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Synthesis, structure and DFT study of asymmetrical NHC complexes of cymantrene derivatives and their application in the dehydrogenative dimerization reaction of thiols



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ABSTRACT

Asymmetrical NHC complexes of cymantrene and methylcymantrene have been synthesised through the photochemical substitution of carbonyl ligands in the presence of the imidazol-2-ylidene salts. The carbene substituents have been varied between compact (L1) and bulky (L2 and L3) substituents to produce an array of differently sized carbene ligands. The solid state crystal structures of three of the complexes confirmed the bonding pattern of the ligand towards available metal centres and an in-depth DFT study provided insight into electronic and steric aspects. Application of the Extended Transition State coupled with Natural Orbitals for Chemical Valence (ETS-NOCV) energy decomposition technique indicated various NOCV channels for each Mn-L bond (L = 3-ethyl-1-methylimidazolylidene carbene, triphenylphosphine or acetonitrile), describing the density and energy changes of specific (σ and π) attributes of each bond. N-heterocyclic carbenes of cymantrene derivatives and their triphenylphosphine-substituted analogue are equivalent σ -donors, with 53% and 56%, respectively, of the total binding energy originating from σ -donation. However, NHC complexes show considerably less π character in the metal-carbene bond. Hydrogen interactions in the NHC complexes were also identified in the ETS-NOCV calculations and provided quantification of the hydrogen interactions witnessed in the solid state structures. Calculated Wiberg bond indices, bond dissociation enthalpies, percentage buried volumes and percentage sigma and pi-bonding characteristics quantified the bonding and electronic aspects of the ligand-metal interactions within the complex.

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1. Introduction

Since the isolation of the first stable, free N-heterocyclic carbene (NHC) by Arduengo in 1991, NHC's have transformed the field of organometallic chemistry [1]. The adjustability of the steric and electronic properties of these ligands has resulted in their persistent use for the synthesis and stabilization of metal complexes capable of cleaving very inert bonds [2]. The majority of synthetic pathways in the synthesis of transition metal (TM) NHC complexes have been thermally initiated [3] whereas photochemical induced pathways have, however, been mostly ignored. This aspect is surprising, especially if taken into consideration the similarities between tertiary phosphines and NHC ligands and the applicability of photochemical reactions in producing highly reactive, coordinatively unsaturated TM-PR₃ species [3]. The photolysis and the

* Corresponding author. E-mail address: marile.landman@up.ac.za (M. Landman). subsequent isomerisation of ruthenium NHC complexes have been reported and indicate the ability of photochemical processes to produce isomeric variations of target complexes (Fig. 1) [3].

Methylcyclopentadienyl manganese tricarbonyl (MMT), and to a far lesser extent, cymantrene have been successfully applied in the fuel industry as supplements in unleaded gasoline. MMT not only increases octane ratings but are particularly useful as anti-knocking agents, improving combustion of fuels [4]. Studies on carbene complexes of MMT and cymantrene complexes are limited in literature and mainly focus on the synthesis of novel, symmetrical N-heterocyclic carbene (NHC's) complexes of MMT and cymantrene (Fig. 2) [4-7]. The synthesis of symmetrical NHC complexes of MMT has been reported as early as 1977 when Lappert [8] prepared complexes of manganese from the Wanzlick dimeric NHC ligand under high thermal conditions. The complexes were stable above 180 °C and displayed exceptional inertness against thermal decomposition. A small variety of symmetrical NHC cymantrene derived carbene complexes have been synthesised by means of photochemical processes and have even found application in the



Fig. 1. Isomerisation of Ru-NHC complexes afforded through photochemical processes [3].



Fig. 2. NHC complexes of cymantrene and MMT (a) and agostic interaction of the cymantrene NHC complex (b).

hydrosilylation of aldehydes and ketones [4]. The study found that the incorporation of at least one mesityl group leads to the most selective and active systems. DFT calculations also indicated the presence of an agostic stabilization when a second carbonyl ligand is removed by photolytic irradiation [5].

Since agostic interactions are also witnessed in the triphenylphosphine analogue [5] and both Cp'Mn(CO)PPh₃ and Cp'Mn(CO) NHC stabilize carbonyl expulsion through agostic interactions rather than with solvent ligation [6], both analogues can be seen as quite similar in chemical nature. Although the synthetic methodology and catalytic potential of symmetric NHC complexes of cymantrene and MMT have been determined for a variety of



Fig. 3. Cymantrene derived NHC complexes of this study.

different reactions and conditions, very limited understanding exists for the structural and electronic effects of different unsymmetrical NHC ligands towards the metal centre. For this purpose, asymmetrical NHC complexes with increasing steric bulk have been synthesised (Fig. 4) and studied with theoretical calculations. This study reports the synthesis of the six novel asymmetrical NHC complexes of cymantrene and MMT, the synthesis of the acetonitrile and triphenylphosphine analogues of the NHC complexes, Xray crystal structures of three of the complexes and a DFT study (Fig. 3). The triphenylphosphine and acetonitrile analogues were synthesised to form a baseline to which the percentage sigma and pi-bonding characteristics of the NHC complexes could be compared.

2. Experimental

2.1. General

All reactions, unless noted otherwise, were performed under inert nitrogen or argon atmospheres using typical Schlenk techniques [9]. All solvents used, were freshly distilled, dried and collected under inert conditions. Column chromatography was carried out under inert nitrogen and argon atmospheres using silica gel (particle size 0.063–0.200 mm) as the stationary phase. Percentage yields were calculated relative to the limiting reactant. Crystallization was done using hexane:DCM or hexane:diethyl ether diffusion methods. The reagents CpMn(CO)₃, MeCpMn(CO)₃, n-butyl lithium (1.6 M solution in hexane) and other commercial reagents were used as purchased. Complexes **B1** [10] and **C1** [11] were synthesised according to literature procedures. NMR spectra were recorded on a Bruker ARX-300. NMR spectra were recorded in



Fig. 4. NHC ligands used in this study.

CD₃CN using the deuterated solvent peak as internal reference. The ¹H and ¹³C NMR spectra were measured at 300.1 and 75.5 MHz, respectively. IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR spectrophotometer as KBr pellets or in hexane and only the vibration bands in the carbonyl-stretching region (ca. 1500-2200 cm⁻¹) are reported.

2.2. Synthesis of complexes 1-6

2.2.1. Synthesis of 1, CpMn(CO)₂L1

All complexes were synthesised according to a similar methodology as reported by Lugan [4]. CpMn(CO)₃ (0.612 g, 3.0 mmol) was dissolved in 40 ml of dry THF and irradiated for 60 min at room temperature. Imidazol-2-ylidene L1 (0.714 g, 3.0 mmol) was added to the reaction mixture via cannula and the reaction allowed to stir for 90 min. The reaction colour turned to deep brown and the mixture was subsequently filtered through a small aluminium oxide column. The solvent was evaporated, the product redissolved and purified with column chromatography with hexane:ether eluent to recover **1** as an orange oil. Yield (0.267 g (31%) %) 1 H NMR(CD₃CN): δ 7.33 (s, 1H, NCH=CHN), 7.30 (s, 1H, NHC=CHN), 4.44 (s, 5H, Cp), 4.27 (q, 2H, J_{HH} = 7.3, NCH₂CH₃), 3.75 (s, 3H, NCH₃), 1.30 (t, 3H, $J_{HH} = 7.3$, NCH₂CH₃) ¹³C{¹H} NMR: δ 235.22 Mn(CO)₂, 195.7 NCN, 124.6 NC=CN, 121.5 NC=CN, 82.6 Cp, 65.4 NCH₃, 45.5 NCH₂CH₃, 16.7 NCH₂CH₃. IR (cm⁻¹): 1922 *v*(CO), 1856 *v*(CO). HRESI⁺-MS, *m*/*z*: 287.0513 (calcd. 287.0592).

2.2.2. Synthesis of 2, MeCpMn(CO)₂L1

A similar methodology as for **1** was followed. Imidazol-2-ylidene **L1** (0.714 g, 3.0 mmol) was added to photo-irradiated MeCpMn(CO)₃ (0.654 g, 3.0 mmol). A single brown-orange oily product of complex **2** was isolated. Yield: 0.271 g (30%) ¹H NMR, ppm (CD₃CN): δ 7.20 (s, 1H, NHC=CHN), 7.15 (s, 1H, NHC=CHN, 4.34 (s br, 2H, NCH₂CH₃), 4.09 (s, 2H, Cp), 4.02 (s, 2H, Cp)), 3.36 (s, 3H, NCH₃), 2.86 (s, 3H, Cp-CH₃), 1.48 (s br 3H, NCH₂CH₃). ¹³C{¹H} NMR, ppm: δ 234.7 Mn(CO)₂, 200.7 NCN, 129.0NC = CN, 128.6 NC=CN, Cp 101.4, Cp 81.5, Cp 79.8, 65.0 NCH₃; NCH₂CH₃ 52.27, Cp-CH₃ 37.5, NCH₂CH₃ 13.7. IR (cm⁻¹): 1918 ν (CO), 1852 ν (CO). HRESI⁺-MS, *m*/*z*: 303.0939 (calcd. 303.0905).

2.2.3. Synthesis of 3, CpMn(CO)₂L2

A similar methodology as for **1** was followed. Imidazol-2ylidene **L2** (0.0481 g, 3.0 mmol) was added to photo-irradiated MeCpMn(CO)₃ (0.612 g, 3.0 mmol). A single yellow solid product of complex **3** was isolated (yield: 0.271 g; 30%).¹H NMR, ppm (CD₃CN): δ 7.42 (s, 1H, NHC=CHN), 7.32 (s, 1H, NCH=CHN), 4.45 (s, 5H, Cp), 3.76 (s, 3H, NCH₃), 3.60 (m, 2H, NCH(CH₃)₂), 1.32 (s, 6H, NCH(CH₃)₂). ¹³C{¹H} NMR, ppm: δ 235.1 Mn(CO)₂, 193.5 NCN, 124.90 NC=CN, 118.7 NC=CN, Cp 82.5, 67.5 NCH₃, 51.9 NCH(CH₃)₂, 25.6 NCH(CH₃)₂. IR (cm⁻¹): 1922 ν (CO), 1856 ν (CO). HRESI⁺-MS, *m*/ *z*: 301.0789 (calcd. 301.0748).

2.2.4. Synthesis of 4, MeCpMn(CO)₂L2

A similar methodology as for 1 was followed. Imidazol-2-

ylidene **L2** (0.481 g, 3.0 mmol) was added to photo-irradiated MeCpMn(CO)₃ (0.654 g, 3.0 mmol). A single yellow solid product of complex **4** was isolated (yield: 0.255 g; 27%).¹H NMR, ppm (CD₃CN): δ 6.85 (s, 1H, NCH=CHN), 6.83 (s, 1H, NCH=CHN), 3.96 (s, 2H, Cp), 3.86 (s, 3H, NCH₃), 3.85 (s, 2H, Cp), 3.76 (s br, 2H, NCH(CH₃)₂), 2.89 (s, 3H, Cp-CH₃), 1.33 (d, 6H, *J*_{HH} = 6.3, NCH(CH₃)₂). ¹³C{¹H} NMR, ppm: δ 235.1 Mn(CO)₂, 195.0 NCN, 124.9 NC=CN, 124.1 NC=CN, 34.7 Cp-CH₃, 102.8 Cp, 81.9 Cp, 80.4 Cp, 60.5 NCH₃, 52.4 NCH(CH₃)₂, 13.7 NCH(CH₃)₂. IR (cm⁻¹): 1943 *v*(CO), 1852 *v*(CO). HRESI⁺-MS, *m/z*: 317.1081 (calcd. 317.1062).

2.2.5. Synthesis of 5, CpMn(CO)₂L3

A similar methodology as for **1** was followed. Imidazol-2ylidene **L1** (0.801 g, 3.0 mmol) was added to photo-irradiated MeCpMn(CO)₃ (0.612 g, 3.0 mmol). A single yellow solid product of complex **3** was isolated (yield: 0.381 g; 35%). ¹H NMR, ppm (CD₃CN): δ 7.45 (s, 1H, NHC=CHN), 7.34 (s br, 5H, Ph), 7.26 (s, 1H, NHC=CHN), 4.44 (m, 2H, NCH₂Bn); 4.38 (s, 5H, Cp), 3.75 (s, 3H, NCH₃), 3.03 (m, 2H, NCH₂CH₂Ph). ¹³C{¹H} NMR, ppm: δ 235.2 Mn(CO)₂, 195.1 NCN, 138.9 Ph_(ipso), 129.3 Ph_(meta), 129.0 Ph_(ortho), 127.0 Ph_(para), 124.5 NC=CN, 122.1 NC=CN, 82.7Cp, 64.4 NCH₃, 52.0 NCH₂Bn, 40.8 NCH₂CH₂Ph, IR (cm⁻¹): 1921 ν (CO), 1855 ν (CO). HRESI⁺-MS, *m/z*: 365.1033 (calcd. 365.1062).

2.2.6. Synthesis of 6, MeCpMn(CO)₂L3

A similar methodology as for **1** was followed. Imidazol-2ylidene **L1** (0.801 g, 3.0 mmol) was added to photo-irradiated MeCpMn(CO)₃ (0.654 g, 3.0 mmol). A single yellow solid product of complex **6** was isolated (yield: 0.374 g; 33%). ¹H NMR, ppm (CD₃CN): δ 7.37 (s br, 4H, Ph), 7.46 (s, 1H NHC=CHN), 7.25 (s, 1H NCH=CHN), 4.46 (m, 2H, NCH₂Bn), 4.26 (s br, 5H, Cp), 3.75 (s, 3H, NCH₃) 3.05 (m, 2H, NCH₂CH₂Ph), 2.51 (s, 3H, Cp-CH₃). ¹³C{¹H} NMR, ppm: δ Mn(CO) 235.3, 196.5 NCN, 124.6 NC=CN, 122.2 NC=CN, 138.9 Ph_(ipso), 129.3 Ph_(meta), 129.0 Ph_(ortho), 127.0 Ph_(para), 103.2 Cp, 82.1 Cp, 80.4 Cp, 64.4 NCH₃, 52.1 NCH₂Bn, 40.8 NCH₂CH₂Ph,35.6 Cp-CH₃. IR (cm⁻¹): 1917 ν (CO), 1852 ν (CO). HRESI⁺-MS, *m/z*: 379.1248 (calcd. 379.1218).

2.3. X-ray crystallography

Data for complexes **3** and **6** and **C1** were collected at 150 K on a Bruker D8 Venture kappa geometry diffractometer, with duo Iµs sources, a Photon 100 CMOS detector and APEX II control software using Quazar multi-layer optics, monochromated Mo-K α radiation and by means of a combination of ϕ and ω scans. Data reduction was performed using SAINT+ and the intensities were corrected for absorption using SADABS [12]. The structures were solved by intrinsic phasing using SHELXTS and refined by full-matrix least squares using SHELXTL and SHELXL-2013 [13]. In the structure refinement, all hydrogen atoms were added in calculated positions and treated as riding on the atom to which they are attached. All nonhydrogen atoms were refined with anisotropic displacement parameters, all isotropic displacement parameters for hydrogen atoms were calculated as X × Ueq of the atom to which they are attached, X = 1.5 for the methyl hydrogens and 1.2 for all other hydrogens. Crystallographic data and refinement parameters are given in Table 1. Ortep drawings [14] of the three structures are included in Fig. 5, Fig. 6 and Fig. 9. The crystal structures (cif) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 1517726–1517728. Data collection, structure solution and refinement details are available in each cif.

2.4. Molecular modelling

The calculations reported in this paper were obtained using the Gaussian 09 [15] suite of programs. Calculations were carried out in the singlet spin state using the hybrid functional B3LYP [16,17]. Geometries of the neutral complexes were optimized in gas phase with the triple- ζ basis set 6-311G^{*} on all atoms except for the metal atoms. Stuttgart/Dresden (SDD) pseudopotential was used to describe the metal electronic core, while the valence electrons were described using def2-TZVPP [18]. No symmetry constraints were applied and only the default convergence criteria were used during the geometric optimizations. Vibrational frequencies [19] were calculated for the optimized geometries and no imaginary frequencies were observed, confirming true minima. Donor-acceptor interactions have been computed using the natural bond order (NBO) method [20]. For the ETS-NOVC analysis, complexes 1, B1 and C1 were optimized in ADF 2014.01 [21], using BP86 with a triple- ζ basis set and with up to 2*p* frozen cores on metal atoms, in the gas phase. Optimized structures were then investigated using the Extended Transition State coupled with Natural Orbitals for Chemical Valence (ETS-NOCV) [22] energy decomposition technique. Mn–L bonds were broken and the corresponding fragments were used as promolecules, without any adjustment of fragment occupations.

2.5. General procedure for the dimerization of thiols

On the basis of literature [23] and for purposes of the comparison of computed percentage buried volume and solid angle predictions to experimental obtainable results, 3 mol% of catalyst, in the presence of the ethylthiol and cyclohexane were irradiated in an inert argon atmosphere for the duration of 2.5 h. The resulting solution was analysed directly by GC/MS using hexadecane as internal standard upon which the dimerization yields were based. All reported yields are based on the average of three runs.

Tab	le	1
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Selected	bond	lengths	and	angles.
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	3	6 ^a		
Bond length (Å)				
Mn-COx (x = $1-2$)	1.7565 (19)	1.761 (4)		
Mn-C6	1.9904 (17)	1.990 (3)		
N1-C6	1.363 (2)	1.373 (4)		
N2-C6	1.367 (2)	1.377 (5)		
Bond angle (°)				
C1-Mn-C2	87.96 (9)	89.44 (15)		
N1-C6-N2	103.08 (14)	102.6 (3)		
N1-C6-Mn	128.79 (12)	128.6 (2)		
N2-C6-Mn	128.12 (12)	128.6 (2)		
Torsion angle (°)				
Mn-C6-N1-C7	-179.94 (12)	-0.5 (4)		
Mn-C6-N2-C8	-179.97 (12)	0.6 (4)		
Plane angle (°)				
Carbene/Cp	31.77	30.40		

^a Bond lengths and angles are average values calculated due to the presence of two units per cell.



Fig. 5. Perspective view of ${\bf 3}$ with thermal ellipsoids drawn at the 50% probability level.

3. Results and discussion

3.1. Synthesis and characterization

Complexes **1–6** were prepared in reasonable yields by photochemical substitution of a carbonyl ligand with the free NHC ligand, generated in situ from the reaction between an imidazolium salt and ^tBuOK (Scheme 1). The imidazolium salts (**L1-L3**) were prepared according to literature procedures [24].

The infrared (IR) spectrum of the complexes have been recorded using hexane as the solvent, and indicated the presence of two stretching frequencies. Both stretching frequencies are attributed to the carbonyl ligands of the $Mn(CO)_2$ -moiety. The observations of these stretching frequencies are supported by literature [4,5]. The structural predictions were also confirmed with X-ray diffraction studies of three complexes and will be presented in the next sections.

3.2. Spectroscopic characterization

Using NMR spectroscopy, with CD₃CN as solvent, the structural aspects of the NHC complexes could be investigated. The ¹H NMR spectroscopic peaks for both the imidazolium salts and the complexated ligands had similarity in their spectral pattern and chemical shifts. The imidazolium ligand salts had a characteristic carbene carbon proton peak around $\delta = 9$ ppm, which disappeared instantly upon deprotonation and coordination to the metal centres, indicating the formation of the desired carbene complexes. The protons peaks on the C4 and C5 ring positions of the imidazolylidene ligand of 1-6 were also clearly visible at chemical shifts between $\delta = 6.83$ and $\delta = 7.46$ ppm. The ¹³C NMR of complexes **1–6** indicated the presence of a single distinct CO peak at ca. 235 ppm, a down-field shift of 10 ppm from the MMT and cymantrene starting synthons. The distinct carbene carbon peak can be witnessed at *ca*. 195 ppm. The NMR spectroscopy data is in accordance with literature [4,5]. The IR spectra of 1–6 were measured in hexane and indicated two stretching frequencies attributed to the CpMn(CO)₂ moiety carbonyl stretching frequencies. The stretching frequencies for the two carbonyls ligands were observed at ca. 1850 (symmetric A') and 2020 (antisymmetric A'') cm^{-1} .



Fig. 6. Perspective view of 6 (molecule A) with thermal ellipsoids drawn at the 50% probability level.



Fig. 7. The angle (°) between the Cp and carbene planes of 3.



Fig. 8. Hydrogen interactions (in Å) witnessed in 3.



Fig. 9. Perspective view of C1 with thermal ellipsoids drawn at the 50% probability level.

3.3. Single crystal X-ray diffraction studies

Selected structural parameters are summarized in Table 1. The conformation of the carbene moiety, as represented by the C7-N1-C6-Mn dihedral angles, deviate from planarity by less than 1° (**3**, see Fig. 5) and 7° (**6**, see Fig. 6). The carbene-metal bond lengths were determined to be 1.9904 (17) Å and 1.990 (3) Å respectively and seem to be insensitive to the size of the carbene substituents. The carbene-metal bond lengths are slightly shorter compared to published literature on symmetrical NHC cymantrene derived complexes [**5**]. The angles between the carbene plane (Mn, C6, N1 and N2) and the Cp ring were measured as 31.77° for **3** and 30.40° for **6** (Fig. 7). Complex **6** crystallized with two molecular units (molecule A and molecule B) in the asymmetric unit and displays intramolecular hydrogen interactions between the carbene substituents and the carbonyl groups.

The incidence of hydrogen interactions can also be witnessed in both **3** and in **6** between the methyl group on the N substituent and the carbonyl ligands of the manganese metal atom. The presence of these hydrogen interactions will be quantified using the (ETS-NOCV) [22] energy decomposition technique in the DFT study section (Fig. 8).



Scheme 1. Synthesis of group VII NHC complexes.

During the synthesis of complex **C1** a single crystal, suitable for X-ray diffraction, was also obtained. **C1** crystallized in a $P2_1/c$ space group and displays a linearly coordinated nitrile functionality (Fig. 9). The Mn-N-C3 displays a bond angle of nearly 180° (175.6°) and a C1-M-C2 bond angle of 91.37° which is bigger compared to the NHC ligated complexes **3** and **6**.

3.4. Theoretical study

Theoretical aspects of manganese carbene complexes are well described in literature [4,25,26]. Computational studies typically focus on the interactions of the frontier orbitals and the predictions that can be made from these interactions on the oxidation and reduction potential trends witnessed for metal centres [26]. Theoretical studies by Whittlesey [5] focused on aspects of agostic interactions witnessed in MMT NHC complexes. These studies have, however, been confined to electronic parameters and limited data have been provided on the steric aspects of NHC-substituted complexes of cymantrene and MMT. A DFT study has thus been considered to describe not only the electronic influences that the carbene moiety imparts on the coordination sphere of metal centres but also structural and steric influences by these ligands on the metal moiety. Complexes 1–6, with varying steric bulk on one of the nitrogen substituents of the carbene ligand, have been studied. The calculated properties of the novel complexes 1-6 and C1 were compared with those of literature complexes A2 [4] and B1 [10] as well as theoretical complex A1 (Fig. 10).

3.4.1. Ligand steric parameters

In this study the steric characteristics of NHC ligands have been determined using two different methods, namely the percentage buried volume (%V_{bur}) and the solid angle measurement of the ligands [27a,28,29]. Increasing the bulkiness of the substituents on the N atoms of the ligand should result in a greater %V_{bur} in relation to the metal-ligand bond distance. The %V_{bur} values were found to be similar irrespective of the identity or bulkiness of R-group

substituents on the N atoms of the NHC ligands (26% for L1, 25% for L2 and *ca.* 26% for L3). The %V_{bur} was slightly higher (28.5%) for A1 and significantly higher (33%) for A2 [4]. Therefore the %V_{bur} values are elevated only when both N-substituents are bulky. Due to size and rotation possibilities, steric repulsion is minimized by rotating the bulky substituents away from the coordination sphere of the manganese metal centre. The steric contour map of complex 3 (Fig. 11(b)), generated with SambVca2 [27b], indicates that the NHC ligand is not seen to be sterically crowding the metal centre. Complexes 1 and 5 show similar steric contour maps (see SI).

Although groups are increasingly bulkier, only hydrogen atoms are allowed to penetrate the coordination centre, while the alkyl and aryl groups are accommodated away from the coordination sphere, minimizing the steric requirements of the substituents. Since the %V_{bur} of all the complexes are similar in value, and the NHC ligands occupy only a quarter of the total available space around the manganese atom, the deduction can be made that the steric demands of the NHC ligands have little consequence on available catalytic space.

Solid angle measurements of ligand steric parameters [30] have been attempted to establish a correlation between the steric bulk of a ligand and chemical and physical characteristics of inorganic and organometallic systems [29,31,32]. Shielded regions would severely limit metal-substrate interactions and affect the catalytic potential of the pre-catalyst. The solid angle parameters are provided in Table 2.

The G_M of **1**, **3**, **5** and the cymantrene starting synthon have been visualized and presented in Fig. 12.

The solid angles of **1–6** indicate the size of the ligand increases in the order of **L1** \approx **L2** < **L3**. The G_M and G_(γ) of the cymantrene synthon has also been calculated and indicates a small decrease in both parameters after the coordination of the NHC moiety. As expected, the G_M and G_(γ) increase when two ethyl groups occupy the carbene nitrogen substituents positions compared to the ethyl methyl substituted ligand Fig. 13. The G_(M) predictions for **1–6** have similar values as also seen in the %V_{bur}. Although the solid angles



Fig. 10. NHC complexes 1–6, A1, A2, phosphine complex B1 and acetonitrile complex C1 of the theoretical study.



Fig. 11. (a) Graphical representation of the sphere defining the %V_{bur} of metal complexes 1–6; (b) steric contour map of 3; and (c) representation of the solid angle and G_M of a complex.

Table 2Solid angle parameters for 1–6.

Ligand	Complex	Solid Angle Steradians ^a	G _M (Complex) %	$G_{(\gamma)}\%$
1	1	3.11	96.88	12.89
1	2	3.20	96.91	13.19
2	3	3.06	96.70	13.87
2	4	3.18	96.93	14.14
3	5	3.34	96.35	15.50
3	6	3.34	96.55	16.03
	A1	4.05	98.04	18.79
	A2	4.92	98.60	25.69
	CpMn(CO) ₃	-	97.07	16.66
	$MeCpMn(CO)_3$	-	95.41	12.08

^a Solid angle of the NHC ligand.

indicate a similar size of **L1** and **L2**, the increasing $G_{(\gamma)}$ values is indicative of increasing steric bulk of the ligands in the order of $L1 < L2 < L3 < L_{A1} < L_{A2}$.

3.4.2. Wiberg bond indices and bond dissociation energies (BDEs)

Literature exists for the determination and applicability of Wiberg bond orders in the endeavour to study NHC ligands [33,34] and the coordination to metal centres [35,36]. The Wiberg bond indices quantified single or double bond character and can be utilized to determine bond strength orders (BSOs). From our calculated results, the Wiberg bond indices (see Table S1 in SI) indicate a relatively strong sigma-donation from the NHC ligand towards the metal centre (BO = 0.73-0.78). The indices are similar in all the NHC complexes and show no variation despite steric difference between the carbene nitrogen substituents. These values correlate

well with dimeric Mn NHC complexes reported recently [29]. The bonding interaction of the NHC ligands was determined to be similar to that of phosphine ligands (M-L bond order of 0.77) and stronger in comparison to the nitrile ligand analogues such as **C1** (BO = 0.66). These values are, however, in line with reported literature values [35].

The bond dissociation energies [29,37] for **1–6** are listed in Table S1 in SI. From the data presented, NHC ligands bound more tightly towards the manganese centre bearing cyclopentadienyl ligands compared to the methylcyclopentadienyl analogues. NHC ligands with ethyl phenyl substituents had greater BDEs followed by isopropyl and finally ethyl groups respectively. The dissociation energies thus decreases in the following trend: CpMn-L3 > MeCpMn-L3 > CpMn-L2 > CpMn-L1 > MeCpMn-L2 > MeCpMn-L1.

The average bond dissociation energy for the NHC ligands were significantly greater compared to both phosphine and nitrile ligands despite the similarity in Wiberg bond orders. The heightened BDEs are ascribed to the superior coordination interactions offered by NHC ligands. Complexes with larger substituents on the nitrogen backbone of the ligands tend to display greater BDE compared to smaller substituents. This finding is supported by literature [38] and the steric effects of the heteroatomic substituents are well described. Increasing the bulkiness of the nitrogen substituents leads to increases in the stability of the NHC ligands and greater donation to the ligated metal centre.

3.4.3. Extended Transition State coupled with Natural Orbitals for Chemical Valence (ETS-NOCV)

ETS-NOCV is a powerful computational tool with which the



Fig. 12. The G_M (Complex) of 1 (a), 3 (b) and 5 (c) and CpMn(CO)₃ (d).



Fig. 13. Solid angle parameters of the (a) MeCpMn(CO)₃, (b) diethyl substituted NHC and (c) complex 2.

formation of an M–C bond can be investigated and analysed in terms of the absorbed or released interaction energy, ΔE_{Int} , as well as the change in electron density, commonly known as the deformation density, $\Delta \rho$, associated with bond formation [21,22]. Both ΔE_{Int} and $\Delta \rho$ can be decomposed into different components to aid interpretation of a bond formation process. The interaction energy can be decomposed into three terms,

$$\Delta E_{Int} = \Delta E_{Elstat} + \Delta E_{Pauli} + \Delta E_{Orb} + \Delta E_{Disp}$$
(1)

where ΔE_{Elstat} gives the change in electrostatic energy upon bringing unperturbed promolecules from an infinite separation to the final bonding distance, ΔE_{Pauli} gives the change in energy required to orthogonalize (ensuring antisymmetry) the promolecular (ensuring antisymmetry) wavefunctions and is commonly known as Pauli repulsion, ΔE_{Orb} gives the change in energy related to the minimization of the energy of the final structure and is commonly known as the orbital interaction term and ΔE_{Disp} is the dispersion energy, usually calculated through empirically-derived functionals. The electrostatic and Pauli energy changes are often combined into a single value, ΔE_{Steric} , to give an indication of the steric (electrostatic + electronic) interaction between promolecules. Similarly, the deformation density can be decomposed into two terms,

$$\Delta \rho = \Delta \rho_{\text{Pauli}} + \Delta \rho_{\text{Orb}} \tag{2}$$

where each terms gives the change in density associated with the energetic term of Eq. (1) (no density change is observed with the change in electrostatic energy) [21,22]. The various decomposition terms of Eq. (1) can be used to compare the properties associated with the formation of different M–C bonds, and the associated density changes can be used for visual inspection [21,22]. Of more interest to us, however, is the further decomposition of the ΔE_{Orb} and $\Delta \rho_{Orb}$ terms into contributions from natural orbitals, as given by the NOCV addition to ETS. Specifically, the total $\Delta \rho_{Orb}$ term can be decomposed into i natural orbitals,

$$\Delta \rho_{Orb} = \sum_{i} \Delta \rho_i \tag{3}$$

and each NOCV channel is associated with a specific change in energy, ΔE^i_{Orb} . The highest occupied NOCV channels can usually be associated with specific components of molecular orbital interactions between promolecules, such as σ and π bonding, giving associated deformation density channels and energy changes for these components, i.e. $\Delta \rho_{\sigma}$ and ΔE^{σ}_{Orb} describing a σ -bonding component of an M–C bond [21,22]. These features of the ETS-

NOCV approach allow qualitative as well as quantitative comparison of specific attributes of different M–C bonds in various systems [21,22].

In this section the bond characteristics of three different ligand systems coordinated to a CpMn(CO)₂ moiety were probed. The formation of various Mn-L bonds in 1, B1 and C1 was investigated theoretically using ETS-NOCV. Of primary interest is the various NOCV channels of each Mn-L bond, describing the density and energy changes of specific (σ and π) attributes of each bond. The primary NOCV channels for the NHC (structure 1) are shown in Fig. 14. $\Delta \rho \sigma$ describes the clear σ -donation from the ligand to the metal with an associated energy change of -146.86 kJ·mol⁻¹, whereas $\Delta \rho \pi 1$ and $\Delta \rho \pi 2$ describe the π -back donation from metal to ligand for two different axes, with a combined energy contribution of $-59.50 \text{ kJ} \cdot \text{mol}^{-1}$. Finally, $\Delta \rho_4$ shows the formation of two hydrogen CH···C interactions, contributing $-5.69 \text{ kJ} \cdot \text{mol}^{-1}$ to the total interaction energy. The NOCV channels for the remaining structures **B1** and **C1** are qualitatively very similar, except for the lack of CH····C interactions in C1. The presence of hydrogen interactions was also witnessed in the solid-state crystal structures of 3 and 6.

In Table 3, decomposition of the total interaction energy into relevant components for each structure is shown; for a complete ETS-NOCV decomposition. Comparing first the total interaction energies, ΔE_{Int} , **1** forms the strongest M–L bond, with the phosphine **B1** and the acetonitrile **C1** weaker by +29.12 and + 125.10 kJ·mol⁻¹, respectively. The biggest contribution to the strength of **1** is a very large electrostatic contribution $(-485.26 \text{ kJ} \cdot \text{mol}^{-1} \text{ as opposed to } -348.61 \text{ and } -227.61 \text{ kJ} \cdot \text{mol}^{-1} \text{ in }$ B1 and C1, respectively, as seen in Table 3). Electronically, however, **1** and **B1** is equivalent, with a total orbital interaction of -233.47 and $-237.61 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. Interestingly, the σ -donation of both **1** and **B1** is very similar (differing by $-7.41 \text{ kJ} \cdot \text{mol}^{-1}$ in favour of 1) but 1 experiences considerably weaker π -back bonding (differing by $-16.78 \text{ kJ} \cdot \text{mol}^{-1}$ in favour of **B1**). On the other hand, **B1** and **C1** show equivalent π contributions, but **C1** forms a considerably weaker σ bond than the other structures. Therefore, the combination of large electrostatic attractions coupled with comparatively small electronic steric repulsions result in 1 forming a stronger M-L bond than **B1**, despite comparative orbital and dispersion interactions.

The ratio of the σ contributions over π contributions for each structure is shown in Table 3. This metric gives us a direct indication of the relative σ -donation over π -back bonding capability of each system. Clearly, **1** shows by far the most σ character (2.47 times more σ -bonding than π -bonding), whereas the phosphine **B1** is slightly more prevalent for σ -bonding (1.83) and the **C1** is more or less equivalent for both σ and π (1.11). However, since the total



 $\Delta E_{Orb}^{\sigma} = -146.9 \text{ kJ} \cdot \text{mol}^{-1}$

 $\Delta E_{Orb}^{\pi 1} = -37.4 \,\mathrm{kJ} \cdot \mathrm{mol}^{-1}$



Fig. 14. Primary NOCV channels and associated orbital energy changes for **1**. Blue and red regions indicate an accumulation and depletion of electron density, respectively. Isosurfaces for $\Delta \rho_{\sigma}$, $\Delta \rho_{\pi_1}$, $\Delta \rho_{\pi_2}$ and $\Delta_{\rho 4}$ are 0.002 au, 0.001 au and 0.00015 au, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3	
Selected ETS-NOCV energy contributions.	

	ΔE_{Int}^{a}	ΔE_{Elstat}^{a}	ΔE_{Pauli}^{a}	ΔE_{Steric}^{a}	ΔE_{Orb}^{a}	ΔE_{Disp}^{a}
1	-276.14	-485.26	+493.96 +405.68 +265.27	+8.70	-233.47	-51.35
B1	-247.02	-348.61		+57.07	-237.61	-66.46
C1	-151.04	-227.61		+37.66	-173.64	-15.21
	ΔE_{Orb}^{σ}	a Δ	E_{Orb}^{π} a	σ/π^{b}	%σ ^c	$\%\pi^{d}$
1	-35.1	10 –	14.22	2.47	53%	22%
B1	-33.3	33 –	18.23	1.83	56%	31%
C1	-20.4	10 –	18.40	1.11	13%	12%

^a All values in kJ·mol⁻¹.

^b Ratio of ΔE^{σ}_{Orb} over ΔE^{π}_{Orb} .

^c Percentage of σ contribution to ΔE_{Int} .

^d Percentage of π contribution to ΔE_{Int} .

interaction energies of each system differ, the final columns of Table 3 present each attribute of bonding as a percentage of the total interaction energy, allowing direct comparison between different ligands.

Complexes **1** and **B1** are equivalent σ -donors, with 53% and 56% of the total binding energy originating from σ -donation, respectively. However, **1** shows considerably less π character than **B1**, with 22% π -back donation for **1** and 31% for **B1**. The acetonitrile **C1** shows equivalent σ and π character (13% and 12%, respectively), and overall lower contributions from electronic interactions. The remaining contributions to the total interaction energy includes

energetically weaker electronic interactions (such as weak noncovalent interactions and various polarizations), as well as stearic effects (including electrostatic interactions and Pauli repulsion). The stronger M-L bond in **1** illustrates the superior ability of the NHC ligand to stabilize the metal centres compared to phosphine and acetonitrile ligands. The ETS-NOCV results also mirror findings of the bond dissociation energies were NHC-M complexes display strong M-L bonds.

3.5. Catalytic study

Catalytic applications of cymantrene [39] include dehydrocoupling reactions of amine-borane adducts [40], dehydrogenative silane alcoholysis [41] and the photoconversion of thiols into disulfides [23]. Of the three reactions mentioned, the final process was chosen to evaluate the catalytic activity of our complexes.

Organosulfur chemistry has always been of particular interest both in the field of chemistry and biology [42]. The transformation of sulfur-containing compounds has attracted much research interest and specifically the oxidation of thiols to disulfides has remained an area of importance [43]. Reactions focussing explicitly on the dimerization of sulfides into disulfides normally require a basic catalyst [44], stoichiometric amounts of oxidants [45] or toxic reagent and long reaction times. Apart from the high demand of these reaction conditions, many synthetic methodologies generate elevated levels of unwanted side-products. The side-products are commonly produced as a result from over oxidation, producing sulfoxides, sulfones, thiosulfinates and thiosulfonates [46–48]. Literature examples have been reported for the employment of rhodium(I) transition-metal complexes that illustrated the ability to selectively oxidize thiols into disulfides as an attractive alternative to the use of hazardous oxidants [23], but such processes have been fairly unexploited. The UV photolysis of cymantrene with thiols at room temperature offered a viable, greener alternative to classic published method of dimerization of thiols and produced H₂ as the only side product [23]. Pre-catalysts **1–6** have been investigated for application in the dimerization of thiols into disulfides [23]. Based on literature [23] and for purposes of the simple comparison of $%V_{bur}$ and solid angle predictions to experimental obtainable results, 3 mol% of catalyst, in the presence of the substrate and cyclohexane were photo-irradiated in an inert argon atmosphere for the duration of 2.5 h to test for catalytic activity.

All six complexes displayed catalytic activity in the dimerization of thiols into disulfides (Table 4). Although lower yields were obtained for complexes 3 and 4, complexes 5 and 6 displayed superior activity with yields of ca. 47% and turn over frequencies (TOF) of 49 h^{-1} . The obtained yields were lower in comparison to literature [23] (ca. 99% for alkyl thiols) for the CpMn(CO)₃-photoconversion of thiols. Complexes displayed diminished activity over the 150 min reaction period, which might indicate the decomposition of the catalysis under the harsh photo-irradiation conditions. The higher catalytic activity of **5** and **6** could thus be explained by the greater stability of these complexes where decomposition is concerned, displaying higher BDE of the metal-carbene bond and slightly larger HOMO-LUMO band gaps (see SI) compared to complexes **1–4**. The dimerization occurs through the substitution of a carbonyl ligand for an ethylthiol group. The ligand exchange can occur at two different carbonyl ligand positions in reference to the substituents on the NHC ligand. Bond dissociation energies of the metalcarbonyl bonds indicate similar dissociation energies for carbonyl ligands CO_a and CO_b (Fig. 15). It can thus be hypothesized that ligand exchange could occur at either carbonyl ligand to initiate the catalytic cycle.

The ligand steric parameter results indicate that the steric trend increases in the order **L1** < **L2** < **L3** and literature associates the steric influences of NHC substituents with the greater stability these ligands afford to the metal moiety. The solid angle and $%V_{bur}$ parameters thus correlate with the stability associated with the pre-catalysts and therefore might suggest a probable explanation for the catalytic activity witnessed. Although the ligands increase in bulkiness, the steric groups do not directly influence the coordination space of the metal moiety (as indicated by the solid angle).

Table 4

Dimerization of ethylthiol by manganese(I) NHC complexes 1-6.



Fig. 15. Possible carbonyl substitution positions CO_a and CO_b available on 1–6.

The ligands thus afford greater stability while not crowding the metal atom. Complexes 5 and 6 contain the most steric ligand L3, according to the steric parameters calculated, which then implies that the most stable complexes were found to have the best catalytic activity. A feasible catalytic cycle is proposed in Fig. 16, describing the catalytic conversion of the thiol substrates into disulfides. The cycle is based on experimental data obtained from the similar study on the dimerization of thiols using cymantrene only as catalyst [23,49]. In the article by Zhang et al. [49], an indepth DFT study on the key intermediates and two possible pathways for this conversion, is described. Their results correlate with the experimental observations of Tan et al. [23]. The cycle is initiated with the photo-induced substitution of a carbonyl ligand for a thiol substrate and terminates with the liberation of disulfides and the regeneration of the active catalyst species. The process is dependent on the availability and lability of carbonyl ligands of the pre-catalyst species and thus might explain the lower activity of our pre-catalysts in comparison with the cymantrene analogue.

4. Conclusion

NHC complexes **1–6** were synthesised in satisfactory yields from MMT and cymantrene synthons. The molecular structures of the novel complexes were confirmed with NMR and IR spectroscopy, and single crystal X-ray diffraction studies of **3** and **6**. Through DFT calculations, it was possible to describe the steric influences the NHC ligands impose on the metal synthon. Wiberg bond indices indicated orders of *ca*. 0.7 for the NHC complexes, which is similar to bonding aspects of triphenylphosphine. Both ligands thus display negligible π -back donation from the metal centre. The frontier orbital analysis indicated increases in the band gaps upon



Catalyst ^{a,c}	Complex	R	R′	Cat. (mol%)	Conversion ^b (%)
	1	Et	Н	3	28
R	2	Et	Me	3	22
R'	3	ⁱ Pr	Н	3	16
N Mn	4	ⁱ Pr	Me	3	6
///co	5	CH ₂ CH ₂ Ph	Н	3	47
	6	CH ₂ CH ₂ Ph	Me	3	48

^a General reaction conditions: Ethylthiol (2.0 mmol), Catalyst (0.06 mmol), Cyclohexane (10 ml), Room temperature, 150 min.

^b Conversion based on internal standard.

^c TOF, as cited in text, was calculated after the first 10 min of the catalytic reaction.



Fig. 16. Catalytic cycle associated with the dimerization of thiol substrates.

the substitution of NHC ligands with larger molecular masses (see SI). Lower mass ligands had smaller band gaps. The increases in the band gaps may indicate higher stability of complexes **5** and **6** or greater inertness towards decomposition pathways. Finally, BDE energies indicated a linear relationship between the associated energies and the molar mass of the NHC moiety. The BDE of the NHC-metal bonds were higher in cymantrenecomplexes compared to MMT analogues.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.03.047.

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