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A mixed halo/n-alkyl compound of chromium(III): synthesis, structure, and reactivity of $Cr(n\text{-}Bu)_2Cl[(Me_2PCH_2)_3CMe]$

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Abstract

$Cr(n\text{-}Bu)_2Cl[(Me_2PCH_2)_3CMe]$ has been synthesized, characterized, and subjected to a single-crystal X-ray structure determination of its toluene solvate. Space group *Pcnb* with (−158°C) a 18.696(7) Å, b 15.055(5), c 21.697(7), $Z = 8$ and $R(F) = 0.0805$. There is no evidence for agostic C−H−Cr interactions in the structure, but the alkyl groups cause a marked lengthening of Cr−P bonds in comparison to chlorine as the group *trans* to P. ^1H NMR spectra of the analogous methyl, ethyl, propyl and butyl compounds reveal that only the γ and δ hydrogens of the alkyl substituent give detectable signals, while all hydrogens on the tripod ligand are observed.

Introduction

In search of synthetic routes to new polyhydrides of chromium containing the sterically-compact and highly-basic phosphine $MeC(CH_2PMe_2)_3$ (tripod) we have discovered that use of borohydride reagents with $(tripod)CrCl_3$ can give rise to unexpected problems [1]. We therefore, redirected our goal to one of hydrogenolysis of a chromium alkyl (e.g., $(tripod)CrR_3$). We report here the unusual synthetic outcome and complete characterization of the reaction product of $(tripod)CrCl_3$ and n-BuLi in hexanes.

Experimental

General procedures

All operations were performed under a nitrogen atmosphere, using standard Schlenk techniques for air- and moisture-sensitive materials. Pentane and diethyl ether were dried and distilled prior to use from solutions containing sodium/potassium benzophenone ketyl. n-BuLi (in hexanes) and MeLi (in Et_2O) were purchased from Aldrich. EtLi and n-PrLi were synthesized by reaction of the

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appropriate halide (CH_3CH_2Cl or $CH_3(CH_2)_2Cl$) with two equivalents of Li metal at −20 °C in Et_2O. ^1H NMR spectra were recorded on a Nicolet NT-360 or a Bruker AM500 spectrometer. For paramagnetic samples, a standard one-pulse sequence experiment was performed using a delay time between pulses of two sec. and a 90° pulse with a duration of 5 μsec and a sweep width of ±74380 Hz (±206 ppm) was employed for all samples. Full width at half-height (Hz) and assignment are shown in parentheses (following chemical shift) for those resonances where this parameter could be measured (i.e., when it was not obscured by overlap with a nearby resonance). The magnetic susceptibility was determined in C_6D_6 (Evans method [2]) at 22 °C. Gas chromatography was accomplished using a Varian Model 3700 gas chromatograph with a J&W DB-5 (0.25 μM) 30 m fused silica capillary column.

Synthesis of chromium alkyls

Cr(n-Bu)$_2$Cl(tripod) (I). In a typical preparation n-BuLi (1.1 ml, 1.65 M) in hexane was added to $CrCl_3$(tripod) [1] (0.25 g; 0.61 mmol) slurried in pentane at 20 °C. The blue slurry immediately turns into a red solution. The reaction mixture was then filtered through a medium porosity frit to yield a bright red homogeneous solution. The solution volume was then reduced to approximately 2 ml and cooled to −20 °C for 24 h to produce red plates. X-ray quality crystals were grown from toluene, by a similar procedure. ^1H NMR (C_6D_6): δ 8.5 ppm (360 Hz), $\gamma(CH_2)$), 4.9 ppm (660 Hz, n-BuCH_3), −0.5 ppm (360 Hz, CCH_3), −7.5 ppm (1497 Hz, PMe_2), and −25 ppm (1900 Hz, CH_2P); Magnetic susceptibility μ 3.7 BM; IR (Nujol, cm^{-1}), 2760s, 1985w, 1915w, 1420s, 1410s, 940s, 917s, 719m.

Cr(n-Pr)$_2$Cl(tripod) (II). Compound II was synthesized in a manner identical to I, using n-PrLi (1.3 M in Et_2O). Microcrystalline material was obtained by cooling (−20 °C) a concentrated pentane solution for 48 h. ^1H NMR (C_6D_6): δ −0.44 ppm (268 Hz, CCH_3), −8.9 ppm (br, PMe_2), −10.9 ppm (br, n-Pr, CH_3), and −25.4 ppm (1134 Hz, CH_2P).

Cr(Et)$_2$Cl(tripod) (III). To $CrCl_3$(tripod) slurried in pentane was added three equivalents of EtLi (0.9 M in Et_2O). This mixture was stirred at room temperature for 35 min, after which time there is an orange precipitate and an orange solution present. The solvent was then removed in vacuo and the remaining orange solid extracted with toluene; the toluene solution was filtered to yield a homogeneous orange solution. Concentrating and cooling this solution yields orange/red microcrystals. ^1H NMR (toluene-d_8): δ −0.48 ppm (150 Hz, CCH_3), −7 ppm (734 Hz, PMe_2), and −25 ppm (v.br, CH_2P).

Cr(Me)$_2$Cl(tripod) (IV). To $CrCl_3$(tripod) (0.3 g; 0.7 mmol) in pentane (20 ml) was added nine equivalents of MeLi (1.4 M in Et_2O). The reaction mixture was then stirred for 2 h after which time a pale orange precipitate had formed. The solvent was then removed in vacuo and the pale orange powder was extracted with toluene (75 ml) and filtered to yield a bright orange solution. This solution was then cooled to −78 °C and CH_2Cl_2 (10 ml) was added and the solution was stirred and allowed to warm to room temperature to quench any excess MeLi. The bright orange solution was then reduced in volume to 20 ml and cooled (−20 °C) overnight to yield dark orange microcrystals. ^1H NMR (toluene-d_8): δ −0.4 ppm (94 Hz, CCH_3), −9 ppm (595 Hz, PMe_2), and −27 ppm (v.br, CH_2P). IR (cm^{-1}), 2770s, 1093m, 1063s, 945s, 920s, 837s, 721m.

Crystallography for (tripod)Cr(n-bu)$_2$Cl · toluene

A suitable, equidimensional crystal was selected and transferred to the goniostat, where it was cooled to −158° for characterization and data collection [3]. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited orthorhombic symmetry and systematic extinctions of $h0l$ for $h + l = 2n + 1$, $0kl$ for $l\text{-}2n + 1$, $hk0$ for $k = 2n + 1$. The choice of the space group *Pcnb* was confirmed by the subsequent solution and refinement of the structure.

Characteristics of the data collected ($6° \leq 2\theta \leq 45°$) appear in Table 1. After averaging of equivalent reflections a set of 3997 unique reflections remained, of which 2218 were considered observed by the criterion $F > 3.0\sigma(F)$. The R for the averaging of equivalent reflections was 0.07 for 2756 reflections observed more than once. Data processing was carried out using an uncertainty factor of 0.10 due to the large number of weak intensities.

The structure was solved by the usual combination of direct methods (MULTAN78) and Fourier techniques. The asymmetric unit contains one full molecule of the Cr complex as well as two half molecules of toluene. Both of the solvent molecules are situated on two-fold axes; one is ordered and the other disordered. One n-butyl group is also disordered (at C(23)); least squares refinement of the occupancy of these atoms (keeping the thermal parameter fixed) lead to occupancies of approximately 50% for each. Subsequently, atoms C(23) and C(23)′ were each assigned a fixed occupancy of 0.5 and the isotropic thermal parameter was allowed to vary. Full matrix least squares refinement was completed using anisotropic thermal parameters on all other atoms in the complex. The solvent molecules were refined using isotropic thermal parameters. In a difference Fourier,

Table 1

Crystal data for $[MeC(H_2PMe_2)_3]Cr[(CH_2)_3CH_3]_2Cl \cdot$toluene

Empirical formula	$C_{26}H_{33}ClCrP_3$
Color	red
Crystal dimensions (mm)	0.30×0.30×0.30
Space group	*Pcnb*
Cell dimensions (−158° C; 16 reflections)	*a* 18.696(7) Å
	b 15.055(5) Å
	c 21.697(7) Å
Molecules/cell	8
Volume (Å^3)	6107.29
Calculated density (gm/cm^3)	1.188
Wavelength (Å)	0.71069
Molecular weight	546.07
Linear absorption coefficient (cm^{-1})	6.203
Number of unique intensities	3997
Number with $F > 0.0$	3508
Number with $F > 3.0\sigma(F)$	2218
Final residuals	
R(F)	0.0805
R_w(F)	0.0832
Goodness of fit for the last cycle	1.888
Maximum Δ/σ for last cycle	0.05

Table 2

Fractional coordinates and isotropic thermal parameters [a,b] for $[MeC(CH_2PMe_2)_3]Cr[(CH_2)_3]_2Cl \cdot$ toluene

	$10^4 x$	$10^4 y$	$10^4 z$	$10 B_{iso}$
Cr(1)	2642(1)	6012(1)	1384(1)	24
P(2)	3171(2)	4791(2)	2036(2)	29
P(3)	1614(2)	4945(2)	1331(2)	23
P(4)	3089(2)	5084(2)	553(2)	25
C(5)	3192(7)	3670(7)	1678(6)	26
C(6)	2622(7)	3486(7)	1196(5)	20
C(7)	1858(7)	3757(7)	1399(6)	28
C(8)	2828(7)	3904(8)	569(6)	26
C(9)	4098(8)	4894(9)	2272(7)	43
C(10)	2730(9)	4591(10)	2777(7)	45
C(11)	1074(7)	4969(8)	622(6)	28
C(12)	916(8)	5049(9)	1913(7)	36
C(13)	2855(8)	5391(10)	−235(7)	42
C(14)	4066(7)	4990(8)	490(7)	36
C(15)	2599(7)	2470(8)	1102(6)	32
Cl(16)	2237(3)	6633(3)	2325(2)	63
C(17)	2098(7)	6887(8)	784(7)	32
C(18)	1506(7)	7463(9)	1064(7)	37
C(19)	1279(7)	8231(9)	658(7)	37
C(20)	659(9)	8748(12)	910(8)	55
C(21)	3603(8)	6762(9)	1312(10)	55
C(22)	3572(9)	7668(11)	1617(14)	106
C(23)	4183(13)	8387(15)	1046(11)	14(4)
C(23)′	4191(16)	8230(19)	1710(13)	36(6)
C(24)	4181(10)	9050(24)	1352(13)	116
C(25)	0*	7500*	2473(13)	71(7)
C(26)	0*	7500*	3152(10)	35(4)
C(27)	−383(8)	8151(10)	3475(7)	43(3)
C(28)	−376(10)	8114(13)	4118(9)	67(5)
C(29)	0*	7500*	4430(13)	64(6)
C(30)	5000*	7500*	4325(11)	46(5)
C(31)	5500(15)	8160(19)	3795(14)	101(7)
C(32)	5249(9)	7822(12)	3191(9)	63(5)
C(33)	5876(19)	8659(23)	3861(16)	51(8)
C(34)	5472(20)	8052(24)	4288(18)	57(8)

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given by W.C. Hamilton, Acta Cryst., 12 (1959) 609. [b] Parameters marked by an asterisk (*) were not varied.

most of the hydrogen atoms on the ordered part of the molecule were evident, and they were included in fixed idealized positions. No hydrogen atoms were assigned to the disordered n-butyl or to the solvent molecules. The final difference Fourier was essentially featureless, the largest peak was 1.2 e/Å^3 in close proximity of the Cr atom; the next largest peak of 1.0 e/Å^3 was in the area of the disordered solvent molecule. Results of the structure determination appear in Tables 2 and 3, as well as Fig. 1. Additional details are available as supplementary material.

Thermolysis of Cr(n-Bu)$_2$Cl(tripod)

A saturated C_6D_6 solution of CrCl(n-Bu)$_2$(tripod) was placed in an NMR tube, which was subsequently placed in a hot water bath at 63° C (previously established

Table 3

Selected bond distances (Å) and angles (deg.) for (tripod)Cr(n-Bu)$_2$Cl

Bonds		Angles			
Cr(1)-Cl(16)	2.371(5)	Cl(16)-Cr(1)-P(2)	85.95(15)	C(7)-P(3)-C(12)	101.8(6)
Cr(1)-P(2)	2.521(4)	Cl(16)-Cr(1)-P(3)	92.69(17)	C(11)-P(3)-C(12)	100.6(6)
Cr(1)-P(3)	2.507(4)	Cl(16)-Cr(1)-P(4)	167.48(16)	Cr(1)-P(4)-C(8)	116.7(4)
Cr(1)-P(4)	2.428(4)	Cl(16)-Cr(1)-C(17)	97.5(4)	Cr(1)-P(4)-C(13)	117.9(5)
Cr(1)-C(17)	2.112(13)	Cl(16)-Cr(1)-C(21)	97.1(5)	Cr(1)-P(4)-C(14)	116.2(5)
Cr(1)-C(21)	2.128(14)	P(2)-Cr(1)-P(3)	81.94(13)	C(8)-P(4)-C(13)	101.5(7)
P(2)-C(5)	1.859(12)	P(2)-Cr(1)-P(4)	82.08(13)	C(8)-P(4)-C(14)	100.9(6)
P(2)-C(9)	1.814(15)	P(2)-Cr(1)-C(17)	171.5(4)	C(13)-P(4)-C(14)	100.9(7)
P(2)-C(10)	1.834(16)	P(2)-Cr(1)-C(21)	95.5(5)	P(2)-C(5)-C(6)	116.0(8)
P(3)-C(7)	1.853(11)	P(3)-Cr(1)-P(4)	82.06(13)	C(5)-C(6)-C(7)	113.8(10)
P(3)-C(11)	1.840(13)	P(3)-Cr(1)-C(17)	90.1(4)	C(5)-C(6)-C(8)	110.9(10)
P(3)-C(12)	1.822(14)	P(3)-Cr(1)-C(21)	169.7(5)	C(5)-C(6)-C(15)	107.0(9)
P(4)-C(8)	1.844(12)	P(4)-Cr(1)-C(17)	93.9(4)	C(7)-C(6)-C(8)	111.8(9)
P(4)-C(13)	1.825(15)	P(4)-Cr(1)-C(21)	87.7(5)	C(7)-C(6)-C(15)	105.8(10)
P(4)-C(14)	1.838(13)	C(17)-Cr(1)-C(21)	91.8(6)	C(8)-C(6)-C(15)	107.1(9)
C(5)-C(6)	1.519(17)	Cr(1)-P(2)-C(5)	115.8(4)	P(3)-C(7)-C(6)	117.4(8)
C(6)-C(7)	1.549(17)	Cr(1)-P(2)-C(9)	118.2(5)	P(4)-C(8)-C(6)	118.4(8)
C(6)-C(8)	1.546(16)	Cr(1)-P(2)-C(10)	115.8(5)	Cr(1)-C(17)-C(18)	117.3(9)
C(6)-C(15)	1.543(15)	C(5)-P(2)-C(9)	100.1(6)	C(17)-C(18)-C(19)	113.9(12)
C(17)-C(18)	1.531(18)	C(5)-P(2)-C(10)	103.1(6)	C(18)-C(19)-C(20)	113.7(12)
C(18)-C(19)	1.513(18)	C(9)-P(2)-C(10)	101.3(7)	Cr(1)-C(21)-C(22)	114.4(12)
C(19)-C(20)	1.499(20)	Cr(1)-P(3)-C(7)	115.2(4)	C(21)-C(22)-C(23)′	123.8(18)
C(21)-C(22)	1.517(23)	Cr(1)-P(3)-C(11)	116.5(4)	C(21)-C(22)-C(23)	101.2(17)
C(22)-C(23)′	1.45(3)	Cr(1)-P(3)-C(12)	117.6(5)	C(22)-C(23)-C(24)	95.9(21)
C(22)-C(23)	2.00(3)	C(7)-P(3)-C(11)	102.7(6)	C(22)-C(23)′-C(24)	114.2(24)
C(23)-C(24)	1.20(4)				
C(23)′-C(24)	1.46(4)				

as the temperature at which decomposition is complete within 1 min). The deep red solution immediately turned dark brown and heterogeneous. The volatiles from this tube were then vacuum transferred to a separate NMR tube which was flame-sealed. ^{1}H and ^{13}C NMR (C_6D_6) showed butane, 1-butene, and *cis*- and *trans*-2-butene in a mole ratio of 3.6/2/1.4/1. ^{31}P NMR (C_6H_6) of the nonvolatile material showed free tripod (−61.3 ppm) and Cr(tripod)$_2$ (31 ppm).

Hydrogenolysis of Cr(n-Bu)$_2$Cl(tripod)

A saturated C_6D_6 solution of Cr(n-Bu)$_2$Cl(tripod) was placed in an NMR tube and the solution was then degassed (freeze pump thaw method; 3 cycles) and placed

Fig. 1. Stereo ORTEP drawing of the nonhydrogen atoms of Cr(n-Bu)$_2$Cl[(Me$_2$PCH$_2$)$_3$CMe], showing atom labeling. Only one occupied site for the disordered carbon (C23) is shown.

under an atmosphere of H_2. After ~ 25 min the solution began to turn dark brown. The solution was then allowed to stand at room temperature for an additional 3 h, at which time, decomposition was complete. At this point, the volatiles were transferred to a separate NMR tube which was then flame-sealed. ^1H NMR (C_6D_6) showed butane (> 90%) and *cis*- and *trans*-2-butene. ^{31}P NMR (C_6H_6) of the nonvolatile material showed Cr(tripod)$_2$ and free tripod.

Hydrogenation and isomerization of 1-hexane

Cr(n-Bu$_2$)Cl(tripod) (0.12 mmol) in benzene (5 ml) was placed in a reaction tube, to which was then added 1-hexene (0.75 g; 8.9 mmol). The solution was then degassed and placed under an atmosphere of H_2 and allowed to stir for 2.5 h. The volatiles from this reaction were then vacuum-transferred to a separate vessel and analyzed by GC, which showed that, of the initial 8.9 mmol 1-hexene, 10.3% (0.91 mmol) had been converted to hexane and 22.5% (2.0 mmol) had been converted to a mixture of *cis*- and *trans*-2-hexenes.

Results

Synthesis and characterization

Reaction of $CrCl_3[(Ph_2PCH_2)_3CMe]$ with three equivalents of n-BuLi at −70 °C in pentane, generates a deep red solution. However, above −50 °C this solution immediately turns black and the only soluble species remaining is the ligand $H_3CC(CH_2PPh_2)_3$. Based on our prior experience with $H_3CC(CH_2PPh_2)_3$ and $H_3CC(CH_2PMe_2)_3$ [1,4] ("tripod"), we felt that the greater basicity and compact size of the methylated ligand should greatly enhance the thermal stability of the chromium alkyls we sought. Indeed, this is the case. When three equivalents of n-BuLi are added to $CrCl_3$(tripod) slurried in pentane at 20 °C, a deep red solution is again produced. Filtering this solution followed by concentrating and cooling to −20 °C for 24 h yields red crystals. ^1H NMR of these crystals showed five broad and shifted resonances, and ^{31}P NMR showed no resonances, all of which is consistent with a paramagnetic species. Three bands in the IR at 2760 (s), 1985 (w), and 1915 (w) cm^{-1} suggested the presence of metal-bound alkyl ligands, or of hydride ligands or of agostic interactions. In search of more detailed structural information, an X-ray structure determination was performed in order to define the composition and connectivity within this species.

Solid-state structure of $Cr(n\text{-}Bu)_2Cl[(Me_2PCH_2)_3CMe]$

The X-ray diffraction study reveals that one halide ligand has not been alkylated, and that the product is a dialkyl chromium(III) complex with approximately octahedral geometry. A solution magnetic susceptibility measurement gave a value of μ 3.7 BM, consistent with octahedral Cr^{III}. The tripod ligand displays a geometry quite typical of that seen in previous tripod/Cr compounds. The P–Cr–P angles (~ 82°) fall in a narrow range and within two degrees of that found [1,5] in (tripod)$CrCl_3$, Cr(tripod)$_2$ and HCr(tripod)$_2{}^+$. The Cr–P distances reflect a considerable *trans* influence, being 0.086 Å (15σ(difference)) shorter for P *trans* to chloride than *trans* to n-butyl. All P–Cr–P angles are less than 90°, and all *trans* P–Cr–C or Cl angles are 8.5–13° less than 180°. The C–Cr–C angle (91.8°) is smaller than the two Cl–Cr–C angles (97°). In spite of the disorder in one n-butyl group, the α and β carbons seem reasonably positioned when compared to the ordered n-butyl, both in terms of Cr–C distances and the Cr–C(α)–C(β) angles. There is no evidence in these angles for an agostic Cr...H–C interaction, and the two Cr–C distances (average value 2.120 Å) are quite typical of Cr^{III}–C(sp^3) distances in six-coordinate compounds.

The definitive characterization of these paramagnetic 15-valence-electron species is difficult, and heavy reliance must be placed on X-ray diffraction. To assist in assignment of the (broad) ^1H NMR spectra, we have also synthesized (tripod)CrR_2Cl species for R = Me, Et, and n-Pr. We find as do Gardner and Girolami [6], that only the γ and δ protons of the R group give detectable resonances. While the tripod resonances are all detected, they are not at all species-specific among the four (tripod)CrR_2Cl compounds. The γ methyl resonance of the n-propyl compound (−10.9 ppm), however, is quite distinct from the γ and δ hydrogens of the n-butyl species (+8.5 and +4.9 ppm).

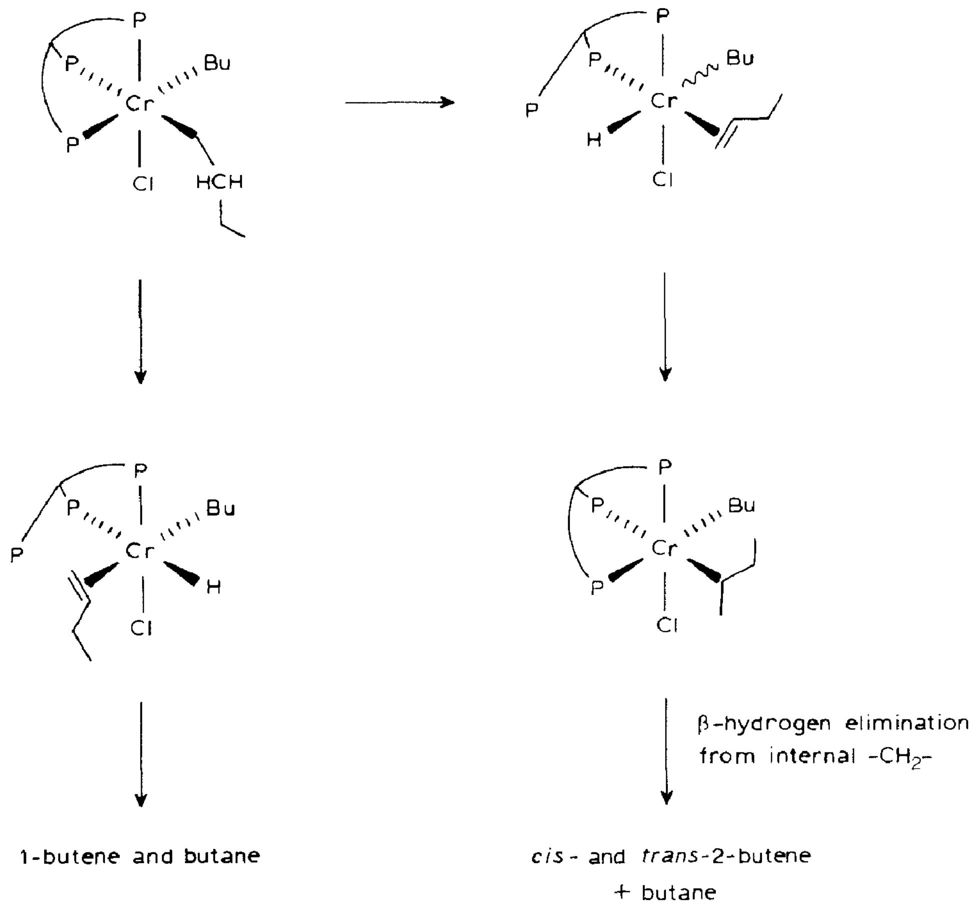
Discussion

It is surprising that n-BuLi reacts with (tripod)$CrCl_3$ (mole ratio 3/1) in pentane to selectively yield a dialkyl monochloro compound. It has been reported [6] that $^tBuSi(CH_2PMe_2)_3CrCl_3$ reacts with RLi (R = Me, n-Bu) in Et_2O to give the trialkyl products. We suggest that the difference lies in the solvents employed, with the polar, donor solvent Et_2O enhancing the reactivity of the alkyllithium reagents. The question then arises as to why (tripod)$CrCl_3$ should be more reactive than (tripod)CrR_2Cl, such that RLi reagent selectivity is only manifest in the last alkylation step. We suggest that replacement of π-donor chloride ligands by alkyl ligands concentrates π-donation in the remaining Cr–Cl bonds. Thus, (tripod)CrR_2Cl has the strongest Cr–Cl bonds of the series of compounds, and thus represents the stage where resistance to alkylation becomes most pronounced. We have also observed this to be the case in polyalkylation of $RhCl_3(PR_3)_3$ [7].

The isolation of the 15-valence electron $Cr(n\text{-}Bu)_2Cl$(tripod) is somewhat remarkable, considering the general instability of unsaturated transition metal alkyl compounds containing β-hydrogens. We propose that this enhanced thermal stability is a result of a modest increase in activation energy for β-hydrogen migration to the metal because of the absence of an empty metal d-orbital. The d^3 configuration (μ 3.7 BM) leaves each available t_{2g} orbital half-filled (i.e., essentially useless for accepting the migrating β-hydrogen). Thus, spin pairing energy would be required for a β-hydrogen shift. Another elimination-resistant alkyl, Cp_2V(n-Bu), is also high spin [8]. The alternative source of an empty metal orbital, ligand dissociation, is known to be a high energy process for octahedral Cr^{III}. Another contributing factor in the stability of this compound is probably the bulky nature of $Cr(n\text{-}Bu)_2Cl$(tripod) which could inhibit the molecule from reaching the geometry necessary to perform a β-hydrogen shift. This argument has been used to explain the stability of $Cr(^tBu)_4$ [9].

When it reacts, however, $Cr(n\text{-}Bu)_2Cl$(tripod) does reveal lability of the β-hydrogens. This is easily demonstrated by allowing a solution of $Cr(n\text{-}Bu)_2Cl$(tripod) to stand at room temperature for 3.5 h, after which time, 20–30% of the compound has decomposed to yield butane and butenes, as determined by ^1H (500 MHz) and ^{13}C

Decomposition Path



Scheme 1

(125 MHz) NMR. Very rapid thermal decomposition occurs with only mild heating (63° C) to also yield butane, 1-butene, and *cis*- and *trans*-2-butene. The production of internal olefins, along with the absence of octane as a product, are sufficient to suggest that butane and butenes were not produced from butyl radicals, but are instead products of the decomposition pathway depicted in Scheme 1. Since Cr(n-Bu)$_2$Cl(tripod) also decomposes in the solid state at room temperature, the observed infrared bands at 1985 and 1915 cm^{-1} may be Cr–H stretches.

Under 1 atm H$_2$, a solution of Cr(n-Bu)$_2$Cl(tripod) has a considerably shorter lifetime (1 h) than it does under N$_2$, with the hydrocarbon products being almost exclusively butane (> 90%), with only trace amounts of *cis*- and *trans*-2-butene. The absence of 1-butene suggested to us that this system might be a hydrogenation catalyst for terminal olefins. To test this proposal, hydrogenolysis of Cr(n-Bu)$_2$Cl(tripod) was carried out in the presence of excess (8.9 mmol) 1-hexene. Indeed, hydrogenation did occur with 0.12 mmol of catalyst producing 0.91 mmol of hexane. Also produced was 2.0 mmol of *cis*- and *trans*-2-hexene. These results suggest that chromium hydrides are produced, and that this system is fairly selective for the conversion of 1-alkenes to 2-alkenes. The fact that 3-alkenes are not produced is probably a result of the diminished ability of internal olefins to coordinate to octahedral systems, particularly in competition with abundant 1-hexene. Cr(tripod)$_2$ is a product of all the reactions.

Conclusion

Although tripod Cr/hydrides are not isolable in our hands, the fact that isomerized butenes are produced during thermal decomposition, that H_2 accelerates decomposition, and that the systems will catalytically hydrogenate 1-hexene, all serve to implicate transient chromium hydrides. The dramatically higher resistance to Cr/C bond rupture of $[{}^t\mathrm{BuSi(CH_2PMe_2)_3]CrR_3}$ (R = Me, n-Bu) in comparison to $\mathrm{[MeC(CH_2PMe_2)_3]Cr(n\text{-}Bu)_2Cl}$ carries the implication that the chloride ligand promotes the decomposition pathway, possibly due to its π-donor character diminishing the spin pairing energy.

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