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Transmetalation of Chromocene by Lithium-Amide, -Phosphide, and -Arsenide Nucleophiles

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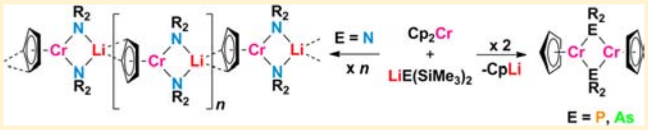
Ⓢ *Supporting Information*



ABSTRACT: The pnictogen-centered nucleophiles LiE(SiMe$_3$)$_2$ (E = N, P, or As) substitute a cyclopentadienide ligand of chromocene (Cp$_2$Cr), with elimination of lithium cyclopentadienide, to give the series of pnictogen-bridged compounds [(μ:η^2:η^5-Cp)Cr{μ-N(SiMe$_3$)$_2$}$_2$Li] (**1**) and [(η^5-Cp)Cr{μ-E(SiMe$_3$)$_2$}]$_2$, with E = P (**2**) or E = As (**3**). Whereas **1** is a heterobimetallic coordination polymer, **2** and **3** are homometallic dimers, with the differences being due to a structure-directing influence of the hard or soft character of the bridging group 15 atoms. For compound **1**, the experimental magnetic susceptibility data were accurately reproduced by a single-ion model based on high-spin chromium(II) ($S = 2$), which gave a g-value of 1.93 and an axial zero-field splitting parameter of $D = -1.83$ cm^{-1}. Determinations of phosphorus- and arsenic-mediated magnetic exchange coupling constants, J, are rare: in the dimers **2** and **3**, variable-temperature magnetic susceptibility measurements identified strong antiferromagnetic exchange between the chromium(II) centers, which was modeled using the spin Hamiltonian $H = -2J(S_{\mathrm{CrA}}\cdot S_{\mathrm{CrB}})$, and produced large coupling constants of $J = -166$ cm^{-1} for **2** and -77.5 cm^{-1} for **3**.

■ INTRODUCTION

Exchange coupling interactions between transition metal ions are of fundamental importance in molecular magnetism.[1] Such interactions have been studied extensively for over half a century following the pioneering work of Bleaney and Bowers on copper(II) acetate dimers,[2] and they have recently taken on additional significance with the development of transition metal single-molecule magnets.[3] With the notable exception of thiolate ligands,[4] the use of ligands with soft donor atoms in molecular magnetism is uncommon, and exchange coupling mediated by phosphorus- and, particularly, arsenic-donor ligands has not been investigated to any significant extent. The potential benefits of exploring the influence of, for example, phosphide and arsenide ligands (R$_2$E$^-$, E = P or As) on the magnetic properties of transition metal ions was highlighted by our study of the manganese(II) dimers [CpMn{μ-E(SiMe$_3$)$_2$}]$_2$ (E = P or As, Cp = cyclopentadienyl), in which spin-crossover (SCO) and simultaneous antiferromagnetic coupling were identified.[5] In the case of the arsenic-bridged compound [CpMn{μ-E(SiMe$_3$)$_2$}]$_2$, the magnetic susceptibility measurements revealed a two-step SCO from the $S = 5/2$ to the $S = 3/2$ spin states of the two manganese(II) ions, and the first SCO step around 96–105 K even showed hysteresis. Also noteworthy was that the antiferromagnetic exchange coupling in the *P*-bridged dimer, although weak with $J = -13.5$ cm^{-1}, was almost an order of magnitude stronger than in the *As*-bridged analogue, with $J = -1.5$ cm^{-1}. A recent study by Wright and co-workers on the reaction of manganocene with *t*-butylphosphine observed formation of the dimer [CpMn(P^{t}BuH$_2$)(μ-P^{t}BuH)]$_2$, in which the introduction of stronger-field primary phosphine and μ-phosphido ligands led to a high-spin to low-spin switch of the manganese(II) ions, with concomitant formation of an unusual Mn–Mn bond.[6]

Thus, there is growing evidence that soft group 15 donor atoms can influence the electronic structure of transition metal ions in unusual ways. To develop our understanding of magnetic exchange between transition metal ions mediated by nitrogen and, in particular, by phosphorus and arsenic, we now turn our attention to chromium(II). Chromium(II) was targeted because chromocene, Cp$_2$Cr, shows similar reactivity to manganocene with respect to Cp ligand substitution by strong nucleophiles; hence a series of isostructural and therefore comparable compounds could be accessible. An additional reason for selecting chromium(II) is that studies of exchange-coupled compounds based on this ion are surprisingly rare. Thus, we report the synthesis, structures, and magnetic properties of the chromium–lithium amido coordination polymer [CpCr{μ-N(SiMe$_3$)$_2$}$_2$Li]$_\infty$ (**1**), and the phosphorus- and arsenic-bridged chromium(II) dimers [CpCr{μ-E(SiMe$_3$)$_2$}]$_2$, with E = P (**2**) and E = As (**3**). The chromium(II) ions in the dimers **2** and **3** are coupled by strong

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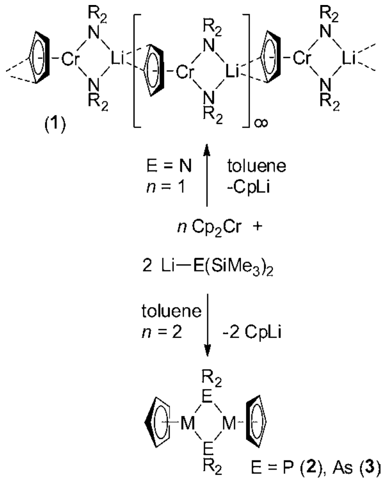
antiferromagnetism, and modeling of the magnetic susceptibility data enabled *J* coupling constants for phosphorus- and arsenic-mediated exchange to be determined for only the second time.

■ SYNTHESIS AND STRUCTURES OF 1−3

Compounds **1**−**3** were synthesized by exploiting the tendency of cyclopentadienyl ligands in "electron deficient" metallocenes to be substituted by strong nucleophiles. Thus, 16-electron Cp_2Cr reacts with the lithium complexes of bis(trimethylsilyl)-amide, -phosphide, and -arsenide, $LiE(SiMe_3)_2$ (E = N, P, As), with elimination of CpLi, according to Scheme 1. The structures of **1**−**3** were determined by X-ray diffraction.

Scheme 1. Synthesis of 1−3 (R = $SiMe_3$)



The outcome of the reaction that results in the formation of **1** is the same when the ratio of Cp_2Cr to $LiN(SiMe_3)_2$ is 1:2 or 1:1. Two unique molecules of $[(\mu{:}\eta^2{:}\eta^5\text{-Cp})Cr\{\mu\text{-N}(SiMe_3)_2\}_2Li]$ are found in the unit cell (**1a** and **1b**), which assemble into coordination polymers, that is, $[\mathbf{1a}]_\infty$ and $[\mathbf{1b}]_\infty$, through $\mu{:}\eta^2{:}\eta^5$-bridging modes of the Cp ligand (Figure 1 and Supporting Information, Figure S1). In **1a**, the η^5-coordination of the Cp ligand to Cr(1) produces Cr−C bond distances in the range 2.359(5)−2.401(4) Å (average 2.381 Å), and the Cr(1)−N(1) and Cr(1)−N(2) bond lengths are 2.0926(17) and 2.1025(19) Å, respectively (Table 1). Assuming that an η^5-Cp ligand occupies three coordination sites, the chromium(II) centers in **1** are five-coordinate and have formal valence electron counts of 14. The Li(1)−N(1) and Li(1)−N(2) bonds lengths are 2.079(4) and 2.065(4) Å, respectively, and the rhombic shape of the CrN_2Li ring is reflected in the N−Cr−N, N−Li−N, Cr−N(1)−Li, and Cr−N(2)−Li angles of 96.28(7), 97.9(2), 82.86(13), and 82.96(13)°. Molecules of **1a** (and **1b**) therefore have approximate C_{2v} point symmetry, although the slight differences in bond lengths show that the two "halves" of the molecule are not strictly symmetry-related. The two relatively short Li−C distances of 2.592(6) and 2.655(6) Å, compared to three much longer distances in the range 3.399(4)−3.769(6) Å, are within the upper limit of Li−C distances recorded in the Cambridge Structural Database (CSD) for lithium cyclopentadienides,[7] suggesting that the bridging interaction between nearest neighbor molecules of **1a** (and **1b**) can be described as $\mu{:}\eta^2$-Cp. The ^1H NMR spectrum of **1** recorded in toluene-D_8 confirms the presence of the Cp ligand ($\delta = 23.41$ ppm); however, a sharp resonance at $\delta = 1.55$ ppm and a broad resonance at 2.85 ppm, likely due to the trimethylsilyl groups, were also observed (Supporting Information, Figure S2). The ^7Li NMR spectrum of **1** in toluene-D_8 (Supporting Information, Figure S3) features a weak, broad resonance with a chemical shift of $\delta = 140.3$ ppm: this is substantially downfield relative to the ^7Li chemical shifts reported for $[Li\{N(SiMe_3)_2\}]$ in various solvents and at various concentrations, which are typically in the range of $\delta \approx \pm 1$ ppm.[8] The position and appearance of ^7Li resonance in particular suggests that a paramagnetic lithium-containing complex is present in solution, although there is no direct evidence to suggest that the solid-state structure of **1** is preserved in toluene solution.

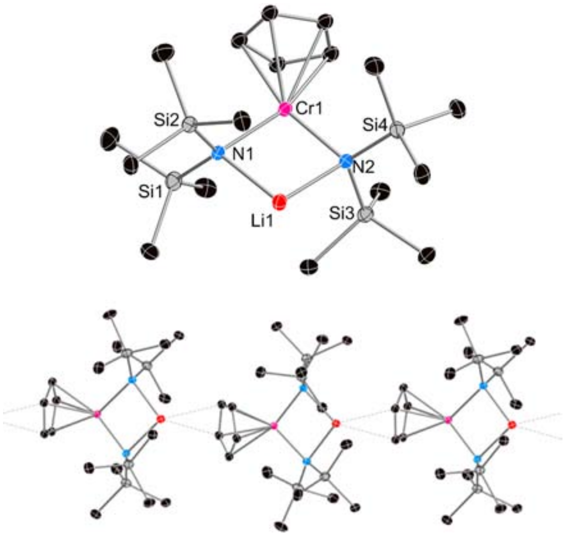


Figure 1. Thermal ellipsoid plot (30% probability) of the molecular structure of **1a**, and a segment of the coordination polymer structure of $[\mathbf{1a}]_\infty$. Unlabeled atoms are carbon (black) and silicon (gray).

As with compound **1**, the syntheses of **2** and **3** were achieved using chromium:pnictogen ratios of 1:1 or 1:2. X-ray crystallography revealed that the molecular structures of **2** and **3** are very similar, each consisting of pnictogen-bridged dimers with the general formula $[(\eta^5\text{-Cp})Cr\{\mu\text{-E}(SiMe_3)_2\}]_2$ (E = P or As). The dimers have molecular D_{2h} symmetry, and the $\{CpCrE_2\}$ coordination environments have approximate C_{2v} symmetry (Figures 2, Supporting Information, Figures S4, S6), and each chromium(II) in **2** and **3** is formally five-coordinate and has a valence electron of 14, as in **1**.

The phosphide-bridged dichromium compound $[CpCr\{\mu\text{-P}(SiMe_3)_2\}]_2$ (**2**) crystallizes with two independent molecules in the unit cell, **2a** and **2b**, which are iso-structural (Figures 2, Supporting Information, Figure S4). The structure of **2a** is a dimer in which the two Cr(II) atoms are bridged by two μ-$[(Me_3Si)_2P]^-$ ligands. The resulting Cr(1)−P(1) and Cr(1)−P(1A) bond lengths are 2.3814(9) and 2.3864(9) Å, respectively, and the P−Cr−P and Cr−P−Cr bond angles are 99.98(3) and 80.02(3)° (Table 1). A search of the CSD for molecular structures containing cyclic $\{Cr_2(\mu\text{-}P_2)\}$ structural units reveals Cr−P bond distances in the range 2.254−2.763 Å, with the mean average of 2.407 Å being similar to the Cr−P distances in **2a** and **2b**.[7] The cyclopentadienyl ligands in **2a** are η^5-coordinated to the chromium atoms, with Cr−C distances in the range 2.276(17)−2.33(2) Å (average 2.292 Å). The Cr(1)···Cr(1A) separation in **2a** is 3.066(1) Å (3.086 Å in **2b**).

Table 1. Selected Interatomic Distances and Bond Angles for 1−3

	1a/1b	2a/2b	3a/3b
Cr−E	2.0926(17), 2.1025(19)/2.1001(19), 2.0841(17)	2.3814(9), 2.3864(9)/2.3858(9), 2.3869(9)	2.4963(5), 2.4992(5)/2.5011(5), 2.5010(4)
Cr−C	2.382(5)−2.401(4)/2.357(3)−2.397(3)	2.276(17)−2.33(2)/2.244(9)−2.297(13)	2.270(11)−2.327(11)/2.281(9)−2.325(11)
Li−N	2.079(4), 2.065(4)/2.055(4), 2.078(4)		
Li−C	2.592(6), 2.655(6) 2.584(5), 2.677(5)		
Cr···M[a]	2.761(4)/2.755(4)	3.066(1)/3.086(1)	3.394(1)/3.419(1)
E−Cr−E	96.28(7)/96.22(7)	99.98(3)/99.43(3)	94.41(2)/93.79(2)
Cr−E−M[a]	82.86(13), 82.96(13)/83.05(13), 82.90(13)	80.02(3)/80.57(3)	85.59(1)/86.21(1)

[a] M = Li in **1**, M = Cr in **2** and **3**

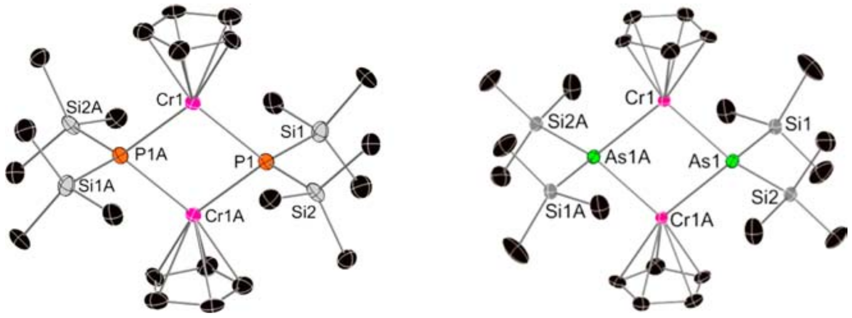


Figure 2. Thermal ellipsoid plots (30% probability) of the molecular structures of **2a** and **3a**. Hydrogen atoms not shown.

The arsenide-bridged dichromium compound [CpCr{μ-As(SiMe$_3$)$_2$}]$_2$ (**3**) also crystallizes with two iso-structural molecules in the unit cell, **3a** and **3b**, (Figure 2, Supporting Information, Figure S6). The Cr(1)−As(1) and Cr(1)−As(1A) distances in **3a** are 2.4963(5) and 2.4992(5) Å, which result in a much longer Cr(1)···Cr(1A) separation of 3.394(1) Å (3.419(1) Å in **3b**) compared to **2a**/**2b**. The Cr−C bond lengths in **3a** are 2.270(11)−2.327(11) Å (average 2.295 Å), and As−Cr−As and Cr−As−Cr bond angles of 94.41(2)° and 85.59(1)°, respectively, were found in **3a**. Surprisingly, very few arsenide-bridged dichromium compounds have been structurally characterized: the example most closely related to **3** is the metal−metal bonded dichromium(I) compound [Cr(μ-AsMe$_2$)(CO)$_4$]$_2$, which features a Cr−As distance of 2.421(2) Å.[9] The Cr(1)···Cr(1A) distances of 3.066(1) Å and 3.394(1) Å in **2a** and **3a**, respectively, (and the analogous distances in **2b** and **3b**, Table 1) lie within the range of chromium−chromium bond distances according to the CSD: range 1.858−3.471 Å, average 2.761 Å, standard deviation 0.218 Å.[7] However, whereas the Cr···Cr distances in **2a** and **2b** are considerably less than the upper limit of a chromium−chromium bond, the distances in **3a** and **3b** are close to the upper limit. Although the possibility of Cr−Cr bonding in **2a** and **2b** in particular cannot be completely discounted based on X-ray crystallography, the magnetic susceptibility measurements on bulk samples of **2** suggest that the chromium(II) centers are exchange coupled via the phosphide bridge and are not directly bonded to each other (see below). The solution-phase ^{1}H NMR spectra of **2** and **3** in benzene-D$_6$ are consistent with the empirical formula [CpCr{E(SiMe$_3$)$_2$}], with broad resonances for the Cp environment being observed at 98.81 ppm in **2** and 34.01 ppm in **3**, and the trimethylsilyl environments occurring with chemical shifts of 3.35 ppm and 2.38 ppm in **2** and **3**, respectively (Supporting Information, Figures S5 and S7).

The only variable in the reactions that produce **1**−**3**, and hence results in the structure of **1** being different to that of the isostructural dimers **2** and **3**, is the group 15 element. The most likely explanation for the contrasting outcomes is therefore the varying hard/soft character of the amide, phosphide, and arsenide donor atoms: rather than eliminate the hard lithium cations as CpLi, the harder *N*-donor ligands in **1** remain coordinated to lithium as well as chromium. In contrast, the softer *P*- and *As*-donors in **2** and **3** preferentially coordinate to the softer chromium(II) centers, and CpLi is precipitated from the reaction. This hypothesis points to a general pnictogen-based structure-directing influence in systems of this type.

■ MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Variable-temperature magnetic susceptibility measurements and isothermal magnetization versus field measurements were conducted on polycrystalline samples of **1**−**3**. In the case of **1**, the molar magnetic susceptibility was determined in the temperature range 2−300 K in fields of H_{dc} = 1000 and 5000 G; however, the outcome was the same irrespective of the field strength. The value of $\chi_M T$ at 300 K is 2.80 cm^3 K mol^{-1}, and is essentially independent of temperature down to about 10 K, when a small decrease to 2.35 cm^3 K mol^{-1} was observed, most likely due to the effects of zero-field splitting (Supporting Information, Figure S8). The isothermal magnetization (M) versus field data were collected at 1.8 and 4 K, with field strengths in the range H = 0−7 T, and for each isotherm the $M(H)$ curves reach saturation approximately at M = 3.5 μB (Supporting Information, Figure S9), in agreement with the presence of four unpaired electrons on the Cr(II) centers. The $\chi_M T(T)$ data and the $M(H)$ curves were accurately reproduced by a spin Hamiltonian (see Supporting Information) that used a chromium(II) ion with S = 2, a g-value of 1.93, and an axial zero-field splitting parameter of D = −1.8 cm^{-1}. The results obtained on **1** are similar to those previously reported g- and D-values for chromium(II) complexes.[10]

For **2** and **3**, the graphs of $\chi_M T$ against T (Figure 3) show that $\chi_M T$ at the high-temperature limit of the experiment is 0.60 cm^3 K mol^{-1} for **2** and is 1.24 cm^3 K mol^{-1} for **3**, both of which are significantly less than the spin-only value of 6.0 cm^3 K mol^{-1} expected for two noninteracting high-spin Cr(II) ions

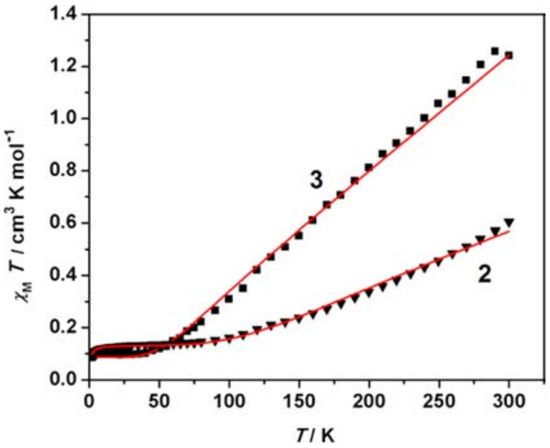


Figure 3. Temperature dependence of $\chi_M T$ for compounds **2** (triangles) and **3** (squares). The red lines represent a theoretical fit of the experimental data (see text for parameters).

(assuming $g = 2$). Upon cooling, $\chi_M T$ for **2** and **3** decreases continuously to reach a value of almost zero at 2 K, which indicates strong antiferromagnetic coupling between the chromium centers, and leads to a diamagnetic ($S = 0$) spin ground state. The nonzero value of $\chi_M T$ at 2 K is likely to be due to the presence of small amounts of a paramagnetic impurity in samples of **2** and **3**.

To quantify the strength of the antiferromagnetic exchange in **2** and **3**, the experimental susceptibility data were fitted with the Heisenberg−Dirac−Van Vleck (HDVV) model,[1] adapted for dimers consisting of two $S = 2$ metal ions. To account for intermolecular magnetic exchange, a $(T - \theta)$ term, where θ is the Weiss constant, was included. The spin Hamiltonian formalism $H = -2J(S_{CrA} \cdot S_{CrB})$, where J is the exchange coupling constant and S_{CrA} and S_{CrB} refer to the spin of the two Cr(II) ions in each dimer, was used.[11] Very good fits to experiment were obtained for both dichromium compounds, using $g = 2$ and $S_{Cr} = 2$, and the following parameters: for **2**, $J = -166$ cm^{-1}, $\theta = -0.7$ K, and $\rho = 0.022$; and for **3**, $g = 2$; $J = -77.5$ cm^{-1}, $\theta = -0.4$ K, and $\rho = 0.014$. The parameter ρ represents the proportion of the paramagnetic impurity in each sample, which was modeled as a monomeric Cr(II) species. The origin of the minor paramagnetic impurity is not immediately obvious; however, the same parameters that were employed to model the susceptibility data produced good fits of the isothermal magnetization versus field plots for **3** (Supporting Information, Figure S10), hence the impurity is unlikely to be an oxidized species.

The temperature dependence of the magnetic susceptibilities in **2** and **3** are qualitatively similar, the major difference being that the antiferromagnetic exchange in **2** is very strong, and more than twice as strong as that in **3**. Given that orbital overlap plays an important role in magnetic exchange, the difference in the two J-values is most likely because the Cr−As bonds in **3** are approximately 0.11 Å longer than the Cr−P bonds in **2**. This is also reflected in the Cr···Cr separations in **3** being on average 0.33 Å longer than those in **2**. In **2**, the Cr−P−Cr bridging angles are also approximately 5−6° more acute than the Cr−As−Cr angles in **3**, and this small structural difference may also contribute to the different magnitude of the exchange coupling constants. The stronger exchange coupling in **2** relative to **3** is also consistent with our observations on the manganese(II) analogues $[CpMn\{E(SiMe_3)_2\}]_2$, where coupling constants of $J = -13.5$ cm^{-1} and -1.5 cm^{-1} were determined for E = P or As, respectively.[5] The much smaller couplings in the manganese analogues is presumably due to the greater ionic character of the Mn−E bonds.[12]

Diamagnetic, polymetallic compounds of chromium in which the metal centers are bridged by *P*- or *As*-donor ligands are well-known. The range of bridging heavy-pnictogen ligands is quite broad, and includes poly pnictogen ligands $[E_n]^{x-}$ and ligands of the type $[R_2E]^-$.[13,14] Such compounds have typically been studied for their intrinsically interesting coordination chemistry and, in some cases, their applications in alkene polymerization catalysis.[14c] Studies of the magnetism in paramagnetic analogues are limited to very few examples, and no exchange coupling constants have been disclosed. Although experimental studies of exchange coupling between transition metals involving phosphorus- or arsenic-*containing* ligands are well-known, for example, phosphonates and arsonates,[15] to the best of our knowledge the exchange coupling constants in compounds **2** and **3** are only the second examples to be determined with phosphorus or arsenic as the bridging atom. In the context of magnetic exchange, by far the most extensively studied chromium compounds are oxygen-bridged cages of chromium(III), in which the metal ions can either couple ferromagnetically or, more commonly, antiferromagnetically.[16] The exchange coupling in **2** and **3** is considerably stronger than the coupling in oxygen-bridged chromium(III) compounds, where coupling constants are typically only several wavenumbers. Studies of exchange-coupled chromium(II) compounds are much less common, presumably because of a tendency to form chromium−chromium bonds, and measurements of exchange coupling constants involving this ion are therefore rare.[17] The chromium(II) centers in the 26-valence-electron triple-decker complex $[\{(\eta^5\text{-Cp*})Cr\}_2(\mu{:}\eta^5{:}\eta^5\text{-}P_5)]^+$, which contains the *cyclo*-$[P_5]^-$ ligand, are thought to be coupled antiferromagnetically; however, it was not possible to determine a J-value for this compound owing to the simultaneous occurrence of a spin crossover at lower temperatures.[18] Fryzuk et al. reported five-coordinate dichromium(II) compounds with chloride or hydride bridges in which the metals couple antiferromagnetically; in the case of the chloride bridge an exchange coupling constant of $J = -12.4$ cm^{-1} was determined, however for the hydride bridge very strong coupling with $J = -139$ cm^{-1} was observed.[19] In the hydride-bridged, mixed-valence compound $[(\eta^5\text{-}C_5Me_4Et)_4(Cr^{III})_3(Cr^{II})(\mu\text{-}H)_5(\mu_3\text{-}H)_2]$ reported by Heintz et al., the effective magnetic moment is temperature-independent, which implies that the J-value is in excess of several hundred wavenumbers.[20] The propensity of the hydride ligand for promoting very strong exchange is well-known; hence, it is noteworthy that the phosphorus-mediated exchange coupling between the chromium(II) centers in **2** can be stronger even than in some hydride-bridged chromium(II) compounds.

■ CONCLUSION

The pnictogen-centered nucleophiles $LiE(SiMe_3)_2$ (E = N, P, As) displace a Cp ligand from chromocene, giving the heterodimetallic compound $[(\mu{:}\eta^2{:}\eta^5\text{-}Cp)Cr\{\mu\text{-}N(SiMe_3)_2\}_2Li]$ (**1**) and the homometallic dimers $[(\eta^5\text{-}Cp)M\{\mu\text{-}E(SiMe_3)_2\}]_2$ with E = P (**2**) or As (**3**). The inclusion of lithium into the coordination polymer structure of **1** is due to the hard−hard lithium−nitrogen interactions, whereas the softer phosphorus and arsenic donors in **2** and **3** preferentially coordinate only to chromium. The magnetic properties of **1**

Table 2. Crystal Data and Structure Refinement for Compounds 1−3

	1	2	3
empirical formula	$C_{17}H_{41}CrLiN_2Si_4$	$C_{22}H_{46}Cr_2P_2Si_4$	$C_{22}H_{46}As_2Cr_2Si_4$
formula weight	444.82	588.89	676.79
T/K	123(1)	123(1)	123(1)
λ/Å	1.54178	1.54178	1.54178
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	16.7360(2)	9.0064(10)	9.1939(3)
b/Å	14.8988(2)	10.8050(13)	10.9303(4)
c/Å	21.2558(3)	17.1383(18)	17.3201(7)
α/deg		90.468(9)	91.042(3)
β/deg	106.434(2)	90.944(9)	90.828(3)
γ/deg		105.076(10)	106.057(3)
V/Å^3	5083.53(13)	1610.0(3)	1672.01(11)
Z	8	2	2
density (calcd.)/Mg m^{-3}	1.162	1.215	1.344
crystal size/mm^3	0.32 × 0.19 × 0.07	0.15 × 0.03 × 0.02	0.13 × 0.09 × 0.05
θ range /deg	2.96−66.60	4.24−67.5	4.21 to 76.39
reflections collected	28031	11022	13531
independent reflections	8792 [R(int) = 0.0344]	6372 [R(int) = 0.0399]	6764 [R(int) = 0.0210]
completeness/%	97.6	99.6	96.3
data/restraints/parameters	8792/0/442	6372/308/529	6764/500/373
goodness-of-fit on F^2	0.919	1.009	1.136
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0400	R_1 = 0.0409	R_1 = 0.0245
	wR_2 = 0.1053	wR_2 = 0.0919	wR_2 = 0.0738
R indices (all data)	R_1 = 0.0448	R_1 = 0.0603	R_1 = 0.0291
	wR_2 = 0.1074	wR_2 = 0.1017	wR_2 = 0.0773
largest diff. peak and hole/e Å^{-3}	0.696, −0.446	0.366, −0.524	0.364, −0.416

were interpreted in terms of a single-ion chromium(II) system, and simulation of the susceptibility and magnetization data produced a zero-field splitting parameter of $D = -1.8$ cm^{-1} with a g-value of 1.93. Compounds **2** and **3** display strong antiferromagnetic coupling between their chromium(II) centers, with exchange coupling constants of $J = -166$ and -77.5 cm^{-1}, respectively. The coupling in **2** is particularly strong, and highlights that phosphorus-mediated exchange can be stronger than the exchange mediated by ligands that are well-known for promoting very strong exchange, such as hydride.

■ EXPERIMENTAL SECTION

General 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 argon that had been passed through several columns of various drying agents and a heated copper catalyst. Chromocene,[21] lithium bis(trimethylsilyl)phosphide[22] and lithium bis(trimethylsilyl)arsenide[23] were synthesized according to literature procedures. Compounds **1**−**3** are pyrophoric when dry and in the case of **2** and **3** a most unsupportable odor is produced. Paramagnetic ^{1}H NMR spectra were acquired using a Bruker Avance III spectrometer across a chemical shift range of ±250 ppm. NMR spectra were acquired using a Bruker Avance III spectrometer operating at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C), and 155.51 MHz (^{7}Li). ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$, and ^{7}Li chemical shifts are reported relative to an external standard of aqueous LiCl.

Compound 1. A solution of Cp_2Cr (0.10 g, 0.55 mmol) in toluene (10 mL) was cooled to −78 °C, and a solution of $[(Me_3Si)_2NLi]$ (0.34 g, 1.10 mmol) in toluene (20 mL) was added dropwise. The blue-black reaction mixture was warmed to room temperature and stirred overnight. The resulting very dark blue solution was filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at −28 °C produced a crop of dark blue block-like crystals (0.05 g, 21% based on chromium). Analysis calculated for $C_{17}H_{41}N_2Si_4LiCr$: C 45.90, H 9.29, N 6.30; found C 45.62, H 8.99, N 6.11. ^{1}H NMR (benzene-D$_6$, 400.13 MHz, 298 K, δ/ppm): 23.41, Cp, fwhm 1073 Hz; 2.85, $SiMe_3$, fwhm 149 Hz; 1.55, $SiMe_3$, fwhm 40 Hz. ^{7}Li NMR (pyridine-D$_5$, 155.51 MHz, 298 K, δ/ppm): −5.11.

Compound 2. A solution of Cp_2Cr (0.10 g, 0.55 mmol) in toluene (10 mL) was cooled to −78 °C, and a solution of $[(Me_3Si)_2PLi\cdot(thf)_{1.8}]$ (0.17 g, 0.55 mmol) in toluene (10 mL) was added dropwise. The dark red reaction mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at −28 °C produced a crop of dark red block-like crystals (0.08 g, 50% based on chromium). Analysis calculated for $C_{22}H_{46}P_2Si_4Cr_2$: C 44.87, H 7.87, P 10.52; found C 44.23, H 7.83, P 10.36. ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K, δ/ppm): 98.82, low intensity; 3.35, fwhm 219.5 Hz, Cp; 0.28, fwhm 5.2 Hz, singlet, $SiMe_3$. No signal was observed in the ^{31}P NMR spectrum.

Compound 3. A solution of Cp_2Cr (0.10 g, 0.55 mmol) in toluene (10 mL) was cooled to −78 °C, and a solution of $[(Me_3Si)_2AsLi\cdot(thf)_2]$ (0.20 g, 0.55 mmol) in toluene (10 mL) was added dropwise. The dark red reaction mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at

−28 °C produced a crop of dark red block-like crystals (0.08 g, 43% based on chromium). Analysis calculated for $C_{22}H_{46}As_2Si_4Cr_2$: C 39.04, H 6.85; found C 39.20, H 6.72. ^1H NMR (benzene-d_6, 400.13 MHz, 298 K, δ/ppm): 34.02, very low intensity, fwhm 466.7 Hz; 2.38, fwhm 82.1 Hz, Cp; 0.28, fwhm 5.3 Hz, singlet, $SiMe_3$.

X-ray Crystallography. The experiments were carried out using an Agilent Gemini R Ultra (**1**) or an Agilent SuperNova (**2**, **3**), and either a multiscan[24] (**2**) or an analytical[25] (**3**) absorption correction was applied to the data (Table 2). The structures of **2** and **3** were solved with SuperFlip,[26] and SHELXL[27] was used for the refinement (Table 2). Disorder is present in all of the structures. The affected $SiMe_3$ and Cp groups were refined employing SAME, SIMU, DELU, and ISOR restraints. The hydrogen atoms were constrained to the corresponding carbon atom and refined according to the riding model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data on **1**−**3** in CIF format. Illustrations of molecular structures of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**. ^1H NMR spectra and details of magnetic susceptibility measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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