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Theoretical investigation of the scope of sequential ligand tuning using a bifunctional scorpionate tris(1,2,4-triazolyl)borate-based architecture

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Abstract

The donor properties of a series of tripodal mixed N-donor/carbene ligands derived through sequential alkylation of hydrotris(1,2,4-triazolyl)borate have been investigated by density functional theory (DFT) methods. The structures of complexes of the form $[Mo(L)(CO)_3]^-$ were optimized (L = $[HB(1,2,4\text{-triazolyl})_n(1,2,4\text{-triazol-5-ylidene})_{3-n}]^-$ (n = 0 – 3), hydrotris(pyrazolyl)borate, hydrotris(3,5-dimethylpyrazolyl)borate and hydrotris(imidazol-2-ylidene)borate) and ν_{CO} frequencies for these complexes and partial charges of their $Mo(CO)_3$ fragments were determined. Results show that ligand donation is highly tunable when compared to similar experimentally known ligands with a shift in the symmetric ν_{CO} stretching mode of -39 cm $^{-1}$ on going from the tris(1,2,4-triazolyl)borate complexes to that of the triscarbene hydrotris(1,2,4-triazol-5-ylidene) and an increase in partial charge (distributed multipole analysis) of the $Mo(CO)_3$ fragment from -0.23 to -0.48.

Keywords: Carbene, triazoles, DFT, scorpionate ligands.

1. Introduction

Hydrotris(pyrazolyl)borate-based tripodal scorpionate ligands (Tp, see Chart 1), originally developed by Trofimenko,[1,2] have become ubiquitous in coordination chemistry. Their complexes have provided a wealth of organometallic chemistry and have been commonly used as ligands in mimics of a variety of metalloproteins.[3]

Analogous scorpionate ligands can also be easily prepared through the use of other heterocycles, for example hydrotris(1,2,4-triazolyl)borate (Ttz) which has similar coodination properties to Tp but yields greater solubility of its complexes in protic and aqueous media and weaker donor capacity.[4-8]

Since the first isolation of a free imidazole based *N*-heterocyclic carbene by Arduengo et al.,[9] this ligand class has also become extremely common.[10] Regarded as analogues and replacements of more traditional phosphine ligands, *N*-heterocyclic carbenes have found widespread utility as supporting ligands in catalysis yielding more stable and catalytically active complexes due to their higher electron donor strengths and stronger metal-ligand bonds.

Hybrids of these two classes of ligands were first introduced in the form of tris-*N*-heterocyclic carbene borates by the group of Fehlhammer.[11,12] By first preparing hydrotris(imidazolyl)borate and subsequently treating this with $[Me_3O][BF_4]$ yielded the tristriazolium carbene precursor. Deprotonation with butyl lithium then led to the isolation of the lithiated triscarbene, hydrotris(imidazol-2-ylidene)borate (Tim), which was then used to prepare several transition metal complexes. More recently, the chemistry of complexes of these ligands and their bulkier second generation tris(imidazolylidene)borate complexes have been explored by several groups including that of Smith.[13-18]

Just as scorpionate ligands moved beyond Tp to greater structural diversity, N-heterocyclic carbenes quickly moved beyond imidazole based frameworks. A commonly encountered analogue to imidazol-2-

ylidenes are 1,2,4-triazol-5-ylidenes.[19] We therefore reasoned that the Ttz ligand framework could be similarly modified as to yield a tricarbene analogue of Tim. The dihydrobis(1,2,4-triazol-5-ylidene)borate bidentate carbene ligand has been reported.[20]

The beauty of the approach using the Ttz parent ligand is that Ttz would be a face capping κ^3-ligand as both its parent tris-N-donor and as its triscarbene derivative. This is not possible with the non-alkylated Tim framework as it cannot chelate due to the divergent directionality of the N-donor atoms. Furthermore, by progressive alkylation of the Ttz parent, access will be available to the monocarbene/bis-N-donor and dicarbene/mono-N-donor. The Ttz ligand framework thus provides for an excellent system for the tuning of both steric and electronic properties (Figure 1).

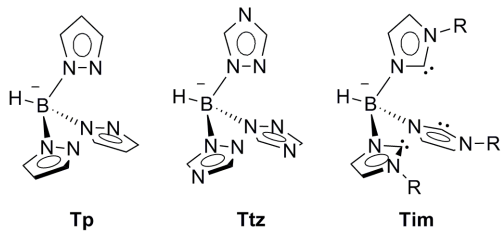
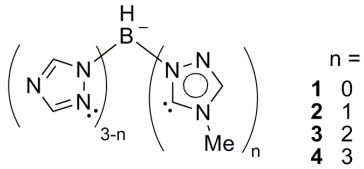


Chart 1



1 - 4

Figure 1. Ttz-based ligands investigated in this study (lone pairs signify coordinating atoms).

There has been renewed interest in the establishment of reliable metrics for the quantification of ligand donor effects. Several recent reports have appeared in the literature detailing the calculation by DFT methods of the donor properties of a wide range of monodentate 2-electron donor ligands,[21] *N*-heterocyclic carbenes[22] and carbones.[23] It might therefore be possible to establish systems for the comparison of the donor properties of tripodal and face capping ligands such as Tp and TTz.

Here, we have embarked on a theoretical DFT survey of the tunability that would be afforded by the

Ttz (**1**) framework in their $Mo(CO)_3$ complexes on going from the parent ligand with progressive modification through the monocarbene/bis-N-donor (**2**) and dicarbene/mono-N-donor (**3**) derivatives and ultimately the tricarbene (**4**).

2. Computational details

The molecular structures of the molybdenum tricarbonyl complexes, $[Mo(\mathbf{1}\text{-}\mathbf{4})(CO)_3]^-$, along with those of the ligands Tp, Tp* and Tim, were optimized using the Stuttgart-Dresden relativistic small core potential for molybdenum[24] and triple-ζ 6-311G* basis sets for boron, carbon, oxygen, nitrogen and hydrogen,[25] using the B3LYP hybrid functional (20 % Hartree-Fock)[26] as implemented in the GAMESS-UK software package.[27] Symmetry constraints were not applied during geometry optimizations. Frequency calculations and partial atomic charge analyses were then carried out for the optimized geometries for all complexes

3. Results and Discussion

The optimized geometries for all complexes, $[Mo(L)(CO)_3]^-$, (L = **1** to **4**) are shown in Figure 2 (for coordinates of the optimized geometries, see Supplementary Information). Due to the known 1,4-disubstitution of monodentate 1,2,4-triazol-5-ylidenes and the 4-position alkylation in the analogous dihydrobis(1,2,4-triaolyl-5-ylidene)borate system, we fully expect Ttz to show the same alkylation reactivity. Hence ligands **2** to **4** are depicted as the product of alkylation at 4-positions of the triazole rings. In order to provide tuning benchmarks for the proposed Ttz-based system, our DFT calculations were therefore extended to a series of analogous complexes using the experimentally known tripodal face-capping ligands hydrotris(pyrazolyl)borate, hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), and the tricarbene tris(3-methylimidazol-2-ylidene)borate.

C-O bond lengths for $[Mo(\mathbf{1})(CO)_3]^-$, $[Mo(Tp)(CO)_3]^-$ and $[Mo(Tp^*)(CO)_3]^-$ match those of experimentally derived X-ray structures within quoted errors.[7] The Mo-N and Mo-CO bond lengths

are comparable but slightly elongated compared to experimental data. On going from [Mo(**1**)(CO)$_3$]$^-$ to [Mo(**4**)(CO)$_3$]$^-$ the C-O bond length increases from 1.170 to 1.173 Å as would be expected for the presence of an increasingly strongly donating ancillary ligand. The Mo-CO bond lengths do not however shorten as might be expected and could be a consequence of the increased steric crowding about the metal due to the methyl substituents of the NHC rings. C-O bond lengths are not the best metric for the comparison of the donor strength of ancillary ligands as the C-O bond length is generally relatively insensitive to change to the ancillary ligand. Infrared stretching frequencies associated with carbonyl ligands are, on the other hand, a far more sensitive measure of the comparative donation.

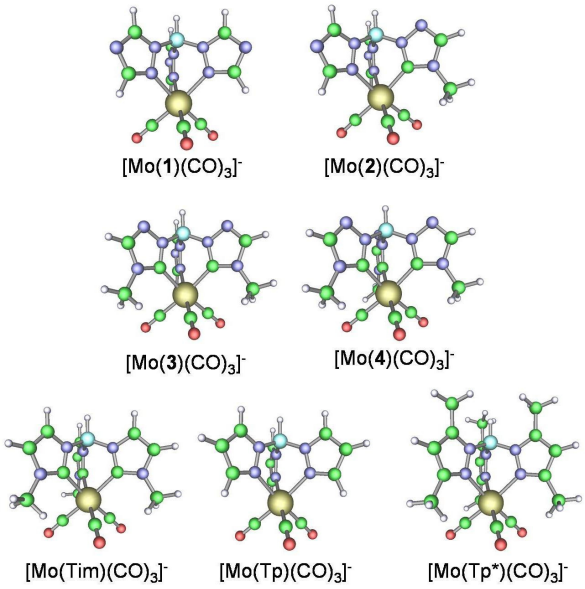


Figure 2. Optimized geometries of complexes.

Infrared stretching frequencies for symmetric and asymmetric ν_{CO} modes were therefore calculated for the optimized geometries of all complexes [Mo(L)(CO)$_3$]$^-$ and are listed in Table 1 along with experimental values where available.[7,28] Calculated values are consistently overestimated by ca. 50 cm^{-1} relative to experimentally derived values. For the complex bearing the parent ligand, [Mo(**1**)(CO)$_3$]$^-$, the symmetric ν_{CO} stretch is calculated at 1965 cm^{-1} with the asymmetric stretches almost coincident at 1823 cm^{-1} consistent with the degeneracy expected for a complex of C_{3v} symmetry.

Table 1. Calculated and experimental ν_{CO} stretching frequencies.

Complex		ν_{CO} / cm^{-1}	
		Calc.	Exp.
$[Mo(\mathbf{1})(CO)_3]^-$	ν_{CO}	1964.7, 1823.7, 1822.7	1906, 1776[a]
	avg. ν_{CO}	1870.4	1819
$[Mo(\mathbf{2})(CO)_3]^-$	ν_{CO}	1956.3, 1829.1, 1794.0	
	avg. ν_{CO}	1859.8	
$[Mo(\mathbf{3})(CO)_3]^-$	ν_{CO}	1942.7, 1822.5, 1780.9	
	avg. ν_{CO}	1848.7	
$[Mo(\mathbf{4})(CO)_3]^-$	ν_{CO}	1926.3, 1790.9, 1790.1	
	avg. ν_{CO}	1835.8	
$[Mo(Tp)(CO)_3]^-$	ν_{CO}	1951.1, 1804.2, 1803.9	1888, 1752[b]
	avg. ν_{CO}	1853.1	1797
$[Mo(Tp^*)(CO)_3]^-$	ν_{CO}	1943.5, 1794.5, 1784.8	1881, 1745[b]
	avg. ν_{CO}	1840.9	1790
$[Mo(Tim)(CO)_3]^-$	ν_{CO}	1922.6, 1789.5, 1779.4	
	avg. ν_{CO}	1830.5	

[a] MeCN, NEt_4^+ salt from ref 7, [b] MeCN, NEt_4^+ salt from ref 28

On going to the monocarbene complex, $[Mo(\mathbf{2})(CO)_3]^-$, the asymmetric stretching modes are no longer degenerate due to the loss of C_{3v} symmetry, and are calculated to appear at 1794 and 1829 cm^{-1}. The symmetric ν_{CO} stretch for $[Mo(\mathbf{2})(CO)_3]^-$ is shifted to lower frequency by 9 cm^{-1} to 1956 cm^{-1} consistent with increased back donation of electron density into the CO π^* orbitals due to the increased donor capacity of the monocarbene moiety.

The ν_{CO} modes for $[Mo(\mathbf{3})(CO)_3]^-$ are similarly shifted to lower frequency on going to the biscarbene

ligand **3** with the asymmetric stretches at 1781 and 1823 cm^{-1} and symmetric stretch at 1943 cm^{-1}.

For the triscarbene complex $[Mo(\mathbf{4})(CO)_3]^-$ where C_{3v} symmetry is restored, the asymmetric stretching modes are again degenerate and are centered at 1790 cm^{-1} with the symmetric stretch appearing at 1926 cm^{-1}.

Figure 3 shows a graphical representation of the ligand dependent tuning of the symmetric ν_{CO} stretching frequencies for ligands **1** to **4** in relation to the known N-donor Tp and Tp* ligands and the triscarbene, Tim. As can be seen, the parent Ttz ligand, **1**, is the weakest electron donor based on ν_{CO} frequency. The donor capability of ligands **2** and **3** straddle those of Tp and Tp*. The triscarbene Tim is the strongest donor with a symmetric ν_{CO} value of 1923 cm^{-1}, some ~ 4 cm^{-1} lower in energy than that for its triazole derived analogue **4** as would be expected from comparison of monodentate imidazole and 1,2,4-triazole derived NHCs.[29] The overall shift in the symmetric ν_{CO} mode of -39 cm^{-1} going from $[Mo(\mathbf{1})(CO)_3]^-$ to $[Mo(\mathbf{4})(CO)_3]^-$ demonstrates the electronic tuning that would be possible through the proposed sequential ligand modification method. An interesting point to note, however, is that the tuning effect of ligands **1** to **4** does not appear to be entirely additive as might be expected and may be an effect of the progressively increasing steric congestion about the metal centre.

Whilst the increased donor capability of the ligands through progressive carbene augmentation is not surprising, the results clearly highlight the attractiveness of such an approach where donor capacity can be tuned over a wide range when compared to Tp, Tp* and Tim through the use of a single ligand architecture rather than through use of a range of independently derived ligand structures. Such polydentate bifunctional ligand systems may therefore open up greater scope for the tuning of the electronic and steric properties of metal complexes.

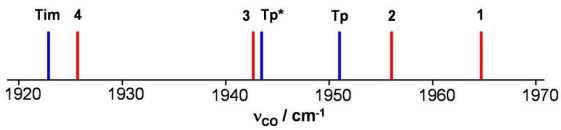


Figure 3. Graphical representation of ligand dependent tuning of the symmetric ν_{CO} stretch for the

complexes $[Mo(L)(CO)_3]^-$.

To further quantify the relative levels of electron donation in the complexes $[Mo(L)(CO)_3]^-$ we derived partial charges for the $Mo(CO)_3$ fragment in all complexes at their optimized geometries from Mulliken and Lowdin population analyses and a distributed multipole analysis (DMA). In each case, net negative charge on the $Mo(CO)_3$ fragment increases in an approximately additive fashion on going from $[Mo(\mathbf{1})(CO)_3]^-$ to $[Mo(\mathbf{4})(CO)_3]^-$ indicative of increasing donation from the tripodal ligand (Table 2). When correlated with the calculated frequencies for the symmetric ν_{CO} modes for all complexes, a near linear plot is obtained (Figure 4). The data show some inconsistencies between the trends in calculated ν_{CO} and partial charge. Indeed, whilst Tp is judged to be a better donor than ligand **2** on the basis of calculated ν_{CO} values, the $Mo(CO)_3$ fragment of $[Mo(\mathbf{2})(CO)_3]^-$ exhibits a greater negative charge than that in $[Mo(Tp)(CO)_3]^-$. This discrepancy may therefore be indicative of the increased steric demands of **2** relative to Tp that may prevent optimal overlap between Mo and CO orbitals and highlights of the difficulty in establishing a single reliable metric for probing relative ligand donor capabilities as has already been noted elsewhere in monodentate systems.[21] In all cases, the greatest negative charge for the $Mo(CO)_3$ fragment is found for $[Mo(Tim)(CO)_3]^-$ consistent with the calculated IR data showing that the ligand Tim is the best donor ligand of those included in this study. Overall, the best correlation is observed using partial charges derived from the DMA calculations (Figure 4).

Table 2. Summed partial atomic charges for the $Mo(CO)_3$ fragment in complexes $[Mo(L)(CO)_3]^-$ (L = **1** to **4**, Tp, Tp* and Tim) and calculated frequencies of their symmetric ν_{CO} stretch.

Ligand	Sym ν_{CO} / cm^{-1}	$Mo(CO)_3$ partial charge		
		Mulliken	Lowdin	DMA
1	1964.7	-0.10	-1.28	-0.23

2	1956.3	-0.18	-1.40	-0.30
3	1942.7	-0.27	-1.52	-0.39
4	1926.3	-0.35	-1.66	-0.48
Tp	1951.1	-0.12	-1.31	-0.27
Tp*	1943.5	-0.10	-1.37	-0.34
Tim	1922.6	-0.36	-1.67	-0.53

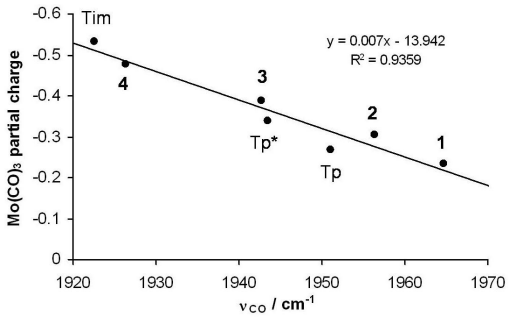


Figure 4. Plot of summed partial atomic charges (distributed multipole analysis) for the $Mo(CO)_3$ in complexes $[Mo(L)(CO)_3]^-$ (L = **1** to **4**, Tp, Tp* and Tim) versus calculated frequency of symmetric ν_{CO} stretch.

4. Conclusions

In conclusion, we have carried out a DFT study of the electronic tuning that would be possible through the successive carbene augmentation of the hydrotris(1,2,4-triazolyl)borate ligand system. We have shown that increasing the carbene content of the scorpionate ligand results in increased electron donation to the metal with consequent reduction in ν_{CO}. Additionally, calculated partial charges for the $Mo(CO)_3$ fragments of their complexes show increased negative charge with increasing carbene content. Moreover, the ligand donor properties would be tunable over a larger range than that covered by experimentally known face-capping ligand systems. We are currently extending our theoretical studies to other metal-based systems since ligand donor capacity has been shown to vary with the nature of the

metal and also other ligands present.[28] We are also investigating other tripodal ligand frameworks of this type that could also be amenable to this successive augmentation approach and we then hope to soon commence synthetic and reactivity studies on these and other systems.

Acknowledgement

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Supporting Information Available. Optimized atomic coordinates for all complexes and plots of $Mo(CO)_3$ partial charge versus CO stretching frequency.

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