What can a synthetic chemist learn from charge density?

Dietmar Stalke

Institut für Anorganische Chemie der Universität Göttingen

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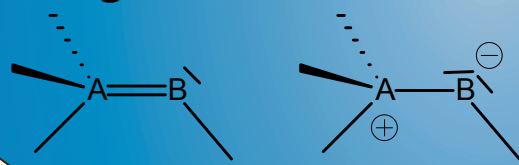
Nature
of a chemical bond

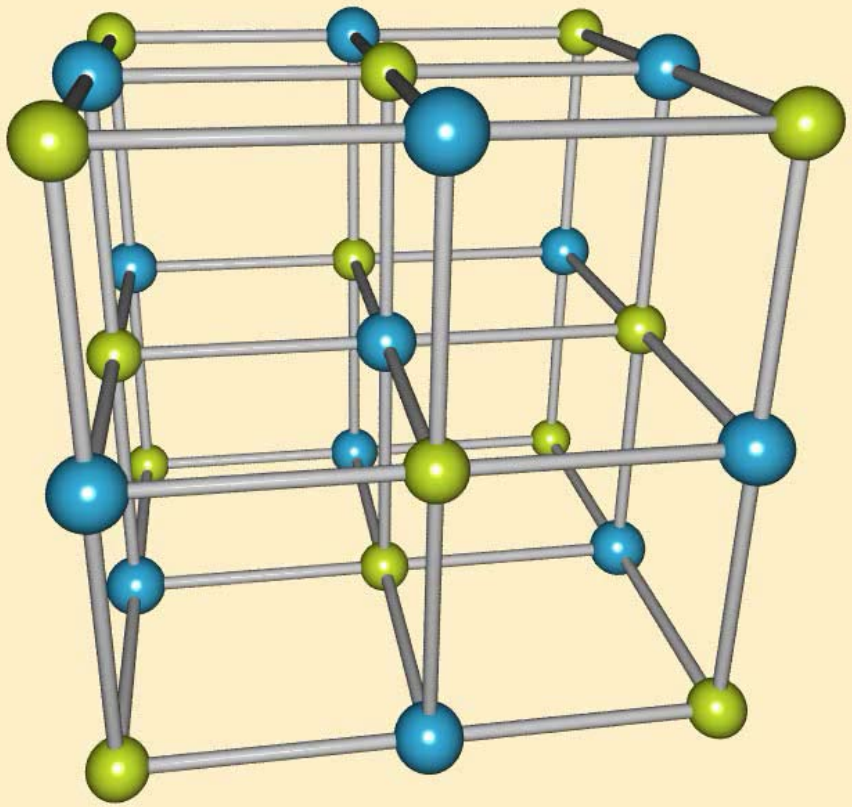
Hypervalency
central atom exceeds the noble gas configuration

Single or **double** bond



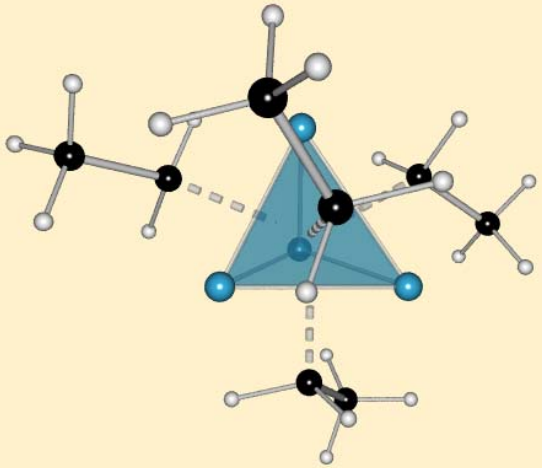
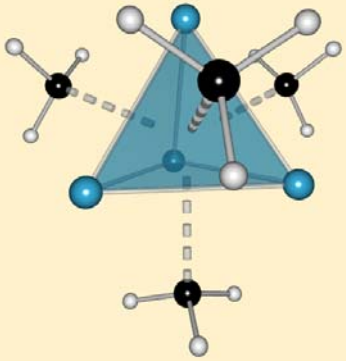
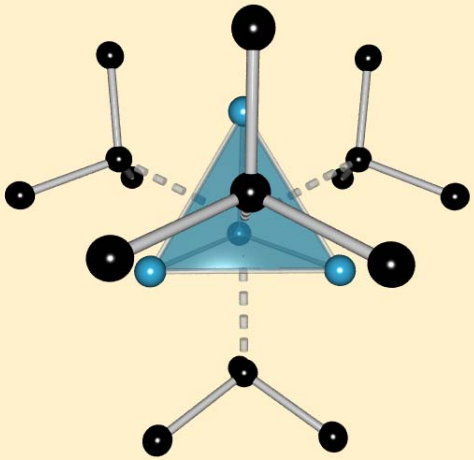
Structure/Reactivity
bond formation or cleavage

Bond or topological connectivity ?

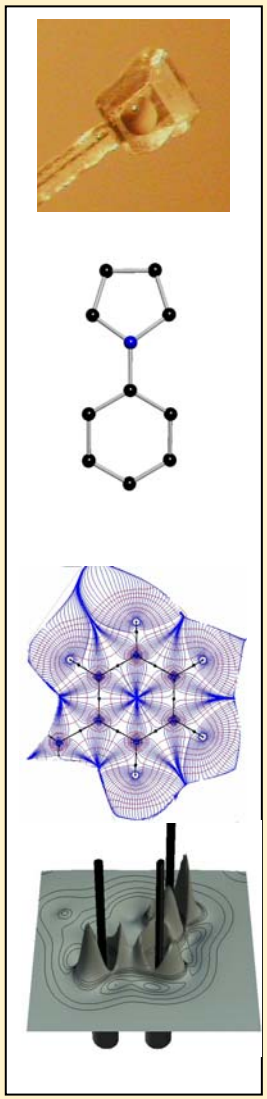


T. Stey, D. Stalke *Lead structures in lithium organic chemistry* in *The Chemistry of Organolithium Compounds*, eds. Z. Rappoport, I. Marek, John Wiley & Sons New York, **2004**, 47-120.

$[(RLi)_4]_n$ - Tetrahedra

	$[(EtLi)_4]$	$[(MeLi)_4]$	$[(tBuLi)_4]$
			
Li - C_α	228	226	225 pm
Li - C_β	250	(236)	237 pm
Li ··· Li	253	259	241 pm
	H. J. Dietrich, *J. Organomet. Chem.* **1981**, *205*, 291.	E. Weiss et al., *Chem. Ber.* **1990**, *123*, 79.	D. Stalke et al., *Angew. Chem. Int. Ed.* **1993**, *32*, 580.

Experimental charge density



High resolution diffraction data (2Θ = 3-110° (MoK_α))

↓

Standard structure determination

↓

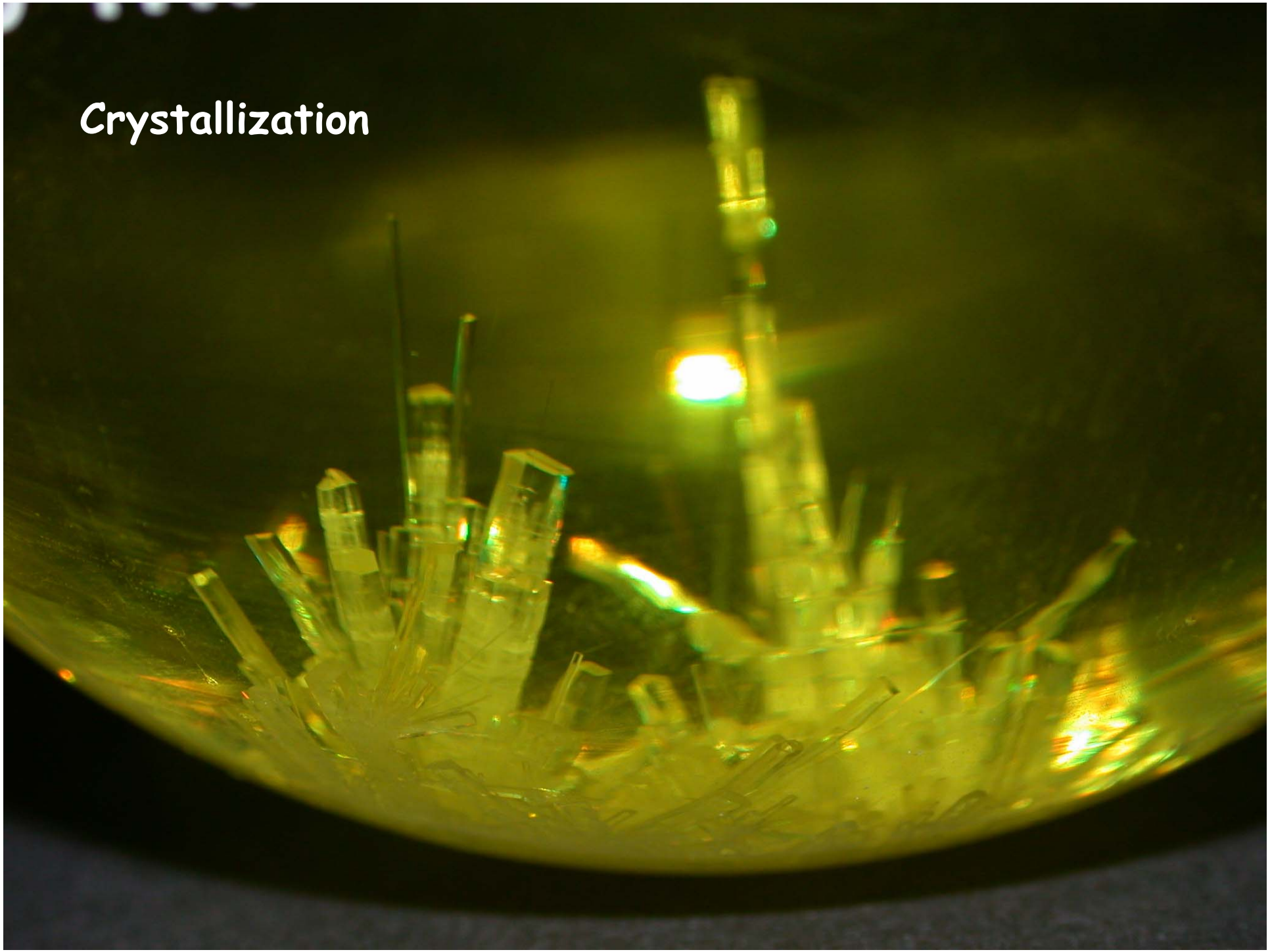
Multipole refinement

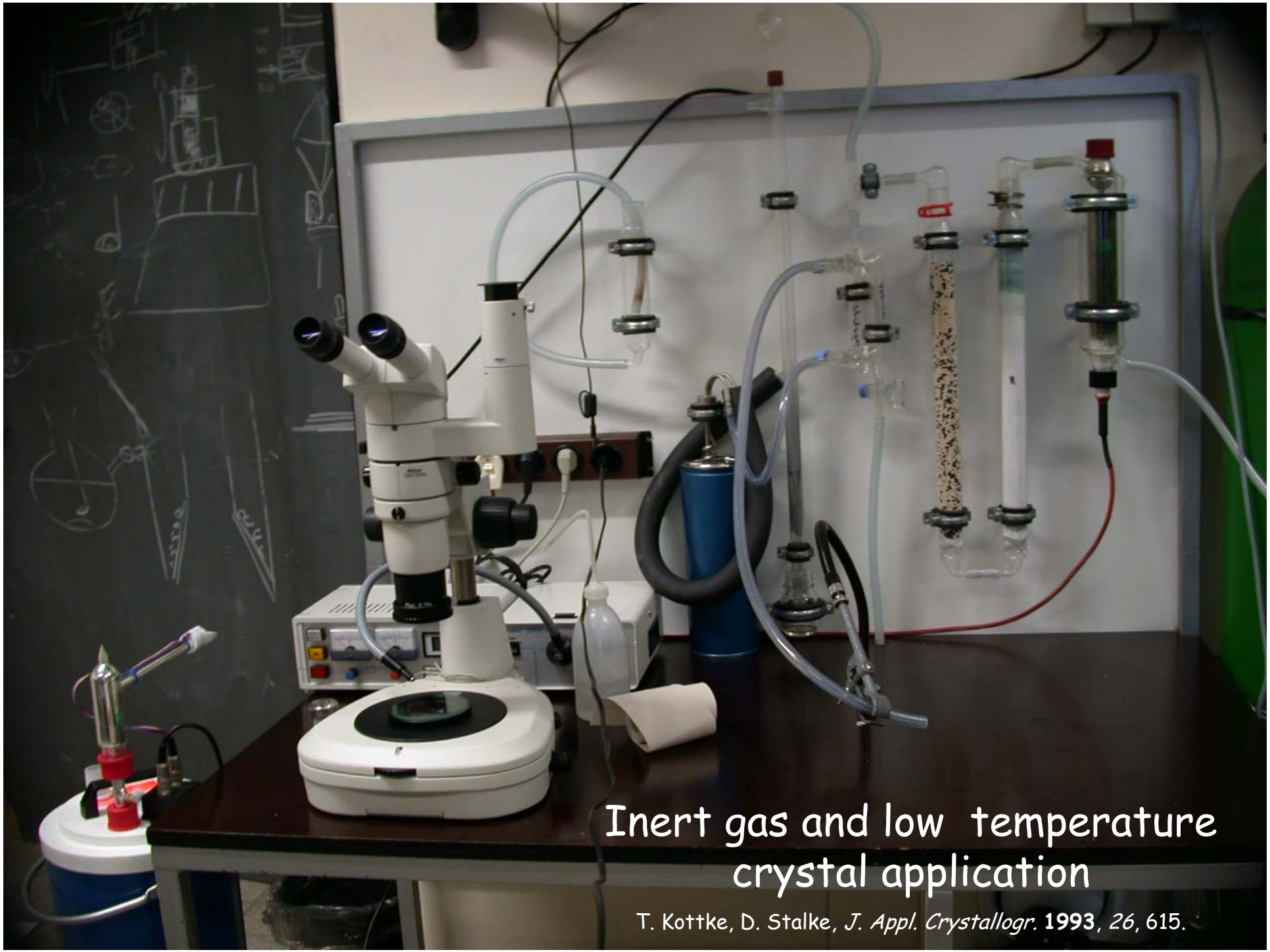
↓

Analyses according to Bader's

„Atoms in Molecules" (AIM) formalism

Crystallization

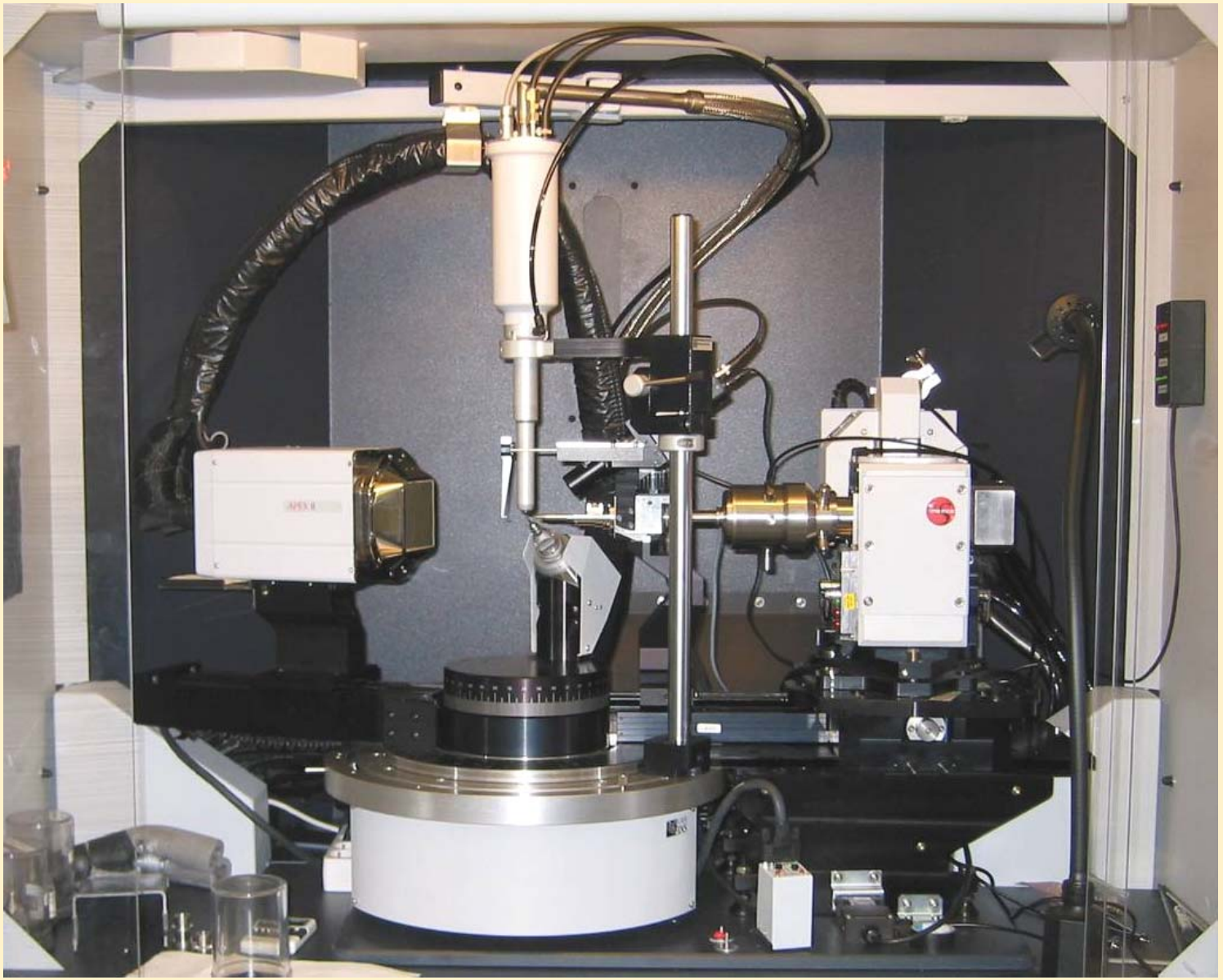




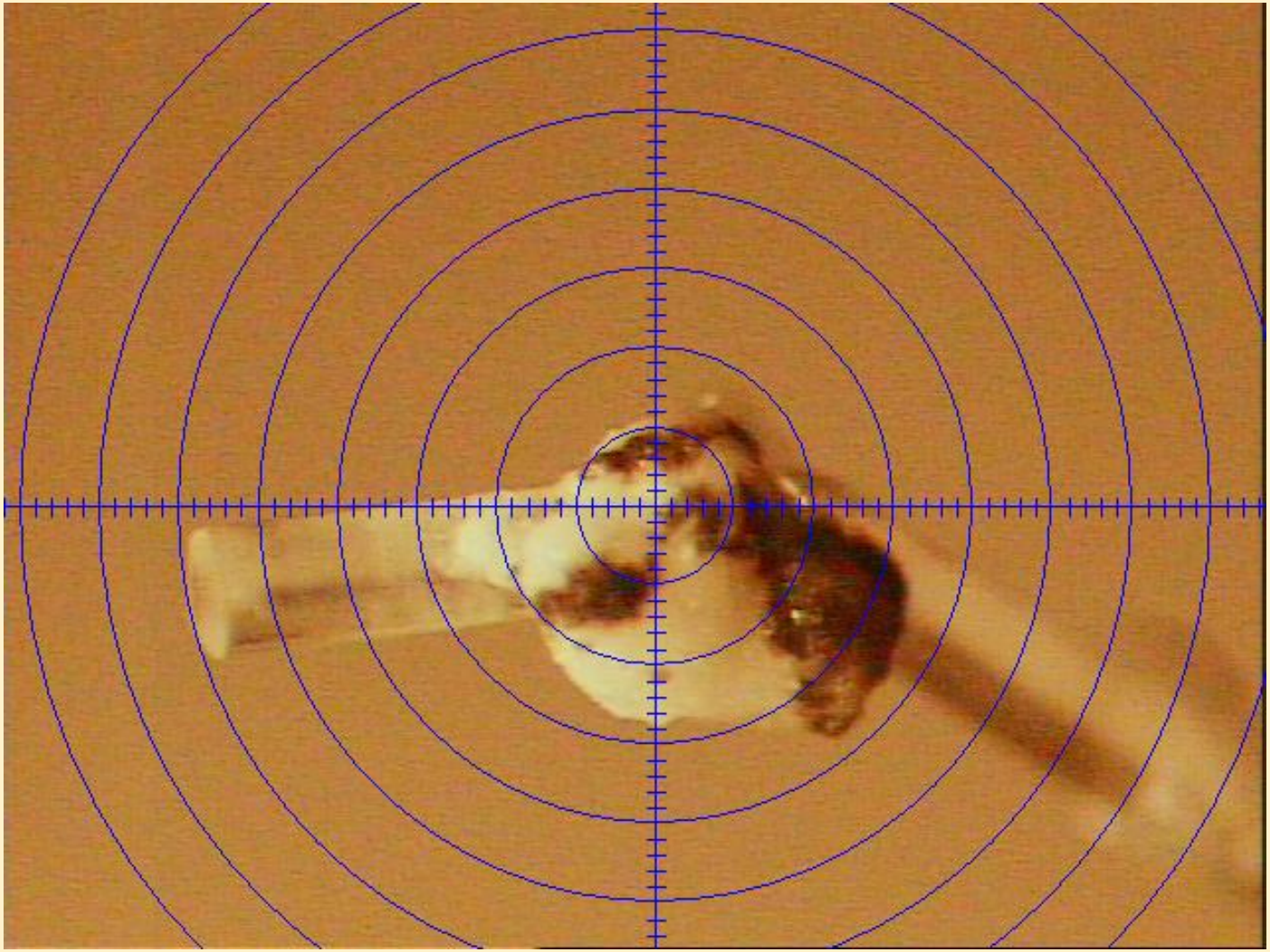
Inert gas and low temperature crystal application

T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

Bruker TXS and INCOATEC Mo mirrors



Beware: Burning crystal

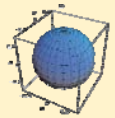


Exquisite data from the Bruker TXS

Resolution	2 θ (MoK_α)	$\frac{\sin\theta}{\lambda}$	% Complete	Red.	Mean I/σ	R_{int}	R_σ
Inf - 1.18	36.13	0.42	99.8	22.43	145.11	0.0159	0.0047
1.18 - 0.93	46.33	0.54	100.0	23.09	117.94	0.0194	0.0058
0.93 - 0.81	53.70	0.62	100.0	20.16	97.26	0.0237	0.0072
0.81 - 0.73	60.16	0.68	99.6	6.43	52.82	0.0222	0.0133
0.73 - 0.68	65.10	0.74	99.0	5.87	46.52	0.0248	0.0150
0.68 - 0.64	69.73	0.78	98.5	6.51	45.91	0.0286	0.0160
0.64 - 0.60	75.15	0.83	98.1	10.00	55.29	0.0328	0.0129
0.60 - 0.57	79.86	0.88	97.6	9.23	44.20	0.0395	0.0168
0.57 - 0.54	85.30	0.93	97.4	6.11	35.16	0.0393	0.0217
0.54 - 0.52	89.43	0.96	94.9	4.16	26.96	0.0382	0.0291
0.52 - 0.50	94.06	1.00	93.1	3.75	20.87	0.0479	0.0390
0.50 - 0.48	99.32	1.04	94.8	3.73	16.95	0.0572	0.0491
0.48 - 0.46	105.38	1.09	94.9	3.75	15.57	0.0628	0.0533
0.46 - 0.45	108.79	1.11	92.5	3.59	14.71	0.0658	0.0577
0.45 - 0.44	112.51	1.14	94.7	3.43	12.82	0.0733	0.0667
0.44 - 0.42	121.18	1.19	75.3	2.13	10.64	0.0770	0.0817
0.52 - 0.42			91.9	3.50	16.37	0.0570	0.0503
Inf - 0.42			95.4	7.67	43.86	0.0201	0.0126

Multipole structure refinement

MONOPOL

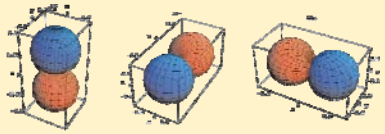


M1

The atomic density is modelled along spherical harmonics

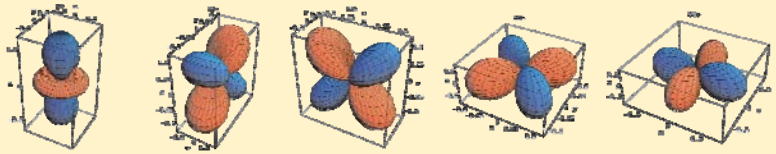
$$\rho_d\left(\kappa' \mathbf{r}\right)=\sum_l \kappa'^3 R_l\left(\kappa' r\right)\sum_{m=-l}^{l} P_{lm} \cdot Y_{lm}\left(\frac{\mathbf{r}}{r}\right)$$

DIPOLE



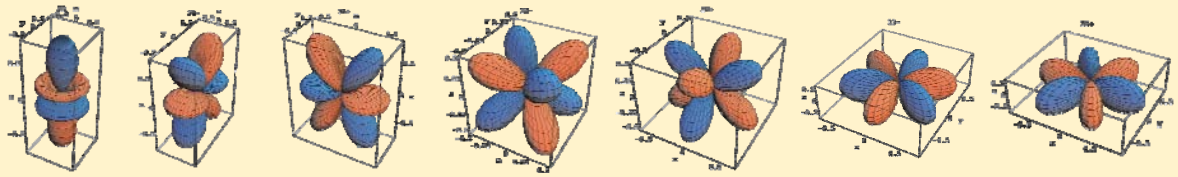
D0 D1- D1+

QUADRUPOLE



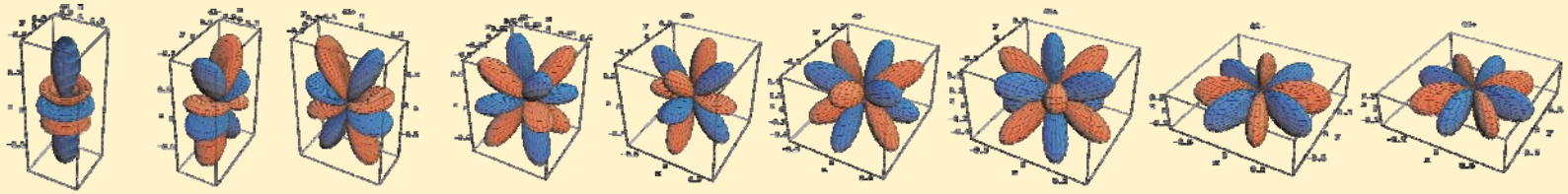
Q0 Q1- Q1+ Q2- Q2+

OCTAPOLE



O0 O1- O1+ O2- O2+ O3- O3+

HEXADECAPOLE

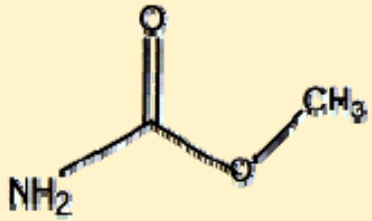


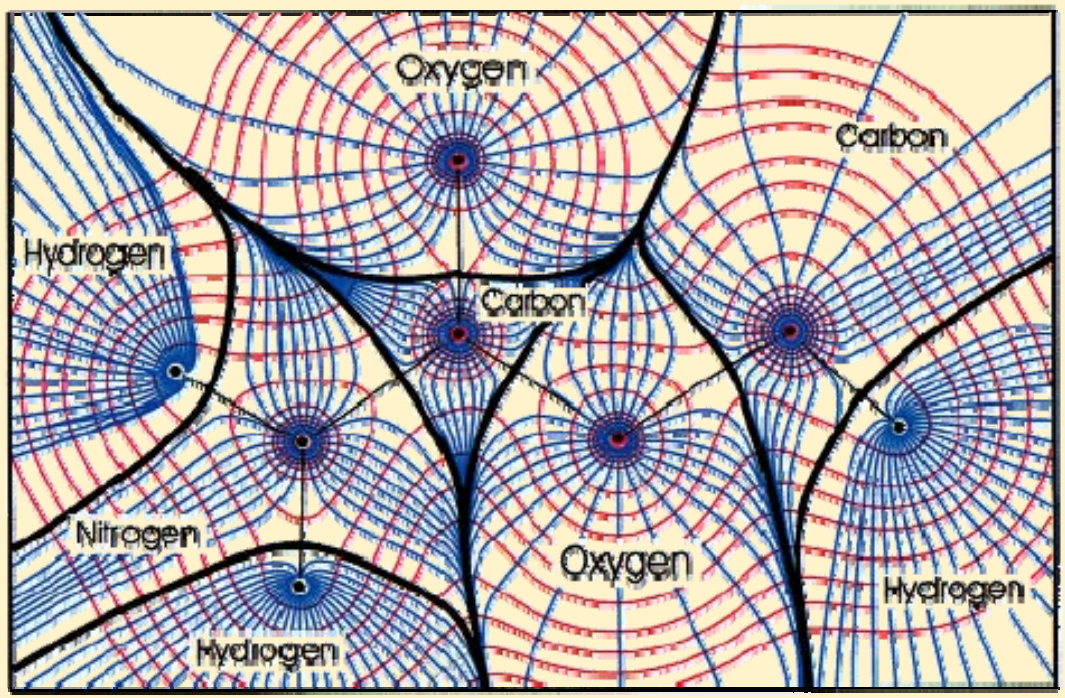
H0 H1- H1+ H2- H2+ H3- H3+ H4- H4+

P. Coppens, *X-ray Charge Densities and Chemical Bonding*, IUCr texts on Crystallography, Oxford Univ. Press, **1997**.

Structure topology

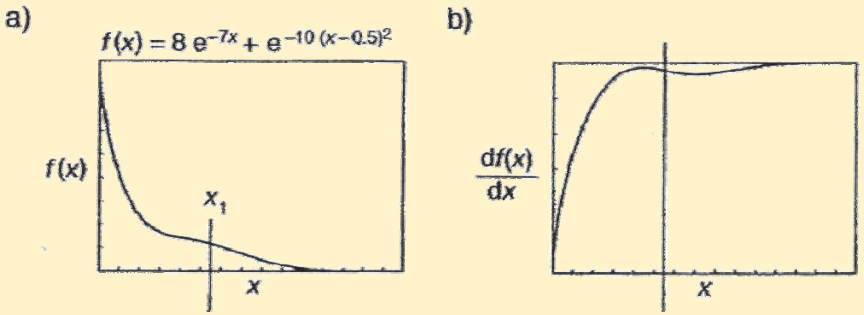
The gradient vector field of methyl carbamide:

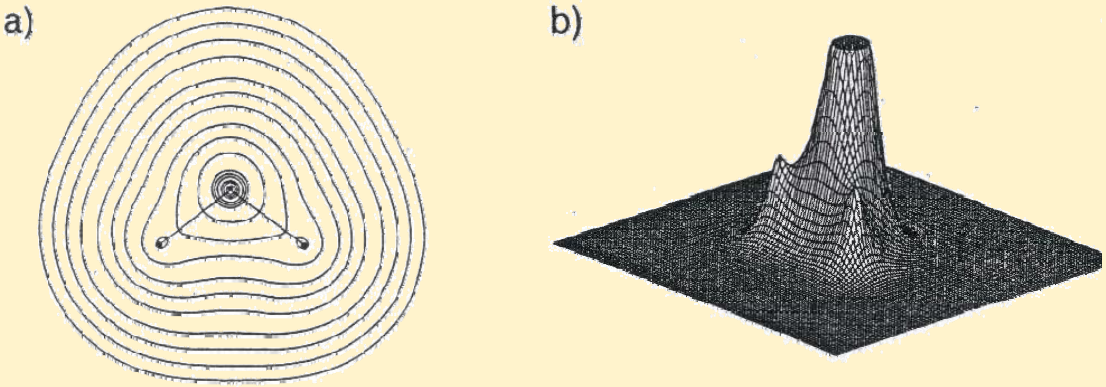




P. Coppens, *X-ray Charge Densities and Chemical Bonding*, IUCr texts on Crystallography, Oxford Univ. Press, **1997**.

Charge density and derivatives

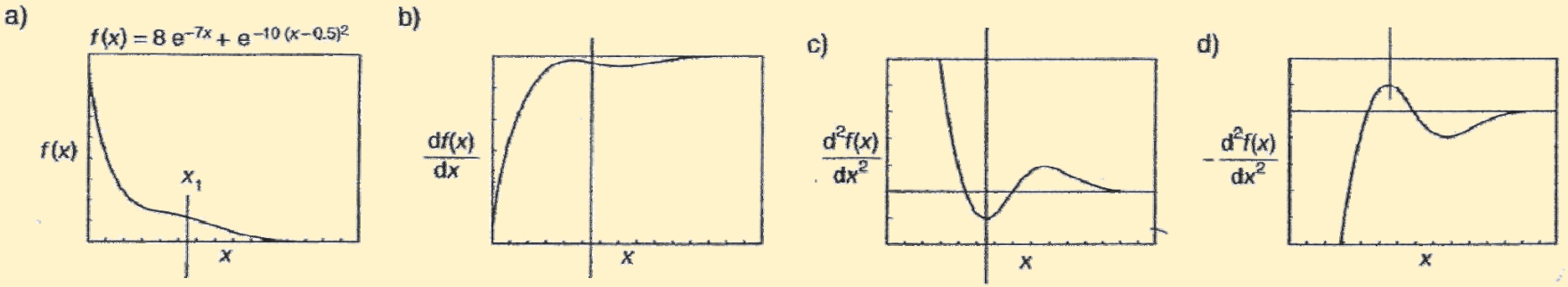


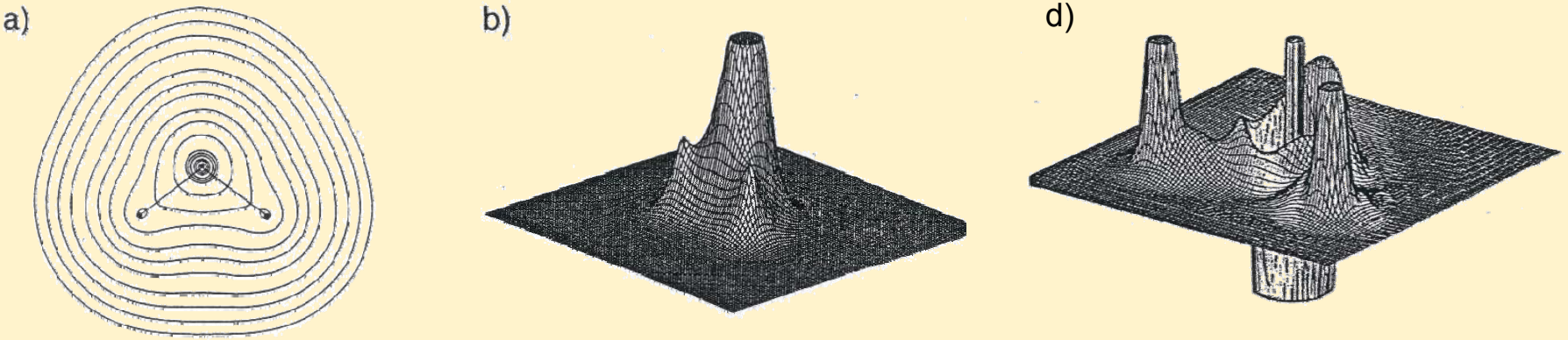


Charge density distribution $\rho = f(\mathbf{r})$

R. J. Gillespie, E. A. Robinson, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495.

Charge density and derivatives



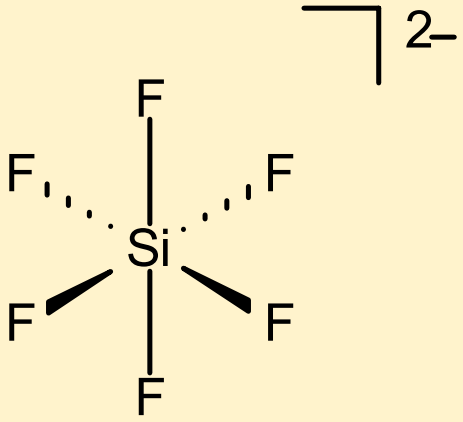


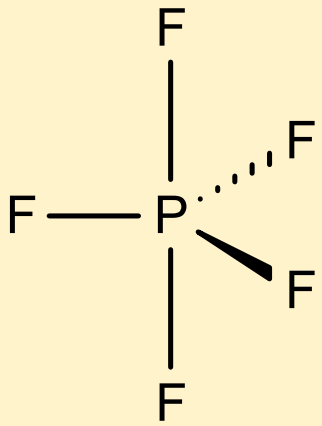
Charge density distribution $\rho = f(\mathbf{r})$

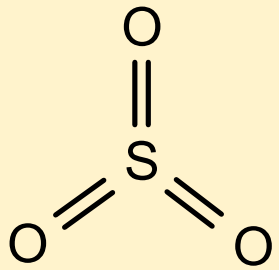
Laplacian $-\nabla^2\rho = -\dfrac{d^2f(\mathbf{r})}{d\mathbf{r}^2}$

R. J. Gillespie, E. A. Robinson, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495.

Hypervalency ??





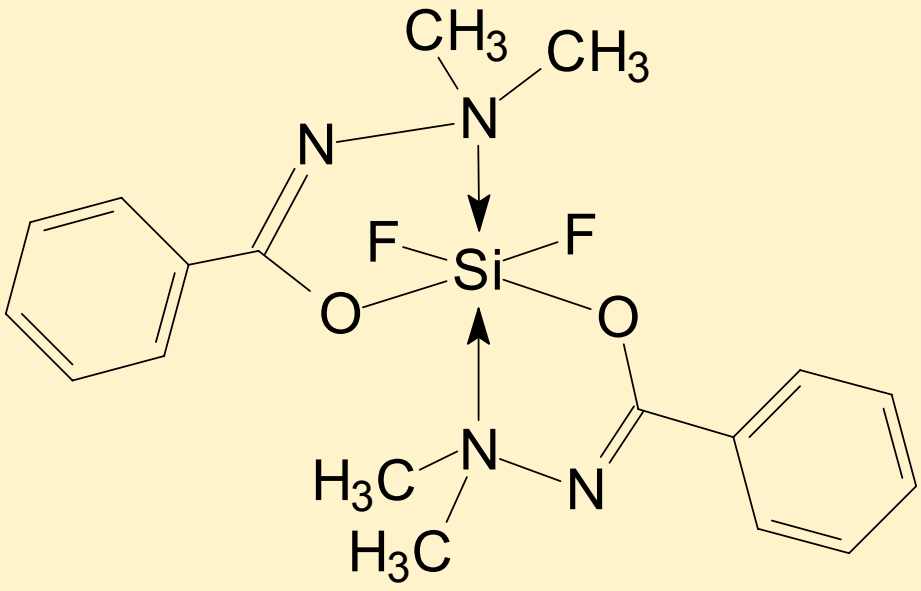


The usual suspects: third (or higher) period central atoms,

$d^n sp^m$ hybridized,

no formal charges.

Independent atom model *vs.* multipole model

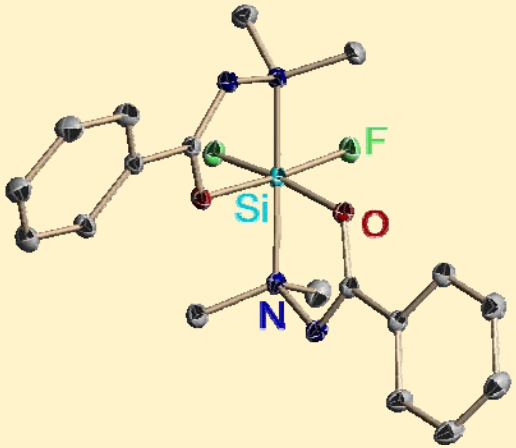


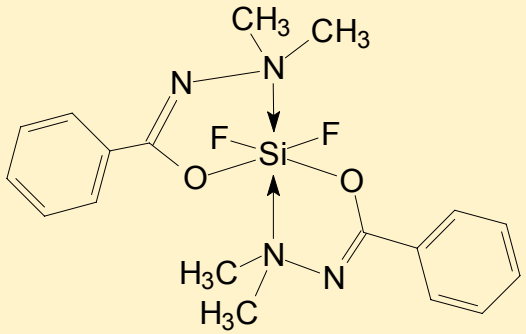
Si←N	Si—N	Si=N
197 pm	174 pm	157 pm
	CCDC 2005	Wiberg et al. 1986

N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, 126, 5563.

Independent atom model *vs.* multipole model

Independent Atom Model (IAM)





Multipole Model

N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, 126, 5563.

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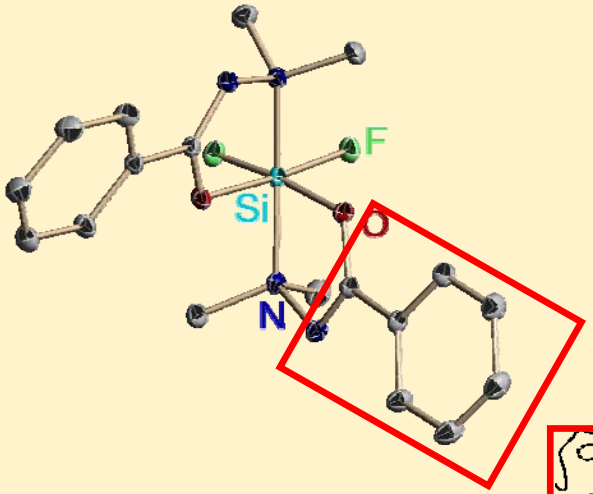
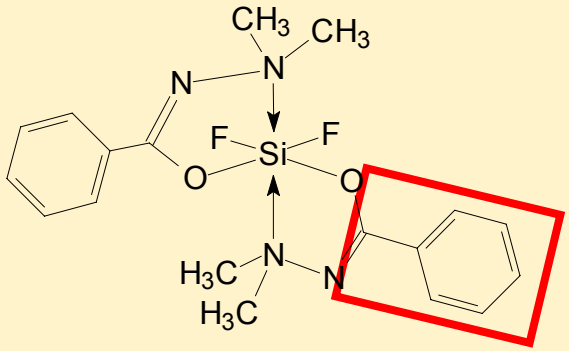


Multipole Model



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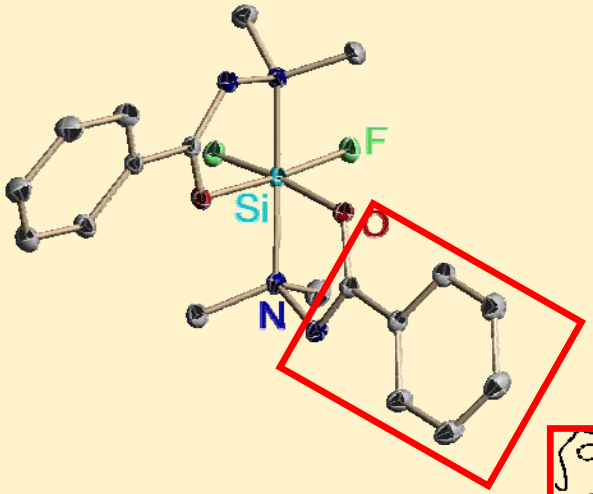
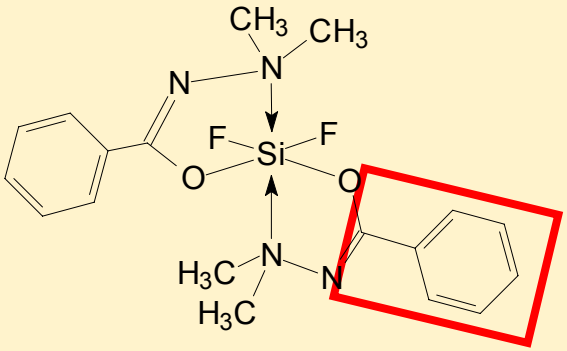
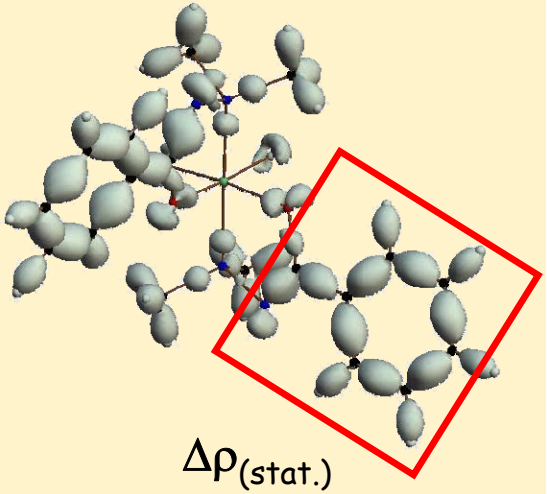
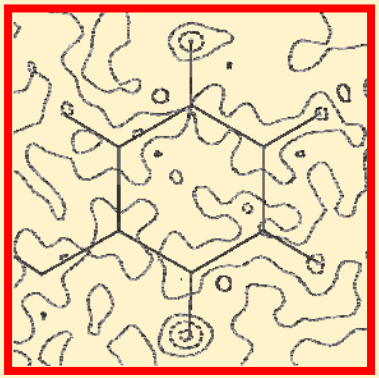




Multipole Model

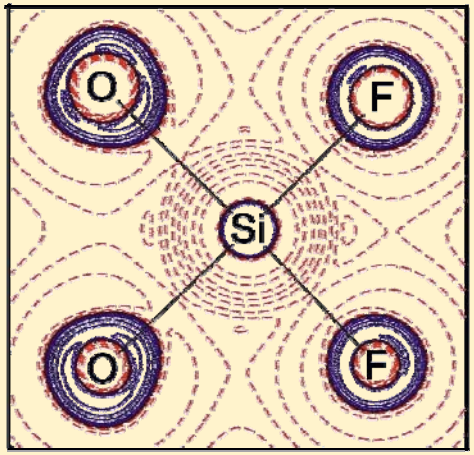


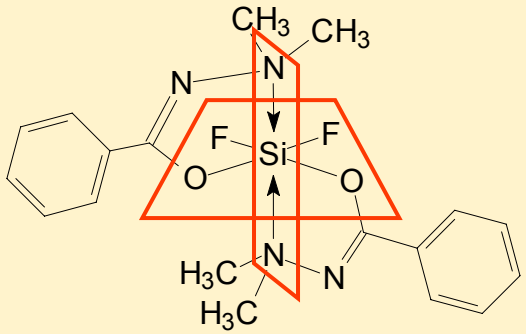
$\Delta\rho_{(stat.)}$



N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, 126, 5563.

Topology of the Si—E-bonding (E = N, O, F)





$\nabla^2\rho(r)$

N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, 126, 5563.

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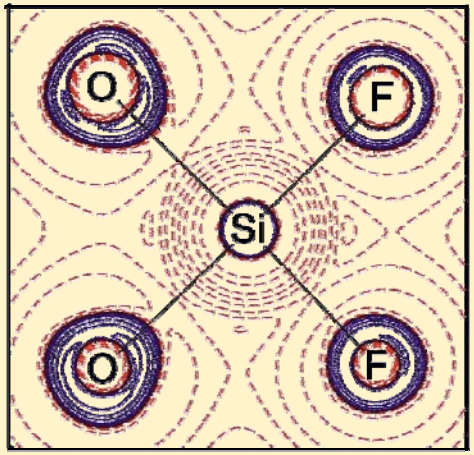
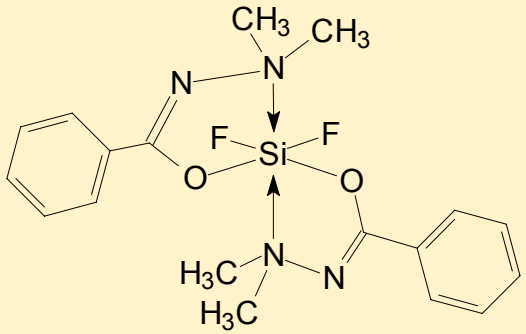
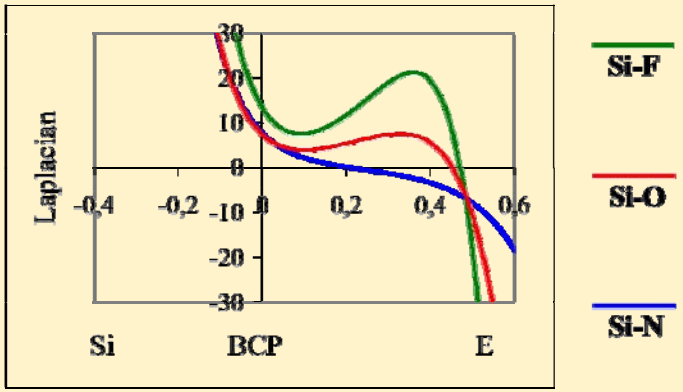






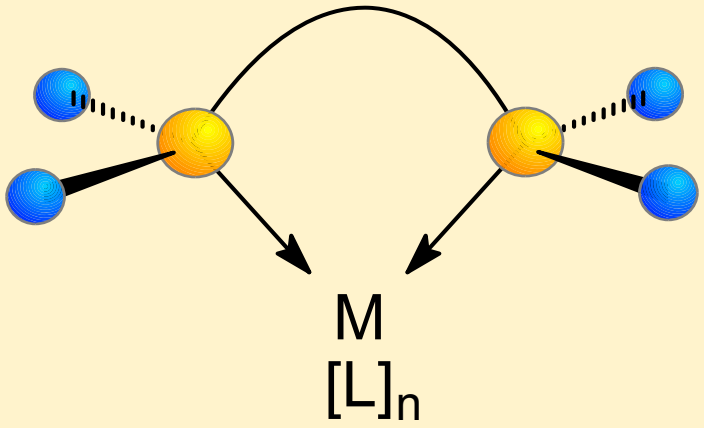
Si: + 2.78 (exp.); + 2.27 (NBO)

$\nabla^2\rho(r)$

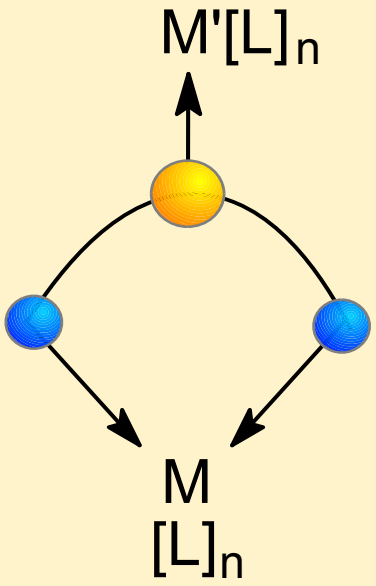
A–B	bond path	$\rho(r_{BCP})$	$\nabla^2\rho(r_{BCP})$	charge (B)	NBO-charge (B)
Si–N	197.03	0.501(16)	7.755(32)	– 0.78	– 0.43
Si–O	177.89	0.766(13)	7.373(29)	– 1.21	– 0.81
Si–F	163.97	1.015(13)	13.472(33)	– 0.80	– 0.66

N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, 126, 5563.

Phosphorus centred *Janus-Head* ligands



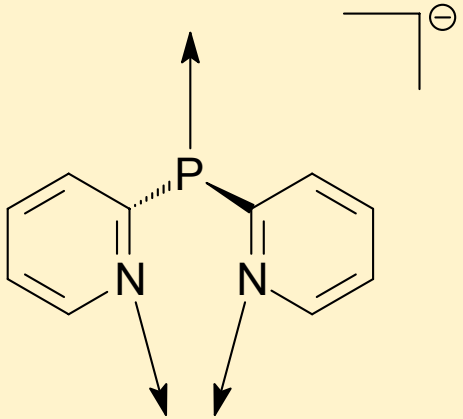
Classical chelating ligands
asymmetrical, chiral, hemilabile

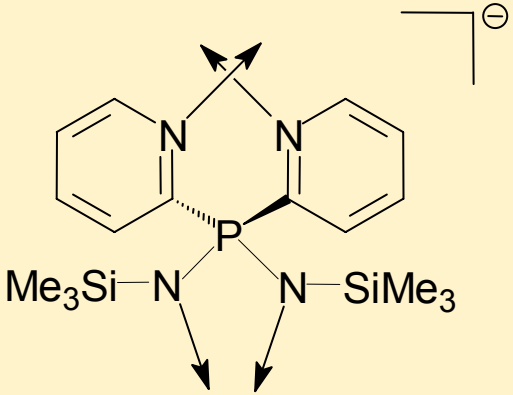


Janus-Head ligands
σ/π coordination *via* the
ligand periphery

Reviews: L. Mahalakshmi, D. Stalke, In *Structure and Bonding*, Springer Verlag Heidelberg, **2002**, *103*, 85.
D. Stalke et al., *J. Organomet. Chem.* **2002**, *661*, 111.

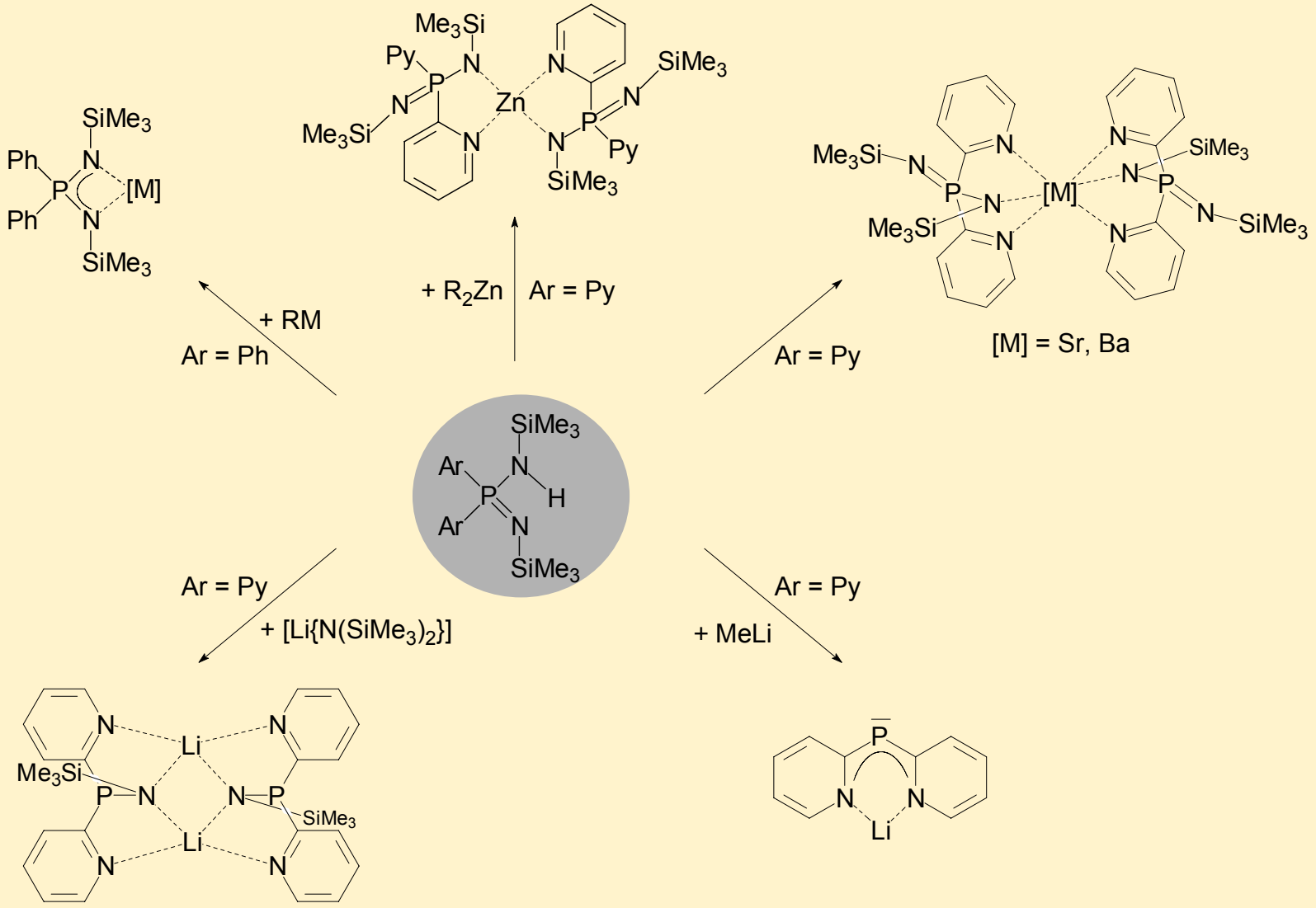
Phosphorus centred *Janus-Head* ligands





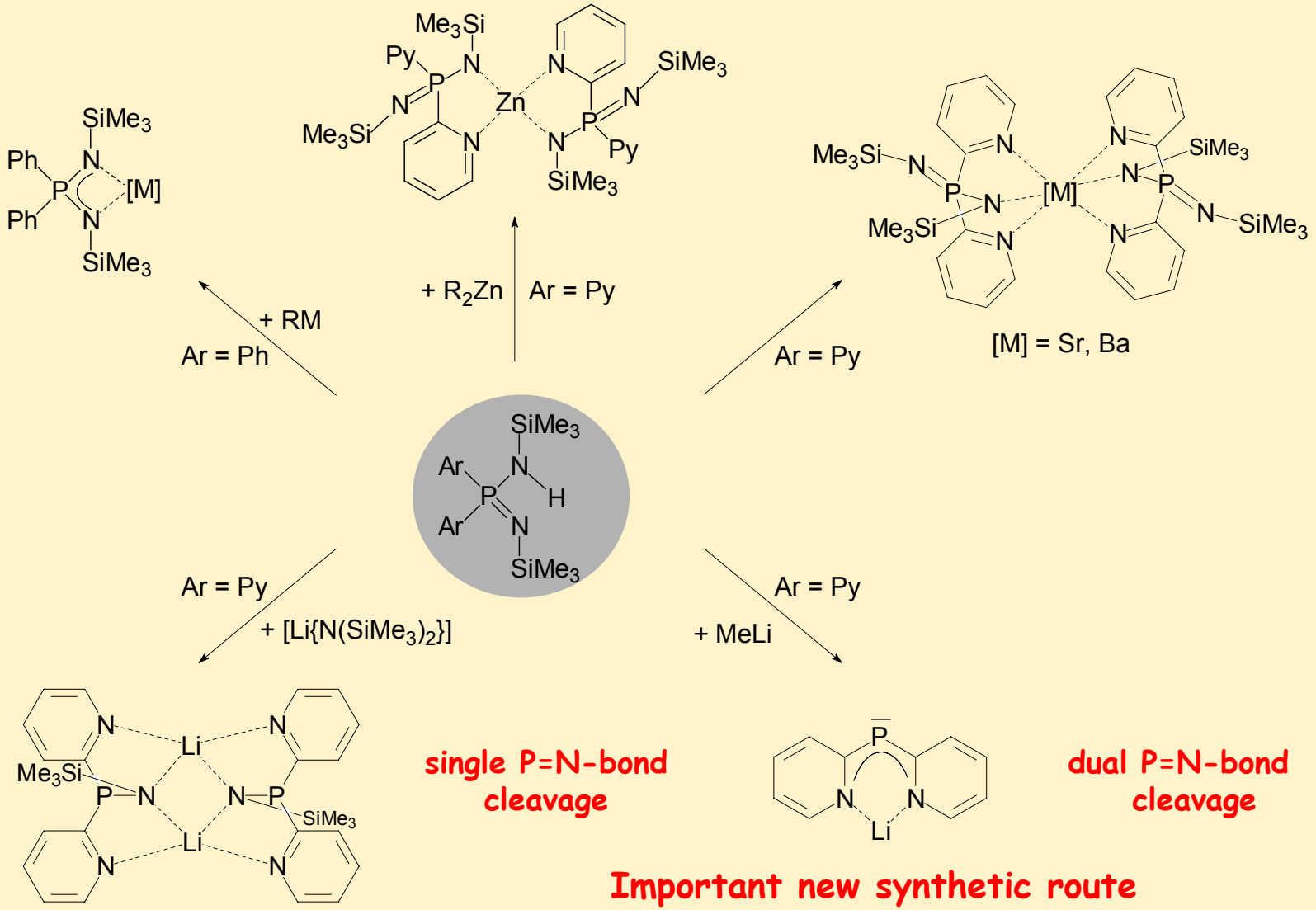
Reviews: L. Mahalakshmi, D. Stalke, In *Structure and Bonding*, Springer Verlag Heidelberg, **2002**, *103*, 85.
D. Stalke et al., *J. Organomet. Chem.* **2002**, *661*, 111.

Aminoiminophosphoranes



Inorg. Chem. **1993**, *32*, 1977; *Inorg. Chem.* **1997**, *36*, 2413; *J. Am. Chem. Soc.* **2001**, *123*, 1381.

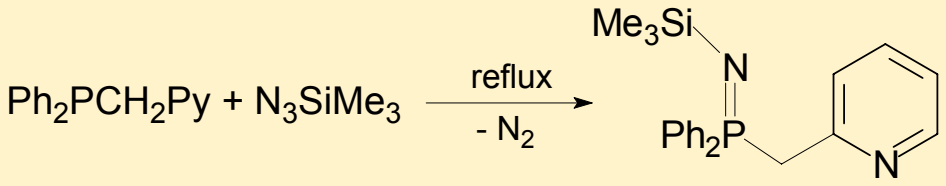
Aminoiminophosphoranes



Important new synthetic route

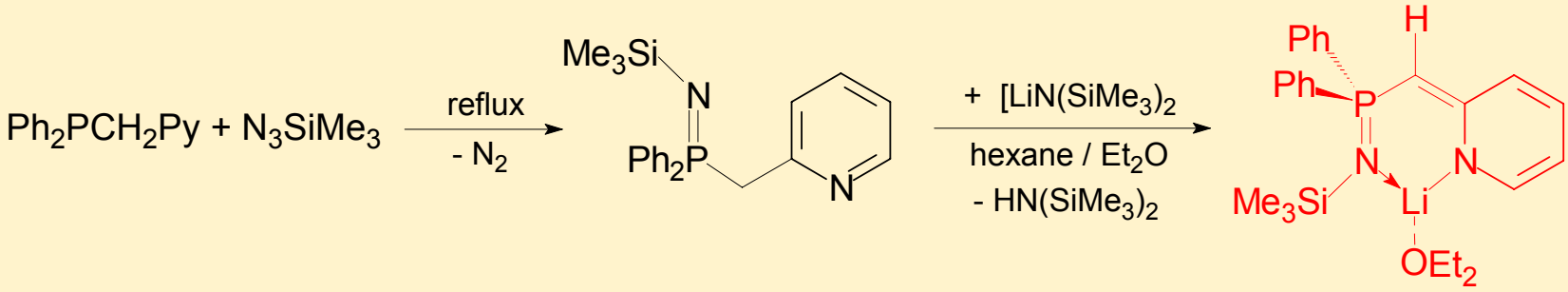
Inorg. Chem. **1993**, *32*, 1977; *Inorg. Chem.* **1997**, *36*, 2413; *J. Am. Chem. Soc.* **2001**, *123*, 1381.

P=N double bond ??



N. Kocher, D. Leusser, A. Murso, D. Stalke, *Chem. Eur. J.* **2004**, *10*, 3622.

P=N double bond ??



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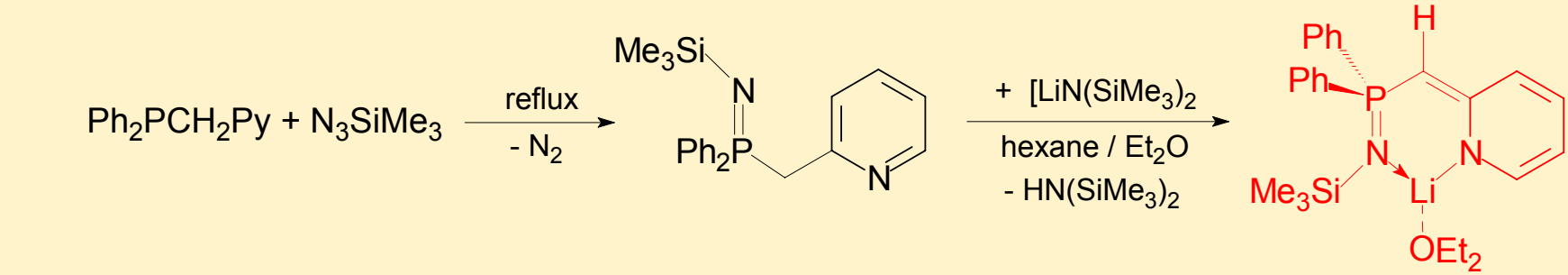
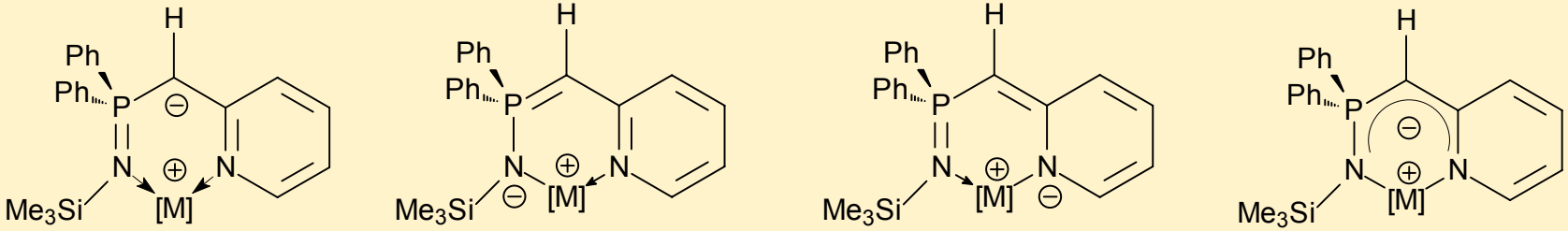


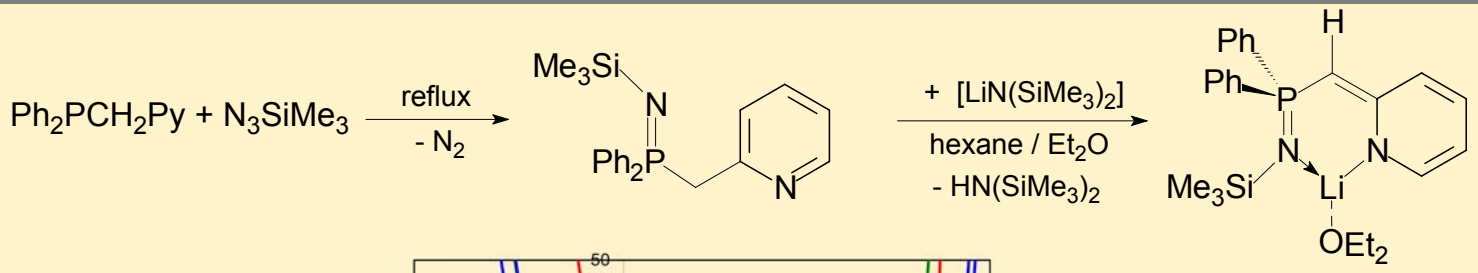


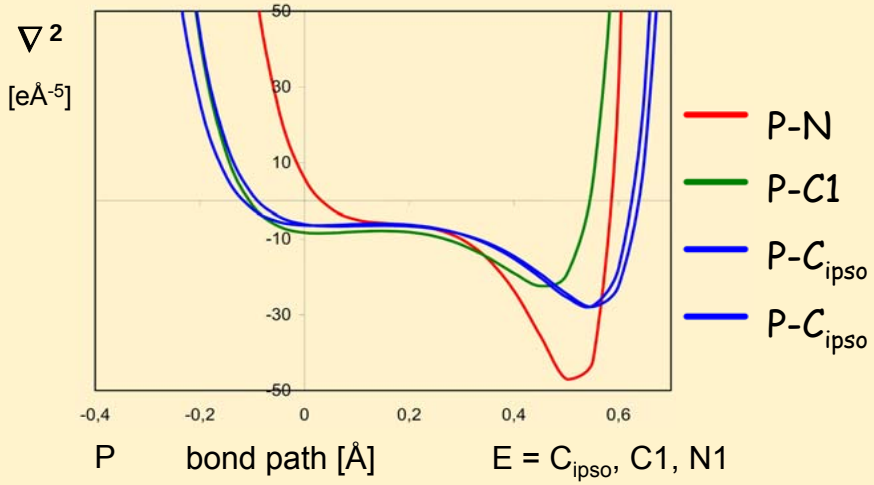
carbanion, ylide | **amide, ylene** | **amide, olefin** | **"delocalised"**

All canonical forms would require hypervalent phosphorus in P–C or P–N multiple bonding.

N. Kocher, D. Leusser, A. Murso, D. Stalke, *Chem. Eur. J.* **2004**, *10*, 3622.

No double bonds at phosphorus





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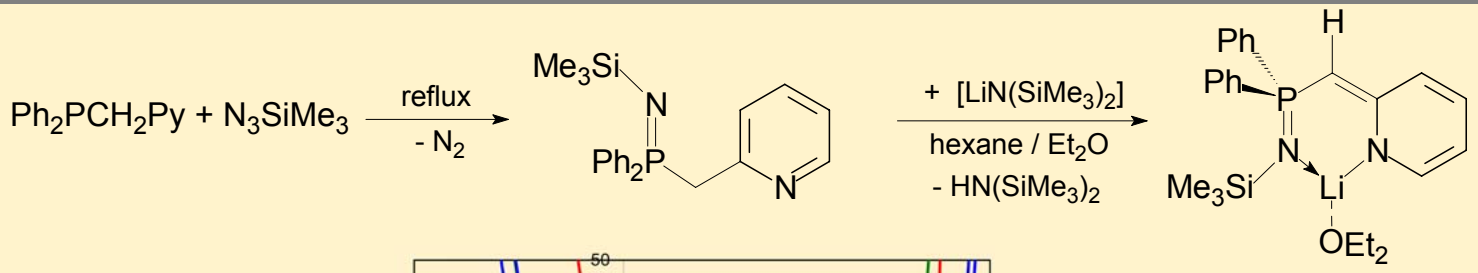

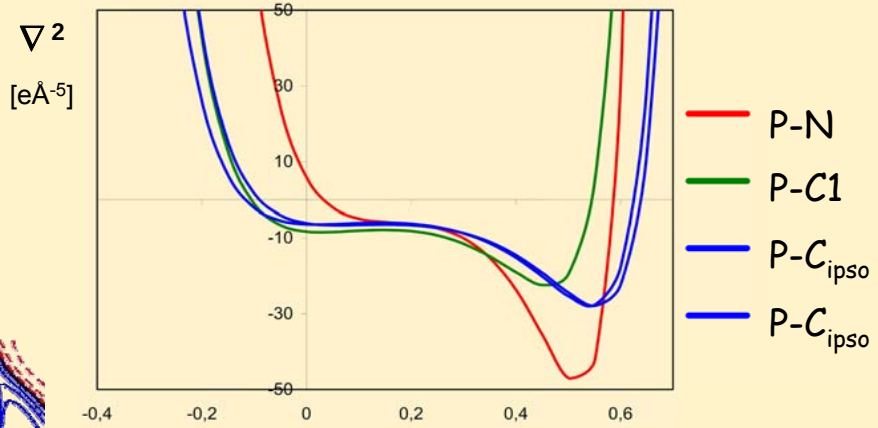

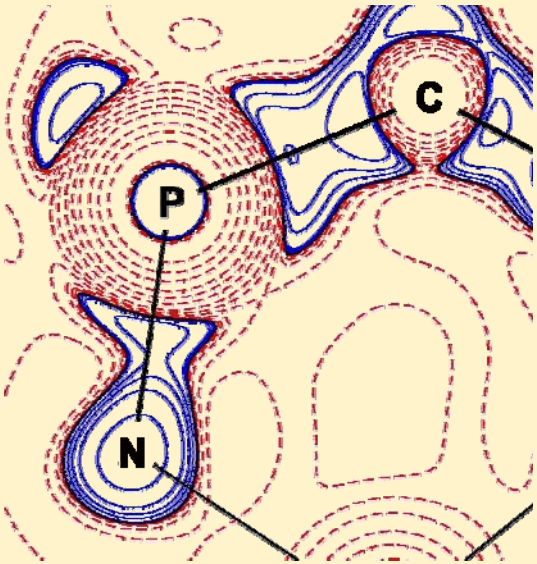

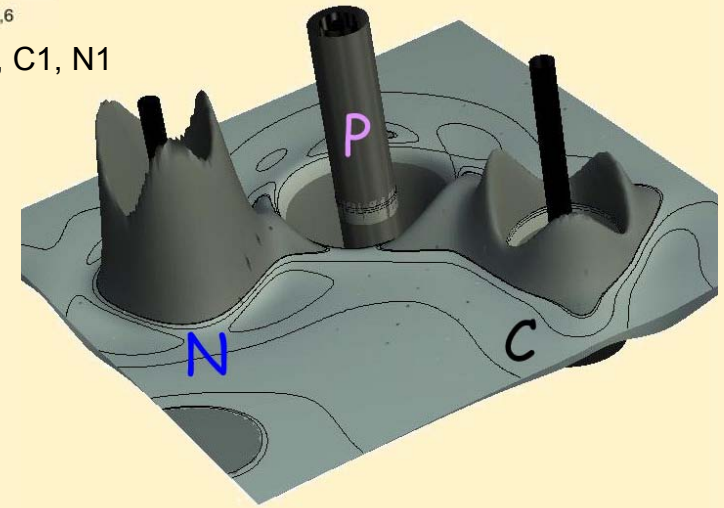

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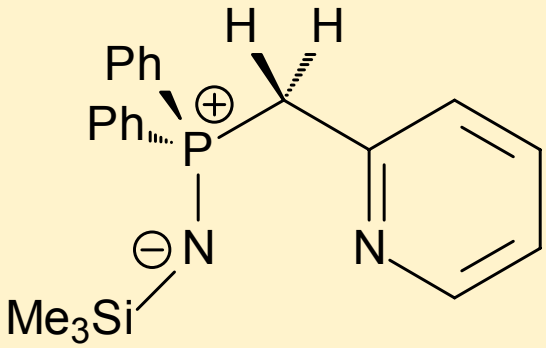
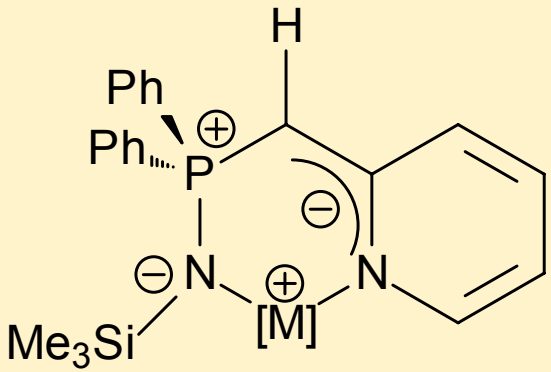
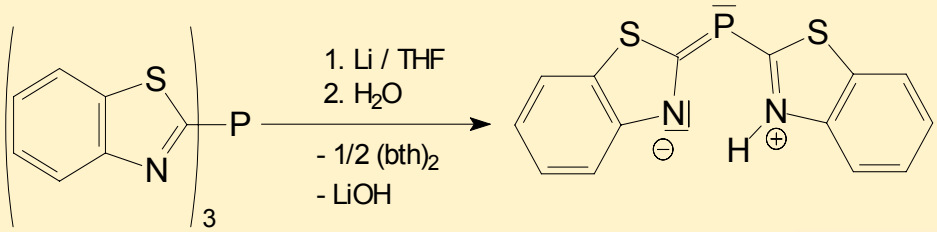
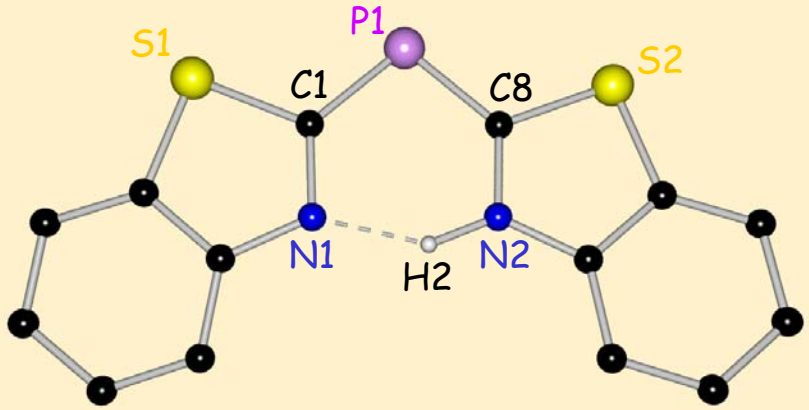




N. Kocher, D. Leusser, A. Murso, D. Stalke, *Chem. Eur. J.* **2004**, *10*, 3622.

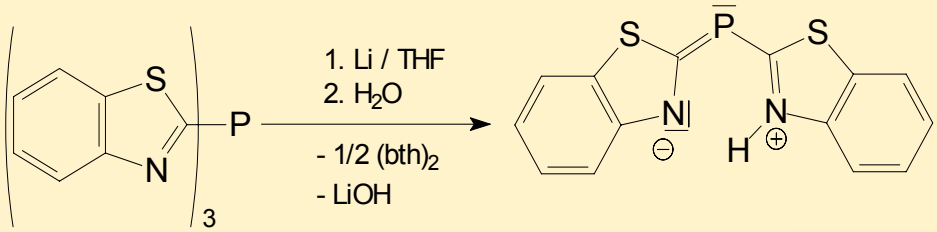
4 e⁻ donor *Janus-Head* ligands

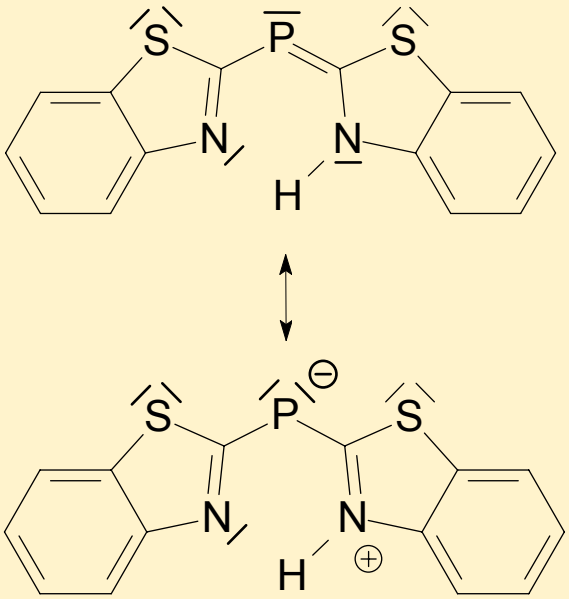


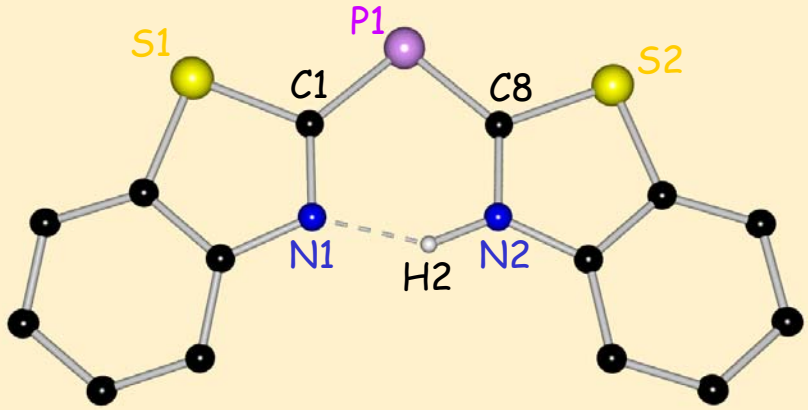


T. Stey, J. Henn, D. Stalke, *Chem. Commun.* **2007**, 413.

4 e⁻ donor *Janus-Head* ligands







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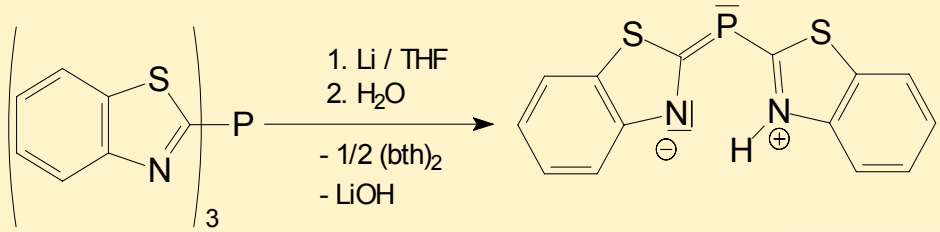

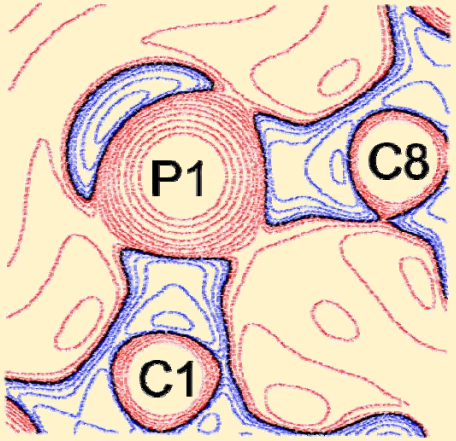

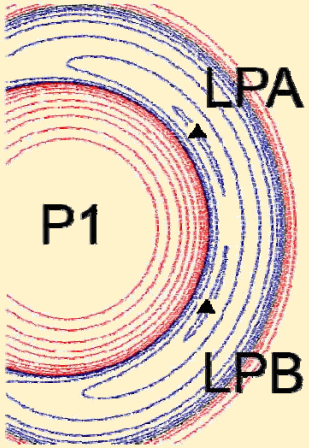

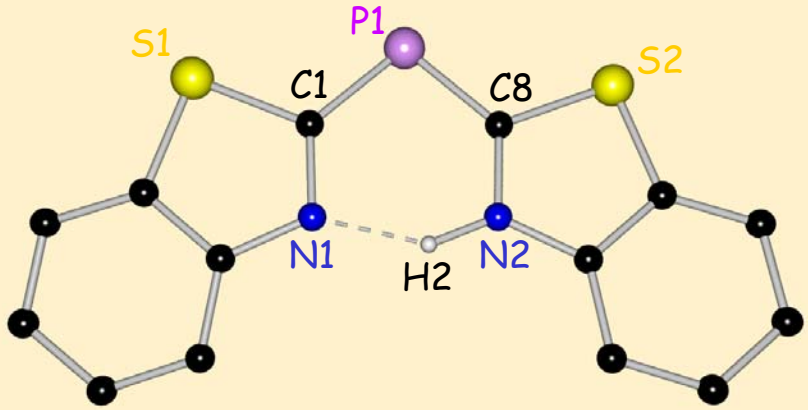

$\nabla^2\rho(r)$

T. Stey, J. Henn, D. Stalke, *Chem. Commun.* **2007**, 413.

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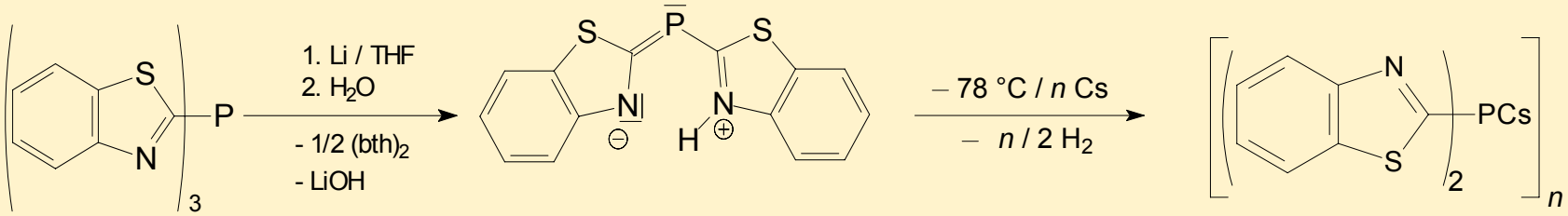
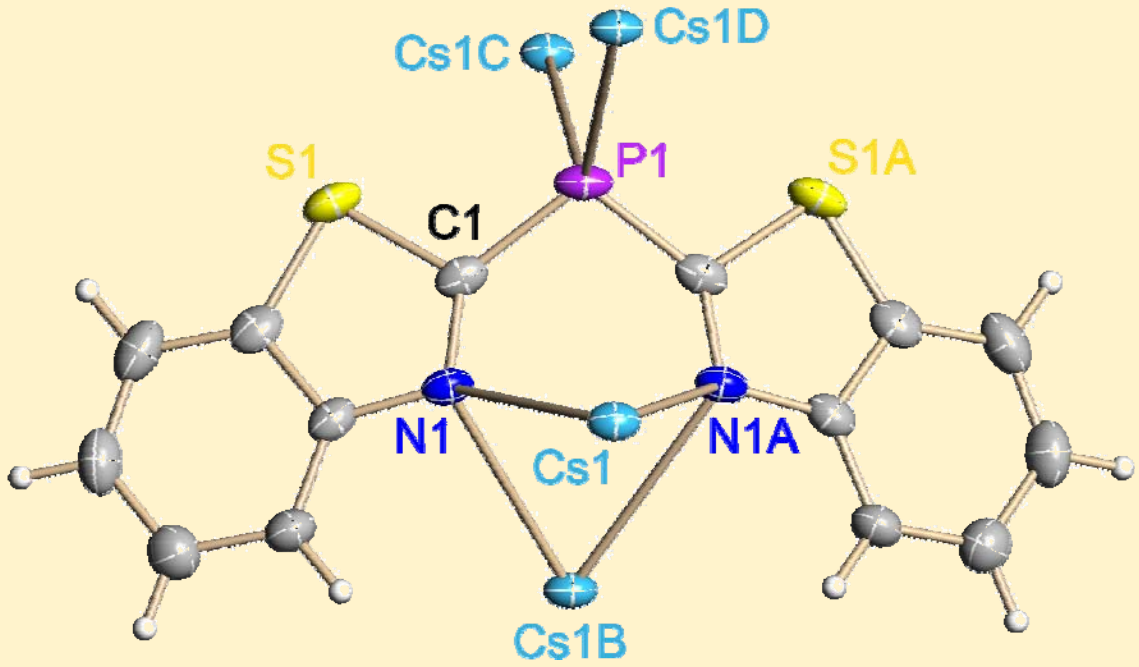
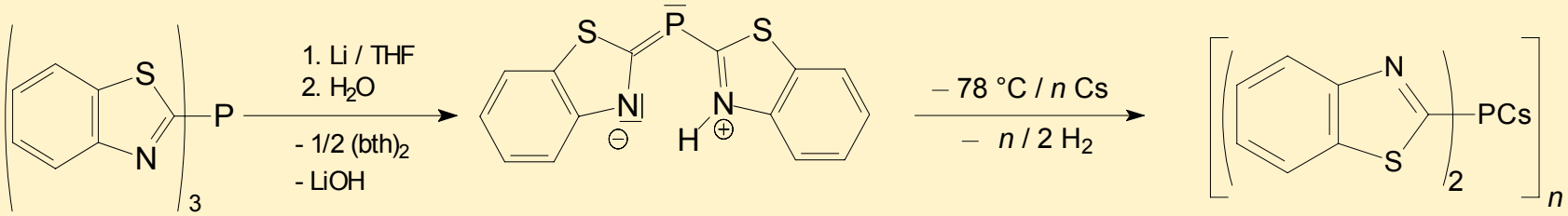
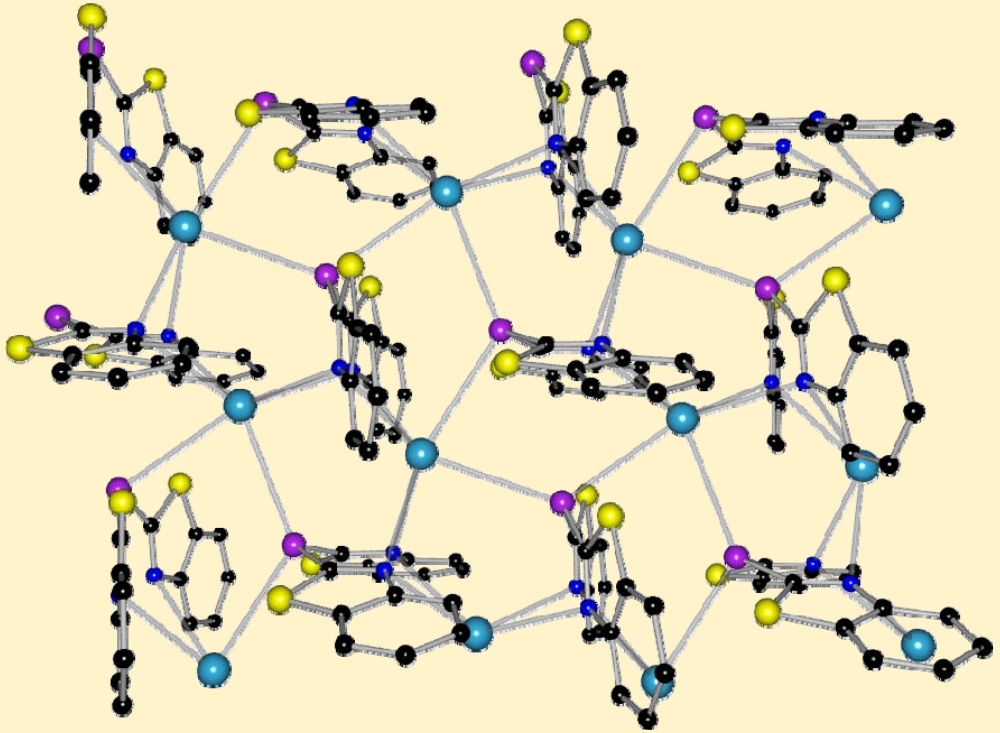




T. Stey, M. Pfeiffer, J. Henn, S. K. Pandey, D. Stalke, *Chem. Eur. J.* **2007**, DOI: 10.1002/Chem200601221.

4 e⁻ donor *Janus-Head* ligands





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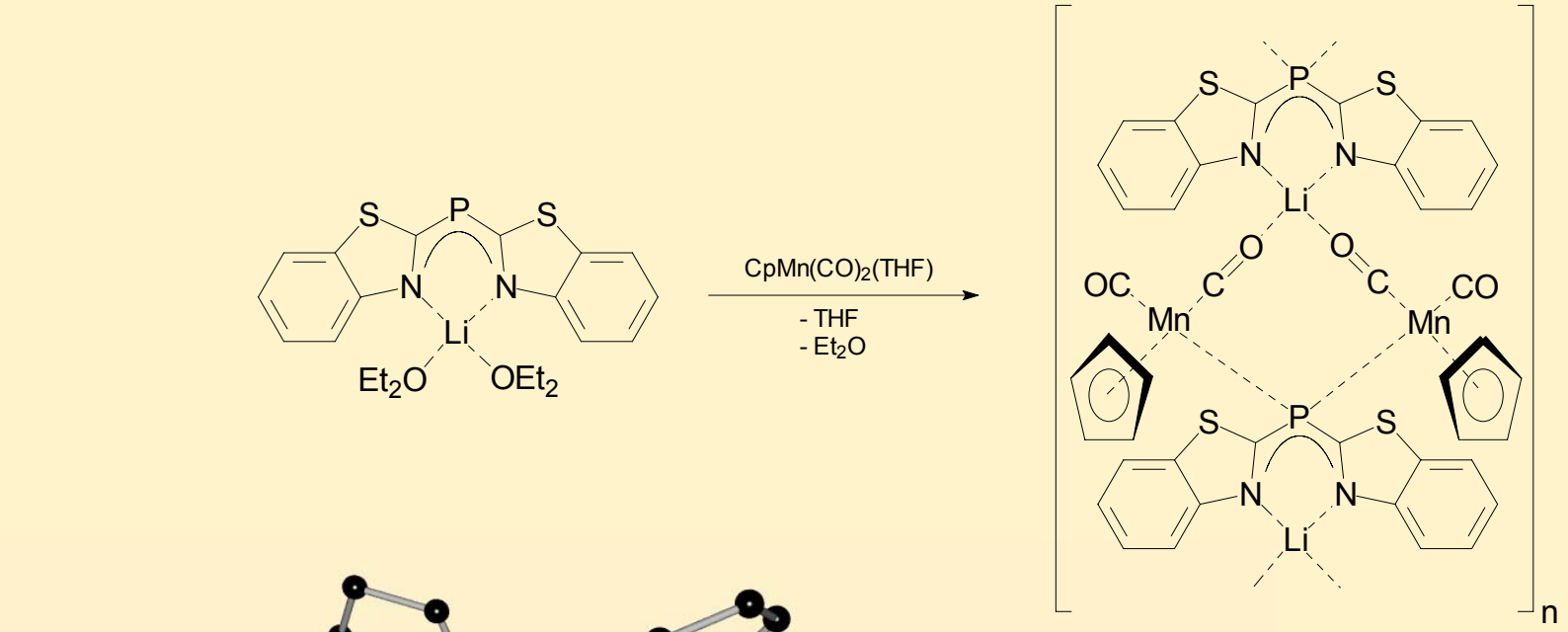
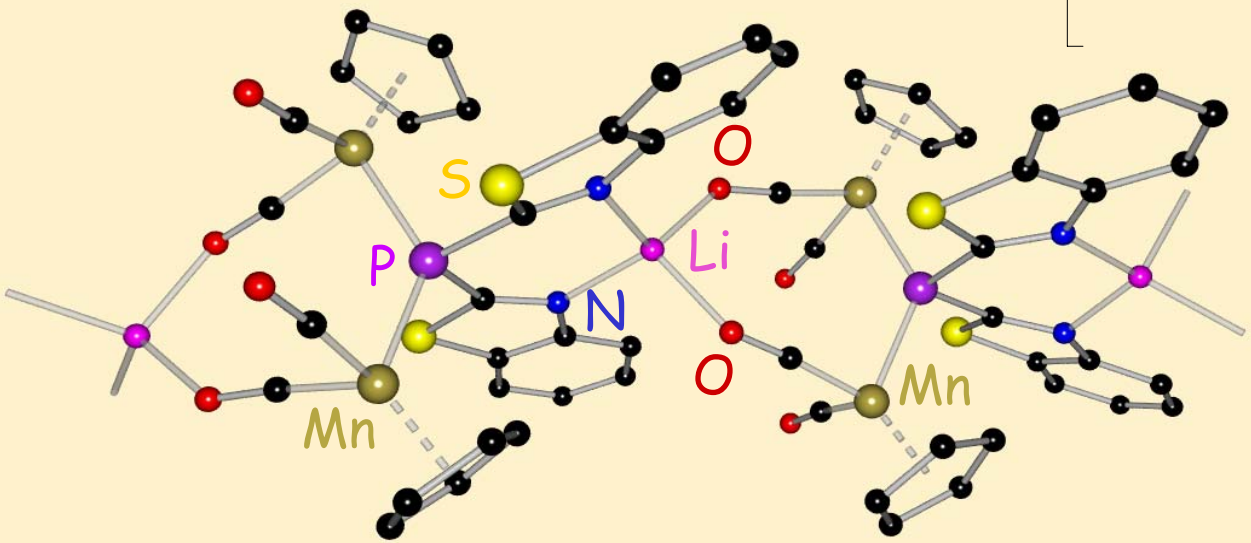
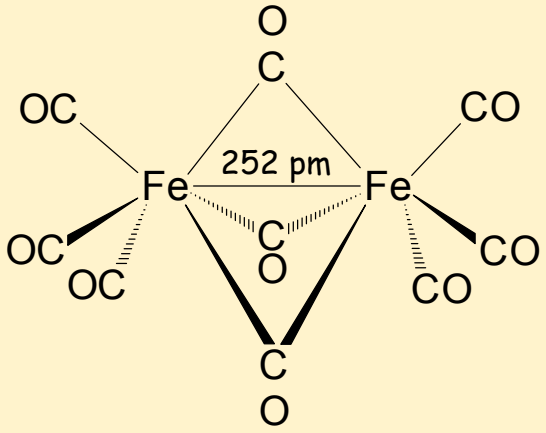


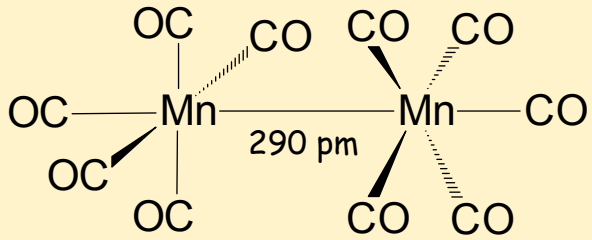


T. Stey, J. Henn, D. Stalke, *Chem. Commun.* **2007**, 413.

d-Block metal–metal bonds



F. A. Cotton et al. *Dalton Trans*. **1974**, 800.



G. Bianchi et al. *Inorg. Chem.* **2000**, *39,* 2360.

P. Macchi et al. *J. Am. Chem. Soc*. **1998**, *120*, 13429.

L. J. Farrugia et al. *Acta Crystallogr. Sect. B* **2003**, *59*, 234.

Review: P. Macchi, A. Sironi, *Coord. Chem. Rev.* **2003**, 238, 383.

Chemical Bonds without "Chemical Bonding"? L. J. Farrugia, C. Evans, M. Tegel, *J. Phys. Chem. A* **2006**, *110*, 7952.

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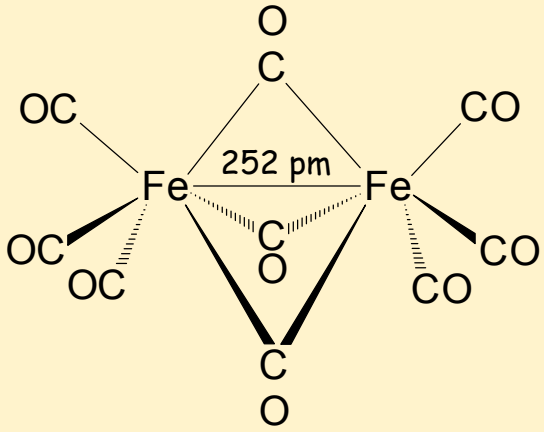

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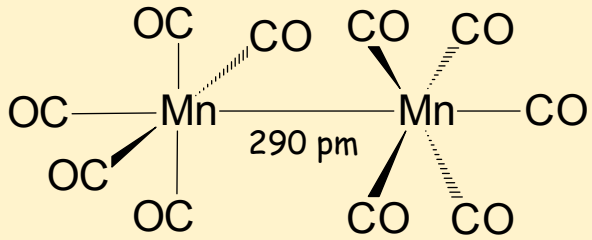

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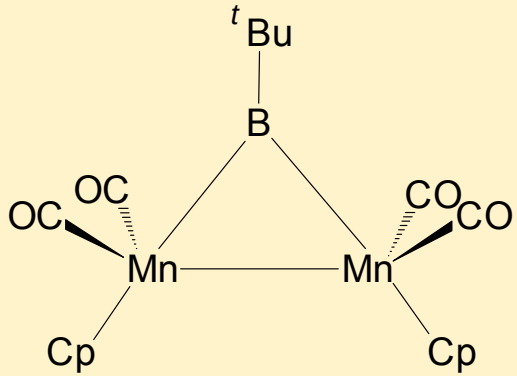

H. Braunschweig et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 4352.

Review: P. Macchi, A. Sironi, *Coord. Chem. Rev.* **2003**, 238, 383.

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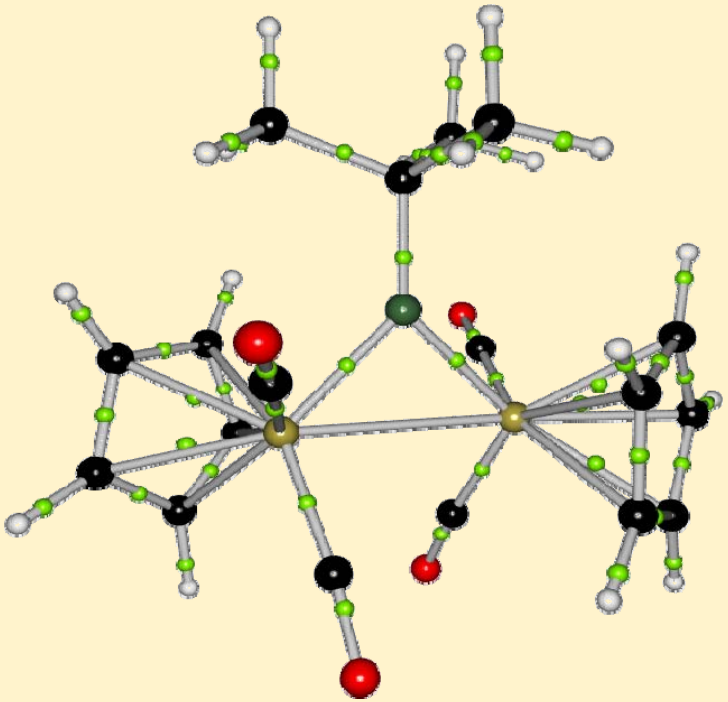
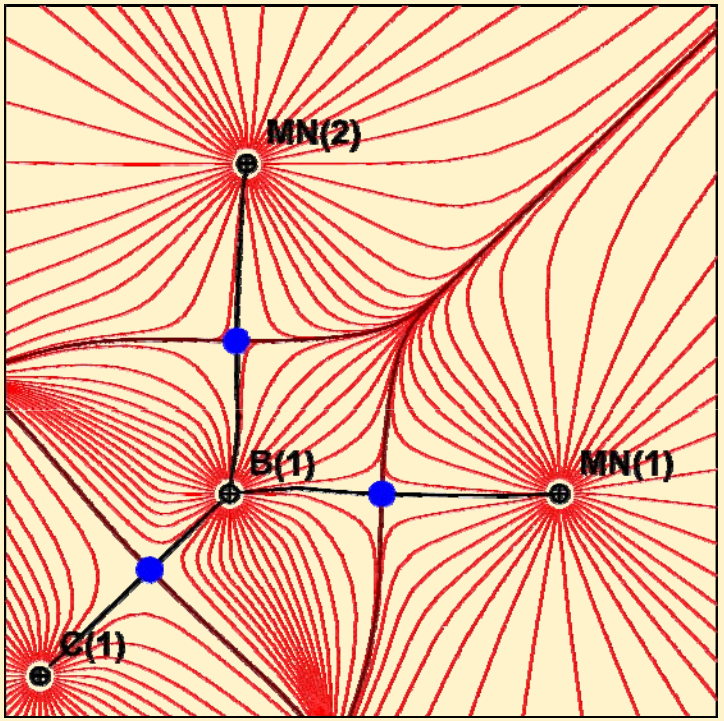
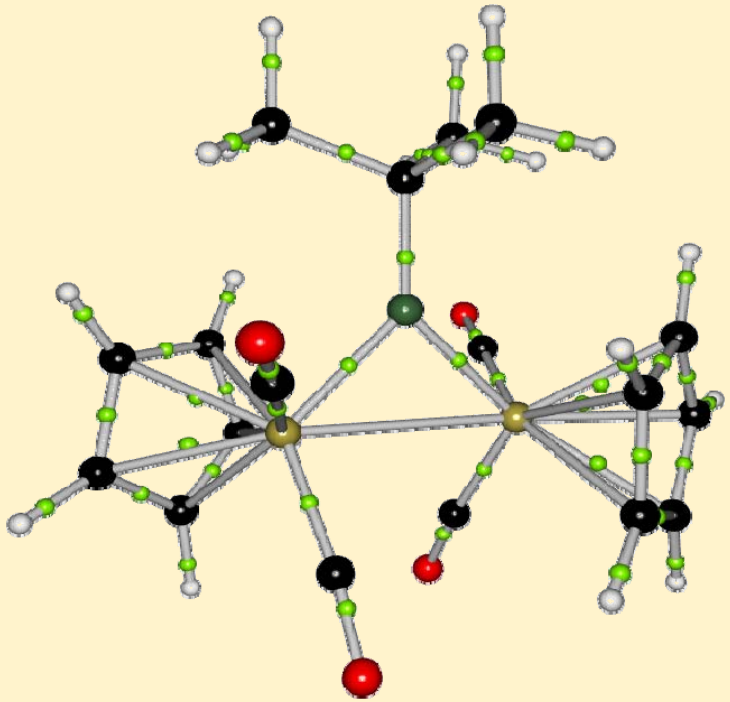


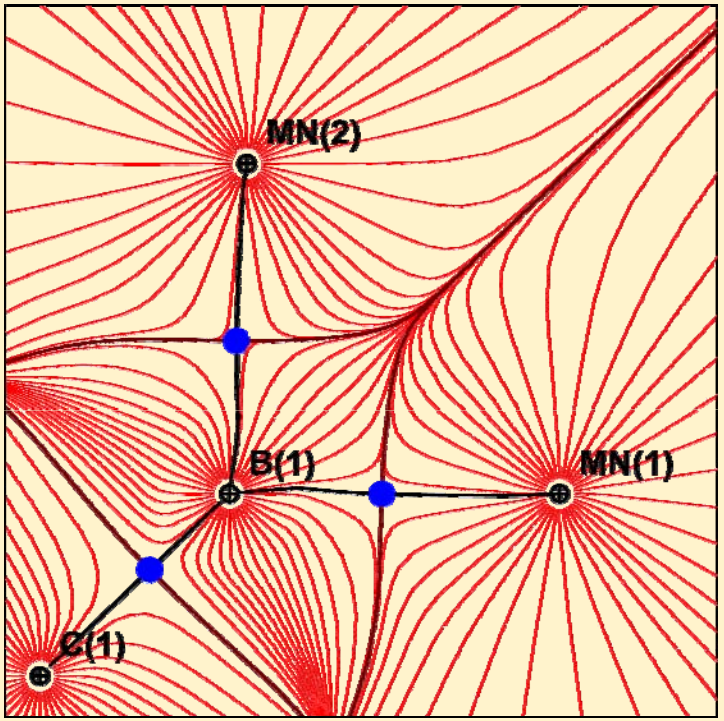


R1 (I>3σ(I)) / wR2 (I>3σ(I)) after multipole ref. to sin θ/λ_{max} = 1.187 [Å]	0.0162 / 0.0281 ($w = 1/\sigma^2$)
no. of unique reflections / R_{int} / R_{sigma}	23961 / 0.0203 / 0.0126
$N_{refl.}$ / $N_{param.}$	53.85

U. Flierler, J. Henn, M. Burzler, H. Braunschweig, H. Ott, D. Leusser, D. Stalke, in preparation.

d-Block metal–metal bonds





A–B	bond lengths	bond paths	$\rho(r_{BCP})$	$\nabla^2\rho(r_{BCP})$
Mn···Mn	2.7820(8)	-	(0.213)	(1.415)
Mn–B	2.0215(3)	2.0217	0.617	2.904
Mn–C	1.7850(3)	1.78450	0.982	14.844

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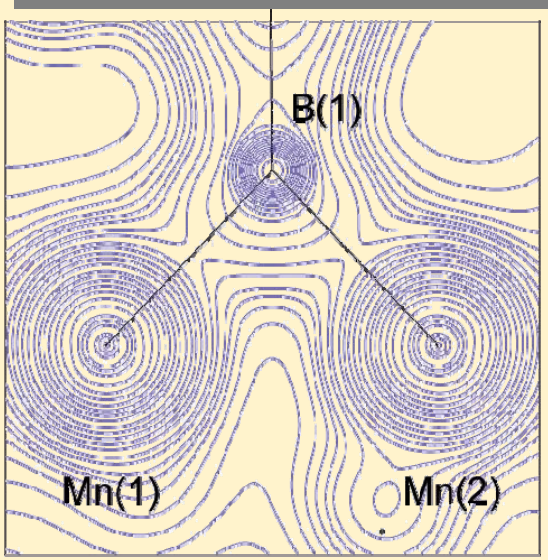
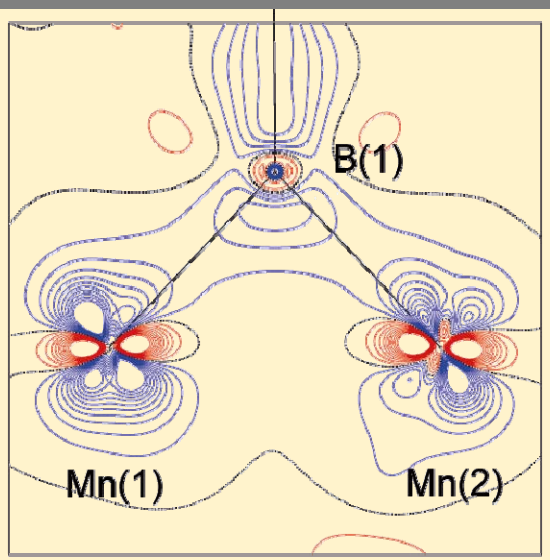
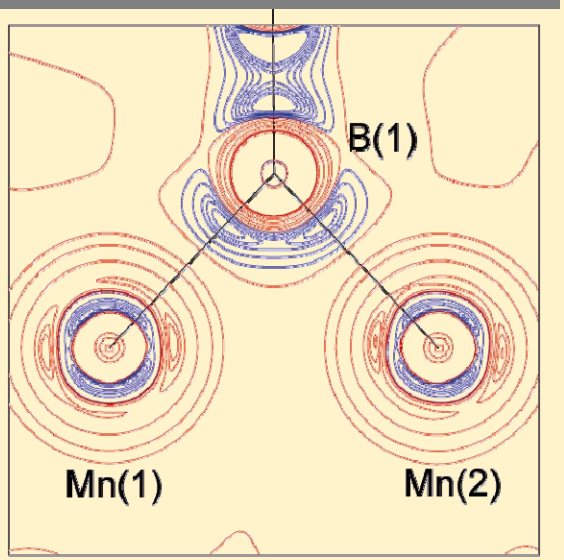


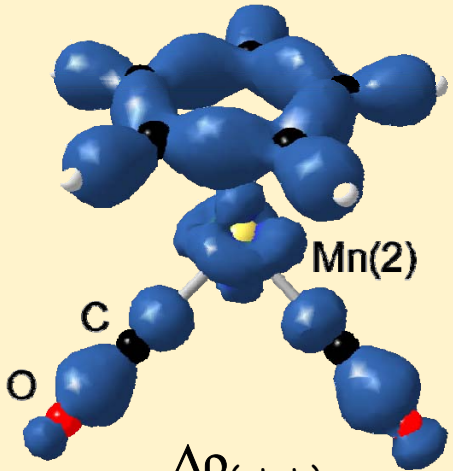
$\rho(r)$



$\Delta\rho_{(stat.)}$



$\nabla^2\rho(r)$



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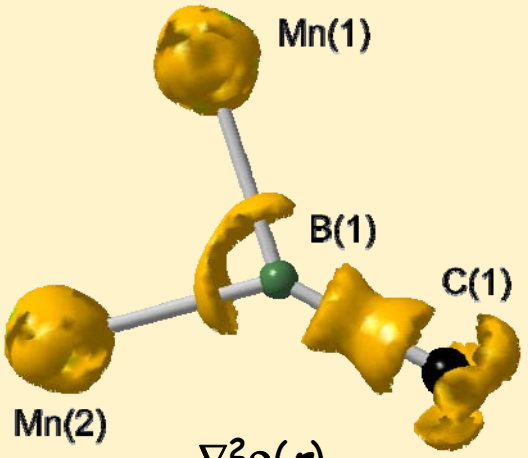


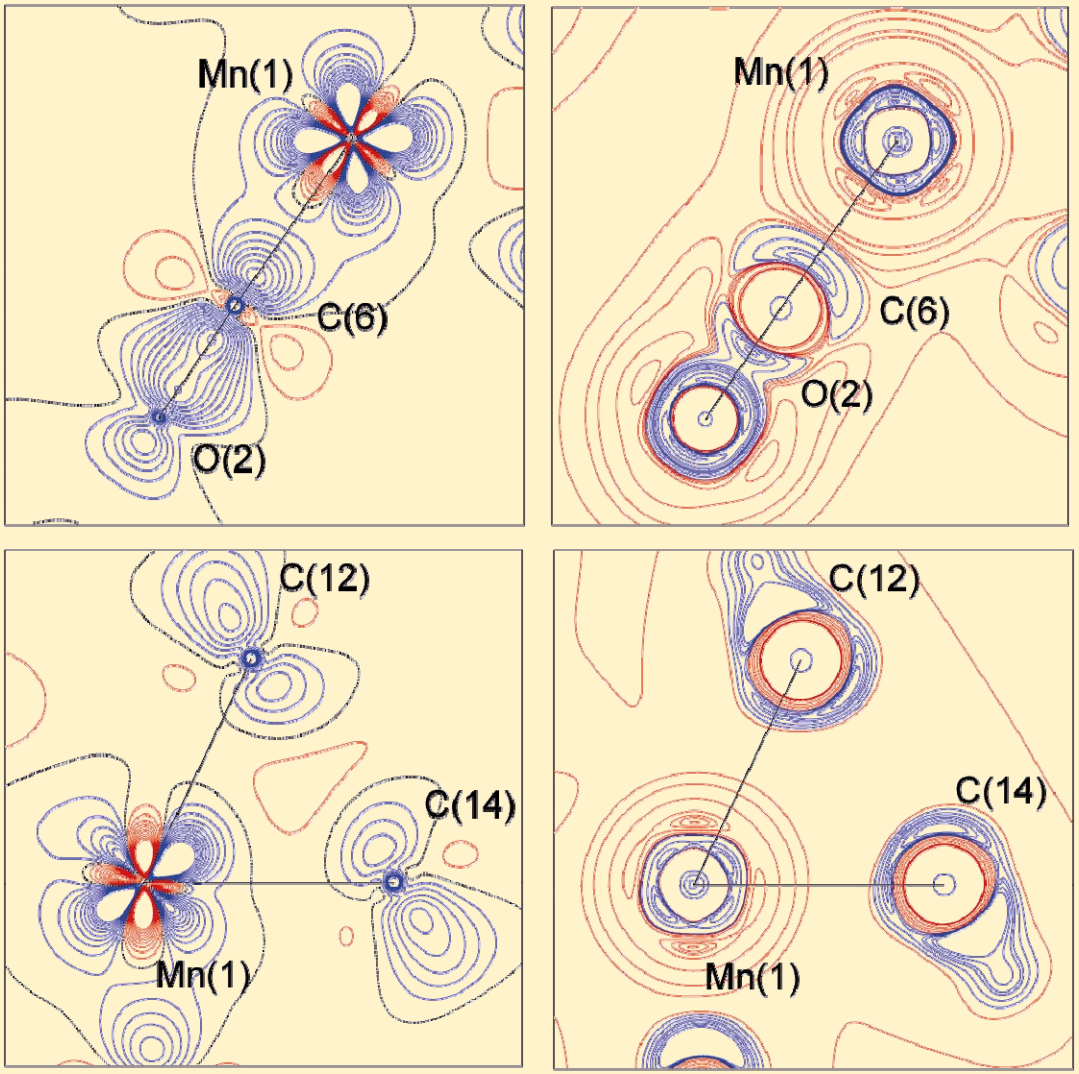
$\nabla^2\rho(r)$

U. Flierler, J. Henn, M. Burzler, H. Braunschweig, H. Ott, D. Leusser, D. Stalke, in preparation.

d-Block metal–metal bonds

static deformation density

$\Delta\rho_{(stat.)}$

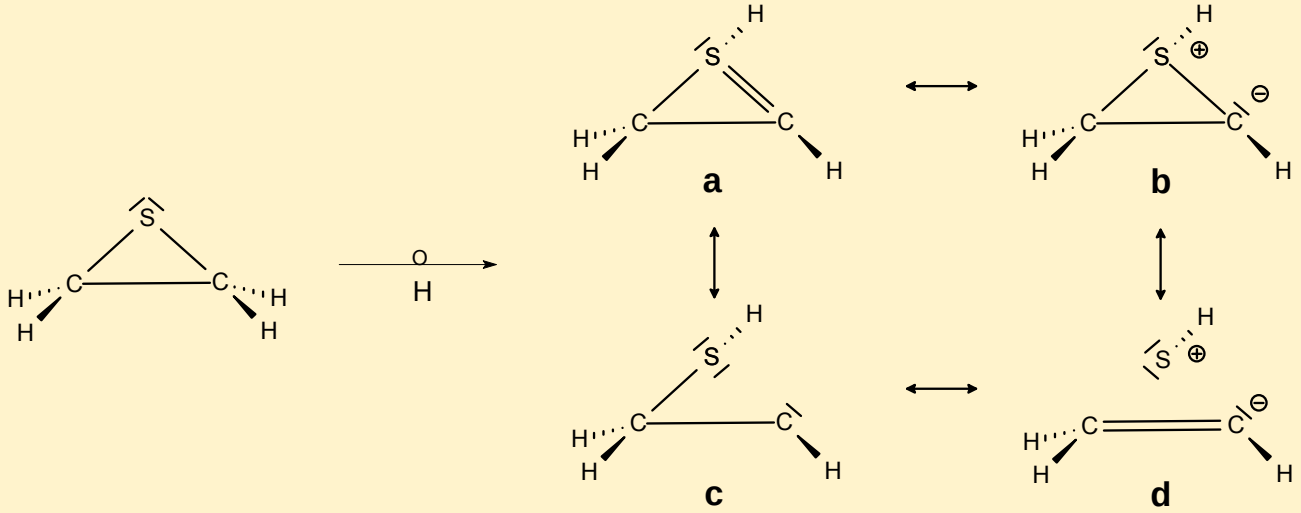


Laplacians

$\nabla^2\rho(r)$

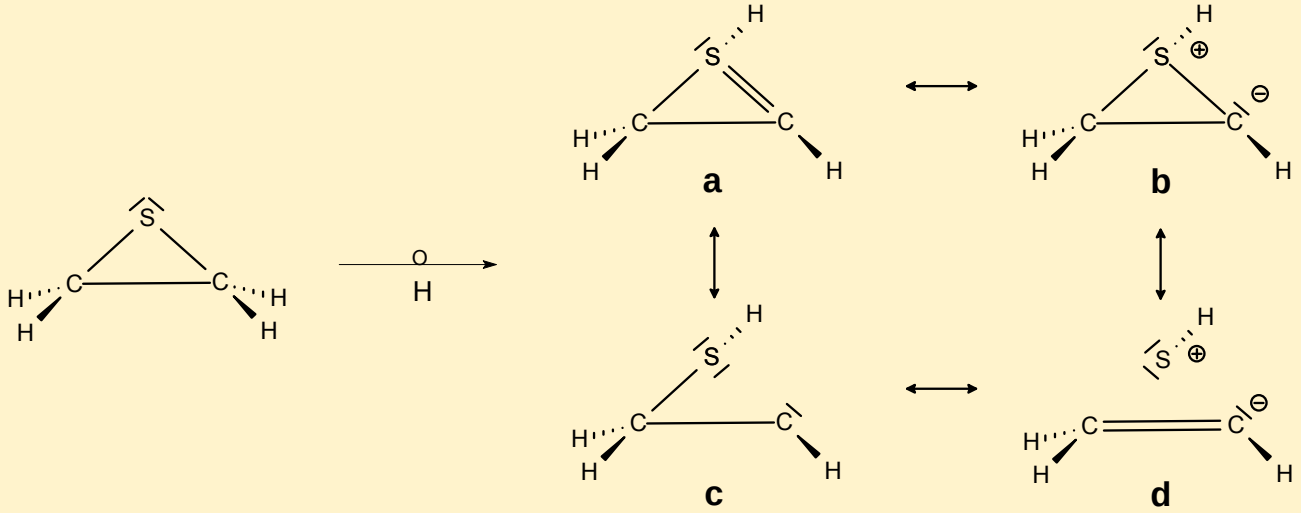
U. Flierler, J. Henn, M. Burzler, H. Braunschweig, H. Ott, D. Leusser, D. Stalke, in preparation.

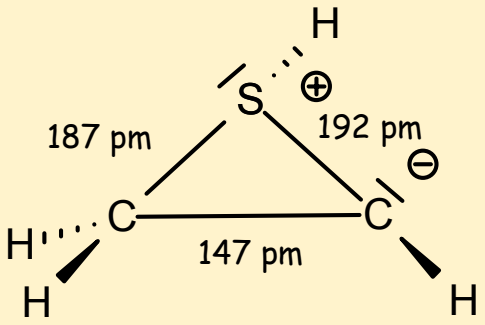
Chemical bonds without "chemical bonding"



J. Henn, D. Stalke, *J. Comput. Chem.*, submitted.

Chemical bonds without "chemical bonding"

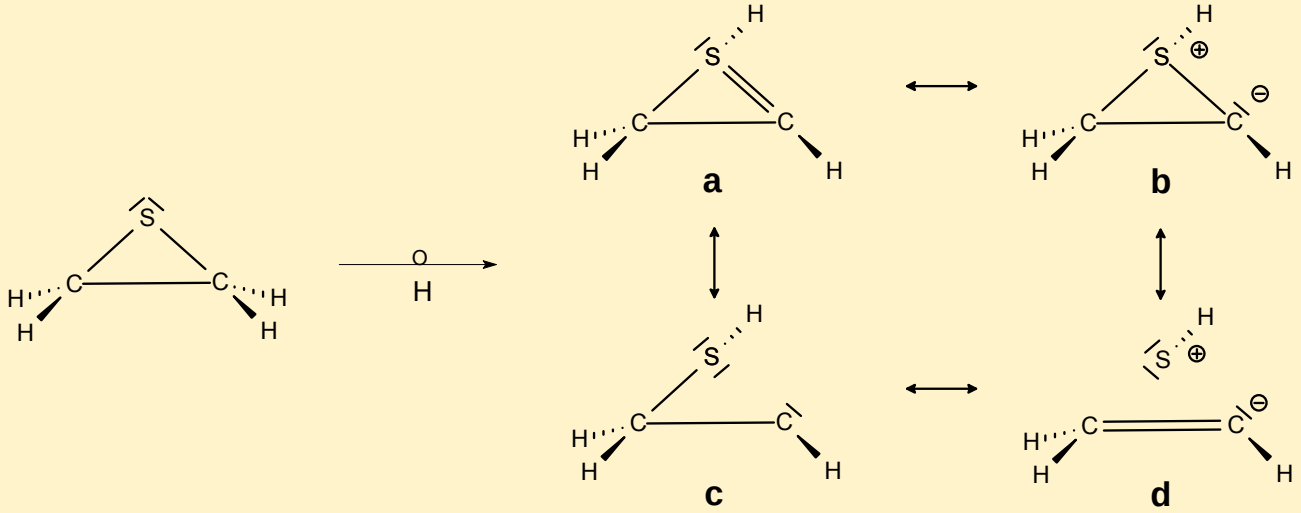


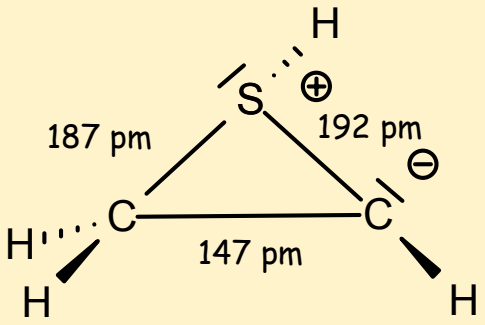


85 % in NRT

J. Henn, D. Stalke, *J. Comput. Chem.*, submitted.

Chemical bonds without "chemical bonding"





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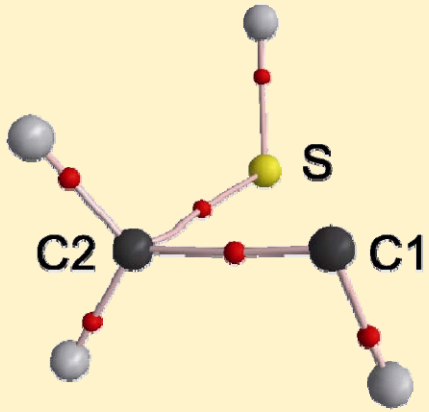
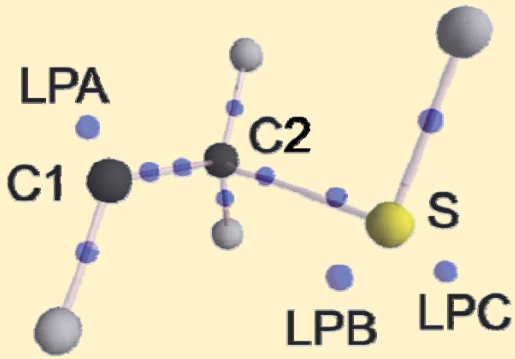


BCPs



VSCCs

in QTAIM

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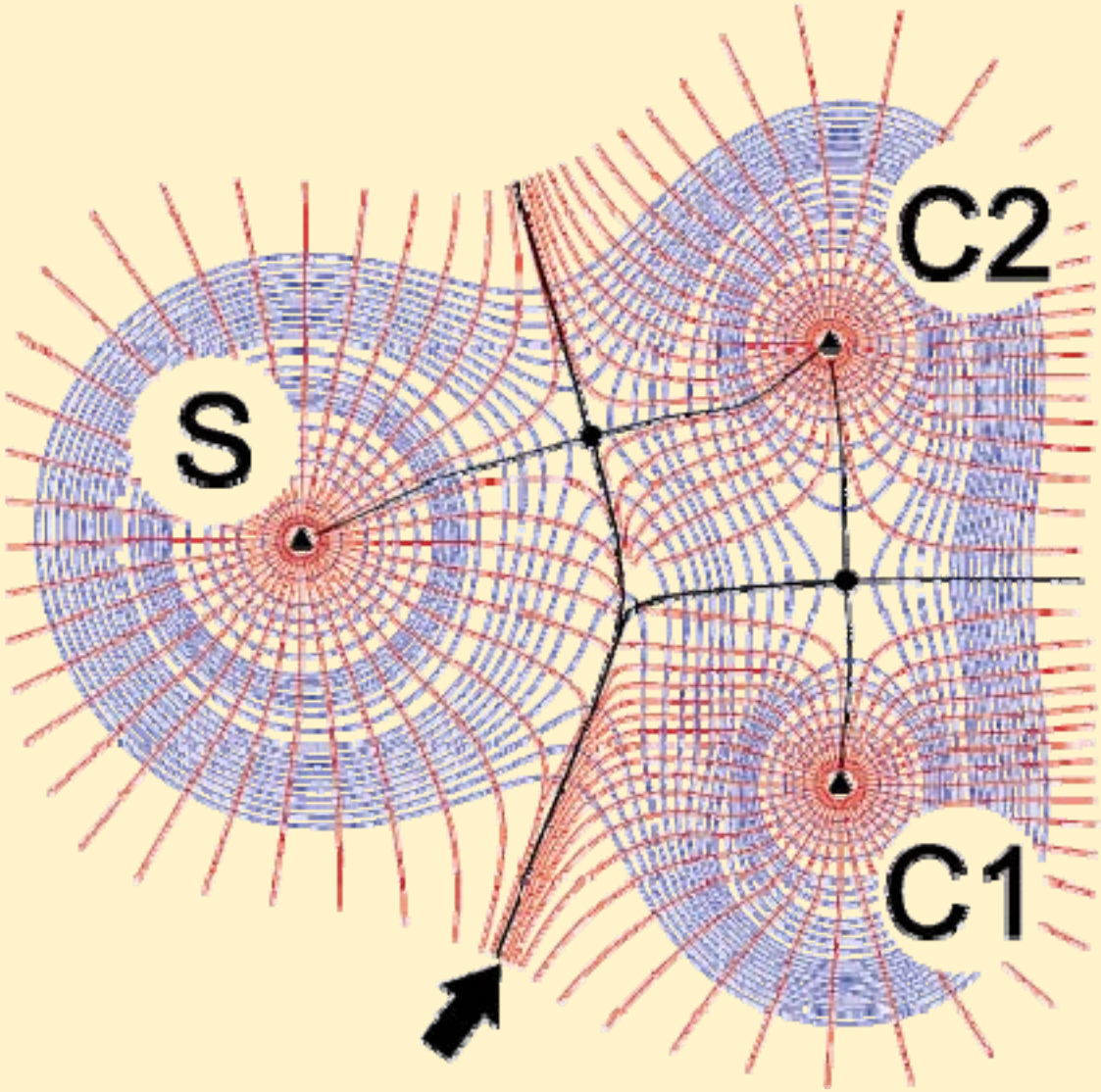

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Lithium organics or lithium amides

According to the literature it is impossible to metalate pyridine directly with *n*-butyllithium, because this base acts as a nucleophile and the ring substitution is in favor of the deprotonation.

B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press 1974.
D. R. Armstrong, R. E. Mulvey, D. Barr, R. Snaith, D. Reed, *J. Organomet. Chem.* **1988**, *350*, 191.
T. Lauterbach, K.-J. Niehues, *Butyllithium-Eigenschaften und Anwendungen*, CHEMETALL.

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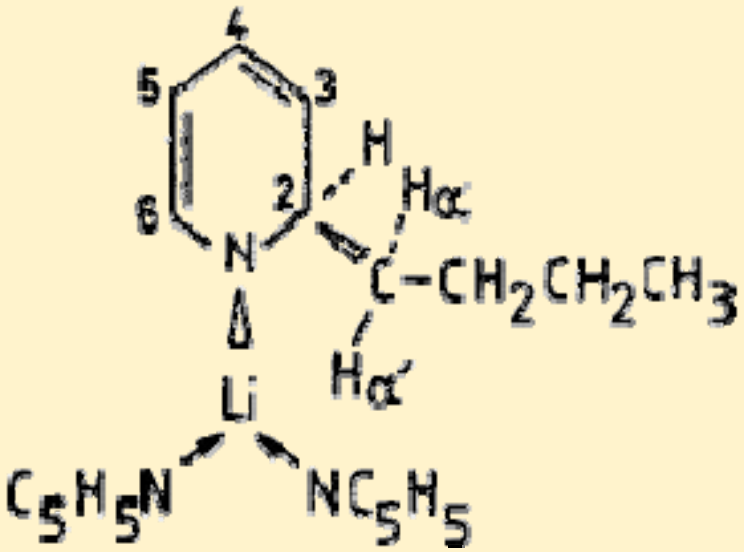

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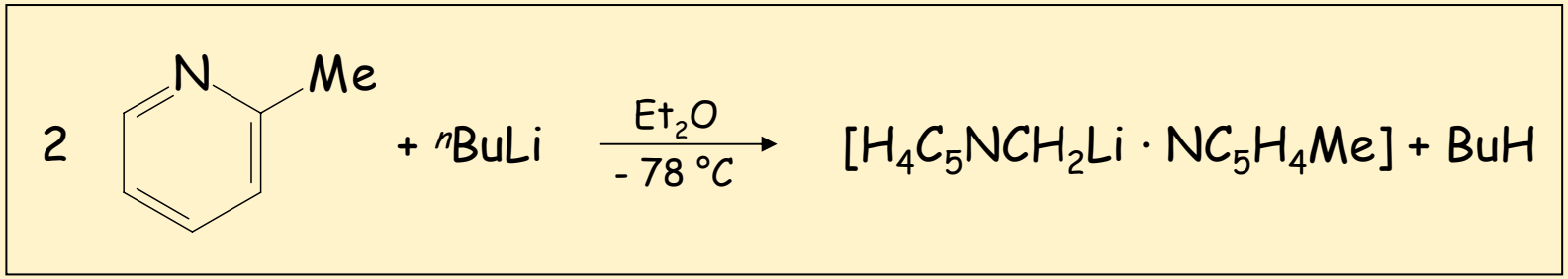

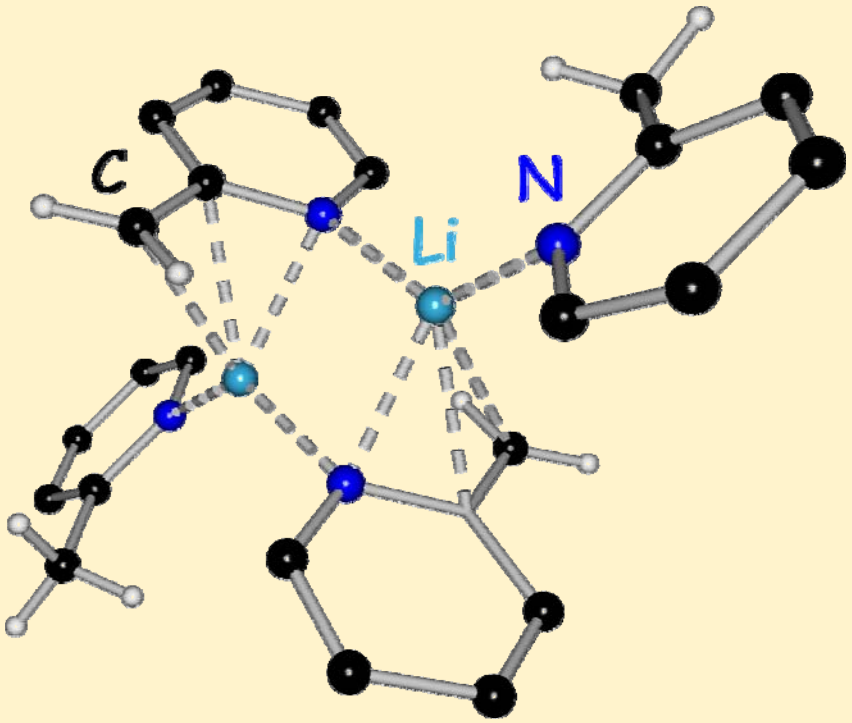

H. Ott, J. Henn, D. Leusser, D. Stalke, in preparation.

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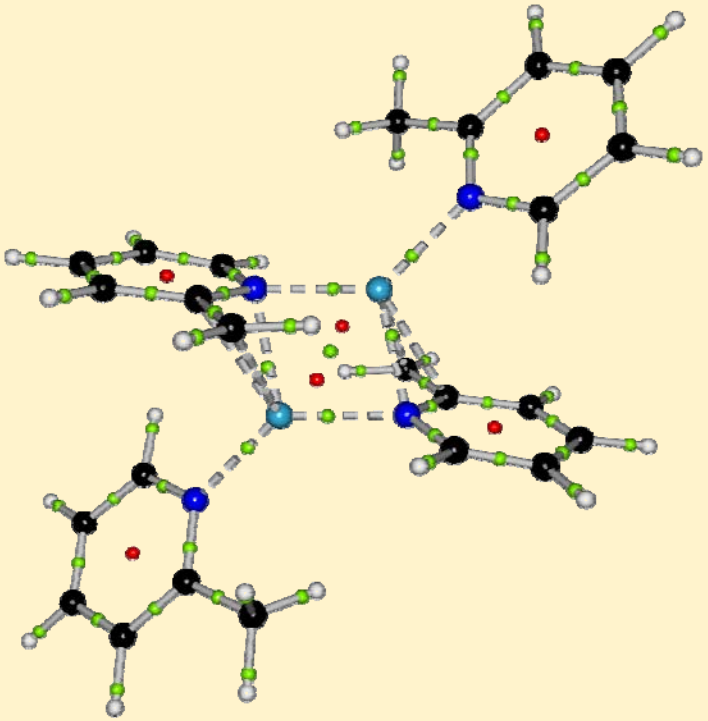

R1 (I>3σ(I)) / wR2 (I>3σ(I)) after multipole ref. to sin θ/λ_{max} = 1.136 [Å]	0.0244 / 0.0417 ($w = 1/\sigma^2$)
no. of unique reflections / R_{int} / R_{sigma}	13125 / 0.0202 / 0.0092
$N_{refl.}$ / $N_{param.}$	24.08

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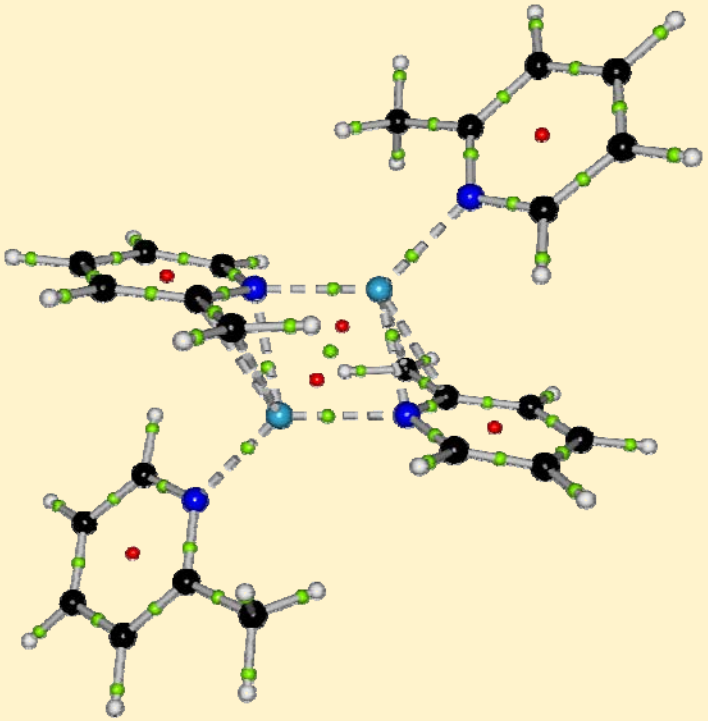

A—B	bond lengths	bond paths	$\rho(\mathbf{r}_{BCP})$	$\nabla^2\rho(\mathbf{r}_{BCP})$
$Li—N_{(carb.)}$	1.9788(4)	1.9789	0.167	4.899
$Li_{(allyl)}—N_{(carb.)}$	2.0489(4)	2.0506	0.123	3.615
$Li\cdots N_{(donor)}$	2.0337(4)	2.0337	0.153	4.435
Li—C	2.4378(5)			

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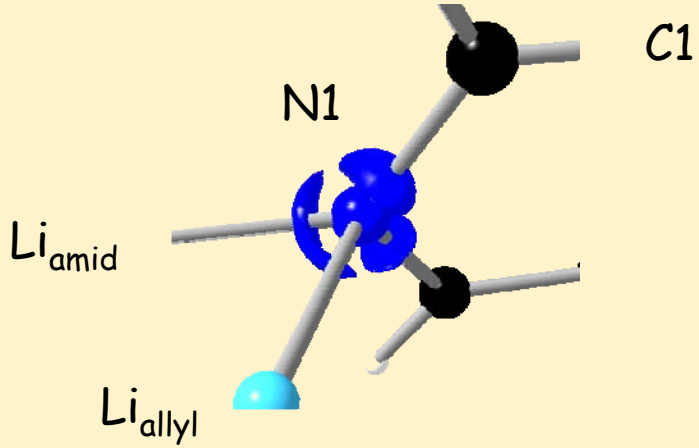
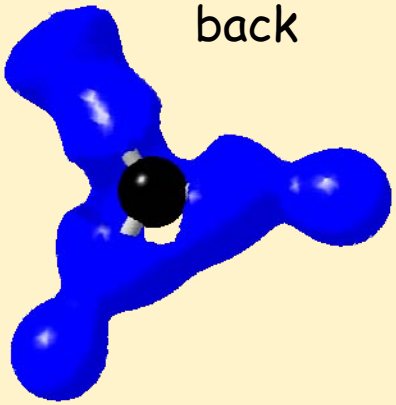
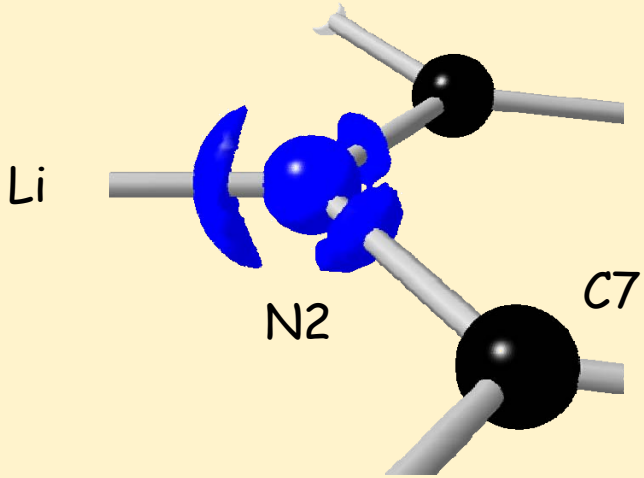
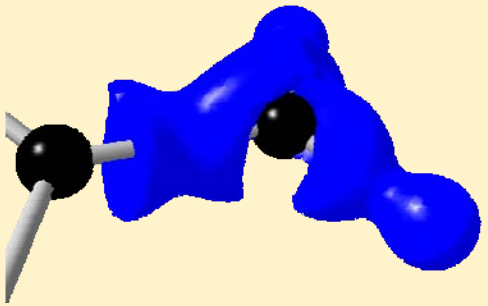


Laplacians

$\nabla^2\rho(r)$







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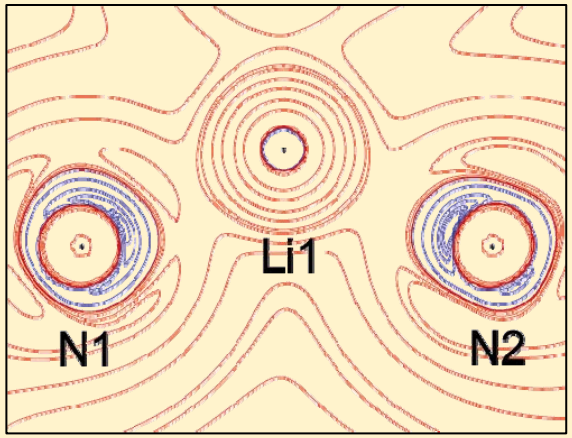
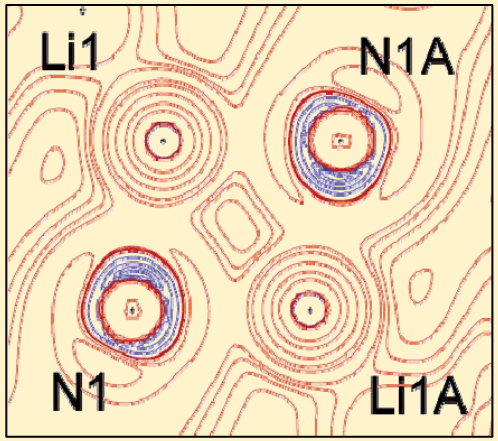
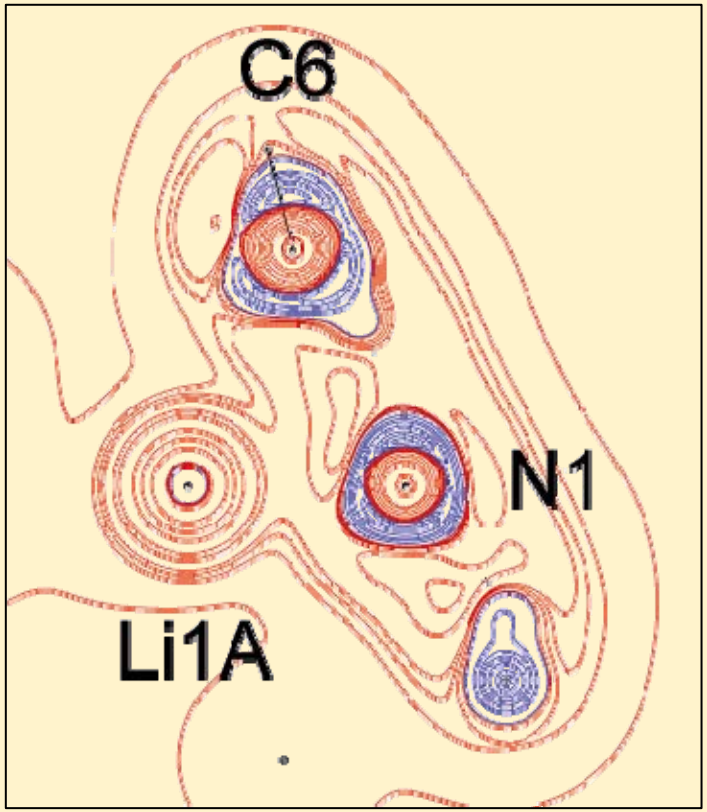
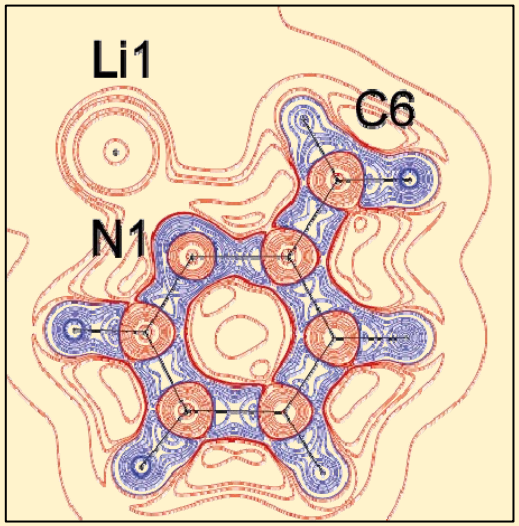
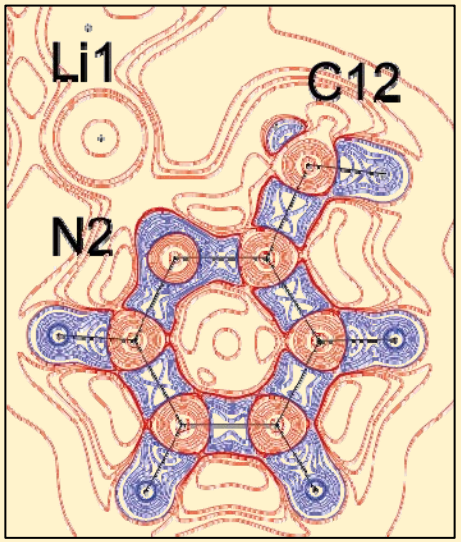










H. Ott, J. Henn, D. Leusser, D. Stalke, in preparation.

MoK_α TXS in life science

Cubic insulin

$C_{257}H_{387}N_{65}O_{66}S_6$ + soup

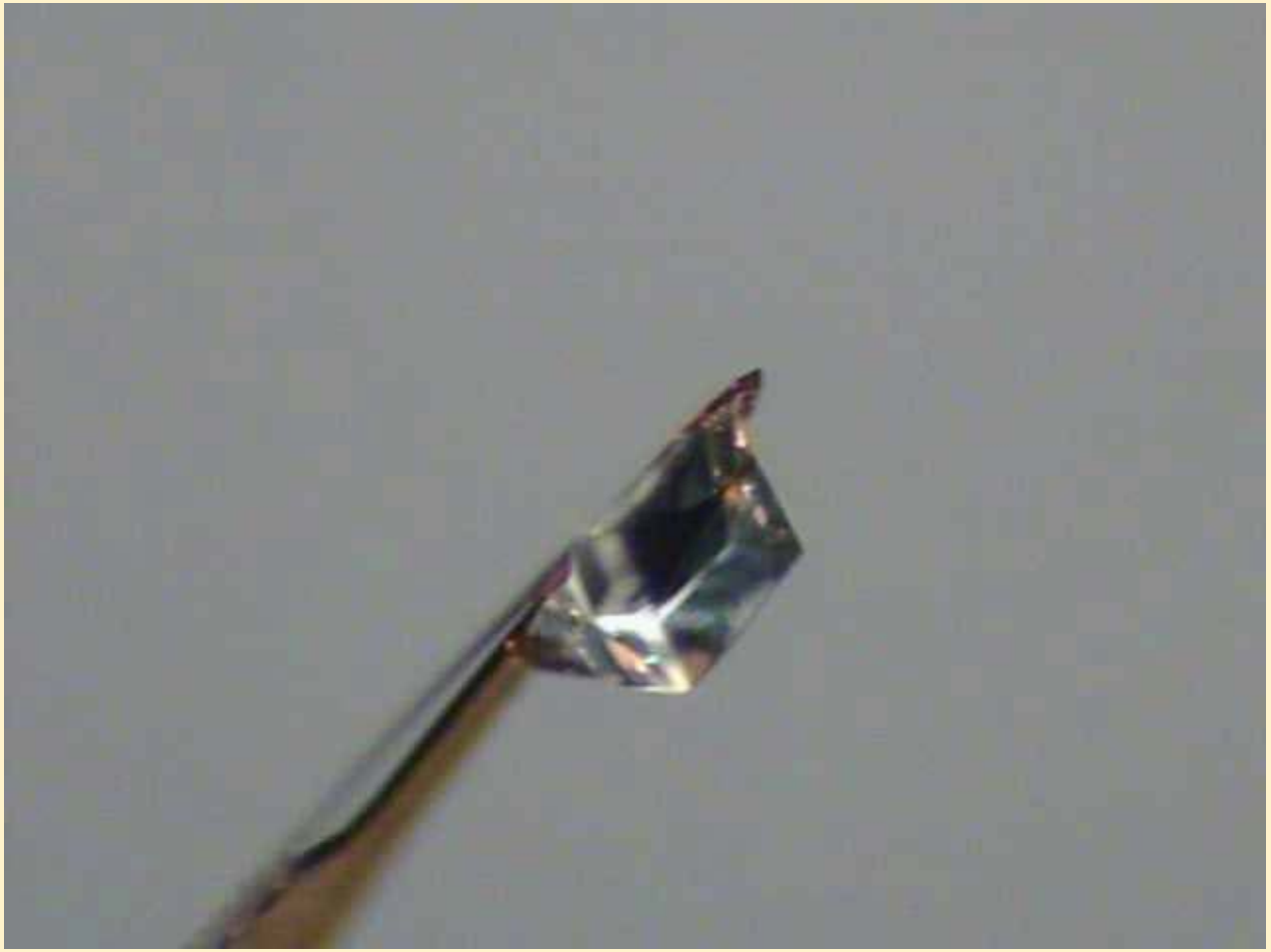
a = 77.8 Å

V = 470.140 $Å^3$

space group = I 2_13

size = 0.30 x 0.31 x 0.38 mm

detector dist. = 75 mm



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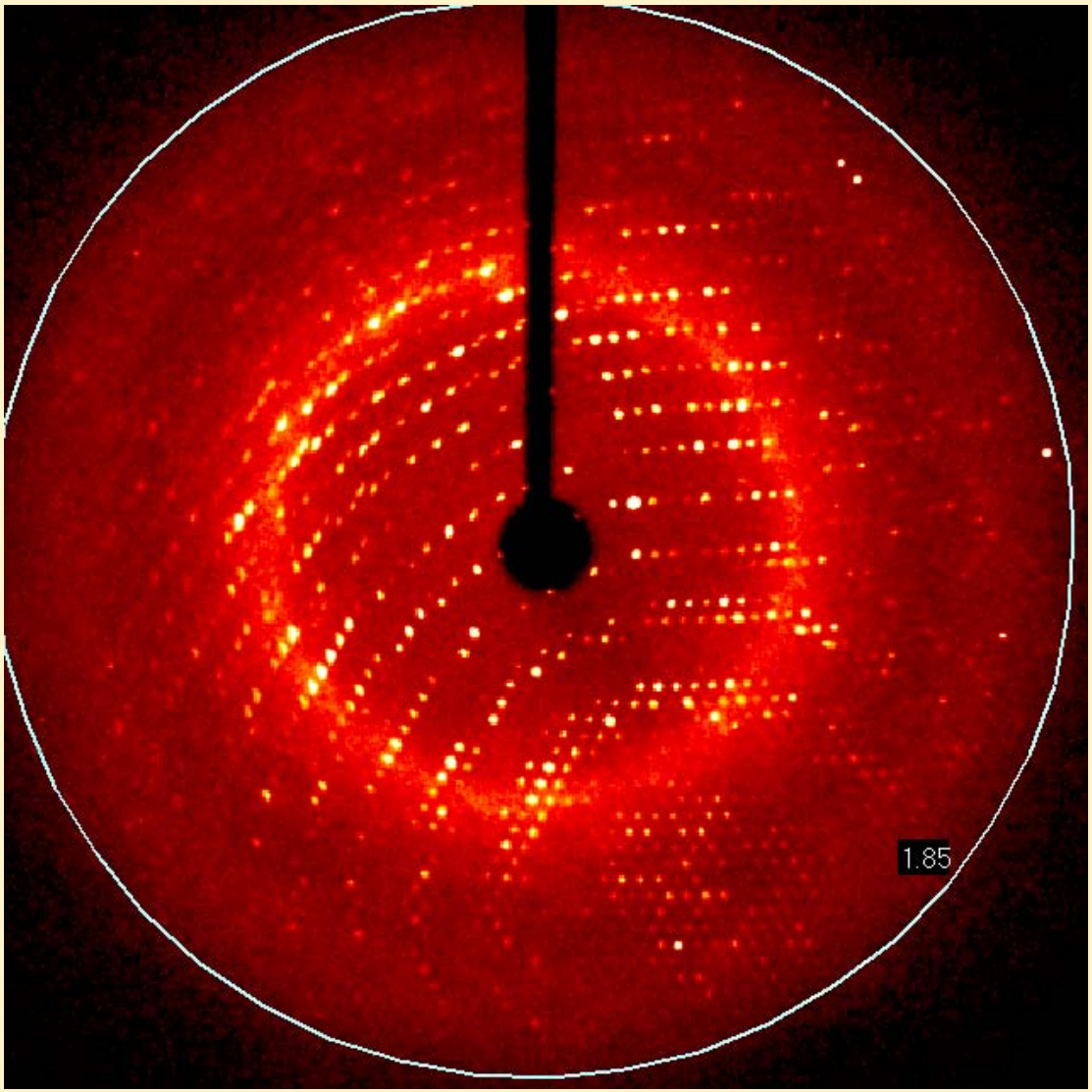

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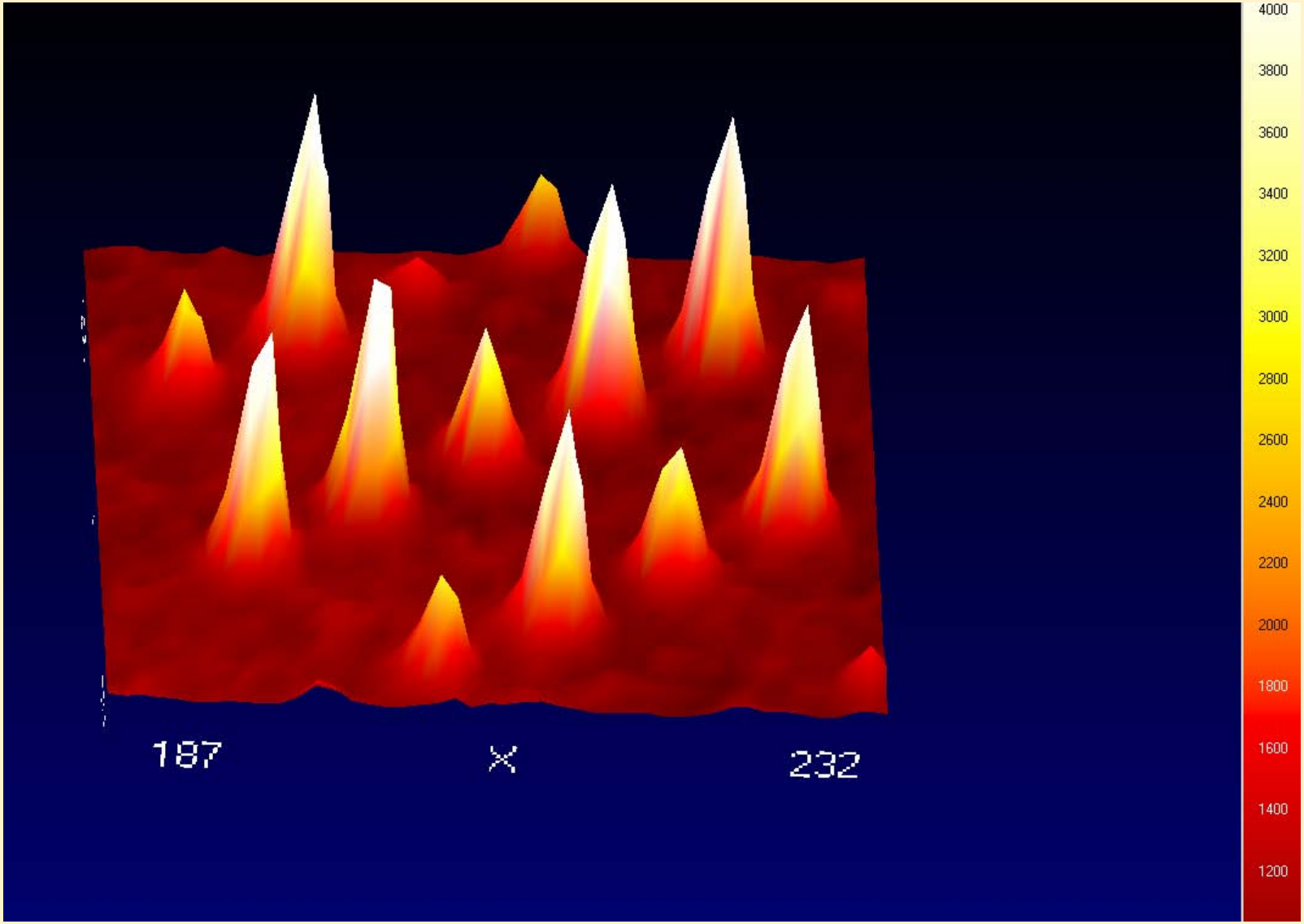

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Acknowledgement

Finances:

ExpED priority program 1178 of the DFG
Graduiertenkolleg 690 of the DFG
Deutscher Akademischer Austauschdienst (ARC, INIDA, PROCOP)
German-Israeli Foundation
CHEMETALL GmbH / Frankfurt