Cover Page for Supporting Information

Synthesis and reactivity of asymmetric Cr(I) dinitrogen complexes

supported by cyclopentadienyl-phosphine ligands

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1) General Methods

Unless otherwise noted, all manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or glovebox techniques. Solvents were purified by an Mbraun SPS-800 Solvent Purification System. KHMDS, "BuLi, 3-hexyne, 2-(2-bromophenyl)acetaldehyde and CrCl₂ were obtained from Strem, Aldrich, TCI, Alfa Aesar, Acros, Adamas-beta, J&K and others. PhSiD₃ was prepared according to the reported method.^[1]

¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker ARX500 spectrometer (FT, 500 MHz for ¹H; 125 MHz for ¹³C; 202 MHz for ³¹P) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Solarix XR FTMS mass spectrometer using ESI (electrospray ionization) source. Susceptibility experiment was performed on Quantum Design MPMS XL-5 SQUID (superconducting quantum inference device) magnetometer on crystalline sample. Elemental analyses were tested on a Vario EL elemental analyzer at the Analytical Center of Peking University. Infrared Spectroscopy was recorded on a Bruker Tensor 27 using a KBr pellet. Using 2-(2-bromophenyl)acetaldehyde instead of 2-bromobenzaldehyde, the neutral cyclopentadienyl-phosphine ligand **L** was prepared according to our reported procedures,^[2] as a mixture of double-bond isomers which cannot be separated from each other.

2) Experimental Details

Preparation of the ligands (1):



A typical procedure for the preparation of 1: Under an atmosphere of nitrogen, the neutral cyclopentadienyl-phosphine ligand (with double-bond isomers, 0.1 mmol) was dissolved in 10 mL Et₂O. Then KHMDS (0.1 mmol in 0.2 mL Toluene) was added in and the mixture was stirred for 12 h. After reaction, precipitate was washed by Et₂O (The double-bond isomers could not be deprotonated and thus would be washed by Et₂O) and dried *in vacuo* to give pure target compounds as yellow powders.

E I a: Yellow powder, isolated yield 25 % (0.025 mmol, 12.3 mg). Crystal suitable for X-ray diffraction was grown from the mixture of THF and toluene at room temperature. ¹H NMR (500 MHz, d^8 -THF) δ: 0.79 (t, J = 7.5 Hz, 6H, CH₃), 1.06 (t, J = 7.5 Hz, 6H, CH₃), 2.23-2.27 (m, 4H, CH₂), 2.45-2.50 (m, 4H, CH₂), 3.94 (s, 2H, CH₂), 6.57-6.60 (m, 1H, CH), 6.82-6.85 (m, 1H, CH), 7.01-7.05 (m, 2H, CH), 7.26-7.34 (m, 10H, CH); ¹³C NMR (125 MHz, d^8 -THF) δ: 19.54 (2CH₃), 20.00 (2CH₃), 20.78 (2CH₂), 20.83 (2CH₂), 32.02 (d, J = 22.0 Hz, CH₂), 108.19 (d, J = 2.5 Hz, Quant. C), 114.51 (2Quant. C), 115.36 (2Quant. C), 125.29 (CH), 129.11 (2CH), 129.15 (2CH), 129.20 (2CH), 129.26 (2CH), 130.92 (CH), 130.97 (CH), 132.19 (CH), 134.46 (d, J = 7.5 Hz, Quant. C), 135.04 (d, J = 12.5 Hz, 2CH), 139.23 (d, J = 7.5 Hz, 2Quant. C), 152.59 (d, J = 14.0 Hz, Quant. C); ³¹P NMR (202 MHz, d^8 -THF) δ: -13.80.

b Ft Vellow powder, isolated yield 20 % (0.020 mmol, 8.5 mg). Crystal suitable for X-ray diffraction was grown from the mixture of THF and toluene at room temperature. ¹H NMR (500 MHz, d^8 -THF) δ: 0.84 (t, J = 5.0 Hz, 6H, CH₃), 0.93-0.96 (m, 6H, CH₃), 1.07 (t, J = 5.0 Hz, 6H, CH₃), 1.16 (m, 6H, CH₃), 2.09-2.15 (m, 2H, CH), 2.31-2.36 (m, 4H, CH₂), 2.45-2.49 (m, 4H, CH₂), 4.14 (d, J = 4.0 Hz, 2H, CH₂), 6.93-6.96 (m, 1H, CH), 7.00-7.07 (m, 2H, CH), 7.29-7.31 (m, 1H, CH); ¹³C NMR (125 MHz, d^8 -THF) δ: 19.62 (2CH₃), 20.02 (4CH₃), 20.13 (2CH₃), 20.67 (2CH₂), 20.79 (2CH₂), 21.03 (CH), 21.23 (CH), 32.45 (d, J = 26.5 Hz, CH₂), 110.98 (d, J = 20 Hz, Quant. C), 114.39 (2Quant. C), 115.25 (2Quant. C), 124.43 (CH), 128.95 (CH), 130.74 (d, J = 6.3 Hz, CH), 132.02 (d, J = 3.8 Hz, CH), 133.49 (d, J = 22.5 Hz, Quant. C), 155.12 (d, J = 30.0 Hz, Quant. C); ³¹P NMR (202 MHz, d^8 -THF) δ: -8.64. **E Ic**: Yellow powder, isolated yield 23 % (0.023 mmol, 11.6 mg). ¹H NMR (500 MHz, d^8 -THF) δ: 0.83 (t, J = 6.0 Hz, 6H, CH₃), 1.05 (t, J = 6.0 Hz, 6H, CH₃), 1.16-1.36 (m, 10H, CH₂), 1.63-1.68 (m, 6H, CH₂), 1.78 (d, J = 10.5 Hz, 2H, CH), 1.93-1.97 (m, 4H, CH₂), 2.30-2.34 (m, 4H, CH₂), 2.44-2.48 (m, 4H, CH₂), 4.10 (d, J = 3.0 Hz, 2H, CH₂), 6.91-6.93 (m, 1H, CH), 6.98-7.03 (m, 2H, CH), 7.29-7.30 (m, 1H, CH); ¹³C NMR (125 MHz, d^8 -THF) δ: 18.46 (2CH₃), 18.88 (2CH₃), 19.65 (2CH₂), 19.73 (2CH₂), 26.57 (2CH₂), 27.07 (d, J = 6.3 Hz, 2CH₂), 27.21 (d, J = 10.0 Hz, 2CH₂), 29.25 (d, J = 8.0 Hz, 2CH₂), 30.87 (d, J = 15.0Hz, 2CH₂), 31.65 (d, J = 22.0 Hz, CH₂), 34.23 (d, J = 12.4 Hz, 2CH), 109.26 (Quant. C), 113.22 (2Quant. C), 114.04 (2Quant. C), 123.16 (CH), 127.62 (CH), 129.93 (d, J = 4..38 Hz, CH), 130.87 (CH), 131.72 (d, J = 14.9 Hz, Quant. C), 154.23 (d, J = 19.9 Hz, Quant. C); ³¹P NMR (202 MHz, d^8 -THF) δ: -18.18.

Preparation of chromium chloride complexes (2)

A typical procedure for the preparation of 2: Under an atmosphere of nitrogen, the yellow THF solution of **1a** (49.1 mg, 0.1 mmol) was added into the suspension of $CrCl_2$ (12.3 mg, 0.1 mmol) in THF (5 mL) at room temperature. The resultant brown mixture was stirred for 12 h and the solvent was removed and dried *in vacuo*. After the addition of Et₂O (8 mL) to the black residue, the solution was filtered through Celite, and the solvent was removed and dried *in vacuo*. Single crystals of **2a** suitable for Xray crystallography were obtained by recrystallization from Et₂O at -30 °C.



2a: Dark red powder, isolated yield 62 % (0.062 mmol, 33.4 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.1 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, *d*⁸-THF) δ : 0.89 (br), 1.12 (br), 2.78 (br), 3.37 (m), 5.33 (br), 6.30 (br), 7.30 (m), 8.16 (br), 11.52 (br),

13.19 (br), 14.75 (br), 18.63 (br). Anal. Calcd. for C₃₂H₃₆ClCrP: C, 71.30; H, 6.73. Found: C, 71.12; H, 7.17. HRMS calcd. for C₃₂H₃₆ClCrP [M]⁺: 538.1643, found 538.1639. IR (KBr, cm⁻¹) v: 2964 (s), 2930 (s), 2871 (s), 1465 (m), 1436 (s), 1096 (w), 1067 (w), 748 (s), 696 (s), 504 (m).



2c: Dark green powder, isolated yield 46 % (0.046 mmol, 25.4 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.0 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. Magnetic susceptibility (SQUID): $\mu_{eff} = 3.5 \ \mu_B$ at room

temperature. ¹H NMR (500 MHz, d^8 -THF) δ : 0.89 (br), 1.12 (br), 1.29 (br), 3.38 (m), 3.41 (br), 3.58 (br), 5.33 (br), 6.66 (br), 7.30 (br), 8.52 (br), 11.34 (br), 13.45 (br), 16.36 (br), 26.13 (br). Anal. Calcd. for C₃₂H₄₈ClCrP: C, 69.74; H, 8.78. Found: C, 69.24; H, 8.85. HRMS calcd. for C₃₂H₄₈ClCrP [M]⁺: 550.2582, found 550.2583. IR (KBr, cm⁻¹) υ : 2961 (m), 2927 (s), 2854 (m), 1449 (m), 1374 (w), 1267 (w), 895 (w), 751 (w), 525 (w), 441 (w).

Preparation of chromium(I) dinitrogen complexes (3)

A typical procedure for the preparation of 3: Under an atmosphere of nitrogen, potassium graphite (14.9 mg, 0.11 mmol) was added into the solution of 2a (53.9 mg, 0.1 mmol) in THF (5 mL) at room temperature. The resultant dark brown mixture was stirred for 6 h and the solvent was filtered and then dried *in vacuo*. The black residue was washed by hexane (10 mL) and dried *in vacuo* to get the raw product. Single crystals of 3a suitable for X-ray crystallography were obtained by recrystallization from Et₂O at -30 °C.



3a: Black powder, isolated yield 67 % (0.022 mmol, 35.6 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 5.2 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, d^8 -THF) δ : 0.89 (br), 1.12 (br), 1.29 (br), 3.38 (m), 3.41 (br), 3.58 (br), 5.33 (br), 6.81 (br), 7.30 (br), 7.34

(br). Anal. Calcd. for C₉₆H₁₀₈Cr₃N₆P₃: C, 72.30; H, 6.83; N, 5.27. Found: C, 72.15; H, 7.25; N, 4.45. IR (KBr, cm⁻¹) υ(N₂): 1933, 1752.



3b: Black powder, isolated yield 68 % (0.034 mmol, 31.5 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 4.2 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, *d*⁸-THF) δ : -1.90 (br), -0.04 (br), 0.89 (br), 1.11 (br), 1.29 (br), 2.04 (br), 3.38 (m), 3.41 (br), 3.58 (br), 3.84 (br), 5.33 (br),

5.68 (br), 7.13 (m), 7.30 (br), 7.33 (br), 8.05 (br). Anal. Calcd. for C₅₂H₈₀Cr₂N₄P₂: C, 67.36; H, 8.70; N, 6.04. Found: C, 67.51; H, 8.68; N, 5.50. IR (KBr, cm⁻¹) υ(N₂): 1957, 1748.

Preparation of chromium complexes 4-7

A typical procedure for the preparation of 4-7: Under an atmosphere of N_2 , phenylsilane (32.5 mg, 0.3 mmol) was added into the solution of **3a** (159.5 mg, 0.1 mmol) in THF (5 mL) at room temperature. The resultant dark brown mixture was stirred for 12 h and then the solvent was removed *in vacuo*. Single crystals of **4** suitable for X-ray crystallography were obtained by recrystallization from hexane at -30 °C.



4: Black powder, isolated yield 35 % (0.053 mmol, 60.6 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.3 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, d^8 -THF) δ : -5.64

(d), -0.87 (br), -0.51 (br), -0.20 (br), -0.04 (br), 0.11 (br), 0.29 (br), 0.89 (br), 1.11 (br), 1.29 (br), 3.38 (m), 3.41 (br), 3.58 (br), 4.89 (br), 7.33 (br), 7.36 (m), 7.39 (br), 7.57 (br), 7.58 (br), 8.72 (br). Anal. Calcd. for C₇₀H₈₀Cr₂N₂P₂Si: C, 73.53; H, 7.05; N, 2.45. Found: C, 74.31; H, 6.96; N, 2.26. IR (KBr, cm⁻¹) υ(N₂): 1761.



5: Black powder, isolated yield 53 % (0.16 mmol, 109.7 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.6 \pm 0.1 \ \mu_B$ in C₆D₆ at 296 K. Magnetic susceptibility (SQUID): $\mu_{eff} = 4.5 \ \mu_B$ at room temperature. ¹H NMR (500 MHz, *d*⁸-THF) δ : -7.54 (br),

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6: Black powder, isolated yield 46 % (0.14 mmol, 95.9 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.8 \pm 0.1 \ \mu_{B}$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, d^{8} -THF) δ : 0.84 (m), 0.85 (br), 0.87 (br), 1.08 (m), 1.13 (br), 1.26 (br), 1.69 (br), 1.99 (m), 2.27 (br), 3.34 (m), 3.36 (br), 3.54 (br), 4.25 (br), 5.30 (br), 6.52

(m), 7.13 (m), 7.15 (m), 7.17 (br), 7.29 (br), 7.31 (br), 7.32 (br), 7.41 (br), 7.88 (br),
7.89 (br), 8.47 (br). Anal. Calcd. for C₄₅H₄₇CrNP: C, 78.92; H, 6.92; N, 2.05. Found:
C, 78.37; H, 7.42; N, 1.92. IR (KBr, cm⁻¹) v: 3056 (w), 2965 (s), 2927 (s), 2869 (m),
1628 (w), 1585 (s), 1480 (s), 1368 (m), 1315 (m), 748 (s), 695 (s), 539 (w).



7: Red powder, isolated yield 45 % (0.14 mmol, 82.6 mg). Magnetic susceptibility (Evans'method): $\mu_{eff} = 3.7 \pm 0.1 \ \mu_{B}$ in C₆D₆ at 296 K. ¹H NMR (500 MHz, *d*⁸-THF) δ : -0.35 (br), 0.78 (br), 1.01 (m), 1.06 (br), 1.19 (br), 1.39 (br), 1.62 (br), 3.26 (br), 3.27 (br), 3.29 (br), 3.30 (br), 3.47 (br), 5.22 (br), 7.24 (br), 9.93

(br), 10.78 (br). Anal. Calcd. for C₄₀H₄₈CrP: C, 78.53; H, 7.91. Found: C, 79.32; H, 8.27. HRMS calcd. for C₄₀H₄₈CrP [M]⁺: 611.2893, found 611.2888. IR (KBr, cm⁻¹) υ: 3055 (w), 2964 (s), 2927 (s), 2870 (m), 1569 (w), 1461 (m), 1092 (w), 1062 (w), 1024 (w), 747 (m), 697 (m), 501 (w).

3) Examination of IR Spectra



Figure S1 IR spectrum of 2a in KBr pellet at room temperature



Figure S2 IR spectrum of 2b in KBr pellet at room temperature



Figure S3 IR spectrum of 2c in KBr pellet at room temperature



Figure S4 IR spectrum of 3a in KBr pellet at room temperature



Figure S5 IR spectrum of 3b in KBr pellet at room temperature



Figure S6 IR spectrum of the product obtained from reduction of 2c with KC8 in THF under N_2



Figure S7 IR spectrum of 4 in KBr pellet at room temperature



Figure S8 IR spectrum of 5 in KBr pellet at room temperature



Figure S10 IR spectrum of 7 in KBr pellet at room temperature

Wavenumber cm 1



4) Copies of NMR Spectra of New Compounds

Figure S12 ¹³C{¹H} NMR of 1a at room temperature

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (gpm) -- 500



Figure S13 ${}^{31}P{}^{1}H$ NMR of 1a at room temperature



Figure S14 ¹H NMR of 1b at room temperature



Figure S15 ¹³C{¹H} NMR of 1b at room temperature



Figure S16 ³¹P{¹H} NMR of 1b at room temperature



Figure S18 ${}^{13}C{}^{1}H$ NMR of 1c at room temperature



Figure S20 ¹H NMR of 2a at room temperature



Figure S21 ¹H NMR of 2b at room temperature



Figure S22 ¹H NMR of 2c at room temperature



Figure S23 ¹H NMR of 3a at room temperature



Figure S24 ¹H NMR of 3b at room temperature



Figure S25 ¹H NMR of 4 at room temperature



Figure S26 ¹H NMR of 5 at room temperature



Figure S27 ¹H NMR of 6 at room temperature



Figure S28 ¹H NMR of 7 at room temperature

5) Copies of SQUID Spectra of Complexes 2c and 5

Magnetic susceptibility measurements (Fig. S29) at variable temperature with a superconducting quantum inference device (SQUID) show that the effective magnetic moment of **2c** at room temperature ($\mu_{eff} \approx 3.5 \,\mu_B$) is higher than the spin-only value (2.8 μ_B) expected for an S = 1 state, suggesting an unquenched orbital momentum contribution.



Figure S29 SQUID spectrum of complex 2c

Magnetic susceptibility measurements (Fig. S30) at variable temperature with a superconducting quantum inference device (SQUID) show that the effective magnetic moment of **5** at room temperature ($\mu_{eff} \approx 4.5 \ \mu_B$) is higher than the spin-only value (3.9 μ_B) expected for an S = 3/2 state, suggesting an unquenched orbital momentum contribution.



Figure S30 SQUID spectrum of complex 5

6) X-ray Crystallographic Studies

Single crystals suitable for X-ray analysis were grown in solution of Et₂O, Hexane, or the mixture of Et₂O and Hexane in -30 °C. Data collections were performed at 180 K on Rigaku diffractometer, using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by SHELXTL or Olex program.^[3,4] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix leastsquares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. H(3)in complex 4 was located from difference electron density map. Crystal data, data collection and processing parameters for compounds 1a, 1b, 2a-c, 3a,b, and 4-7 are summarized in following tables. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1907376 (1a), CCDC-1860877 (1b), CCDC-1860868 (2a), CCDC-1860867 (2b), CCDC-1903190 (2c), CCDC-1860876 (3a), CCDC-1860875 (3b), CCDC-1907372 (4), CCDC-1907373 (5), CCDC-1907375 (6), CCDC-1907374 (7). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre. Solvent molecules in some crystals could not be located appropriately. Thus, the diffused electron density associated with these solvent molecules were removed by SQUEEZE routine in PLATON.



Figure S31 ORTEP drawing of **1a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Selected Bond Lengths (Å) and Angles (deg) for 1	a.
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	1a
CCDC number	1907376
Empirical formula	C ₁₂₈ H ₁₄₄ K ₄ P ₄
Formula weight	1962.70
Temperature/K	89.9(5)
Crystal system	triclinic
Space group	P-1
a/Å	17.9093(6)
b/Å	18.1403(8)
c/Å	20.5737(7)
α/°	113.944(4)
β / °	100.357(3)
γ / °	108.053(3)
Volume/Å ³	5437.1(4)
Z	2
ρ _{calc} , g/cm ³	1.199
µ/mm⁻ ¹	0.272
F(000)	2096.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
2Θ range for data collection/^	6.876 to 54.968
Index ranges	-23 \leq h \leq 23, -23 \leq k \leq 23, -26 \leq l \leq 26
Reflections collected	72066
Independent reflections	24866 [R _{int} = 0.0548, R _{sigma} = 0.0784]
Data/restraints/parameters	24866/0/1241
Goodness-of-fit on F^2	1.029
$R_1 [I \ge 2\delta (I)]$	0.0746
wR ₂ [all data]	0.1926
Largest diff. peak/hole / e Å ⁻³	1.35/-0.54

Table S2 X-ray crystallographic data for 1a



Figure S32 ORTEP drawing of **1b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S3 Selected Bond Lengths (Å)) and Angles	(deg) for 1b .
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C(1)—C(6)	1.412(4)
C(6)—C(7)	1.514(4)
P(1)—C(1)—C(6)	120.4(2)
C(1)—C(6)—C(7)	123.1(3)

	1b
CCDC number	1860877
Empirical formula	C ₁₀₄ H ₁₆₀ K ₄ P ₄
Formula weight	1690.59
Temperature/K	179.98(11)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	21.0786(4)
b/Å	24.3001(5)
c/Å	21.1776(4)
α / °	90
β/°	91.440(2)
γ / °	90
Volume/Å ³	10844.0(4)
Z	4
$ ho_{calc},g/cm^{3}$	1.036
µ/mm⁻ ¹	0.263
F(000)	3680.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2 Θ range for data collection/°	6.932 to 52.044
Index ranges	-26 \leq h \leq 26, -29 \leq k \leq 30, -26 \leq l \leq 26
Reflections collected	188963
Independent reflections	20261 [R _{int} = 0.0413, R _{sigma} = 0.0214]
Data/restraints/parameters	20261/0/1041
Goodness-of-fit on F ²	1.039
R ₁ [I>=2δ (I)]	0.0769
wR ₂ [all data]	0.2023
Largest diff. peak/hole / e Å- ³	1.05/-0.64

Table S4 X-ray crystallographic data for 1b



Figure S33 ORTEP drawing of **2a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 55 Selected Dolld Lenguis (A) and Angles (deg) for 2	2a.
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Cr(1)——CI(1)	2.2819(4)
Cr(1)——P(1)	2.4320(4)
Cl(1) — Cr(1) — P(1)	106.336(15)

	2a
CCDC number	1860868
Empirical formula	C ₃₂ H ₃₆ CICrP
Formula weight	539.03
Temperature/K	179.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4291(3)
b/Å	12.2337(3)
c/Å	13.0486(5)
αlo	65.497(3)
β / °	71.852(3)
γ / °	73.717(3)
Volume/Å ³	1417.35(9)
Z	2
$ ho_{calc}$, g/cm 3	1.264
µ/mm⁻ ¹	1.263
F(000)	568.0
Crystal size/mm ³	0.2 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
2 Θ range for data collection/°	6.992 to 54.968
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflections collected	24131
Independent reflections	6463 [R _{int} = 0.0262, R _{sigma} = 0.0244]
Data/restraints/parameters	6463/0/320
Goodness-of-fit on F ²	1.056
R ₁ [I>=2δ (I)]	0.0293
wR ₂ [all data]	0.0805
Largest diff. peak/hole / e Å ⁻³	0.52/-0.36

Table S6 X-ray crystallographic data for 2a



Figure S34 ORTEP drawing of **2b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S7 Selected Bond Lengths (Å) and Angles (deg) for 2
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Cr(1)——Cl(1)	2.2844(7)
Cr(1)——P(1)	2.4296(6)
Cl(1) — Cr(1) — P(1)	104.03(2)

	2b
CCDC number	1860867
Empirical formula	C ₂₆ H ₄₀ CICrP
Formula weight	471.03
Temperature/K	179.97(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0749(4)
b/Å	11.1730(3)
c/Å	11.5235(3)
α / °	75.066(2)
β / °	72.107(3)
γ / °	73.390(3)
Volume/Å ³	1277.56(7)
Z	2
$ ho_{calc},g/cm^{3}$	1.2244
µ/mm⁻¹	0.625
F(000)	505.3
Crystal size/mm ³	0.2 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2Θ range for data collection/°	7.36 to 54.96
Index ranges	-15 \leq h \leq 15, -15 \leq k \leq 15, -16 \leq l \leq 15
Reflections collected	22696
Independent reflections	5836 [R _{int} = 0.0260, R _{sigma} = 0.0266]
Data/restraints/parameters	5836/0/270
Goodness-of-fit on F ²	1.032
R ₁ [I>=2δ (I)]	0.0443
wR ₂ [all data]	0.1225
Largest diff. peak/hole / e Å- ³	1.66/-0.61

Table S8 X-ray crystallographic data for 2b



Figure S35 ORTEP drawing of **2c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S9Selected	Bond	Lengths	(Å)) and	Angles	(deg)	for 2c .
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Cr(1)——Cl(1)	2.3080(4)
Cr(1)——P(1)	2.4382(3)
Cl(1) — Cr(1) — P(1)	108.803(13)

	2c
CCDC number	1903190
Empirical formula	C ₃₂ H ₄₈ ClCrP
Formula weight	551.12
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	20.2829(4)
b/Å	9.1944(2)
c/Å	16.1826(3)
α / °	90
β / °	99.695(2)
γ / °	90
Volume/Å ³	2974.78(10)
Z	4
ρ _{calc} , g/cm ³	1.231
µ/mm⁻ ¹	0.547
F(000)	1184.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2⊙ range for data collection/°	7.308 to 54.96
Index ranges	-26 \leq h \leq 26, -11 \leq k \leq 11, -19 \leq l \leq 21
Reflections collected	62546
Independent reflections	6787 [R _{int} = 0.0363, R _{sigma} = 0.0185]
Data/restraints/parameters	6787/0/320
Goodness-of-fit on F ²	1.030
R ₁ [l>=2δ (l)]	0.0277
wR ₂ [all data]	0.0762
Largest diff. peak/hole / e Ä ⁻³	0.38/-0.28

Table S10 X-ray crystallographic data for 2c



Figure S36 ORTEP drawing of **3a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S11	Selected Bond Lengths (Å) and Angles (deg) for 3a

Cr(1)——N(1)	1.855(3)
Cr(1)—N(3)	1.815(2)
Cr(2)—N(4)	1.877(2)
Cr(2)——N(5)	1.799(3)
Cr(3)——N(6)	1.873(3)
N(1) — N(2)	1.127(4)
N(3) — N(4)	1.162(3)
N(5) N(6)	1.176(4)
N(1) — Cr(1) N(3)	93.54(11)
N(4) — Cr(2) N(5)	98.07(11)
N(6) — Cr(3) – P(3)	108.00(8)

	За
CCDC number	1860876
Empirical formula	C ₉₆ H ₁₀₈ Cr ₃ N ₆ P ₃
Formula weight	1594.79
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	26.5505(5)
b/Å	17.7159(2)
c/Å	41.6344(5)
۵⁄۰	90.00
β / °	92.826(2)
γ / °	90.00
Volume/Å ³	19559.6(5)
Z	8
$ ho_{calc}$, g/cm 3	1.083
µ/mm⁻¹	0.420
F(000)	6744.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
2 Θ range for data collection/°	7.06 to 54.96
Index ranges	$-34 \le h \le 34,-23 \le k \le 22,-54 \le l \le 48$
Reflections collected	117360
Independent reflections	22324 [Rint = 0.0429, Rsigma = 0.0401]
Data/restraints/parameters	22324/47/985
Goodness-of-fit on F ²	1.043
R ₁ [I>=2δ (I)]	0.0664
wR ₂ [all data]	0.2090
Largest diff. peak/hole / e Å ⁻³	1.19/-0.56

Table S12 X-ray crystallographic data for 3a



Figure S37 ORTEP drawing of **3b.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S13	Selected Bond Lengths (A	Å) and Angles ((deg) for 3b .

Cr(1)——N(1)	1.8907(12)
Cr(2)——N(2)	1.7784(12)
Cr(2)——N(3)	1.8754(13)
N(1) — N(2)	1.1841(17)
N(3) —— N(4)	1.1243(18)
N(1) — Cr(1) P(1)	95.72(4)
N(2) — Cr(2) N(3)	93.61(5)

	3b
CCDC number	1860875
Empirical formula	$C_{52}H_{80}Cr_2N_4P_2$
Formula weight	927.14
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0838(3)
b/Å	13.0546(3)
c/Å	18.0075(4)
α/°	95.386(2)
β / °	98.078(2)
γ / °	95.760(2)
Volume/Å ³	2551.24(11)
Z	2
ρ _{calc} , g/cm ³	1.207
µ/mm ⁻¹	0.526
F(000)	996.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
2⊙ range for data collection/°	7.264 to 54.966
Index ranges	$-14 \le h \le 14, -16 \le k \le 16, -23 \le l \le 23$
Reflections collected	48986
Independent reflections	11667 [R _{int} = 0.0316, R _{sigma} = 0.0274]
Data/restraints/parameters	11667/0/557
Goodness-of-fit on F ²	1.018
R ₁ [I>=2δ (I)]	0.0313
wR ₂ [all data]	0.0793
Largest diff. peak/hole / e Å- ³	0.33/-0.27

Table S14 X-ray crystallographic data for 3b



Figure S38 ORTEP drawing of **4.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S15 Selected Bond Lengths (A) and Angles (deg) for

Cr(1)——P(1)	2.2922(5)
Cr(1)——N(1)	1.7747(15)
Cr(1)——Si(1)	2.3590(6)
N(1) — N(2)	1.175(2)
P(1) — Cr(1) — N(1)	89.67(5)
P(1) — Cr(1) — Si(1)	118.40(2)
Cr(1) N(1) N(2)	177.81(15)

	4
CCDC number	1907372
Empirical formula	C ₇₆ H ₉₄ Cr ₂ N ₂ P ₂ Si
Formula weight	1229.56
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	17.7239(4)
b/Å	21.5839(5)
c/Å	17.9159(4)
α/°	90
β / °	94.801(2)
γ / °	90
Volume/Å ³	6829.7(3)
Z	4
$ ho_{calc}, g/cm^3$	1.196
µ/mm⁻ ¹	0.425
F(000)	2624.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2⊙ range for data collection/°	7.104 to 52.044
Index ranges	-21 \leq h \leq 21, -26 \leq k \leq 26, -22 \leq l \leq 22
Reflections collected	100316
Independent reflections	13368 [R _{int} = 0.0387, R _{sigma} = 0.0215]
Data/restraints/parameters	13368/3/768
Goodness-of-fit on F ²	1.031
$R_1 [I \ge 2\delta (I)]$	0.0383
WK ₂ [all data]	0.1079
Largest diff. peak/hole / e A-3	1.09/-0.40

Table S16 X-ray crystallographic data for 4



Figure S39 ORTEP drawing of 5. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S17	Selected Bond Lengths (Å) and Angles (deg) for	5.

Cr(1)——N(1)	1.9449(16)
Cr(1)——N(2)	1.9423(16)
Cr(1)——P(1)	2.4302(5)
N(1) — N(2)	1.434(2)
N(1) — Cr(1) — P(1)	94.50(5)
N(2) — Cr(1) — N(1)	43.30(6)
N(2) — N(1) — Cr(1)	68.25(9)

	5
CCDC number	1907373
Empirical formula	C ₄₇ H ₅₃ CrN ₂ P
Formula weight	728.88
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3491(4)
b/Å	11.6086(4)
c/Å	17.2859(6)
alo	96.567(3)
β / °	98.370(3)
γ / °	115.198(3)
Volume/Å ³	1998.76(13)
Z	2
$ ho_{calc}, g/cm^3$	1.211
µ/mm⁻ ¹	0.360
F(000)	776.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2⊖ range for data collection/°	7.084 to 52.042
Index ranges	$-14 \le h \le 13, -14 \le k \le 13, -21 \le l \le 21$
Reflections collected	31054
Independent reflections	7834 [R _{int} = 0.0238, R _{sigma} = 0.0225]
Data/restraints/parameters	7834/0/465
Goodness-of-fit on F ²	1.071
R ₁ [l>=2δ (l)]	0.0405
wR ₂ [all data]	0.1149
Largest diff. peak/hole / e Å- ³	1.64/-0.49

Table S18 X-ray crystallographic data for 5



Figure S40 ORTEP drawing of **6.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S19	Selected Bond Lengths (Å) and Angles (deg) for 6.

Cr(1)——N(1)	1.9555(17)
Cr(1)——C(1)	2.073(2)
Cr(1)——P(1)	2.4354(5)
N(1) ——C(1)	1.409(3)
N(1) — Cr(1) — P(1)	98.89(5)
C(1) Cr(1) N(1)	40.82(7)
C(1) – N(1) – Cr(1)	74.06(11)

	6
CCDC number	1907375
Empirical formula	C ₄₉ H ₅₇ CrNOP
Formula weight	758.92
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.6433(2)
b/Å	14.5073(4)
c/Å	15.3365(4)
α/°	66.709(2)
β / °	70.729(2)
γ / °	85.951(2)
Volume/Å ³	2240.74(10)
Z	2
$ ho_{calc}$, g/cm 3	1.125
µ/mm⁻¹	0.325
F(000)	810.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2⊖ range for data collection/°	6.946 to 54.97
Index ranges	-15 \leq h \leq 14, -18 \leq k \leq 18, -19 \leq l \leq 19
Reflections collected	40018
Independent reflections	10238 [R _{int} = 0.0300, R _{sigma} = 0.0255]
Data/restraints/parameters	10238/0/484
Goodness-of-fit on F ²	1.084
R ₁ [l>=2δ (l)]	0.0524
wR ₂ [all data]	0.1718
Largest diff. peak/hole / e Å ⁻³	1.42/-0.58

Table S20 X-ray crystallographic data for 6



Figure S41 ORTEP drawing of **7.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S21	Selected Bond Lengths (Å) and Angles (deg) for 7.

Cr(1)——C(1)	2.0511(18)
Cr(1)——P(1)	2.4061(6)
C(1) — C(2)	1.354(3)
C(2) — C(3)	1.483(3)
C(1) — Cr(1) — C(4)	83.02(8)
P(1) — Cr(1) — C(1)	90.73(6)
Cr(1) — C(1) — C(2)	111.22(14)

	7
CCDC number	1907374
Empirical formula	C ₄₀ H ₄₈ CrP
Formula weight	611.75
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.9809(3)
b/Å	19.7635(6)
c/Å	20.9170(7)
αl°	102.713(3)
β / °	97.631(3)
γ / °	101.586(3)
Volume/Å ³	3486.4(2)
Z	4
$ ho_{calc}$, g/cm ³	1.165
µ/mm⁻ ¹	0.399
F(000)	1308.0
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	ΜοΚα (λ = 0.71073)
2⊙ range for data collection/°	7.084 to 52.042
Index ranges	$-11 \le h \le 11, -24 \le k \le 24, -25 \le l \le 25$
Reflections collected	33298
Independent reflections	13363 [R _{int} = 0.0376, R _{sigma} = 0.0472]
Data/restraints/parameters	13363/0/773
Goodness-of-fit on F ²	1.043
R ₁ [I>=2δ (I)]	0.0388
wR ₂ [all data]	0.0340
Largest diff. peak/hole / e A-3	0.977-0.28

Table S22 X-ray crystallographic data for 7

7) Studies of the Hydride Ligand in Complex 4

The doublet at -5.6 ppm (Fig. S42) might be assigned to the hydride, which disappeared if it is substituted by the deuteride in the reaction between 3a and PhSiD₃.



Figure S42 ¹H NMR spectra of hydride and deuteride in complex 4

The generation of H₂ was detected at 4.55 ppm by ¹H NMR (Fig. S43) in the quenching reaction between complex **4** and the acid $[H(OEt_2)_2][B\{C_6H_3(m-CF_3)_2\}_4]$.



Figure S43 In situ ¹H NMR of quenching reaction between 4 and [H(OEt₂)₂][B{C₆H₃(*m*-CF₃)₂}₄]



The signal at -3.3 ppm (Fig. S44) might be assigned to the deuteride in the product obtained from the reaction between **3a** and PhSiD₃.

Figure S44 ²H(D) NMR spectrum of the product obtained from reaction between 3a and PhSiD₃



Figure S45 ²H(D) NMR spectrum of PhSiD₃

8) Calculational Details

Table 525 The relationship between 5 and energy of 5a				
S	S=1/2	S=3/2	S=5/2	S=7/2
Energy/Hartree	-8208.79718545	-8208.79814890	-8208.82674870	-8208.73158987

Table S23 The relationship between S and energy of 3a

Table S24 The relationship between S and energy of 3b

			••	
S	S=0	S=1	S=2	S=3
Energy/Hartree	-5019.98938298	-5020.02801418	-5020.05349330	-5019.99628679

The calculation part was carried out with the GAUSSIAN 09 program package.^[5] The energy was calculated at the M06L/def2TZVP level.^[6] According to the results of energy calculations (Tables S23-S24), the electron configurations (for **3a**, S = 5/2, the lowest energy is about -8208.827 a.u.; for **3b**, S = 2, the lowest energy is about - 5020.053 a. u.) can be assigned to the ground states of **3a** and **3b**, which indicates the numbers of unpaired electrons in **3a** and **3b** are 5 and 4, respectively. In addition, the complexes **3a** and **3b** have solution magnetic moments of $5.2 \pm 0.1 \mu_B$ and $4.2 \pm 0.1 \mu_B$ measured by Evans' method in C₆D₆ at 296 K, which indicates the numbers of unpaired electrons in **3a** and **3b** are 4.25 and 3.32, respectively. Therefore, the experimental results are generally consistent with the calculational results.

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