

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

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The development of N-heterocyclic carbene (NHC) chemistry has advanced enormously since the pioneering work of Wanzlick and Schönher, 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 E₂ (E = Si, Ge, P, As)^[5–8] and P₂²⁺.^[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(C₆F₅)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]

Herein, we report the first example of a transition metal complex containing anionic N-heterocyclic dicarbene ligands K[{:C[N(2,6-*i*Pr₂C₆H₃)]₂(CH)C₂Mn(mes)(thf)]·THF (2).

Reaction of 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) with Mn₃(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

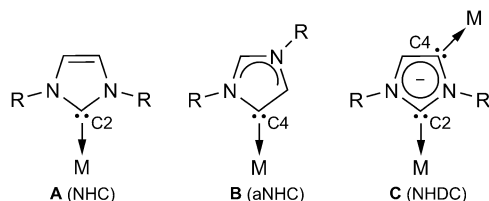


Figure 1. Bonding modes of N-heterocyclic carbenes including the classical coordination mode (A), the abnormal coordination mode (B) and the deprotonated anionic dicarbene (C).

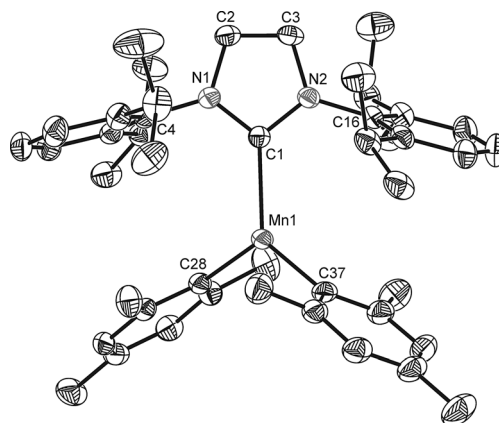


Figure 2. Molecular structure of 1 (anisotropic displacement ellipsoids set at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Mn1–C1 2.195(2), Mn1–C28 2.122(2), Mn1–C37 2.125(2), C1–N1 1.364(2), C1–N2 1.359(2), N1–C2 1.390(2), N2–C3 1.389(2), 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)(CH₂SiMe₃)₂] and [Mn(IPr){CH(SiMe₃)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 [$\chi_{\text{mol}} = N_{\text{A}}\mu_{\text{B}}^2\mu_{\text{eff}}^2/3k(T-\Theta)$] and exhibits an effective magnetic moment of 6.042(6) μ_B, which is comparable to the spin-only value of 5.92 μ_B expected for an *S* = 5/2 system.

The chemical reduction of **1** using KC₈ was found to give rise to the highly air- and moisture-sensitive pseudo-tetrahedral bis(dicarbene) complex K[{:C[N(2,6-*i*Pr₂C₆H₃)₂(CH)C]₂Mn(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*Pr₂C₆H₃)₂(CH)C]₂Mn(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*Pr₂C₆H₃)₂(CH)C]₂ (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

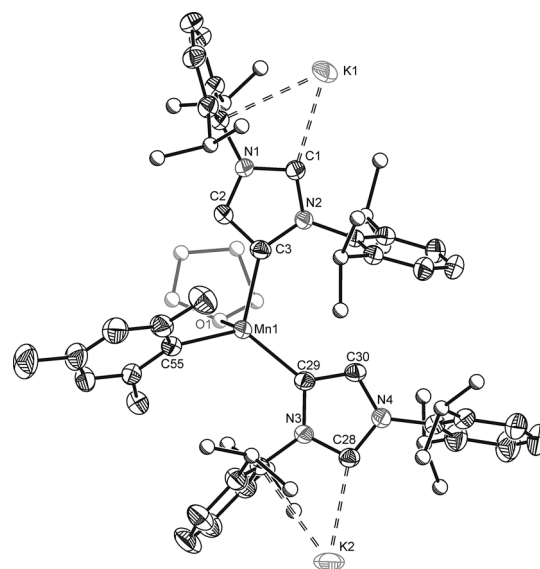


Figure 3. Molecular structure of **2** (anisotropic displacement ellipsoids set at 50% probability). Solvent of crystallization and hydrogen atoms have been omitted for clarity. Atoms of the *i*Pr groups and the THF molecule are pictured as spheres of arbitrary radii. Selected bond distances [Å] and 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).

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.

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) μ_B, is consistent with these findings.

The presence of [{:C[N(2,6-*i*Pr₂C₆H₃)₂(CH)C]₂Mn(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

$i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{CH})\text{C}_2\text{Mn}(\text{mes})^-$ (100%), 1189.1 $[\text{K}(2,2,2\text{-crypt})]\text{-}[\text{C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)](\text{CH})\text{C}_2]$ (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 $[(\text{CH}_3\text{CH}_2)_3\text{Al}\{\text{C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)](\text{CH})\text{C}_2\text{Mn}(\text{mes})+\text{H}\}]^+$ (59%), 1894.7 $[\text{K}(2,2,2\text{-crypt})]_2[(\text{CH}_3\text{CH}_2)_3\text{Al}\{\text{C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)](\text{CH})\text{C}_2\text{Mn}(\text{mes})\}]^+$ (39%), 2008.8 $[\text{K}(2,2,2\text{-crypt})]_2\text{-}[\text{K}(\text{CH}_3\text{CH}_2)_3\text{Al}\{\text{C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)](\text{CH})\text{C}_2\text{Mn}(\text{mes})\}]^+$ (100%). SQUID magnetometry: $\mu_{\text{eff}} = 5.903(6) \mu_{\text{B}}$.

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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