

Synthesis and Characterisation of Low-Coordinate Transition-Metal Complexes Stabilised by Sterically Demanding Carbazolido Ligands

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The synthesis and characterisation of the homoleptic transition-metal complexes $(1,8\text{-Ph}_2\text{-}3,6\text{-Me}_2\text{C}_{12}\text{H}_4\text{N})_2\text{M}$ ($\text{M} = \text{Cr}$, **1**; $\text{M} = \text{Mn}$, **2**; $\text{M} = \text{Fe}$, **3**; $\text{M} = \text{Co}$, **4**) are described. Formally two-coordinate, the solid-state structures of **2** and **3** reveal near-linear N–M–N geometries and significant bending of the flanking phenyl groups towards the metal centres. Solid-state magnetic measurements reveal high spin metal centres

in **1–4**; computational calculations for the model complexes $\text{M}(1,8\text{-Ph}_2\text{C}_{12}\text{H}_6\text{N})_2$ ($\text{M} = \text{Cr–Co}$) confirm the presence of high-spin configurations within these bis-carbazolido compounds and an orbital ordering of $\delta < \pi < \sigma$ for these systems.

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Introduction

The use of sterically demanding amido ligands has allowed the isolation of a number of low-coordinate open-shell transition-metal species. In particular, much attention has been focussed on diphenylamido and disilylamido ligands Ph_2N^- and $(\text{Me}_3\text{Si})_2\text{N}^-$, which have allowed the isolation of transition-metal centres with coordination numbers as low as three.^[1–3] The steric demands of these ligands have been found to be insufficient to stabilise two-coordinate transition-metal centres in the solid state, the homoleptic $\text{M}(\text{NR}_2)_2$ species consisting of dimers formed through amido bridges giving rise to three-coordinate metal atoms.^[2,3] However, cryoscopic measurements on $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ have revealed that this system is monomeric in cyclohexane solution.^[4] Additionally, mass spectrometry and electron-diffraction measurements on $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) have revealed the presence of monomers in the gas phase.^[4,5] Although open-shell transition-metal complexes featuring amido ligands have been well researched, two-coordinate homoleptic examples of these compounds remain comparatively rare.

Power and co-workers have utilised very bulky arylsilylamido $\text{N}(\text{SiMe}_n\text{Ph}_{3-n})_2^-$ ($n = 0, 1, 2$) and arylborylamido

NRBR'_2^- ($\text{R} = \text{Ph}$, $\text{R}' = \text{Mes}$; $\text{R} = \text{R}' = \text{Mes}$ where $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) ligands in the stabilisation and structural authentication of two-coordinate complexes of Cr^{II} through to Ni^{II} .^[6–10] The stabilisation of two-coordinate Fe^{II} amido complexes has also been reported by the groups of Lappert, Lee and Girolami who have used the $\text{N}(\text{SiMe}_3)\text{C}(\text{tBu})\text{CH}(\text{C}_{10}\text{H}_7\text{-}1)^-$, $\text{N}(\text{CH}_2\text{tBu})(\text{C}_6\text{H}_3\text{iPr}_2\text{-}2,6)^-$ and tBu_2N^- ligands, respectively.^[11–13]

Recent investigations into monodentate 3,6-dimethyl-1,8-diphenylcarbazolido and 1,8-dimesityl-3,6-dimethylcarbazolido ligands have revealed frameworks with significant steric demands, and have been used in the stabilisation of highly reactive group 13 centres.^[14,15] Given our interest in fundamental studies of structure, bonding and reactivity of coordinatively and electronically unsaturated transition-metal complexes such as $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{M}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$),^[16] and the similarities which have been drawn between 1,8-diarylcarbazolido and *m*-terphenyl ligands (Figure 1),^[15] we have sought to examine these sterically demanding carbazolido systems in the stabilisation of low-coordinate, open-shell transition-metal complexes. Herein,

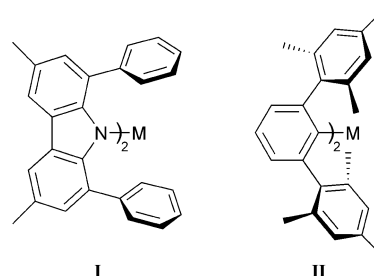


Figure 1. Homoleptic metal(II) 1,8-diphenyl-3,6-dimethylcarbazolido (**I**) and 2,6-dimesitylphenyl (**II**) complexes.

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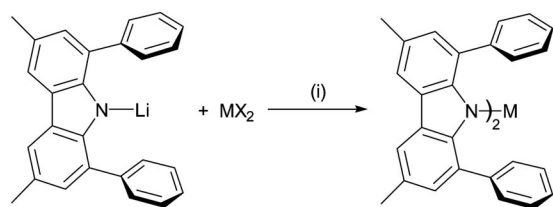
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we describe the synthesis and characterisation of a series of transition-metal amido compounds stabilised by these sterically demanding carbazolido ligands, which have not, as yet, been examined for this purpose.

Results and Discussion

Although monoanionic carbazolido ligands have been exploited in the stabilisation of transition-metal complexes, no homoleptic open-shell systems have been structurally authenticated, for example, the manganese(II) complex $\text{Mn}(\text{C}_{12}\text{H}_8\text{N})_2(\text{THF})_3$ exists as the tris-THF adduct.^[17] In order to stabilise transition metal carbazolido complexes featuring lower coordination numbers than previously characterised, it was therefore thought necessary to provide steric shielding in the 1 and 8 positions of the carbazole framework.

The reaction between two equivalents of (1,8- Ph_2 -3,6- $\text{Me}_2\text{C}_{12}\text{H}_4\text{N}$)Li and CrCl_2 , MnCl_2 , $\text{FeCl}_2(\text{THF})_{1.5}$ or $\text{CoBr}_2(\text{DME})$ ($\text{DME} = 1,2$ -dimethoxyethane) at room temperature in a mixture of toluene and THF gives rise to the homoleptic complexes (1,8- Ph_2 -3,6- $\text{Me}_2\text{C}_{12}\text{H}_4\text{N}$)₂M ($\text{M} = \text{Cr}$, **1**; $\text{M} = \text{Mn}$, **2**; $\text{M} = \text{Fe}$, **3**; $\text{M} = \text{Co}$, **4**) in good yields, according to Scheme 1. Compounds **1–4** are highly air sensitive, but can be stored at room temperature under argon for an indefinite period. These compounds are thermally stable, crystals of **1–4** turning black in the temperature range 90–145 °C. Complexes **1–4** have been unambiguously identified by spectroscopic techniques and, in the case of **2** and **3**, by the results of single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of 3,6-dimethyl-1,8-diphenyl-3,6-carbazolido complexes (1,8- Ph_2 -3,6- $\text{Me}_2\text{C}_{12}\text{H}_4\text{N}$)₂M ($\text{M} = \text{Cr}$, **1**; Mn , **2**; Fe , **3**; Co , **4**). Reaction conditions: (i) toluene/THF, 16 h, $-78^\circ\text{C} \rightarrow$ room temp., -2LiX .

Single crystals of suitable quality for X-ray diffraction were obtained by slow diffusion of hexane into a saturated toluene solution of the complex, giving rise to yellow and orange crystals of **2** and **3**, respectively. The crystal structure of **2** can be seen in Figure 2. The single-crystal X-ray diffraction measurements on **2** and **3** reveal monomeric complexes where the metal centres are free from coordinating solvent; which contrasts with that found for complexes containing diphenylamido and disilylamido ligands, which exist as amide-bridged and/or donor-containing systems in the solid state^[2,3,18] and also the Mn^{II} complex featuring the parent carbazolido ligand, $\text{Mn}(\text{C}_{12}\text{H}_8\text{N})_2(\text{THF})_3$.^[17] The monomeric, donor-free formulations for **2** and **3** in the

solid state are presumably a consequence of the high steric shielding afforded by the flanking phenyl rings in the 1 and 8 positions on the carbazolido ligands in these systems.

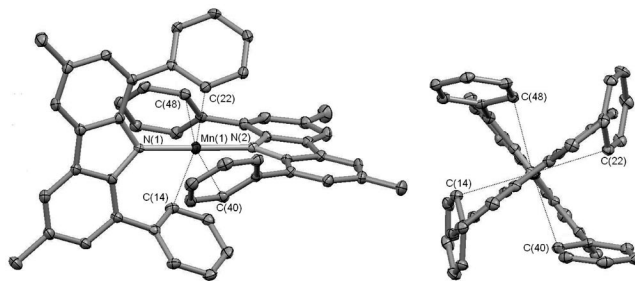


Figure 2. Molecular structure of (1,8- Ph_2 -3,6- $\text{Me}_2\text{C}_{12}\text{H}_4\text{N}$)₂Mn (**2**) viewed from the side (left) and along the N–Mn–N bond (right), with thermal ellipsoids set at the 40% probability level. Hydrogen atoms (both pictures) and 3,6-methyl groups (right hand picture) omitted for clarity.

Relevant bond lengths and angles for **2** and **3** can be found in Table 1. As would be expected on the basis of the decrease in ionic radius on going from Mn^{2+} to Fe^{2+} ,^[19] **2** has longer M–N distances than those found in **3** [for **2** Mn–N 2.0405(15) and 2.0442(14) Å; for **3** Fe–N 1.9715(18) and 1.9758(18) Å]. The average M–N distances for **2** [2.0424(15) Å] and **3** [1.9737(18) Å] are comparable to those found in the arylborylamido complexes $\text{Mn}[\text{NMesBMe}_2]_2$ [ave. Mn–N 2.046(4) Å] and $\text{Fe}[\text{NMesBMe}_2]_2$ [ave. Fe–N 1.938(2) Å],^[8,10] systems that are thought to consist predominantly of a σ bonding interaction between the amido ligands and the metal centres.

Of interest are the N–M–N angles for **2** [178.58(6)°] and **3** [177.92(9)°], which are only slightly deviated from linearity compared to the gas-phase structures of the amido complexes $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ (which have N–M–N angles of 180° for $\text{M} = \text{Mn}$, Fe)^[5] and that of $(t\text{Bu}_2\text{N})_2\text{Fe}$ [N–Fe–N 179.45(8)°].^[13] Indeed, the majority of metal amido complexes have N–M–N angles significantly deviated from linearity, viz. Mn amido [which fall in the range 79.9(3)° for $\text{Mn}\{\text{N}(\text{Dipp})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Dipp}\}_2$ ($\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) to 170.7(1)° for $\text{Mn}\{\text{N}(\text{SiMePh}_2)_2\}_2$] and Fe amido complexes [which fall in the range 153.6(1)° for $\text{Fe}\{\text{N}(\text{SiMe}_3)\text{-C}(t\text{Bu})\text{CH}(\text{C}_{10}\text{H}_7\text{-1})\}_2$ to 172.1(1)° for $\text{Fe}\{\text{N}(\text{SiMe}_2\text{-Ph})\}_2$].^[6–8,10–12,20]

The two metal-substituted carbazolido moieties are near perpendicular to each other (torsion angles between the two carbazole planes are 87.92° and 87.76° for **2** and **3**, respectively). This differs significantly from that in $(t\text{Bu}_2\text{N})_2\text{Fe}$ [80.5(1)°], and is presumably in part due to the differing steric requirements of the 1,8- Ph_2 -3,6- $\text{Me}_2\text{C}_{12}\text{H}_4\text{N}$ and $t\text{Bu}_2\text{N}$ ligand frameworks.

Of particular interest are the angles formed between the carbazolido planes and the phenyl moieties in **2** and **3**; they are neither parallel nor perpendicular to their parent carbazoles, but are instead skewed such that one of the *ortho*-CH groups of each lies in close proximity to the metal atom (see, for example Figure 2). The interplanar angles between the best planes of the phenyl rings and the parent carbazole

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **3**.

	(1,8-Ph ₂ -3,6-Me ₂ C ₁₂ H ₄ N) ₂ Mn (2)	(1,8-Ph ₂ -3,6-Me ₂ C ₁₂ H ₄ N) ₂ Fe (3)
M–N	2.0442(15) (Mn1–N1) 2.0405(15) (Mn1–N2)	1.9715(18) (Fe1–N1) 1.9758(18) (Fe1–N2)
N–M–N	178.58(6)	177.92(9)
Carbz–carbz dihedral angle ^[a]	87.92	87.76
M···C (<i>ortho</i> -C of phenyl)	2.7054(19) (Mn1···C14) 2.7036(19) (Mn1···C22) 2.6825(19) (Mn1···C40) 2.6906(19) (Mn1···C48)	2.7135(26) (Fe1···C4) 2.6661(22) (Fe1···C7) 2.6811(26) (Fe1···C10) 2.6966(21) (Fe1···C32)
M···H (<i>ortho</i> -CH of phenyl)	2.6224(3) (Mn1···H141) 2.5270(3) (Mn1···H221) 2.5216(3) (Mn1···H401) 2.6230(3) (Mn1···H481)	2.4846(4) (Fe1···H41) 2.4733(4) (Fe1···H71) 2.5996(4) (Fe1···H101) 2.5816(4) (Fe1···H321)
M···H–C angles (<i>ortho</i> -CH of phenyl)	85.08(11) (Mn1···H141–C14) 90.44(11) (Mn1···H221–C22) 88.95(11) (Mn1···H401–C40) 83.41(11) (Mn1···H481–C48)	93.84(16) (Fe1···H41–C4) 91.64(12) (Fe1···H71–C7) 84.54(15) (Fe1···H101–C10) 86.70(12) (Fe1···H321–C32)
Angle (Carbz plane–phenyl plane)	49.18, 49.40, 50.56, 56.11	48.84, 48.99, 50.57, 56.04

[a] Defined as the angle between the best mean planes of the two metal-substituted carbazole rings.

are between 49.18 and 56.11° and 48.84 and 56.04° for **2** and **3**, respectively. There are close contacts between the metal centres and the *ortho*-carbon atoms on the phenyl rings [falling in the range 2.6825(19)–2.7054(19) Å for **2** and 2.6661(22)–2.7135(26) Å for **3**] which are significantly (ca. 1 Å) less than the sum of the Van der Waals radii.^[21] The M···HC contacts for **2** and **3** are 2.5216(3)–2.6230(3) Å and 2.4733(4)–2.5996(4) Å, respectively; the corresponding M···H–C bond angles are small [83.41(11)–90.44(11)° for **2** and 84.54(15)–91.64(12)° for **3**]. Although the short M···HC contacts for **2** and **3** are longer than generally recognised for an agostic interaction (ca. 1.8–2.3 Å)^[22] the presence of a very weak intramolecular interaction cannot be ruled out. However, examination of the space-filling models for the structures of **2** and **3** (see for example, Figure 3) suggests that these close contacts may also be necessary in order to avoid unacceptably short contacts between phenyl rings.

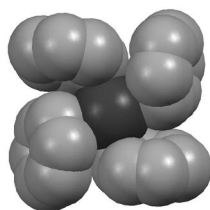


Figure 3. Space-filling model highlighting the orientation of the phenyl groups (light grey) around the central iron atom (dark grey) in **3**. Hydrogen atoms and carbazolido moieties omitted for clarity.

The UV/Vis spectra of **1–4** are dominated by a very intense absorption between 200 and 400 nm due to π – π^* transitions involving the 3,6-dimethyl-1,8-diphenylcarbazolido ligand. At wavelengths longer than 400 nm there are less intense absorptions due to metal d–d transitions for these systems.

Due to the paramagnetic nature of **1–4** the resulting ¹H NMR spectra were paramagnetically shifted, but were found to be broad and uninformative. Solid state magnetic moments for **1–4** were measured using a SQUID magne-

tometer in the temperature range 5–300 K; these compounds are paramagnetic and were found to obey the Curie–Weiss law in the temperature range 50–300 K. The magnetic moments of **1–4** are 4.78, 5.81, 4.73 and 4.00 μ_B , this, together with the near-linear N–M–N configurations for these systems give rise to high spin d⁴, d⁵, d⁶ and d⁷ metal centres, respectively. These magnetic data are supported by the results of DFT calculations on model transition metal bis-carbazolido complexes.

In order to model the electronic structure of paramagnetic compounds **1–4** and to estimate the relative energies of possible spin states, density functional calculations were carried out on the model complexes M(1,8-Ph₂C₁₂H₆N)₂, where the methyl groups on the ligand were substituted by H atoms. It was considered necessary to retain the phenyl groups due to their close proximity to the metal, all molecules had their geometry optimised with C₂ symmetry resulting in a final structure with S₄ symmetry. The variation in the optimised M–N bond lengths is given in Table 2. Generally, there is good agreement between the measured values for the M–N distances in **2** and **3** and that calculated for high spin complexes of Mn(1,8-Ph₂C₁₂H₆N)₂ (2.04 Å) and Fe(1,8-Ph₂C₁₂H₆N)₂ (1.98 Å). The closest approach of a phenyl hydrogen to the central metal fell in the range 2.29–2.54 Å. The relative energies of the various spin states are also shown in Table 2. All compounds were predicted to be high-spin, and are, as such in agreement with the experimental magnetic data.

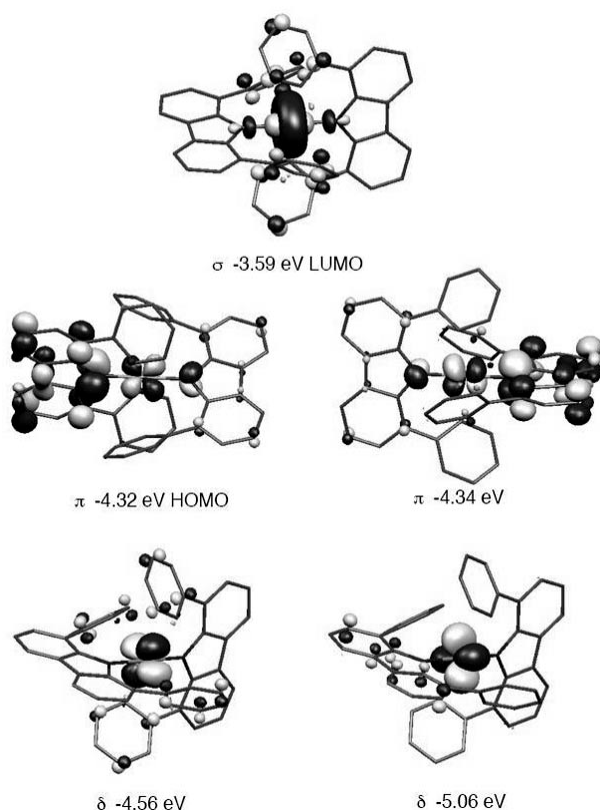
Selected orbitals for Cr(1,8-Ph₂C₁₂H₆N)₂ are shown in Figure 4. The ordering is $\delta < \pi < \sigma$, where the orbitals are classified according to their symmetry around the metal ligand axes. The σ LUMO is predominantly a s–d(z²) hybrid. The corresponding s+d(z²) hybrid forms a bond with the two σ lone pairs on the carbazole N atoms. However, the hybridisation produces effectively a non-bonding orbital that lies within 0.73 eV of the HOMO. The π orbitals, which are effectively degenerate as a consequence of the S₄ molecular symmetry, mix significantly with the ligand orbitals and have an anti-bonding interaction with the carbazole N

Table 2. Relative energies of the various spin states for $M(1,8\text{-Ph}_2\text{C}_{12}\text{H}_6\text{N})_2$ ($M = \text{Cr-Co}$).

Metal	S	Configuration	$d(\text{M-N})$ [Å]	Rel. energy [eV]
Cr	2	$\delta^2\pi^2$	2.07	0
	1		2.06	1.09
Mn	5/2	$\delta^2\pi^2\sigma^1$	2.04	0
	3/2		1.99	1.33
Fe	2	$\delta^3\pi^2\sigma^1$	1.98	0
	1		1.95	0.93
Co ^[a]	3/2	$\delta^3\pi^3\sigma^1$	1.97	0

[a] Calculation for $M = \text{Co}$ with $S = 1/2$ failed to converge.

π electrons. The δ orbitals are more metal-localised and non-degenerate, with the higher of the two having a repulsive interaction with the phenyl rings. The π and δ orbitals span an energy range of 0.73 eV.

Figure 4. Energy-level ordering of selected orbitals for $\text{Cr}(1,8\text{-Ph}_2\text{C}_{12}\text{H}_6\text{N})_2$.

In $\text{Mn}(1,8\text{-Ph}_2\text{C}_{12}\text{H}_6\text{N})_2$ with $S = 5/2$ the σ orbital is singly occupied. The $s/d(z^2)$ hybridisation discussed above keeps its energy sufficiently low for favourable exchange effects to be the determining factor in the selection of spin state. Single occupancy of the σ orbital is also found for lowest energy states of the Fe and Co compounds leading to prediction of high-spin configurations for these metal bis-carbazolido complexes.

In order to test whether any energetic benefit was derived from direct interaction of the phenyl substituents with the metal, the structure of $[\text{Mn}(1,8\text{-H}_2\text{C}_{12}\text{H}_6\text{N})_2]_2$ where H replaced the phenyl substituents was investigated. The ener-

gies of the carbazolido and diphenylcarbazolido ligands were also calculated and the metal ligand binding energies of the two complexes compared. The two binding energies differed by only 2 kJ mol^{-1} , that is they were identical to within computational error supporting the hypothesis that the orientation of the phenyl groups are a result of packing forces.

Conclusions

Sterically demanding 1,8-diphenyl-3,6-carbazolido ligands have been used to stabilise low-coordinate, open-shell M^{II} amido complexes. The solid-state structures of **2** and **3** reveal a high degree of steric congestion for the 1,8-diphenyl-3,6-carbazolido systems. The magnetic moments for **1–4** indicate high spin metal centres, and are generally in agreement with the calculated values for these complexes.

Experimental Section

General: All manipulations were carried out under nitrogen or argon using standard Schlenk line or glove box techniques. Hexane, THF and toluene were pre-dried with Na wire prior to passing through a column of alumina (hexane) or distillation from sodium-benzophenone ketyl (THF) or sodium (toluene). $[\text{D}_6]\text{Benzene}$ (Goss) was dried with potassium and degassed with three freeze-pump-thaw cycles prior to use. CrCl_2 and MnCl_2 (Strem) were used as received. $(1,8\text{-Ph}_2\text{-3,6-Me}_2\text{C}_{12}\text{H}_4\text{N})\text{Li}$, $\text{FeCl}_2(\text{THF})_{1.5}$ and $\text{CoBr}_2(\text{DME})$ were prepared by minor modification of literature methods.^[14,23,24] NMR spectra for complexes **1–4** are not reported as they were found to be broad and uninformative. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, and by the departmental service at the University of Oxford. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Elemental analyses were performed by Stephen Boyer, London Metropolitan University.

Crystallographic Method

Crystalline samples of **2** and **3** were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit. Data for the compounds **2** and **3** were collected with an Enraf Nonius Kappa CCD diffractometer equipped with a $\text{Mo-K}\alpha$ radiation source ($\lambda = 0.71073 \text{ Å}$). Intensity data were processed using the DENZO-SMN package; the structure was solved using the direct-methods program SIR92, which located all non-hydrogen atoms and subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.^[25] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Similarity restraints were applied to the thermal parameters of directly-bonded pairs of N and C atoms. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebyshev polynomial weighting Scheme was applied. Crystal data and refinement parameters for **2** and **3** are given below.

CCDC-698934 (for **2**) and -698935 (for **3**) contain the supplementary data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for Compound 2: $C_{52}H_{40}MnN_2$, $M_r = 747.83$, $T = 150$ K, $\lambda = 0.71073$ Å, yellow plate, $0.05 \times 0.22 \times 0.22$ mm, monoclinic, space group $P2_1/c$, $a = 18.3004(2)$ Å, $b = 9.7885(2)$ Å, $c = 21.0179(2)$ Å, $\beta = 92.2670(5)^\circ$, $U = 3762.06(9)$ Å³, $Z = 4$, $D_c = 1.320$ Mg m⁻³, $\mu = 0.392$ mm⁻¹; 50271 reflections measured, 8548 unique ($R_{int} = 0.059$), final $Goof = 0.9637$, no. of observed reflections 5619 [$I > 2\sigma(I)$]; $R_1 = 0.0442$, $wR_2 = 0.1141$ for observed unique reflections [$F^2 > 2\sigma(F_2)$]. Min. and max. residual electron densities: 0.62 and -0.71 e Å⁻³.

Crystal Data for Compound 3: $C_{52}H_{40}N_2Fe$, $M_r = 748.75$, $T = 150$ K, $\lambda = 0.71073$ Å, orange plate, $0.05 \times 0.30 \times 0.30$ mm, monoclinic, space group $P2_1/c$, $a = 18.3306(4)$ Å, $b = 9.7911(2)$ Å, $c = 20.9988(4)$ Å, $\beta = 91.9890(13)^\circ$, $U = 3766.53(13)$ Å³, $Z = 4$, $D_c = 1.320$ Mg m⁻³, $\mu = 0.441$ mm⁻¹; 40380 reflections measured, 8480 unique ($R_{int} = 0.053$), final $Goof = 0.9168$, no. of observed reflections 4692 [$I > 2\sigma(I)$]; $R_1 = 0.0460$, $wR_2 = 0.1085$ for observed unique reflections [$F^2 > 2\sigma(F_2)$]. Min. and max. residual electron densities: 0.58 and -0.58 e Å⁻³.

Syntheses

Synthesis of (1,8-Ph₂-3,6-Me₂C₁₂H₄N)₂M (M = Cr, 1; Mn, 2; Fe, 3; Co, 4): Typically, to a suspension of MnCl₂ (0.071 g, 0.6 mmol) in toluene (30 mL) at -78°C was added dropwise a solution of (1,8-Ph₂-3,6-Me₂C₁₂H₄N)Li (0.399 g, 1.1 mmol) in a mixture of toluene (25 mL) and THF (5 mL). The reaction mixture was warmed to room temperature and stirred overnight, resulting in a yellow solution. Removal of volatiles in vacuo yielded a yellow solid which was washed with cold hexane (2×20 mL). Extraction into hexane (80 mL) yielded **2** as a yellow microcrystalline solid. Isolated yield: 0.304 g (73%). Crystals of **2** and **3** suitable for X-ray diffraction were obtained from a solution in toluene layered with hexane.

Characterising Data for 1: M.p. 255–260 °C (from hexane; darkens between 95–150 °C). $\mu_{eff} = 4.78$ μ_B. UV/Vis (hexane): strong absorption between 200 and 400 nm with shoulders at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) = 213 (36458), 237 (42262), 304 (15476), 327 (9881), 355 (7143), 391 (4071) nm, peak at 479 (498) nm. EI-MS: $m/z = 744$ (12) [M^+], 692 (12) [$M - Cr$]⁺, 398 (3) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)Cr]⁺, (100) 347 [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)⁺]; exact mass: calcd. 744.2591, found 744.2586. $C_{52}H_{40}CrN_2$ (744.26): calcd. C 83.85, H 5.41, N 3.76; found C 83.76, H 5.48, N 3.81. IR (KBr disk): $\tilde{\nu} = 2964$ (md), 2920 (md), 2855 (md), 1652 (wk), 1405 (wk), 1261 (st), 1209 (md), 1097 (br. st), 1043 (st), 920 (wk), 848 (wk), 803 (st), 774 (md), 668 (md) cm⁻¹.

Characterising Data for 2: M.p. 148–154 °C (from hexane; darkens between 130–145 °C). $\mu_{eff} = 5.81$ μ_B. UV/Vis (hexane): strong absorption between 200 and 400 nm with shoulders at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) = 205 (33898), 234 (49934), 304 (36175), 322 (25115), 360 (17281), 391 (10599) nm. EI-MS: m/z (%) = 747 (20) [M^+], 401 (75) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)Mn]⁺, 347 (100) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)⁺]; exact mass: calcd. 747.2567, found 747.2560. $C_{52}H_{40}MnN_2$ (747.26): calcd. C 83.52, H 5.39, N 3.75; found C 83.64, H 5.49, N 3.71. IR (KBr disk): $\tilde{\nu} = 3058$ (wk), 3032 (wk), 2962 (md), 2924 (md), 2862 (md), 1602 (md), 1490 (st), 1444 (st), 1404 (st), 1348 (wk), 1259 (md), 1239 (st), 1208 (st), 1164 (wk), 1100 (wk), 1074 (wk), 1029 (md), 855 (st), 802 (md), 773 (st), 752 (wk), 717 (wk), 703 (md), 580 (md) cm⁻¹.

Characterising Data for 3: M.p. 160 °C (from hexane; darkens between 100–120 °C). $\mu_{eff} = 4.73$ μ_B. UV/Vis (hexane): strong absorption between 200 and 400 nm with shoulders at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) = 208 (34719), 235 (49044), 307 (31090), 318 (27723), 367 (13019), 382 (12907) nm, peak at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) 499 (6454) with shoulder at 477 (5892) nm. EI-

MS: m/z (%) = 748 (10) [M^+], 402 (20) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)Fe]⁺, 347 (100) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)⁺]; exact mass: calcd. 748.2535, found 748.2539. $C_{52}H_{40}FeN_2$ (748.25): calcd. C 83.42, H 5.38, N 3.74; found C 83.57, H 5.40, N 3.71. IR (KBr disk): $\tilde{\nu} = 3058$ (wk), 3029 (wk), 2949 (wk), 2918 (md), 2848 (wk), 1596 (md), 1489 (st), 1444 (st), 1401 (st), 1343 (wk), 1285 (wk), 1253 (md), 1236 (st), 1206 (st), 1158 (md), 1101 (br. wk), 1072 (wk), 1029 (wk), 918 (wk), 891 (md), 772 (st), 751 (md), 717 (md), 704 (st), 674 (wk), 652 (md), 601 (st), 551 (wk) cm⁻¹.

Characterising Data for 4: M.p. 205 °C (from hexane; darkens between 90–110 °C). $\mu_{eff} = 4.00$ μ_B. UV/Vis (hexane): strong absorption between 200 and 400 nm with shoulders at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) = 230 (81188), 297 (32500), 317 (24125) 335 (17937), 381 (11688) nm, peaks at λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$) 492 (2407), 598 (4002), 701 (7763) nm. EI-MS: m/z (%) = 751 (5) [M^+], 405 (20) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)Co]⁺, 347 (100) [(1,8-Ph₂-3,6-Me₂C₁₂H₄N)⁺]; exact mass: calcd. 751.2518, found 751.2518. $C_{52}H_{40}CoN_2$ (751.51): calcd. C 83.07, H 5.36, N 3.73; found C 82.97, H 5.33, N 3.66. IR (KBr disk): $\tilde{\nu} = 3072$ (wk), 3029 (wk), 2964 (wk), 2919 (md), 2848 (wk), 1597 (md), 1490 (md), 1443 (md), 1399 (md), 1322 (wk), 1261 (md), 1237 (st), 1204 (st), 1150 (wk), 1109 (md), 1094 (md), 1058 (md), 1029 (md), 917 (wk), 882 (md), 853 (st), 802 (md), 772 (st), 750 (md), 705 (md), 668 (md), 643 (wk), 578 (md), 507 (md) cm⁻¹.

Calculations: Density functional calculations were carried out using the Amsterdam Density Functional program suite ADF 2007.01.^[26] The generalised gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair together with the nonlocal exchange correction by Becke and non-local correlation corrections by Perdew. TZP basis sets were used with triple- ζ accuracy sets of Slater type orbitals and two polarisation functions added. The cores of the atoms were frozen up to 1s for C and O and 2p for the metal atoms.

Supporting Information (see also the footnote on the first page of this article): Full experimental data for complexes **1–4** and crystallographic data for **2** and **3**.

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