**Supplementary: Summary of key results from Unrestricted-Density Functional computations on 9b and on Models, and ORTEP plot of 5a.**

Computations on **9b** produced alterations in the bond lengths from the starting crystallographic geometry in accord with expected trends, since the crystallographic geometry is composed predominantly of the doubly reduced ene-diamide form of the ligand. Hence, C-C and C-N bonds within the diazadiene fragment went from 1.37 and 1.42 to 1.43 and 1.35 Å, respectively. These computed values are similar to those found in crystals of known diazadiene radical complexes (e.g., 1.41 and 1.34 Å for C-C and C-N in [AlI$_2$**1**], Baker *et al*, *Dalton Trans* 2002, 3844). The overall conformation of the ligand is little changed. The computed B-Cl lengths (1.87 Å) compare with crystallographic lengths in **9b** of 1.89 Å that are probably overestimates based on the boron position being primarily from the **9a** form, in which, as a 3-co-ordinate centre, its B-N lengths would be shorter. The computed value compares well with crystallographic cases in which a 4-co-ordinate N$_2$BCl$_2$ co-ordination sphere exists. B-N, B-Cl in Clyburne's diazaborolium cation (Jenkins *et al*, *Can. J. Chem.*, 2002, 80, 1398).averaged 1.56 and 1.84 (computed from **9b**: 1.54 and 1.87 Å).
PDB and Gaussian .out provided for **9b**.

Computations on models to investigate C-C coupling of **8**.
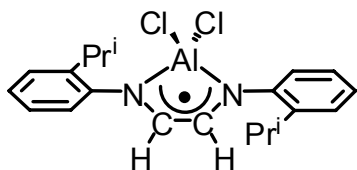Full Gaussian .out files are also provided.

Model:
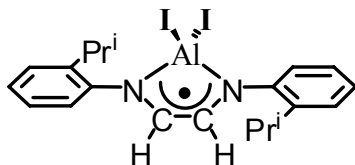
Basis set: dgdzvp on I 6-311G(d,p) on others	Computed G	Experimental G[1]	Computed Mulliken spin density
N	5.56	6.75	0.25
H	6.17	5.95	0.0135
Al	7.2	2.85	0.003
I	8.75	0.38	0.019
C	5.95	-	0.22

1. see R. J. Baker et al., *Chem. Eur. J.*, 2005, **11**, 2972.

Model:

Basis set: 6-311G(d,p)	Comp. G	Experim. G	Comp. Mulliken spin density
N	3.232	-	0.275
H	5.74	-	0.0138
Al	7.99	-	0.0106
Cl	1.337	-	0.078
C	1.05	-	0.21

Notes: The model used is not exactly identical to ligand **1**, having only 1 isopropyl group rather than 2 on each phenyl, but the point is established that these isopropyl nuclei have negligibly small couplings to the unpaired spin. It does result in a slight skewing of the aryls from orthogonality, allowing some modest delocalization of spin density into them. (see Figures 1S). This would be expected to be less the case where ligand **1** proper was used.
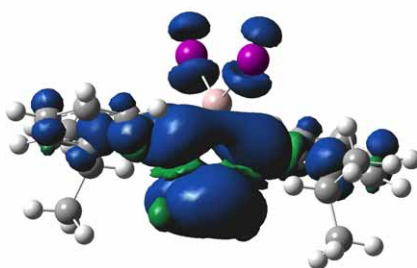

Figure 1S. Total Spin density plot computed for AlI$_2$.**1**

Though agreement in I couplings is poor, agreement with N and H couplings, key in the principal locality of unpaired spin (the diazadiene radical anion), is good at the higher basis. At 6-311G(d,p), the nitrogen coupling is underestimated in comparison to reported measured values, but recent computational work suggests these are overestimated. Agreement between bases in Mulliken atomic spin density is reasonable for H and N, and is similar for the different basis sets, hence comparability in the carbon figures is expected, and found. A very similar set of data is reported in the supplementary

information to H. M. Tuononen and A. F. Armstrong, *Dalton Trans*., 2006, 1885. This
paper also calls into question the experimentally derived Iodine couplings from Baker *et
al*. Though our calculations use inferior basis sets to those employed by Tuononen and
coworkers, they give qualitatively analogous results.

The overall conclusion from these studies, and from our own, is that diazadiene radical
anion spin densities are rather insensitive to different halides, metals, and diazadiene N-
substituents, and hence the observation in the solid state of the C-C coupled dimer **8**
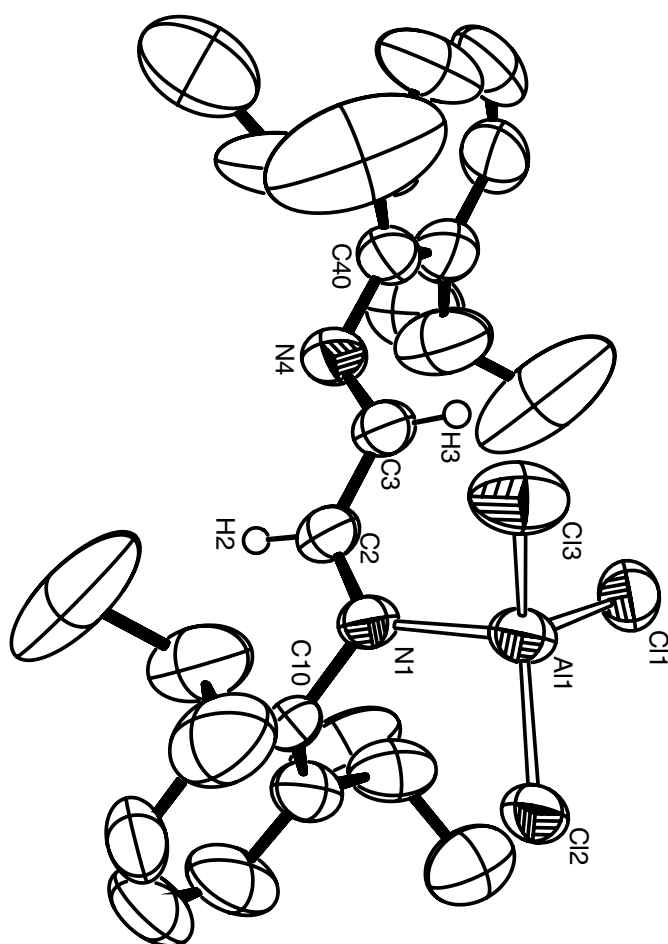cannot be due to electronic differences resulting from substitution of Cl for I.

Figure 2S: Ortep plot of Isomer **5a**; (**5b** is presented in the main manuscript). All cifs are
available a supplementary data, and from the CCDC, deposition numbers 658384–
658391.