

to imagine a chiral environment of the coordinated nitrogen due to different solvation of the two hydrogens.^{18,19} Thus, although our mechanism (Figure 7) is a very probable one, we cannot from the present evidence exclude other possibilities. Different models can be expected to provide different kinetic

responses to hydrogen ion activity, and studies along these lines are in progress.

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Registry No. I, 86309-45-7; II, 30538-13-7; III, 86309-46-8; IV, 86309-47-9; V, 86362-14-3.

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Notes

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Synthesis and Properties of Tetrahydrofuran Complexes of Chromium(III). $[\text{Cr}(\text{THF})_3\text{X}_3]$ (X = Cl, Br, I), $[\text{Cr}(\text{THF})_2\text{X}_4]$ (X = Cl, Br, I, NCS), and $[\text{Cr}(\text{THF})_6](\text{BF}_4)_3$

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Since its preparation in 1958,² trichlorotris(tetrahydrofuran)chromium(III), $[\text{Cr}(\text{THF})_3\text{Cl}_3]$, has been widely used as a starting material for the synthesis of coordination and organometallic³ compounds of chromium. Surprisingly little is known about other Cr(III)-THF adducts,⁴ although solutions of CrX_3 (X = Br, I) in THF have been prepared (from anhydrous CrX_3 , THF, and zinc dust) and used in situ to prepare tertiary phosphine complexes.⁵ In our experience the latter approach is not completely satisfactory since (a) some CrX_3 usually remains unreacted, making it difficult to control the Cr:ligand ratio accurately, and (b) the large excess of THF present as solvent can compete with weak donor ligands for the chromium. Even with polydentate phosphines, we have found that better yields and purer products are obtained from $[\text{Cr}(\text{THF})_3\text{Cl}_3]$ and L in CH_2Cl_2 or $\text{CH}_2\text{Cl}_2/\text{toluene}$ than in neat THF. Here we report the synthesis and properties of the title compounds, which are valuable starting materials for the preparation of Cr(III) complexes.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously.⁶ Tetrahydrofuran (BDH Ltd.) was dried by refluxing over sodium wire for 3 days and distilled from LiAlH_4 immediately before use. Anhydrous chromium trichloride (Fluka) was used as supplied.

Anhydrous CrBr_3 was made in a manner similar to that described for PaBr_5 .⁷ Electrolytic grade chromium metal (20 mmol) was crushed and placed in a silica apparatus (20-mm diameter by 250-mm length) with a small side arm. The apparatus was flamed out under vacuum and cooled and then a 2-fold excess of anhydrous bromine

(BDH) was transferred into the side arm. After suitable degassing, the silica apparatus was sealed off from the vacuum line. The tube was placed horizontally with the end containing the chromium inside a tube furnace at 500 °C. After approximately 2 days the tube was cooled, the excess bromine condensed in the side arm, and the tube sealed off. Yields were estimated to be in excess of 95% on the basis of bromine used.

For anhydrous CrI_3 no side arm was required, and the tube was held in a vertical position. The lower end of the tube was heated to 500 °C for 3 days. The excess iodine was sublimed away from the CrI_3 with the tube held horizontally.

$[\text{Cr}(\text{THF})_3\text{Cl}_3]$. This was prepared in essentially quantitative yield as described.² Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{CrO}_3$: C, 38.5; H, 6.4; Cl, 28.4; Cr, 13.9. Found: C, 38.7; H, 6.4; Cl, 29.4; Cr, 14.3.

$[\text{Cr}(\text{THF})_3\text{Br}_3]$. This was prepared by extraction of a mixture of anhydrous CrBr_3 (ca. 5 g) and zinc dust (0.5 g) with THF (250 cm^3) in a Soxhlet apparatus under nitrogen for 24 h. The brown solution was concentrated under reduced pressure, dry petroleum ether added, and the mixture stirred to give a fine powder. This was filtered off, dried in vacuo (ambient temperature (0.1 torr) throughout), and stored in sealed ampules (60%). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{Br}_3\text{CrO}_3$: C, 28.3; H, 4.7; Br, 47.2. Found: C, 28.0; H, 4.9; Br, 47.6.

$[\text{Cr}(\text{THF})_3\text{I}_3]$. This was prepared in a manner similar to that for the bromide (40–60%). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{CrI}_3\text{O}_3$: C, 22.2; H, 3.7. Found: C, 22.4; H, 3.7.

$[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{X}_4]$ (X = Cl, Br, I). $[n\text{-Bu}_4\text{N}]\text{X}$ were dried by heating at 80 °C (0.01 torr) for 2 days. The appropriate finely powdered $[n\text{-Bu}_4\text{N}]\text{X}$ (2 mmol) was added to $[\text{Cr}(\text{THF})_3\text{X}_3]$ (2 mmol) in dichloromethane (25 cm^3) and the mixture stirred for 3 h. For X = Br, the solution rapidly became green, but for X = Cl or I, no obvious color change occurred. The solutions were filtered and concentrated in vacuo at room temperature and the resulting oils/solids stirred with dry petroleum ether (40–60 °C). The resulting solids were dried in vacuo.

$[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Cl}_4]$. Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Cl}_4\text{CrNO}_2$: C, 49.6; H, 9.0; Cl, 24.4; N, 2.4. Found: C, 49.7; H, 9.6; Cl, 23.6; N, 2.2.

$[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Br}_4]$. Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Br}_4\text{CrNO}_2$: C, 37.9; H, 6.8; Br, 42.2; N, 1.8. Found: C, 37.4; H, 6.6; Br, 42.6; N, 1.7.

$[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{I}_4]$. Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{CrI}_4\text{NO}_2$: C, 30.4; H, 5.5. Found: C, 29.7; H, 6.0.

$[\text{K}][\text{Cr}(\text{THF})_2(\text{NCS})_4]$. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1.1 g, 4 mmol) and KCNS (2.3 g, 24 mmol) were refluxed in ethanol (50 cm^3) for 5 h, and the mixture was concentrated and filtered. The blue filtrate was stirred with petroleum ether until it produced a solid material, which was dried in vacuo. The material was refluxed for several hours with THF (30 cm^3), producing a purple solution, which was filtered and concentrated to yield a purple solid. This was washed with petroleum ether and dried (60 °C). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{CrKN}_4\text{O}_2\text{S}_4$: C, 29.8; H, 3.3; N, 11.6; NCS, 48.7. Found: C, 30.4; H, 3.5; N, 11.8; NCS, 49.3.

$[\text{Cr}(\text{THF})_6](\text{BF}_4)_3$. A solution of $[\text{Cr}(\text{THF})_3\text{Cl}_3]$ (0.37 g, 1 mmol) in THF (20 cm^3) was stirred overnight with AgBF_4 (0.59 g, 3 mmol) and the precipitated AgCl filtered off. The deep green filtrate decomposed on evaporation to yield a purple oil.

Results and Discussion

The brown $[\text{Cr}(\text{THF})_3\text{X}_3]$ (X = Br, I) were made by reaction of the appropriate anhydrous CrX_3 with THF and a

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Table I. Physical Data

complex	IR (THF bands), ^a cm ⁻¹		
	$\nu(\text{COC})_{\text{sym}}$	$\nu(\text{COC})_{\text{asym}}$	far-IR, ^b cm ⁻¹
[Cr(THF) ₃ Cl ₃] (purple)	855 (s)	1018 (s), 1042 (s)	370, 338, 315
[Cr(THF) ₃ Br ₃] (brown)	850 (s)	1015 (m), 1050 (m)	330-290 (vbr)
[Cr(THF) ₃ I ₃] (greenish brown)	845 (s)	1010 (s), 1045 (w)	
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ Cl ₄] (purple)	870 (s)	1028 (s), 1068 (s)	348, 316
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ Br ₄] (green)	870 (s)	1028 (s), 1070 (s)	284, 266
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ I ₄] (dk brown)	880 (s)	1022 (s), 1052 (br)	
K[Cr(THF) ₂ (NCS) ₄] (purple)	865 (s)	1015 (m), 1055 (s)	365 ^c
electronic spectra			
complex	soln $E_{\text{max}} \times 10^{-3}$, cm ⁻¹ (mol)		diffuse reflectance $E_{\text{max}} \times 10^{-3}$, cm ⁻¹
[Cr(THF) ₃ Cl ₃]	14.04 (18), 14.70 (20), 20.32 (40), 26.59 (8)		14.04, 14.61, 20.49, 26.88
[Cr(THF) ₃ Br ₃]	14.28 (26), 20.16 (48), 20.83 (50), 28.50 (390)		13.0 (br), 18.38, 25.0
[Cr(THF) ₃ I ₃]	14.28 (29), 18.24 (134), 22.72 (sh) (1620), 27.47 (10 020)		13.52, 16.66, 21.08, 24.75
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ Cl ₄]	13.15 (69), 14.36 (90), 19.08 (116)		13.08, 18.11, 19.53 (sh), 26.59 (sh)
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ Br ₄]	12.72 (45), 17.24 (70)		13.15 (br), 16.66 (sh), 18.51 (sh), 24.50
[<i>n</i> -Bu ₄ N][Cr(THF) ₂ I ₄]	12.34 (w), 14.93 (...), 18.86 (...) ^d		12.34 (w), 15.72 (sh), 16.72, 24.27
K[Cr(THF) ₂ (NCS) ₄]	17.73 (89), 12.55 (sh) (41), 23.47 (sh) (93), 24.39 (100)		17.79, 18.51 (sh), 25.51 (sh), 27.77 (sh)
"[Cr(THF) ₆](BF ₄) ₃ " (green soln)	15.43 (...), 21.73 (...), 28.08 (...)		

^a Nujol mulls. Free THF absorption (cm⁻¹): 909, $\nu(\text{COC})_{\text{sym}}$; 1070, $\nu(\text{COC})_{\text{asym}}$ (Bellamy, L. J. "The IR Spectra of Complex Molecules"; Wiley: New York, 1958). ^b 400-200-cm⁻¹ bands tentatively assigned as $\nu(\text{Cr-X})$. ^c $\nu(\text{CN})$ 2100, $\nu(\text{NCS})$ 480 cm⁻¹. ^d Some decomposition in solution.

zinc dust "catalyst", but in contrast to the synthesis of [Cr(THF)₃Cl₃], which is straightforward,² their preparations are very dependent upon the particular CrX₃ sample used. Some commercial samples of CrBr₃ were unreactive, and "anhydrous" CrX₃ made by dehydration of the hydrated halides with 2,2-dimethoxypropane or thionyl halides (X = Cl, Br) gave impure products. Best results were achieved with CrX₃ (X = Br, I) made by direct combination of the elements in sealed tubes. The [Cr(THF)₃X₃] (X = Br, I) are quite moisture sensitive, although pure samples can be manipulated quickly in air (impure materials are very much more moisture sensitive). Previous studies^{8,9} have shown [Cr(THF)₃Cl₃] to be the *mer* isomer, and the other halo complexes are tentatively assigned a similar structure on the basis of their electronic reflectance spectra (Table I). The far-IR spectrum of [Cr(THF)₃Br₃] contains only a very broad band at 330-280 cm⁻¹, which could not be resolved and probably results from overlapping $\nu(\text{Cr-X})$ and $\nu(\text{Cr-O})$ modes.

Attempts to isolate [Cr(THF)₃F₃] were unsuccessful; anhydrous CrF₃ did not react with THF/Zn dust, and treatment of [Cr(THF)₃Cl₃] with 3 equiv of silver(I) fluoride in THF gave an exceedingly moisture-sensitive pink-brown oil that could not be solidified or satisfactorily characterized. Anhydrous Cr₂(SO₄)₃¹⁰ also failed to react with THF, and K₃[Cr(NCS)₆] and THF gave K[Cr(THF)₂(NCS)₄] (*vide infra*), not the neutral [Cr(THF)₃(NCS)₃].

The reactions of [Cr(THF)₃X₃] (X = Cl, Br, I) with the corresponding [*n*-Bu₄N]X¹¹ in THF in a 1:1 ratio gave the [*n*-Bu₄N][Cr(THF)₂X₄] salts. These materials are very moisture sensitive in solution, and the solid chloro and bromo complexes decompose immediately on exposure to air, although curiously the solid iodo complex is rather more stable. The electronic reflectance spectra of the [Cr(THF)₂X₄]⁻ anions show that the two expected visible absorption bands (⁴A_{2g} → ⁴T_{2g}, ⁴T_{1g}(F), O_h symmetry) are considerably split, suggesting the ions have trans (*D*_{4h}) rather than cis (*C*_{2v}) structures.¹²

The far-IR spectra of *trans*-[Cr(THF)₂X₄]⁻ (X = Cl, Br) (Table I) each show two bands that are tentatively assigned as the E(Cr-X) mode split by solid-state effects. The lack of coincident absorption between the two anions and the presence of only weak bands in this region of the spectrum of [Cr(THF)₂I₄]⁻ rule out assignment of one component as A_{2u} (Cr-O), which are thought to be weak.

The purple K[Cr(THF)₂(NCS)₄] is produced by refluxing K₃[Cr(NCS)₆] in THF. It is much less moisture sensitive than the halide analogues. The presence of single bands in the IR spectrum assignable as $\nu(\text{CN})$, $\nu(\text{Cr-N})$, and $\delta(\text{NCS})$ (the $\nu(\text{CS})$ occurs in a region where THF absorbs) indicates a *trans* (*D*_{4h}) structure for the anion,⁹ but in contrast to the case of the halides, the two electronic spectral bands show little splitting, which is attributed to the similar spectrochemical positions of NCS (*Dq* = 1770 cm⁻¹)¹² and THF (1543 cm⁻¹ (estimated)).

Treatment of [Cr(THF)₃Cl₃] in THF with 3 equiv of AgBF₄ gives a green, chloride-free solution that probably contains [Cr(THF)₆]³⁺, but attempts to isolate this material caused decomposition to a brown-pink oil (cf. the AgF reaction). Green [Cr((CH₃)₂SO)₆](BF₄)₃ has recently been prepared electrochemically.¹³

All the THF complexes isolated in this study exhibited three IR bands attributed to coordinated THF (Table I), but no bands corresponding to uncoordinated THF were present.^{8,14} It is noteworthy that the low-frequency shifts in $\nu(\text{COC})_{\text{asym}}$ (which also splits) and $\nu(\text{COC})_{\text{sym}}$ from the values in free THF are greater in [Cr(THF)₃X₃] than in [Cr(THF)₂X₄]⁻. The moisture sensitivity and the ease with which the THF is displaced by other donors restricted solution measurements, although electronic spectra in THF solution are reported in Table I. The [*n*-Bu₄N][Cr(THF)₂X₄] and K[Cr(THF)₂(NCS)₄] were insoluble in halocarbons and changed color on dissolution in nitromethane or acetonitrile. The conductivities in THF (10⁻³ M) lay in the range 2.1-4.0 Ω⁻¹ cm² M⁻¹, compared with immeasurably small conductances for [Cr(THF)₃X₃] and 3.2 Ω⁻¹ cm² M⁻¹ for [*n*-Bu₄N]BF₄, supporting the 1:1 electrolyte formulation, although the low values clearly make THF an unsatisfactory solvent for these measurements.

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Thermogravimetric analyses of $[\text{Cr}(\text{THF})_3\text{X}_3]$ and $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]^{15}$ in dry argon showed weight losses corresponding to the loss of the THF.

$[\text{Cr}(\text{THF})_3\text{Cl}_3]$ and $[\text{Cr}(\text{THF})_3\text{I}_3]$ lose three molecules of THF in one step over the temperature ranges 150–200 and 80–130 °C, respectively. In the case of $[\text{Cr}(\text{THF})_3\text{Br}_3]$, one molecule of THF is lost at 90–120 °C and two molecules of THF are lost at 160–200 °C. For $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$ the weight loss occurs in two ill-defined steps at ca. 150 and 350 °C.

We have used the THF adducts here as starting materials for the synthesis of chromium(III) complexes of a wide range of neutral ligands, details of which will be reported elsewhere. As examples of their use may be cited the preparations of $[\text{Cr}(\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)_2(\text{NCS})_4)]^{-9}$ from $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$, of $[\text{n-Bu}_4\text{N}][\text{Cr}(\text{L-L})\text{X}_4]$ (L-L = $\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, *cis*- $\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2$) from $[\text{Cr}(\text{THF})_2\text{X}_4]^{-16}$ of $[\text{Cr}(\text{L-L-L})\text{X}_3]$ (L-L-L = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{CH}_3\text{C}(\text{CH}_2\text{AsMe}_2)_3$) from $[\text{Cr}(\text{THF})_3\text{X}_3]^{17}$ and of $[\text{Cr}(\text{L-L-L})_2](\text{BF}_4)_3$ from $[\text{Cr}(\text{THF})_6]^{3+}$.

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Registry No. $[\text{Cr}(\text{THF})_3\text{Cl}_3]$, 10170-68-0; $[\text{Cr}(\text{THF})_3\text{Br}_3]$, 86286-48-8; $[\text{Cr}(\text{THF})_3\text{I}_3]$, 86217-22-3; $[\text{n-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Cl}_4]$, 86217-24-5; $[\text{n-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Br}_4]$, 86217-26-7; $[\text{n-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{I}_4]$, 86217-28-9; $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$, 86217-29-0; $[\text{Cr}(\text{THF})_6](\text{BF}_4)_3$, 86217-31-4.

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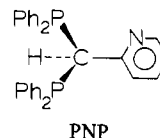
Synthesis and X-ray Structural Characterization of a Rhodium(I) Complex of a Pyridyldiphosphine (PNP) Tridentate Ligand

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There has been much recent interest in the use of cationic rhodium(I) complexes that contain chelating diphosphine ligands for catalytic hydrogenation¹⁻⁴ and decarbonylation⁵⁻⁷ reactions. Results from our laboratory on the catalytic decarbonylation of aldehydes using $[\text{Rh}(\text{diphosphine})_2]^+$ complexes strongly implicate a mechanism that involves an initial Rh-P bond rupture that leads to a catalytically active three-coordinate complex.^{7,8} In order to test this possibility, a study that makes use of complexes of chelating phosphorus-nitrogen (PN) donor ligands was initiated. With such ligands the N donor end is known to be labile.⁹ As part of this general investigation a PNP ligand was synthesized.

Metallo compounds of this potentially tridentate ligand should serve as reasonable models for catalytic decarbonylation



intermediates, and they are of interest in their own right because bridged binuclear complexes of the well-known face-to-face and A-frame type are likely.¹⁰⁻¹⁸ The ligand also offers a choice of P-P or P-N bidentate or PNP tridentate coordination with four- and/or five-membered chelate rings. In this paper we report the reaction of PNP with a solution of $[(\text{nbd})\text{RhCl}]_2$ (nbd = nornbornadiene) and AgBF_4 and the complete characterization of the resulting new complex $[\text{Rh}(\text{nbd})(\text{PNP})]\text{BF}_4$ (**1**). In addition, some preliminary results on the novel reaction chemistry of **1**, which yields bridged binuclear compounds, is discussed.

Experimental Section

Physical Measurements. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 120.5 MHz and at 25 °C on a Nicolet NT-300 spectrometer. The chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4 with positive shifts downfield. IR spectra were recorded on a Beckman Model 4250 grating spectrometer using KBr disks.

Preparation of Compounds. $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CHC}_5\text{H}_4\text{N}$ (PNP) was prepared by the reaction of 1 mol of 2-picolone anion with 2 mol of chlorodiphenylphosphine. All manipulations were carried out under a purified atmosphere on a N_2 by using standard Schlenk techniques. The red 2-picolone anion is formed by the slow addition of *n*-butyllithium (31.5 mL of 2 M hexane solution; 0.063 mol) to a stirred solution of 2-picolone (6.2 mL, 0.063 mol) and tetramethylethylenediamine (12 mL, 0.080 mol) in 10 mL of dry thf at -78 °C. The suspension of 2-picolone anion is slowly added via a cannula tube to chlorodiphenylphosphine (22.6 mL, 0.126 mol) at 0 °C and with constant stirring. After the solution is stirred for 1 h, its volume is reduced by vacuum distillation, and upon addition of 10 mL of ethanol and 5 mL of distilled water a white globular precipitate forms. This mixture is heated to reflux to dissolve the solid, and after rapid filtration white crystals separate on cooling. The crystals are collected by filtration and washed respectively with hexane and distilled water until

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