Chromium–Chromium Interaction in a Binuclear Mixed-Valent Cr$^{\text{I}}$–Cr$^{\text{II}}$ Complex

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ABSTRACT: A mixed-valent Cr$^{\text{I}}$–Cr$^{\text{II}}$ binuclear complex, \{κ$^{1}$,κ$^{2}$,κ$^{3}$-N,P,P-cyclo[(Ph)PCH$_{2}$N(CH$_{2}$Ph)CH$_{2}$]$_{2}$[CrCl$_{2}$][Cr(μ-Cl)-(AlClMe$_{2}$)]·4toluene (1), of a P$_{2}$N$_{2}$ cyclic ligand was obtained upon treatment of the chromium precursor with alkylaluminum. Complex 1 was accessible from either its trivalent or divalent precursors, and density functional theory calculations revealed the presence of only σ- and π-orbital interactions in the Cr$^{\text{I}}$–Cr$^{\text{II}}$ bond.

INTRODUCTION

Stabilizing the monovalent state of chromium without the aid of CO ligands is challenging and yet desirable because of the involvement of this oxidation state in selective ethylene tri- and tetramerization. Depending on the nature of the ligand, carbonyl-free monovalent chromium complexes may generate short intermetallic contacts, thought to be the result of direct metal-to-metal multiple bonds. One of the features of Cr$^{\text{I}}$–Cr$^{\text{II}}$ multiple bonds is a pronounced variability of the intermetallic distance, which directly affects the strength of the intermetallic interaction and electron coupling. The formation of short Cr$^{\text{I}}$–Cr$^{\text{II}}$ distances in multinuclear complexes, whether or not it indicates the presence of an attractive intermetallic force, certainly introduces a stabilization, for example, sufficient to suppress the metal catalytic behavior for olefin oligomerization. Therefore, of particular interest could be binucleating ligands capable of rigidly holding two monovalent Cr atoms at distances where no direct Cr$^{\text{I}}$–Cr$^{\text{II}}$ interaction may occur yet allowing cooperative interactions of the two metals on the same olefin substrate.

Monovalent Cr might be accessible via the controlled oxidation of zerovalent complexes stabilized by carbonyls and/or phosphines. Another possibility is to generate such species via the reduction of di- or trivalent complexes where suitable ligands have been previously coordinated to the metal. Incidentally, this is part of a catalyst activation process, normally carried out with alkylaluminate reagents. What remains unclear is whether the monovalent state may be reached via a simultaneous two-electron reduction of a trivalent precursor (e.g., from the reductive elimination of a doubly alkylated metal center) or via the transient formation of divalent intermediates. Furthermore, divalent species have been shown to oxidize to the trivalent state in the presence of alumimates, most likely via a disproportionation reaction. Given this complex scenario, we were interested in studying the ability of the N$_{2}$N-dibenzyl-P$_{2}$P-diphenyl-1,5-diaza-3,7-diphosphacyclooctane, [(Ph)PCH$_{2}$NCH$_{2}$(CH$_{2}$Ph)]$_{2}$ ligand [P$_{2}$N$_{2}$] to afford facially coordinated monovalent species under Ziegler–Natta activation types of conditions. In particular, we wished to probe the possibility of obtaining monovalent species under these particular reaction conditions. Reaching the monovalent state would open the door for the possible formation of Cr$^{\text{I}}$–Cr$^{\text{II}}$ multiple bonds. It should be reminded that the P$_{2}$N$_{2}$ ligand was successfully used by Bullock for the preparation of rare examples of terminally bonded cis- and trans-dinitrogen complexes of zerovalent chromium. This reiterates the ability of ligands containing combinations of P- and N-donor atoms to afford Cr in its lower-valent states.

By treating either a di- or trivalent catalyst precursor with a nonparticularly reducing aluminate, Me$_{3}$Al (TMA), we have now obtained an intriguing mixed-valent Cr$^{\text{I}}$–Cr$^{\text{II}}$ complex containing a Cr$^{\text{I}}$–Cr$^{\text{II}}$ bond. Herein we describe its full characterization and electronic structure.

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**RESULTS AND DISCUSSION**

The ligand $\text{P}^{\text{Ph}}\text{N}^{\text{Bn}}_2$ was prepared according to a literature procedure.\textsuperscript{16} Treatment of the chromium(III) chloride complex of the $\text{P}^{\text{Ph}}\text{N}^{\text{Bn}}_2$ ligand with 5 equiv of TMA or, as an alternative, a chromium(II) chloride precursor with 3 equiv of [PPh$_2$Cl$_2$]$\mu$Cl was prepared according to a literature procedure. (Scheme 1). Inorganic Chemistry

Complex I exhibits a Cr1–Cr2 bond distance of 2.0387(8) Å (Figure 1). One of the Cr atoms, Cr2, is in a trigonal-bipyramidal geometry, with two Cl atoms [(Cr2–Cl2 = 2.329(1) Å, Cr2–Cl3 = 2.315(1) Å, and Cl3–Cr2–Cl2 = 123.81(4)°) and the second Cr atom occupying the equatorial plane [Cr1–Cr2 = 2.0387(8) Å]. Two N-donor atoms from two different ligands [Cr2–N2 = 2.234(3) Å, Cr2–N4 = 2.210(3) Å, and N4–Cr2–N2 = 172.0(1)°] occupy the axial positions. The geometry around the second Cr atom is octahedral, with the four P atoms defining the equatorial plane [the Cr–P distances range from 2.375(1) to 2.3497(10) Å, and the P–Cr–P angles range from 79.73(3)° to 80.51(3)° and from 175.79(4)° to 178.48(4)°] and the other Cr and one Cl atom [Cr1–Cl1 = 2.677(1) Å and Al1–Cl1–Cr1 = 155.71(6)°] on the axial positions. Four molecules of toluene per dimeric unit complete the crystal structure (see Tables S1–S7 in the Supporting Information, SI).

The asymmetric structure of I indicates a mixed-valence species composed by two nonequivalent Cr atoms in the formal mono- and divalent oxidation states. The Cl atoms bonded to the two metal atoms also display very different features. However, the long Cr1–Cl1 distance may also be related not only to the different oxidation state but also to the axial position trans to the Cr–Cr multiple bond.\textsuperscript{5} In addition, the nature of the Cr1–Cl1 and Cr2–Cl(2,3) interactions is different because of the fact that Cl(2,3) atoms have only one metal–ligand contact, while Cl1 is involved in the two Cr1–Cl1 and Al1–Cl1 interactions. Therefore, the donor strength of Cl1 and the covalent bonding in Cr1–Cl1 are weakened relative to Cl(2,3). The particular arrangement of the ligand donor atoms may suggest that the monovalent metal is probably the one surrounded by the soft P atoms. The variable-temperature magnetic moment of I was probed using a SQUID magnetometer operating between temperatures of 1.8 and 300 K. At room temperature, I exhibited an effective magnetic moment value of 2.97 $\mu_B$, which is slightly higher than the expected spin-only value for two unpaired electrons (2.83 $\mu_B$) and lower than the expected spin-only value for three unpaired electrons (3.87 $\mu_B$) (Figure 2). A slight gradual decrease of the magnetic susceptibility upon a decrease of the temperature is observed up to 10 K. This could be attributed to the depopulation of excited states assuming the interactions between the unpaired electrons of the two Cr ions are strong because of the presence of the metal–metal bond. However, magnetic anisotropy of the Cr ions can also lead to such a negative deviation of the magnetic susceptibility. Below 10 K, a much steeper decrease can be seen with a low temperature (1.8 K) value of 2.15 $\mu_B$. This final decrease might also be, in part, contributed by an intermolecular interaction between neighboring d nicular units having 7.33 Å as the closest intermolecular Cr···Cr distance.

![Figure 1. Thermal ellipsoid plot of I with ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg) for 1: Al1–C62 = 1.956(6), Al1–C61 = 1.981(7), Al1–C4 = 2.075(3), Al1–C11 = 2.28(2), Cr2–Cr1–P4 = 92.46(3), Cr2–Cr1–P1 = 91.74(3), Cr2–Cr1–P3 = 91.58(3), P1–Cr1–P3 = 99.87(4), Cr2–Cr1–P2 = 89.88(3), P4–Cr1–P2 = 99.79(4), Cr2–Cr1–Cl1 = 173.82(4), P4–Cr1–Cl1 = 83.93(4), P1–Cr1–Cl1 = 91.91(4), P3–Cr1–Cl1 = 92.70(4), P2–Cr1–Cl1 = 85.81(4), Cr1–Cr2–N4 = 93.52(8), Cr1–Cr2–N2 = 94.44(7), Cr1–Cr2–Cl3 = 116.84(3), N4–Cr2–Cl3 = 87.62(8), N2–Cr2–Cl3 = 88.96(8), Cr1–Cr2–Cl2 = 119.35(4), N4–Cr2–Cl2 = 88.99(8), N2–Cr2–Cl2 = 86.95(7), Cl4–Al1–Cl1 = 103.1(1).](Image 1)
To rule out the possible presence of paramagnetic impurities, we have carried out magnetization experiments at 100 K and their simulation. The linear fit indicates that the sample is reasonably clean (Figure 3).

In order to determine the presence of any orbital angular momentum contribution to the susceptibility (i.e., magnetic anisotropy), magnetization measurements were also carried out at variable fields (Figure 4). The $M$ versus $H$ data below 7 K demonstrate a rapid increase in the magnetization at low magnetic fields and a less sharp increase at higher fields reaching 1.59 $\mu_B$ under 7 T without saturation at 1.8 K. The $M$ versus $H/T$ data for 1 also display similar behavior, where at high fields there is no saturation or overlay onto a single master curve. This indicates the presence of large magnetic anisotropy. It is worth reminding that the presence of low-lying excited states could also yield similar behavior.

Given the value of the Cr–Cr distance [2.0387(8) Å] and the behavior of the magnetic moment, both the doublet ($S = 1/2$) and quartet ($S = 3/2$) spin states were used as input for density functional theory (DFT) calculations. Calculations at the spin-unrestricted PBE/TZVP level were carried out using nuclear positions of the heavy atoms from the X-ray crystal structure. To reduce the time of the computational treatment, four phenyl groups at the periphery of the complex were replaced by H atoms. The other four phenyl groups (attached to the P atoms) were retained in the structure. All H-atom positions in the structure were optimized. DFT calculations of the quartet spin state at the X-ray geometry gave a substantially higher value of the total electronic energy (37.1 kcal mol$^{-1}$), indicating the doublet spin state as the electronic ground state at that particular geometry. In this ground state, the Cr1 and Cr2 atoms have unpaired electron spin densities of $-1.19$ and $+2.09$ au, respectively (Figure 5), indicating an antiferromagnetic coupling between the two Cr atoms (Scheme 2; the Cr 3d orbitals are shown in the same molecular orientation as that shown in Figure 4). Analysis of the electronic structure descriptors revealed the nature of the Cr–Cr interaction. The frontier molecular orbitals (MOs) are mainly Cr-centered with high 3d character (Figure 6 and Table S8 in the SI). However, the Cr atom contributions to these MOs are not identical, and this has an important impact on the covalent coupling between the two Cr atoms. The $\alpha$- and $\beta$-HOMOs (HOMO = highest occupied molecular orbital) are localized on the Cr1 atom (with the main contribution coming from the $d_{xy}$ orbital). The $\alpha$- and $\beta$-HOMOs are practically identical: their orbital overlap is 0.99 (Table S9 in the SI). Thus, this Cr1 $d_{xy}$-based orbital is doubly occupied (Scheme 2), and this impedes $\delta$ bonding between the two Cr atoms in
the dπ orbitals of the two Cr atoms) contribute to the σ bond between two Cr atoms (Figure 6). Depopulation of these spin orbitals causes a more significant drop in the Cr—Cr bond order [from 2.22 in the ground state to 1.92 (α-HOMO—4) and 1.84 (β-HOMO—1)], α- and β-HOMO—2, β-HOMO—3, β-HOMO—4, α- and β-HOMO—5, and α-HOMO—7 (the bonding combinations of dπ orbitals of the two Cr atoms mixed with the ligand orbitals) contribute to the π bonding between the two Cr atoms. Depopulation of these spin orbitals also causes a drop in the Cr—Cr bond order [from 2.22 in the ground state to 1.87 (α-HOMO—2), 1.92 (β-HOMO—2), 1.92 (β-HOMO—3), 2.09 (β-HOMO—4), 2.04 (α-HOMO—5), and 2.08 (β-HOMO—5)]. The contributions to the total value of the Cr—Cr bond order from the occupied α- and β-spin MOs are nearly equal (1.12 and 1.10, respectively). In the first quartet spin state, the Mayer bond order for the Cr—Cr interaction is, as expected, slightly lower (1.96) at the geometry corresponding to the X-ray structure and should be lower in the geometry corresponding to its energy minimum, with a longer Cr—Cr bond.

To probe the response of the Cr—Cr interaction to the axial coordination and to the metal oxidation state, several experiments have been carried out. Coordinating solvents, such as tetrahydrofuran (THF) or N,N-dimethylformamide, extracted the AlR2Cl residue, affording the corresponding monomeric AlR2Cl(THF). In these cases, the chromium-containing residue remained ill-defined because only oily materials were isolated. Similar results were obtained during reactions with a few ammonium and phosphonium bromides aiming at replacing the axial aluminate group. A change of the chromium oxidation state was also attempted via both reduction (with metallic Li and K and KH) and oxidation (with Ag(triflate) and [Ph3PBr]Br). Unfortunately, only intractable materials have been invariably obtained.

In conclusion, we have isolated an interesting dinuclear chromium complex, even though the first intention was to investigate the catalytic behavior of the interesting facial PNP ligand system. Formation of the mixed-valent CrII—CrIV complex 1 obtained from the treatment with TMA adds further evidence to the formation of the monovalent state of chromium during the interaction of chromium precursors with aluminum alkyls.

**EXPERIMENTAL SECTION**

All reactions were carried out under an inert atmosphere using Schlenk techniques or in a purified nitrogen-filled drybox. Solvents were dried using a purification system composed of aluminum oxide. Elemental analysis was carried out with a PerkinElmer 2400 CHN analyzer. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at 300 K. All chemical reagents were purchased from commercial sources and used as received. Trimethylaluminum (TMA) was purchased from Strem and used as received.

**Preparation of [C(6,6-cyclo-P4,N,P-aryl)-cyclop(Ph)PC2,N(CH2Ph)-CHCH][Cr2(Cl)2][Cr2Cl2][Al(IEt)4] (1). Method A: From the CrCl3(THF)3 Precursor.** A solution of the cyclic PNPN ligand (0.64 g, 1.0 mmol) in toluene (10 mL) was treated with CrCl3(THF)3 (0.37 g, 1.0 mmol), and a dark-blue precipitate formed. After 12 h of stirring at room temperature, the mixture was cooled to −40 °C, and TMA (0.36 g, 5.0 mmol) was added dropwise. Stirring was continued for 30 min while room temperature was reached. The suspension was then centrifuged and the supernatant concentrated, layered with hexanes (3 mL), and stored in a freezer at −40 °C for 3 days. The resulting brown crystals of 1 were filtered, washed with cold hexanes (10 mL), and dried in vacuo at room temperature (0.35 g, 0.28 mmol, 28%).

The brown solid was analyzed for C39H36Cl2Cr2N4P4 (found): C, 58.73 (58.65); H, 5.56 (5.49); N, 4.42 (4.37).
Magnetization data were collected at 100 K to check for ferromagnetic from 0 to 7 T and at temperatures between 1.8 and 300 K.

Magnetic Measurements. Magnetic susceptibility measurements for I were obtained using a Quantum Design SQUID MPMS-XL7 magnetometer operating between 1.8 and 300 K for applied direct-current (dc) fields ranging from −7 to +7 T. dc analyses were performed on a crushed polycrystalline sample sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and at temperatures between 1.8 and 300 K. Magnetization data were collected at 100 K to check for ferromagnetic impurities that were absent in I. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

Computational Details. DFT calculations were performed using the Gaussian 09 package using the PBE16 exchange-correlation functional and the TZVP16 basis set at the spin-unrestricted level. Tight self-consistent-field convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for analysis of the electronic structure, including generation of the initial open-shell wave functions, Mulliken population analysis (MPA),26 calculation of the Mayer bond order indices,21 and orbital occupancy-perturbed bond orders,22 and evaluation of the overlap between α- and β-spin MOs were performed using the AOMix software package.23

**REFERENCES**


