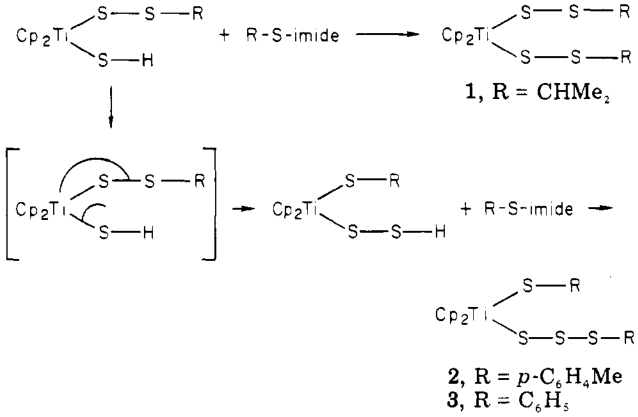
Scheme II



1, R = CHMe$_2$

2, R = p-C$_6$H$_4$Me
3, R = C$_6$H$_5$

Ti-S distances (Ti-S1 = 2.439 (3) Å, Ti-S4 = 2.381 (3) Å), but this may not be entirely due to its unsymmetrical structure since similar asymmetry was observed for 4 and $Cp_2V(SPh)_2$.[21] The two S-S distances (S1-S2 = 2.053 (3) Å, S2-S3 = 2.011 (3) Å) are within the ranges observed for trisulfides,[23] and the variation between them is presumably a consequence of the different substituents terminating the S_3 chain.

The isolation of 3 is another example of the tendancy for chain growth in the Cp_2Ti system. The complex may be considered to be a model of a possible intermediate in the reactions that lead to Cp_2TiS_5 from unblocked sulfur transfer reagents. Scheme II depicts possible routes to 1–3 starting from $Cp_2Ti(SSR)SH$ which is the most reasonable first product[25] from the reaction of $Cp_2Ti(SH)_2$ with 2 equiv of RS–imide. Aryl thiolate anions are much better leaving groups than alkyl ones[26] which may explain the difference between 1 and 2, 3. The formation of sulfur-sulfur bonds on transition-metal templates[18] would appear to be a promixing new area of study with potential applications to organosulfur chemistry.

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Registry No. 1, 87434-23-9; 2, 87434-24-0; 3, 87434-25-1; $Cp_2Ti(SH)_2$, 12170-34-2; 2-[(1-methylethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione, 15199-26-5; 2-[(4-methylphenylthio]-1*H*-isoindole-1,3(2*H*)-dione, 15199-26-5; 1-(phenylthio)-2,5-pyrrolidinedione, 14204-24-1.

Supplementary Material Available: Tables of positional and thermal parameters, structure factors, and bond distances and angles with their estimated standard deviations for complex 3 (8 pages). Ordering information is given on any current masthead page.

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[23] The trans conformation, the SSS bond angle (109.3 (1)°), and the dihedral angles TiS1S2/S1S2S3 = 70.44 (8)° and S1S2S3/S2S3C21 = 78.98 (8)° are also within the ranges observed for trisulfides.[24]

[24] Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3.

[25] As suggested by a reviewer, a similar rearrangement of $Cp_2Ti(SSR)_2$ could lead to 2 and 3. No new complexes were detected upon the decomposition of 1.

[26] Field, L. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977.

Crystal and Molecular Structure of $Cr(C_6H_5)_3(OC_4H_8)_3$

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Summary: Although triphenyltris(tetrahydrofuran)chromium(III) is a classic "textbook" compound in the organometallic literature, its molecular structure has never been established unequivocally. In particular, the question of whether the compound has a cis(facial) or trans(meridional) configuration has remained unresolved. In this paper we show that the compound has a cis(facial) geometry, with three σ-bonded phenyl ligands.

Chromium–aryl complexes are among the very first organometallic compounds ever synthesized, chiefly as a result of Hein's pioneering work in the 1920s and 1930s.[1,2] The very interesting and widely studied reaction[2-5] of phenyl Grignard with chromium(III) halides shows a strong dependence on the choice of solvent, reaction temperature, and the particular stoichiometry of the reactants. While no recognizable product is obtained at room temperature in diethyl ether,[6] at low temperature a threefold excess of reducing agent produces a mixture of π-arene/chromium complexes.[7] However, in tetrahydrofuran the reaction leads to a σ-bonded complex, $Cr(C_6H_5)_3(OC_4H_8)_3$, a key intermediate of the above reaction.[8] Though the σ complex was made as early as 1957 during the extensive investigations by Zeiss and co-workers on the $CrCl_3$/PhMgBr/THF system, its molecular geometry has remained elusive. Over the years, it has been represented as having either a cis(facial)[9] or trans(meridional)[10] configuration. In solution, $CrPh_3(THF)_3$ selectively loses one molecule of THF,[12] and on this basis it has been suggested to have a trans structure.[4,13] A more interesting aspect of its chemical behavior is an unusual reaction whereby it irreversibly rearranges to π-arene/chromium compounds upon loss of solvated molecules either under heat, under reduced pressure, or on treatment with diethyl ether.[8] How this rearrangement is brought about is not clear; however, some speculations regarding possible mechanisms have been made.[3] We thus feel that it is important to establish the correct geometry of the parent complex, which would not only provide a more meaningful starting point for any proposed mechanism of the σ/π transformation but would also establish the geometry of a large

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[1] An excellent and comprehensive review of Hein's early work is given by Zeiss.[2]

[2] Zeiss, H. *ACS Monogr.* **1960**, *No. 147*, 380.

[3] Zeiss, H. H.; Sneeden, R. P. A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 435.

[4] Sneeden, R. P. A. "Organochromium Compounds"; Academic Press: New York, 1975.

[5] Cotton, F. A. *Chem. Rev.* **1955**, *55*, 551.

[6] Bennett, G. M.; Turner, E. E. *J. Chem. Soc.* **1914**, 1057.

[7] (a) Zeiss, H.; Tsutsui, M. *J. Am. Chem. Soc.* **1959**, *81*, 1367. (b) Zeiss, H.; Tsutsui, M. *Ibid.* **1957**, *79*, 3062. (c) Zeiss, H.; Herwig, W. *Ibid.* **1956**, *78*, 5959. (d) Zeiss, H.; Tsutsui, M. *Naturwissenschaften* **1957**, *44*, 420.

[8] (a) Herwig, W.; Zeiss, H. *J. Am. Chem. Soc.* **1957**, *79*, 6561. (b) Herwig, W.; Zeiss, H. *Ibid.* **1959**, *81*, 4798.

[9] See Figure 8.4 of ref 2.

[10] See, for example: (a) Scheme 1-1 (page 2) and structure 68 (page 139) of ref 4; (b) structure 9a (page 437) of ref 3; and (c) page 557 of ref 11.

[11] Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978.

[12] Hakle, J.; Stolze, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1964**, *19B*, 1081.

[13] Daly, J. J.; Sneeden, R. P. A. *J. Chem. Soc. A* **1967**, 736.

0276-7333/83/2302-1896$01.50/0

Table I. Average Distances (Å) and Angles (deg) in $CrPh_3(THF)_3$

	Bond Distances		
Cr-O	2.225 (10)	C-C(THF)	1.510 (13)
Cr-C	2.060 (10)	C-C(Ph)	1.415 (8)
C-O	1.485 (6)		
	Bond Angles		
O-Cr-O	83.2 (3)	O-Cr-C(trans)	172.0 (4)
C-Cr-C	93.9 (4)	O-Cr-C(cis)	91.2 (6)

number of organochromium complexes which have been derived from the title complex via ligand exchange. This communication therefore reports the results of the X-ray diffraction studies on $CrPh_3(THF)_3$.

$Cr(C_6H_5)_3(OC_4H_8)_3$ was synthesized from anhydrous $CrCl_3$ according to literature methods.[8b] However, it was observed that running the reaction for longer periods of time (24–30 h) at −30 °C gives a better yield: i.e., one obtains material almost free of the side product $Cr(C_6H_5)_3 \cdot 3MgBrCl \cdot 6THF$. Large red needles of the complex were obtained through repeated recrystallizations from THF. These pyrophoric crystals showed a pronounced tendency to decompose when removed from the mother liquor in a dry atmosphere. Thus the crystals were mounted under a continous flow of argon in a glass capillary at low temperature by using a specially designed cross-shaped glass device.[14] Once mounted, the crystals were found to be stable at room temperature.

The X-ray diffraction data were collected at room temperature on a Nicolet/Syntex $P2_1$ diffractometer using Mo Kα radiation. The complex crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules per unit cell: a = 17.330 Å, b = 15.634 Å, c = 21.931 Å, β = 94.09°, and Z = 8. The initial positions of the chromium atoms were obtained through direct methods,[15] while the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. The structure was refined[16] by full-matrix least-squares techniques to a final agreement factor of R = 0.102 for the 2698 independent reflections with $I > 3\sigma(I)$. The relatively high R factor is undoubtedly due to the fact that the THF ligands are partially disordered,[17] a commonly observed phenomenon.[18]

An ORTEP plot of the molecule is shown in Figure 1, and average distances and angles listed in Table I. Other results of the structural analysis are available as supplementary material (see paragraph at end of paper for details). As expected, the Cr atom is octahedrally coordinated by three σ-bonded phenyl ligands and three THF molecules. Most importantly, the molecule is found to exist in a cis(facial) configuration. It is interesting to note that the six ligands are arranged in three mutually perpendicular planes: each opposing pair of Ph and THF ligands are approximately coplanar and are perpendicular to the other two Ph/Cr/THF planes. The Cr–C bonds are all significantly shorter than the Cr–O bonds, probably reflecting the presence of pπ–dπ back-bonding on the part of the "soft" phenyl ligands as opposed to the lack of such interactions for the "hard" THF ligands. The average Cr–C distance compares well with those of several closely related structures[13,19] including that of the $[Cr(C_6H_5)_5]^{2-}$ anion.[19c]

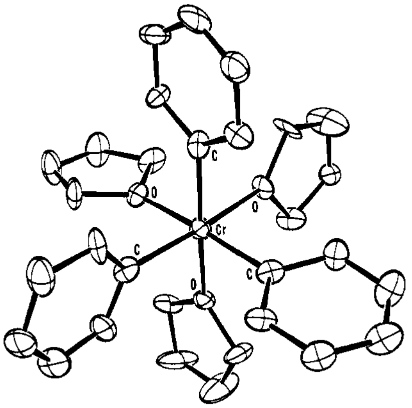

Figure 1. Molecular plot of $CrPh_3(THF)_3$.

Acknowledgment. We thank the National Science Foundation for support of this research through Grant CHE-81-01122.

Supplementary Material Available: Listings of the final atomic coordinates (Table A), thermal parameters (Table B), and selected distances and angles (Table C) of $CrPh_3(THF)_3$, and final observed and calculated structure factors for the structure determination (23 pages). Ordering information is given on any current masthead page.

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[14] The cross-shaped glass device was designed such that one of the horizontal side arms was attached to the glass capillary for crystal loading purposes, whereas the other horizontal side arm contained a glass fiber that was used to push the crystal into the capillary tube. The top vertical arm of the cross contained a septum cap fitted with a long copper wire with a little grease at the end to pick up crystals, and finally the bottom end of the cross was fitted into the Schlenk tube. We thank Dr. Peter G. Edwards for the design of this apparatus.

[15] MULTAN: a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368).

[16] Major computations in this work were performed on the USC IBM 370/158 computer using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

[17] Many of the THF carbon atoms have large thermal parameters. This is because at room temperature some of the THF ligands appear to be planar (in contrast to a normal puckered conformation), indicating a disordered superposition of two or more nonplanar conformers.

[18] (a) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567. (b) Bau, R.; Chiang, M. Y.; Ho, D. M.; Gibbins, S. G.; Koetzle, T. F., submitted for publication.

[19] (a) Daly, J. J.; Sanz, F.; Sneeden, R. P. A.; Zeiss, H. H. *Helv. Chim. Acta* **1974**, *57*, 1863. (b) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1972**, 2584. (c) Müller, E.; Krause, J.; Schmiedeknecht, K. *J. Organomet. Chem.* **1972**, *44*, 127.

Synthesis and Reactions of a Dinuclear Iron Nitrosyl Radical Anion and Di- and Mononuclear Dimethylnitrosyliron Complexes. Migratory Insertion of Coordinated Nitric Oxide

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Summary: Reduction of $[CpFe(NO)]_2$ (**1**) with sodium in DME gives the novel radical anion salt $Na[CpFe(NO)]_2 \cdot 1.5$ DME (**3**). Complex **3** can be doubly methylated, leading to **2**; this material rearranges to mononuclear complex **4** in which migratory insertion of NO occurs in the presence of PMe_3.

Although migratory insertion reactions involving metal alkyls and coordinated nitric oxide are less well-known than those[1] involving CO, several recent studies suggest