Supporting information for:

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

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General synthetic considerations. Toluene was dried by refluxing under nitrogen for several hours over sodium-potassium alloy. Benzene-d_6 was distilled from sodium-potassium alloy and stored over activated 4 Å molecular sieves. Solids were manipulated using an MBraun LabMaster glovebox under an argon atmosphere, and solutions were transferred using a Schlenk line under nitrogen that had been passed through several columns of various drying agents and a heated copper catalyst. Lithium bis(trimethylsilyl)phosphide[1] and lithium bis(trimethylsilyl)arsenide[2] were all synthesized according to literature procedures. Anhydrous chromium(II) chloride was purchased from Aldrich and used as supplied. Paramagnetic ^{1}H NMR spectra were acquired using a Bruker Avance III spectrometer across a chemical shift range of ±250 ppm. Elemental analysis results were obtained using the elemental analysis service of London Metropolitan University, U.K. (Mr. S. Boyer).

[(η^5-Cp*)Cr(μ$_3$-P)]$_4$ (1). LiCp* (75 mg, 0.5 mmol) and $CrCl_2$ (65 mg, 0.5 mmol) were combined as solids, cooled to –78°C, and thf (10 mL) was added. The mixture was warmed to room temperature, giving a blue solution, which was stirred for one hour and then cooled to –78°C again. A solution of $[LiP(SiMe_3)_2\cdot(thf)_{0.98}]$ (158 mg, 0.5 mmol) in thf (5 mL) was then added dropwise, and the reaction was warmed to room temperature. After stirring overnight, the thf solvent was removed from the dark brown reaction mixture and the residue dissolved in toluene. The solution was filtered (diatomaceous earth) and the volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel. A homogenous solution was obtained by gentle heating, and storage at –28 °C produced dark brown crystals (isolated yield 36 mg, 33% based on chromium). Melting point: 156°C, with decomposition. Analysis calculated for $C_{40}H_{60}P_4Cr_4$: C 55.05, H 6.93, P 14.20; found C 54.97, H 6.83, P 13.91.^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K):

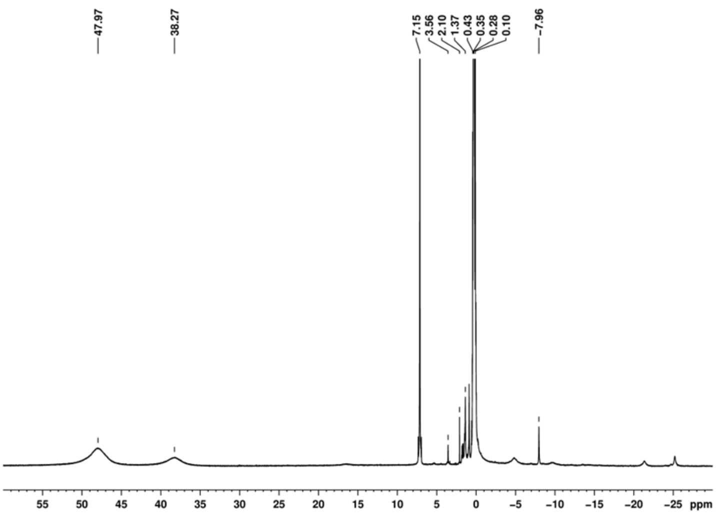

Figure S1. ^{1}H NMR spectrum of [(η^5-Cp*)Cr(μ$_3$-P)]$_4$ (**1**).

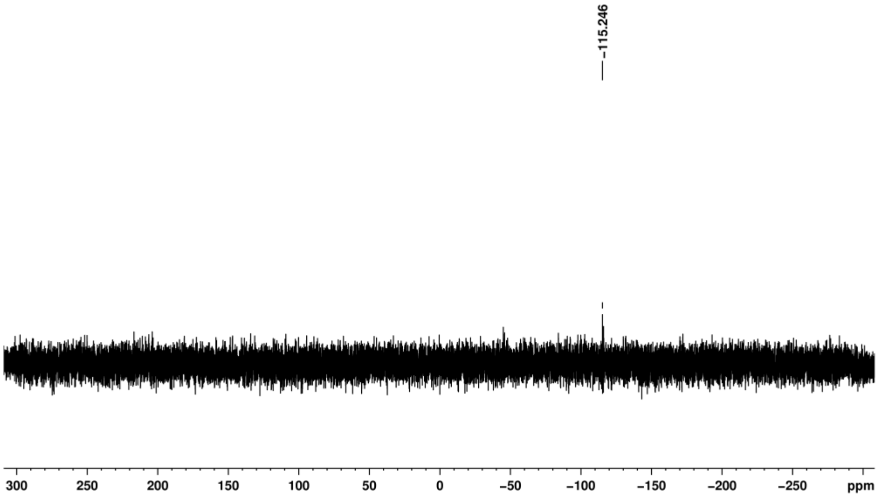

Figure S2. ^{31}P NMR spectrum of $[(\eta^5\text{-Cp*})Cr(\mu_3\text{-P})]_4$ (**1**). The low-intensity signal at $\delta(^{31}P)$ 115.25 ppm is the only discernible feature of the spectrum, however assignment of this peak to the phosphorus environment in **1** cannot be made with any certainty.

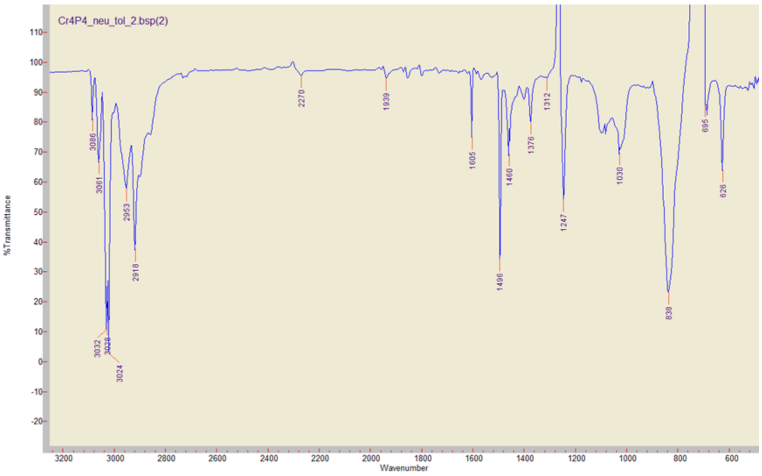

Figure S3. Infrared spectrum of **1** recorded in toluene solution.

[{(η^5-Cp*)Cr}$_3$(μ_3-As)$_2$] (2). LiCp* (75 mg, 0.5 mmol) and CrCl$_2$ (65 mg, 0.5 mmol) were combined as solids, cooled to –78°C, and thf (10 mL) was added. The mixture was warmed to room temperature, giving a blue solution, which was stirred for one hour and then cooled to –78°C again. A solution of [LiAs(SiMe$_3$)$_2$·(thf)$_{0.94}$] (170 mg, 0.5 mmol) in thf (5 mL) was then added dropwise, and the reaction was warmed to room temperature. After stirring overnight, the thf solvent was removed from the dark brown reaction mixture, and the residue dissolved in toluene. The solution was filtered (diatomaceous earth) and the volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel. A homogenous solution was obtained by gentle heating, and storage at –28 °C produced dark brown crystals (isolated yield 66 mg, 42% based on chromium). Melting point: 168°C, with decomposition. Analysis calculated for C$_{30}$H$_{45}$As$_2$Cr$_3$: C 50.64, H 6.37; found C 50.22, H 6.23. ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K, δ/ppm):

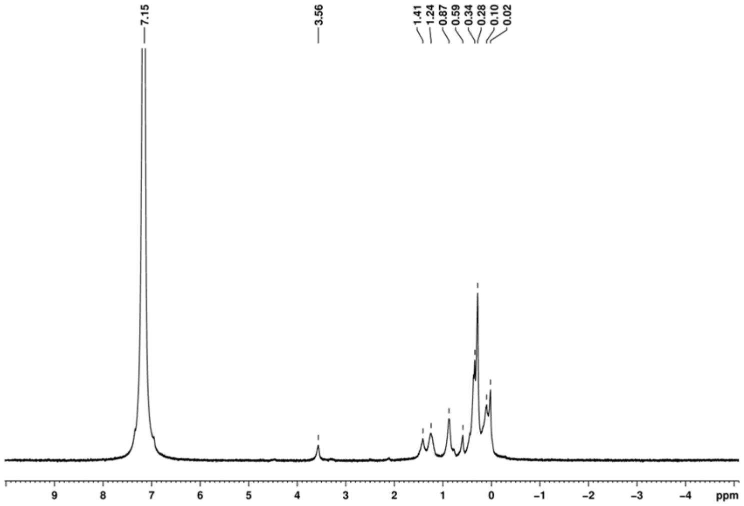

Figure S4. ^{1}H NMR spectrum of [{(η^5-Cp*)Cr}$_3$(μ_3-As)$_2$] (**2**).

Figure S5. Infrared spectrum of **2** recorded in toluene solution.

Magnetic susceptibility measurements. The magnetic properties of polycrystalline samples of **1** and **2** were measured using a Quantum Design MPMS-7 SQUID magnetometer at temperatures in the range 2-300 K. In a glove box, the polycrystalline samples were transferred to Kel-F capsules, which were then sealed with an O-ring cap, and the capsules were then placed in plastic straws. One end of the straw was then sealed with a cap, and the other end was sealed with Blu-Tac. The straw was then sealed in a Schlenk tube and taken to the magnetometer. The straw was removed from the Schlenk tube and the Blu-Tac quickly replaced with the carbon fibre rod, and then the sample was quickly transferred to the purged sample space of the MPMS.

X-ray crystallography

The experiments were carried out at an Agilent Technologies SuperNova A CCD diffractometer and analytical absorption corrections were applied.[3] The structures were solved by SIR-97[4] and refined with ShelX-97 (full-matrix least-squares on F^2)[5] employing the Olex^2 software.[6]

Table S1. Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{40}H_{60}P_4Cr_4$	$C_{30}H_{45}As_2Cr_3$
Formula weight	872.76	711.50
T/K	123.0(1)	123.0(1)
λ/Å	1.54178 (Cu)	1.54178 (Cu)
Crystal system	tetragonal	orthorhombic
Space group	*I*	*Pbca*
a/Å	11.9954(1)	15.3898(3)
b/Å	11.9954(1)	18.4053(3)
c/Å	13.9537(3)	21.8004(4)
V/Å^3	2007.79(5)	6175.05(19)
Z	2	8
ρ_{calc}/Mg m^{-3}	1.444	1.531
μ_{calc}/mm^{-1}	10.395	11.039
Crystal size/mm^3	0.07 × 0.05 × 0.04	0.29 × 0.17 × 0.13
Crystal colour and shape	dark brown octahedron	dark brown octahedron
2θ range for data collection/°	9.72 to 149.00	8.12 to 148.54
Reflections collected	5961	119504
Independent reflections	1985 [R_{int}=0.0339]	6281 [R_{int}=0.0419]
Completeness/%	99.1	99.8
Data / restraints / parameters	1985/0/115	6281/0/331
Goodness-of-fit on F^2	1.072	1.031
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0356$, $wR_2 = 0.0922$	$R_1 = 0.0280$, $wR_2 = 0.0754$
R indices (all data)	$R_1 = 0.0363$, $wR_2 = 0.0929$	$R_1 = 0.0284$, $wR_2 = 0.0757$
Largest diff. peak and hole/e.Å^{-3}	0.47/–0.49	0.47/–0.92
Flack parameter	0.494(7)	–

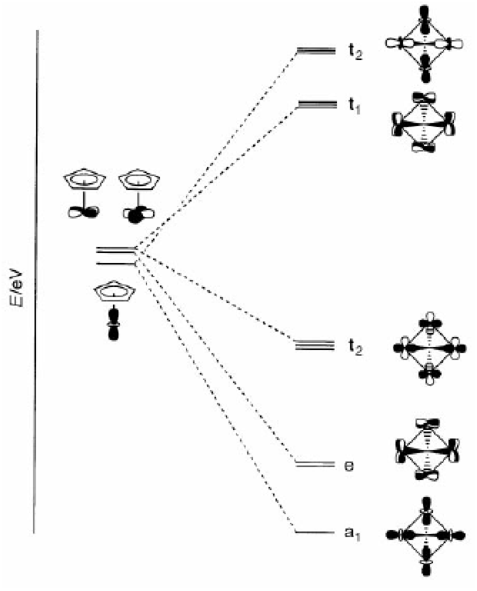

Figure S6. Schematic molecular orbital energy level diagram for **1**, from *J. Chem. Soc., Dalton Trans*. **1999**, 1393 (manuscript reference 23c) for cubanes of the type $[(\eta^5\text{-Cp})M(\mu_3\text{-S})]_4$ (M = transition metal).

Density Functional Theory Calculations on 1 and 2

For computational details see text.

Table S2. Relative energies of the different spin multiplicities of **1**, calculated at the PBE/TZVP level of theory.

Total spin, S	Spin multiplicity	Relative energy / kJ mol^{-1}
		PBE/TZVP
4	9	178.6
3	7	99.3
2	5	0.0
1	3	19.9
0	1	25.4

Table S3. Relative energies of the different spin multiplicities of **2**, calculated at the PBE/TZVP and PBE0/TZVP levels of theory.

Total spin, S	Spin multiplicity	Relative energy / kJ mol^{-1}	
		PBE/TZVP	PBE0/TZVP
9/2	10	0.0	0.0
7/2	8	66.0	104.6
5/2	6	73.7	117.7
3/2	4	55.0	69.1
1/2	2	82.2	120.5

Table S4. Calculated Mayer bond orders (MBO) for the electronic ground-state of **1** with $S = 2$.

Bond type	MBO range (PBE/TZVP)
Cr–P	0.94-1.00
Cr–C(ring)	0.37-0.41
Cr–Cr	0.22-0.24

Table S4. Calculated Mayer bond orders for the electronic ground-state of **2** with $S = 9/2$.

Bond type	MBO range	
	PBE/TZVP	PBE0/TZVP
Cr–As	0.82-0.98	0.76-0.94
Cr–C(ring)	0.21-0.45	0.21-0.43
Cr–Cr	0.06-0.10	0.07-0.12

References

1. G. Fritz, H. Schäfer, W. Holderich, *Z. Anorg. Allg. Chem.*, **1974**, *407*, 266.
2. R. L. Wells, M. F. Self, J. D. Johansen, J. A. Laske, S. R. Aubuchon, L. J. Jones III, *Inorg. Synth.*, **1997**, *31*, 150.
3. Agilent Technologies **2006-2013**, CrysAlisPro Software system, different versions, Agilent Technologies UK Ltd, Oxford, UK; R. C. Clark, J. S. Reid, *Acta Cryst.* **1995**, *A51*, 887.
4. A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Cryst.* **1993**, *26*, 343.
5. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009** *42*, 339.