Kurzmitteilung / Short Communication

Dialkyl(η^5-cyclopentadienyl)chromium Derivatives with Extreme Values of $^{1(2)}$H-NMR Parameters[1)]

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Received January 13, 1989

Key Words: Dialkylchromium(III) half-sandwich molecules / Paramagnetic $^{1(2)}$H- and ^{13}C-NMR data

The title compounds $CpCrR_2(PR'_3)$ (R = CH_3, $CH_2C_6H_5$, CH_2SiMe_3) and $Cp^*Cr(CH_3)_2(PMe_3)$ (3b) have been prepared, and a piano-stool geometry has been established for 3b by X-ray structure analysis. Convenient observation of the hydrogen atoms 1′-H of R is only possible by ^{2}H NMR giving signals which are up to 6200 Hz broad and shifted up to −1373 ppm.

One of the most recent applications of cyclopentadienyl (Cp = C_5H_5, Cp* = C_5Me_5) as a co-ligand for the stabilization of transition-metal hydrocarbyl complexes is the access to magnetic derivatives of the general formula $CpMR_nL_m$ [2)]. Important examples include M = V, Cr, W, and Re with up to four groups R bound to M. A key feature of these compounds is their increased reactivity originating from the unpaired electrons. The potential of this chemistry is, however, limited by the lack of a rapid and efficient analytical method. In particular, NMR spectroscopy seemed to be unsuitable because the most important ^{1}H-NMR signals, those of R = CH_3 and the like, were missing. The same applies for the paramagnetic dialkylmetal compounds $MR_2(R'_2PCH_2CH_2PR'_2)_2$ [3)]. We have now synthesized a series of formerly unknown dialkylchromium half-sandwich compounds $CpCrR_2L$ (L = PR'_3), which allows *all* hydrogen atoms to be routinely identified by paramagnetic NMR spectroscopy.

Bluish green antiferromagnetic $[CpCrCl_2]_2$ (**1a**)[4)] and $[Cp^*CrCl_2]_2$ (**1b**)[5)] are cleaved quantitatively to give the dark blue paramagnetic half-sandwich compounds $CpCrCl_2(PR'_3)$ (**2a**−**c**)[6)]. When **2a** is treated with two equivalents of MeMgI or MeLi a bluish violet air-sensitive product is isolated which is soluble in pentane, toluene, or ethers without decomposition and which must be formulated as $CpCrMe_2(PMe_3)$ (**3a**) according to the elemental analysis. Similarly bluish violet (in solution) $Cp^*CrMe_2(PMe_3)$ (**3b**), deep red $CpCr(CH_2C_6H_5)_2(PEt_3)$ (**3c**), and deep blue $CpCr(CH_2SiMe_3)_2(PMe_3)$ (**3d**) have been obtained in 58−82% yield. In the mass spectrum (EI, 70 eV) we can identify the molecular ion of **3c** only. The compounds **3a**−**d** are thermally unstable producing other magnetic species, e. g. chromocene.

$[CpCrCl_2]_2$
1a

$CpCrCl_2(PR'_3)$
2a: R′ = Me
c: R′ = Et

$Cp^*CrCl_2(PMe_3)$
2b

$[Cp^*CrCl_2]_2$
1b

$CpCrR_2(PMe_3)$
3a: R = Me
d: R = CH_2SiMe_3

$Cp^*CrMe_2(PMe_3)$
3b

$CpCr(CH_2C_6H_5)_2(PEt_3)$
3c

$CpCr(CD_3)_2(PMe_3)$
4a

$Cp^*(CD_3)_2(PMe_3)$
4b

$CpCr(CD_2C_6D_5)_2(PEt_3)$
4c

Cp* = C_5Me_5

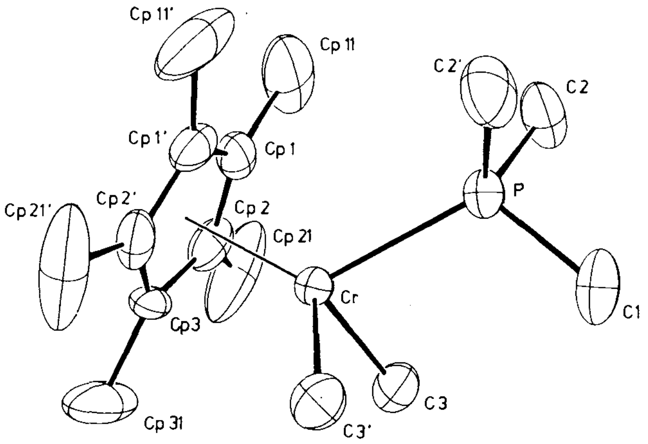

Figure 1. Structure of **3b** in the crystal (ORTEP, displacement ellipsoids 50%, hydrogen atoms omitted). Selected distances [Å] and angles [°]: Cr−C3 2.067(5), Cr−P 2.426(2), Cr−D 1.948, C3−Cr−C3′ 92.8(3), C3−Cr−P 91.5(2), C3−Cr−D 122.5, P−Cr−D 126.6 with D = center of gravity of Cp*

We have established the structure of the dialkylchromium derivatives by a crystallographic study of **3b**. As shown in Figure 1, **3b** is a mononuclear molecule having the crystallographic symmetry C_s, and chromium is coordinated tetrahedrally. The Cr−C3 distance [2.067(5) Å] seems to be typical[2c,e,f)] for chromium(III)−alkyl fragments, and the methyl groups of Cp* are bent away from the metal (average 3.7°). The rather large angles C3−Cr−C3′ and C3−Cr−P [92.8(3) and 91.5(2)°] reflect the π-donor effect of Cp*[4b)].

Among the NMR data[7)] the shift of $\delta^{para}(^1H) \approx -180$ for the signal of the Cp protons is characteristic and of diagnostic value. The comparison with analogous dihalides $CpCrCl_2L$[4b,6)] having $\delta^{para}(^1H) = -230$ to -250 indicates that the three unpaired electrons are delocalized less efficiently on the Cp ligands of **3a, c, d**. The temperature dependence of all $\delta^{para}(^1H)$ values does not deviate

Chem. Ber. 122 (1989) 897−899 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1989 0009−2940/89/0505−0897 $ 02.50/0

strongly from the Curie law and confirms mononuclear species in solution.

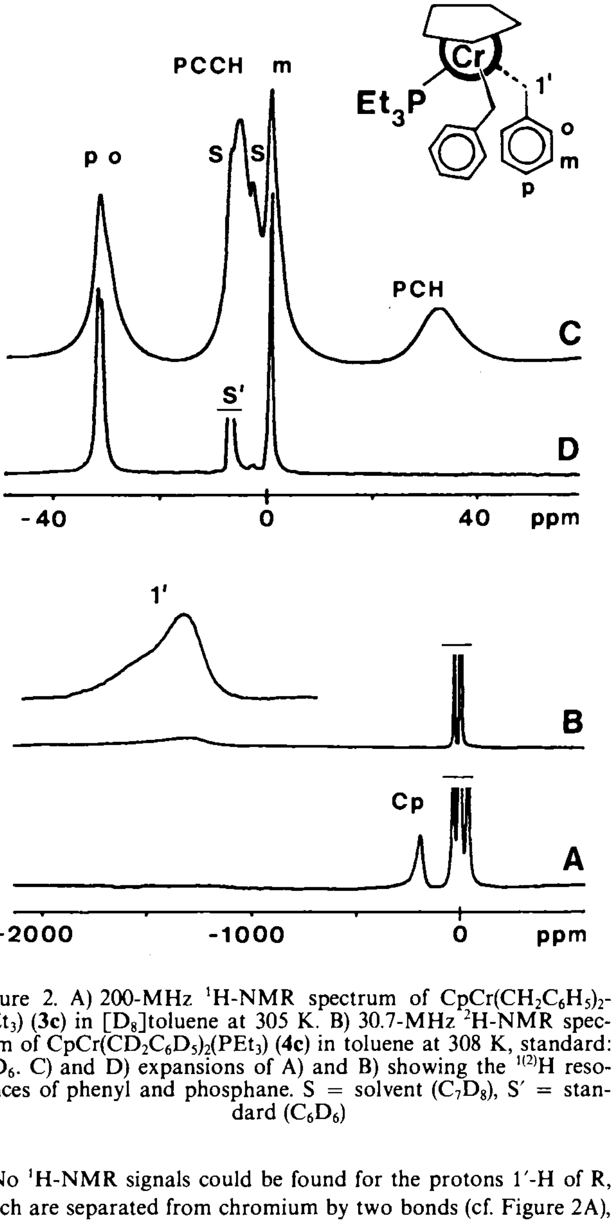

Figure 2. A) 200-MHz ^{1}H-NMR spectrum of CpCr(CH$_2$C$_6$H$_5$)$_2$(PEt$_3$) (**3c**) in [D$_8$]toluene at 305 K. B) 30.7-MHz ^{2}H-NMR spectrum of CpCr(CD$_2$C$_6$D$_5$)$_2$(PEt$_3$) (**4c**) in toluene at 308 K, standard: C$_6$D$_6$. C) and D) expansions of A) and B) showing the $^{1(2)}$H resonances of phenyl and phosphane. S = solvent (C$_7$D$_8$), S' = standard (C$_6$D$_6$)

No ^{1}H-NMR signals could be found for the protons 1'-H of R, which are separated from chromium by two bonds (cf. Figure 2A), although corresponding signals have long been known for alkyluranium derivatives[8]. A study of Cp$_2$V$-$R shows[9] that the signals in question may have large shifts and line widths W. Substituting ^{1}H for ^{2}H reduces W in ^{2}H NMR[10a], and a test with [H$_{10}$/D$_{10}$]chromocene gave a signal narrowing factor of 37[10b]. Actually, at 305 K CpCr(CD$_3$)$_2$(PMe$_3$) (**4a**) shows a signal with $\delta^{para}(^2H) = -1373 \pm 10$ and $W = 1900$ Hz after few accumulations. We conclude that the corresponding ^{1}H-NMR signal should be up to 80 kHz broad and difficult to detect. Similar data[11] are obtained from Cp*(CD$_3$)$_2$(PMe$_3$) (**4b**) and CpCr(CD$_2$C$_6$D$_5$)$_2$(PEt$_3$) (**4c**); most striking is a signal splitting of 170 ppm (Figure 2B) for the diastereotopic deuterons 1'-H of **4c**. Figure 2C/D illustrates the general increase of the signal resolution in ^{2}H NMR, which allows to distinguish *ortho/para*-H of **4c**. Much less shifted signals are found for 1'-H of dinuclear derivatives (e.g. [CpCr(CD$_2$C$_6$D$_5$]$_2$(μ-Cl)$_2$ with $\delta^{para}(^2H) = -612$) due to antiferromagnetism.

The extreme NMR parameters may be traced to selective spin transfer from chromium to hydrogen by σ-π interaction[9]. The same should apply to many other magnetic hydrocarbyl compounds and allow detailed studies including hyperconjugation. We currently use these results to investigate the thermal reactivity of the dialkylchromium derivatives.

This contribution has been supported by the *Fonds der Chemischen Industrie* and the *Degussa AG.*

Experimental

Dibenzyl(η^5-cyclopentadienyl)(triethylphosphine)chromium (**3c**): When 1.2 ml (8.1 mmol) of PEt$_3$ was added under argon to a suspension of 1.50 g (4.0 mmol) of [CpCrCl$_2$]$_2$ (**1a**) in 150 ml of ether a dark blue solution of CpCrCl$_2$(PEt$_3$) (**2c**) was obtained. On cooling to -20°C and slow addition of 35 ml of a 0.47 M solution of C$_6$H$_5$CH$_2$MgCl (16.5 mmol) in ether the mixture turned red. Replacing ether for hexane and cooling to -78°C afforded analytically pure black crystals of **3c**. Yield 2.77 g (82%).

C$_{25}$H$_{34}$CrP (417.5)	Calcd.	C 71.92	H 8.21	Cr 12.45	P 7.42
	Found	C 71.36	H 8.21	Cr 12.91	P 7.12
	Mol. mass 417 (MS)				

Analogously have been prepared:

(η^5-Cyclopentadienyl)dimethyl(trimethylphosphine)chromium (**3a**): From 1 ml (9.7 mmol) of PMe$_3$, 1.16 g (3.1 mmol) of **1a**, and 7.5 ml of a 1.67 M solution of MeLi (12.5 mmol) in ether dark bluish violet crystals of **3a** were obtained. Yield 930 mg (67%).

C$_{10}$H$_{20}$CrP (223.2)	Calcd.	C 53.80	H 9.03
	Found	C 52.58	H 8.78

Dimethyl(pentamethyl-η^5-cyclopentadienyl)(trimethylphosphine)-chromium (**3b**): From 0.6 ml (5.8 mmol) of PMe$_3$, 1.18 g (2.3 mmol) of **2b**, and 6.9 ml of a 1.45 M solution of MeLi (10.0 mmol) in ether dark bluish violet crystals of **3b** were obtained. Yield 800 mg (59%).

C$_{15}$H$_{30}$CrP (293.4)	Calcd.	C 61.41	H 10.31	Cr 17.72
	Found	C 60.33	H 10.01	Cr 18.01

(η^5-Cyclopentadienyl)(trimethylphosphine)bis[(trimethylsilyl)-methyl]chromium (**3d**): From 0.4 ml (3.9 mmol) of PMe$_3$, 0.55 g (1.5 mmol) of **1a**, and 17.4 ml of a 0.34 M solution of (CH$_3$)$_3$SiCH$_2$Li (5.9 mmol) in ether deep blue crystals of **3d** were obtained. Yield 630 mg (58%).

C$_{16}$H$_{36}$CrPSi$_2$ (367.6)	Calcd.	C 52.28	H 9.87
	Found	C 51.05	H 9.57

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors of **3b**

ATOM	X/A	Y/B	Z/C	U(eq.)
CR	0.06031(6)	0.25000	0.0426(1)	0.037
P	-0.0662(1)	0.25000	0.1931(3)	0.048
C1	-0.1509(5)	0.25000	0.058(1)	0.083
C2	-0.0885(3)	0.3553(5)	0.3295(9)	0.074
C3	0.0218(3)	0.3623(4)	-0.1192(7)	0.060
CP1	0.1443(3)	0.3018(4)	0.2530(8)	0.057
CP2	0.1749(3)	0.3357(4)	0.1051(9)	0.037
CP3	0.1937(4)	0.25000	0.0057(9)	0.059
CP11	0.1227(4)	0.3656(8)	0.401(1)	0.167
CP21	0.1873(4)	0.4410(6)	0.060(1)	0.066
CP31	0.2333(6)	0.25000	-0.158(1)	0.208

X-ray Structure Analysis of **3b**: Single crystals of **3b** were obtained from pentane solutions at -42°C. C$_{15}$H$_{30}$CrP, M_r = 293.376, orthorhombic, space group *Pnma*, a = 16.748(1), b = 13.325(1), c = 7.857(1) Å, V = 1753.4 Å^3, d_{calcd} = 1.111 g/cm^3, μ(Mo-K_α) = 7.1 cm^{-1}, Z = 4, $F(000)$ = 636, T = 23°C. 3821 measured reflections; 1792 independent (R_{int} = 0.02) and 1211 "observed" with $F_o \geq 4.0\,\sigma(F_o)$ [$(\sin \vartheta/\lambda)_{max}$ = 0.617, $+h$, $\pm k$, $+l$, $\vartheta - 2\vartheta$ scan, Mo-K_α radiation, λ = 0.71069 Å, Enraf-Nonius CAD4]. Structure solution by Patterson methods, R (R_w) = 0.066 (0.055), $w = 1/\sigma^2(F_o)$ (85 refined parameters, anisotropic, H constant, SHELX-76). $\Delta\varrho_{fin}$(max/min) = 0.42/−0.36 e/Å^3. Further details of the crystal structure analysis are available from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53492, the names of the authors, and the journal citation.

CAS Registry Numbers

1a: 64024-36-8 / **1b**: 119456-15-4 / **2a**: 119456-16-5 / **2b**: 119456-18-7 / **2c**: 119456-17-6 / **3a**: 119456-19-8 / **3b**: 119456-21-2 / **3c**: 119456-22-3 / **3d**: 119456-20-1 / **4a**: 119456-23-4 / **4b**: 119456-24-5 / **4c**: 119456-25-6 / $CrCl_3(THF)_3$: 10170-68-0 / Cp*Li: 51905-34-1 / $(CH_3)_3SiCH_2Li$: 1822-00-0

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[5] From Cp*Li and $CrCl_3(THF)_3$ in 67% yield; ^1H NMR ($CDCl_3$, 303 K: δ^{para} = 52.2. ^{13}C NMR ($CDCl_3$, 337 K): δ^{para} = 49 [$\mathit{C}_5(CH_3)_5$], −311 [$C_5(\mathit{C}H_3)_5$], negative sign for signals at high frequency; H. Zeh, *Diplomarbeit*, Techn. Univ. München, 1986. See also H. Benn, G. Wilke, D. Henneberg, *Angew. Chem.* **85** (1973) 1052; *Angew. Chem. Int. Ed. Engl.* **12** (1973) 1001.

[6] ^1H NMR ([D_8]toluene, 305 K): **2a**, δ^{para} = −231 (C_5H_5), 33.3 (PCH); **2b**, δ^{para} = 0.9 [$C_5(CH_3)_5$], 31.2 (PCH); **2c**, δ^{para} = −231 (C_5H_5), 45.7 (PCH), −5.4 (PCCH). – ^{13}C NMR ([D_8]toluene, 305 K): **2a**, δ^{para} = −83.0 (C_5H_5), −327 (PC); **2b**, δ^{para} = 51.7 [$\mathit{C}_5(CH_3)_5$], −411 [$C_5(\mathit{C}H_3)_5$], −224 (PC); **2c**, δ^{para} = −80.0 (C_5H_5), −272 (PC), 34.6 (PC*C*).

[7] ^1H NMR ([D_8]toluene, 305 K): **3a**, δ^{para} = −174 (C_5H_5), 18.8 (PCH); **3b**, δ^{para} = −26.4 [$C_5(CH_3)_5$], 20.6 (PCH); **3c**, δ^{para} = −184 (C_5H_5), 37.3 (PCH), −4.6 (PCCH), −26 (*o*-H), 23.7 (PCH), 8.2 (*m*-H), −27.7 (*p*-H); **3d**, δ^{para} = −179 (C_5H_5), 2.0 (SiCH). – ^{13}C NMR ([D_8]toluene, 305 K): **3a**, δ^{para} = −105 (C_5H_5), −1018 (PC).

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[11] ^2H NMR (toluene, 305 K): **4b**, δ^{para} = −1300, W = 2400 Hz (1′-H); **4c**, δ^{para} = −1340 and −1510, $W \approx$ 6200 Hz.

[8/89]