Accessibility of 17-Electron Structures for Cyclopentadienylchromium(III) Compounds. 1. Experimental Studies on the Dichloride and Dimethyl Compounds

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Adducts of the $CpCrX_2$ (X = Cl, CH_3) fragments with the bidentate ligands $Me_2PCH_2PMe_2$ (dmpm), $Me_2PCH_2CH_2PMe_2$ (dmpe), and $Ph_2PCH_2CH_2PPh_2$ (dppe) are described. Depending on the amount of ligand used, dinuclear 2:1 adducts or mononuclear 1:1 adducts are obtained. The dinuclear adducts have a $CpX_2Cr(\mu\text{-}\eta^1\text{:}\eta^1\text{-L-L})CrX_2Cp$ structure featuring 15-electron Cr centers, as shown by X-ray structural determinations on $[CpCrCl_2]_2$(dppe), $[CpCrCl_2]_2$(dmpe), and $[CpCr(CH_3)_2]_2$(dmpe). The reaction between $[CpCrCl_2]_2$(L-L) and L-L affords the mononuclear $CpCrCl_2$(L-L) derivatives. A ^{31}P-NMR monitoring of this reaction for L-L = dmpm reveals a quantitative reaction, followed by release of free dmpm. This phenomenon is interpreted as a dmpm-induced isomerization of $[CpCrCl_2]_2$(dmpm) to $[CpCrCl(dmpm)]^+[CpCrCl_3]^-$. The mononuclear adducts have a 15-electron configuration $CpCrX_2(\eta^1\text{-L-L})$ with a dangling phosphine ligand, both in the solid state, as shown by an X-ray crystal structure of $CpCrCl_2$(dmpm), and in solution, as shown by ^{31}P-NMR, UV−visible, and EPR spectroscopies. The hypothetical 17-electron configuration where the bidentate L-L ligand adopts a chelating configuration, $CpCrX_2(\eta^2\text{-L-L})$, is not experimentally observed for any of the systems investigated.

Introduction

In classical (Werner-type) coordination chemistry, the behavior of Cr(III) and Mo(III) is fairly similar. In each case, the overwhelming tendency is to form octahedral complexes.[2] In the valence-electron formalism, these are 15-electron systems, 12 electrons being donated by the ligand set and 3 additional electrons residing in the metal-based t_{2g} set of orbitals in a parallel fashion, to give rise to a spin quartet ground state. In spite of its larger size with respect to Cr^{3+}, the Mo^{3+} ion does not have any tendency to increase its coordination number in order to reach a more saturated electronic configuration when being surrounded by the classical ligands that characterize Werner-type coordination chemistry (e.g. halides, N-donor ligands, ethers, tertiary phosphines, etc.).[2] The only example of higher coordination for Mo(III) appears to be $[Mo(CN)_7]^{4-}$.[3]

When softer carbon-based ligands are present, on the other hand, the coordination chemistry of Mo(III) is profoundly different from the corresponding chemistry of Cr(III). Mo(III) gives rise to an extensive series of organometallic complexes based on the half-sandwich motif, the metal being bonded to one cyclopentadienyl ring and four additional ligands, resulting in a 17-electron, four-legged piano stool structure (**I**; Chart 1).[4] Three-legged piano stool Mo(III) compounds (**II**), isolobal with the large number of octahedral Werner-type complexes, are unknown. On the other hand, cyclopentadienylchromium(III) compounds are almost invariably 15-electron, three-legged piano stool systems with a spin quartet ground-state configuration,[5−8] just like octahedral Werner-type complexes. It is fair to state that Cr(III) has a greater tendency to behave as a Werner-type system, even with soft organic ligands, whereas the properties of the Mo(III) center are modified by the soft ligand environment toward the more typical behavior of low-valent organometallics (i.e. tendency to reach an electronically saturated configuration). This phenomenon is best exemplified by the comparison of the structures of $[Cp^‡MX_2]_2$ (M = Cr, Mo; $Cp^‡$ = variety of $\eta^5\text{-}C_5R_4R'$ ligands; X = Cl, Br, I) systems. For M = Mo, the structure features four bridging halides and a metal−metal bond to achieve a saturated 18-electron configuration (**III**),[9−12] whereas the structure of Cr systems has only two bridging halides and no metal−metal bond giving rise to two antiferromagnetically

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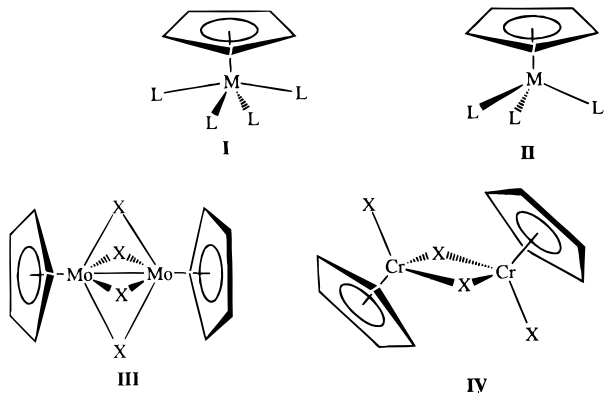
Chart 1



coupled $S = {}^3/_2$, 15-electron metal centers (**IV**).[13−16] The only 17-electron Cr(III) system that appears to be stable (albeit only below room temperature) is $CpCr(\eta^3\text{-}C_3H_5)_2$,[17] where the metal is completely surrounded by soft organic ligands. It could be argued that differences in sterics (the smaller size of Cr^{3+} with respect to Mo^{3+} and the smaller size of the Cp ligand with respect to the isoelectronic XL_2 set[18] of ligands) and metal−ligand bond strength (the M−L bond dissociation energy generally increases upon descending a group of transition metals)[19] are responsible for this variation of structure and stability, but other indirect observations, to be presented and discussed later in this paper, show that these effects alone do not explain all facts.

In this paper, we present experimental studies carried out on cyclopentadienyl chromium(III) systems with bidentate phosphine ligands, $CpCrX_2(L\text{-}L)$ (X = Cl, CH_3). These studies were spurred by the idea that the added chelate effect may force the system to adopt a 17-electron configuration (**I**) akin that of Mo(III) analogues. Our results show that the 15-electron configuration is strongly preferred for Cr(III) even under these circumstances.

Experimental Section

General Methods. All operations were carried out under an atmosphere of dinitrogen or argon with standard Schlenk-line techniques. Solvents were purified and dried by conventional methods and distilled under argon prior to use. FT-IR spectra were recorded on a Perkin-Elmer 1800 spectrophotometer with KBr disks (Nujol mulls). NMR spectra were obtained with Bruker WP200 and AF200 spectrometers; the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (^{1}H) 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 used as the reference. EPR spectra were recorded on a Bruker ER200 spectrometer upgraded to ESP300 and equipped with an X-band microwave generator. The elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. $CrCl_3(THF)_3$ was prepared as previously described.[20] dppe, dmpm, and dmpe (Strem) were used without further purification. CpNa was prepared from freshly cracked CpH and sodium sand in THF, isolated as a white CpNa·*x*THF solid by precipitation with heptane from a concentrated THF solution, and titrated with 0.1 M HCl to determine the effective molecular weight. A 1.4 M solution of MeLi in heptane (Aldrich) was used as received. $CpCrCl_2(PMe_3)$ and $CpCr(CH_3)_2(PMe_3)$ were prepared according to the procedure described in the literature.[6]

Preparation of $[CpCrCl_2]_2$(dppe). To a solution of $CpCrCl_2(THF)$ in 25 mL of THF, prepared in situ from $CrCl_3(THF)_3$ (375 mg, 1.00 mmol) and $CpNa(THF)_{0.38}$ (124 mg, 1.07 mmol), was added dppe (180 mg, 0.45 mmol) dissolved in 5 mL of THF at room temperature. The solution turned slightly darker blue. After ca. 2 h of stirring the solution was evaporated to dryness and the residue taken up in 25 mL of CH_2Cl_2. The solution was then filtered and concentrated to ca. 5 mL. The product was precipitated by addition of 20 mL of heptane, filtered out, washed with heptane, and dried under vacuum. Yield: 253 mg (69%). Anal. Calcd for $C_{36}H_{34}Cr_2Cl_4P_2$: C, 55.84; H, 4.43. Found: C, 55.73; H, 5.09. ^{1}H-NMR ($CDCl_3$, δ): 255 (br, $w_{1/2}$ = 5500 Hz, Cp), 9.2 and 7.2 (br, $w_{1/2}$ = 104 and 52 Hz, Ph), −22 (br, CH_2). UV/vis (CH_2Cl_2, nm (ϵ, M^{-1} cm^{-1})): λ_{max} 660 (390), 482 (140). Crystals of this compound were grown by layering a CH_2Cl_2 solution of $CpCrCl_2$(dppe) (see below) with heptane.

Preparation of $[CpCrCl_2]_2$(dmpm). To a solution of $CpCrCl_2(THF)$ in 25 mL of THF, prepared in situ from $CrCl_3(THF)_3$ (260 mg, 0.69 mmol) and $CpNa(THF)_{0.38}$ (90 mg, 0.78 mmol), was added dmpm (0.05 mL, 0.31 mmol) at room temperature. The solution turned slightly darker blue. After ca. 2 h of stirring the solution was evaporated to dryness and the residue taken up in 25 mL of CH_2Cl_2. The solution was then filtered and concentrated to ca. 5 mL. The product was precipitated by addition of 20 mL of heptane, filtered out, washed with heptane, and dried under vacuum. Yield: 113 mg (71.5%). Anal. Calcd for $C_{15}H_{24}Cr_2Cl_4P_2$: C, 35.18; H, 4.72. Found: C, 34.25; H, 4.33. ^{1}H-NMR ($CDCl_3$, δ): 253 (br, $w_{1/2}$ = 3200 Hz, Cp), −27.8 and −33.4 (br, total $w_{1/2}$ = 1900 Hz, PCH_3 and PCH_2). UV/vis (CH_2Cl_2, nm (ϵ, M^{-1} cm^{-1})): λ_{max} = 639 (1020), 477 (275).

Preparation of $[CpCrCl_2]_2$(dmpe). $CpCrCl_2(THF)$ was prepared in situ from $CrCl_3(THF)_3$ (450 mg, 1.20 mmol) and $CpNa(THF)_{0.38}$ (148 mg, 1.28 mmol) in 30 mL of THF. The resulting blue solution was evaporated to dryness and extracted in CH_2Cl_2 (25 mL). To this solution was added dmpe (90 μL, 0.54 mmol) at room temperature. The solution turned slightly darker blue with formation of a blue precipitate within 5 min. After ca. 2 h of stirring, the solution was left standing overnight without stirring, producing additional product as blue needle-shaped crystals. The product was filtered out, washed with heptane, and dried under vacuum. Yield: 121 mg (43.7%). Anal. Calcd for $C_{16}H_{26}Cr_2Cl_4P_2$: C, 36.53; H, 4.98. Found: C, 37.02; H, 4.67. ^{1}H-NMR ($CDCl_3$, δ): 262 (br, $w_{1/2}$ = 2900 Hz, Cp), −32.1 (br, $w_{1/2}$ = 1100 Hz, PCH_3 and PCH_2). UV/vis (CH_2Cl_2, nm (ϵ, M^{-1} cm^{-1})): λ_{max} = 599 (1130), 472 (200). The needles obtained as described above were used for the X-ray analysis.

Preparation of $CpCrCl_2$(dppe). To a solution of $CpCrCl_2(THF)$ in 25 mL of THF, prepared in situ from $CrCl_3(THF)_3$ (400 mg, 1.06 mmol) and $CpNa(THF)_{0.38}$ (133 mg, 1.15 mmol), was added dppe (450 mg, 1.12 mmol) dissolved in 10 mL of THF at room temperature. The solution turned slightly darker blue. After ca. 2 h of stirring the solution was evaporated to dryness and the residue taken up in 25 mL of CH_2Cl_2. The solution was then filtered and concentrated to ca. 5 mL. The

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blue product was precipitated by addition of 20 mL of heptane, filtered out, washed with heptane, and dried under vacuum. Yield: 444 mg (71.5%). Anal. Calcd for $C_{31}H_{29}CrCl_2P_2$: C, 63.5; H, 4.9. Found: C, 61.1; H, 5.0. The low analysis is attributed to inevitable contamination by the dimeric species, $[CpCrCl_2]_2$(dppe) (see Results section). ^{1}H-NMR ($CDCl_3$, δ): 255 (br, $w_{1/2}$ = 4500 Hz, Cp), 9.2 and 7.2 (br, $w_{1/2}$ = 130 and 64 Hz, Ph), −22 (br, $w_{1/2}$ = 1800 Hz, $CrPCH_2$). ^{31}P-NMR ($CDCl_3$, δ): 83.8 (br, $w_{1/2}$ = 330 Hz, dangling P), −12.8 (free dppe). UV/vis (CH_2Cl_2, nm): λ_{max} = 657, 486.

Preparation of $CpCrCl_2$(dmpm). To a solution of $CpCrCl_2$(THF) in 30 mL of THF, prepared in situ from $CrCl_3(THF)_3$ (550 mg, 1.46 mmol) and $CpNa(THF)_{0.38}$ (190 mg, 1.65 mmol), was added dmpm (0.250 mL, 1.58 mmol) at room temperature. The solution turned slightly darker blue. After ca. 1 h of stirring the solution was evaporated to dryness and the residue taken up in 45 mL of toluene. The solution was then filtered, concentrated to ca. 25 mL, and placed at −20 °C, yielding a heterogeneous blue precipitate containing needle-shaped crystals, one of which was used for the X-ray analysis. Yield: 214 mg (45.3%). Anal. Calcd for $C_{10}H_{19}CrCl_2P_2$: C, 37.0; H, 5.9. Found: C, 35.7; H, 5.7. The low analysis is attributed to inevitable contamination by the dimeric species, $[CpCrCl_2]_2$(dmpm) (see Results section), which also accounts for the heterogeneity. ^{1}H-NMR ($CDCl_3$, δ): 253 (br, $w_{1/2}$ = 3200 Hz, Cp), 1.5 (br, $w_{1/2}$ = 95 Hz, $CrPCH_2P(CH_3)_2$), −34.7 (br, $w_{1/2}$ = 800 Hz, $CrPCH_3$ and $CrPCH_2$). ^{31}P-NMR ($CDCl_3$, δ): −28.1 (br, $w_{1/2}$ = 260 Hz, dangling P), −54.8 (free dmpm). ^{31}P-NMR (C_6D_6, δ): −8.1 (br, $w_{1/2}$ = 220 Hz), −54.8 (free dmpm). UV/vis (CH_2Cl_2, nm): λ_{max} = 630, 480. μ_{eff} = 3.80 μ_B (by the NMR method[21] in CD_3CN).

Preparation of $CpCrCl_2$(dmpe). $CpCrCl_2$(THF) was prepared in situ from $CrCl_3(THF)_3$ (230 mg, 0.61 mmol) and $CpNa(THF)_{0.38}$ (75 mg, 0.65 mmol) in 25 mL of THF. The resulting blue solution was evaporated to dryness, extracted in CH_2Cl_2 (25 mL), and filtered. To this solution was added dmpe (0.110 mL, 0.66 mmol) at room temperature. The solution turned slightly darker blue. After ca. 2 h of stirring the solution was then filtered and concentrated to ca. 3 mL. The product was precipitated by addition of 15 mL of heptane, filtered out, washed with heptane, and dried under vacuum. Yield: 118 mg (57.3%). ^{1}H-NMR ($CDCl_3$, δ): 250 (br, $w_{1/2}$ = 3200 Hz, Cp), 1.0 (br, $w_{1/2}$ = 40 Hz, free dmpe + $CrPCH_2CH_2P(CH_3)_2$) −33.2 (br, $w_{1/2}$ = 1100 Hz, $CrPCH_3$ and $CrPCH_2$). ^{31}P-NMR ($CDCl_3$, δ): −25.1 (br, $w_{1/2}$ = 96 Hz, dangling P), −46.6 (free dmpe). UV/vis (CH_2Cl_2, nm): λ_{max} = 612, 474.

^{31}P-NMR Study of the $[CpCrCl_2]_2$(dmpm) + dmpm Reaction. $[CpCrCl_2]_2$(dmpm) (14 mg, 0.027 mmol) was dissolved in 1 mL of $CDCl_3$. This solution was then introduced in a NMR tube. To the NMR tube was then added dmpm (4.3 μL, 0.027 mmol) and the reaction monitored by ^{31}P-NMR (see Results section).

Preparation of $[CpCrCl(dppe)]^+PF_6^-$. To a solution of $CpCrCl_2$(dppe) (137 mg, 0.23 mmol) in 20 mL of THF was added $TlPF_6$ (80 mg, 0.23 mmol). A white precipitate (TlCl) formed immediately, while the color of the solution became blue-purple. After being stirred at room temperature for 5 h, the solution was filtered, concentrated to ca. 10 mL, and cooled to −20 °C. This resulted in the formation of purple colored crystals, which were filtered off and dried under vacuum. Yield: 24 mg (16.5%). Diffusion of heptane layer into the mother solution gave additional blue solid to bring the total yield to 36 mg (29%). The elemental analysis (C, H) for this material gave unacceptably low results, which are attributed to contamination by TlCl. In agreement with this hypothesis, dissolution of the crystalline product in CH_3CN leads to the subsequent formation of small amounts of a white precipitate. ^{1}H-NMR (CD_3CN, δ): 314 (br, $w_{1/2}$ = 4615 Hz, Cp), 12.8, 10.2 (br, $w_{1/2}$ = 54 Hz, *p*−Ph), 9.9 (br, $w_{1/2}$ = 49 Hz, *m*-Ph), −15 (br, $w_{1/2}$ = 1154 Hz, CH_2), −38.0 (br, $w_{1/2}$ = 1730 Hz, CH_2). ^{31}P-NMR (CD_3CN, δ): −142.8 (septet, J_{PF} = 704 Hz).

Reaction of $[CpCrCl(dppe)]^+PF_6^-$ with PPN^+Cl^-. Compound $[CpCrCl(dppe)]^+PF_6^-$ (18 mg, 0.028 mmol) and PPN^+Cl^- (16 mg, 0.028 mmol) were dissolved together in 1 mL of CD_3CN. The resulting ^{31}P-NMR spectrum showed the resonances of $CpCrCl_2$(dppe) and free dppe, in addition to those of the PPN^+ and PF_6^- ions (see Results section).

Formation of $PPN^+[CpCrCl_3]^-$ and Reaction with dmpm. $CpCrCl_2$(THF) was prepared in situ from $CrCl_3(THF)_3$ (150 mg, 0.40 mmol) and $CpNa(THF)_{0.38}$ (46 mg, 0.40 mmol) in 15 mL of THF. The blue solution was evaporated to dryness, and the residue was extracted in CH_2Cl_2 (20 mL). The resulting solution was filtered, and PPN^+Cl^- (230 mg, 0.40 mmol) was added. An aliquot of the solution was used for the ^{1}H-NMR characterization: δ 216 (br, $w_{1/2}$ = 1900 Hz) in acetone-d_6 and 232 (br, $w_{1/2}$ = 3000) in $CDCl_3$. To the remaining solution was added dmpm (65 μL, 0.41 mmol), which changed the color to darker blue, and a second aliquot of the solution was inspected by ^{1}H- and ^{31}P-NMR in acetone-d_6, showing two resonances in the region which is characteristic of the $CpCr^{III}$ protons, i.e. at δ 249 and 216 in an approximate 1:2 ratio.

^{1}H-NMR Study of the Reaction between $CpCrCl_2$(dmpm) and PPN^+Cl^-. $CpCrCl_2$(dmpm) (17 mg, 0.052 mmol) and PPN^+Cl^- (25 mg, 0.043 mmol) were dissolved together in 1 mL of CD_2Cl_2. The ^{1}H-NMR spectrum of the solution showed two resonances in the region characteristic of $CpCr^{III}$ protons, at δ 245 and 225 in an approximate 2:1 ratio. The same experiment was also run in acetone-d_6, to yield resonances at δ 249 and 216 in an approximate 1:2 ratio.

Preparation of $[CpCrMe_2]_2$(dmpe). $CpCrCl_2$(THF) was prepared in situ from $CrCl_3(THF)_3$ (280 mg, 0.74 mmol) and $CpNa(THF)_{0.38}$ (91 mg, 0.79 mmol) in 25 mL of THF. To the resulting blue solution was added dmpe (60 μL, 0.36 mmol), yielding a blue precipitate. The mixture was then cooled to −78 °C and treated with MeLi (1.0 mL of a 1.4 M heptane solution, 1.4 mmol), following by slow warming to room temperature. The mixture turned purple. After being stirred at room temperature for 1 h, the mixture was evaporated to dryness. The residue was extracted with toluene (20 mL), the mixture was filtered, and the resulting solution was concentrated to ca. 5 mL and cooled to −20 °C, yielding 54 mg (35%) of dark purple crystals. ^{1}H-NMR (C_6D_6, δ): 188 (br, $w_{1/2}$ = 2600 Hz, Cp), −17.1 (br, $w_{1/2}$ = 640 Hz, PCH_3), −33.6 (br, $w_{1/2}$ = ca. 1000, PCH_2). No resonances were observed in the ^{31}P-NMR spectrum. Anal. Calcd for $C_{20}H_{38}Cr_2P_2$: C, 54.12; H, 8.56. Found: C, 53.78; H, 8.52. UV/vis (THF, nm): λ_{max} = 530, 390. A single crystal was used for the X-ray analysis.

Formation of $[CpCrMe_2]_2$(dmpm). By a procedure identical to that described above for the preparation of $[CpCrCl_2]_2$(dmpe), a purple solution of $[CpCrMe_2]_2$(dmpm) was prepared from $CrCl_3(THF)_3$ (260 mg, 0.69 mmol), $CpNa(THF)_{0.38}$ (89 mg, 0.77 mmol), dmpm (50 μL, 0.32 mmol), and MeLi (1.0 mL, 1.4 mmol). The residue after evaporation of the final THF solution showed solubility in toluene and ether, but a solid material could not be obtained from either solution. ^{1}H-NMR (C_6D_6): 187 (br, $w_{1/2}$ = 2900 Hz, Cp), −15.7 (br, $w_{1/2}$ = 640 Hz, PCH_3), −31.7 (br, $w_{1/2}$ = 1000 Hz, PCH_2). No resonances were observed in the ^{31}P-NMR spectrum. UV/vis (THF, nm): λ_{max} = 573, 387.

Attempts To Generate a Solution of $[CpCrMe_2]_2$(dppe). By a procedure identical to that described above for the preparation of $[CpCrCl_2]_2$(dmpe), the preparation of a solution of $[CpCrMe_2]_2$(dppe) was attempted starting from $CrCl_3(THF)_3$ (150 mg, 0.40 mmol), $CpNa(THF)_{0.38}$ (52 mg, 0.45 mmol), dppe (75 mg, 0.19 mmol), and MeLi (0.60 mL, 0.84 mmol). The resulting toluene solution, however, had a green rather than purple color. The investigation of this material was abandoned.

Formation of $CpCrMe_2$(L-L) (L-L = dmpe, dmpm, dppe). Solutions of these three complexes were obtained by

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Table 1. Crystallographic Data for All Compounds

	compound			
	$[CpCrCl_2]_2$(dppe)	$[CpCrCl_2]_2$(dmpe)	$CpCrCl_2$(dmpm)	$CpCrMe_2$(dmpe)
formula	$C_{36}H_{34}Cl_4Cr_2P_2$	$C_{16}H_{26}Cl_4Cr_2P_2$	$C_{10}H_{19}Cl_2CrP_2$	$C_{20}H_{38}Cr_2P_2$
fw	774.38	526.11	324.09	444.44
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	9.7894(14)	6.6354(7)	6.441(3)	6.6168(6)
b, Å	14.974(2)	13.7755(14)	9.995(3)	13.954(2)
c, Å	12.041(2)	12.2663(12)	12.479(3)	12.4150(11)
α, deg	90	90	72.03(2)	90
β, deg	105.937(14)	97.881(2)	83.41(3)	90.046(8)
γ, deg	90	90	79.82(3)	90
V, Å^3	1697.2(4)	1110.6(2)	750.5(4)	1146.3(2)
Z	2	2	2	2
T, K	153(2)	173(2)	153(2)	153(2)
λ, Å	0.71073	0.71073	0.710 73	0.710 73
ρ_{calcd}, g/cm^3	1.515	1.573	1.434	1.288
μ, mm^{-1}	1.076	1.601	1.301	1.088
T_{max}/T_{min}			1.53	1.23
$R(F_o)^a$ ($I > 2\sigma(I)$)	0.1294	0.0564	0.0505	0.1498
$R_w(F_o^2)^b$ ($I > 2\sigma(I)$)	0.2766	0.1002	0.1151	0.3718

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

procedures identical with that described above for the preparation of $[CpCrCl_2]_2$(dmpe), except that twice the molar amount of the diphosphine ligand was used. Crystalline products, however, could not be isolated from these solutions. Cooling a heptane solution of $CpCrMe_2$(dmpm) to −80 °C did produce a crystalline sample, but after the mother liquor was decanted away at low temperature and the sample dried under vacuum, the solid melted to a viscous oil upon warming to room temperature. The solution of $CpCrCl_2$(dppe) had a greenish color, while the solutions of the other two complexes were purple. All the three compounds, however, gave NMR spectra consistent with the presence of the desired Cr(III) products with a η^1-coordination for the diphosphine ligand.

$CpCrMe_2$(dmpe). ^{1}H-NMR (C_6D_6, δ): 185 (br, $w_{1/2} = 2900$ Hz, Cp), 1.2−0.8 (m, free dmpe + $CrPCH_2CH_2P(CH_3)_2$), −13.0 (br, $w_{1/2} = 650$ Hz, $CrPCH_3$), −34.0 (br, $w_{1/2} = 970$ Hz, $CrPCH_2$). ^{31}P-NMR (C_6D_6, δ): −6.5 (br, $w_{1/2} = 170$ Hz, dangling P). A resonance at δ −46.6 due to free dmpe is also observed in the ^{31}P-NMR. UV/vis (THF, nm): $\lambda_{max} = 561$, 390.

$CpCrMe_2$(dmpm). ^{1}H-NMR (C_6D_6, δ): 185 (br, $w_{1/2} = 2500$ Hz, Cp), 2.8 (br, $w_{1/2} = 160$ Hz, $CrPCH_2P(CH_3)_2$), −15.7 (br, $w_{1/2} = 625$ Hz, $CrPCH_3$), −31.5 (br, $w_{1/2} = 950$ Hz, $CrPCH_2$). ^{31}P-NMR (C_6D_6, δ): 109 (br, $w_{1/2} = 640$ Hz, dangling P). A resonance at δ −54.8 due to free dmpm is also observed in the ^{31}P-NMR. UV/vis (THF, nm): $\lambda_{max} = 600$, 387.

$CpCrMe_2$(dppe). ^{1}H-NMR (C_6D_6, δ): 186 (br, $w_{1/2} = 3000$ Hz, Cp), −15.0 (br, $w_{1/2} = 900$ Hz, $CrPCH_2$). ^{31}P-NMR (C_6D_6, δ): 103 (br, $w_{1/2} = 500$ Hz, dangling P). A resonance at δ −12.8 due to free dppe is also observed in the ^{31}P-NMR.

Thermal Treatment of $CpCrMe_2$(dmpe) in THF and Toluene. A THF solution of $CpCrMe_2$(dmpe), prepared in situ as described above, was heated to the reflux temperature for 10 h. No color change was noticed during this period, and a ^{1}H- and ^{31}P-NMR investigation of the final solution exhibited only the resonances of the unreacted starting compound. A thermal treatment in refluxing toluene slowly deposited a brown insoluble precipitate, which did not dissolve in CH_2Cl_2, and whose nature was not further investigated.

X-ray Crystallography. $[CpCrCl_2]_2$(dppe). A blue crystal with dimensions 0.40 × 0.15 × 0.10 mm was placed and optically centered on the Enraf-Nonius CAD-4 diffractometer. The cell parameters and crystal orientation matrix were determined from 25 reflections in the range $9.2 < 2\theta < 40.6°$ and were confirmed with axial photographs. Data collection and reduction and the structure solution and refinement were routine. No correction for decays was necessary, while the data were corrected for absorption by the ψ-scan method ($T_{max}/T_{min} = 1.42$). The averaging of equivalent reflections gave $R_{int} = 0.0676$. The systematic absences from the data uniquely determined the space group as the monoclinic $P2_1/n$ (No. 14). Direct methods (SHELXS-86) allowed the successful location of the four heavy atoms in the asymmetric unit (Cr, two Cl and P). The remaining non-hydrogen atoms were found from two subsequent difference-Fourier maps. The structure was refined with SHELXL-93. Hydrogen atoms were placed in calculated positions and used for structure factor calculations but not refined. The low diffracting power of the crystal and the resulting low number of observed reflections allowed only the Cr, Cl, and P atoms to be refined anisotropically. Crystal data are assembled in Table 1. Other data are available as Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[CpCrCl_2]_2$(dmpe)[a]

Cr(1)−Cl(1)	2.298(2)	Cr(1)−P(1)	2.414(2)
Cr(1)−Cl(2)	2.284(2)	Cr(1)−CNT	1.884(3)
Cl(1)−Cr(1)−Cl(2)	99.02(6)	Cl(2)−Cr(1)−P(1)	93.01(6)
Cl(1)−Cr(1)−P(1)	90.88(6)	Cl(2)−Cr(1)−CNT	124.3
Cl(1)−Cr(1)−CNT	123.0	P(1)−Cr(1)−CNT	118.4

[a] CNT is the Cp ring centroid.

$[CpCrCl_2]_2$(dmpe). Crystals of this compound were too small for measurement on a regular diffractometer. Therefore, the structure of this compound was determined with a Siemens SMART diffractometer equipped with a CCD area detector at Northern Illinois University. A blue needle with dimensions 0.30 × 0.04 × 0.04 mm was mounted on the diffractometer, and the intensity data were gathered at −100 °C. The space group was determined to be the centric $P2_1/n$ (No. 14) from the systematic absences. A summary of data collection parameters is given in Table 1. The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{eq}$(C). The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom ($B = 1.2U_{eq}$(C)). Refinement of non-hydrogen atoms was carried out with anisotropic temperature factors. Selected bond distances and angles are reported in Table 2.

$CpCrCl_2(\eta^1$-dmpm). A blue needle with dimensions 0.15 × 0.15 × 0.45 mm was placed on the Enraf-Nonius CAD-4 diffractometer. The cell parameters and crystal orientation matrix were determined from 25 reflections in the range $15.6 < 2\theta < 21.8°$ and confirmed with axial photographs. Data collection and reduction and the structure solution and refinement were routine. No correction for decays was necessary, while the data were corrected for absorption by the ψ-scan method ($T_{max}/T_{min} = 1.53$). The averaging of equivalent reflections gave $R_{int} = 0.0644$. Intensity statistics clearly favored the centrosymmetric space group $P\bar{1}$ (No. 2). Direct

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $CpCrCl_2(dmpm)$[a]

Cr(1)−Cl(1)	2.281(2)	Cr(1)−P(1)	2.410(2)
Cr(1)−Cl(2)	2.295(2)	Cr(1)−CNT	1.882(7)
Cl(1)−Cr(1)−Cl(2)	100.08(8)	Cl(2)−Cr(1)−P(1)	88.59(7)
Cl(1)−Cr(1)−P(1)	92.80(7)	Cl(2)−Cr(1)−CNT	124.8(2)
Cl(1)−Cr(1)−CNT	122.5(2)	P(1)−Cr(1)−CNT	119.3(2)

[a] CNT is the Cp ring centroid.

methods allowed the location of the Cr, two Cl, and two P atoms. Subsequent difference-Fourier maps revealed the location of all of the remaining non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and used for structure factor calculations but not refined. Crystal data are assembled in Table 1, and selected bond distances and angles are reported in Table 3.

$[CpCr(CH_3)_2]_2(dmpe)$. A black crystal with dimensions 0.40 × 0.15 × 0.05 mm was placed on the Enraf-Nonius CAD-4 diffractometer. The cell parameters and crystal orientation matrix were determined from 25 reflections in the range $16.1 < 2\theta < 20.1°$ and confirmed with axial photographs. Data collection and reduction and the structure solution and refinement were routine. No correction for decays was necessary, while the data were corrected for absorption on the basis of ψ-scan reflections ($T_{max}/T_{min} = 1.23$). The averaging of equivalent reflections gave $R_{int} = 0.0785$. The systematic absences from the data clearly determined the nonstandard centrosymmetric monoclinic space group $P2_1/n$ (No. 14). Direct methods allowed the location of the Cr and P atoms. The remaining non-hydrogen atoms were found from two subsequent difference-Fourier maps. Hydrogen atoms were placed in calculated positions and used for structure factor calculations but not refined. A final difference-Fourier map included many peaks with the largest near the two heavy atoms and as large as 2.13 e·Å^{-3}; it is clearly apparent that one or more other moieties are partially occupying the same space as the molecule of interest, but their elucidation proved futile with many minor peaks and no clear solution as to what the moiety(ies) should have been. Possibilities for the nature of these other low-occupancy components are one or more different orientations of the molecule of interest and/or solvent molecules. A figure showing the spacial relationship between the residual peaks and the main molecule is provided in the Supporting Information. Crystal data for the $[CpCr(CH_3)_2]_2$(dmpe) molecule are assembled in Table 1. All other data are available as Supporting Information.

Results

A. Chloride Systems. A1. The $[CpCrCl_2]_2$ Precursor. Compounds $[CpCrCl_2]_2$ and $CpCrCl_2(THF)$ have previously been obtained from $[Cp_2Cr][CpCrCl_3]$ by standing in chloroform or by dissolution in THF, respectively,[5,13] the ionic precursor being in turn obtained from chromocene. THF can be easily removed from the mononuclear complex to generate the dinuclear one.[5] We have generated these compound more conveniently by direct transmetalation of NaCp and $CrCl_3(THF)_3$ in THF (eq 1), by analogy to the more recent

$$CrCl_3(THF)_3 + NaCp \rightarrow CpCrCl_2(THF) + NaCl + 2THF \quad (1)$$

$$2CpCrCl_2(THF) \rightleftarrows [CpCrCl_2]_2 + 2THF \quad (2)$$

synthesis of the Cp* analogue.[14] Although the direct product of this reaction is the THF adduct, removal of the THF solvent and dissolution in chlorinated hydrocarbons produce a substantial amount of the dimer (eq 2) as verified by ^{1}H-NMR.

The room-temperature ^{1}H-NMR spectrum (in $CDCl_3$) shows a broad and paramagnetically shifted resonance centered at δ 268 ($w_{1/2} = 3400$ Hz), which is assigned to the Cp protons in the mononuclear $CpCrCl_2(THF)$ product. Although the NMR of this compound has not previously been reported to the best of our knowledge, similar resonances have been assigned to the Cp protons in analogous compounds (e.g. δ 231 for $CpCrCl_2(PMe_3)$ and $CpCrCl_2(PEt_3)$,[6] 233.6 for $[CpCrCl_3]^-$, and 247.0 for $CpCrCl_2(py)$[13]). In addition, resonances due to the coordinated THF ligand are evident at δ 37.5 ($w_{1/2} = 1000$ Hz) for the α protons and 11.8 ($w_{1/2} = 280$ Hz) for the β protons (see Table 4). The latter assignment is based on the expected larger contact shift and greater broadening for the protons that are closer to the paramagnetic metal center. Similar shifts for the THF α and β protons have been reported for other d^3, 15-electron complexes.[22,23] The same spectrum shows also a less shifted Cp resonance at δ 158 ($w_{1/2} = 2400$ Hz), assigned to the antiferromagnetic dimer $[CpCrCl_2]_2$ (reported at ca. δ 150 in the literature[13]). The ^{1}H-NMR of the product after several cycles of vacuum drying and redissolution in $CDCl_3$ showed the increase of the dimer resonance at δ 158 at the expenses of the resonances assigned to the mononuclear THF adduct, whereas the addition of THF to the NMR solution resulted in the opposite change. We observed only one Cp resonance for the dimeric $[CpCrCl_2]_2$ compound, while two different resonances, assigned to cis and trans isomers, have previously been reported.[13]

A2. Dinuclear $[CpCrCl_2]_2$(L-L) Adducts. The addition of the bidentate ligands $Ph_2PCH_2CH_2PPh_2$ (dppe), $Me_2PCH_2CH_2PMe_2$ (dmpe), and $Me_2PCH_2PPMe_2$ (dmpm) to the THF solution of $CpCrCl_2(THF)$ in a 1:2 ratio leads to the formation of compounds that analyze as $Cp_2Cr_2Cl_4$(L-L) (eq 3).

$$2CpCrCl_2(THF) + \text{L-L} \rightarrow Cp_2Cr_2Cl_4(\text{L-L}) + 2THF \quad (3)$$

$$\text{L-L} = \text{dppe, dmpe, dmpm}$$

The products are fairly soluble in CH_2Cl_2 for L-L = dmpm and dppe and are recovered as powders by addition of heptane. The dmpe complex is only sparingly soluble in CH_2Cl_2 and precipitates directly from solution. The ^{1}H-NMR spectra for all derivatives (Table 4) show broad, shifted resonances for the Cp protons around δ 250, similar to those found for other $CpCr^{III}$ complexes. This indicates that these phosphine derivatives have a three-legged piano stool coordination geometry and a spin quartet ground state as has been established for other 15-electron $CpCr^{III}$ derivatives, for instance $[CpCrX_3]Li$ (X = Cl, Me, Ph).[24] The aliphatic phosphine proton resonances (all dmpm and dmpe protons and the methylene protons of dppe) are upfield shifted to the δ −20 to −35 region [cf. δ −33.3 for $CpCrCl_2(PMe_3)$].[6] No ^{31}P-NMR resonance is observed for any of these compounds, presumably because of the proximity of the phosphorus nucleus to the paramagnetic metal center. The optical spectra are in accord

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Table 4. NMR Properties of $CpCr^{III}$ Compounds[a]

compd	^{1}H-NMR Cp	^{1}H-NMR other protons	^{31}P-NMR	solvent
$CpCrCl_2(THF)$	268	THF, 37.5 (α), 11.8 (β)		$CDCl_3$
$[CpCrCl_2]_2$	158			$CDCl_3$
$[CpCrCl_2]_2$(dppe)	255	Ph, 9.2−7.2; PCH_2, −22		$CDCl_3$
$[CpCrCl_2]_2$(dmpe)	262	PCH_3 and PCH_2, −32.1		$CDCl_3$
$[CpCrCl_2]_2$(dmpm)	253	PCH_3, −27.8; PCH_2, −33.4		$CDCl_3$
$CpCrCl_2$(dppe)	255	Ph, 9.2−7.2; PCH_2, −22	+83.8	$CDCl_3$
$CpCrCl_2$(dmpe)	250	PCH_3 and PCH_2, −33.2; PCH_3,[b] ca. 1.0	−25.1	$CDCl_3$
$CpCrCl_2$(dmpm)	253	PCH_3 and PCH_2, −34.7; PCH_3,[b] 1.5	−28.1	$CDCl_3$[c]
$[CpCrMe_2]_2$(dmpe)	188	PCH_3, −17.1; PCH_2, −33.6		C_6D_6
$[CpCrMe_2]_2$(dmpm)	187	PCH_3, −15.7; PCH_2, −31.7		C_6D_6
$CpCrMe_2$(dppe)	186	PCH_2, −15.0	+103	C_6D_6
$CpCrMe_2$(dmpe)	185	PCH_3, −13.0; PCH_2, −34.0; PCH_3,[b] ca. 1.0	−6.5	C_6D_6
$CpCrMe_2$(dmpm)	185	PCH_3, −15.7; PCH_2, −31.5, PCH_3,[b] 2.8	+109	C_6D_6

[a] Solvent = $CDCl_3$; $T = 294 \pm 1$ K. [b] Dangling group. [c] ^{31}P-NMR: −8.2 in C_6D_6.

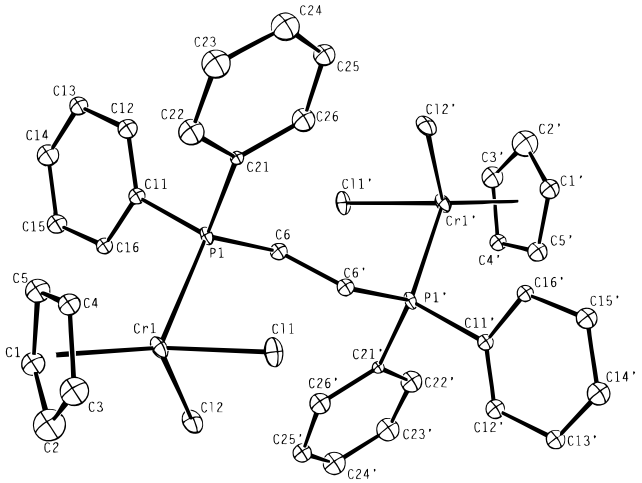

Figure 1. ORTEP view of compound $[CpCrCl_2]_2$(dppe) showing the labeling scheme used. The ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

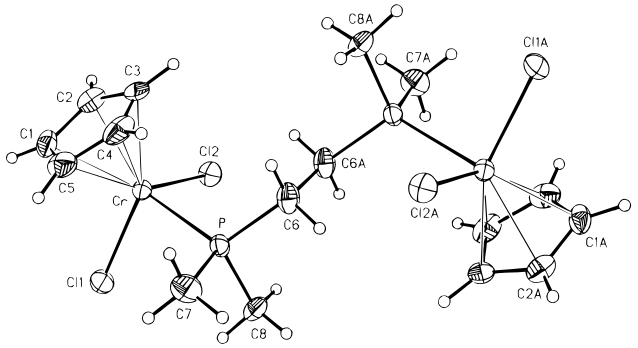

Figure 2. ORTEP view of compound $[CpCrCl_2]_2$(dmpe) showing the labeling scheme used. The ellipsoids are drawn at the 50% probability level.

with the proposed geometry and spin state, the maximum absorptions being essentially superimposable with those of $CpCrCl_2(PMe_3)$ (vide infra). These spectra have the same general shape as those reported for $[CpCrCl_3]^-$ and $[CpCr(H_2O)_3]^{2+}$,[25] with the position of the absorption maxima being very close to those reported for the trichloro complex (624 and 492 nm).

The molecular geometry is confirmed by a single-crystal X-ray investigation on compounds $[CpCrCl_2]_2$(dppe) and $[CpCrCl_2]_2$(dmpe), whose ORTEP drawings are shown in Figures 1 and 2. In each compound, each chromium atom is bonded to a Cp ring, two chlorine atoms, and one phosphorus atom of the bidentate ligand, which serves as bridge between the two metal centers. The crystals of the dppe compound had a very low diffracting power, resulting in a rather unprecise structural determination. For this reason, no emphasis is placed on the metric parameters for this compound, and full results are reported and discussed only for the dmpe compound (see Table 2). The average distances to the chlorine atoms (2.291(7) Å) and Cp ring (center of gravity, 1.884(3) Å) compare quite well with analogous distances in compounds $[CpCrCl_2]_2$ [Cr−Cl(terminal), 2.274(4) Å; Cr−Cp, 1.867 Å][13] and $[Cp^*CrCl_2]_2$ [Cr−Cl(terminal), 2.290(4) Å; Cr−Cp*, 1.88 Å],[14] while the Cr−P distance of 2.414(2) Å is similar to those found in $Cp^*CrMe_2(PMe_3)$ [2.426(2) Å][6] and in other trialkylphosphine-containing, non-cyclopentadienyl-substituted Cr(III) coordination compounds, e.g. $[CrCl_2(dmpe)_2]BPh_4$ [2.445(5) Å].[26] The structure of the dmpm complex as obtained from the synthetic methodology described above is assumed to be identical with those of the dppe and dmpe analogues.

A3. Mononuclear $CpCrCl_2$(L-L) with Dangling Phosphine. When the interaction between $CpCrCl_2$(THF) and L-L was carried out in a 1:1 molar ratio, solutions containing the mononuclear compounds $CpCrCl_2$(L-L) were obtained (eq 4). The same solutions could also be obtained by addition of 1 equiv of L-L to the isolated dinuclear $[CpCrCl_2]_2$(L-L) compounds.

$$CpCrCl_2(THF) + \text{L-L} \rightarrow CpCrCl_2(\text{L-L}) + THF \qquad (4)$$

$$\text{L-L} = \text{dppe, dmpe, dmpm}$$

The physical and spectroscopic properties of these solutions are very similar to those deriving from the 2:1 interaction of eq 3. In particular, the ^{1}H-NMR spectra (Table 4) show the downfield contact shifted Cp resonance and the upfield contact-shifted phosphine (aliphatic α proton) resonance that are characteristic of the quartet state for the 15-electron $CpCrX_2L$ structure. The spin state has been confirmed by a magnetic susceptibility measurement (Evans' method) on $CpCrCl_2$(dmpm) ($\mu_{eff} = 3.80\ \mu_B$). However, contrary to the above dinuclear complexes, the ^{31}P-NMR spectrum of all these mononuclear complexes is characterized by a broad,

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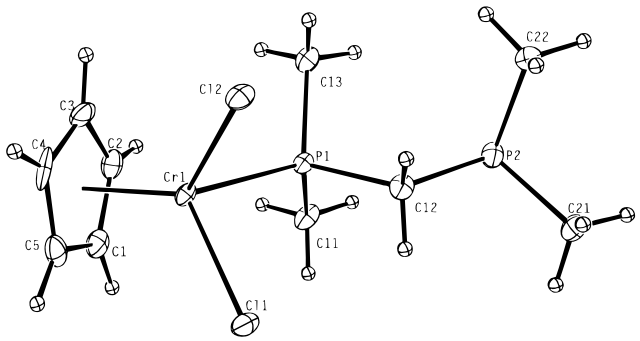


Figure 3. ORTEP view of compound $CpCrCl_2(\eta^1$-dmpm) showing the labeling scheme used. The ellipsoids are drawn at the 40% probability level.

contact-shifted resonance (see Table 4), which is assigned to the dangling phosphorus nucleus. These spectra also invariably exhibit the sharp resonance of free L-L, even when the ligand L-L had been added in substoichiometric amount. Solid samples of crude $CpCrCl_2$(L-L), obtained by vacuum drying the solutions and washed with heptane in order to eliminate any unreacted free L-L, gave again, upon dissolution in $CDCl_3$, a ^{31}P-NMR spectrum exhibiting the broad resonance of the dangling ligand and the sharper resonance due to free L-L. This phenomenon can only indicate the presence of a rapid equilibrium (on the time scale of the solid dissolution and the recording of the NMR spectrum) between the mononuclear compound on one side and the dinuclear compound and free ligand on the other side; see eq 5. The observation of separate

$$2CpCrCl_2(L\text{-}L) \rightleftarrows Cp_2Cr_2Cl_4(L\text{-}L) + L\text{-}L \qquad (5)$$

resonances for the dangling phosphorus and free ligand shows, on the other hand, that the ligand exchange is slow on the NMR time scale. Equilibrium (5) prevented us from obtaining analytically pure solid samples of the mononuclear compound, and indeed, the analytical results on the isolated mononuclear complexes always show low C and H contents, consistent with the presence of substantial amounts of dinuclear material. The methyl protons of the dangling dmpm and dmpe ligands show a broad peak at δ 1.0−1.5, which is the same region as the protons of free phosphine, indicating that the 5- and 6-bond distances of these protons from the paramagnetic Cr center allow the transmission of a negligible amount of spin density onto these nuclei. The resonances due to the aliphatic β protons of the dangling dmpe and dppe ligands could not be identified unambiguously.

We were fortunate to obtain single crystals of complex $CpCrCl_2$(dmpm) by low-temperature crystallization, and these were investigated by X-ray crystallography. The structure (Figure 3) shows the expected three-legged piano stool and the dangling phosphine ligand. The conformation chosen by the dangling phosphine is such as to place the long arm (CH_2PMe_2) of the coordinated phosphorus atom anti with respect to the Cp ring, e.g. the conformation around the Cr−P bond can be described as a staggered pseudo-ethane with the two largest groups in relative anti positions. The same conformation across the Cr−P bond is observed for the dinuclear dppe and dmpe complexes (see Figures 1 and 2). Selected distances and angles for this compound are collected in Table 3. All distances and angles for this compound are quite close to those discussed above for the dinuclear $[CpCrCl_2]_2$(dmpe) structure (cf. Table 3 with Table 2).

The reaction between the isolated dinuclear compound $[CpCrCl_2]_2$(dmpm) and 1 equiv of free dmpm in $CDCl_3$ (eq 6) was monitored by ^{31}P-NMR in order to gain

$$[CpCrCl_2]_2(dmpm) + dmpm \rightleftarrows 2CpCrCl_2(dmpm) \qquad (6)$$

further insight into the apparent equilibrium between mononuclear and dinuclear phosphine adducts. The results of this experiment, however, are unexpected and rather puzzling. A representative run is illustrated in Figure 4. The immediate recording of the spectrum (within 1 min from the introduction of the phosphine in the NMR tube) shows the expected formation of the $CpCrCl_2(\eta^1$-dmpm) monomer as indicated by the broad paramagnetically shifted ^{31}P-NMR resonance for the dangling phosporus atom and the *complete disappearance* of the free phosphine resonance. Subsequently, however, the free phosphine resonance reappears in the spectrum and grows until it reaches a constant intensity. The results of this experiment were reproduced several times. This observation indicates that eq 6 is quantitative but that the monomer product subsequently engages in a slower equilibrium which involves release of free phosphine in solution.

The addition of the phosphine and all other operations were conducted at constant temperature; thus, a change of the equilibrium position for the hypothetical equilibrium between the dinuclear $CpCl_2Cr(\mu$-L-L)$CrCl_2Cp$ and the mononuclear $CpCrCl_2(\eta^1$-L-L) as the experiment progresses is not a possible explanation of this phenomenon. From the kinetic point of view, the occurrence of a quantitative reaction followed by its coming back to an observable equilibrium position is not acceptable for a transformation as mechanistically simple as the present one. The explanation of this phenomenon, therefore, must involve the quantitative formation of $CpCrCl_2(\eta^1$-dmpm) followed by a slower release of dmpm to afford a new compound, i.e. different than the starting dinuclear $[CpCrCl_2]_2$(dmpm). Incidentally, this behavior is consistent with the observation of the instability of $CpCrCl_2$(L-L) toward loss of diphosphine (*vide supra*).

Since no new phosphorus resonance other than those of free dmpm and $CpCrCl_2(\eta^1$-dmpm) appears in the spectrum, any new compound must have either no coordinated phosphine or a chelating dmpm ligand (i.e. both P donors bonded to the paramagnetic metal center). A reasonable hypothesis for this equilibrium is indicated in eq 7. The relative intensity of the free phosphine and

$$2CpCrCl_2(\eta^1\text{-dmpm}) \rightleftarrows [CpCrCl(\eta^2\text{-dmpm})]^+[CpCrCl_3]^- + dmpm \qquad (7)$$

dangling phosphine resonances at equilibrium (Figure 4) shows that equilibrium 7 is largely shifted to the left. A concurrent ^{1}H-NMR investigation did not help substantiate the hypothesis of equilibrium 7, because the alleged ionic product is formed only in small amounts and its ^{1}H-NMR resonances would be broad and largely overlapping with those of the $CpCrCl_2(\eta^1$-dmpm) compound.

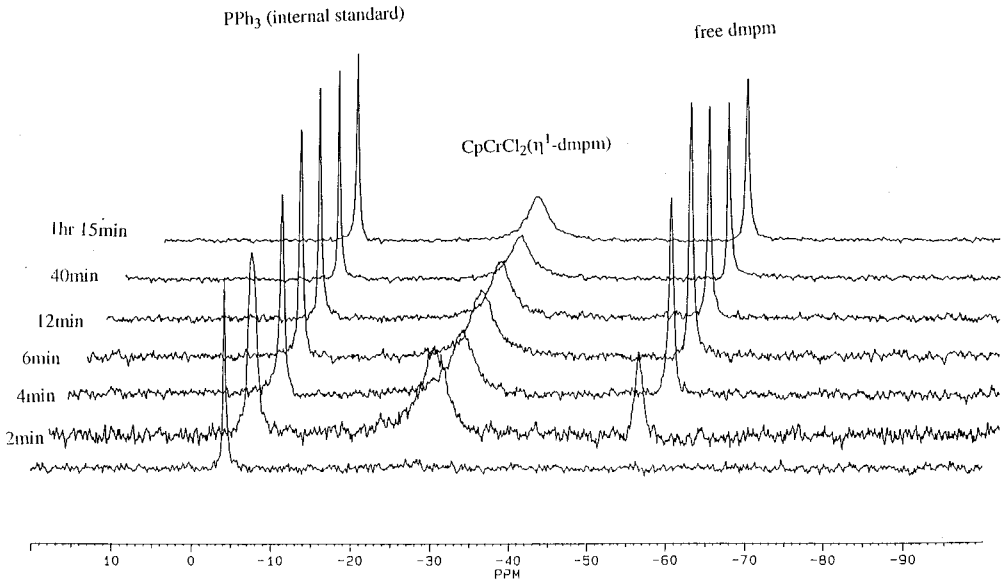
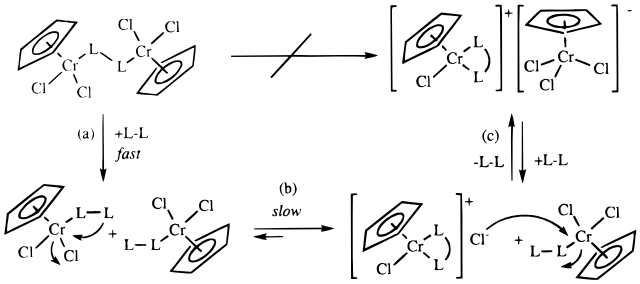


Figure 4. ^{31}P-NMR study of the reaction between $[CpCrCl_2]_2$(dmpm) and dmpm. Solvent = $CDCl_3$, room temperature.

Scheme 1



An important implication of this hypothesis is that among the two isomeric forms $[CpCrCl_2]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-dmpm})$ and $[CpCrCl(\eta^2\text{-dmpm})]^+[CpCrCl_3]^-$, only the former would be produced under kinetically controlled conditions during the synthesis, while the latter could only form through the catalytic intervention of free dmpm. Indeed, the preparation of the neutral dmpm dimer was carried out by using a defect amount of free phosphine. A possible mechanistic pathway that leads from the dinuclear $[CpCrCl_2]_2(\mu\text{-L-L})$ structure to the isomeric ionic form is depicted in Scheme 1. The rate-limiting step during the isomerization reaction could be either the intramolecular substitution of chloride by the dangling phosphorus donor (step b) or the replacement of L-L by free Cl^- (step c). The position of the equilibrium for step b would also be expected to affect the rate of isomerization if step c is rate limiting. When the same experiment was carried out with a substoichiometric amount (0.75 equiv) of dmpm, the same results were obtained, except that the free dmpm resonance reached this time a smaller relative intensity.

The individual steps in Scheme 1 have been tested stoichiometrically. The equilibrium of step b can be simplified as illustrated in eq 8. A salt of [CpCrCl-

$$CpCrCl_2(\text{L-L}) \rightleftarrows [CpCrCl(\text{L-L})]^+Cl^- \quad (8)$$

$$CpCrCl_2(\text{L-L}) + TlPF_6 \rightarrow [CpCrCl(\text{L-L})]^+PF_6^- + TlCl \quad (9)$$

$(\text{L-L})]^+$ with a noncoordinating anion (PF_6^-) has been prepared and reacted with Cl^- to regenerate the neutral $CpCrCl_2$(L-L) species. Attempts to prepare such compound with L-L = dmpm by eq 9 were not successful, because of the interference of the formation of complexes between the Tl^+ cation and the phosphine ligand. The use of $AlCl_3$ as Lewis acid led to similar problems. These results will be reported separately later.[27] However, we were successful in the synthesis of the analogous dppe complex. Reaction of $CpCrCl_2$(dppe) with the equimolar amount of $TlPF_6$ in THF leads to precipitation of TlCl and formation of $[CpCrCl(dppe)]^+PF_6^-$ (eq 9). A related ionic complex with a chelating diphosphine ligand, $[(\eta^5\text{-}C_5Me_5)Cr(CH_3)(dmpe)]^+PF_6^-$, has been previously prepared by the same strategy.[8]

The NMR spectroscopic properties of $[CpCrCl(dppe)]^+PF_6^-$ are as expected (see Experimental Section). In particular, no ^{31}P-NMR resonance other than the typical septet feature of the PF_6^- anion is observed. The Cp resonance in the ^{1}H-NMR spectrum is further shifted dowfield with respect to those of neutral $CpCrCl_2(PR_3)$ complexes, i.e. to δ 314. Addition of the stoichiometric amount of $[Ph_3PNPPh_3]^+Cl^-$ (PPN^+Cl^-) produces the spectrum shown in Figure 5, featuring the resonances of the dangling phosphorus of $CpCrCl_2(\eta^1\text{-dppe})$ (obtained through equilibrium 8) and of free dppe (supposedly obtained through an equilibrium process identical to that shown for the dmpm system in eq 7), in addition to the resonances of the PF_6^- anion and the PPN^+ cation. Therefore, it is established that equilibrium 8 can be shifted to the right (by Tl^+) or to the left (by Cl^-).

The equilibrium of step c in Scheme 1 can be simplified as illustrated in eq 10. The occurrence of equilib-

$$CpCrCl_2(\text{dmpm}) + Cl^- \rightleftarrows [CpCrCl_3]^- + \text{dmpm} \quad (10)$$

$$CpCrCl_2(\text{THF}) + PPNCl \rightarrow [PPN][CpCrCl_3] + \text{THF} \quad (11)$$

rium (10) has been demonstrated by investigating the reaction in both directions. The $[PPN]^+[CpCrCl_3]^-$ compound was prepared by addition of PPN^+Cl^- to

(27) Mattamana, S. P.; Poli, R. Unpublished results.

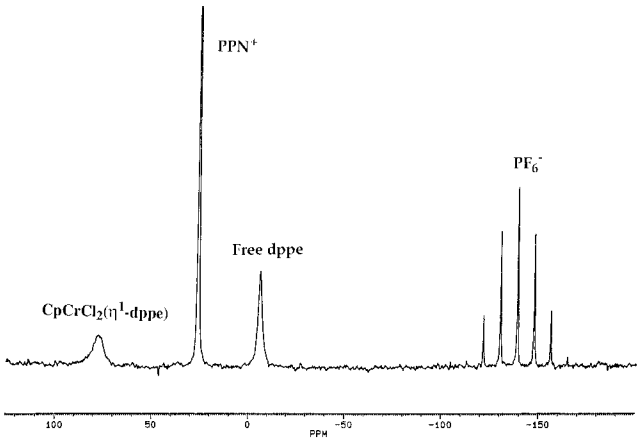


Figure 5. ^{31}P-NMR of the solution obtained by adding $[Ph_3PNPPh_3]Cl$ to $[CpCrCl(dppe)]PF_6$. Solvent = CD_3CN, room temperature.

$CpCrCl_2(THF)$ (which is in equilibrium with $[CpCrCl_2]_2$ as discussed above; see eq 2) in CH_2Cl_2; see eq 11. The compound shows a broad ^{1}H-NMR resonance at δ 216 in acetone-d_6, 225 in CD_2Cl_2, and 232 in $CDCl_3$, the latter one comparing fairly well with the value of 233.6 reported for the corresponding chromocenium salt in $CDCl_3$.[13]

The reaction of either $CpCrCl_2$(dmpm) with PPN^+Cl^-, or $[CpCrCl_3]^-$ with dmpm, in stoichiometric amounts afford the same equilibrium mixture of $CpCrCl_2$(dmpm) and $[CpCrCl_3]^-$ in approximately 1:2 ratio in acetone-d_6 or 2:1 ratio in CD_2Cl_2.

The result of the addition of dmpm to $[CpCrCl_2]_2$-(dmpm) (Figure 4), initially carried out in $CDCl_3$, is therefore satisfactorily explained by the isomerization process outlined in Scheme 1. Since the product of this isomerization is ionic, we tested the same process in the more polar solvents acetone (ϵ = 20.7) and acetonitrile (ϵ = 37.5; vs ϵ = 4.806 for chloroform). The results were essentially identical, featuring the initial disappearance of the free phosphine resonance, followed by its recovery. The final relative intensity of $CpCrCl_2(\eta^1$-dmpm) and free dmpm resonances was essentially the same in the three solvents. Analogous experiments on the dmpe system were hampered by the low solubility of the dinuclear starting material. Addition of 1 equiv of dmpe to $[CpCrCl_2]_2(\mu$-dmpe) caused the rapid dissolution of the precipitate, but the phenomenon of disappearance and subsequent recovery of the free phosphine resonance was not observed. Equally, such a phenomenon was not observed for the dppe system. However, in both cases the final solution exhibited the resonance of residual free phosphine, even when this was added in a substoichiometric amount.

B. Methyl Systems. B1. Dinuclear $[CpCrMe_2]_2$-(L-L) Compounds. Treatment of the chloride complexes $Cp_2Cr_2Cl_4$(L-L) with 2 equiv of methyllithium provided access, in each case, to the dinuclear methylated derivatives $[CpCrMe_2]_2$(L-L), eq 12.

$$Cp_2Cr_2Cl_4(L\text{-}L) + 4MeLi \rightarrow [CpCrMe_2]_2(L\text{-}L) + 4LiCl \quad (12)$$

L-L = dmpe, dmpm, dppe

All these compounds are quite soluble in apolar solvents. The dppe system is exceedingly sensitive and

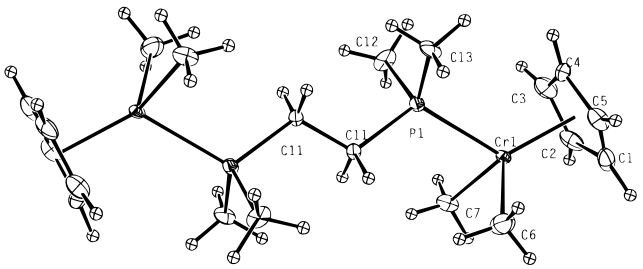


Figure 6. ORTEP view of compound $[CpCrMe_2]_2$(dmpe) showing the labeling scheme used. The ellipsoids are drawn at the 40% probability level.

eluded our characterization attempts, and the dmpm compound could not be obtained in the crystalline state. A crystal structure of compound $[CpCrMe_2]_2$(dmpe) (see Figure 6) shows the expected molecular dinuclear geometry, identical to that already established for the $[CpCrCl_2]_2$(L-L) (L-L = dppe, dmpe) complexes (vide supra). A severe disorder problem (see Experimental Section) did not allow a satisfactory refinement of the structure; therefore, the X-ray result is used only as a verification of the molecular geometry.

These dinuclear compounds exhibit similar optical and NMR properties, which are consistent with their formulation as 15-electron compounds. Neither compound shows a ^{31}P-NMR signal, consistent with binding of both phosphorus atoms to a paramagnetic Cr center. The ^{1}H-NMR resonance of the Cp hydrogen atoms (Table 4) is found at δ 187−188, showing a substantial decrease of spin density at the ring hydrogen nuclei on going from the dichloride to the dimethyl derivatives. The optical spectra show a similar pattern as the corresponding dichloride compounds, with a blue shift of the absorption bands by ca. 100 nm, which corresponds to a change of color from blue for the dichloride compounds to purple for the dimethyl analogues. This is as expected, given the stronger ligand field of alkyl ligands with respect to Cl.

B2. Mononuclear $[CpCrMe_2]_2$(L-L) Compounds. Solutions containing the mononuclear $CpCrMe_2$(L-L) complexes have been obtained by the same synthetic procedure that affords the dinuclear derivatives described above, except for the use of twice the amount of the diphosphine ligand (eq 13). These products are

$$CpCrCl_2(THF) + L\text{-}L + 2MeLi \rightarrow CpCrMe_2(L\text{-}L) + 2LiCl + THF \quad (13)$$

extremely soluble in hydrocarbons and could not be crystallized as pure materials. Crystals of $CpCrMe_2$-(dmpm) were obtained at low temperature, but these melted upon warming to room temperature. As for the dinuclear systems described above, the dppe complex appeared less stable, but its presence in the final solution is nevertheless demonstrated by NMR spectroscopy (vide infra). In all these solutions, free phosphine is always observed. A possible equilibrium between the mononuclear and the dinuclear compound (or an ionic isomer of the latter as for the chloride system described above) seems thus indicated. Indeed, the cationic and anionic alkyl complexes $[CpCrMe(dmpe)]^+PF_6^-$ and $Li[CpCrMe_3]$ are known.[8,24] However, given the extreme air sensitivity of these compounds, we did not pursue a detailed study of such equilibrium process.

The presence in solution of the molecular 15-electron species $CpCrMe_2(\eta^1\text{-L-L})$ with a dangling phosphine ligand is directly indicated by the broad ^{31}P-NMR resonance attributed to the uncoordinated P nucleus (Table 4). In addition, ^{1}H-NMR resonances attributed to the dangling PMe_2 groups are also observed for the dmpm and dmpe compounds, these being sufficiently distinct from the resonance of the free phosphine which is also present. It is interesting to compare the ^{31}P-NMR paramagnetic shift experienced by the various derivatives on going from free phosphine to the dangling phosphine in the dichloride and dimethyl complexes. dppe is shifted downfield from δ −12.8 to +83.8 upon coordination to the "$CpCrCl_2$" moiety, a shift of 95 ppm, and a further downfield shift of 19 ppm is observed upon replacing the two Cl with Me ligands. For the dmpe derivatives, these shifts are 21.7 and 18.4 ppm, whereas for the dmpm derivatives they are 26.7 and 137 ppm, respectively. Thus, the chemical shift qualitatively moves downfield in the series L-L < $CpCrCl_2$(L-L) < $CpCrMe_2$(L-L) but, from the quantitative point of view, the chemical shifting pattern is different for each system for reasons that are presently unclear. We should also observe that there is a considerable solvent dependence of the dangling phosphorus chemical shift, this value for $CpCrCl_2$(dmpm) being −28.1 ppm in $CDCl_3$ and −8.2 in C_6D_6. The other dichloride derivatives were not sufficiently soluble in C_6D_6 to record a ^{31}P-NMR spectrum, whereas the dimethyl derivatives decomposed in $CDCl_3$ to afford blue solutions of the corresponding dichlorides. The optical spectra of solutions containing the $CpCrMe_2$(L-L) materials (vide infra) are essentially superimposable with those of the corresponding dinuclear $[CpCrMe_2]_2$(L-L) complexes.

Compound $CpCrMe_2$(dmpe) was found to be thermally stable in refluxing THF (no noticeable decomposition over 10 h). This result is in contrast with the observed spontaneous reduction by alkyl radical elimination of compound $Cp^*Cr(CH_2Ph)_2$(THF) upon treatment with the bidentate 2,2′-bipyridyl (bipy) ligand, to afford the 16-electron Cr(II) product $Cp^*Cr(CH_2Ph)$(bipy).[28]

C. Absence of 17-Electron Species. We have demonstrated the adoption of 15-electron structures for compounds $CpCrX_2$(L-L) (X = Cl, Me) by ^{1}H- and ^{31}P-NMR in solution and by an X-ray structural determination on $CpCrCl_2$(dmpm) in the solid state. However, the data discussed so far cannot rule out the presence of a minor equilibrium amount of a 17-electron species (e.g. $CpCrX_2(\eta^2\text{-L-L})$). Such a 17-electron species should display dramatically different optical properties with respect to those characteristic of the 15-electron, spin quartet geometry. The optical spectra of solutions of the mononuclear $CpCrX_2$(L-L) complexes (also containing all the other species in equilibrium with them for X = Cl; vide supra), on the other hand, match very well the spectrum of the corresponding $CpCrX_2(PMe_3)$ (see Figure 7). This indicates that if a 17-electron species is present, its relative amount must be very small.

Direct evidence for a 17-electron species should be provided by EPR spectroscopy. All the 15-electron configurations for Cr(III) are characterized by a spin quartet ground state. Although relatively sharp EPR spectra are observed for Werner-type octahedral com-

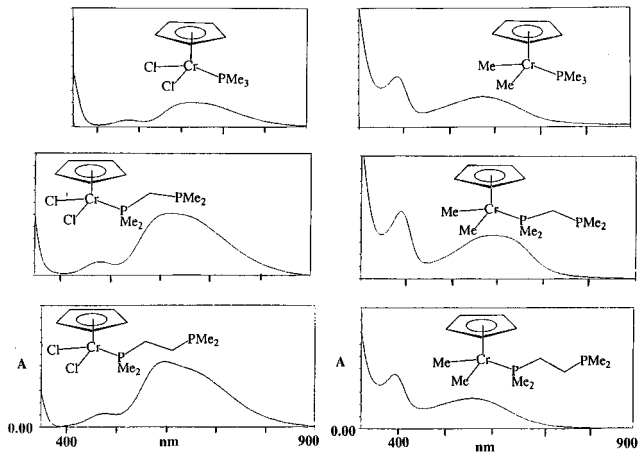


Figure 7. Visible spectra of the $CpCrX_2$(L-L) species (X = Cl, Me; L-L = dppe, dmpe, dmpm) in comparison with those of $CpCrX_2(PMe_3)$.

plexes of Cr(III),[29] the electronic relaxations are apparently much faster for spin quartet half-sandwich compounds, leading to EPR silent solutions at room temperature.[30] In fact, we find that compounds $CpCrX_2(PMe_3)$ (X = Cl, CH_3) are EPR silent in isotropic solution down to the freezing point of the toluene solvent. Furthermore, addition of an excess PMe_3 to these solution does not generate any isotropic EPR signal. At the liquid-N_2 temperature, a typical EPR spectrum for a $S = {}^3/_2$ d^3 center is observed such as that reported[30] for $CpCrCl(CH_3)(PMe_3)$. A hypothetical 17-electron structure, however, must necessarily have an orbitally nondegenerate spin doublet ground state, for which relatively sharp EPR signals are expected even at room temperature, as have been reported for the corresponding Mo(III) systems, $CpMoCl_2(PR_3)_2$.[31−33] Solutions of any of the compounds $CpCrX_2$(L-L) (X = Cl, Me; L-L = dppe, dmpe, dmpm) do not show an EPR signal down to the freezing point of the solvent,[34] therefore indicating that the 17-electron structure $CpCrX_2(\eta^2\text{-L-L})$ is energetically inaccessible. The spectra at liquid-nitrogen temperature are, again, consistent with $S = {}^3/_2$ d^3 systems (e.g. see the spectrum of $CpCr(CH_3)_2$(dmpe) in Figure 8) and do not show signals in the $g = 2$ region that could be attributed to a $S = {}^1/_2$ species. Estimating an EPR detection limit of 10^{-5} M and given the concentrations used for the experiment (up to 5×10^{-2} M), we estimate an upper limit of 2×10^{-4} for the molar fraction of $CpCrX_2(\eta^2\text{-L-L})$ in solution at 300 K. This, in turn, sets a lower limit of 21.2 kJ (5.1 kcal) for the free energy of $CpCrX_2(\eta^2\text{-L-L})$ relative to $CpCrX_2(\eta^1\text{-L-L})$.

Discussion

This work was spurred by the question of what determines the structural and electronic preference of

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(34) EPR signals due to 17-electron Cr(III) species have been observed in our laboratory for other $CpCrX_2L_2$ systems (e.g. X = CN). These results will be reported in due course.

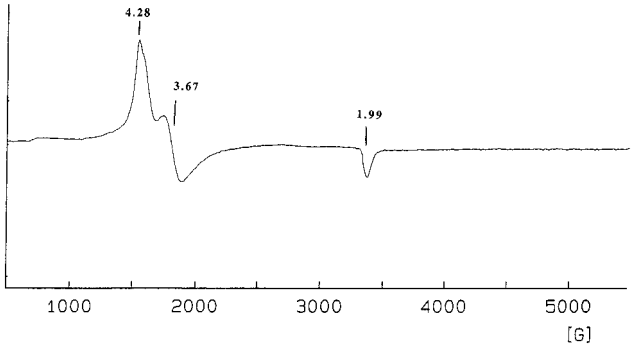

Figure 8. EPR spectrum of compound $CpCr(CH_3)_2(dmpe)$ at 77 K in a frozen toluene glass.

half-sandwich group 6 M(III) compounds: 15-electron, $S = {}^3/_2$, for Cr and 17-electron, $S = {}^1/_2$, for Mo. The paucity of 17-electron Cr(III) systems has also been pointed out in a recent review article.[18] A simple answer to this question could be based on a combination of steric and bond energy factors: Cr^{3+} is much smaller than Mo^{3+}, thus one could imagine that the interligand repulsion in the 17-electron Cr system exceeds the M−L bond strength. A similar situation was discussed for the Cr−Cr bond formation in the $[CpCr(CO)_2(L)]_2$ dimers (L = CO or $P(OMe)_3$).[35] In addition, the M−L bond strength is expected to be smaller for Cr relative to Mo.[19] However, the situation must be more complex. To illustrate why, we simply need to compare the nonexistence of the 17-electron $CpCrX_2(PR_3)_2$ systems for either X = Cl or CH_3 with the existence and stability of isosteric 16-electron $CpVX_2(PR_3)_2$ (X = Cl or alkyl).[36,37] In fact, the vanadium systems are stable with sterically more demanding phosphine ligands (e.g. PEt_3) than those with which Cr cannot form more than a three-legged piano stool structure. For instance, $CpCrCl_2(PMe_3)$ will not form a hypothetical 17-electron $CpCrCl_2(PMe_3)_2$. Fourteen-electron complexes of type $CpVX_2L$ have been reported only with sterically encumbering ligands, e.g. $CpV(CH_2CMe_3)_2(PMe_3)$.[38] This comparison demonstrates that Cr(III) has the steric ability to form 17-electron, four-legged piano stool structures. Another interesting observations is that the half-sandwich V(II) system $CpVXL_2$ (X = halide or alkyl, L = tertiary phosphine), isoelectronic with the Cr(III) system, also exists as a spin quartet 15-electron species and has no tendency to bind another ligand.

A rationalization of the different structural preference for half-sandwich compounds of Cr(III) and V(II) on one hand, and V(III) on the other, may be found when considering the energetic effect of electron pairing.[39,40] For the three-legged piano stool structure, the three valence orbitals that remain available after formation of the metal−ligand σ bonds are occupied by three metal electrons for the complexes of the d^3 Cr(III) and V(II) metal centers, while the corresponding d^2 V(III) center

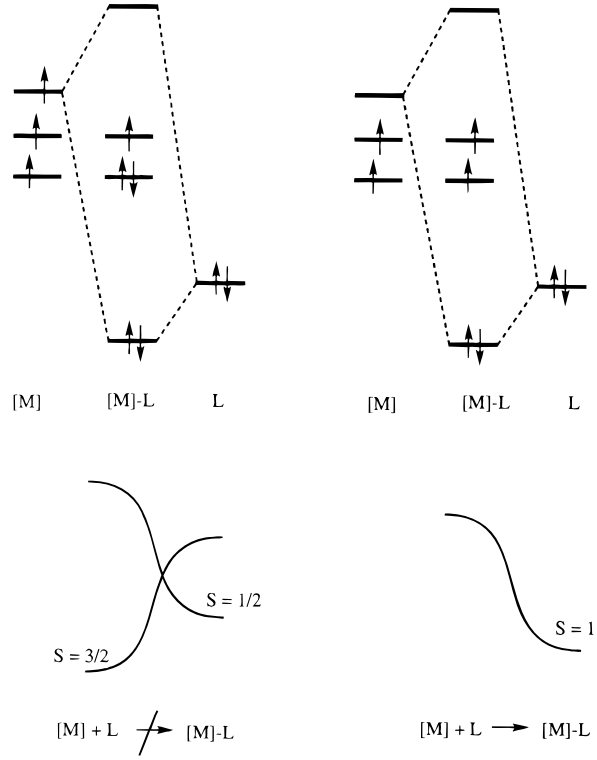

Figure 9. Qualitative orbital interaction diagram (top) and reaction coordinate (bottom) for the reaction between [M] and L ([M] = 15-electron $CpVXL_2$ or $CpCrX_2L$ (left) or 14-electron $CpVX_2L$ (right)).

provides only two electrons. The experimentally determined magnetic properties indicate a quartet ground state for the V(II) and Cr(III) complexes and a spin triplet ground state for the V(III) complexes. The hypothetical interaction with an additional 2-electron donor, resulting in the formation of a new metal−ligand bond, requires the availability of an empty metal orbital. Thus, the process will take place for the d^3 metal centers only at the expense of pairing two electrons to produce a spin doublet product, while the ligand addition to the d^2 V(III) center does not require electron pairing (see Figure 9). Hence, the formation of a new V(III)−L bond to afford a 16-electron $CpVX_2L_2$ complex is only hindered sterically, whereas the formation of a new V(II)−L or Cr(III)−L bond to afford a 17-electron $CpVXL_3$ or $CpCrX_2L_2$ complex is a trade-off of the energetic cost of pairing the electrons (plus the increase of steric repulsion) and the energetic gain of the new M−L bond. The results already available in the literature indicate that this trade-off favors the less saturated and higher spin geometries for V(II) and Cr(III), whereas it favors the more saturated, spin-paired geometry for Mo(III). The well-documented stability of spin doublet, 17-electron $CpMoX_2L_2$ systems[4] finds a rationalization in the expected stronger Mo−L bonds and lower Mo pairing energy (the cost of pairing the electrons is less in the more diffuse 4d orbitals of Mo with respect to the 3d orbitals of Cr or V). These qualitative considerations are supported by preliminary theoretical calculations, which will be presented in detail in a separate contribution.[41]

The results presented in this contribution show that the thermodynamic help of the chelate effect is not sufficient to tilt the balance in favor of a more saturated

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structure for the half-sandwich $CpCrX_2$(L-L) (X = Cl, CH_3) system. The formation of a chelate ring should provide an ideal increase of 8.0 eu in translational entropy with respect to the formation of the corresponding structure with two enthalpically equivalent monodentate ligands,[42] which corresponds to a free energy contribution ($-T\Delta S$) of 2.4 kcal/mol at 298 K. The enthalpic equivalence is not necessarily guaranteed because a hypothetical $CpCrX_2L_2$ (L = monodentate ligand) may adopt a trans geometry, while the $CpCrX_2$-(L−L) structure would presumably adopt a cis geometry as found for the structurally characterized $CpMoBr_2$-(dppe).[32] In addition, there is likely to be some strain in the metallacycle, which should be minimal, however, for the five-membered rings with the dmpe and dppe ligands.[43] These enthalpic effects oppose the entropic help; thus, an overall free energy gain of 2.4 kcal/mol is the maximum expected under ideal circumstances. The sum of this chelate effect gain and the estimated minimum energy of 5.1 kcal/mol for the 17-electron $CpCrX_2(\eta^2$-L-L) with respect to the 15-electron $CpCrX_2$-(η^1-L-L) indicates that the hypothetical 17-electron $CpCrX_2(L)_2$ with X = Cl or L and L = phosphine ligand could be 7.5 kcal/mol or more higher in energy than the $CpCrX_2L$ + L system.

Conclusion

We propose that half-sandwich Cr(III) compounds prefer to adopt a 15-electron, spin quartet configuration instead of adding another ligand and reaching a 17-electron configuration as is the case of Mo(III), because the cost of pairing the electron into the required spin doublet configuration exceeds the energetic gain of forming the new bond. The chelate effect of ligands such as dmpe is not sufficient to overcome this unfavorable energy differential. The stabilization of the less saturated configuration by metal−ligand π bonding is not sufficiently important for this system, because analogous results were obtained for the dichloride and the dimethyl systems. It is not unlikely, though, that 17-electron half-sandwich complexes with a spin $^1/_2$ ground state may exist with other ligand systems[34] or that they could represent intermediates in organometallic reactions such as ligand exchange. Experiments to test these hypotheses are currently in progress.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9508521) for support of this work. The EPR spectrometer was upgraded in part with NSF funds (Grant CHE-9225064).

Supporting Information Available: For compounds $[CpCrCl_2]_2$(dppe), $[CpCrCl_2]_2$(dmpe), $CpCrCl_2$(dmpm), and $[CpCr(CH_3)_2]_2$(dmpe), tables of crystal data, fractional atomic coordinates and *U* values, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and *U* values (24 pages). Ordering information is given on any current masthead page.

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