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 $K\alpha$ 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]

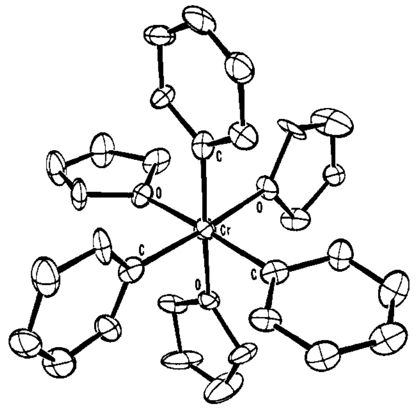

Figure 1. Molecular plot of $CrPh_3(THF)_3$.

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

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that this situation may be changing.[2] In light of these discoveries, we were intrigued by a report of Brunner and Wachsmann, which has been in the literature for several years, concerning the chemistry of the cyclopentadienylnitrosyliron dimer **1**.[3] These workers reported that chemical reduction of dimer **1** leads to the iron dianion $[CpFeNO]_2^{2-}$, which may be alkylated to give dinuclear dialkyl complex **2**.[4]

Little was reported about the chemical properties of **2**, other than an indication of its equilibration with paramagnetic $[CpFe(NO)(CH_3)]$. Because of the possibility that **2** might be a source of complexes capable of undergoing nitric oxide migratory insertion, we have undertaken a reexamination of this system. We wish to report some unexpected results, which include the following: (1) The material formed on chemical reduction of dimer **1** is not a dianion but is instead the paramagnetic dinuclear radical anion **3**. (2) Despite the fact that complex **3** possesses only one negative charge rather than two, it is in fact the material that leads to dinuclear dimethyl complex **2**, in analogy to the behavior of the isoelectronic dinuclear cobalt carbonyl radical anion $[CpCo(CO)]_2^{-}\cdot$.[5] (3) Compound **2** is not thermally stable and does not cleanly sublime but instead undergoes an alkyl transfer reaction giving the new mononuclear dialkyl complex **4**. Dialkyl complex **4** can be induced to undergo nitric oxide migratory insertion, although this reaction is considerably less efficient than the corresponding process observed for $CpCo(NO)(CH_3)$.[2a,b]

By reduction of Brunner's doubly bonded dimer **1** with sodium dispersion in DME, followed by filtration and recrystallization, we have been able to isolate an intensely colored red solid, for which ^1H NMR in CD_3CN shows only the resonances of free DME. The IR spectrum of this material in CH_3CN or DME shows a single absorption in the metal-bound nitrosyl region at 1404 cm^{-1}, approximately 100 cm^{-1} lower in energy than that of the neutral dimer **1** at 1506 cm^{-1} and indicative of a bridging nitrosyl moiety in a highly reduced compound. Thus we made the tentative assignment of the reduction product of dimer **1** as the paramagnetic solvated radical anion salt $Na[CpFe(NO)]_2\cdot 1.5DME$ (**3**).[6] Assuming this constitution (see below), the yield of this complex was 73%.

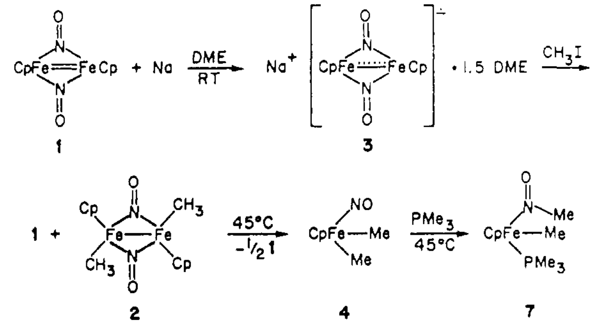
This assignment was supported by the room-temperature ESR spectrum of **3** in THF that shows a single line with $g = 2.06$, a width of 22 G, and no hyperfine coupling. The lack of hyperfine coupling may be indicative of the unpaired electron being in an orbital not localized on an atom with spin (e.g., nitrogen); alternatively, the coupling may be unresolvable due to the 22-G line width. The ESR spectrum of **3** in a dilute α-MeTHF glass (0.1 M) at 11 K showed only the anistropy of the **g** tensor, but no hyperfine coupling. An acceptable elemental analysis could not be obtained for highly air-sensitive **3**.[7] However, conductivity measurements in CH_3CN gave an average value of Λ_M = 130 Ω^{-1} cm^2 mol^{-1}. This is well within the acceptable range of 120–160 Ω^{-1} cm^2 mol^{-1} for a 1:1 electrolyte.[8] Semidifferential cyclic voltammetry[9] measurements on **3** (1×10^{-3} M) in 0.1 M tetraethylammonium perchlorate in CH_3CN at 22 °C (Pt electrode) show a reversible one electron wave at −1.38 V relative to $Ag/AgNO_3$ (0.01 M) (rest potential −0.325 ± 0.010 V) and no further reduction in CH_3CN. This is consistent with **3** being the one electron reduction product from **1** and means that $[CpFe(NO)]_2^{-}\cdot$ is 0.33 V more reducing[5b] than $[CpCo(CO)]_2^{-}\cdot$. By analogy to $Na[CpCo(CO)]_2$, **3** is best described as a "class III" or completely delocalized mixed valence compound with each metal atom in the formal Fe (+1.5) oxidation state (counting NO as a 1^- charged ligand). This is confirmed by the strong similarities between the UV–visible/near-infrared electronic spectra of **3** and $Na[CpCo(CO)]_2$ (Table I), especially the long wavelength bands at 870 and 1280 nm which have been observed for other class III complexes.[10]

Table I. Ultraviolet-Visible/Near-Infrared Absorptions for Nitrosyliron and Carbonylcobalt Radical Anions

compound	λ_{max}, nm (±1 nm)	ϵ, M^{-1} cm^{-1} (±20%)
$Na[CpFe(NO)]_2\cdot 1.5DME$	221	173000
	253	39000
	352	5500
	460 sh	
	530	1200
	604 sh	
	870	250
	1280	640
$Na[CpCo(CO)]_2$ [a]	325 sh	
	372	4800
	580 sh	
	715	34
	835 sh	
	1180	36

[a] Unpublished results of Neil E. Schore and Robert G. Bergman. See also ref 5b.

Scheme I



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(1) (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (c) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 260–288.

(2) (a) Weiner, W. P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612. (b) Weiner, W. P.; Bergman, R. G. *Ibid.* **1983**, *105*, 3922. (c) Wailes, P. C.; Weigold, H.; Bell, A. Ap. *J. Organomet. Chem.* **1972**, *34*, 155. (d) Shortland, A. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 873. (e) Middleton, A. R.; Wilkinson, G. *Ibid.* **1981**, *1888*, 1898. (f) Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880. (g) Clement, R. A.; Klabunde, U.; Parshall, G. *J. Mol. Catal.* **1978**, *4*, 87. (h) Klein, H.; Karsch, H. *Chem. Ber.* **1976**, *109*, 1453.

(3) Brunner, H. *J. Organomet. Chem.* **1968**, *14*, 173.

(4) Brunner, H.; Wachsmann, H. *J. Organomet. Chem.* **1968**, *15*, 409.

(5) (a) Schore, N. E.; Ilenda, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436. (b) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *Ibid.* **1977**, *99*, 1781. (c) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056.

(6) The amount of DME of crystallization was measured by integration of the ^1H NMR resonances of DME against the resonance of a known amount of hexamethylbenzene added as an internal standard.

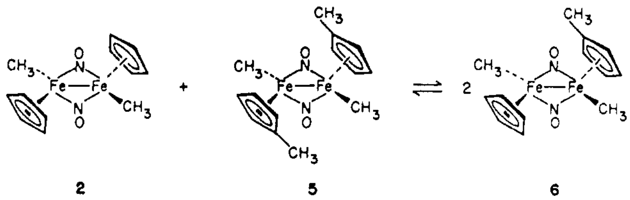
(7) Anal. Calcd for $C_{16}H_{25}Fe_2N_2NaO_5$: C, 41.77; H, 5.48; N, 6.09. Found: C, 42.33; H, 5.80; N, 5.66. Magnetic susceptibility measurements have also given erratic results. Both of these problems may be due to the presence of small amounts of paramangetic impurities. We are attempting to address this by seeking relatives of **3** (e.g., MeCp derivatives; salts with other cations) which may be brought to a higher level of purity.

(8) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(9) (a) Goto, M.; Ishii, D. *J. Electroanal. Chem.* **1975**, *61*, 361; (b) Dalrymple-Alford, P.; Goto, M.; Oldham, K. B. *Ibid.* **1977**, *85*, 1.

(10) (a) Brown, D. B., Ed. "Mixed Valence Compounds"; D. Reidel Publishing Co.: Boston, MA, 1980. (b) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. (c) Garito, A. F.; Heeger, A. J. *Ibid.* **1974**, *7*, 232.

Scheme II



The dimers 1 and 2 are the observed organometallic products of the reaction of 3 with methyl iodide at room temperature in DME. By integration against a known amount of internal standard, the amount of iron in salt 3 is completely accounted for in the quantity of 1 and 2 formed. Thus the total yield of these products is essentially quantiative, and in order for this to be true the sample of 3 used cannot contain substantial impurities, unless they are paramagnetic and lead to the same products. A bit more 1 than 2 (52:48 ratio) was formed, indicating that a small amount of 3 is simply oxidized directly to dimer 2, rather than forming dialkyl complex as well. After a number of unsuccessful attempts at reducing and methylating 2, it was discovered that simple thermolysis of 2 at 45 °C gives 4, along with 1 and an as yet uncharacterized organometallic product with a single ^{1}H NMR resonance at δ 4.40 in benzene-d_6 (Scheme I).

Complex 4 decomposes at a rate comparable to that of its formation (we believe by migratory insertion; see below), and this complicates its isolation. By working rapidly, 4 can be isolated as a green, air-sensitive, and highly volatile solid in analytically pure form in 7.4% yield.[12] Upon following the disappearance of 2 in C_6D_6 at 23.8 °C, its conversion to 4 was found to be cleanly first order over 3 half-lives with an observed rate constant of 1.2×10^{-6} s^{-1}. To determine whether or not 2 also dissociates into monomeric CpFe(NO)Me fragments under these reaction conditions, the methylcyclopentadienyl analogue of 2 was prepared from $[MeCpFe(NO)]_2$[13] in a manner similar to that by which 2 was prepared. Mixtures of 2 and 5 were found to give complete equilibration with the mixed dimer 6 (Scheme II) within seconds at room temperature in C_6D_6 solution, much faster than alkyl transfer.[14] The overall reaction was observed by ^{1}H NMR, and integration of the iron-bound methyl resonances gave $K_{eq} = ([6]^2/[2][5]) = 4.2$. This is indicative of little, if any, thermodynamic preference for one particular dimer. We presume this interchange reaction occurs by reversible dissociation of 2 and 5 into the paramagnetic $CpFe(NO)CH_3$ monomers proposed initially by Brunner.

Although monomeric dialkyl complex 4 decomposes slowly at room temperature to give a variety of products, in the presence of excess trimethylphosphine the trapped insertion product 7 (Scheme I) is formed in 60% yield (^{1}H NMR). This sensitive material can be obtained analytically pure, albeit with significant decomposition during chromatography, in 12% yield.[15] A similar adduct can be observed by ^{1}H NMR with dimethylphenylphosphine, but decomposition of 4 is unaffected by the presence of excess triphenylphosphine. It should further be noted that the extent to which the insertion product can be trapped is the same irrespective of the concentration of trimethylphosphine. This is consistent with rate-determiing migratory insertion followed by rapid trapping, as proposed for the migratory insertion observed[2a,b] for CpCo(NO)-(CH_3).

In summary, reduction of Brunner's dimer 1 leads to a dimeric radical anion, rather than a dianion, which upon alkylation provides a route via a dimethyl dimer to a new monomeic dialkylnitrosyliron complex. Furthermore, NO migratory insertion for the latter is quite facile. We are, therefore, confident that other examples of migratory insertion will be observable and that the paucity of such observations will diminish as the number of known alkyl nitrosyl complexes increases.

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Registry No. 1, 52124-51-3; 2, 87597-73-7; 3, 87597-74-8; 4, 87597-75-9; 5, 87597-76-0; 6, 87597-77-1; 7, 87597-78-2; Na-$[CpCo(CO)]_2$, 62602-00-0; $[MeCpFe(NO)]_2$, 87597-79-3.

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[11] Yields determined by ^{1}H NMR. Isolated yields are lower as reported by Brunner and Wachsmann in ref 4.

[12] Data for 4: mp 56 °C dec; IR (benzene) 1785 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.31 (s, 5 H), 1.03 (s, 6 H); ^{13}C NMR (benzene-d_6, ^{1}H decoupled) δ 94.64 (Cp), −4.14 (CH_3); MS (CI), *m/e* 181 (M^+), 166 (base). Anal. Calcd for $C_7H_{11}Fe(NO)$: C, 46.45; H, 6.12; N, 7.74. Found: C, 46.53; H, 6.16; N, 7.58.

[13] Data for 5: mp 70 °C dec; IR (benzene) 1523 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.40 (t, 2 H, J = 2.2 Hz), 4.22 (t, 2 H, J = 2.1 Hz), 1.64 (s, 3 H), −0.01 (s, 3 H); MS (EI), *m/e* 344 (M − CH_4^+), 78 (base). Anal. Calcd for $C_{14}H_{20}Fe_2N_2O_2$: C, 46.71; H, 5.60; N, 7.78. Found: C, 47.47; H, 5.38; N, 7.75. $[MeCpFe(NO)]_2$ was prepared from $[MeCpFe(CO)_2]_2$ and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in toluene at reflux. Details of the synthesis and characterization of $[MeCpFe(NO)]_2$ will be published elsewhere.

[14] The ^{1}H NMR resonances assigned to 6 in benzene-d_6 are δ 4.48 (s, 5 H), 4.38 (t, 2 H, J = 2.1 Hz), 4.19 (t, 2 H, J = 2.1 Hz), 1.61 (s, 3 H), 0.06 (s, 3 H), −0.06 (s, 3 H).

[15] Data for 7: mp 69 °C dec; IR (KBr) 1309 (s), 1291 (s), 1277 (s), 960 (s, sh), 950 (s), 817 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.27 (s, 5 H), 3.36 (d, 3 H, J = 2.9 Hz), 1.51 (d, 3 H, J = 8.3 Hz), 0.84 (d, 9 H, J = 9.4 Hz); MS (EI), *m/e* 257 (M^+), 61 (base). Anal. Calcd for $C_{10}H_{20}FeNOP$: C, 46.72; H, 7.84; N, 5.45. Found: C, 47.05; H. 7.69; N, 5.51.

Bis(cyclopentadienyl(1,3-diborolenyl)cobalt)tin. A Stannocene Analogue with a Bent Tetradecker Sandwich Structure[†]

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Summary: The preparation of $[(C_5H_5)Co(C_2B_2C)]_2Sn$ (**2**, C_2B_2C, 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) from the sandwich anion $[(C_5H_5)Co(C_2B_2C)]^-$ (**1**$^-$) and $SnCl_2$ is reported. **2** is the first tetradecker sandwich complex containing a non transition metal. It exhibits a bent structure in which the Co–Sn vectors form a 130° angle. The bending angles of the two crystallographically independent molecules are 112 and 114°, respectively.

[†] Dedicated to Professor Dr. Dr. h. c. mult. E. O. Fischer on the occasion of his 65th birthday.

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