Electronic Supplementary Information for

Unique Group 1 Cations Stabilised by Homoleptic Neutral Phosphine Coordination

Marina Carravetta, Maria Concistre, William Levason, Gillian Reid* and Wenjian Zhang

School of Chemistry, University of Southampton, Southampton UK SO17 1BJ UK.

E-mail: G.Reid@soton.ac.uk

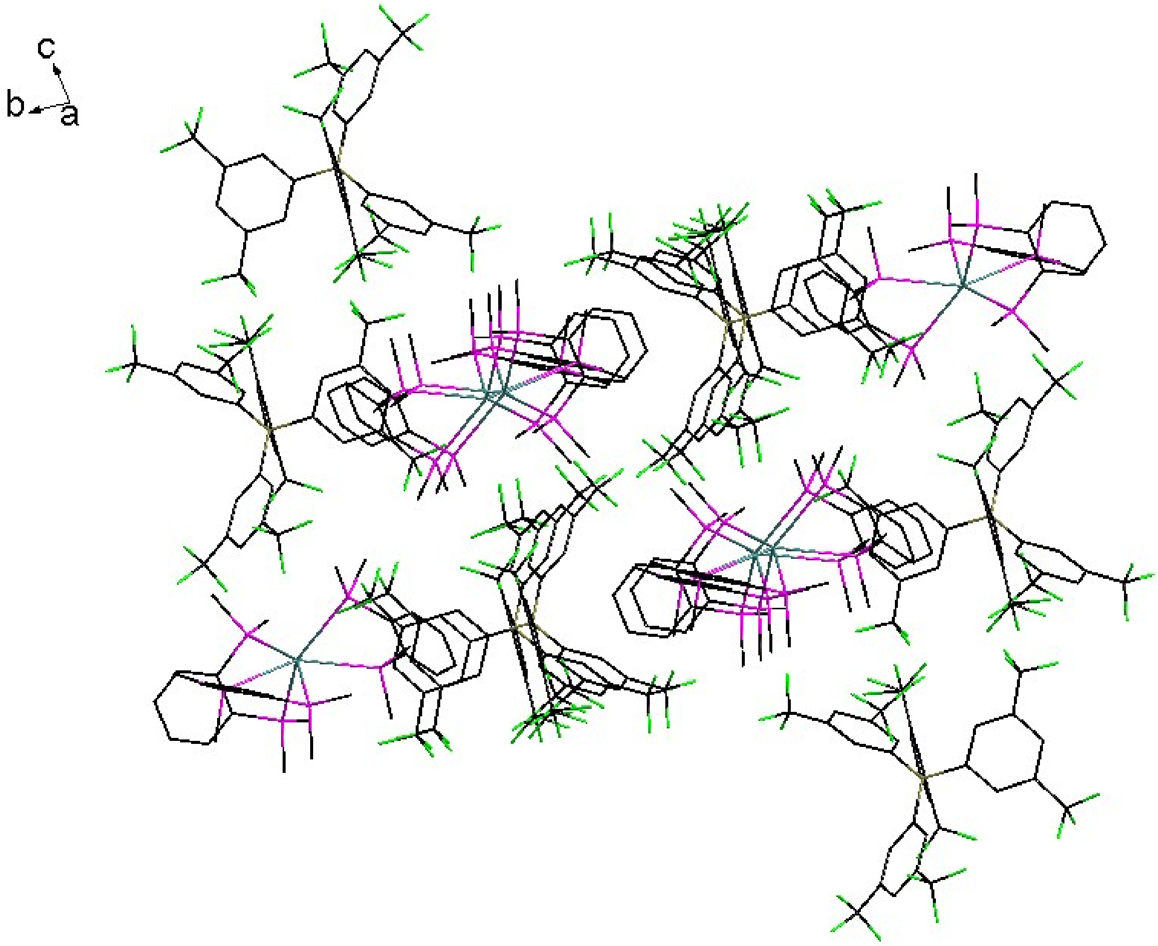

Figure S1 Packing diagram for [Na(diphos)$_3$][BAr^F]

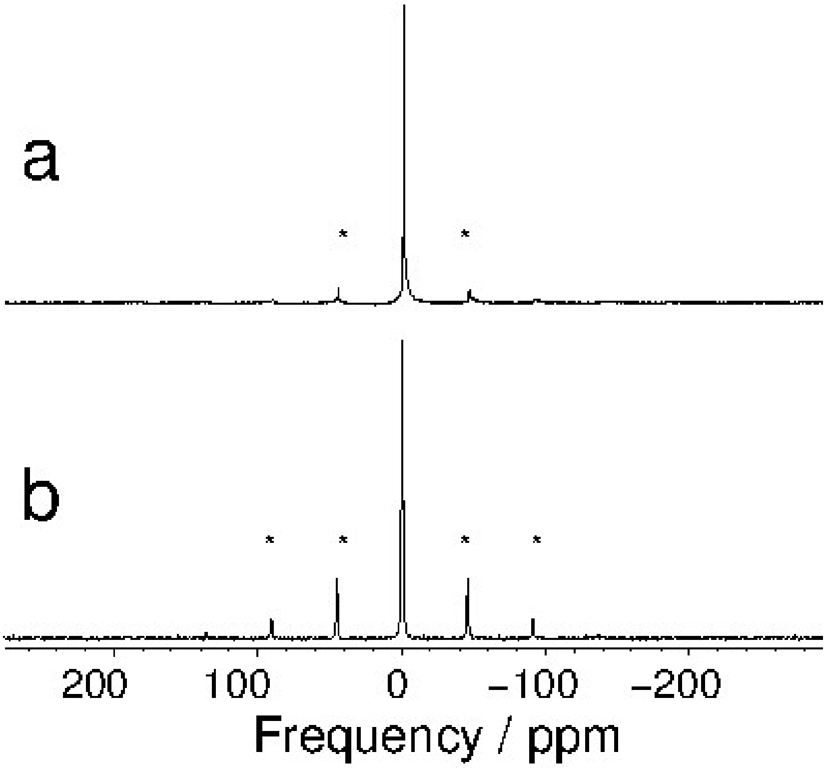

Figure S2. MAS direct excitation ^{7}LI NMR spectra at 7.1 kHz spinning frequency. Spinning sidebands are indicated with asterisks. (a) [Li(dmpe)$_3$][Al{OC(CF$_3$)$_3$}$_4$]. The spectrum is an average of 32 scans with inter-pulse delay of 15 s. The signal is at –0.7 ppm. (b) [Li(diphos)$_3$][Al{OC(CF$_3$)$_3$}$_4$]. The spectrum is an average of 4 scans with inter-pulse delay of 600 s. The peak is at +0.4 ppm.

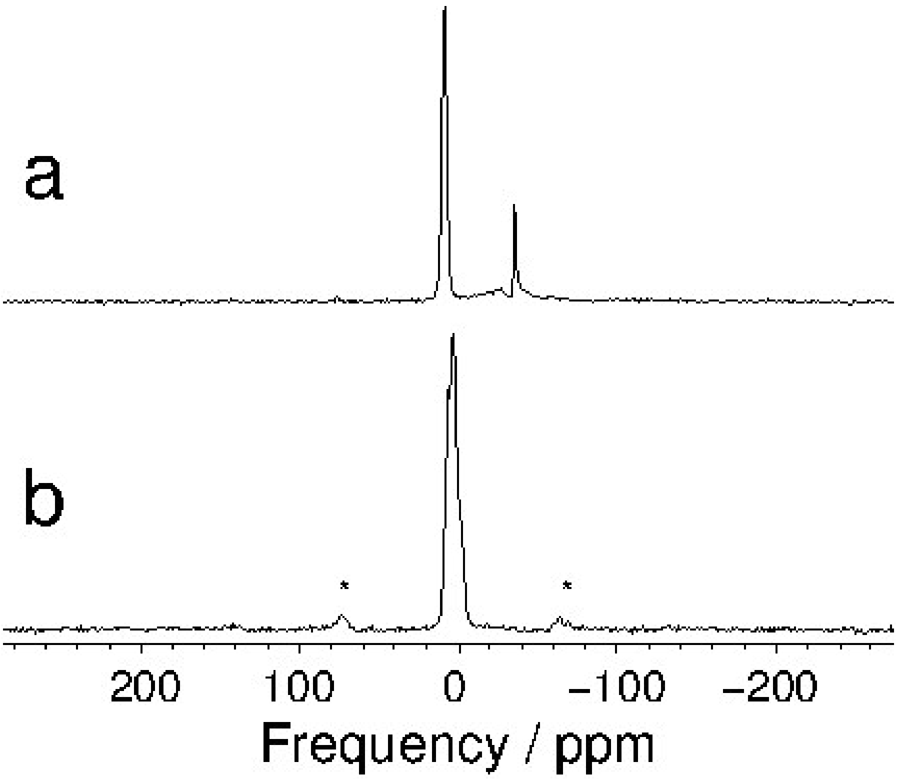

Figure S3. MAS direct excitation ^{23}Na NMR spectra at 7.1 kHz spinning frequency spinning frequency. Spinning sidebands are indicated with asterisks. (a) [Na(dmpe)$_3$][BAr^F]. The spectrum is an average of 128 scans with inter-pulse delay of 3 s. The main peak at 8.9 ppm is due to the complex. The weaker peak at -35.5 ppm is due to Na[BAr^F], confirmed in a separate experiment on the pure precursor compound. (b) [Na(diphos)$_3$][BAr^F]. The spectrum is an average of 128 scans with inter-pulse delay of 7 s. The peak is at 3.8 ppm.

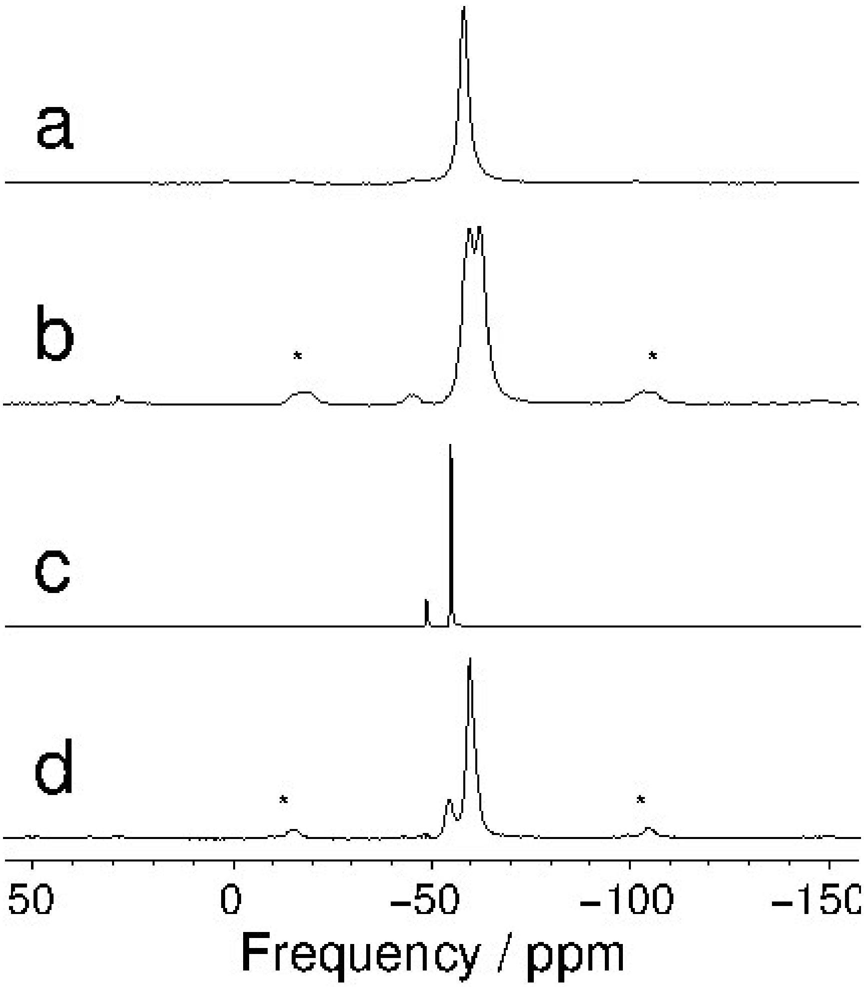

Figure S4. MAS direct acquisition ^{31}P NMR spectra at 7.1 kHz. Spinning sidebands are indicated with asterisks. **(a)** $[Na(dmpe)_3][BAr^F]$. The spectrum is an average of 8 scans with inter-pulse delay of 60 s. The peak is at –57.4 ppm. **(b)** $[Na(diphos)_3][BAr^F]$. The spectrum is an average of 16 scans with inter-pulse delay of 250 s. Two major peaks with approximately equal integrals appear for $[Na(diphos)_3][BAr^F]$ at –61.5 ppm and –59.0 ppm, with an additional minor impurity near –44.5 ppm. We attribute the peaks near –60 ppm to inequivalent crystallographic sites of the coordinated diphos ligand in the complex. Two dimensional correlation experiments with the PDSD method (data not shown) indicate a very strong correlations of the two peaks near –60 ppm. **(c)** $[Li(dmpe)_3][Al\{OC(CF_3)_3\}_4]$. The spectrum is an average of 8 scans with inter-pulse delay of 60 s. Two peaks were observed at –54.5 ppm (major) and –48.5 ppm (minor); the latter is attributed to a small amount of 'free' dmpe. (d) $[Li(diphos)_3][Al\{OC(CF_3)_3\}_4]$. The spectrum is an average of 16 scans with inter-pulse delay of 120 s. The main peak (–59.2 ppm) is attributed to $[Li(diphos)_3][Al\{OC(CF_3)_3\}_4]$, while the minor peak (–54.1 ppm) is close to the expected position of the uncomplexed diphos ligand (–55 ppm),[S1] resulting from a small amount of decomposition of the sample during data acquisition.

Supporting Information References

S1. R. J. Burt, J. Chatt, W. Hussain and G. J. Leigh, *J. Organomet. Chem.* 1979, **182**, 203.

S2. E. P. Kyba, S. T. Liu and R. L. Harris, *Organometallics*, 1983, **2**, 1877.