k^2(\mathbf{r}) - \Psi_{-k}^2(\mathbf{r})] = \sum_{k=1}^{N/2} \Delta\rho_k(\mathbf{r})$$

Michalak, A.; Mitoraj, M.; Ziegler, T. J. *Phys. Chem. A* **2008**, *112*, 1933

Mitoraj, M; Michalak, A.; Ziegler, T. J. *Chem. Theor. Comput.* **2009**, *5*, 962.

» **Electrostatic component:**

- Molecular electrostatic potential (MEP):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Approximation to local hardness

Calculation of these quantities

$$\left[\frac{\partial Q}{\partial N} \right]_v$$

» Electronic chemical potential (- electronegativity):

$$\mu_A = -\chi_A = \left(\frac{\partial E_A}{\partial N_A} \right)_{v_A}$$

» Chemical hardness:

$$\eta_A = \left(\frac{\partial \mu_A}{\partial N_A} \right)_{v_A} = \left(\frac{\partial^2 E_A}{\partial N_A^2} \right)_{v_A}$$

» Fukui function:

$$f_A(\mathbf{r}) = \left[\frac{\delta \partial E_A}{\delta v_A(\mathbf{r}) \partial N_A} \right] = \left(\frac{\delta \mu_A}{\delta v_A(\mathbf{r})} \right)_{N_A} = \left(\frac{\partial \rho_A(\mathbf{r})}{\partial N_A} \right)_{v_A}$$

$$Q = E$$

» Perdew, Parr, Levy and Balduz : dependence of electronic energy E on the number of electrons N

Perdew, J. P. ; Parr, R. G. ; Levy, M. ; Balduz, Jr., J. L. *Phys. Rev. Lett.* **1982**, 49, 1691.

» Plot of E versus N : series of straight line segments, with derivative discontinuities at the integer values of N

» These manifest themselves as integer discontinuities in the exact exchange-correlation potential

» As a result, the exchange-correlation potentials on the electron deficient and electron abundant sides of the integer, denoted v_{XC}^- and v_{XC}^+ , respectively, will differ by some system-dependent positive constant Δ_{XC}

$$v_{XC}^+ - v_{XC}^- = \Delta_{XC}$$

» Using the fact that the E is linear with respect to N and Janak's theorem, the orbital energies of the $N-f$ and $N+f$ electron system become equal to the exact ground state vertical ionization energy and electron affinity respectively

$$\mu^- = \left. \frac{\partial E}{\partial N} \right|_{N-f} = \epsilon_N(N-f) = -I^0$$

where $0 < f < 1$

$$\mu^+ = \left. \frac{\partial E}{\partial N} \right|_{N+f} = \epsilon_{N+1}(N+f) = -A^0$$

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» In practical applications, one uses the average of both quantities as the estimate of the chemical potential of the system

$$\mu^0 = \frac{\mu^- + \mu^+}{2} = -\frac{I^0 + A^0}{2}$$

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» In practical applications, one uses the average of both quantities as the estimate of the chemical potential of the system

$$\mu^0 = \frac{\mu^- + \mu^+}{2} = -\frac{I^0 + A^0}{2}$$

» Since $\mu = -\chi$, this approximation reduces to the Mulliken definition for the electronegativity

» Within the ensemble approach, the hardness would be zero for non-integer N and undefined for integer values of the electron number

» One obtains values for this concept for integer N using a finite difference approximation of the chemical potentials μ^+ and μ^- , i.e.

$$\eta^0 \equiv \frac{1}{2}(\mu^+ - \mu^-) = \frac{1}{2}(-A^0 + I^0) = \frac{I^0 - A^0}{2}$$

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» these estimates can also be obtained by assuming a quadratic relationship between E and N , for which arguments can be given (Ayers et al.)

» Alternative, often used approximations :

$$\mu^0 \approx \frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2}$$

$$\eta^0 \approx \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2}$$

- originates from Koopmans' theorem
- use of Kohn-Sham HOMO and LUMO orbital energies

$$Q = \rho(\mathbf{r})$$

» PPLB also showed that the electron density entering the definition of the energy functional for a non-integer number of electrons is also an ensemble sum

$$\rho_{N+f} = (1 - f)\rho_N + f\rho_{N+1}$$

again with $0 < f < 1$

» The Fukui functions can thus be computed as

$$f_A^+(\mathbf{r}) = \rho_{A,N+1}(\mathbf{r}) - \rho_{A,N}(\mathbf{r}) \quad \text{nucleophilic attack}$$

$$f_A^-(\mathbf{r}) = \rho_{A,N}(\mathbf{r}) - \rho_{A,N-1}(\mathbf{r}) \quad \text{electrophilic attack}$$

» Recently: analytic evaluation

Yang, W.; Cohen, A. J.; De Proft, F.; Geerlings, P. *J. Chem. Phys.* **2012**, *136*, 144110.

Fukui function :

» Nucleophilic attack :
$$f_A^+(\mathbf{r}) = \left(\frac{\partial \rho_A(\mathbf{r})}{\partial N} \right)_v^+ = \rho_{A,N+1}(\mathbf{r}) - \rho_{A,N}(\mathbf{r})$$

Condensed Fukui function (on atom k):

$$f_{A,k}^+ = N_{A,N+1,k} - N_{A,N,k}$$

Frontier MO approximation (no orbital relaxation)

$$f_A^+(\mathbf{r}) \cong \left| \phi_{LUMO,A}(\mathbf{r}) \right|^2$$

» Electrophilic attack : $f_A^-(\mathbf{r}) = \left(\frac{\partial \rho_A(\mathbf{r})}{\partial N} \right)_v^- = \rho_{A,N}(\mathbf{r}) - \rho_{A,N-1}(\mathbf{r})$

Condensed Fukui function (on atom k):

$$f_{A,k}^- = N_{A,N,k} - N_{A,N-1,k}$$

Frontier MO approximation (no orbital relaxation)

$$f_A^-(\mathbf{r}) \cong \left| \phi_{HOMO,A}(\mathbf{r}) \right|^2$$

Local softness: $s^-(\mathbf{r}) = S f^-(\mathbf{r})$

$$s^+(\mathbf{r}) = S f^+(\mathbf{r})$$

Local electrophilicity: $\omega(\mathbf{r}) = \omega f^+(\mathbf{r})$

Non-covalent interaction index

» Plots of reduced density gradient s vs. electron density

$$s = \frac{1}{(2(3\pi^2)^{1/3})} \frac{|\nabla\rho|}{\rho^{4/3}}$$

» Weakly bound complex: signal in low gradient-low density region

» Distinguishing interaction types: eigenvalues of electron density Hessian (Laplacian):

$$\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3 \quad (\lambda_1 \leq \lambda_2 \leq \lambda_3)$$

» Sign of λ_2 : bonded ($\lambda_2 < 0$) vs. nonbonded interactions ($\lambda_2 > 0$)

Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-Garcia, J.; Cohen, A.; Yang, W. *J. Am. Chem. Soc.* **2010**, *132*, 6498.

Complexation energies

» BSSE corrected MP2 interaction energies

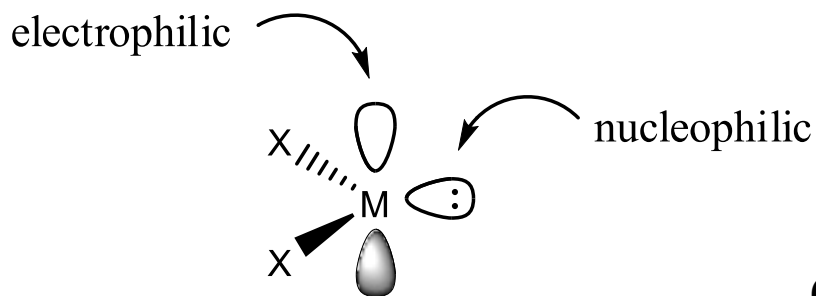
» DFT interaction energies (+ empirical dispersion correction)

» Ziegler-Rauk type energy decomposition: $\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$

with:
$$\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elec}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$$

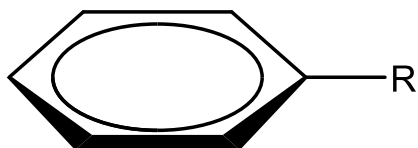
2. Divalent compounds of Sn (stannylenes): σ - and π -complexation

» Singlet stannylenes: complexation by σ - or π - donors



Central metal M = Sn

Substituents -X = -F, -Cl, -Br or -I



» Strength of the σ - vs. (possible ?) π -complexations

» Correlation with molecular properties: electrophilicity of M

Reactivity indices (1)

» Global electrophilicities ω and nucleophilicities ω^- (kcal mol⁻¹)

molecule	ω	ω^-	molecule	ω	ω^-
GeI ₂	46.5	4.9			
GeBr ₂	44.9	4.6	SnBr ₂	45.2	4.7
GeCl ₂	43.6	4.4	SnCl ₂	44.4	4.5
GeF ₂	41.1	3.8	SnF ₂	42.0	4.1
GeH ₂	39.3	5.3	SnH ₂	37.9	5.8
Ge(CH ₃) ₂	29.0	7.2	Sn(CH ₃) ₂	30.0	7.2
Ge(OCH ₃) ₂	27.6	6.9	Sn(OCH ₃) ₂	29.7	6.8

- Most electrophilic: halogenated compounds
- Sequence: (I) > Br > Cl > F

Reactivity indices (2)

» Local electrophilicities on the metal center k : ω_k^-

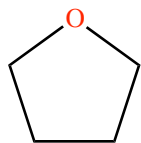
molecule	atom k	ω_k^+	molecule	atom k	ω_k^+
GeI ₂	Ge	30.0	SnBr ₂	Sn	35.6
	I	8.3		Br	4.8
GeBr ₂	Ge	32.0	SnCl ₂	Sn	37.3
	Br	6.5		Cl	3.6
GeCl ₂	Ge	34.0	SnF ₂	Sn	39.7
	Cl	4.8		F	1.1
GeF ₂	Ge	37.7	SnH ₂	Sn	39.9
	F	1.7		H	-1.0
GeH ₂	Ge	41.0	Sn(CH ₃) ₂	Sn	26.1
	H	-0.8		C	-0.9
Ge(CH ₃) ₂	Ge	24.0	Sn(OCH ₃) ₂	Sn	25.7
	C	-0.9		O	0.4
	H*	1.1		C	-0.2
Ge(OCH ₃) ₂	Ge	22.8		H*	0.6
	O	0.9			
	C	-0.2			
	H*	0.6			

» Halogenated compounds still most electrophilic but F > Cl > Br (> I)

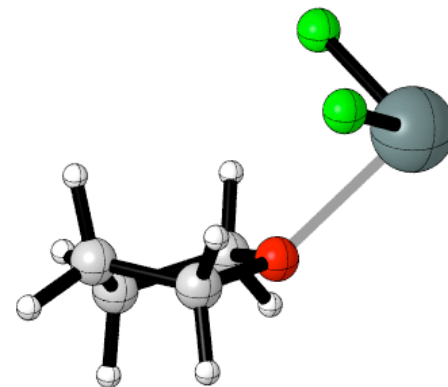
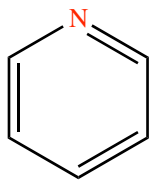
Complexation energies (1)

» Some selected complexation energies of most electrophilic species SnF_2

σ -complexations (kcal mol^{-1}):

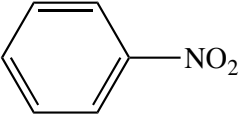
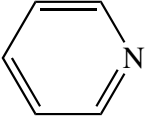
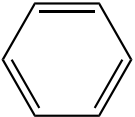
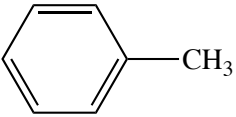
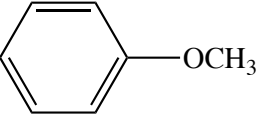
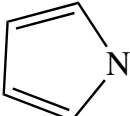


Lewis base	$\Delta E_{\text{complexation}}$
THF	-16.4
Pyridine	-19.4



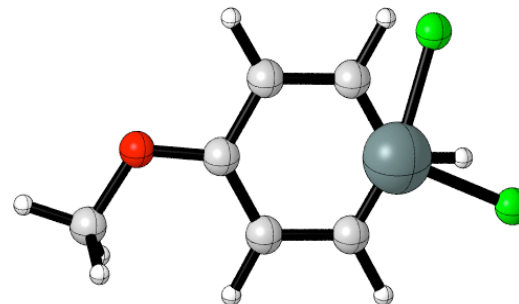
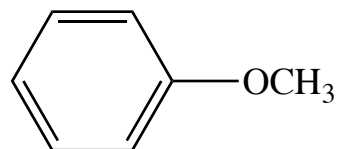
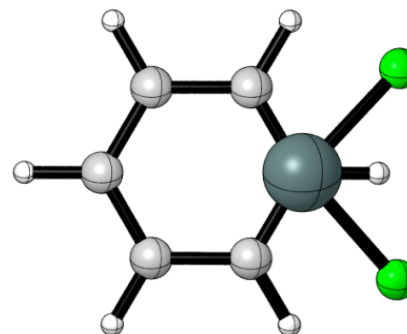
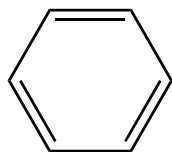
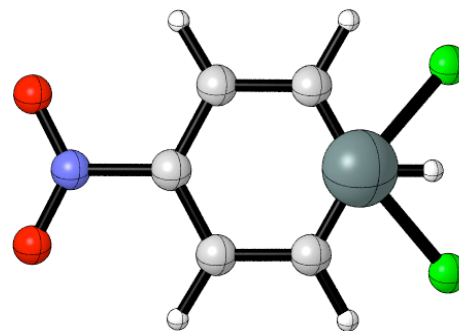
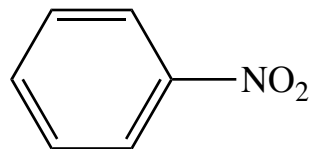
Complexation energies (2)

π -complexations:
(kcal mol⁻¹)

	Lewis base	$\Delta E_{\text{complexation}}$
	Nitrobenzene	-0.8
	Pyridine	-2.8
	Benzene	-4.4
	Toluene	-4.8
	Anisole	-5.0
	Pyrrole	-7.4

Geometries

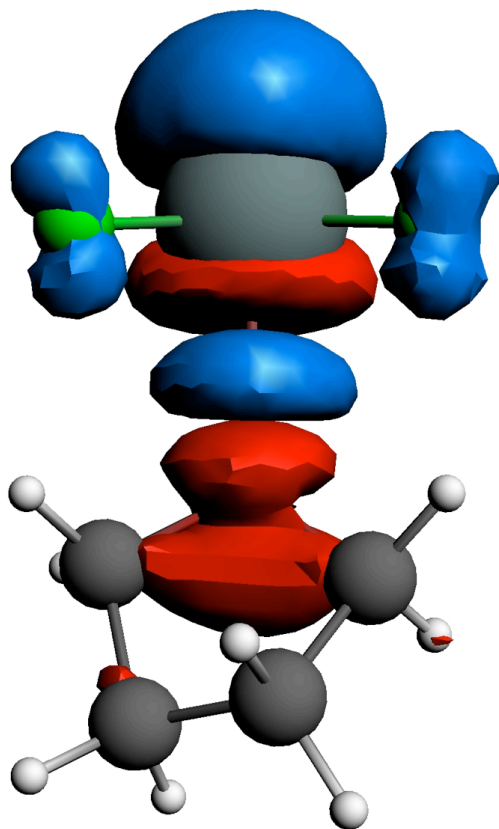
» π -complex geometries:



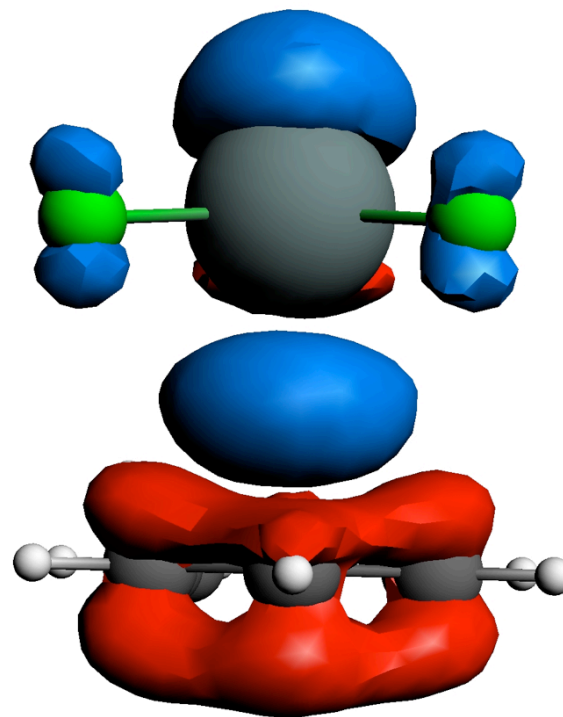
Broeckaert, L.; Geerlings, P.; Růžička, A.; Willem, R.; De Proft, F. *Organometallics* **2012**, *31*, 1605.

Natural Orbitals for Chemical Valence (NOCV)

SnF₂...THF



SnF₂...anisole



■ $\Delta\rho < 0$
■ $\Delta\rho > 0$

Broeckaert, L.; Frenking, G.; De Proft, F., in preparation

Energy contributions (kcal mol⁻¹)

Lewis base	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}	ΔE
THF	49.8	-42.3 (64)	-24.1 (36)	-16.5	-15.2
Anisole	22.1	-15.6 (55)	-13.1 (45)	-6.6	-6.2

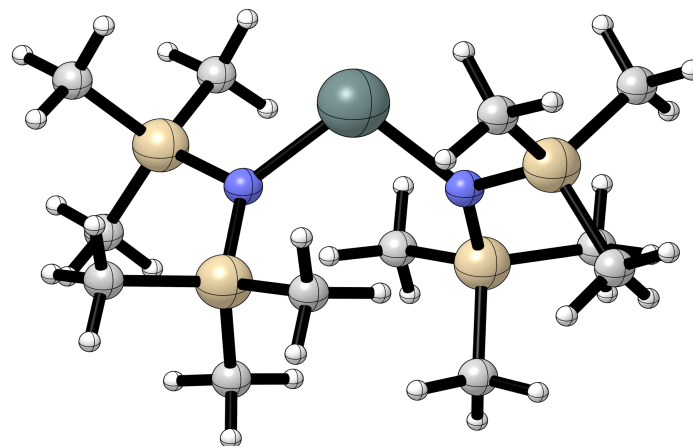
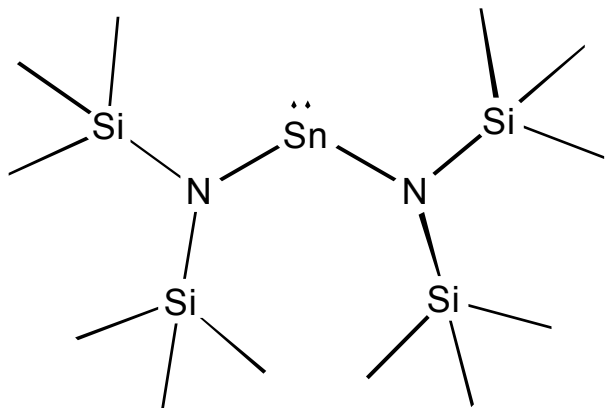
» Orbital interaction contributions:

Lewis base	% σ	% π	% rest
THF	69	23	8
Anisole	0	74	26

Broeckert, L.; Frenking, G.; De Proft, F., in preparation

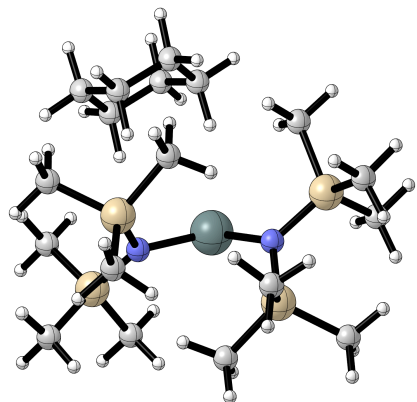
Experimental evidence for π -complexation: NMR chemical shifts

» Stannylene: $\text{Sn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$ (Lappert)

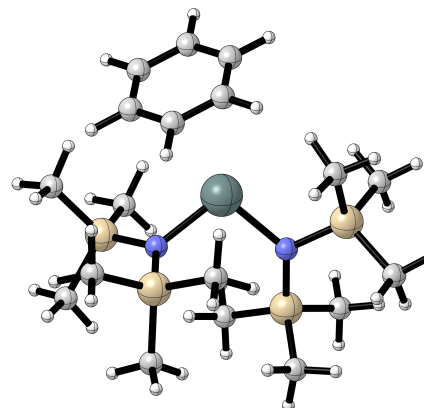


» Measurement & computation of ^{119}Sn chemical shifts in different solvents

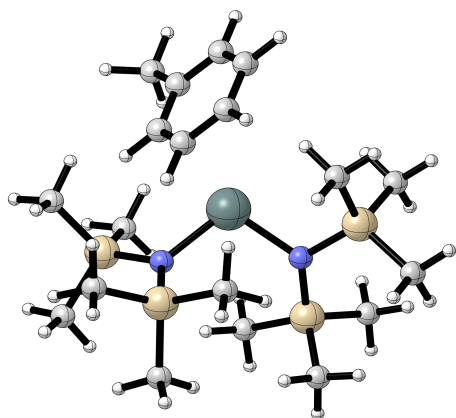
Geometries of 1/1 Sn{N[Si(CH₃)₃]₂}-solvent(donor) complexes



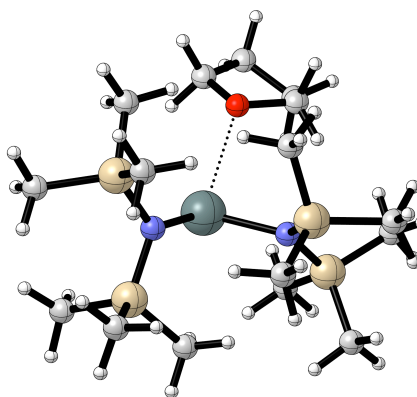
Sn{N[Si(CH₃)₃]₂}-cyclohexane



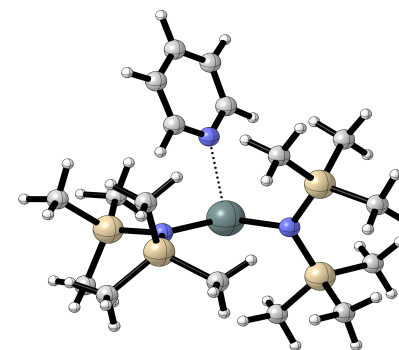
Sn{N[Si(CH₃)₃]₂}-benzene



Sn{N[Si(CH₃)₃]₂}-toluene



Sn{N[Si(CH₃)₃]₂}-THF



Sn{N[Si(CH₃)₃]₂}-pyridine

Calculated and experimental ^{119}Sn chemical shifts of $\text{Sn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}$

$\delta^{119}\text{Sn}/\text{ppm}$			
Solvent (donor)	A	B	Exptl
cyclohexane- d_{12}	677	794	779
benzene- d_6	641	740	767
toluene- d_8	645	758	770
THF- d_8	397	440	602
pyridine- d_5	130	96	145

A: calculated ^{119}Sn NMR chemical shifts (in ppm) of optimized 1/1 stannylene-donor complexes

B: calculated ^{119}Sn NMR chemical shifts (in ppm) of the optimized 1/1 stannylene-donor complexes in a COSMO solvent model with the corresponding dielectric constant of the donor (solvent) molecule

Broeckaert, L.; Turek, J.; Olejník, R.; Růžička, A.; Biesemans, M.; Geerlings, P.; Willem, R.; De Proft, F. *Organometallics* **2013**, *32*, 2121.

Calculated and experimental ^{119}Sn chemical shifts of $\text{Sn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}$

$\delta^{119}\text{Sn}/\text{ppm}$			
Solvent (donor)	A	B	Exptl
cyclohexane- d_{12}	677	794	779
benzene- d_6	641	740	767
toluene- d_8	645	758	770
THF- d_8	397	440	602
pyridine- d_5	130	96	145

**Highest chemical shift:
nondonating solvent**

A: calculated ^{119}Sn NMR chemical shifts (in ppm) of optimized 1/1 stannylene-donor complexes

B: calculated ^{119}Sn NMR chemical shifts (in ppm) of the optimized 1/1 stannylene-donor complexes in a COSMO solvent model with the corresponding dielectric constant of the donor (solvent) molecule

Broeckaert, L.; Turek, J.; Olejník, R.; Růžička, A.; Biesemans, M.; Geerlings, P.; Willem, R.; De Proft, F. *Organometallics* **2013**, *32*, 2121.

Calculated and experimental ^{119}Sn chemical shifts of $\text{Sn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}$

$\delta^{119}\text{Sn}/\text{ppm}$			
Solvent (donor)	A	B	Exptl
cyclohexane- d_{12}	677	794	779
benzene- d_6	641	740	767
toluene- d_8	645	758	770
THF- d_8	397	440	602
pyridine- d_5	130	96	145



**Important upfield shift:
 σ -complexation**

A: calculated ^{119}Sn NMR chemical shifts (in ppm) of optimized 1/1 stannylene-donor complexes

B: calculated ^{119}Sn NMR chemical shifts (in ppm) of the optimized 1/1 stannylene-donor complexes in a COSMO solvent model with the corresponding dielectric constant of the donor (solvent) molecule

Broeckaert, L.; Turek, J.; Olejník, R.; Růžička, A.; Biesemans, M.; Geerlings, P.; Willem, R.; De Proft, F. *Organometallics* **2013**, *32*, 2121.

Calculated and experimental ^{119}Sn chemical shifts of $\text{Sn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}$

$\delta^{119}\text{Sn}/\text{ppm}$			
Solvent (donor)	A	B	Exptl
cyclohexane- d_{12}	677	794	779
benzene- d_6	641	740	767
toluene- d_8	645	758	770
THF- d_8	397	440	602
pyridine- d_5	130	96	145



**Smaller upfield shift:
weak π -complexation**

A: calculated ^{119}Sn NMR chemical shifts (in ppm) of optimized 1/1 stannylene-donor complexes

B: calculated ^{119}Sn NMR chemical shifts (in ppm) of the optimized 1/1 stannylene-donor complexes in a COSMO solvent model with the corresponding dielectric constant of the donor (solvent) molecule

Broeckaert, L.; Turek, J.; Olejník, R.; Růžička, A.; Biesemans, M.; Geerlings, P.; Willem, R.; De Proft, F. *Organometallics* **2013**, *32*, 2121.

3. Halogen Bonding: HSAB Perspective

» Interaction between a halogen atom (Lewis acid) and a Lewis Base:



A: Electron withdrawing group (Acceptor)

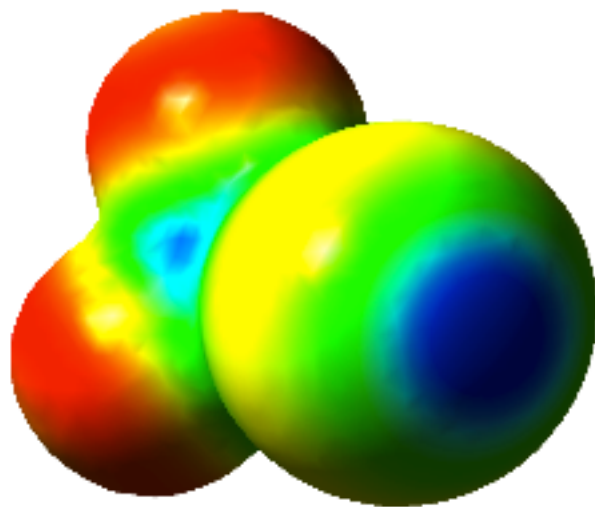
X: Halogen

D: Lewis base (Donor)

» cf. Hydrogen bonding: $A - H \cdots D$

» Applications in many fields such as e.g. supramolecular chemistry, ...

» Fundamental characteristics: σ -hole electrostatic potential

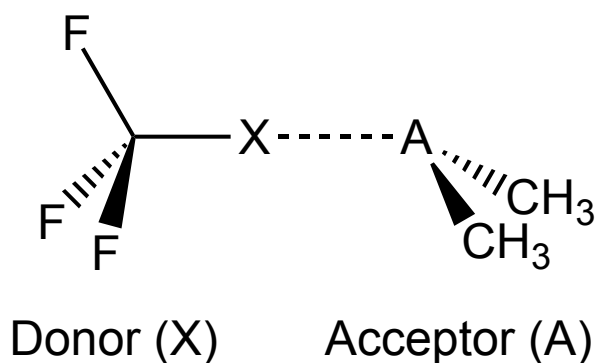


CF₃I

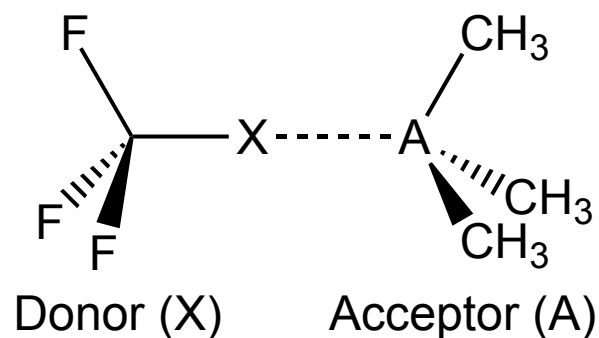
» Also: charge transfer contribution to interaction energy

» This study: importance of electrostatic (hard) and orbital overlap contributions (soft)

» Analysis of different halogen bonded complexes with varying softness of donor and acceptor atoms:



X = Cl, Br, I
A = O, S
(DME, DMS)



X = Cl, Br, I
A = N, P
(TMA, TMP)

Interaction energies/kJ mol⁻¹

	ΔE_{DFT}	ΔE_{MP2}	$\Delta H^{\circ}_{\text{calc}}(\text{LNg})$	$\Delta H^{\circ}_{\text{exp}}(\text{LNg})$
CF ₃ Cl·DME	-12.4	-11.2	-5.1	-6.3(3)
CF ₃ Br·DME	-17.6	-16.1	-11.1	-10.2(1)
CF ₃ I·DME	-24.0	-21.5	-17.6	-15.5(1)
CF ₃ Cl·DMS	-13.7	-11.2	-4.0	n.a.
CF ₃ Br·DMS	-20.8	-16.5	-9.4	-9.5(5)
CF ₃ I·DMS	-30.8	-23.0	-15.2	-17.4(1)
CF ₃ Cl·TMA	-18.9	-15.2	-7.0	-8.9(2)
CF ₃ Br·TMA	-30.2	-25.0	-18.6	-18.3(1)
CF ₃ I·TMA	-44.0	-37.1	-31.9	-28.7(1)
CF ₃ Cl·TMP	-11.8	-8.9		
CF ₃ Br·TMP	-20.7	-15.0		
CF ₃ I·TMP	-35.4	-23.3		

ΔE_{DFT} : PBE(ZORA)/TZ2P//MP2/aug-cc-pVDZ(-PP) + Grimme dispersion correction

ΔE_{MP2} : MP2/aug-cc-pVTZ(-PP)//MP2/aug-cc-pVDZ(-PP)

$\Delta H^{\circ}_{\text{calc}}(\text{LNg})$ ΔE_{MP2} + Monte Carlo Free Energy Perturbation calculations coupled with statistical thermodynamics

Reactivity indices

	A [eV]	I [eV]	S [1/eV]	$q(X)$	$f^+(X)$	$s^+(X)$
CF ₃ Cl	-2.942	13.131	0.062	-0.016	0.956	0.060
CF ₃ Br	-1.822	12.044	0.072	0.020	0.947	0.068
CF ₃ I	-0.603	10.812	0.088	0.038	0.935	0.082
	A [eV]	I [eV]	S [1/eV]	$q(A)$	$f(A)$	$s^-(A)$
DME	-0.669	10.542	0.089	-0.337	0.497	0.044
DMS	-0.862	8.807	0.103	-0.221	0.693	0.072
TMA	-0.640	8.838	0.106	-0.330	0.719	0.076
TMP	-0.642	8.639	0.108	-0.263	1.005	0.108

Decomposition of DFT Interaction energies/kJ mol⁻¹

	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{disp}	ΔE_{DFT}
CF ₃ Cl·DME	14.1	-15.4 (66)	-7.2 (34)	-5.0	-12.4
CF ₃ Br·DME	24.6	-24.1 (66)	-12.7 (34)	-5.4	-17.6
CF ₃ I·DME	38.0	-35.9 (64)	-20.3 (36)	-5.7	-24.0
CF ₃ Cl·DMS	14.9	-13.4 (58)	-9.7 (42)	-5.4	-13.7
CF ₃ Br·DMS	28.0	-24.2 (56)	-18.7 (44)	-5.8	-20.8
CF ₃ I·DMS	47.2	-39.1 (54)	-32.9 (46)	-6.0	-30.8
CF ₃ Cl·TMA	27.3	-25.9 (65)	-14.1 (35)	-6.2	-18.9
CF ₃ Br·TMA	58.6	-51.0 (63)	-29.9 (37)	-7.8	-30.2
CF ₃ I·TMA	102.3	-85.1 (62)	-52.3 (38)	-8.8	-44.0
CF ₃ Cl·TMP	11.3	-12.8 (64)	-7.1 (36)	-3.2	-11.8
CF ₃ Br·TMP	27.0	-26.2 (60)	-17.4 (40)	-4.1	-20.7
CF ₃ I·TMP	59.1	-50.9 (57)	-38.7 (43)	-4.9	-35.4

» Increasing importance of orbital interaction with increasing polarizability (softness) of donor and acceptor atoms

Orbital interaction through orbital σ -hole

Fukui function

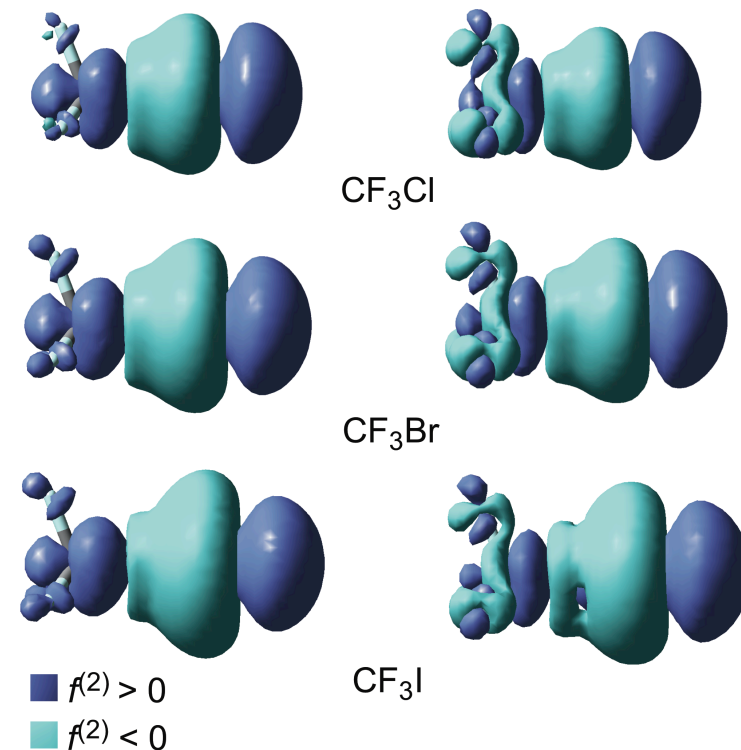
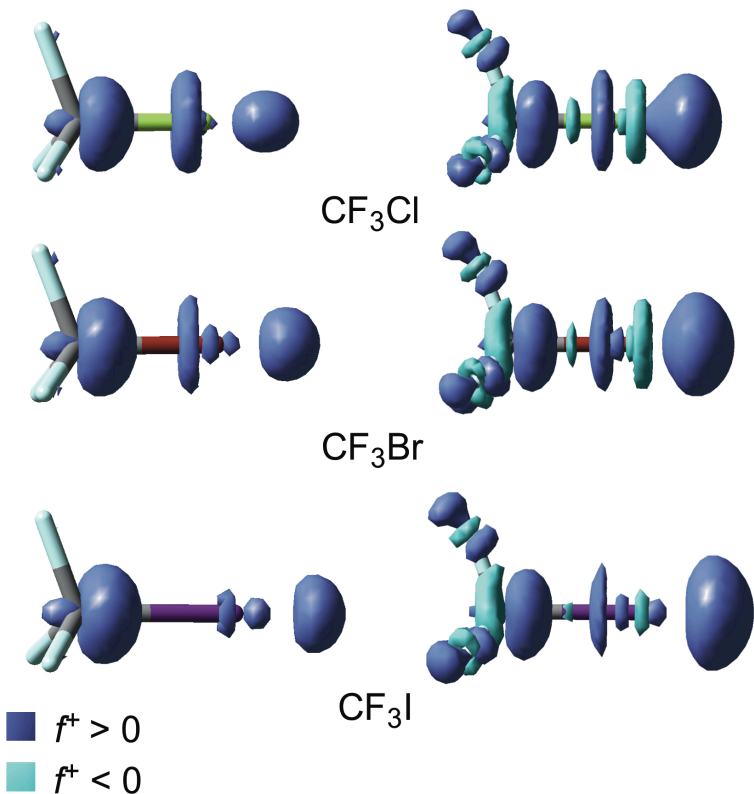
Dual descriptor

orbital based

finite diff. appr.

finite diff. appr.

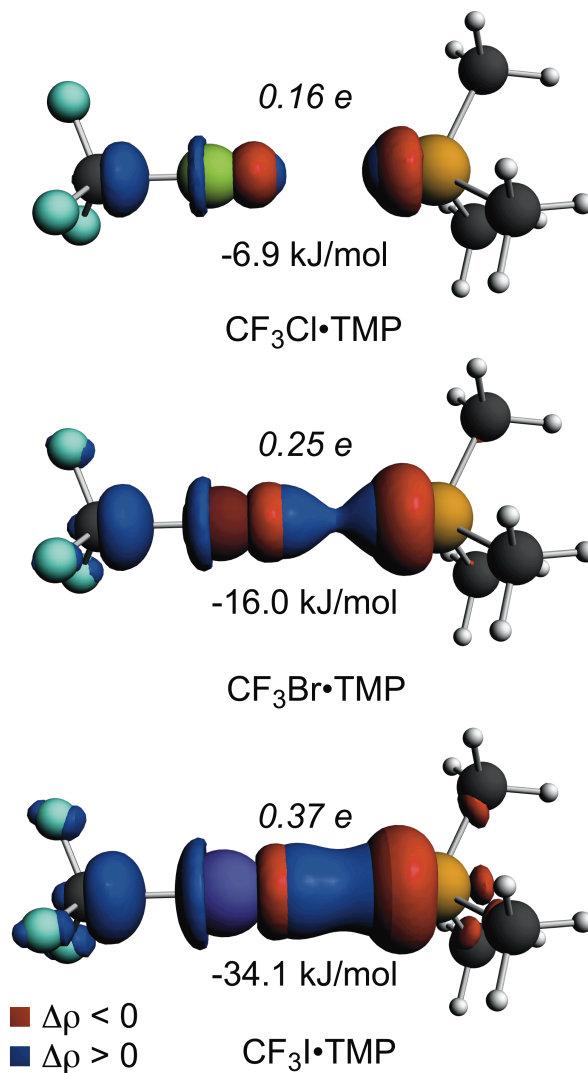
orbital based



» Both functions indicate an 'orbital σ -hole' – strongly directional

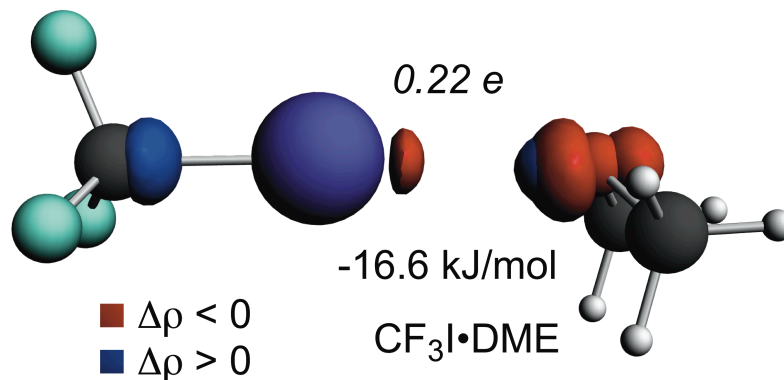
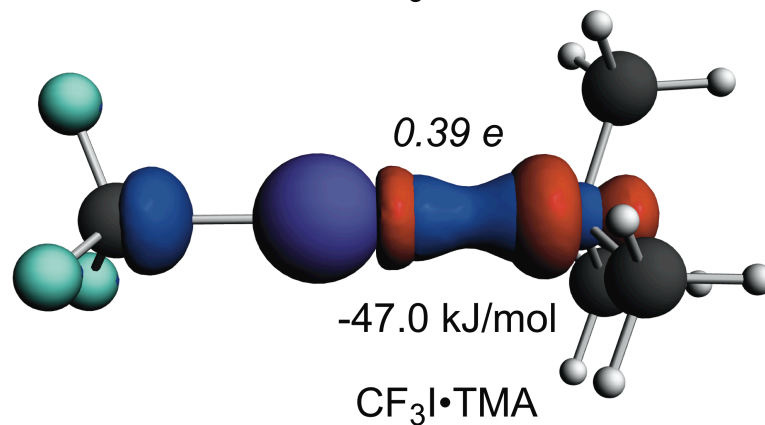
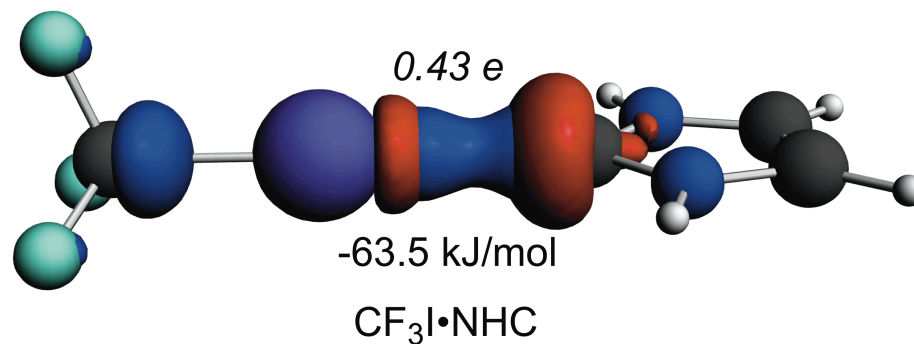
Pinter, B.; Nagels, N.; Herrebout, W. A. De Proft, F. *Chem. Eur. J.* **2013**, *19*, 519.

Natural Orbitals for Chemical Valence (NOCV) (1)

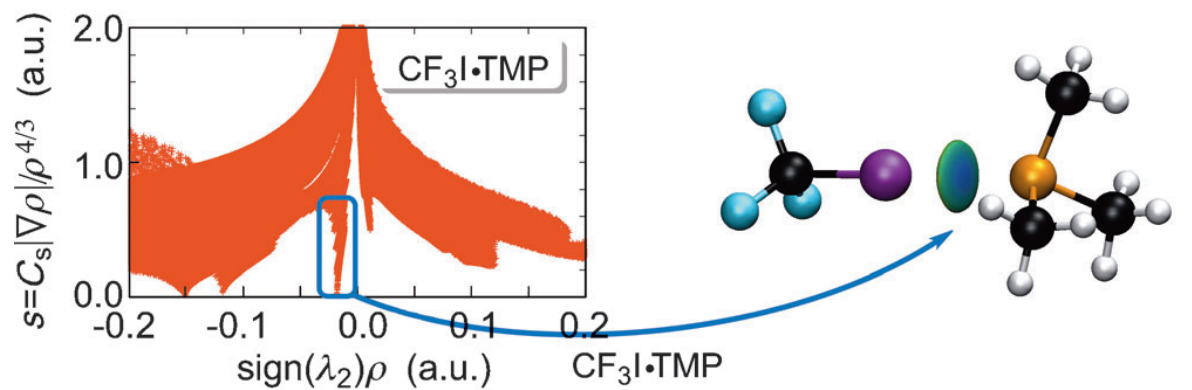
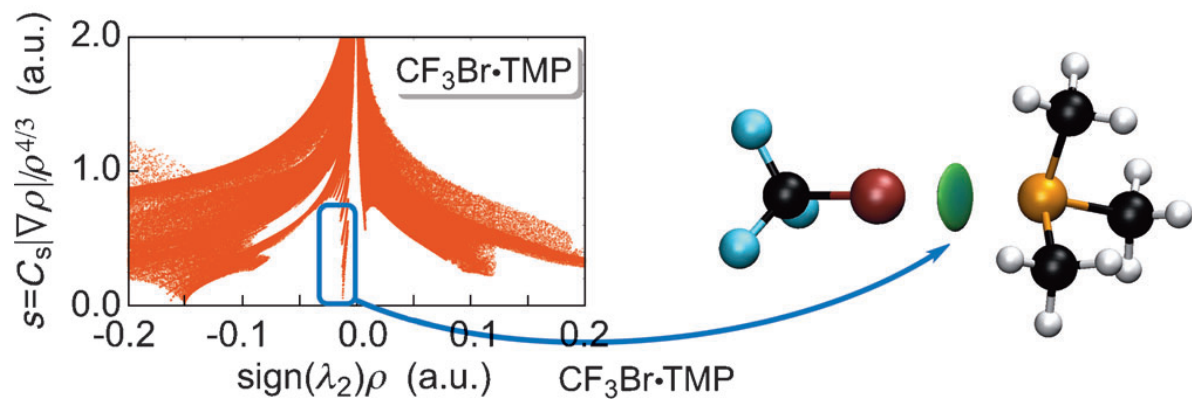
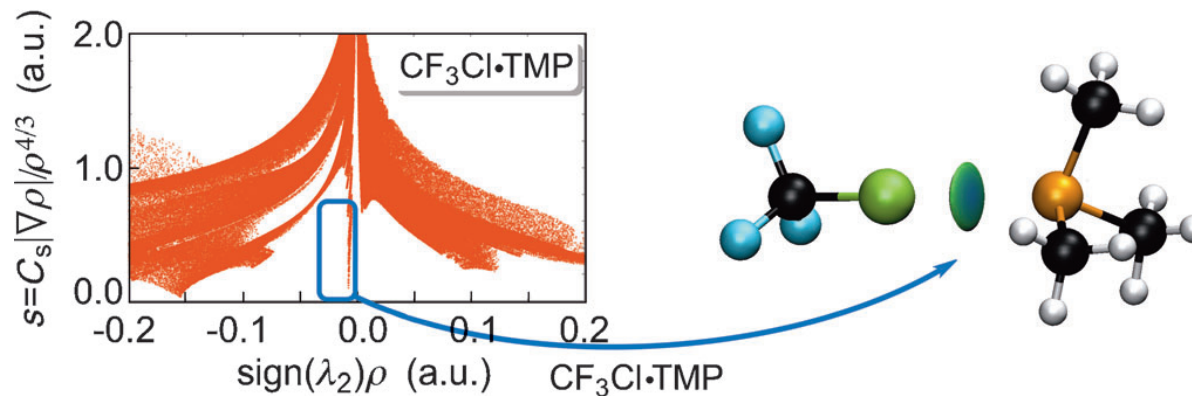


» Orbital interaction: $n \rightarrow \sigma^*$

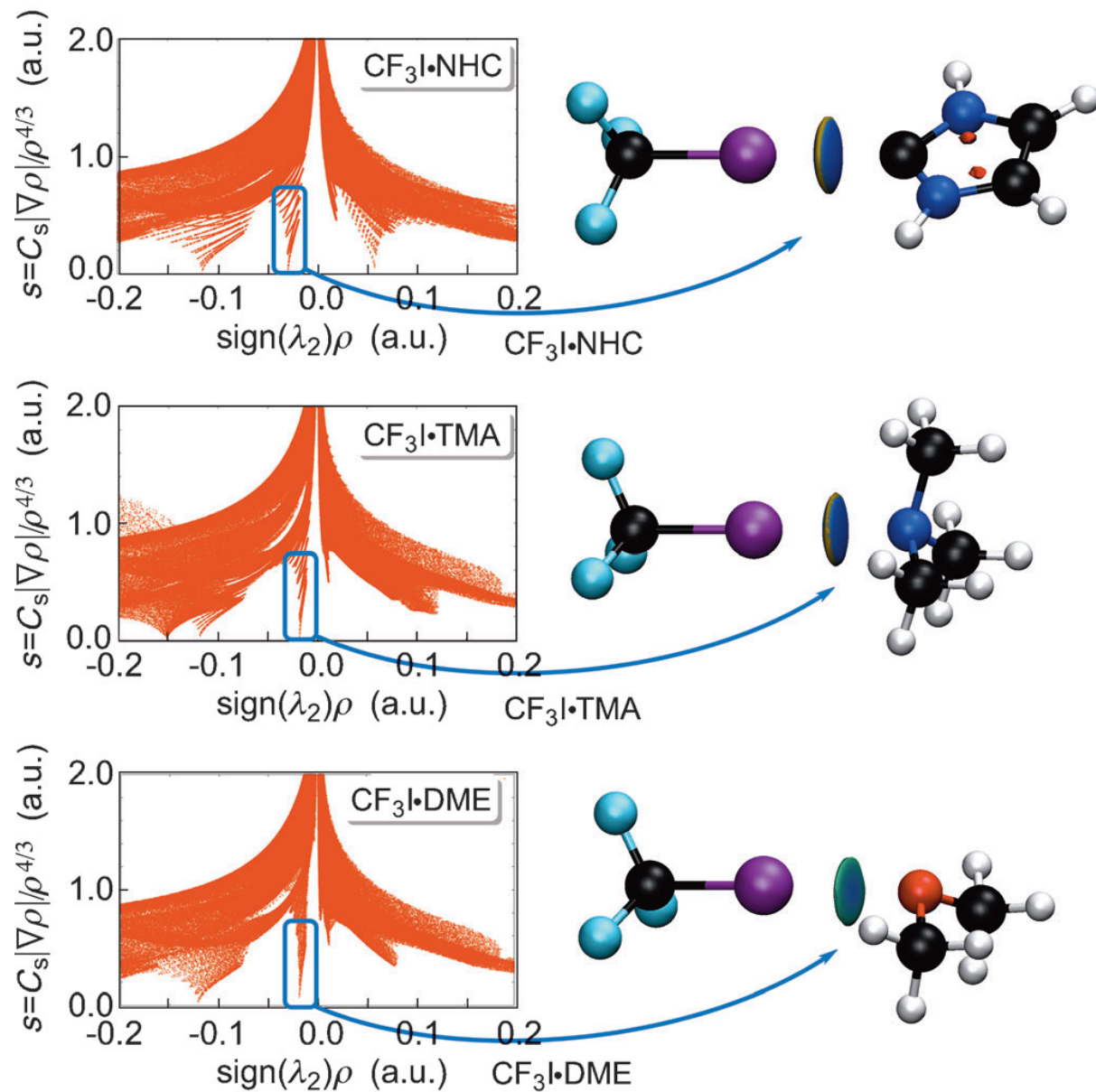
Natural Orbitals for Chemical Valence (NOCV) (2)



NCI index (1)



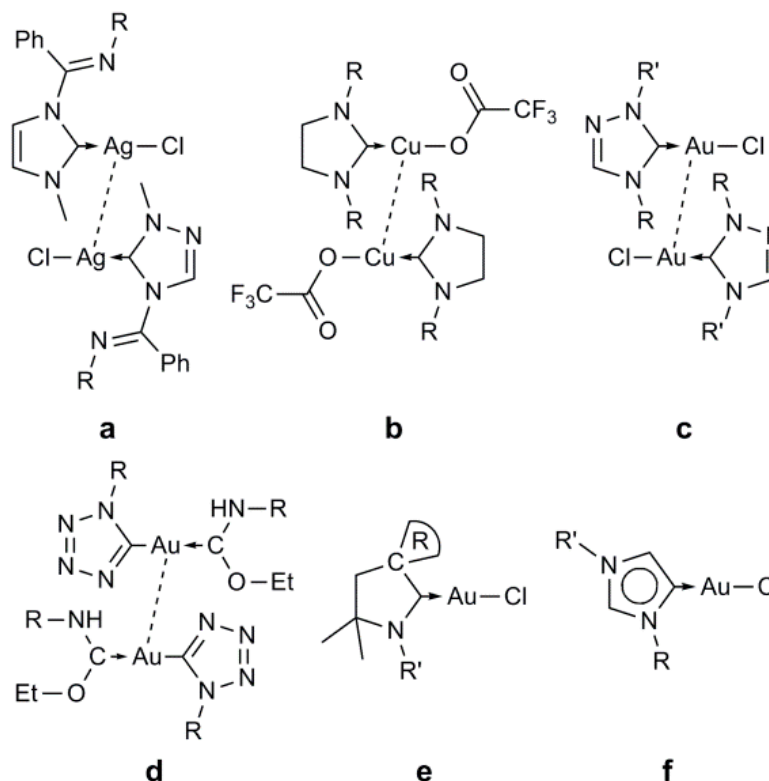
NCI index (2)



3. Metallophilic Interactions in Dimers of N-Heterocyclic Carbene Copper, Silver and Gold Halides

- » Past two decades: strong new impulses in chemistry of coinage metals (especially gold)
- » Often: N-heterocyclic carbenes used as stabilizing ligands

» Representative examples:



» Metallophilic contacts

» Metallophilic attraction: predominantly dispersion driven interaction between closed shell monomers, containing gold or other metals

Muniz, J.; Wang, C.; Pykkö, P. *Chem. Eur. J.* **2011**, *17*, 368 and references therein.

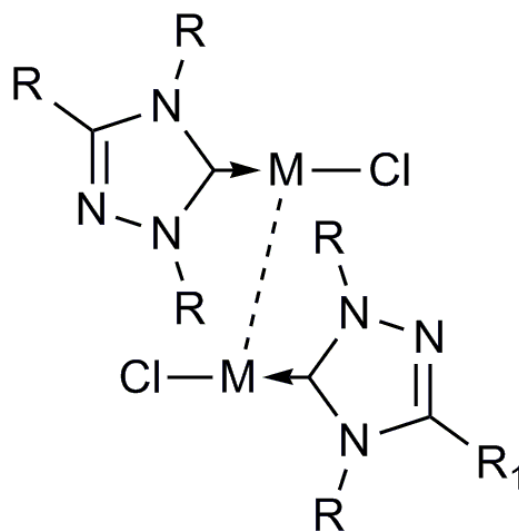
» Auophilic interaction: $\text{Au}^{\text{I}} \cdots \text{Au}^{\text{I}}$ closed shell interaction

» Many theoretical studies on these interaction have been performed

» Our approach: theoretical analysis of different NHC-coinage metal complexes

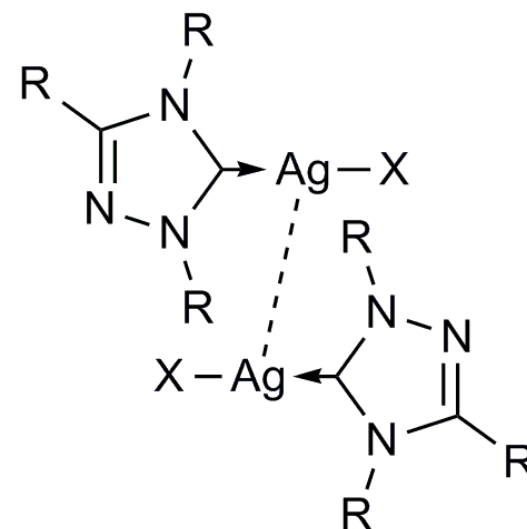
» Use of various electron density based techniques

» Systems investigated:



M = Cu, Ag, Au

a

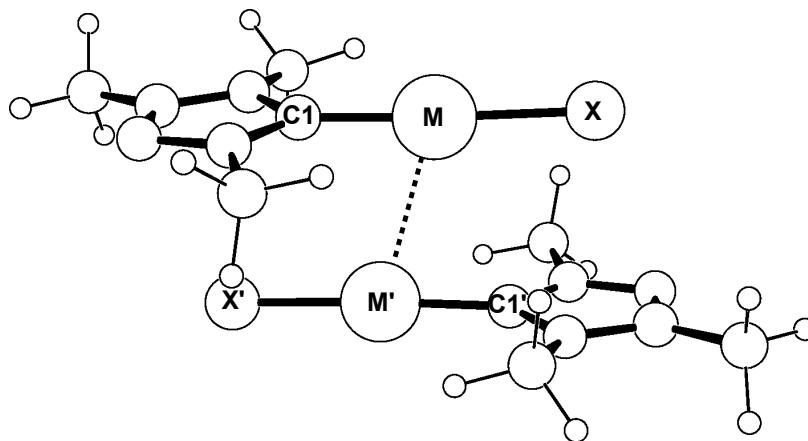


X = F, Cl, Br, I

b

Geometries

» MP2/aug-cc-pVDZ(-PP) geometries



» Head-to-tail arrangement

» M-M distances: cuprophilic, argentophilic and aurophilic interactions

» $[(\text{NHC})\text{AuCl}]_2$: good agreement with crystal structure

» Secondary interaction: Halogen X \leftrightarrow carbene ring

Dimerization energies (1)

» MP2/aug-cc-pVTZ(-PP)//MP2/aug-cc-pVDZ(-PP); values in kcal mol⁻¹
(influence of solvent: PCM)

Dimer	ΔE_{dim}	ΔG_{dim}	$\Delta G_{\text{dim}}^{\text{sol}}$
$[(\text{NHC})\text{CuCl}]_2$	-19.7	-4.2	+2.5
$[(\text{NHC})\text{AgCl}]_2$	-24.8	-8.8	+0.0
$[(\text{NHC})\text{AuCl}]_2$	-24.9	-11.1	-4.4

» Argentophilic and aurophilic interactions comparable strengths

» Interaction between Cu-based fragments: weaker

DFT Dimerization energies and components

» ZORA PBE/TZ2P+ (and D3 for dispersion)

Dimer	ΔE_{disp}	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}	ΔE_{prep}	ΔE
$[(\text{NHC})\text{CuCl}]_2$	-9.4 (22)	+23.4	-24.1 (56)	-9.3 (22)	-19.5	+1.0	-18.5
$[(\text{NHC})\text{AgCl}]_2$	-10.4 (17)	+39.4	-38.1 (61)	-13.5 (22)	-22.6	+1.6	-21.0
$[(\text{NHC})\text{AuCl}]_2$	-19.7 (17)	+45.8	-39.7 (61)	-13.9 (22)	-18.7	+1.5	-17.2

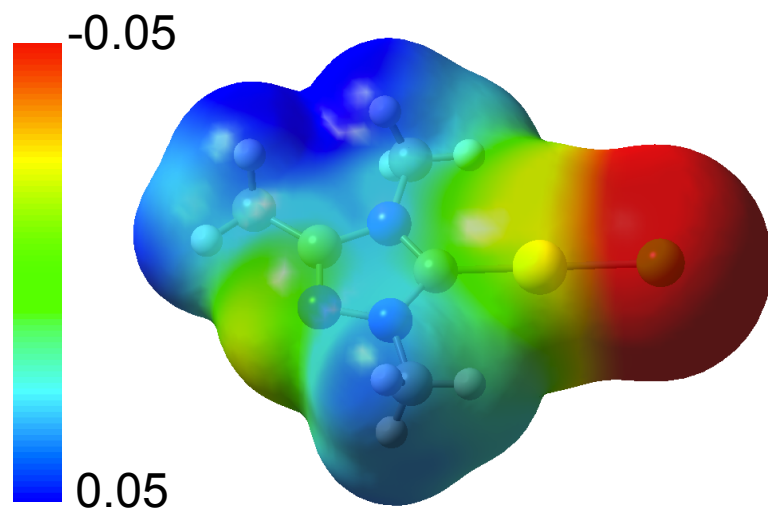
» Dominance of electrostatics

» Dispersion and orbital interaction approximately equal in weight

Electrostatic interaction (hard-hard interactions)

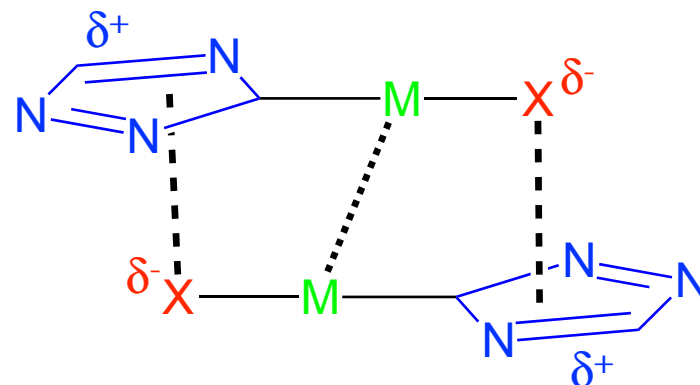
» Importance: counterintuitive at first (metal centers: +1 formal charge)

» Insight from electrostatic potential:



(NHC)AuCl

a



..... metallophilic int.

- - - electrostatic int.

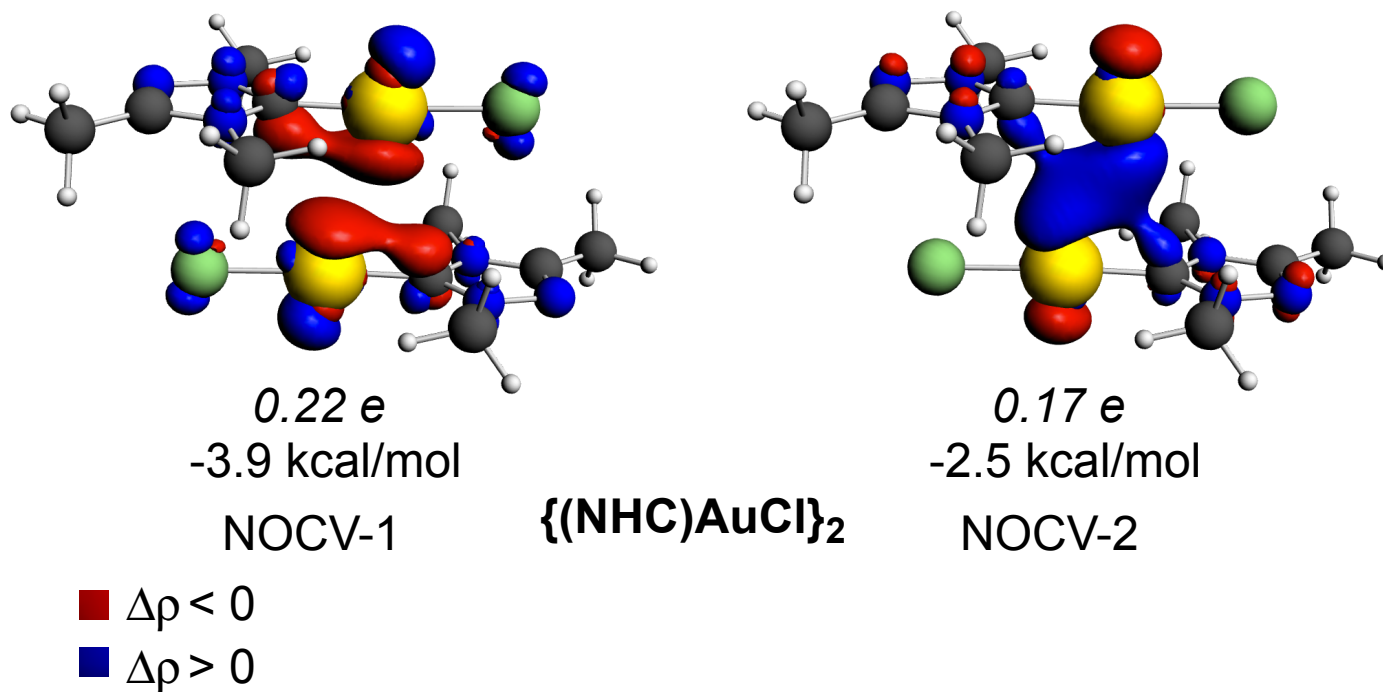
$\{(NHC)MX\}_2$

b

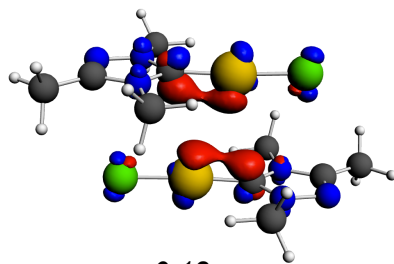
Orbital interaction: NOCV

» Dominant NOCV: weakening of π -backdonation from metal to carbene

» Second NOCV: accumulation of electron density between metal centers

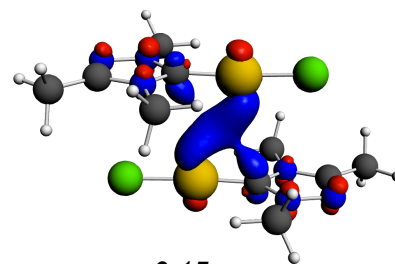


Orbital interaction: NOCV



0.18 e
-2.0 kcal/mol

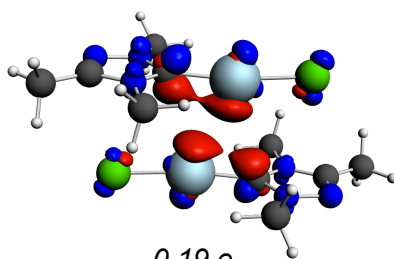
NOCV-1



0.15 e
-1.5 kcal/mol

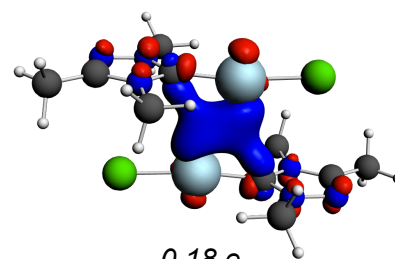
NOCV-2

$\{(NHC)CuCl\}_2$



0.19 e
-2.8 kcal/mol

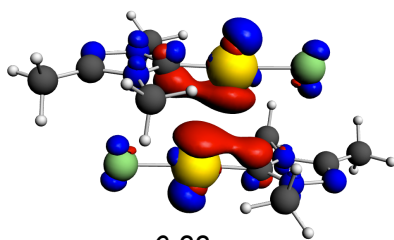
NOCV-1



0.18 e
-2.7 kcal/mol

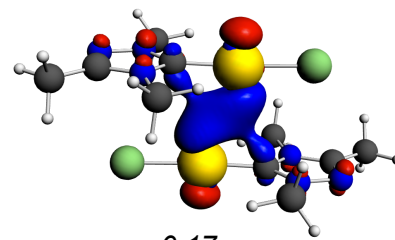
NOCV-2

$\{(NHC)AgCl\}_2$



0.22 e
-3.9 kcal/mol

NOCV-1



0.17 e
-2.5 kcal/mol

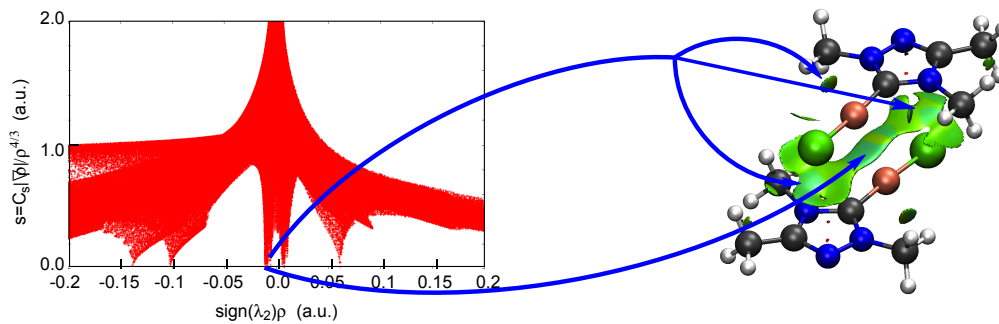
NOCV-2

$\{(NHC)AuCl\}_2$

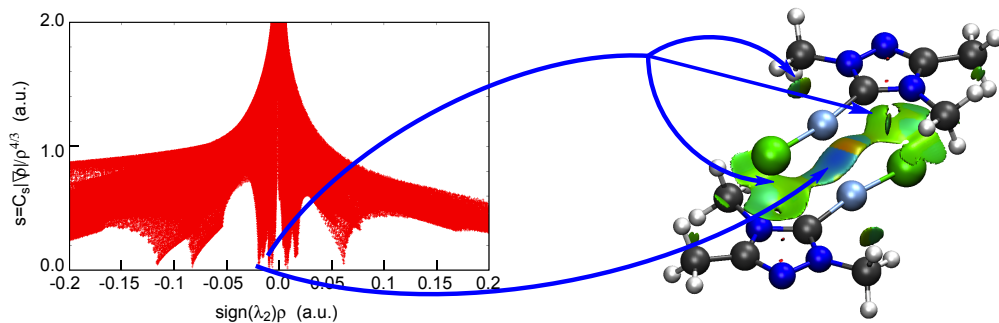
■ $\Delta\rho < 0$

■ $\Delta\rho > 0$

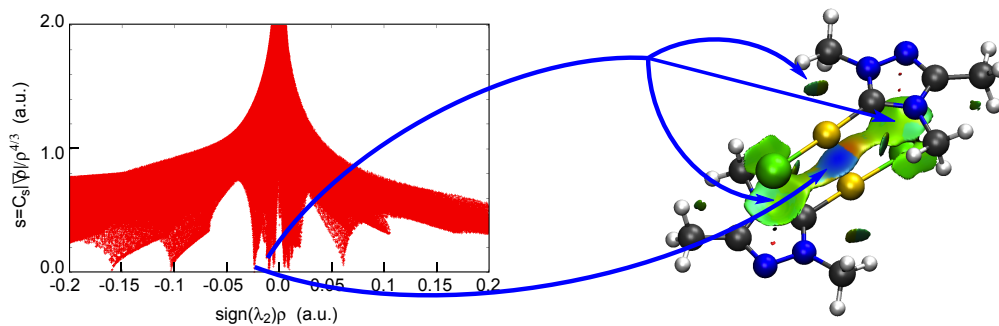
NCI index



$\{(NHC)CuCl\}_2$



$\{(NHC)AgCl\}_2$



$\{(NHC)AuCl\}_2$

- » Strengthening of metal-metal interactions from Cu to Ag to Au

- » Strongest interaction: appears in same regions as hydrogen bonding (competition)

Pinter, B.; Broeckaert, L.; Turek, J.; Růžička, A.; De Proft, F., submitted.

5. Conclusions

- » Intermolecular interactions: main group metals, transition metals, halogens
- » DFT based reactivity indices: charge-transfer vs. electrostatic contributions
- » Combined use of DFT based reactivity indices and other electron density based quantities provide useful insights

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