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New $CpCrCl_2(PR_3)$ complexes: physical properties and reduction chemistry†

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Abstract—Compounds $CpCrCl_2L$ (L = PMe_2Ph, **1**; $PMePh_2$, **2**; PPh_3, **3**) have been prepared. Their magnetic moment is in accord with the presence of three unpaired electron and a variable temperature ^1H NMR investigation of **1** shows Curie–Weiss behavior. The ^1H NMR, EPR and UV-visible spectra are in agreement with those of other previously reported compounds of the same family. An electrochemical investigation shows the accessibility of an irreversible reduction process. A parallel sodium reduction investigation of complexes $CpCrCl_2L$ (L = PMe_3 and η^1-dppe) suggests that the reduction process is followed by immediate chloride loss, and then by a ligand redistribution process to afford chromocene and unstable inorganic phosphine complexes of Cr(II). © 1998 Elsevier Science Ltd. All rights reserved

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We have investigated in some detail a class of stable organometallic radicals based on the $CpMoCl_2(PR_3)_2$ stoichiometry and have shown that they undergo a dissociative phosphine exchange process [1]. The supposed 15-electron $CpMoCl_2(PR_3)$ intermediate is probably favored by the release of pairing energy, since it is calculated to adopt a spin quartet ground state [2,3], while the associative path is disfavored by sterics and the high energy HOMO of the precursor. Attempts to stabilize and isolate such an intermediate, which is isostructural and isoelectronic with stable Cr(III) complexes, have been to date unfruitful [4,5]. The relative stability of the 17-electron $S = 1/2$ structure for CpMo(III) complexes and of the 15-electron $S = 3/2$ structure for CpCr(III) complexes have been rationalized on a theoretical standpoint by differences in M—PR_3 bonding and electron pairing energy [2,3].

We have thus become interested in examining the corresponding phosphine exchange process on the 15-electron Cr(III) compounds. For this purpose, a larger number of complexes was required than previously available and an exchange reaction that would be amenable to a kinetic study. We report here the synthesis of these complexes, a study of their physical properties to complement those already available in the literature, and an electrochemical and chemical reduction study. The phosphine exchange kinetic studies are in progress and will be presented in a later contribution.

EXPERIMENTAL

All operations were carried out under an atmosphere of dinitrogen. Solvents were dehydrated by conventional methods and distilled directly from the dehydrating agent prior to use (THF and Et_2O from Na/benzophenone, hexane from Na/K, heptane and toluene from Na, and CH_2Cl_2 from P_2O_5). NMR spectra were recorded on a Bruker AC200 spectrometer; the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (^1H) or downfield of external 85% H_3PO_4 (^{31}P). For each ^{31}P-NMR spectrum, a sealed capillary containing H_3PO_4 was immersed in the same NMR solvent used for the measurement and this was

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used as the external reference. Visible spectra were recorded on a Kontron Uvikon 810/820 spectrophotometer. EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an X-band microwave generator. The cyclic voltammograms were obtained with a Radiometer analog potentiostats (model PRT30-01) or with a Radiometer digital electrochemical analyzer (model DEA332). The electrochemical cell was a locally modified Schlenk tube with fittings for a platinum disk working electrode, a Pt wire counterelectrode, an SCE reference electrode, and a nitrogen inlet. Bu_4NBF_4 (ca 0.1 M) was used as supporting electrolyte. All potentials are reported relative to the ferrocene standard, which was added to each solution and measured at the end of the experiments. The magnetic susceptibility measurements were carried out with a Johnson Matthey magnetic balance, which operates by a modified Gouy method. The molar susceptibilities for the calculation of the magnetic moments were corrected for the diamagnetism of the ligands by using Pascal's constants. The elemental analyses were by M-H-W Laboratories, Phoenix, Arizona or were carried out at the Université de Bourgogne with a Fisons Instruments EA1108 analyzer. $CrCl_3(THF)_3$ was prepared according to the literature from $CrCl_3 \cdot 6H_2O$ and $SOCl_2$ in THF [6]. Solid $CpNa(THF)_x$ was prepared from Na and freshly cracked CpH in THF, followed by evaporation, precipitation by addition of hexane, filtration, and vacuum drying. The amount of residual THF was determined by acid-base titration after quenching with degassed water. Compounds $CpCrCl_2L$ (L = PMe_3, PEt_3, η^1-dppe) were prepared as previously described [7,8]. PMe_2Ph (Aldrich), $PMePh_2$ (Strem) and PPh_3 (Aldrich) were used as received without further purification.

Synthesis of $CpCrCl_2(PMe_2Ph)$, **1**

A blue solution of $CpCrCl_2(THF)$ was prepared *in situ* from $CrCl_3(THF)_3$ (0.496 mg, 1.325 mmol) and $NaCp(THF)_{0.46}$ (0.17 g, 1.4 mmol) in THF (20 ml). The ligand PMe_2Ph (0.2 ml, 1.4 mmol) was added, causing an immediate change of color to a deeper blue. The mixture was evaporated to dryness and the residue is extracted with CH_2Cl_2 (2 ml). After filtration, the slow diffusion of a hexane layer (15 ml) produced 0.364 g of blue crystals of **1** (84% yield). Elemental analysis: calculated for $C_{13}H_{16}Cl_2CrP$: C, 47.88; H, 4.94. Found: C, 47.92; H, 4.83. ^1H NMR ($CDCl_3$ δ/ppm ($w_{1/2}$/Hz)): 250 (3600) (Cp), 11.4 (49) (p-Ph), 5.28 (61) (m-Ph), −27 (740) (Me). $\mu_{eff} = 3.81$ μ_B ($\chi_g = 18.6 \cdot 10^{-6}$ cgsu, molar diamagnetic correction: $5.6 \cdot 10^{-2}$ cgsu). EPR (toluene, 105 K): $g_x = 4.480$; $g_y = 3.590$; $g_z = 1.990$. Visible (CH_2Cl_2, λ_{max}/nm (ε/cm^{-1} M^{-1})): 458 (394), 620 (666).

Synthesis of $CpCrCl_2(PMePh_2)$, **2**

A blue solution of $CpCrCl_2(THF)$ was prepared *in situ* from $CrCl_3(THF)_3$ (0.740 mg, 1.97 mmol) and $NaCp(THF)_{0.46}$ (0.24 g, 2.0 mmol) in THF (30 ml). The ligand $PMePh_2$ (0.28 ml, 2.0 mmol) is added, causing an immediate change of color to a deeper blue. The mixture was evaporated to dryness and the residue was extracted with CH_2Cl_2 (2 ml). After filtration, the slow diffusion of a hexane layer (20 ml) produced 0.598 g of blue crystals of **2** (78% yield). Elemental analysis: calculated for $C_{18}H_{18}Cl_2CrP$: C, 55.69; H, 4.67. Found: C, 55.90; H, 4.65. ^1H NMR (acetone-d^6, δ/ppm ($w_{1/2}$/Hz)): 255 (2700) (Cp), 9.75 (48) (p-Ph), 7.13 (70) (m-Ph), −21 (600) (Me). $\mu_{eff} = 3.73$ μ_B ($\chi_g = 14.7 \cdot 10^{-6}$ cgsu, molar diamagnetic correction: $7 \cdot 10^{-2}$ cgsu). EPR (toluene, 105 K): $g_x = 4.489$; $g_y = 3.590$; $g_z = 1.994$. Visible (CH_2Cl_2, λ_{max}/nm (ε/cm^{-1} M^{-1})): 480 (230), 666 (926).

Synthesis of $CpCrCl_2(PPh_3)$, **3**

A blue solution of $CpCrCl_2(THF)$ was prepared *in situ* from $CrCl_3(THF)_3$ (0.493 mg, 1.31 mmol) and $NaCp(THF)_{0.46}$ (0.17 g, 1.4 mmol) in THF (30 ml). The ligand PPh_3 (0.378 g, 1.44 mmol) was added, causing an immediate change of color to a deeper blue. The mixture evaporated to dryness and the residue is extracted with CH_2Cl_2 (2 ml). After filtration, the slow diffusion of a hexane layer (20 ml) produced blue crystals of **3**. These were recrystallized several times by the same procedure, until the ^1H and ^{31}P NMR spectra indicated the complete elimination of free PPh_3. Yield 0.204 g, 34%. Elemental analysis: calculated for $C_{23}H_{20}Cl_2CrP$: C, 61.35; H, 4.48. Found: C, 60.64; H, 4.43. ^1H NMR ($CDCl_3$, δ/ppm ($w_{1/2}$)): 260 (4500) (Cp), 9.32 (46) (p-Ph), 7.97 (73) (m-Ph). $\mu_{eff} = 3.76$ μ_B ($\chi_g = 12.77 \cdot 10^{-6}$ cgsu, molar diamagnetic correction: $2.32 \cdot 10^{-2}$ cgsu). EPR (toluene, 105 K): $g_x = 4.306$; $g_y = 3.635$; $g_z = 1.989$. Visible (CH_2Cl_2, λ_{max}/nm (ε/cm^{-1} M^{-1})): 518 (135), 662 (461).

Sodium reduction of $CpCrCl_2(PMe_3)$

Compound $CpCrCl_2(PMe_3)$ (0.689 g, 2.62 mmol) was dissolved in THF (60 ml) and the resulting blue solution was transferred into a Schlenk where 1% sodium amalgam (64 mg, 2.8 mmol of Na) had previously been prepared. The resulting mixture was stirred at room temperature for 12 h to afford rapid precipitation of a white solid, presumably NaCl. The final solution had a dark color. After filtration through Celite, the dark solution was evaporated to dryness and the residue was extracted with hexane and filtered. Cooling the resulting yellow-brown solution to −80°C afforded brown crystals, which were identified as Cp_2Cr by elemental analysis and comparison of the ^1H NMR ($\delta_{Cp} = 320$ ppm) and cyclic voltammetric properties (rev. oxidation at $E_{1/2} = -1.1$ V vs Cp_2Fe) with those reported in the literature [9]. Further work-up of the residue of the

hexane extraction did not lead to other soluble products.

Sodium reduction of $CpCrCl_2(\eta^1$-dppe)

Compound $CpCrCl_2(\eta^1$-dppe) (2.039 g, 3.48 mmol) was dissolved in THF (30 ml) and the resulting blue solution was transferred into a Schlenk where 1% sodium amalgam (80 mg, 3.5 mmol of Na) had previously been prepared. The resulting mixture was stirred at room temperature for 12 h to afford a brown suspension with precipitation of a white solid. After filtration through Celite, the solution was evaporated to dryness and the residue was extracted with hexane and filtered. Cooling the resulting yellow-brown solution to −80 C afforded brown crystals of Cp_2Cr (see previous section). The residue of the extraction is a beige solid which is soluble in THF. Its ^1H and ^{31}P NMR spectrum in C_6D_6 shows only the presence of free dppe. After nitric acid attack, the solution gives a positive test for the chloride ion.

A solid identical in appearance and solubility properties to this beige residue is obtained by sodium amalgam reduction of $CrCl_3(THF)_3$. Treatment of this solid with dppe in THF does not lead to any observable change.

RESULTS AND DISCUSSION

The new compounds $CpCrCl_2L$ (L = PMe_2Ph, **1**; $PMePh_2$, **2**; PPh_3, **3**) have been prepared by following the same protocol previously used for the analogous compounds where L = PMe_3, PEt_3, η^1-dmpm, η^1-dmpe, and η^1-dppe [7,8]. This consists of exchange of THF by the appropriate phosphine on compound $CpCrCl_2(THF)$, which is obtained *in situ* from $CrCl_3(THF)_3$ and NaCp.

The spin quartet ground state for the class of 15-electron CpCr(III) compounds has previously been established [10]. In accordance with previous findings, the measured magnetic moments for compounds **1–3** is close to the spin-only value expected for three unpaired electrons. The ^1H-NMR properties of compounds **1–3** are also in accord with those reported for similar compounds [7,8]. The relatively short electronic relaxation times for the magnetic states of the spin quartet compounds are responsible for the observation of paramagnetically shifted but relatively sharp NMR resonances for the protons. Only the resonance of the *ortho* phenyl protons could not be clearly identified. Furthermore, the coordinated P nucleus does not lead to the observation of any resonance in the ^{31}P NMR spectrum. The short electronic relaxation times are also responsible for the absence of an EPR spectrum at room temperature for these complexes. A rhombic spectrum, however, can be observed in the glassy state at low temperature, in conformity with previous analogues [8,11].

A variable temperature magnetic study had apparently not been carried out on any of the previously reported complexes of this class. Compound **1** has been investigated in detail in $CDCl_3$. The position of the ^1H NMR resonances for the various observed protons as a function of the inverse temperature gives straight lines (see Fig. 1), in accordance with the expected Curie–Weiss behavior of the magnetically diluted complex.

Complexes **1–3,** like the previously reported analogues, are blue. Visible absorption bands are therefore expected. Indeed, compounds **1–3** show a strong (ε = 500–1000 cm^{-1} M^{-1}) and broad absorption in the 600–750 nm region, which is probably the overlap of two or more transitions, in addition to a weaker (ε = 150–500) and more blue-shifted (450–500 nm) absorption. These spectra are similar to those previously reported for $CpCrCl_2(L)$ (L = η^1-dmpm, -dmpe, and -dppe) [8]. Although qualitatively similar, the spectra of the various compounds show significant differences, with the more methyl-substituted derivatives showing slightly blue shifted and more intense absorption bands relative to more phenyl-substituted derivatives. This feature is being exploited for the determination of the ligand exchange kinetics by stopped-flow with visible monitoring. A preliminary ^1H NMR investigation shows that the $CpCrCl_2(PMe_3)/PMe_3$ self-exchange process is too slow for accurate kinetics to be determined by the line-broadening technique, while the use of PMe_3-d^9 shows that it is too fast for a classic mixing and monitoring study.

To the best of our knowledge, an electrochemical

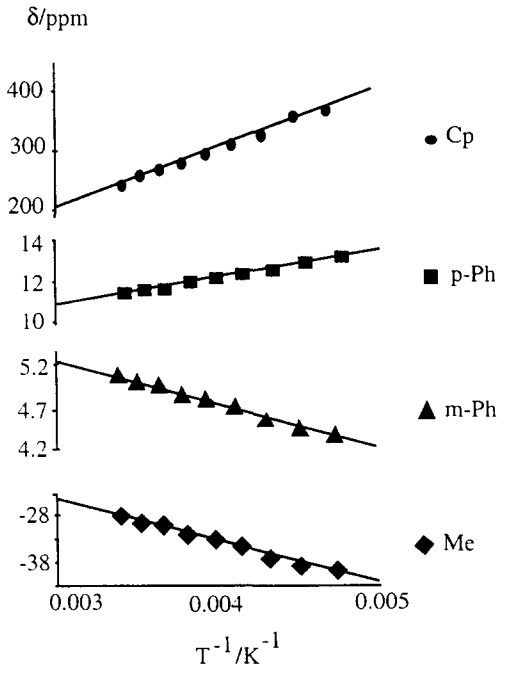


Fig. 1. Chemical shifts for compound **1** as a function of temperature. Solvent = $CDCl_3$.

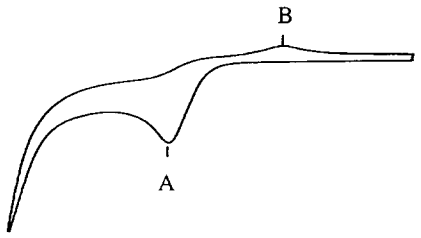


Fig. 2. A typical cyclic voltammogram for compounds $CpCrCl_2L$ in CH_2Cl_2 (see Table 1 for the list of L ligands and potentials for waves A and B).

Table 1. Cyclic voltammetric parameters for the study of compounds $CpCrCl_2L$ in CH_2Cl_2 at room temperature[a]

L	$E_{p,c}$ (A)[b] V	$E_{p,a}$ (B)[b] V
PMe_3	−1.60	−1.10
PMe_2Ph	−1.58	−1.06
$PMePh_2$	−1.51	−0.89
PPh_3	−1.61	−1.02
PEt_3	−1.72	−1.08
η^1-dppe	−1.58	−1.14

[a] Values of potentials are relative to the ferrocene internal standard.

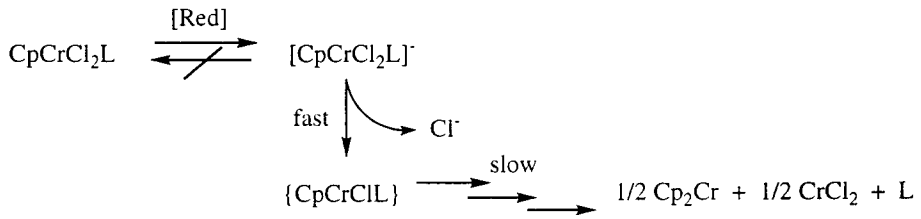
[b] See Fig. 2 for the definition of waves A and B.

investigation has never been reported for dichloride CpCr(III) complexes of this stoichiometry. On the other hand, coordination compounds of Cr(III) are known to afford, by reduction, related complexes of Cr(II). The related alkyl derivative $[Cp^*CrMe(dmpe)]^+$ has been shown to undergo a reversible electrochemical and chemical reduction to the neutral Cr(II) complex [12]. We have therefore carried out a cyclic voltammetric investigation on compounds **1**–**3**, as well as on the previously reported analogous complexes with PMe_3, PEt_3, and η^1-dppe ligands. As expected, a reduction process takes place (wave A in Fig. 2). This, however, is irreversible and is followed by a smaller intensity, irreversible oxidation wave at a more positive potential (wave B in Fig. 2). The spectrum is qualitatively identical for all compounds investigated, with the related potentials being collected in Table 1. The voltammogram of compound $CpCrCl_2(\eta^1$-dppe) is characterized also by a second reduction wave at $E_{p,c} = -1.98$ V.

The results of a chemical reduction study suggest a possible explanation for the cyclic voltammetric results. A sodium amalgam reduction was carried out on compounds $CpCrCl_2(PMe_3)$ and $CpCrCl_2(\eta^1$-dppe). The PMe_3 complex gave rise to a mixture of Cp_2Cr and uncharacterized inorganic species. The dppe complexes analogously gave rise to Cp_2Cr and free dppe, accompanied by a beige solid that contains chloride and that appears identical to a solid obtained by sodium amalgam reduction of $CrCl_3(THF)_3$. Therefore, we propose the mechanism shown in Scheme 1 for both the electrochemical and chemical reductions.

Following the reduction process to the 16-electron Cr(II) anion, a fast chemical process must occur according to the electrochemical study. This is likely to be loss of the chloride ion, since the chemical reduction study shows rapid precipitation of a white solid, presumably NaCl. The presumed CpCrClL intermediate is not susceptible to oxidation at accessible potentials, since the oxidation scan of the voltammogram does not show oxidation waves of the same intensity as the initial reduction wave. Given that this complex is electron deficient (14-electron), it is reasonable to imagine that its oxidation might be difficult. This proposed intermediate proceeds to an apparent ligand redistribution reaction, since chromocene has been identified as one of the products for the reduction of both PMe_3 and dppe complexes. Isolated chromocene shows an oxidation process at a potential corresponding to process B in Fig. 2.

The stoichiometry of the ligand redistribution process in Scheme 1 allows a second product of stoichiometry $CrCl_2L_2$. However, a $CrCl_2(PMe_3)_2$ complex is not known and our attempts to characterize the inorganic material produced by the reduction of the PMe_3 complex have been unfruitful. The same ligand redistribution process occurs for the reduction of the dppe complex. In this case, a 6-coordinate $CrCl_2(dppe)_2$ complex might be obtained. This would be similar to the reported $CrCl_2(LL)_2$ complexes with LL = dmpe [13] and dippe [14]. However, a previous report shows that the $CrCl_2(dppe)_x$ complex is rather unstable and easily loses dppe [15]. Our



Scheme 1.

observations are fully consistent with these previous findings.

It is to be noted that, while a 14-electron $CpCrCl(PMe_3)$ intermediate is likely to gain stability by formation of a di-μ-chloro bridged dimer, opening the way to ligand scrambling with formation of the proposed products of Scheme 1, the corresponding $CpCrCl(\eta^1$-dppe) intermediate also has the possibility of stabilizing itself by chelation and formation of a mononuclear 16-electron $CpCrCl(\eta^2$-dppe). The result of the electrochemical and chemical reduction studies clearly indicate that either this does not occur, or the phosphine chelation process must be a fast and reversible process. Interestingly, however, the analogous 16-electron $Cp^*Cr(CH_3)$(dmpe) complex is stable [12]. This difference could be attributed to the ability of the chloride ligand to bridge the two metals and/or to the greater ionic character of the Cr—Cl bond relative to the Cr—CH_3 bond, also favoring the ligand exchange process.

In conclusion, we have synthesized a greater number of 15-electron complexes of the $CpCrCl_2L$ family and thoroughly investigated their physical and spectroscopic properties. A preliminary investigation shows that a study of the phosphine exchange kinetics is accessible by fast mixing methods. The reduction of these derivatives to the Cr(II) state triggers a ligand redistribution reaction with formation of chromocene and unstable inorganic Cr(II)-phosphine complexes.

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