



Synthesis and redox reactivity of a phosphine-ligated dichromium paddlewheel



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ABSTRACT

A pentadentate ligand platform, bis[2-(diisopropylphosphino-methylamino)phenyl]ether (**1**), abbreviated as H₂(PNONP), is introduced that enables the isolation of homodinuclear chromium complexes. In a one-step metalation using Cr(III) and Cr(II) chloride reagents, the bimetallic compounds, [Cr(μ-Cl)(PNONP)]₂ (**2**) and [Cr(PNONP)]₂ (**3**), respectively, were synthesized. These complexes have been characterized by X-ray diffraction, NMR spectroscopy, cyclic voltammetry, magnetometry, UV–Vis–NIR spectroscopy, combustion analysis, and computational methods. Complex **3** has a reasonably short Cr–Cr bond length of 2.1342(5) Å. Quantum chemical calculations support a diradical singlet ground-state with a formal triple bond between the chromium centers. By cyclic voltammetry, **3** exhibits two reversible oxidations at $E_{1/2} = -470$ and -750 mV versus FeCp^{9/+}. The one- and two-electron oxidized analogues, **3**⁺ and **3**²⁺, were generated *in situ* via chemical oxidation using ferrocenium. Based on *in situ* characterization of **3**⁺ and **3**²⁺, we hypothesize the oxidations are metal-based to yield Cr₂⁵⁺ and Cr₂⁶⁺ cores, respectively.

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1. Introduction

Dichromium paddlewheels feature prominently in the history of metal–metal multiple bonds [1–5]. Despite the vast number of multiply bonded Cr₂⁴⁺ paddlewheels, only one species, a dichromium tetraguanidinate complex, Cr₂(DPPC)₄ (where DPPC is (PhN)₂CN(CH₂)₄; Fig. 1a), was reported to exhibit reversible oxidation processes by cyclic voltammetry (CV), with two redox couples at $E_{1/2}$ of 0.02 and 1.10 V (versus Ag/AgCl) [6]. The Cr₂⁵⁺ analogue was subsequently isolated and characterized by X-ray diffraction. A high-field (W-band) EPR spectroscopic study proved definitively that the unpaired spin resided at chromium, thus supporting the formation of an oxidized Cr₂⁵⁺ core [7]. The unique redox behavior was attributed to the extreme σ and π basicity of the guanidinate ligands. Recently, a Cr₂⁶⁺ species was isolated via oxidation of a Cr₂⁴⁺ paddlewheel, Cr₂(dpa)₄ (where dpa is dipyridylamide) using two equiv. of AgOTf [8]. The solid-state structure revealed a complete rupture of the Cr–Cr bond with a long Cr···Cr distance of 3.197(3) Å, attesting to the challenge in isolating higher valent Cr₂⁵⁺ and Cr₂⁶⁺ paddlewheels (Fig. 1b).

Herein, we report a Cr₂⁴⁺ paddlewheel supported by new pentadentate ligand that comprises mixed phosphine, amide, and ether

donors. The ligand binds dichromium in a 2:1 ratio, thus saturating all the available coordination sites of the Cr₂⁴⁺ unit (Fig. 1c). Phosphine ligands are rare in the coordination chemistry of multiply-bonded dichromium. To our knowledge, the only structurally characterized complex is Li₂[Cr₂(CH₂PMe₂)₆] [9]. This is in contrast to the heavier Group 6 metals, Mo and W, for which numerous examples of phosphine-supported multiply bonded cores have been isolated, including a family of M₂(PR₃)₄X₄ complexes, where M is either Mo or W, and X is a halide [10,11]. The Cr₂⁴⁺ paddlewheel with the mixed P,N,O-donor set was characterized by a suite of physical methods, including X-ray diffraction, cyclic voltammetry, and magnetic susceptibility measurements. Theoretical studies were also conducted to elucidate its electronic structure and bonding. The combined physical and theoretical data support a triply bonded dichromium core that is capable of undergoing two one-electron oxidations. The oxidized counterparts were generated *in situ*, and preliminary characterization suggests metal-based oxidations to Cr₂⁵⁺ and Cr₂⁶⁺ species.

2. Experimental

2.1. General procedures

All manipulations were performed under a dinitrogen atmosphere inside a glovebox. Standard solvents were deoxygenated

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by sparging with N₂ and dried by passing them through activated alumina columns of an SG Water solvent purification system. Bis(2-amino-phenyl)ether and [FeCp₂][BAR₄^F] were prepared according to literature methods [12,13]. Deuterated solvents were purchased from Cambridge Isotope Laboratories, dried over calcium hydride and distilled, degassed via freeze–pump–thaw cycles, and stored over activated 4 Å molecular sieves. All reagents were purchased from Aldrich or Strem and used without further purification. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ) and Robertson Microlit Laboratories (Ledgewood, NJ). ¹H NMR spectra were recorded on a Bruker 500 MHz, or a Varian 300 or 500 MHz spectrometer at rt unless otherwise stated. All ¹H and ¹³C NMR spectra are referenced to the internal solvent residual. Variable temperature NMR experiments were performed on a Varian 300 MHz spectrometer. The temperature of the NMR probe was calibrated against an external methanol standard. UV–Vis–NIR spectra were collected on a HP8453 (190–1000 nm) diode array spectrophotometer. Low temperature UV–Vis–NIR experiments were performed using an Unisoku low temperature UV–Vis cell holder. Cyclic voltammetry was conducted using a CH Instruments 600 electrochemical analyzer. The one-cell setup utilized a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO₃ reference electrode in CH₃CN. Analyte solutions were prepared in a THF solution of 0.4 M [ⁿBu₄N][PF₆] and referenced internally to the FeCp₂^{0/+} redox couple. Perpendicular-mode X-band EPR spectra were recorded at 20 K with a Bruker ESP 300 spectrometer equipped with an Oxford ESR 910 liquid helium cryostat and an Oxford temperature controller. X-band EPR spectra were simulated by using EPR program (version W95) written by Professor Frank Neese (MPI-CEC, Mülheim, Germany). Magnetic susceptibility of **2** was determined by the Evans' Method [14], measured in C₆D₆ at 300 K using a Bruker 500 MHz spectrometer, and a sealed glass capillary containing 2:1 C₆D₆:C₆H₆. Magnetic susceptibility data were measured from powder samples of solid material over the temperature range 2–290 K using a SQUID susceptometer with a field of 1.0 T (MPMS-7, Quantum Design, calibrated with a standard palladium reference sample, error <2%). The experimental data were corrected for underlying diamagnetism using tabulated Pascal's constants ($\chi_{\text{dia}} < 0$) [15,16] as well as for temperature-independent paramagnetism ($\chi_{\text{TIP}} > 0$) [17]. Specifically, the value of χ_{TIP} used for **3** was 180×10^{-6} emu.

2.2. Preparation of bis[2-(diisopropylphosphino-methylamino)phenyl]ether, H₂PNONP (**1**)

A mixture of paraformaldehyde (0.508 g, 16.9 mmol), ⁱPr₂PH (2.00 g, 16.9 mmol) and 15 mL *n*-hexane was stirred at 55 °C for 3 h. The solvent was removed in vacuo and to the resulting oil was added 15 mL THF and bis(2-amino-phenyl)ether (1.74 g, 8.67 mmol). This reaction mixture was stirred for 12 h at 65 °C, and then the solvent was removed in vacuo. The crude product was dissolved in 20 mL pentane, filtered, and added to the top of a short silica plug. The plug was washed with 60 mL hexane, and the product eluted with 60 mL of a 9:1 hexane/THF mixture. Evaporation of the eluent in vacuo yielded a colorless oil (3.12 g, 6.77 mmol, 80% yield). ¹H NMR (500 MHz, C₆D₆) δ 7.03 (t, *J* = 11 Hz, 2H), 6.84 (d, *J* = 13 Hz, 2H), 6.77 (d, *J* = 13 Hz, 2H), 6.57 (t, *J* = 11 Hz, 2H), 4.45 (br, 2H, NH), 3.13 (dd, *J* = 1.5 & 5 Hz, 4H), 1.60 (septet of d, *J* = 3 & 7 Hz, 4H), 0.99 (dd, *J* = 7 & 14 Hz), 0.95 (dd, *J* = 7 & 11 Hz); ³¹P (282 MHz, C₆D₆) δ 2.4; ¹³C NMR (125 MHz, C₆D₆) δ 143.5, 140.3, 124.4, 117.5, 116.7, 111.3, 37.8 (d, *J* = 18 Hz), 22.6 (d, *J* = 14 Hz), 20.0 (d, *J* = 12.5 Hz), 18.8 (d, *J* = 12.5 Hz). ESI-MS-TOF *m/z*: [M+Na]⁺ calcd for C₂₆H₄₂N₂O₂Na 483.2665; found, 483.2718.

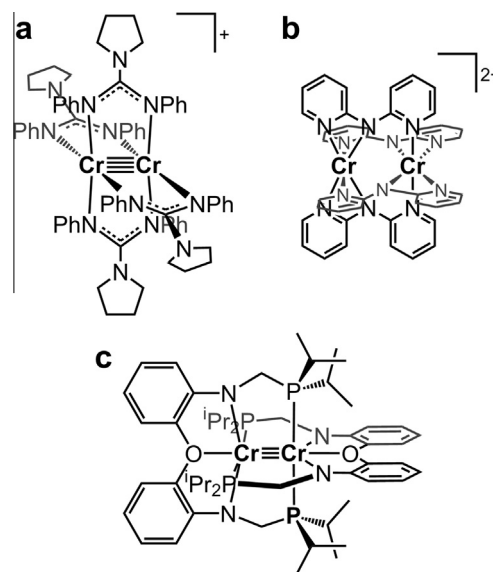


Fig. 1. Dichromium paddlewheels.

2.3. Preparation of [Cr(μ-Cl)(PNONP)]₂ (**2**)

To a frozen Et₂O solution of **1** (92.0 mg, 0.200 mmol), ⁿBuLi (2.50M in hexanes, 0.160 mL, 0.400 mmol) was added dropwise. The stirring reaction was allowed to warm to rt immediately and was stirred for an additional 2 h. After removing the solvent in vacuo, the crude residue was dissolved in 10 mL THF and added to a stirring THF slurry of CrCl₃(THF)₃ (75.0 mg, 0.200 mmol) at –50 °C. Upon warming to rt and stirring overnight the solvent was removed in vacuo. The crude residue was washed with 10 mL pentane, dissolved in 15 mL benzene, and filtered through a pipette containing a plug of glass filter paper. The filtrate was reduced in vacuo to yield a salmon-colored solid (53.8 mg, 0.107 mmol, 55% yield). ¹H NMR (500 MHz, C₆D₆) δ 68, 20, 16.7, 1.9, –4.7, –8.4, –17.9, –26.6. UV–Vis–NIR (THF) λ_{max} , nm (ϵ , M^{–1} cm^{–1}): 430 (1,100); 680 sh (150); 850 sh (80). Evans' method (C₆D₆): $\mu_{\text{eff}} = 3.87 \mu_{\text{B}}$. Anal. Calc. for **2**, C₅₂H₈₀N₄O₂P₄Cr₂: C, 57.19; H, 7.38; N, 5.13. Found: C, 56.07; H, 7.09; N, 4.89%.

2.4. Preparation of [Cr(PNONP)]₂ (**3**)

To a frozen Et₂O solution of **1** (230 mg, 0.50 mmol), ⁿBuLi (2.50M in hexanes, 0.400 mL, 1.00 mmol) was added dropwise. The stirring reaction was allowed to warm to rt immediately and was stirred for an additional 2 h. After removing the solvent in vacuo, the crude residue was dissolved in 10 mL THF and added to a stirring THF slurry of CrCl₂ (61.5 mg, 0.500 mmol) at –50 °C. Upon warming to rt and stirring overnight the solvent was removed in vacuo. The resulting solid was washed with 20 mL pentane, dissolved in 15 mL benzene, filtered and dried in vacuo to yield a bronze-colored crystalline solid (107 mg, 0.105 mmol, 62% yield). ¹H NMR (500 MHz, C₆D₆) δ 7.43 (d, *J* = 8 Hz, 2H), 7.07 (t, *J* = 8 Hz, 2H), 6.65 (d, *J* = 8 Hz, 2H), 6.36 (t, *J* = 8 Hz, 2H), 4.28 (s, 4H), 2.19 (septet, *J* = 7 Hz), 1.05 (d, *J* = 6 Hz, 12H), 0.77 (d, *J* = 5 Hz, 12H). ³¹P (282 MHz, C₆D₆) δ 19.8; ¹³C NMR (125 MHz, C₆D₆) δ 151.6, 144.6, 124.2, 113.2, 111.5, 109.6, 54.4, 26.4, 20.2, 20.0. UV–Vis–NIR (THF) λ_{max} , nm (ϵ , M^{–1} cm^{–1}): 290 (37000); 331 (41600); 428 sh (4590); 500 sh (1900); 619 (845); 762 sh (110). Anal. Calc. for **3**, C₅₂H₈₀N₄O₂P₄Cr₂: C, 61.16; H, 7.90; N, 5.49. Found: C, 61.02; H, 8.01; N, 5.46%.

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