Electronic Supplementary Information (ESI)

belonging to

Pincer/Pseudo-Pincer Isomerism in Palladium(II) Complexes bearing κ^3*C*,*S*,*C* ligands

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Computational details, optimised complex and ligand geometries, plots of σ(HOMO)s

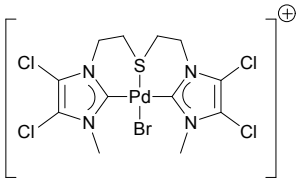
Computational Methods. All calculations were carried out using hybrid density functional theory (DFT) employing the B3LYP functional[1] and the Gaussian 09 software.[2] The nature of all stationary points was confirmed by frequency analysis, and all geometries were found to represent minima on the potential energy surface. For the optimisation of complex geometries and the calculation of their Gibbs free energies, palladium and bromine were described with a cc-pVDZ-PP basis set in combination with the corresponding electronic core potential (ECP),[3] while the lighter elements were treated with the cc-pVDZ basis set.[4] The optimisation of truncated ligand geometries was carried out using a cc-pVDZ basis set on all elements and Kohn-Sham orbitals were calculated for the optimised structures using the aug-cc-pVTZ basis set.[4,5] All basis sets were obtained from the EMSL Basis Set Library.[6]

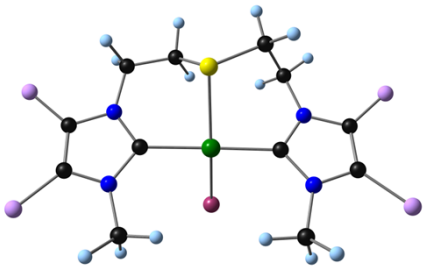
The choice of the B3LYP functional and (aug)-cc-pVxZ-(PP) basis sets was based on our previous, favourable experiences with this level of theory in accurately describing the electronic structure of N-heterocyclic carbenes.[7]

Optimised complex geometries: Bond distances (Å) and angles (deg)

	NHC backbone				
	1	**2**	**3**	**4**	**5**
Pd1-C1	2.0841	2.0760	2.0847	2.0864	2.0781
Pd1-C2	2.0478	2.0418	2.0450	2.0456	2.0781
Pd1-S1	2.3784	2.3881	2.3783	2.3729	2.3314
Pd1-Br1	2.4672	2.4669	2.4686	2.4744	2.4663
C1-Pd1-S1	87.37	87.26	87.79	89.12	91.26
C1-Pd1-Br1	91.82	91.86	92.19	91.39	89.22
C2-Pd1-S1	92.61	92.01	92.16	92.23	91.26
C2-Pd1-Br1	88.86	89.20	88.46	87.70	89.22
C1-Pd1-C2	177.91	178.53	178.11	178.26	174.07
S1-Pd1-Br1	161.55	163.34	161.68	160.78	170.09
Pd1-C1	2.0393	2.0259	2.0388	2.0370	2.0418
Pd1-C2	2.0538	2.0470	2.0548	2.0532	2.0528
Pd1-Br1	2.5153	2.5156	2.5212	2.5163	2.5257
Pd1-Br2	2.5078	2.5092	2.5130	2.5110	2.5098
C1-Pd1-Br1	88.82	88.58	89.33	89.14	87.74
C1-Pd1-Br2	89.00	88.54	88.44	88.76	89.55
C2-Pd1-Br1	92.57	92.45	92.08	93.33	94.43
C2-Pd1-Br2	91.07	92.11	91.74	90.05	89.41
C1-Pd1-C2	168.73	167.96	168.60	169.53	169.47
Br1-Pd1-Br2	172.03	171.18	171.42	172.38	169.47

Dichloroimidazolin-2-ylidene, pincer complex





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C	-4.189296000	0.603606000	0.105322000
C	-4.223974000	-0.677057000	-0.364706000
C	2.078523000	-0.021842000	-0.181328000
C	-2.051700000	-0.105535000	-0.151358000
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H	3.120693000	2.848690000	1.092008000
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H	-1.689928000	2.118342000	1.522152000
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H	0.716940000	2.361160000	1.364191000
H	1.006323000	3.874988000	0.445764000
C	-1.564749000	2.930662000	-0.510907000
H	-2.160743000	2.926445000	-1.435211000
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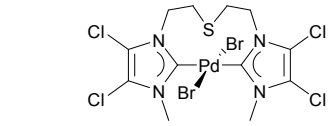
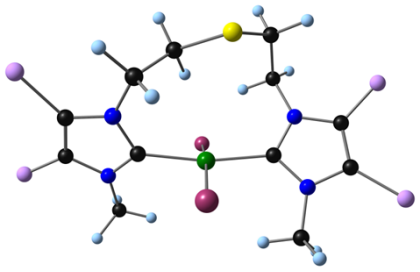
Cl	5.573755000	1.670468000	0.277832000
Cl	5.548339000	-1.762759000	-0.545006000

Dichloroimidazolin-2-ylidene, pseudo-pincer complex





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C	-4.021681000	0.497731000	0.361347000
C	-4.195953000	-0.727587000	-0.207539000
C	2.083840000	-0.366784000	-0.070032000
C	-1.981963000	-0.460855000	0.158332000
N	3.118996000	-1.166146000	0.288130000
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N	-2.657239000	0.652165000	0.586977000
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C	1.868464000	1.930504000	-1.036013000
H	1.275795000	1.496149000	-1.853405000
H	2.587971000	2.638047000	-1.464595000
C	-2.067852000	1.773612000	1.332264000
H	-1.140709000	1.391374000	1.775257000
H	-2.750005000	1.994117000	2.168309000
C	0.942048000	2.622040000	-0.013938000
H	0.727688000	1.927963000	0.809908000
H	1.406742000	3.527910000	0.405104000
C	-1.838202000	3.075072000	0.554466000
H	-2.773393000	3.430133000	0.094449000
H	-1.530995000	3.841333000	1.285794000
C	-2.688465000	-2.635506000	-0.862348000
H	-3.313195000	-3.369564000	-0.334064000

H	-2.913621000	-2.654106000	-1.937329000
H	-1.628172000	-2.862890000	-0.716689000
C	2.983624000	-2.531109000	0.786199000
H	3.555906000	-3.219502000	0.148313000
H	3.346171000	-2.592809000	1.821604000
H	1.919413000	-2.786718000	0.760932000
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Br	-0.024366000	-0.876044000	-2.429013000
Cl	-5.204063000	1.671624000	0.780172000
Cl	-5.641673000	-1.502057000	-0.712083000
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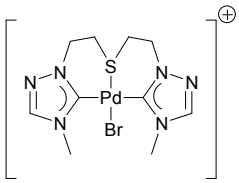
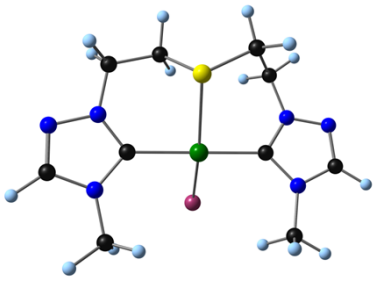
1,2,4-triazolin-5-ylidene, pincer complex





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Br	-0.009511000	-2.189634000	1.077794000
C	4.228708000	-0.509187000	-0.418001000
H	5.125790000	-1.085335000	-0.630135000
C	-4.210424000	-0.469243000	-0.408877000
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C	-2.041921000	-0.085783000	-0.170202000
N	2.953724000	-0.995851000	-0.570362000
N	2.892505000	1.011107000	0.127266000
N	-2.810145000	0.909250000	0.314504000
N	-2.955465000	-0.981452000	-0.642896000
C	2.590875000	2.412820000	0.440078000
H	2.963920000	3.019071000	-0.399671000
H	3.183962000	2.679694000	1.327352000
C	-2.337540000	2.174660000	0.863003000

H	-1.739759000	1.981573000	1.765685000
H	-3.236455000	2.731529000	1.160362000
C	1.129963000	2.724610000	0.716913000
H	0.764681000	2.212447000	1.617656000
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C	-1.561913000	2.982587000	-0.177197000
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H	-1.339244000	3.991395000	0.201568000
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C	2.651225000	-2.341928000	-1.068415000
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H	1.724396000	-2.312678000	-1.650509000
N	4.225018000	0.722436000	0.004417000
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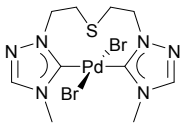
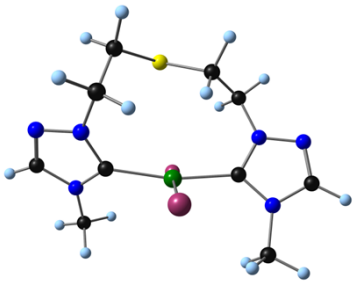
1,2,4-triazolin-5-ylidene, pseudo-pincer complex





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C	-4.098785000	-0.925670000	-0.162591000
H	-5.023827000	-1.392914000	-0.489423000
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C	-1.921574000	-0.602383000	0.129275000
N	3.225120000	-0.765000000	0.132411000
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C	1.739810000	2.344858000	-0.787815000
H	1.257831000	2.066056000	-1.736661000
H	2.472731000	3.135901000	-0.984375000
C	-2.235403000	1.488955000	1.519522000
H	-1.276527000	1.197943000	1.965016000
H	-2.969698000	1.579407000	2.334230000
C	0.682756000	2.796258000	0.247542000
H	0.598263000	2.044984000	1.044710000
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H	4.323390000	-2.460137000	0.665094000
H	2.663508000	-2.370878000	1.356760000
H	2.895697000	-2.779127000	-0.374925000
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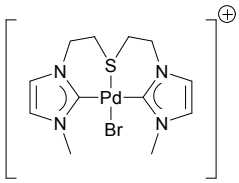
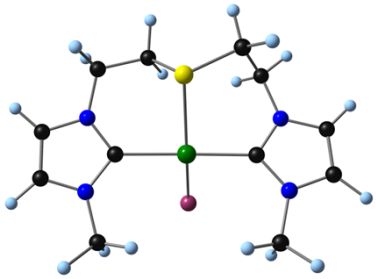
Imidazolin-2-ylidene, pincer complex





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C	4.258724000	0.596591000	0.020556000

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C	-2.042847000	-0.067489000	-0.197714000
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N	-2.913960000	-0.981825000	-0.691621000
C	2.607396000	2.395428000	0.413482000
H	2.960068000	2.997999000	-0.439420000
H	3.188394000	2.703779000	1.296996000
C	-2.297569000	2.159584000	0.876813000
H	-1.664315000	1.929406000	1.746367000
H	-3.150019000	2.752318000	1.238959000
C	1.147637000	2.712652000	0.692879000
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H	1.064233000	3.800410000	0.837528000
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H	-2.141800000	3.099207000	-1.082451000
H	-1.311618000	3.986192000	0.218713000
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H	-2.517143000	-3.055301000	-0.608293000
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H	-1.578174000	-2.139716000	-1.818435000
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H	2.550428000	-3.104960000	-0.282216000
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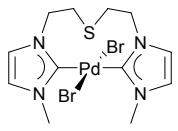
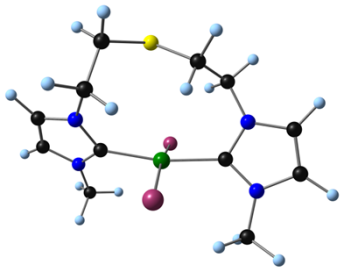
Imidazolin-2-ylidene, pseudo-pincer complex





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H	-4.485135000	2.200580000	0.364115000
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C	4.116174000	-1.046662000	0.322660000
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H	4.966522000	-1.591768000	0.718792000
C	-2.107611000	-0.054898000	0.080142000
C	1.925243000	-0.610633000	-0.058587000
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N	2.708121000	0.333911000	-0.665710000
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H	-0.535470000	1.922024000	-1.081501000
H	-1.010829000	3.634526000	-0.924910000
C	2.153290000	2.810730000	-0.947594000
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H	3.159602000	-2.842453000	2.067215000
H	1.440757000	-2.552072000	1.675392000
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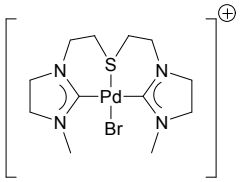
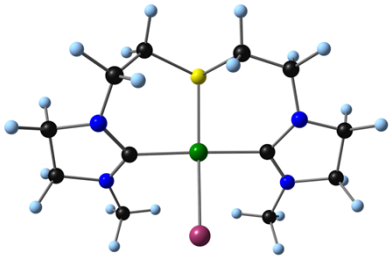
H	-3.137858000	-2.776128000	0.514302000
Br	-0.332937000	-0.966326000	-2.452058000
Br	-0.099248000	-0.428559000	2.533712000

Imidazolidin-2-ylidene, pincer complex



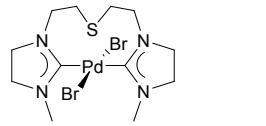


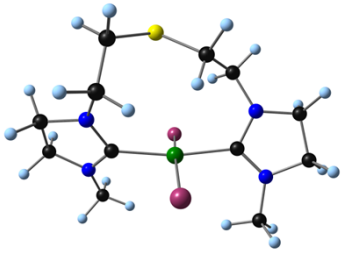
G = -1631.78668 a.u.

Pd	0.001655000	-0.025755000	-0.190891000
S	0.015728000	2.271407000	-0.785612000
Br	-0.022357000	-2.083495000	1.183145000
C	4.278762000	-0.829659000	-0.313891000
C	4.320734000	0.650397000	0.070746000
H	4.919074000	-1.077299000	-1.172711000
H	4.738272000	1.282569000	-0.733778000
C	-4.235063000	0.658981000	0.181408000
C	-4.263975000	-0.755408000	-0.415997000
H	-4.819455000	0.745571000	1.107930000
H	-4.903586000	-0.838766000	-1.306186000
C	2.087689000	-0.015494000	-0.230000000
C	-2.042843000	-0.092230000	-0.178651000
N	2.857079000	-1.023755000	-0.647329000
N	2.888239000	0.967469000	0.260084000
N	-2.793026000	0.839197000	0.446372000
N	-2.848138000	-0.979913000	-0.766306000
C	2.576181000	2.390221000	0.352072000
H	2.926903000	2.897354000	-0.568346000
H	3.170236000	2.807152000	1.182627000
C	-2.251805000	2.091759000	0.947907000
H	-1.547599000	1.888623000	1.769587000
H	-3.084528000	2.668148000	1.378613000
C	1.126783000	2.763749000	0.615070000
H	0.754346000	2.308017000	1.542930000
H	1.065090000	3.859663000	0.694581000
C	-1.587008000	2.939834000	-0.143199000
H	-2.233455000	3.027843000	-1.028979000
H	-1.369582000	3.956470000	0.218937000
C	-2.458436000	-2.202382000	-1.449190000
H	-2.628888000	-3.081261000	-0.806590000
H	-3.050881000	-2.306947000	-2.371566000
H	-1.394655000	-2.155455000	-1.704109000
C	2.437115000	-2.301996000	-1.199417000
H	3.055175000	-2.524209000	-2.083874000
H	2.557227000	-3.109060000	-0.460028000
H	1.384406000	-2.251629000	-1.492342000
H	4.550728000	-1.492578000	0.525062000
H	4.888535000	0.844370000	0.991880000
H	-4.586445000	-1.514173000	0.317823000

H	-4.594119000	1.422496000	-0.531666000

Imidazolidin-2-ylidene, pseudo-pincer complex



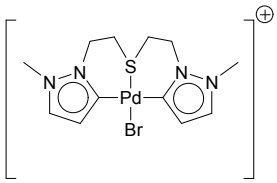


G = -2048.91733 a.u.

Pd	0.125890000	-0.533553000	0.024491000
S	-0.962447000	3.200332000	-0.508238000
C	4.430595000	-0.101520000	0.055375000
C	3.982348000	1.266736000	-0.476767000
H	4.802545000	-0.044622000	1.095276000
H	4.416418000	2.108933000	0.081642000
C	-4.119883000	0.130055000	0.424720000
C	-4.133700000	-1.138223000	-0.438500000
H	-4.548458000	-0.042295000	1.429469000
H	-4.819701000	-1.912906000	-0.062398000
C	2.105915000	-0.074462000	-0.109641000
C	-1.922937000	-0.627520000	0.119350000
N	3.177828000	-0.868321000	0.016396000
N	2.521990000	1.198915000	-0.296932000
N	-2.679287000	0.415562000	0.540549000
N	-2.736738000	-1.581504000	-0.355820000
C	1.645798000	2.272178000	-0.786474000
H	1.090136000	1.898274000	-1.660384000
H	2.299487000	3.089568000	-1.123965000
C	-2.226632000	1.474575000	1.434583000
H	-1.257112000	1.172435000	1.848986000
H	-2.926318000	1.504880000	2.291694000
C	0.656259000	2.782908000	0.283761000
H	0.483725000	1.984137000	1.016689000
H	1.053826000	3.659318000	0.819690000
C	-2.160944000	2.892707000	0.850241000
H	-3.126334000	3.187689000	0.406850000
H	-1.966314000	3.591329000	1.681559000
C	-2.319423000	-2.801876000	-1.016540000
H	-2.920134000	-3.647189000	-0.641052000

H	-2.442387000	-2.724811000	-2.109963000
H	-1.260369000	-2.980332000	-0.799666000
C	3.148910000	-2.258085000	0.425325000
H	3.429241000	-2.364874000	1.487730000
H	2.132025000	-2.644845000	0.293150000
H	3.848353000	-2.843402000	-0.193852000
Br	0.400645000	-0.825692000	2.508631000
Br	0.011849000	-0.533446000	-2.483930000
H	5.206458000	-0.575464000	-0.564628000
H	4.227949000	1.392502000	-1.547183000
H	-4.395750000	-0.925237000	-1.490771000
H	-4.660749000	0.967462000	-0.040132000

Pyrazolin-5-ylidene, pincer complex

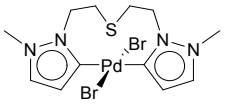


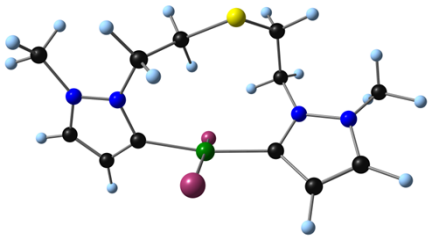
G = -1629.34185 a.u.

Pd	0.000002000	0.258485000	-0.106326000
C	2.870065000	1.431012000	-0.550785000
C	4.189074000	1.025090000	-0.599164000
H	2.490312000	2.430794000	-0.728312000
H	5.100899000	1.577145000	-0.814421000
C	-2.870057000	1.430991000	-0.550849000
C	-4.189067000	1.025068000	-0.599219000
H	-2.490304000	2.430767000	-0.728409000
H	-5.100890000	1.577116000	-0.814498000
C	2.075305000	0.313428000	-0.198794000
C	-2.075299000	0.313420000	-0.198813000
N	-2.964893000	-0.712737000	-0.035326000
N	-4.252323000	-0.291113000	-0.298404000
N	2.964898000	-0.712734000	-0.035340000
N	4.252329000	-0.291102000	-0.298396000
C	5.439101000	-1.113120000	-0.113532000
H	5.564282000	-1.407206000	0.940216000
H	5.409729000	-2.008048000	-0.751872000

H	6.301954000	-0.504647000	-0.410033000
C	-5.439096000	-1.113123000	-0.113507000
H	-5.409729000	-2.008072000	-0.751816000
H	-5.564271000	-1.407173000	0.940253000
H	-6.301949000	-0.504658000	-0.410022000
C	-2.738342000	-2.149204000	0.149844000
H	-2.842564000	-2.665086000	-0.820680000
H	-3.519388000	-2.539735000	0.818046000
C	2.738346000	-2.149207000	0.149790000
H	2.842544000	-2.665060000	-0.820752000
H	3.519405000	-2.539761000	0.817962000
C	1.400445000	-2.488858000	0.787363000
H	1.262276000	-1.958202000	1.739954000
H	1.371003000	-3.575370000	0.960411000
C	-1.400428000	-2.488842000	0.787397000
H	-1.262243000	-1.958169000	1.739976000
H	-1.370982000	-3.575351000	0.960462000
S	-0.000003000	-2.061902000	-0.333071000
Br	-0.000013000	2.635277000	0.552216000

Pyrazolin-5-ylidene, pseudo-pincer complex



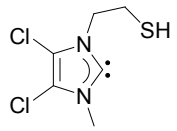


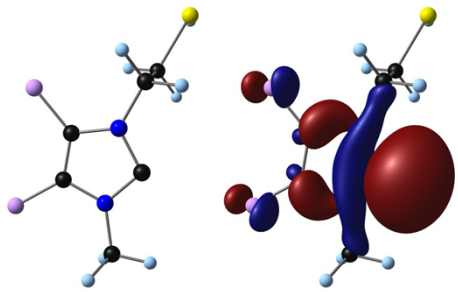
G = -2046.46328 a.u.

Pd	0.119276000	0.330796000	-0.801904000
S	-0.668494000	-0.487931000	2.892807000
C	4.358881000	-0.328897000	-0.696394000
H	5.397415000	-0.508731000	-0.964263000
C	-4.054721000	1.242431000	-0.504543000
H	-5.002727000	1.771068000	-0.574728000
C	2.137073000	0.090529000	-0.602370000
C	-1.920998000	0.485430000	-0.635977000
N	2.633323000	-0.107714000	0.647649000
N	-2.678560000	-0.366051000	0.109581000
C	1.872127000	0.000625000	1.901583000
H	1.338466000	0.960646000	1.836980000
H	2.578803000	0.058414000	2.738520000

C	-2.273966000	-1.618976000	0.744445000
H	-1.399814000	-1.956058000	0.171690000
H	-3.060939000	-2.369062000	0.561290000
C	0.863566000	-1.153805000	2.094839000
H	0.590609000	-1.554574000	1.109311000
H	1.285095000	-1.968866000	2.704870000
C	-1.988863000	-1.592136000	2.255119000
H	-2.871906000	-1.264296000	2.827812000
H	-1.783528000	-2.632003000	2.561051000
Br	0.054786000	-1.952111000	-1.880578000
Br	0.338934000	2.691882000	0.020498000
C	-2.813946000	1.519093000	-1.033504000
C	3.248882000	-0.053321000	-1.470729000
H	-2.531630000	2.393134000	-1.610579000
H	3.215387000	0.021137000	-2.552566000
N	-3.977618000	0.098746000	0.225837000
N	3.986236000	-0.370254000	0.607361000
C	4.811848000	-0.593226000	1.775919000
H	5.822898000	-0.831533000	1.422102000
H	4.865864000	0.303592000	2.413613000
H	4.441688000	-1.443046000	2.370113000
C	-5.081927000	-0.718058000	0.690983000
H	-4.900519000	-1.089881000	1.709308000
H	-5.975288000	-0.080829000	0.712464000
H	-5.272261000	-1.572049000	0.019247000

Dichloroimidazolin-2-ylidene, truncated ligand



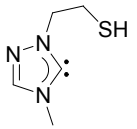


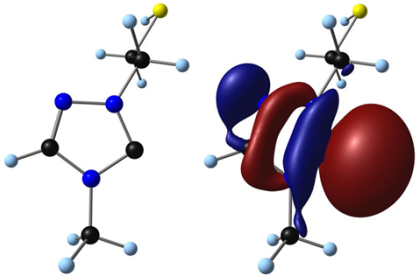
HOMO-1 = -0.2411 a.u.

C	0.333710000	-1.714811000	-0.379526000
C	-1.734572000	-0.384376000	-0.705122000
H	-1.922744000	0.511625000	-1.315204000
H	-2.014758000	-1.272489000	-1.286679000
C	-2.533180000	-0.326088000	0.598852000

H	-2.241189000	0.555894000	1.188118000
H	-2.338458000	-1.235791000	1.185515000
S	-4.332363000	-0.217145000	0.184718000
H	-4.771188000	-0.163898000	1.467908000
N	1.626234000	-1.367506000	-0.082789000
N	-0.301006000	-0.497883000	-0.453413000
C	1.789690000	0.007877000	0.028126000
C	0.564439000	0.561918000	-0.203292000
C	2.688389000	-2.347701000	0.081998000
H	3.486432000	-2.189680000	-0.659572000
H	3.124814000	-2.286332000	1.090661000
Cl	0.112192000	2.226599000	-0.221412000
Cl	3.289772000	0.783152000	0.378340000
H	2.234046000	-3.333991000	-0.066808000

1,2,4-triazolin-5-ylidene, truncated ligand



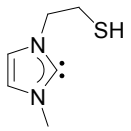


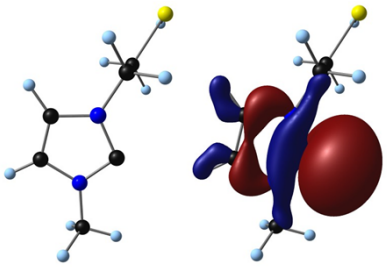
HOMO = -0.2397 a.u.

C	1.348279000	-0.953694000	-0.246897000
C	-0.983090000	-0.171128000	-0.697608000
H	-1.266066000	0.526124000	-1.501154000
H	-1.077171000	-1.200477000	-1.067299000
C	-1.861062000	0.053004000	0.534527000
H	-1.715678000	1.076013000	0.910322000
H	-1.586985000	-0.665691000	1.321284000
S	-3.631472000	-0.187496000	0.057439000
H	-4.150458000	0.116765000	1.273957000
N	2.457366000	-0.199056000	0.071774000
N	0.424307000	0.029364000	-0.387102000
C	2.130614000	1.139326000	0.102836000
C	3.777245000	-0.755434000	0.322997000
H	4.505483000	-0.392388000	-0.419236000
H	4.130025000	-0.488559000	1.331501000
H	3.694789000	-1.845749000	0.244533000

H	2.831231000	1.941523000	0.324048000
N	0.870679000	1.321112000	-0.174973000

Imidazolin-2-ylidene, truncated ligand

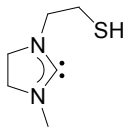


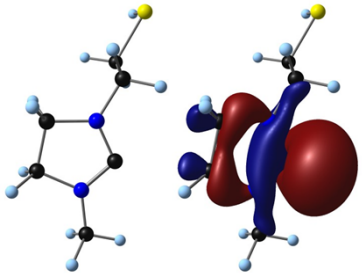


HOMO = -0.2248

C	1.240756000	-0.822616000	-0.387408000
C	-1.005700000	0.171788000	-0.712322000
H	-1.334855000	1.119440000	-1.168065000
H	-1.114199000	-0.627241000	-1.458159000
C	-1.846588000	-0.147890000	0.526366000
H	-1.715251000	0.633612000	1.290521000
H	-1.524024000	-1.113735000	0.941464000
S	-3.628872000	-0.234519000	0.037907000
H	-4.100347000	-0.565303000	1.266852000
N	2.423084000	-0.276597000	0.036967000
N	0.409974000	0.271030000	-0.385408000
C	2.333623000	1.089578000	0.294551000
H	3.175545000	1.690678000	0.626555000
C	1.046336000	1.439099000	0.029824000
H	0.547165000	2.402280000	0.090601000
C	3.640459000	-1.055751000	0.181550000
H	4.429037000	-0.685798000	-0.493899000
H	4.013824000	-1.013851000	1.217703000
H	3.400345000	-2.094058000	-0.076375000

Imidazolidine-2-ylidene, truncated ligand

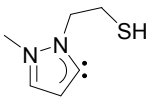


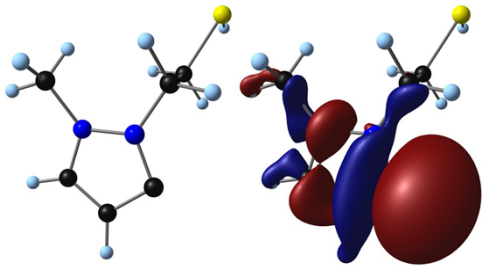


HOMO = -0.2182

C	1.246531000	-0.913511000	-0.293151000
C	-1.043150000	-0.079121000	-0.680005000
H	-1.357533000	0.712505000	-1.385077000
H	-1.132540000	-1.046587000	-1.193116000
C	-1.950392000	-0.062397000	0.557110000
H	-1.830541000	0.878472000	1.116357000
H	-1.685467000	-0.904196000	1.213679000
S	-3.713926000	-0.220109000	0.017503000
H	-4.251158000	-0.227655000	1.263959000
N	2.429468000	-0.342609000	0.012982000
N	0.352482000	0.102958000	-0.339422000
C	2.379449000	1.112491000	0.254869000
H	2.609851000	1.338471000	1.312420000
C	0.926338000	1.448973000	-0.118437000
H	0.399132000	1.994494000	0.680761000
C	3.655983000	-1.076175000	0.213893000
H	4.456908000	-0.712039000	-0.455921000
H	4.019345000	-0.982065000	1.255147000
H	3.460845000	-2.134077000	-0.001574000
H	3.118014000	1.645919000	-0.367283000
H	0.853745000	2.054504000	-1.039999000

Pyrazolin-5-ylidene, truncated ligand





HOMO = -0.2027

C	-1.384672000	-1.589968000	0.345728000
C	0.654597000	-0.204312000	0.729991000
H	0.803563000	0.760197000	1.241799000
H	0.909058000	-1.006276000	1.433293000
C	1.530866000	-0.298955000	-0.521915000
H	1.220904000	0.447611000	-1.269297000
H	1.422152000	-1.303351000	-0.955500000
S	3.292274000	0.003002000	-0.045126000
H	3.821619000	-0.269216000	-1.264778000
N	-0.754899000	-0.396048000	0.416436000
C	-2.697887000	0.125807000	-0.465392000
H	-3.480134000	0.771366000	-0.862195000
C	-1.218878000	2.068928000	0.149195000
H	-1.278871000	2.296181000	1.227850000
H	-0.224392000	2.356046000	-0.223678000
H	-1.967799000	2.674514000	-0.378615000
N	-1.496648000	0.670359000	-0.125533000
C	-2.662094000	-1.229849000	-0.211782000
H	-3.473247000	-1.925185000	-0.418140000

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