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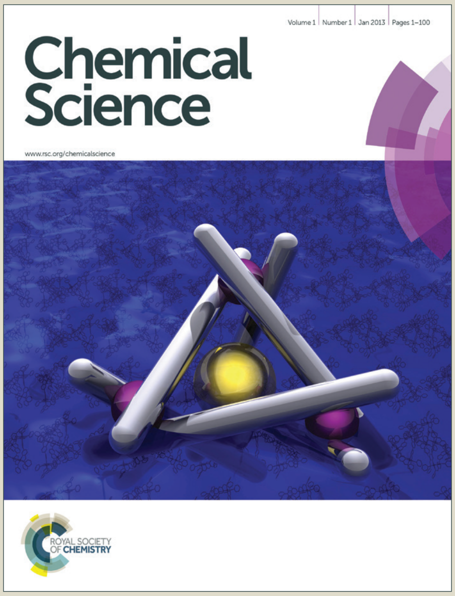

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ARTICLE

Addition of pnictogen atoms to chromium(II): synthesis, structure and magnetic properties of a chromium(IV) phosphide and a chromium(III) arsenide

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Chromium(II) chloride reacts with lithium pentamethylcyclopentadienide (LiCp*, Cp* = C_5Me_5) and $LiE(SiMe_3)_2$ (E = P or As) to give the heterocubane chromium phosphide $[(\eta^5\text{-}Cp^*Cr)(\mu_3\text{-}P)]_4$ (**1**) or the chromium arsenide cage $[(\eta^5\text{-}Cp^*Cr)_3(\mu_3\text{-}As)_2]$ (**2**), respectively. The crystal and molecular structures of both compounds have been determined by X-ray crystallography. The reactions represent unusual oxidative additions of pnictogen atoms to chromium(II), which in the case of **1** results in the formation of the unusual chromium(IV) formal oxidation state, and in the case of **2** provides access to chromium(III). Compound **1** is also a rare example of a transition metal μ_3-phosphide-ligated cubane. Magnetic susceptibility and magnetization measurements, with support from DFT calculations, indicate $S = 2$ and $S = 9/2$ ground states for **1** and **2**, respectively, which can be rationalized by considering the electronic structure in terms of chromium-chromium bonding.

Introduction

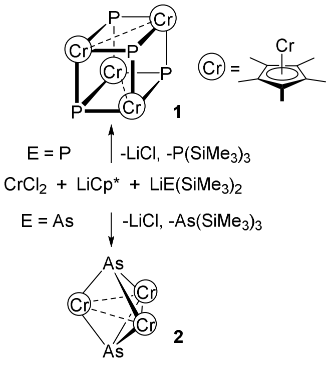
Cluster compounds containing unsubstituted group 15 element ligands of the type $[E_n]$ (E = P or As, $n \geq 1$), or so-called ‘naked’ pnictogen ligands, continue to attract considerable interest due to their remarkable structural diversity, and also because of the opportunities for using the clusters themselves as novel ligands and in supramolecular chemistry.[1] Synthetic routes to $[E_n]$-containing coordination compounds are well developed, particularly in the case of phosphorus, with activation reactions of white phosphorus, P_4, proving to be a particularly successful source of $[P_n]$ complexes, including complexes of P_4 itself.[2] Although somewhat less extensive owing to greater technical challenges, analogous chemistry with yellow arsenic, As_4, leading to complexes of $[As_n]$ ligands, has also been reported.[3] Recently, Cummins *et al.* have also developed a series of transition metal complexes based on the naked mixed-pnictogen starting material P_3As.[4]

One branch of coordination chemistry in which the potential of $[E_n]$ ligands has been underexploited is molecular magnetism. Indeed, there is a general paucity of studies addressing the magnetic properties of compounds containing *P*- and *As*-donor ligands of the type $[R_xE]^{y-}$, where $x = 2$ and $y = 1$, $x = 1$ and $y = 2$, or $x = 0$ and $y = 3$.[5] We recently reported studies of the *P*- and *As*-mediated exchange coupling in the phosphide- and arsenide-bridged dimers $[(\eta^5\text{-}Cp)M\{\mu\text{-}E(SiMe_3)_2\}]_2$, with M = Cr(II)[6] or Mn(II),[7] and determined the exchange coupling constants via phenomenological spin Hamiltonians. In the case of the chromium(II) dimers, the antiferromagnetic super-exchange coupling between the high-spin $S = 2$ ions was found to be strong and also pnictogen-dependent, with exchange coupling constants of $J = -166\ cm^{-1}$ for E = P and $J = -77.5\ cm^{-1}$ for E = As (2*J* formalism). The antiferromagnetic exchange in the manganese(II) analogues is more than an order of magnitude weaker, but these compounds are more noteworthy because of their $S = 5/2$ to $S = 3/2$ spin crossover properties. In the case of the arsenide-bridged manganese(II) dimer, the spin crossover is a two-step process that shows hysteresis at 96-105 K in the temperature dependence of the magnetic susceptibility.

The spin configurations of first-row transition metal Cp complexes can be very sensitive to the ligand substituents, particularly in the case of manganese(II)[8] and, to a lesser extent, chromium(II).[9] Chromocene itself has a low-spin, $S = 1$ configuration,[10] but substituting a $[Cp]^-$ ligand by $[(Me_3Si)_2E]^-$ to give $[CpCr\{\mu\text{-}E(SiMe_3)_2\}]_2$ (E = P or As) evidently weakens the ligand field sufficiently to give high-spin $S = 2$ chromium(II).[6] In an attempt to induce thermal spin crossover in $[CpCr\{\mu\text{-}E(SiMe_3)_2\}]_2$ by forcing the ground state of the metal to switch from $S = 2$ to $S = 1$ with the aid of a stronger ligand field, we have targeted the analogous pentamethylcyclopentadienyl (Cp*) dimers $[(Cp^*)Cr\{\mu\text{-}E(SiMe_3)_2\}]_2$.

Results and discussion

The method used to synthesize $[CpCr\{\mu\text{-}E(SiMe_3)_2\}]_2$, in which Cp_2Cr is transmetallated by $[(Me_3Si)_2ELi]$ with concomitant elimination of LiCp, was initially used to target $[Cp^*Cr\{\mu\text{-}E(SiMe_3)_2\}]_2$, but only starting materials were recovered. An alternative, two-step approach was then attempted, in which chromium(II) chloride and lithium pentamethylcyclopentadienide (LiCp*) were combined as solids in a 1:1 stoichiometry, cooled to –78°C, and then thf was added. The reaction mixtures were slowly warmed to room temperature, which resulted in the formation of a blue solution. The solution was cooled to –78°C, and $[(Me_3Si)_2PLi]$ or $[(Me_3Si)_2AsLi]$ (1 stoichiometric equivalent) in thf was added. Once again, the reactions were warmed to room temperature and stirred overnight. In the case of the phosphorus-containing reaction, the thf was evaporated and replaced with toluene, and the resulting solution was filtered, concentrated and stored at –30°C for several days, which resulted in the formation of dark brown crystals of the heterocubane chromium phosphide $[(\eta^5\text{-Cp*Cr})(\mu_3\text{-P})]_4$ (**1**), which was isolated in a yield of 33% based on the chromium starting material. For the arsenic-containing reaction, the same procedure led to the formation of large, brown crystals of the arsenide-bridged trimetallic cage $[(\eta^5\text{-Cp*Cr})_3(\mu_3\text{-As})_2]$ (**2**) in 42% yield based on the chromium starting material (Scheme 1). The moderate yields of **1** and **2** are a consequence of their high solubility, even in hydrocarbon solvents, at the temperature used for the recrystallizations. Although both **1** and **2** are very air-sensitive, both compounds can be heated to reflux in toluene for brief periods with obvious signs of decomposition, and they appear to be stable indefinitely at room temperature under an inert atmosphere of nitrogen or argon.



Scheme 1.

Compound **1** (Figure 1) crystallizes in the tetragonal space group $I\bar{4}$, and the molecular structure consists of four symmetry-related chromium centres arranged in a tetrahedron, with Cr···Cr distances of 2.931(2) Å and 2.935(1) Å, and a P···P separation of 3.431(1) Å (Figure 1). The Cr-Cr-Cr and P-P-P angles are all 60.0° within standard deviations. Each chromium is coordinated by an η^5-Cp* ligand, with Cr–C distances in the range 2.235(3)- 2.248(4) Å. The chromium atoms are bridged by three μ_3-phosphide ligands, which produce very similar Cr–P distances of 2.2609(9), 2.2646(8) and 2.2610(9) Å, and P-Cr-P angles of 98.59(3), 98.32(3) and 98.59(3)°. Thus each chromium resides in a classical $\{Cp^*CrP_3\}$ piano stool coordination environment and formally exists as chromium(IV) (see below for discussion of electronic structure).

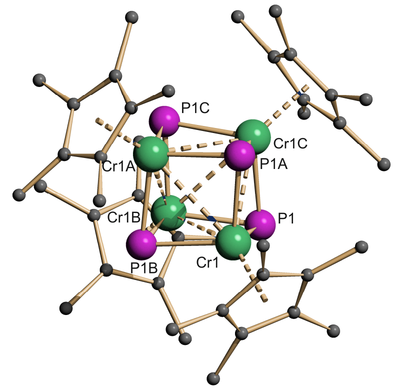


Fig. 1. Ball-and-stick representation of the molecular structure of **1.** Cr = green; P = purple; C = grey (hydrogen atoms not shown).

Compound **2** crystallizes in the orthorhombic space group *Pbca*, and the molecular structure consists of a triangle of $\{(\eta^5\text{-Cp*})Cr\}$ units capped by two μ_3-arsenide ligands (Figure 2). Although the three chromium atoms are not related by crystallographic symmetry, the close approximation to molecular D_{3h} symmetry (regarding the Cp* ligands as undergoing ring whizzing) is reflected in the Cr(1)–Cr(2), Cr(1)–Cr(3) and Cr(2)–Cr(3) distances of 2.7658(5), 2.7869(4) and 2.7677(4) Å, respectively, and the Cr(3)-Cr(1)-Cr(2), Cr(1)-Cr(2)-Cr(3) and Cr(2)-Cr(3)-Cr(1) angles of 59.79(1), 60.48(1) and 59.73(1)°. Within each $\{(\eta^5\text{-Cp*})Cr\}$ unit, the Cr–C distances are in the range 2.227(2)-2.238(2) Å for Cr(1), 2.224(2)-2.238(2) Å for Cr(2), and 2.226(2)-2.240(2) Å for Cr(3). The D_{3h} symmetry of molecules of **2** is underscored by the similarity of the lengths of the Cr–As bonds, which are 2.4304(4)-2.4381(4) Å to As(1) and 2.4258(4)-2.4316(4) Å to As(2). The As(1)-Cr(1)-As(2), As(1)-Cr(2)-As(2) and As(1)-Cr(3)-As(2) angles are 97.85(1), 97.59(1) and 97.48(1)°, respectively. In contrast to **1**, the chromium centres in **2** are present formally as Cr(III).

Several examples of five-vertex coordination cages containing $\{M_3E_2\}$ cores are known for M = Fe with E = P or As,[11] and for M = Co with E = P, including the closely related $[(Cp''Co)_3(\mu_3\text{-P})_2]$ ($Cp'' = C_5H_3{}^tBu_2$).[12] However, compound **2** is the first example of such a cluster to contain chromium. The formation of **1** is even more remarkable, for four reasons. Firstly, whereas clusters containing the $\{M_4S_4\}$ (E = O, S) unit are extremely well known,[13] only two molecular compounds containing $\{M_4P_4\}$ heterocubane units have been structurally characterized, both of which have M = Co and were formed either in low yield[14] or as part of a mixture resulting from the thermolysis of $[Cp^RCo(CO)_2]$ with $[Cp^*Fe(P_5)]$.[12a] The iron phosphide $[(CpFe)_4(P_2)_2]$ is reminiscent of **1**, however its structure differs in that the triangulated dodecahedral core comprises $\{P_2\}$ ligands with a P–P bond distance of ca. 2.30 Å, which is more than 1.1 Å longer than the P···P separation in **1**.[15] The nickel phosphide $[(CpNi)_3(\mu_3\text{-P})(P_4)]$, which contains a branched $\{P_4\}$ ligand,[16] and the vanadium phosphorus cluster

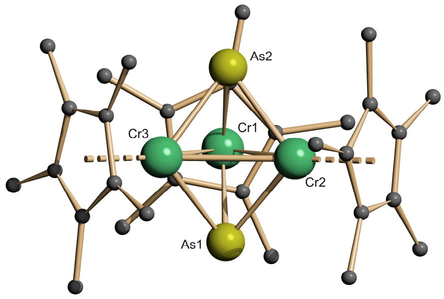


Fig. 2. Ball-and-stick representation of the molecular structure of **2.** Cr = green; As = yellow; C = grey (hydrogen atoms not shown).

$[(CpV)_4(P_3)_2]$, which contains triphosphaallyl ligands,[17] also bear some structural similarities to **1**. The synthesis of the cubane $[(PhSn)(\mu_3\text{-}P)]_4$ was reported in 1968, and although the structural properties were not characterized in detail the tin(IV) phosphide is thought to be essentially isostructural to **1**.[18] Secondly, the chromium(II) starting material has been formally oxidized to chromium(IV) in **1**, which is an uncommon oxidation state for this metal[19] and, indeed, is also an unusual reaction for chromium(II), which tends to be oxidized to chromium(III) or chromium(VI),[20] or to engage in metal-metal (multiple) bonding.[21] Furthermore, although chromium heterocubanes of the type $[CpCr(\mu_3\text{-}E)]_4$ are known with E = O, S or Se,[22] these species feature the formal chromium(III) oxidation state, rather than chromium(IV) as proposed for **1**. Thirdly, the majority of chromium(IV) complexes feature hard oxygen- or nitrogen-donor ligands,[23] rather than soft ligands such as phosphide or cyclopentadienide, and organometallic chromium(IV) is particularly rare.[24] Fourthly, to the best of our knowledge, compound **1** is the first polymetallic chromium(IV) compound.

The mechanism(s) through which **1** and **2** form are currently unclear, with NMR studies being hampered by the paramagnetism of both compounds. A reasonable assumption is that salt metathesis occurs in the initial step, generating '$[Cp^*CrCl]$' followed by $[Cp^*Cr\{E(SiMe_3)_2\}]$, with lithium chloride as the by-product. Our previously reported chromium(II) compounds $[(\eta^5\text{-}Cp)Cr\{\mu\text{-}E(SiMe_3)_2\}]_2$ can therefore be regarded as models for the proposed intermediates, although these stable complexes were synthesized using a different route involving transmetallation of Cp_2Cr by $LiE(SiMe_3)_2$.[6] Generation of the naked pnictogen ligands may then occur by nucleophilic attack of $LiE(SiMe_3)_2$ on the E–Si bonds in $[(\eta^5\text{-}Cp^*)Cr\{\mu\text{-}E(SiMe_3)_2\}]_2$, liberating $E(SiMe_3)_3$ as the by-product. However, analysis of the crude reaction mixture accompanying the formation **1** by the ^{31}P NMR spectroscopy did not produce any definitive information for the formation of $P(SiMe_3)_3$ owing to the poor signal-to-noise ratio arising from the paramagnetism of **1** (Figure S2). Indeed, assignment of the NMR spectra of **1** and **2** cannot be made with any certainty owing to the effects of the unpaired spin density.

Precedent for the reactivity proposed to account for the formation of **1** and **2** stems from our work on the synthesis of *tris*(phosphino)phosphines of the type $P(PR_2)_3$ (R = various alkyl, Ph),[25] in which the P–Si bonds in intermediates species such as $R_2P–P(SiMe_3)_2$ are sequentially cleaved by $[LiP(SiMe_3)_2]$. The formation of chromium(IV) in the presence of phosphorus, and the formation of chromium(III) in the presence of arsenic, is intriguing feature of the chemistry depicted in Scheme 1. The different chromium oxidation states in **1** and **2** can be explained by considering that the energies of the valence orbitals of chromium(IV) should be lower than those of chromium(III), and therefore closer in energy to those of phosphorus. In contrast, the higher energy of the arsenic valence orbitals may be better matched to those of chromium(III).

An important consideration in **1** and **2** is the possibility of chromium-chromium bonding. A search of the Cambridge Structural Database (CSD) reveals that the range of chromium-chromium single bonds is 1.858-3.471 Å, with a mean value of 2.755 Å,[26] suggesting that such interactions are at least possible in **1** and **2**. Studies on the bonding in related chalcogen-bridged heterocubanes of general formula $[(CpM)_4(\mu_3\text{-}E)_4]^{n+}$ (M = Ti, V, Cr, Mo, Fe, Ru, Co, Ir; E = O or S; *n* = 0, +1, +2) have considered two limiting possibilities, one in which the unpaired spin density is delocalized into metal-metal bonds, and one in which the spin density is localized in the metal d-orbitals, which can lead to magnetic exchange coupling via the ligands. To gain insight into the electronic structure in **1** and **2**, the temperature dependence of the molar magnetic susceptibility (χ_M), and the field (*H*) dependence of the magnetization (*M*) of polycrystalline samples of both compounds were measured.

In an applied field of H_{dc} = 1000 Oe, $\chi_M T$ for **1** at 300 K is 2.85 cm^3 K mol^{-1}, and remains essentially constant down to about 10 K, when a sharp decrease is observed, and then a value of 2.05 cm^3 K mol^{-1} is reached at 2 K (Figure 3). The isothermal magnetization of **1** at *T* = 2 K shows a steep increase to reach *M* = 2.46 Nμ_B at *H* = 2.0 T, and then increases at a slower rate at higher fields, reaching *M* = 3.67 μ_B at *H* = 7.0 T, but without saturation (Figure 3). The $\chi_M T$ value of **1** in the range 10-300 K is less than the upper limit of 4.00 cm^3 K mol^{-1} predicted for four Cr(IV) ions with *S* = 1,[27] and the magnetization at 7 T and 2 K is significantly less than the value of 8 Nμ_B predicted for this system (assuming *g* = 2.00). Because $\chi_M T$ is essentially temperature-independent down to 10 K, any antiferromagnetic exchange is likely to be extremely weak, therefore an alternative explanation involving metal-metal bonding should be considered in order to account for the susceptibility and the magnetization in **1**.

A molecular orbital (MO) energy-level scheme to describe the bonding in cubanes of the type $[(CpM)_4E_4]$ (E = O, S) has been proposed by Dahl *et al*., and developed by others for cubanes with a range of d-electron counts.[28] The metal-metal cluster bonding MOs consist of the d_{z^2} orbitals oriented towards the centre of the cubane, with the d_{xy} and $d_{x^2-y^2}$ orbitals

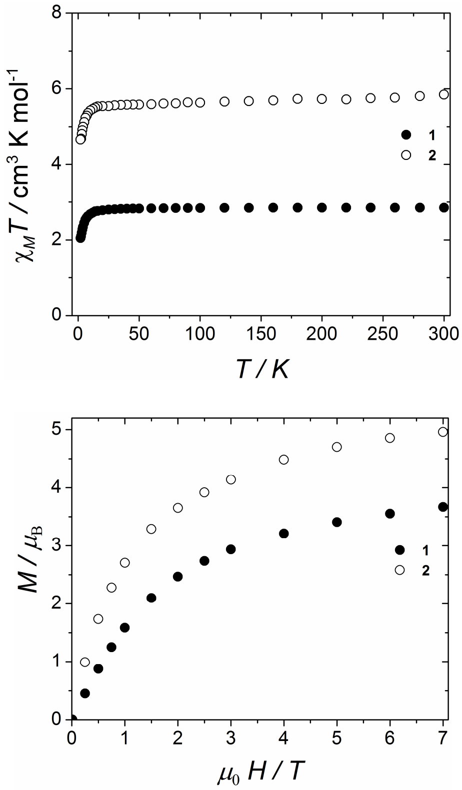


Fig. 3. Temperature dependence of $\chi_M T$ in an applied field of 1 kG (upper), and magnetization (*M*) versus magnetic field (*H*) at 2 K (lower), for **1** (shaded circles) and **2** (unshaded circles).

overlapping around the cluster periphery. These interactions produce a simplified energy-level diagram with low-lying a_1, e and t_2 bonding MOs, and t_1 and t_2 antibonding orbitals (Figure S6). In the case of **1**, populating the frontier MOs with eight electrons can produce two configurations, either $(a_1)^2\ (e)^3\ (t_2)^3$ with a total spin of $S = 2$, or $(a_1)^2\ (e)^4\ (t_2)^2$ with a total spin of $S = 1$. The expected value of $\chi_M T$ for a cluster with $S = 2$ and $g = 2.00$ is 3.00 cm^3 K mol^{-1},[27] which agrees well with the values measured for **1** down to 10 K. Furthermore, the value of the magnetization at $H = 7$ T is also close to the expected value of 4 $N\mu_B$ for an $S = 2$ system. The magnetic susceptibility and magnetization measurements therefore indicate that **1** occupies an $S = 2$, spin quintet ground state.

To obtain further support for the assignment of the magnetic ground states of **1** and **2**, we performed density functional calculations using the Gaussian suite of programs.[29] Stability analysis was applied to ensure that a true minimum was obtained in the Kohn-Sham solutions. Calculations were attempted within the generalized gradient approximation using the PBE exchange-correlation functional,[30] and its derivative PBE0.[31] The hybrid DFT calculations were plagued by the presence of instabilities: in the case of **2**, removing the instabilities was straightforward, **1** proved very difficult to treat using PBE0 (calculations using the B3LYP hybrid functional were also unsuccessful). Consequently, for **1** we report calculations only at the PBE/TZVP level.[32] For **2**, it was possible to obtain stable solutions at both PBE/TZVP and PBE0/TZVP levels, with both levels producing the same ordering of spin state energies. PBE has previously been shown to be successful in describing metal-metal bonds,[33] and we accordingly have confidence in its use here.

In the case of **1**, the spin quintet was indeed found to be the ground state, with the other spin multiplicities lying above the ground state by: singlet ($S = 0$) +25 kJ/mol; triplet ($S = 1$) +20 kJ/mol; septet ($S = 3$) +99 kJ/mol; nonet ($S = 4$) +179 kJ/mol (Table S2). The spin density plot for the ground state of **1** (Fig. 4) reveals that the unpaired spin resides almost entirely on the chromium(IV) centres. The presence of chromium-chromium bonding in **1** is also substantiated by the calculated Cr–Cr Mayer bond orders for the ground-state quintet, which, at 0.22-0.24, are non-negligible (Table S4).

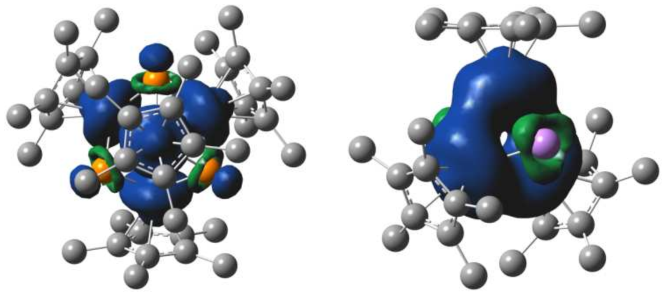


Fig. 4. PBE/TZVP spin density plot for the ground state of **1** (left) and **2** (right) (isosurface value = 0.004 a.u.).

The magnetic properties of **2** are more straightforward to interpret. Under the same experimental conditions as for **1**, the $\chi_M T$ product for **2** at 300 K is 5.85 cm^3 K mol^{-1}, with this value decreasing slightly down to about 10 K, when a sharper decrease is observed, reaching 4.65 cm^3 K mol^{-1} at 2 K. The 2 K magnetization of **2** reaches $M = 4.96\ N\mu_B$ at $H = 7.0$ T. A system containing three Cr(III) ions, each with $S = 3/2$, would be expected to show a maximum of $\chi_M T = 5.63$ cm^3 K mol^{-1} at 300 K, and $M = 4.5$ at 2 K;[22] the similarity of the theoretical values to those observed experimentally suggests that **2** occupies an $S = 9/2$ ground state, i.e. a spin decet. DFT calculations are in good agreement with the experimental data, with the excited spin states being destabilized relative to the ground state as follows (PBE/TZVP): doublet ($S = 1/2$) +82 kJ/mol; quartet ($S = 3/2$) +55 kJ/mol; sextet ($S = 5/2$) +74 kJ/mol; octet ($S = 7/2$) +66 kJ/mol (Table S3). The same spin state ordering was found at the PBE0/TZVP level. The Cr–Cr Mayer bond orders for **2** are in the range 0.07-0.10, and hence much smaller than those in **1** (Table S5).

Conclusions

In summary, we have discovered a new route to chromium complexes of naked phosphide and arsenide ligands, which involves formal oxidative addition of the pnictogen atom to chromium(II) using simple starting materials. Of particular note is that the synthetic route provides convenient access to a rare example of a phosphide-ligated heterocubane (**1**), which contains chromium in the unusual formal +4 oxidation state. Magnetic susceptibility and magnetization measurements confirm that the spin ground state of **1** can be described by an $S = 2$ system with chromium-chromium bonding. The spin ground state of **2** was determined experimentally to be $S = 9/2$, and support for the assignment of the spin ground states was provided by DFT calculations. The general implication of the current study is that the synthetic method may represent a general route to transition metal complexes of naked pnictogen ligands, potentially with the metals present in uncommon oxidation states and unusual coordination environments. Our ongoing work will explore this possibility.

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Notes and references

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Electronic Supplementary Information (ESI) available: CCDC reference codes 984791 (**1**) and 984792 (**2**). Details of the synthesis, crystallography, magnetic property measurements and DFT calculations. See DOI: 10.1039/b000000x/

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