PERKIN 2
COMMUNICATION

A ‘triylide carbocycle’: cyclononane-1,4,7-triammonium triylide

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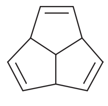
A postulated triylide carbocycle is explored using *ab initio* quantum chemistry, and the importance of such compounds discussed, in the context of macrocyclic chemistry.

Macrocyclic ligands have been shown to have a very extensive coordination chemistry involving a wide range of metal ions.[1] The ligands usually consist of a carbon framework in which two or more carbon atoms are replaced with donor atoms including O (crown ethers), N (aza-crowns, porphyrins, phthalocyanines), S (thiacrowns) and P (phospha-crowns). The use of macrocyclic ligands in coordination chemistry permits donor atom type and ring size to be modified so that the properties of the resulting complexes are optimal for a specific application.

The one donor atom largely neglected by macrocyclic chemists is carbon itself. The organometallic chemistry of carbon-based ligands is of enormous importance but macrocyclic ligands with purely metal–carbon bonds are not common. One elegant example of a nine-membered ring reported by Codding and co-workers[2] is tricyclo[5.2.1.1^{4,10}]deca-2,5,8-triene (triquinacene, **1**) which bonds *via* three alkene π-interactions in a face-capping mode to an $Mo(CO)_3$ fragment. However for our purposes we define a macrocyclic donor as a large ring (nine or more members) carbocyclic system in which three or more donor atoms may be simultaneously σ-bonded to a single metal centre. Macrocyclic ligands such as **2** (1,4,7-triazacyclononane[3]) and **3** (1,4,7-trithiacyclononane[4]) have very extensive coordination chemistries, characterised by the three donor atoms occupying *cis* sites at a metal centre.



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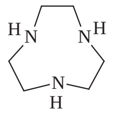

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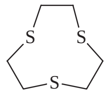

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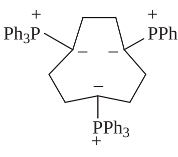

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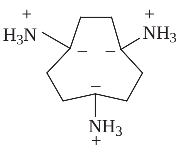

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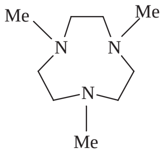

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The aim here is to point out that for almost any macrocycle there is, in principle, an associated polyylide carbocycle with potentially quite different thermodynamic and kinetic properties as a ligand. The very high basic strength of such lone pair-bearing carbon atoms has recently been illustrated in the context of hydrogen bonded complexes theoretically[5,6] with similar interactions confirmed experimentally.[7] The choice of donor group is largely directed by the need to reduce the charge of a potential tridentate ligand. The use of a simple nine-membered tri-anionic ligand such as 1,4,7-trilithiocyclononane is probably not feasible due to the excessive charge that would be built up upon low-valent metal ions. For this reason we are currently undertaking the synthesis of neutral cyclic triylides typified by structure **4**.

The coordination chemistry of chelating ylides is relatively sparse. Relevant examples include the report by Booth *et al.* for Ni complexes of simple chelating ylides such as $Ph_3PCH(CH_2)_n$-$CHPPh_3$ ($n = 1$–3),[8] in which the chelate rings with up to six members could be isolated as air stable complexes of the formula $[NiPh_3PCH(CH_2)_nCHPPh_3(\eta\text{-}C_5H_5)]PF_6$. Schmidbaur *et al.*[9] examined the Ni^{II} coordination chemistry of the chelating ylidic anion $[Ph_2PCHPPh_2CH_2]^-$. However, to date no examples of cyclic or tridentate ylide based ligands have been reported.

Here we assess *via* an *ab initio* approach the relative stabilities and simple complexation properties of neutral cyclotriylides as macrocyclic, face-capping ligands. This naturally involves a study of the preferred (ground state) conformers and electronic structure. We choose the compound which can be considered as the prototype triylide carbocycle, namely cyclononane-1,4,7-triammonium triylide **5** (hereafter CTT). This is isomeric with 1,4,7-trimethyl-1,4,7-triazacyclononane **6** (hereafter Me_3-TACN). We have therefore compared the results for CTT and some of its simple complexes with the analogous Me_3TACN complexes at the same level of theory. In a following paper, we hope to present a more detailed study in addition to an analysis of the charge distributions, bonding and electrostatic properties of simple diylide and triylide carbocycle transition metal complexes.[10] The calculations employed GAUSSIAN94/DFT,[11] running on the Columbus supercomputer at the Rutherford-Appleton Laboratories.

CTT and Me_3TACN were initially optimized within three different point group symmetries at the Hartree–Fock (HF) level using standard 3-21G basis sets.[12] Harmonic frequency calculations were performed on all species at this level, in order

Table 2 HF/3-21G zero-point energies of the complexes

	CTT		Me_3TACN	
Complex with	ZPE/ kJ mol^{-1}	Imag. Freqs?	ZPE/ kJ mol^{-1}	Imag. Freqs?
Li^+	873.9	0	877.9	0
Na^+	867.8	0	871.0	0
K^+	862.8	0	866.9	0

Table 1 HF/3-21G electronic and zero-point energies of CTT and TACN in different symmetries

	CTT			Me_3TACN		
Point group	Energy (a.u.)	ZPE/kJ mol^{-1}	Imag. Freqs?	Energy (a.u.)	ZPE/kJ mol^{-1}	Imag. Freqs?
(2,1) C_s	−513.13349	845.0	1	−513.44019	855.0	2
(3,0) C_s	−513.13238	845.1	1	−513.43605	858.2	2
C_3	−513.13863	845.2	0	−513.44631	858.5	0
C_{3v}	−513.11039	845.1	3	−513.41532	852.8	6

Table 3 HF/6-31+G(d) geometrical parameters and BLYP/6-31+G(d)//HF/6-31+G(d) cation binding energies (BE)

	CTT			Me$_3$TACN		
Complex with	r(C···M)/Å	d^a/Å	BE^b/kJ mol^{-1}	r(N···M)/Å	d^a/Å	BE^b/kJ mol^{-1}
Li$^+$	2.124	1.203	540.8	2.010	1.106	362.6
Na$^+$	2.483	1.686	413.3	2.399	1.659	248.9
K$^+$	2.951	2.292	285.5	2.861	2.266	157.5

[a] Perpendicular distance of the metal ion to the mean plane of the three coordinating atoms, as defined in Fig. 1. [b] Including HF/3-21G ZPE corrections scaled by 0.89.[15]

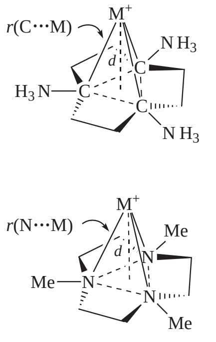

Fig. 1 Geometries of CTT and Me$_3$TACN complexes.

to estimate zero-point energies (ZPE's) and to establish which structures were stable. It is also necessary to consider two different conformations for both CTT and Me$_3$TACN in the C_s point group—a conformation we denote as (2,1) in which two of the methyl (or ammonium) groups are 'up' and one 'down', and a (3,0) conformer in which all three exocyclic substituents are 'down'. The results of these calculations are presented in Table 1, which shows that a C_3 conformer is preferred for both CTT and Me$_3$TACN, all other structures corresponding to saddlepoints on their respective potential energy surfaces. C_3 symmetry was then applied in optimizations of CTT and Me$_3$TACN with Li$^+$, Na$^+$ and K$^+$ respectively (see Table 2). All complexes exist in energetic minima (no imaginary frequencies) and are characterized by a macrocycle/carbocycle which has been optimized to a (3,0) conformation, with all exocyclic substituents on the opposite face of the macrocycle/carbocycle to the cation (as indicated in Fig. 1).

Subsequent optimizations on the lowest energy C_3 conformers of CTT and Me$_3$TACN were then carried out at the HF level with 6-31+G(d) basis sets[13] except for potassium, where no literature 6-31+G(d) basis set is available. In this case, the TZV+(d) basis set of Wachters was used.[14] Finally, BLYP/6-31+G(d) single point calculations were performed on all structures optimized at the HF/6-31+G(d) level. This enables an estimate of electron correlation effects to be included in the binding energies. Some key geometrical parameters (defined in Fig. 1) and the computed cation binding energies are reported in Table 3. These include ZPE changes computed at the 3-21G level and scaled by the empirical factor 0.89.[15] Since the aim here is an initial demonstration of the stronger binding energies of CTT complexes relative to those of Me$_3$TACN, more detailed corrections to the binding energy (such as counterpoise corrections) have not been included here. (*Ab initio* calculations on other macrocycles such as crown ethers[16] indicate that counterpoise corrections affect alkali metal cation binding energies by approx. 1%.) The binding energies in Table 3 show that the cationic complexes of CTT have significantly larger values than the corresponding Me$_3$TACN complexes, despite the fact that the N···M$^+$ distances in the macrocyclic complexes are consistently shorter (by approx. 0.1 Å) than the C···M$^+$ carbocycle distances. There appear to be at least two possible explanations for this. Firstly, the carbon ylide lone pairs are far more diffuse and extended than the nitrogen lone pairs of the triaza macrocycle. Secondly, the metal cations in the triylide complexes certainly experience some electrostatic repulsion from the cationic ammonium groups. This will be analysed in some detail in the subsequent full paper.[10]

In summary: this communication demonstrates that a C_3-symmetric carbocycle (in principle) exists, isomeric with 1,4,7-trimethyl-1,4,7-triazacyclononane, in which three identical lone pair-bearing carbons may coordinate to metal ions forming high binding energy complexes (*i.e.* in comparison with the analogous triaza-macrocycle). This compound is characteristic of an entirely new class of carbocycles, even so far as *ab initio* or modelling studies are concerned. It should be reiterated that nitrogen ylides are notoriously difficult to stabilize, and it may be that the CTT compound we concentrate on in this communication will never be isolated. However, it is of fundamental importance as ostensibly the simplest triylide carbocycle, and as a model for other polyylide carbocycles which may indeed be synthesizable. A triphosphonium carbocycle related to the recently synthesised 1,5,9-triphosphacyclododecane[17] is one example of a more accessible synthetic target. Such phosphorus ylides should certainly be more stable than their nitrogen analogues, and would be less susceptible to basic elimination reactions. STH thanks the EPSRC for access to the Columbus national supercomputing facility.

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