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Complexes of 3d Metals with a Bulky Carbazoyl Ligand

Michelle Kaiser,^[a] Lucas Winkler,^[a] and Alexander Hinz^{*[a]}Dedicated to Prof. Cameron Jones on the occasion of his 60th birthday.

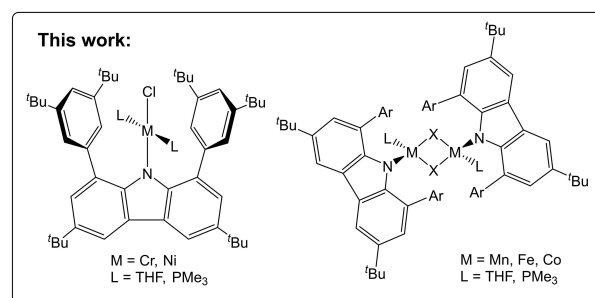
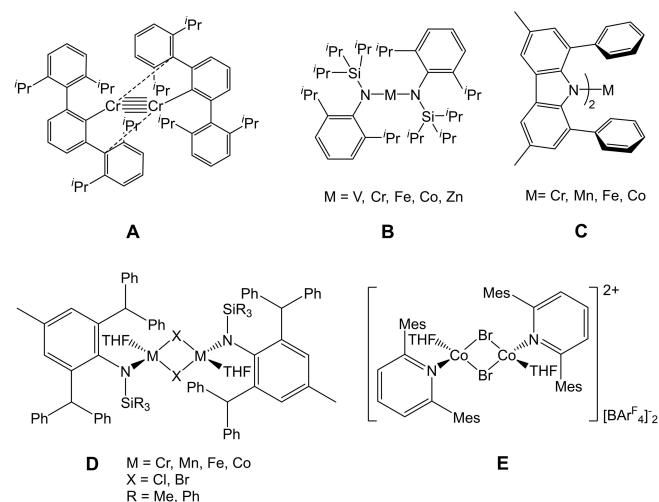
In this contribution, the synthesis and properties of nine novel 3d metal complexes are reported. As supporting ligand scaffold, the bulky 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazole (R) was employed. After deprotonation and salt metathesis reactions, a series of four complexes, the dimeric [RMn(THF)(μ-Cl)]₂ (**1a**), [RFe(THF)(μ-Cl)]₂ (**2a**), and [RCo(THF)(μ-Cl)]₂ (**3a**) as well as a monomeric [RCr(THF)₂(Cl)] (**4a**), were obtained, while the analogous Ni(II) complex remained elusive. However,

incorporation of PMe₃ as stronger donor molecule in comparison sufficed to stabilise also the Ni(II) complex [RNi(PMe₃)₂(Cl)] (**5b**). The series was completed by treatment of **1a–4a** with PMe₃, which afforded the related phosphine complexes **1b–4b**. All complexes were characterised in the solid state by single crystal structure elucidation and their magnetic moments in solution were determined by NMR experiments with the Evans method.

Introduction

Sterically demanding ligands were employed already quite early in transition metal chemistry, as it had become apparent that the coordination number of any metal atom is not only dependent on the preferences of the metal atoms but even more so on the properties of the employed ligand systems. Secondary interactions may help stabilise unusual structural motifs, and ligands may also participate electronically, thus becoming less “innocent”.^[1] Early work on transition metal complexes with the bulky amido ligand bis(trimethylsilyl)amide N(SiMe₃)₂ was conducted by Bürger and Wannagat.^[2] In 1963 they presented the three-coordinated iron complex Fe[N(SiMe₃)₂]₃, which was later confirmed by single-crystal XRD as monomeric complex with coordination number 3.^[3a] The ligand continuously is investigated, and recent discoveries for instance by Werncke and coworkers highlight their undiminished potential.^[3b,c,d] In 1985 Eaborn, Smith, and co-workers reported the first two-coordinated manganese complex Mn[C(SiMe₃)₃]₂ who was also structurally characterised.^[4] In the following years, the number of these “low-coordinate” complexes continuously expanded as more varied ligand systems were employed. Nowadays, in this context the term low-coordinate describes a complex with a coordination number of three or less.^[5] The group of Power pioneered this research area and employed for

instance silylamido or borylamido ligands such as N(SiMePh₂)₂ and N(Mes)BMe₂^[6] before the rise of terphenyl ligands, culminating in the synthesis of Ar'CrCrAr' (Ar' = C₆H₃-2,6(C₆H₃-2,6-*i*-Pr₂)₂), a compound with a quintuple bond between two Cr(I) centers in 2005 (Scheme 1, A).^[7] In a subsequent investigation with an even bulkier terphenyl, Wolf and Power



Scheme 1. Selected examples for 3d transition metal complexes featuring bulky monodentate monoanionic ligands (Ar = 3,5-ditertbutylphenyl).

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obtained monomeric chromium(I) complexes instead of the quintuply bonded dimers.^[8]

Recent works by Power and Tilley are more focused on the use of silylamido ligands and their dispersion interaction as a stabilising driving force for homoleptic two-coordinate transition metal complexes (**B**).^[9] Some of these examples show reactivity in various subsequent reactions, like the formation of methyl-bridged dimeric complexes, homoleptic metal(I) anions, various hydride complexes and polymers.^[10] Furthermore, the Tilley group reported on low-coordinate Ni[N(SiMe₃)(C₆H₃-2,6-ⁱPr₂)]₂ complexes with Ni in oxidation states from 1 to 3,^[12] which catalyse Kumada cross-coupling reactions.^[13]

Related homoleptic complexes with a carbazole-based ligand were presented by Kays who reported on a series of open shell transition metal complexes (1,8-Ph₂-3,6-Me₂C₁₂H₄N)₂M (**C**, M=Cr, Mn, Fe, Co).^[11]

However, in the formation of homoleptic compounds by salt metathesis, complexes "RMX" are frequent intermediates, which can dimerise by formation of halide bridges. These can be versatile starting materials in their own right.^[14] A landmark example of the reduction of such complexes was reported by Jones, who generated "inorganic Grignard reagents" by reduction with dimeric Mg(I) compounds, which allowed the formation of unsupported M–Mg bonds.^[15] Further examples for "RMX"-type complexes were also provided by Jones who reported a series of first row transition metal(II) halide complexes with extremely bulky silylamido ligands L' and L'' (L'/L''=N(Ar*)₂(SiR₃), Ar*=C₆H₂{C(H)Ph₂}₂Me-2,6,4; R=Me (L') or Ph (L'')).^[14d] In this series eight dimers of the elements Cr, Mn, Fe and Co and two monomeric Zn compounds were presented (**D**). The Aldridge group employed pyridine donor ligands to obtain the dication [(2,6-Mes₂py)Co(THF)(μ-Br)₂]²⁺ as a bis[BAR₄^F]⁻ salt (**E**).^[14c]

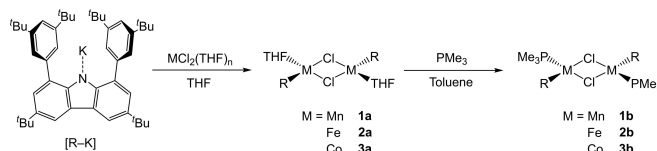
As we have recently endeavoured the generation of dicoordinate heteroleptic Cu complexes by using the bulky carbazolyl ligand 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazole (**R**),^[17] we subsequently aimed for an extension of this chemistry to other 3d metals.^[16] In this contribution we show the synthesis and characterisation of the dimeric "RMX"-type complexes of the 3d transition metals Mn, Fe, Co and the monomeric Cr and Ni complexes with **R** as sterically demanding ligand system.

Results and Discussion

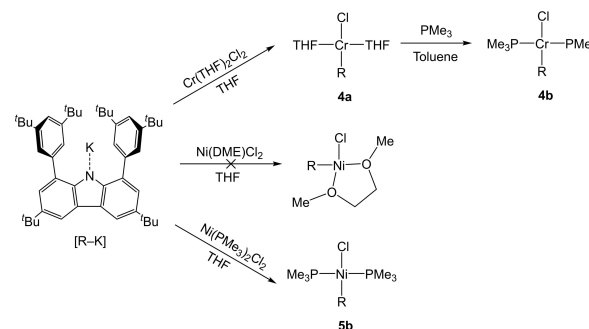
As established in prior investigations, the most facile route towards such carbazolyl compounds is a metathesis approach. Deprotonation of the 9H-carbazole with benzyl potassium cleanly afforded the corresponding potassium carbazolate. This was then used as starting material for the reactions with divalent transition metal halides. However, the insolubility of these salts in common non-polar solvents precludes the reactions in benzene or toluene. Even when coordinating solvents such as THF are present, the reactions with MCl₂ (M=Cr, Mn, Fe, Co) proceed only sluggishly. More suitable starting materials are complexes of the type [M(THF)_nCl₂].^[18] The thus

obtained THF-solvated transition metal dihalide complexes are better suited for the metathesis reactions with the potassium carbazolate [R–K], but the presence of coordinated THF-molecules can not be avoided. Three different reactivity patterns were observed: In the reaction of [R–K] with [M(THF)_nCl₂] (M=Mn, Fe, Co), the metathesis proceeded smoothly. After filtration and crystallisation of the products, dimeric complexes of the general formula [RM(THF)(μ-Cl)]₂ were obtained in good yield as pale yellow (M=Mn, **1a**), yellow (M=Fe, **2a**) or brown (M=Co, **3a**) substances (Scheme 2). Despite similar behaviour in the reaction, the metathesis of [R–K] with [Cr(THF)₂Cl₂] afforded the monomeric complex [RCr(THF)₂(Cl)] (**4a**) as yellowish green crystalline material (Scheme 3). In contrast to these observations, an analogous Ni(II) complex could not be isolated. The nickel(II) chloride ethylene glycol dimethyl ether (DME) complex was chosen as a suitable starting material. A salt metathesis reaction with [R–K] appeared to provide the desired product, however, the resulting crude solid was found to be insoluble in toluene, hexane, and fluorobenzene and decomposed rapidly so that no nickel-containing product could be obtained.

As a working hypothesis, the requirement for stronger donors such as phosphines for the stabilisation of the Ni(II) complex was considered. Accordingly using the bis(phosphine) Ni(PMe₃)₂Cl₂ precursor enabled isolation of the monomeric complex [RNi(PMe₃)₂(Cl)] (**5b**) as a dark green crystalline material (Scheme 3). For the four other 3d metals Mn, Fe, Co and Cr, the THF-containing complexes **1a–4a** could be converted into the phosphine-containing derivatives by straightforward addition of PMe₃, affording the corresponding products **1b–4b**. The change from THF to PMe₃ as donor on the metal centre caused a relatively small change in colour: The Mn(II) complex [RMn(PMe₃)(μ-Cl)]₂ **1b** appears as pale yellow compound, the Fe(II) complex [RFe(PMe₃)(μ-Cl)]₂ **2b** appears



Scheme 2. Synthesis of the dimeric complexes **1a–3a** and **1b–3b**.



Scheme 3. Synthesis of the monomeric complexes **4a**, **4b** and **5b**.

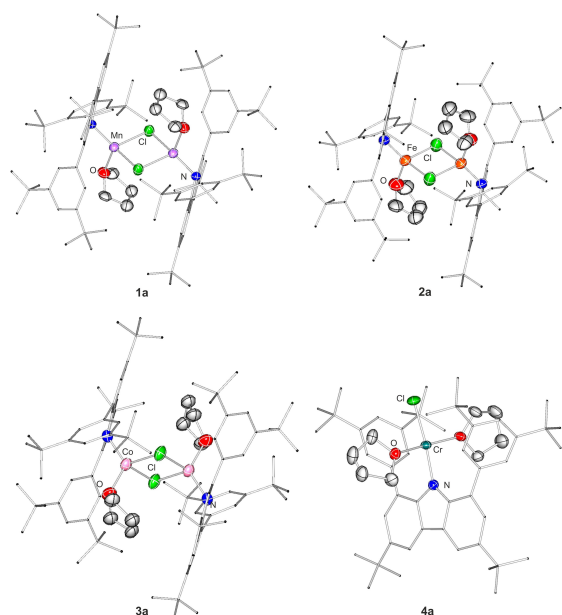


Figure 1. Molecular structures of the carbazole based transition metal complexes **1 a–4 a**. Thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

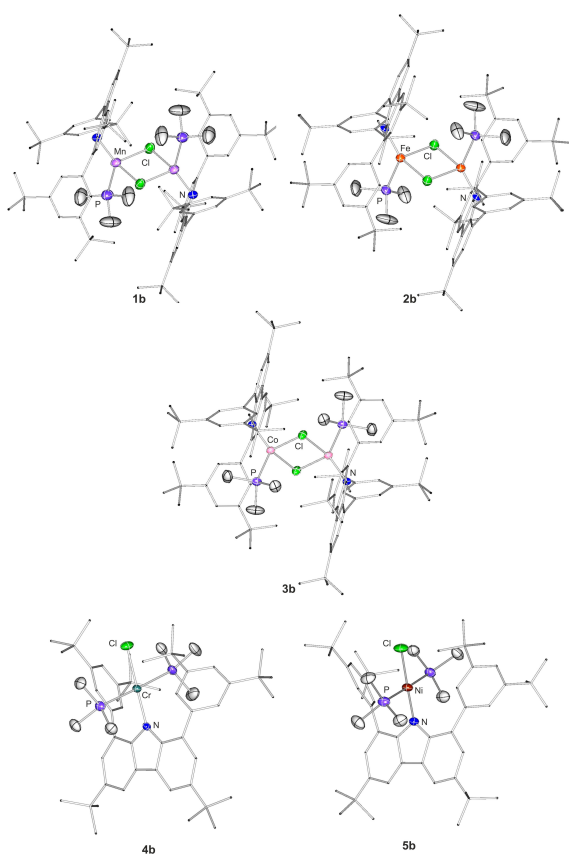


Figure 2. Molecular structures of the carbazole based transition metal complexes **1 b–5 b**. Thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

orange, the Co(II) complex $[\text{RCo}(\text{PMe}_3)(\mu\text{-Cl})_2]$ **3 b** is purple and the monomeric Cr(II) complex $[\text{RCr}(\text{PMe}_3)_2(\text{Cl})]_2$ **4 b** turned yellow.

Crystallographic Characterisation

For all novel complexes, single-crystal XRD allowed the determination of their molecular structures, which are shown in Figure 1 and Figure 2. Selected distances and angles are presented in Table 1.

In complexes **1 a–3 a** and **1 b–3 b**, the metal atoms are in a distorted tetrahedral coordination environment, the N–M–Cl angles deviate up to 10° from the ideal tetrahedral angle. The dimeric $\text{M}_2(\mu\text{-Cl})_2$ core is nearly perfectly square-shaped and located on crystallographic centre of inversion. The M–Cl–M' and the Cl–M–Cl' angles each approach 90° . The carbazole scaffolds are located coplanarly to each other, but their arene groups are in an angled arrangement with twisted dihedral angles from 76° to almost 90° . The THF or PMe_3 molecules are bent sharply to enable the fit into the pocket provided by both carbazolyl moieties. The metal atoms in the dimeric complexes deviate significantly from the carbazole plane by between $1.408(2)$ Å (**3 a**) and $1.581(1)$ Å (**1 b**). This results in decreasing effective steric bulk of that carbazole moiety, as the metal atoms are shifted away from the central region between the flanking arenes. Related carbazolyl-based alkali metal complexes by Aldridge and Kays show similar deviations of the metal ion from the carbazole backbone, but in these cases additional η^5 -coordination of the metal ions with another carbazolyl ligand was observed.^[19]

In the series of **1 a**, **2 a**, **3 a** and **1 b**, **2 b**, **3 b** the M–N and the M–Cl bond lengths decrease with increasing molecular weight of the used metal. Comparing the THF and the PMe_3 complexes there is no strict order according to which the bond lengths or angles decrease or increase.

These complexes are structurally resemblant of the work of Jones mentioned in the beginning, in which a dimeric species of the type $[\{\text{L}'/\text{L}''\text{M}(\text{THF})(\mu\text{-X})_2\}_2]$ were generated using MnBr_2 , FeBr_2 and CoCl_2 . The M–N bond lengths of **1 a–4 a** and **1 b–4 b** compare well to the literature known ones.^[14d] In two of the complexes with the more bulky ligand L'' intramolecular interaction with flanking arene moieties is observed, which competes with the THF coordination. In contrast to these compounds we did not observe competing intramolecular coordination phenomena. The complexes can be recrystallised in different solvents such as toluene, hexane or fluorobenzene without change of the central motif. For cobalt, the related complex $[\{\text{Ar}'\text{Co}(\text{THF})(\mu\text{-Br})_2\}_2]$ shows great resemblance of the structural parameters, even though the slightly less bulky Ar' substituent allows a more linear coordination of the THF molecule.^[14a]

The structures of the monomeric complexes **4 a**, **4 b** and **5 b** show the Cr and Ni atoms, respectively, in a slightly distorted square planar coordination sphere. The N–M–Cl bond angles differ only slightly between **4 a** and **4 b** and are close to 180° , while the N–Cr–O/P and Cl–Cr–O/P angles are close to 90° . The

Table 1. Selected interatomic distances and angles for **1a–4a** and **1b–5b**.

	1a	1b	2a	2b	3a	3b	4a	4b	5b
N–M [Å]	2.023(2)	2.036(1)	1.967(2)	1.959(3)	1.930(2)	1.946(1)	2.036(1)	2.038(1)	1.890(1)
M–Cl [Å]	2.442(1)/ 2.427(8)	2.448(4)/ 2.446(4)	2.385(7)/ 2.392(6)	2.353(1)/ 2.436(1)	2.344(3)/ 2.353(4)	2.350(4)/ 2.328(4)	2.317(5)	2.314(5)	2.168(4)
M–M' [Å]	3.465(6)	3.458(5)	3.445(6)	3.379(9)	3.326(6)	3.273(5)			
M–Carb [Å]	1.564(5)	1.581(1)	1.509(3)	1.538(8)	1.408(2)	1.507(3)	0.380(5)	0.718(6)	0.807(3)
N–M–Cl [°]	118.9(6)/ 116.4(7)	114.9(3)/ 113.1(3)	117.5(5)/ 117.3(5)	106.9(1)/ 122.5 (1)	112.6 (1)/ 114.9(1)	109.4(4)/ 117.8(3)	174.0(4)	178.3(4)	178.6(4)
N–M–O/ N–M–P [°]	121.8(7)	134.5(1)	123.0(4)	131.2(1)	122.5(1)	126.6(4)	88.06(5)/ 91.29(5)	87.63(4)/ 94.04(4)	89.42(4)/ 91.89(4)
Cl–M–O/ Cl–M–P [°]	100.9(6)/ 103.8(6)	97.21(1)/ 97.43(1)	102.6(4)/ 102.2(3)	98.23(5)/ 97.72(5)	105.6(9)/ 106.4(1)	104.5(2)/ 101.2(2)	90.37(4)/ 91.09(4)	92.09(2)/ 86.24(2)	91.90(2)/ 86.80(2)
M–Cl–M' [°]	90.72(3)	89.91(1)	92.30(2)	89.75(4)	90.18(9)	88.77(1)			
Cl–M–Cl' [°]	89.28(3)	90.10(1)	87.70(2)	90.25(4)	89.82(1)	91.23(1)			
O–M–O/ P–M–P [°]							171.73(5)	178.32(2)	178.66(2)
∠ Aryl groups [°]	84.57(2)	86.80(4)	85.02(2)	89.81(2)	76.28(3)	82.92(9)	53.77 (2)	74.66(3)	76.30(2)

Cr–N bond length is between 2.036(1) Å (**4a**) and 2.039(1) Å (**4b**) which fits in the range of typical chromium(II) amides and changes only marginally upon introduction of the phosphine ligands.^[20]

The Cr atoms of **4a** and **4b** protrude from the carbazole plane by 0.380(5) Å (**4a**) and 0.718(6) Å (**4b**) respectively. The bond angles in **5b** also differs slightly from a distorted square planar structure with a N–Ni distance of 1.890(1) Å. Like the metal atom in complexes **4a** and **4b**, the Ni atom in **5b** deviates from the carbazole plane by 0.807(3) Å. The flanking arenes of the carbazole ligand are in an angled arrangement like in **1a–3b** but with smaller angles from 53° to 76°.

Due to their monomeric structure complexes **4a** and **4b** are unlike other literature known chromium(II) compounds with sterically demanding ligands, such as the amido or terphenyl ligands based complexes published by Jones^[14d] ([{L'Cr(THF)(μ-Cl)}₂]) and [{L''Cr(μ-Cl)}₂]) and Power^[8b,14b] ([{Ar'Cr(μ-Cl)}₂]) and ([{Ar^{CF3}Cr(μ-F)}₂]). The so far known dimeric species are structurally more like **1a–3a** and **1b–3b** with bridging halides, but with a square planar coordination of the chromium ions with either a THF stabilisation or an intermolecular η²-phenyl interaction of the ligand.

Based on this similar structural motif it can be deduced that the formation of a dimeric species is necessary to stabilise the 3d metals. In our work the ligand system seems to be too bulky to allow the formation of a dimeric species with a square planar coordination of the Cr(II) ions so that instead the monomeric species can be observed.

In addition, these examples make clear that a certain steric demand and further saturation by donor molecules are important. The abstraction of these stabilisers may lead to the formation of extremely unsaturated and hence highly active compounds that could be used as attractive starting materials for subsequent reactions.

Furthermore, the square planar coordination geometry of **5b** suggests that the Ni atom is in a low spin state. This was confirmed via NMR spectroscopy and a diamagnetic behaviour and will be discussed below.

Spectroscopic measurements

The compounds appear as colourful reagents (except for **1a** and **1b**) which appear indefinitely stable both in solution and as a solid under inert atmosphere at ambient temperature. Due to the paramagnetic nature of compounds **1a–4a** and **1b–4b** Evans experiments^[21] were carried out to determine the effective magnetic moments of all compounds. These experiments show magnetic moments of 4.4 μ_B for **4a** and 4.2 μ_B for **4b** which confirm that both complexes are in a d⁴-high spin state. The complexes **1a–3a** and **1b–2b** showed magnetic moments of 6.2 μ_B (**1a**), 6.7 μ_B (**1b**), 7.0 μ_B (**2a**) and 5.9 μ_B (**2b**) and 5.0 μ_B (**3a**) per dimer. For **3b**, poor sample solubility prevented reliable Evans measurements. The values for **1a** and **1b** are certainly lower than the spin only values for dimers with non-interacting Mn(II) ions (8.36 μ_B) but fit well to the values of the previous mentioned examples by Jones, [{L'Mn(THF)(μ-Br)}₂] (5.90 μ_B) and [{L''Mn(THF)(μ-Br)}₂] (6.85 μ_B). As an explanation for this behaviour an antiferromagnetic coupling of the metals between each other was given. The determined values of **2a** and **3a** fit very well to the spin only values for dimers Fe (6.93 μ_B), and Co (5.40 μ_B) so that it can be assumed that in **2a** and **3a** also some weak antiferromagnetic couplings of the metal ions are present.

Due to the square planar coordination geometry of the Ni(II) ion in **5b** it can be assumed, that the Ni(II) ion is in a low-spin state and diamagnetic. NMR spectra of **5b** confirm this. In the ¹H NMR spectra the singlet at 0.22 ppm was assigned to the PMe₃ group. The ^tBu-protons of the aryl groups and the carbazole backbone merge to a broad singlet at 1.46 ppm, which can be unambiguously assigned with the aid of ¹H-¹³C-HSQC NMR experiments. The C^{2,7} and C^{4,5} protons of the carbazole backbone were observed as doublets at 7.42 ppm and 8.46 ppm, respectively. The triplet at 7.70 ppm originates from the *para* protons of the aryl rings. The *ortho* protons do not show the expected doublet signal, but instead were observed as broad singlet resonance 8.36 ppm, indicating some dynamic effect in solution. The multiplicity of the neighboring

para protons confirms the present of the *ortho* protons. Furthermore, the corresponding ^{13}C NMR resonance at 126.6 ppm is also broad. The ^{31}P resonance of the PMe_3 is shifted to lower field compared to that of free PMe_3 and can be found at -26.9 ppm.

^1H NMR spectra of **1a–4b** show either no paramagnetic signals for Mn and Cr or broad paramagnetic shifted signals for Fe and Co in the range of approximately 100 ppm to -50 ppm, which can not be assigned to individual protons of the compounds.

As the variety in colours of the carbazoyl complexes was already mentioned, UV/Vis spectra of **2a–4a** and **2b–5b** were recorded.

In the Fe complexes also one absorption band each is expected due to the transition of the ^5E to the $^5\text{T}_2$ components of the ^5D ground term of the tetrahedral iron(II) ion. UV/Vis spectra of **2a** shows and absorption at 418 nm and **2b** at 461 nm. For the Co complexes the ^4F ground term of the tetrahedral Co(II) ion splits into three components $^4\text{A}_2$, $^4\text{T}_2$ and $^4\text{T}_1$. The $^4\text{T}_1$ term of the excited ^4P term interacts with the ground term. Three spin-allowed transitions are therefore expected. In the UV/Vis spectra of **3a** and **3b** are three transitions visible (**3a**: 475 nm, 640 nm and 735 nm, **3b**: 492 nm, 679 nm and 755 nm). The first absorption bands are each very broad with a shoulder at 530 nm for **3a** and 561 nm for **3b**. As for Cr(II) ions square planar coordination geometry the ^5D ground term splits in four components (A_{1g} , E_g , B_{2g} and B_{1g}), three transitions should be observed. For **4a** and **4b** the UV/Vis spectra show one broad and weak absorption band each at 644 nm (**4a**) and 670 nm (**4b**), which is comparable with the UV/Vis spectra of Powers structurally similar terphenyl dimer ($[\{\text{Ar}^{\text{CF}_3}\text{Cr}(\mu\text{-F})\}_2]$).^[8b] However, two more shoulders each, which are located in the fading absorption of the carbazole backbone, at 436 nm, 455 nm (**4a**) and 457 nm, 546 nm (**4b**) are observed, respectively. These three absorptions would then be due to the respective transition from $^5\text{A}_{1g}$, $^5\text{E}_g$, or $^5\text{B}_{2g}$ states to the $^5\text{B}_{1g}$ level. In the Ni complex **5b** one absorption band at 595 nm was observed. As for a square planar complex, again three transitions would be expected, it is likely that the remaining two transitions are in the range of the carbazoyl ligand absorption at higher energies and hence were not identified. This leads to the unexpected green colour which is unusual for square planar low-spin Ni compounds and more common in octahedral high-spin complexes.

Conclusions

In conclusion, the synthesis of nine novel transition metal complexes with a bulky carbazoyl ligand was described. For Cr the first monomeric representatives of this kind of complexes could be obtained. The dimeric complexes of Mn, Fe and Co are structurally comparable with some examples of the literature. A phosphine-based Ni complex could also be obtained, which is isostructural to the Cr complexes. Due to its square-planar coordination geometry it is low-spin and diamagnetic.

These complexes are promising precursors for a variety of follow-up reactions. For example, the donor effects of the phosphine ligands could support and stabilise the reduction to metal(I) complexes. The removal of the donor molecules by heating or the addition of a Lewis-acid could provide access to low-coordinate, highly reactive species.

Experimental Section

General Methods

All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. Et_2O , THF, *n*-hexane and benzene were dried over sodium and distilled prior to use. Fluorobenzene was dried over Calcium hydride and distilled prior to use. MgSO_4 (Sigma-Aldrich, 99.5%), NaOH (Honeywell, 99%), *n*-BuLi (Sigma-Aldrich, 2.5 M in hexane), 1-bromo-3,5-di-*tert*-butylbenzene (98% ArkPharm, procured via ChemPur) were used without further purification. C_6D_6 (Roth, 99.5%) was dried over sodium and distilled prior to use. The protonated ligand **RH** was prepared according to literature protocols.^[17] IR spectra were recorded on a Bruker Alpha spectrometer using the attenuated total reflection (ATR) technique on powdered samples. Elemental analyses were obtained with a Vario Micro Cube (Elementar Analysensysteme GmbH) in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT). NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer and a Magritek Spinsolve Phosphorous 80 MHz spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were reported against TMS and $^{31}\text{P}\{^1\text{H}\}$ against H_3PO_4 . Further, chemical shifts are referenced to the ^1H and ^{13}C NMR resonances of the deuterated solvent.^[22] Coupling constants *J* are given in Hertz as positive values regardless of their real individual sign. ^1H , ^{13}C and ^{31}P NMR spectra were obtained at 400.1, 100.6 and 162 MHz, respectively. Evans Experiments were carried out in a mixture of C_6D_6 and C_6H_6 in a ratio of 50:1. The UV/vis spectra were recorded using a Shimadzu PC-150 UV/vis spectrophotometer and a Mettler-Toledo Spektralphotometer UV7 in quartz cuvettes ($d=1$ cm) in solution. To subtract the solvent, the sample was measured relative to the pure solvent. Single crystals were mounted in perfluoropolyalkyl ether oil on a cryo loop and then brought into the cold nitrogen stream of a low-temperature device (Oxford Cryosystems Cryostream unit) so that the oil solidified. Diffraction data were collected using a Stoe IPDS II diffractometer and graphite-monochromated Mo- $\text{K}\alpha$ (0.71073 Å) or Ga- $\text{K}\alpha$ (1.34143 Å) radiation. The structures were solved by direct methods with SHELXS^[23] intrinsic phasing with SHELXT^[24] followed by full-matrix least-squares refinement using SHELXL-2014/7^[25] and the ShelXle GUI.^[26] All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model.

Preparation of **1a**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes **RK** as a yellow fluorescent solution has formed. To this solution $\text{MnCl}_2(\text{THF})_2$ (126 mg, 0.466 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to a pale yellow solution and a white precipitate. The solution was separated and volatiles were removed in vacuo. The residue was washed with hexane, dissolved in fluorobenzene and filtered via a syringe filter. The resulting solution

was concentrated affording pale yellow crystals of **1a** (89.0 mg, 0.109 mmol, 48% relating to 0.5 eq. RH) suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2961 (s), 2902 (w), 2864 (vw), 1591 (w), 1476 (w), 1462 (w), 1391 (w), 1361 (s), 1287 (w), 1268 (vw), 1246 (m), 1226 (vs), 1202 (vw), 1186 (vw), 1016 (w), 864 (vs), 846 (m), 825 (vw), 785 (vw), 716 (s), 700 (w), 677 (vw), 644 (w), 623 (vw), 603 (vw), 579 (w), 567 (w), 548 (w), 535 (m), 512 (s), 483 (m), 462 (s), 455 (s), 426 (s), 414 (vs), 402 (vs), 394 (s). EA found (calc. for C₁₀₄H₁₄₂Cl₂Mn₂N₂O₂): C 75.49 (76.49), H 8.76 (8.76), N 1.70 (1.72). **Magnetic moment** μ : 6.2 μ_B .

Preparation of **1b**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution MnCl₂(THF)₂ (126 mg, 0.466 mmol) was added. The mixture was stirred for two days at ambient temperature, which caused a colour change to a pale yellow solution and a white precipitate. Volatiles were removed in vacuo. The residue was washed with hexane and dissolved in toluene. PMe₃ (0.1 ml, 0.970 mmol) was added and the mixture was stirred for two days. The resulting solution was dried in vacuo affording a pale yellow solid of **1b** (279 mg, 0.170 mmol, 74% relating to 0.5 eq. RH). Recrystallisation of **1b**, performed from a saturated solution in toluene, afforded single crystals suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2955 (vs), 2903 (w), 2865 (w), 2225 (vw), 2167 (vw), 2143 (vw), 2052 (vw), 2015 (vw), 2001 (vw), 1987 (vw), 1974 (vw), 1910 (vw), 1590 (m), 1477 (m), 1392 (m), 1361 (vs), 1287 (m), 1246 (s), 1226 (vs), 1202 (w), 1151 (vw), 1074 (vw), 951 (w), 901 (vw), 865 (vs), 845 (m), 787 (vw), 771 (vw), 732 (w), 716 (vs), 699 (m), 674 (vw), 644 (w), 567 (vw), 545 (w), 531 (w), 507 (s). EA found (calc. for C₁₀₂H₁₄₆Cl₂Mn₂N₂P₂): C 75.28 (74.56), H 8.51 (8.96), N 1.52 (1.71). **Magnetic moment** μ : 6.7 μ_B .

Preparation of **2a**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution FeCl₂(THF)_{1.5} (110 mg, 0.467 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to dull yellow. Volatiles were removed in vacuo and the residue was extracted with toluene, filtered via a syringe filter and dried again in vacuo affording a yellow solid of **2a** (311 mg, 0.190 mmol, 83% relating to 0.5 eq. RH). Recrystallisation of **2a**, performed from a saturated solution in fluorobenzene, afforded single crystals suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3467 (vw), 3055 (vw), 2958 (vs), 2904 (w), 2866 (w), 1590 (m), 1491 (w), 1476 (m), 1462 (w), 1392 (m), 1362 (s), 1286 (s), 1266 (w), 1245 (s), 1225 (m), 1201 (vw), 1151 (vw), 1073 (vw), 1022 (vw), 978 (vw), 923 (vw), 899 (vw), 867 (vs), 847 (w), 824 (vw), 787 (vw), 770 (vw), 755 (vw), 717 (m), 699 (w), 674 (vw), 654 (w), 645 (w), 603 (vw), 548 (vw), 511 (vw), 499 (vw), 465 (vw), 406 (w), 385 (vw). EA found (calc. for C₁₀₄H₁₄₂Cl₂Fe₂N₂O₂): C 76.68 (76.41), H 8.48 (8.76), N 1.47 (1.71). **UV/Vis** λ_{max} : 418 nm. **Magnetic moment** μ : 7.0 μ_B .

Preparation of **2b**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution FeCl₂(THF)_{1.5} (110 mg, 0.467 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to dull yellow. Volatiles were removed in

vacuo and the residue was dissolved in toluene and filtered via a syringe filter. PMe₃ (0.1 ml, 0.98 mmol) was added and the mixture was stirred overnight, causing a colour change to orange. Volatiles were removed in vacuo and the residue was extracted with toluene, filtered via a syringe filter and dried again in vacuo affording an orange solid of **2b** (335 mg, 0.203 mmol, 88% relating to 0.5 eq. RH). Recrystallisation of **2b**, performed from a saturated solution in fluorobenzene afforded single crystals suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2954 (vs), 2903 (m), 2866 (w), 1590 (m), 1477 (m), 1462 (m), 1430 (w), 1392 (m), 1360 (vs), 1287 (3), 1270 (w), 1246 (s), 1233 (s), 1202 (m), 948 (m, br), 866 (vs), 851 (w), 844 (w), 731 (vw), 715 (vw), 700 (w), 647 (w), 513 (w), 503 (w), 401 (w). EA found (calc. for C₁₀₂H₁₄₆Cl₂Fe₂N₂P₂): C 74.32 (74.48), H 8.83 (8.95), N 1.87 (1.70). **UV/Vis** λ_{max} : 461 nm. **Magnetic moment** μ : 5.9 μ_B .

Preparation of **3a**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution CoCl₂(THF)_{1.5} (108 mg, 0.457 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to deep red. Volatiles were removed in vacuo and the residue was extracted with toluene, filtered via a syringe filter and dried again, affording **3a** (305 mg, 0.186 mmol, 81% relating to 0.5 eq. RH) as a brown solid. Recrystallisation of **3a**, performed from a saturated solution in fluorobenzene afforded single crystals suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2953 (m), 2902 (vw), 2863 (vw), 1591 (w), 1477 (w), 1391 (w), 1361 (s), 1287 (w), 1269 (vw), 1246 (w), 1224 (s), 1203 (vw), 1184 (vw), 1152 (vw), 1014 (vw), 931 (vw), 901 (vw), 865 (vs), 847 (m), 825 (vw), 761 (vw), 715 (s), 701 (w), 676 (vw), 643 (vw), 622 (vw), 601 (vw), 579 (vw), 555 (vw), 526 (vw), 513 (w), 500 (vw), 466 (vw), 418 (w), 408 (w), 397 (s), 381 (w). EA found (calc. for C₁₀₄H₁₄₂Cl₂Co₂N₂O₂): C 77.44 (76.12), H 8.71 (8.72), N 1.65 (1.71). **UV/Vis** λ_{max} : 475 nm, 640 nm, 735 nm. **Magnetic moment** μ : 5.0 μ_B .

Preparation of **3b**

3a (300 mg, 0.183 mmol) was dissolved in 20 ml of toluene. At ambient temperature PMe₃ (0.04 ml, 0.40 mmol) was added. The mixture was stirred overnight and turned purple. The resulting solution was concentrated affording dark purple crystals of **3b** (39.4 mg, 0.024 mmol, 13%) suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2954 (s), 2903 (w), 2866 (w), 1590 (w), 1477 (m), 1429 (vw), 1392 (m), 1361 (s), 1287 (m), 1267 (w), 1245 (m), 1223 (vs), 1203 (w), 1151 (vw), 1075 (vw), 957 (w), 899 (vw), 866 (vs), 845 (m), 787 (vw), 770 (vw), 750 (vw), 732 (w), 715 (s), 699 (w), 677 (vw), 642 (w), 511 (w), 465 (w), 406 (w), 699 (vw), 674 (vw), 644 (vw), 567 (vw), 545 (vw), 531 (vw), 507 (vw). EA found (calc. for C₁₀₂H₁₄₆Cl₂Co₂N₂P₂): C 73.81 (74.20), H 8.25 (8.91), N 1.42 (1.70). **UV/Vis** λ_{max} : 492 nm, 679 nm, 755 nm.

Preparation of **4a**

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution CrCl₂(THF) (93 mg, 0.479 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to light green. Volatiles were removed in vacuo and the residue was extracted with toluene, filtered via a syringe filter and dried again in vacuo, affording **4a** as a light green solid (338 mg, 0.455 mmol, 99% relating to RH). Recrystallisation of **4a**, performed from a saturated solution in hexane, afforded single

crystals suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3468 (vw), 3056 (vw), 2954 (m), 2903 (w), 2867 (w), 1587 (w), 1476 (w), 1461 (w), 1433 (vw), 1393 (w), 1376 (w), 1362 (m), 1340 (vw), 1287 (w), 1265 (vw), 1244 (w), 1224 (s), 1204 (w), 1182 (vw), 1154 (vw), 1075 (vw), 1021 (m), 979 (vw), 956 (vw), 925 (vw), 898 (vw), 867 (vs), 844 (m), 793 (vw), 769 (vw), 760 (vw), 723 (w), 699 (w), 679 (vw), 643 (vw), 603 (vw), 547 (vw), 532 (vw), 519 (vw), 502 (vw), 460 (vw), 422 (vw), 390 (w). EA found (calc. for C₅₆H₇₈ClCrNO₂): C 75.68 (76.03), H 8.50 (8.89), N 1.42 (1.58). UV/Vis λ_{max} : 644 nm. Magnetic moment μ : 4.4 μ_B .

Preparation of 4b

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution CrCl₂(THF) (93 mg, 0.479 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change light green. Volatiles were removed in vacuo and the residue was dissolved in toluene and filtered via a syringe filter. PMe₃ (0.1 ml, 0.98 mmol) was added and the mixture was stirred overnight, causing a colour change to dark yellow. The resulting solution was concentrated affording yellow crystals of **4b** (85.0 mg, 0.095 mmol, 21% relating to RH) suitable for X-ray diffraction. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2961 (w), 2952 (w), 2905 (w), 2866 (vw), 1587 (vw), 1477 (vw), 1461 (vw), 1431 (vw), 1393 (vw), 1362 (w), 1305 (w), 1282 (w), 1226 (vs), 1203 (s), 1149 (s), 1126 (s), 1064 (vw), 982 (s), 958 (w), 945 (w), 900 (vw), 868 (m), 843 (w), 807 (w), 758 (vw), 744 (w), 732 (w), 721 (w), 697 (vw), 676 (vw), 643 (w), 554 (vw), 507 (w, br), 466 (vw). EA found (calc. for C₅₄H₈₂ClCrNP₂): C 72.35 (72.50), H 8.73 (9.24), N 1.23 (1.57). UV/Vis λ_{max} : 670 nm. Magnetic moment μ : 4.2 μ_B .

Preparation of 5b

RH (300 mg, 0.457 mmol) and benzyl potassium (60 mg, 0.457 mmol) were added in a Schlenk tube and dissolved in THF. After a few minutes RK as a yellow fluorescent solution has formed. To this solution NiCl₂(PMe₃) (130 mg, 0.460 mmol) was added. The mixture was stirred overnight at ambient temperature, which caused a colour change to dark green. Volatiles were removed in vacuo and the residue was extracted with hexane, filtered via a syringe filter and dried again in vacuo, affording **5b** as a dark green solid (266 mg, 0.295 mmol, 65% relating to RH). Recrystallisation of **5b**, performed from a saturated solution in hexane, afforded single crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, C₆D₆): δ (ppm) = 0.22 (s, 18 H, H-PMe₃), 1.46–1.47 (m, 54 H, Ar-^tBuH, Carb-^tBuH), 7.42 (d, 2 H, C^{2,7}H), 7.70 (t, 2H, *p*-CH), 3.36 (s br, 4H, *o*-CH), 8.46 (d, 2H, C^{4,5}H). ¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 12.6 (s, P(CH₃)₃), 32.0 (s, Ar-C(CH₃)), 32.3 (s, Carb-C(CH₃)), 34.5 (s, Ar-C(CH₃)), 35.5 (s, Carb-C(CH₃)), 115.3 (s, C^{2,7}H), 123.0 (s, *p*-CH), 126.6 (s br, *o*-CH), 128.7 (s, C^{4,5}H), 130.2 (s, C^{4a,4b}), 130.4 (s, C^{1,8}), 138.7 (s, C^{8a,9a}), 145.6 (s, C^{3,6}), 148.0 (s, *i*-C), 150.7 (s, *m*-C). ³¹P NMR (162 MHz, C₆D₆): δ (ppm) = -26.90 (s, PMe₃). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2958 (vs), 2866 (w), 1588 (m), 1477 (m), 1426 (vw), 1392 (m), 1361 (s), 1287 (m), 1246 (m), 1223 (vs), 1205 (m), 1176 (w), 900 (vw), 868 (vs), 845 (s), 740 (m), 717 (s), 698 (w), 677 (w), 643 (w), 615 (vw), 496 (w), 448 (vw), 433 (vw), 402 (m), 385 (w), 642 (m), 511 (vs), 465 (m), 406 (s), 699 (w), 674 (vw), 644 (vw), 567 (vw), 545 (vw), 531 (w), 507 (w). EA found (calc. for C₅₄H₈₂ClNiNP₂): C 71.74 (71.96), H 9.29 (9.17), N 1.26 (1.55). UV/Vis λ_{max} : 595 nm.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Transition metals · Bulky ligand · Synthesis · Crystal structures · Evans method

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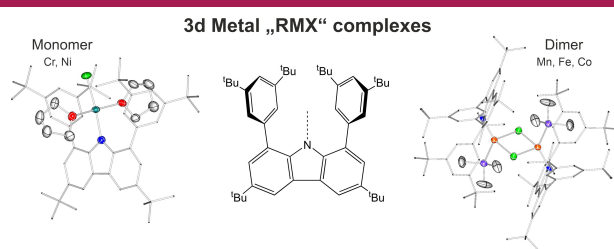
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RESEARCH ARTICLE



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**Complexes of 3d Metals with a
Bulky Carbazoyl Ligand**

