NHC Complexes

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# Transition Metal Complexes of Anionic N-Heterocyclic Dicarbene Ligands**

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The development of N-heterocylic carbene (NHC) chemistry has advanced enormously since the pioneering work of Wanzlick and Schönherr, and that of Öfele.[1] Arguably, one of the most significant breakthroughs in this area was the isolation of the first stable N-heterocyclic carbene (NHC), 1,3-bis(adamantyl)-imidazol-2-ylidene, by Arduengo and co-workers.[2] Since this species was first reported, NHCs have gone from chemical curiosities to ubiquitous ligands in the span of just twenty years.[3] Their use as supporting ligands for the formation of transition metal complexes with varied chemical properties has been extensively documented.[4] Similarly, the exploitation of their strong sigma-donor ability has been used in main-group chemistry for the stabilization of numerous low-coordinate complexes containing elements in low oxidation states, including the remarkable group 14 and 15 diatomic species $E_2$ (E = Si, Ge, P, As)[5–8] and $P_2^{2+}$.[9]

The chemistry of NHCs is dominated by ligand coordination through the C2 atom in the so-called classical mode (**A**, Figure 1). However, following the discovery of the first transition metal complex of an abnormal NHC (aNHC, **B**, Figure 1) by Crabtree and co-workers,[10] numerous additional examples of such abnormally bonded species have been isolated,[11] including the first example of an isolated metal-free abnormal carbene.[12] A closely related, metal-free mesoionic carbene was also isolated by Bertrand and co-workers.[13] More recently, Robinson and co-workers reported the first example of an anionic N-heterocyclic dicarbene, that is, an NHC in which one of the sites of the imidazol-2-ylidene backbone has been deprotonated, giving rise to an NHC capable of coordinating through the C2 and C4 positions simultaneously (NHDC, **C**, Figure 1).[14] A related anionic NHC which can be rationalized as an adduct of a dicarbene and $B(C_6F_5)_3$ was also recently reported.[15] Whereas lanthanide complexes of an N-heterocyclic dicarbene have previously been isolated,[16] to our knowledge no examples of transition metal complexes of N-heterocyclic dicarbenes have been reported to date. Related neutral dicarbenes based on 1,2,4-triazole-3,5-diylidenes were first identified in coordination polymers of silver(I) salts.[17]

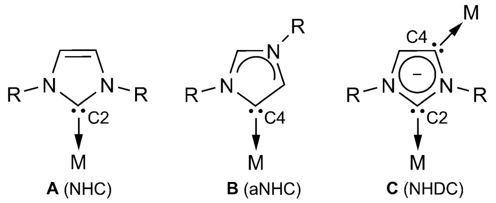

*Figure 1.* Bonding modes of N-heterocyclic carbenes including the classical coordination mode (**A**), the abnormal coordination mode (**B**) and the deprotonated anionic dicarbene (**C**).

Herein, we report the first example of a transition metal complex containing anionic N-heterocyclic dicarbene ligands $K[\{:C[N(2,6\text{-}i\text{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)(thf)]\cdot THF$ (**2**).

Reaction of 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) with $Mn_3(mes)_6$ in diethylether afforded the complex $[Mn(IPr)(mes)_2]$ (**1**; Figure 2) as an insoluble off-white solid in near quantitative yields. Crystals suitable for single crystal X-ray diffraction could be obtained by slow diffusion of diethylether into a pyridine solution of **1** at 4 °C.[18] Analogous reactions giving rise to related three

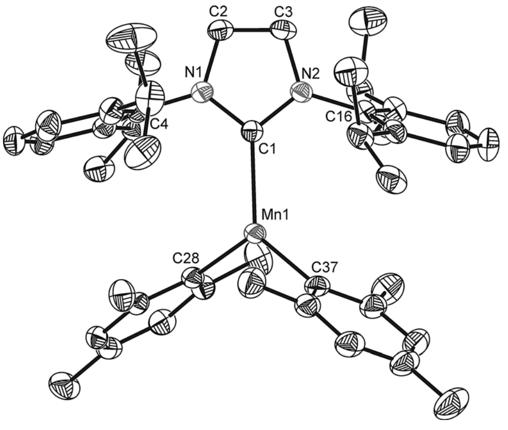

*Figure 2.* Molecular structure of **1** (anisotropic displacement ellipsoids set at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Mn1–C1 2.195(2), Mn1–C28 2.122(2), Mn1–C37 2.125(2), C1–N1 1.364(2), C1–N2 1.359(2), N1–C2 1.390(2), N2–C3 1.389(2), C2–C3 1.347(3), N1–C4 1.446(2), N2–C16 1.446(2); C1-Mn1-C28 116.49(6), C1-Mn1-C37 122.57(7), C28-Mn1-C37 120.94(7).

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coordinate trigonal planar manganese(II) NHC complexes have previously been reported.[19]

The Mn–C1 distance in **1** is 2.195(2) Å, which is slightly shorter than the values of 2.236(2) and 2.277(4) Å reported for the closely related bis-alkyl species [Mn(IPr)(CH$_2$SiMe$_3$)$_2$] and [Mn(IPr){CH(SiMe$_3$)$_2$}$_2$], respectively.[19] The C1-Mn1-C28, C1-Mn1-C37, and C28-Mn1-C37 bond angles are 116.49(6), 122.57(7), and 120.94(7)°, respectively, which are very close to the value of 120° expected for a trigonal planar complex. Compound **1** is only sparingly soluble in most organic solvents, yet exhibits excellent solubility in pyridine, which gives rise to dark red solutions. Such intensely colored solutions are consistent with metal–ligand charge transfer in a hypothetical pyridine adduct of **1**, however owing to the paramagnetic nature of this complex, its behavior in solution could not be investigated by NMR spectroscopy.

DFT calculations on **1** show that the sextet ($S = 5/2$) state is the lowest energy electronic configuration, with the quartet ($S = 3/2$) and doublet states ($S = 1/2$) states located at higher energies by 57.5 and 137.2 kJ mol$^{-1}$, respectively. Bond metric data for the sextet state were found to be the most closely related to the structure, as determined by single crystal X-ray diffraction (see the Supporting Information for details). These results are consistent with superconducting quantum interference device (SQUID) magnetic measurements, which show that **1** obeys the Curie–Weiss law [$\chi_{\mathrm{mol}} = N_{\mathrm{A}}\mu_0 \mu_{\mathrm{B}}{}^2 \mu_{\mathrm{eff}}{}^2/3k(T-\Theta)$] and exhibits an effective magnetic moment of 6.042(6) $\mu_{\mathrm{B}}$, which is comparable to the spin-only value of 5.92 $\mu_{\mathrm{B}}$ expected for an $S = 5/2$ system.

The chemical reduction of **1** using KC$_8$ was found to give rise to the highly air- and moisture-sensitive pseudo-tetrahedral bis(dicarbene) complex K[{:C[N(2,6-$i$Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)(thf)]·THF (**2**) along with additional unidentified reaction products. Compositionally pure crystals of **2** suitable for single crystal X-ray diffraction could be grown by slow diffusion of hexanes into the filtered reaction mixture in moderate (25–30 %) yields.[18]

The crystal structure of **2** contains an anionic [{:C[N(2,6-$i$Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)(thf)]$^-$ moiety consisting of a manganese(II) metal center that is bonded to a mesityl group, a THF molecule, and to two deprotonated IPr (aIPr-H) ligands in an abnormal fashion through the C4 atoms (Figure 3). In turn, these two anionic carbene ligands interact with the potassium cations through the classical carbene positions, ultimately giving rise to infinite one-dimensional coordination polymers of potassium separated anionic moieties. Each potassium cation is coordinated in a linear fashion by two dicarbene ligands (K1–C1 2.844(3) Å; K2–C28 2.832(3) Å). Bond metric data within the dicarbene units are closely related to those recorded for the salt reported by Robinson et al., [Li(thf)][:C{N(2,6-$i$Pr$_2$C$_6$H$_3$)}$_2$(CH)C] (see the Supporting Information).[14a] The manganese–carbene distances observed for **2** are 2.183(3) and 2.157(3) Å, which are slightly shorter than the value of 2.195(2) Å observed for **1**, and consistent with an increase in the ionic character of the metal–ligand interaction. Conversely, the M–C bond distance to the mesityl substituent, 2.188(3) Å, is significantly longer than those observed in **1** (2.122(2) and 2.125(2) Å), this is presumably due to the increase in coordination number and steric bulk around the manganese center. Coordination about the manganese(II) metal center is pseudo-tetrahedral, with a weakly bonded THF molecule (Mn–O 2.291(2) Å) distorting an otherwise trigonal planar structure. This is manifested in the bond angles around the central manganese; the angles between dicarbene and mesityl substituents are rather close to 120°, as expected for a trigonal planar structure (117.17(10), 109.93(10), and 124.97(10)°), whereas the angles between the coordinated THF molecules and the mesityl and dicarbene ligands are more acute (103.70(10), 93.10(9), and 100.61(9)°). The five-membered carbene ring systems are nearly coplanar owing to the steric bulk of the diisopropylphenyl groups.

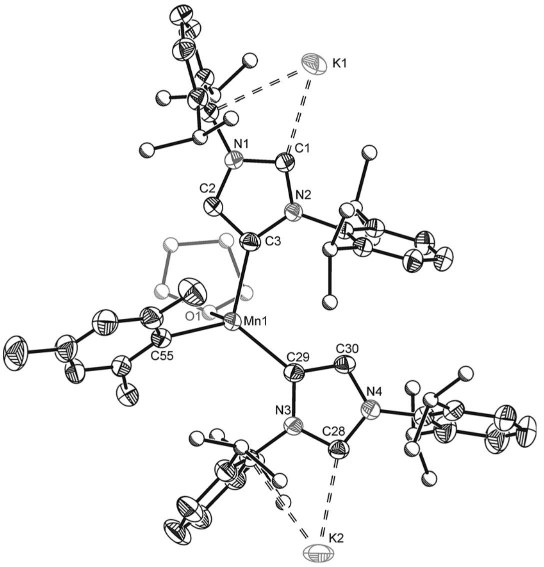

***Figure 3.*** Molecular structure of **2** (anisotropic displacement ellipsoids set at 50 % probability). Solvent of crystallization and hydrogen atoms have been omitted for clarity. Atoms of the $i$Pr groups and the THF molecule are pictured as spheres of arbitrary radii. Selected bond distances [Å] and angles [°]: Mn1–C3 2.183(3), Mn1–C29 2.157(3), Mn1–C55 2.188(3), Mn1–O1 2.291(2), K1–C1 2.844(3), C1–N1 1.363(3), C1–N2 1.361(3), N1–C2 1.391(4), N2–C3 1.423(3), C2–C3 1.362(4), K2–C28 2.832(3), C28–N3 1.363(4), C28–N4 1.361(4), N3–C29 1.418(3), N4–C30 1.397(4), C29–C30 1.367(4); C3-Mn1-C29 117.17(10), C3-Mn1-C55 109.93(10), C29-Mn1-C55 124.97(10), C3-Mn1-O1 93.10(9), C29-Mn1-O1 100.61(9), C55-Mn1-O1 103.70(10).

As with **1**, unrestricted DFT geometry optimizations on **2** reveal that the sextet state is the lowest energy spin state, 45.7 kJ mol$^{-1}$ lower in energy than the quartet state and 142.9 kJ mol$^{-1}$ below the total bonding energy of the doublet state. The geometry of the optimized structure for the sextet was found to most closely match the geometry determined by single crystal X-ray diffraction (see the Supporting Information for details). The magnetic moment measured for **2**, 5.943(2) $\mu_{\mathrm{B}}$, is consistent with these findings.

The presence of [{:C[N(2,6-$i$Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)]$^-$ in solution was confirmed by electrospray mass-spectrometry of a THF solution of **2**, which showed the molecular ion at an $m/z$ value of 948.6 in the negative-ion-mode spectrum. The positive-ion-mode mass spectrum also revealed the presence of the anion paired with two potassium cations at 1027.3 Da.

The dicarbenic nature of the ligands in **2** was probed by reacting the complex with two molar equivalents of triethylaluminium in the presence of the cation sequestering agent 2,2,2-crypt. This yielded the complex [K(2,2,2-crypt)]-$[\{(CH_3CH_2)_3Al{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)]$ (**3**; Figure 4). Single crystals of **3** suitable for X-ray diffraction were grown from a THF/hexanes mixture and reveal an anionic metal complex where the two dicarbene ligands are coordinated to the metal center in an abnormal fashion, as with **2**. There is no solvent coordinated to the metal center in **3**, which indicates that the interaction with a THF molecule present in **2** is presumably very weak and unnecessary to stabilize the complex in solution. The classical carbene C2 positions interact with the Lewis acidic $Al(CH_2CH_3)_3$ fragments, thus giving rise to a 1:2 adduct. Bond metric data for the anionic metal complex are very similar to those observed for **2** (see the Supporting Information for details).

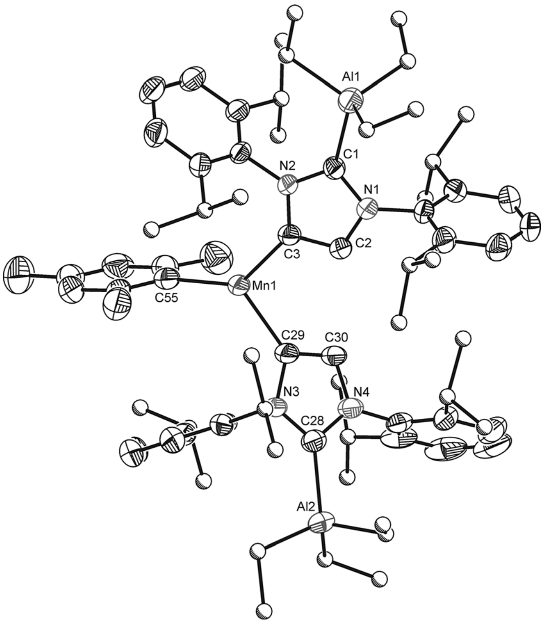

***Figure 4.*** Single crystal X-ray structure of the anionic moiety in **3** (anisotropic displacement ellipsoids set at 50% probability). The $[K(2,2,2\text{-crypt})]^+$ countercation and all hydrogen atoms have been omitted for clarity. Carbon atoms of Et and *i*Pr groups are pictured as spheres of arbitrary radii. Selected bond distances [Å] and angles [°]: Mn1–C3 2.153(4), Mn1–C29 2.163(4), Mn1–C55 2.102(5), Al1–C1 2.094(4), C1–N1 1.365(5), C1–N2 1.367(5), N1–C2 1.391(5), N2–C3 1.412(5), C2–C3 1.357(6), Al2–C28 2.103(4), C28–N3 1.361(6), C28–N4 1.363(6), N3–C29 1.420(5), N4–C30 1.395(5), C29–C30 1.336(7); C3-Mn1-C29 104.12(16), C3-Mn1-C55 137.33(17), C29-Mn1-C55 117.38(19).

As with **2**, the ESI-MS spectra of THF solutions of **3** prove the presence of the complex in solution. The negative-ion-mode spectrum reveals a mass-envelope at an *m*/*z* value of 1177.1 corresponding to the parent anion. There is also evidence of additional peaks arising from complex fragmentation/decomposition during the ionization process. Similarly, the positive-ion-mode spectrum reveals a peak at 2008.8 Da, which arises from the molecular ion paired with two $\{[K(2,2,2\text{-crypt})]^+$ cations.

In summary, we have shown that the chemical reduction of transition metal complexes of N-heterocyclic carbenes represents a viable route towards the synthesis of species containing dicarbenic NHC ligands. This is a noteworthy observation, as NHCs have been extensively employed as supporting ligands for the isolation of complexes of elements in low oxidation states (often generated by the chemical reduction of the NHC adducts of element halides). Our observations suggest that the generation of dicarbene ligand complexes is one of several possible outcomes upon reduction of metal–NHC compounds; as such it is surprising that such systems have gone largely unnoticed until now.

## Experimental Section

$[Mn(IPr)(mes)_2]$ (**1**): $Mn_3(mes)_6$ (0.57 g, 1.96 mmol) and IPr (2.00 g, 5.87 mmol) were dissolved in diethylether (50 mL). The mixture was left to stir under argon for 24 h until all of the dark solid had reacted, with concomitant precipitation of a cream-colored product. The solvent was removed under dynamic vacuum and the off-white powder dried for 3 h. Yield: 3.20 g (86%). Crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of diethylether into a pyridine solution of the product at 4°C. Anal. Calcd for $MnC_{45}H_{58}N_2$: C 79.26%, H 8.57%, N 4.11%. Found: C 78.42%, H 8.50%, N 4.32%. EI-MS measurements showed no evidence of the molecular ion owing to complex fragmentation during ionization. SQUID magnetometry: $\mu_{\mathrm{eff}} = 6.042(6)\ \mu_B$.

$K[\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)(thf)]\cdot THF$ (**2**): A mixture of **1** (1.00 g, 1.47 mmol) and $KC_8$ (0.198 g, 1.47 mmol) were weighed into a Schlenk tube inside a glovebox. THF (20 mL) was added under argon on a Schlenk line and the resulting dark brown mixture stirred for 24 h. The mixture was concentrated to 10 mL, filtered through a Celite plug and layered with hexanes to yield off-white crystals of **2** suitable for single crystal X-ray diffraction (409 mg; 26% crystalline yield, based on Mn). Elemental analyses were consistently (and reproducibly) found to be low in carbon, this is presumably due to the formation of metal carbides. Anal. Calcd for $MnC_{71}KO_2H_{97}N_4$: C 75.29%, H 8.63%, N 4.95%. Found: C 73.00%, H 8.28%, N 5.32%. ESI-MS (negative ion mode, THF): *m*/*z* 412.5 $[Mn(mes)_3]^-$ (8%), 606.7 (unidentified, 22%), 680.8 $[\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}Mn(mes)_2]^-$ (50%), 948.6 $[\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)]^-$ (100%), 991.3 $[\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)+K^+]^-$ (8%). ESI-MS (positive ion mode, THF): 429.8 $[K\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}+H^+]^+$ (100%), 816.63 $[2\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}^-+K^++2H^+]^+$ (58%), 1027.3 $[K_2\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)]^+$ (40%). SQUID magnetometry: $\mu_{\mathrm{eff}} = 5.943(2)\ \mu_B$.

$[K(2,2,2\text{-crypt})][\{(CH_3CH_2)_3Al\}_2\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)]_2(CH)C\}_2Mn(mes)]$ (**3**): A mixture of **2** (105 mg, 0.10 mmol) and 2,2,2-crypt (37 mg, 0.10 mmol) were weighed into a vial in an inert atmosphere glovebox and dissolved in THF (5 mL). The solution was stirred for 5 min, after which $Al(CH_2CH_3)_3$ (28 μL, 0.20 mmol) was added and the solution left to stir for an additional 5 min. It was subsequently filtered through a Celite plug into a crystallization ampoule and layered with hexanes (20 mL). Crystals of the product grew after approximately 3 days, were isolated by filtration, and dried under dynamic vacuum for 1 hour. Yield: 110 mg (85%). As with **2**, elemental analyses carried out on **3** were consistently low in carbon. Anal. Calcd for $C_{93}H_{147}Al_2KMnN_6O_6$: C 70.09%, H 9.30%, N 5.28%. Found: C 65.56%, H 8.79%, N 5.25%. ESI-MS (negative ion mode, THF): *m*/*z* 1075.0 $[K[K(2,2,2\text{-crypt})]\{(CH_3CH_2)_3Al\}\{{:}C[N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)](CH)C\}(mes)]^-$ (29%), 1177.1 $[\{(CH_3CH_2)_3Al\}_2\{{:}C[N(2,6\text{-}$

$i\mathrm{Pr_2C_6H_3})]_2(\mathrm{CH})\mathrm{C}\}_2\mathrm{Mn(mes)}]^-$ (100 %), 1189.1 [K(2,2,2-crypt)]-{:C[N(2,6-$i\mathrm{Pr_2C_6H_3}$)](CH)C}$_2$] (57 %); the spectrum also exhibits numerous intense mass-envelopes below 900 Da arising from sample fragmentation/decomposition. ESI-MS (positive ion mode, THF): *m*/*z* 1064.2 [$(\mathrm{CH_3CH_2})_3$Al{:C[N(2,6-$i\mathrm{Pr_2C_6H_3}$)](CH)C}$_2$Mn-(mes)+H]$^+$ (59 %), 1894.7 {[K(2,2,2-crypt)]$_2$[$(\mathrm{CH_3CH_2})_3$Al{:C[N(2,6-$i\mathrm{Pr_2C_6H_3}$)](CH)C}$_2$Mn(mes)]}$^+$ (39 %), 2008.8 {[K(2,2,2-crypt)]$_2$-[{$(\mathrm{CH_3CH_2})_3$Al}$_2${:C[N(2,6-$i\mathrm{Pr_2C_6H_3}$)](CH)C}$_2$Mn(mes)]}$^+$ (100 %). SQUID magnetometry: $\mu_{\mathrm{eff}} = 5.903(6)\ \mu_{\mathrm{B}}$.

CCDC 894200 (**1**), 894201 (**2**), and 894202 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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