between the bond distance, d, and the π bond order, p:

$$d = S - (S - D)p \tag{3}$$

where S and D are standard single and double bond distances: S = 1.517 and 1.470 Å and D = 1.337 and 1.290 Å for C-C and C_1-N distances, respectively.[22] The changes in the pyridine bond distances (Δ_{MO}) were calculated to be +0.0175, −0.0140, and +0.0102 Å for C_1-N, C_1-C_2, and C_2-C_3, respectively. The last column of Table II lists the sum of the absolute values of the residuals between "observed" and calculated normalized bond length changes for the 32 solutions. Solutions 1, 3, 6, 7, 11, 13, and 14 all show sums of residuals near 0.3, significantly lower than the remaining solutions. Among this set, solutions 1 and 3 have significantly better deuterium residuals than the remainder.

Solutions 1 and 3 differ only in the sign of the origin shift of mode 8, the Fe-N stretching mode. This coordinate is not strongly mixed into the other modes, and the excited-state distortions differ mainly in the sign of the Fe-N bond length change. Figure 4 illustrates the similarity in the form of the excited-state distortion provided by solution 1 and the MO calculation. We expect a contraction of the Fe-N bond, since the Fe→ py charge-transfer transition increases the positive charge on Fe and the negative charge on py, thereby increasing the bond polarity. Consequently solution 1, which has the best deuterium residual, a satisfactory MO bond displacement residual, and the expected sign of the Fe-N displacement, is provisionally assigned as the correct solution. It corresponds to an excited-state geometry in which the C_1-C_2 bonds are contracted by about as much as the N-C_1 and C_2-C_3 bonds are expanded (0.012-0.016 Å) and the Fe-N bond is contracted by a slightly larger amount, 0.020 Å. The scaling depends on the accuracy of the MO calculation, and could be corrected by an absolute intensity measurement, or by a complete analysis of the excitation profiles.[16]

Acknowledgment. We thank Professor A. Warshel and W. L. Peticolas for helpful comments. This work was supported by NIH Grant HL 12526 and NSF Grant CHE 74-00055.

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η^5-Cyclohexadienyltricarbonylchromium(0) Complexes from Addition of Carbon Nucleophiles to η^6-Benzenetricarbonylchromium(0). Formation, Chemical and Spectroscopic Features, and X-ray Diffraction Analysis

**M. F. Semmelhack,* H. T. Hall, Jr., R. Farina, M. Yoshifuji,
G. Clark, T. Bargar, K. Hirotsu, and J. Clardy**

*Contribution from the Department of Chemistry, Cornell University,
Ithaca, New York 14853.* *Received August 4, 1978*

Abstract: The addition of reactive carbanions to η^6-benzenetricarbonylchromium(0) produced η^5-(6-alkylcyclohexadienyl)tricarbonylchromium(0) anion complexes, as the lithium salts. Reaction with a variety of oxidizing agents (iodine, cerium(IV), oxygen) removes the hydrogen from C-6 and detaches the $Cr(CO)_3$ unit, to produce a substituted arene. Reaction with electrophiles (potential hydride acceptors) leads to cleavage of the carbon-carbon bond at C-6 with regeneration of η^6-benzenetricarbonylchromium(0). Solution spectral (^{1}H NMR, IR) data are consistent with an η^5-cyclohexadienyl structure. X-ray diffraction analysis on the crystalline adduct of η^6-benzenetricarbonylchromium(0) and 2-lithio-1,3-dithane defines the mode of addition (exo), the deformation (38.6°) of C-6 from the plane of carbons 1-5 in the cyclohexadienyl ligand, and the preferred conformation of the $Cr(CO)_3$ unit.

Introduction

The π complex (**1**) of the chlorobenzene with the chromium tricarbonyl unit undergoes nucleophilic substitution for chloride under mild conditions, providing an overall conversion parallel with classical nucleophilic aromatic substitution.[1] The $Cr(CO)_3$ group enhances the reactivity of the arene ligand to a degree similar to the nitro substituent in p-chloronitrobenzene.[1] The preparative aspects of this reaction have been explored recently, focusing on carbon nucleophiles of special interest in organic synthesis.[2] The mechanism has been discussed[3] in terms of cyclohexadienyl anionic intermediates such

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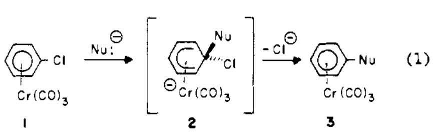
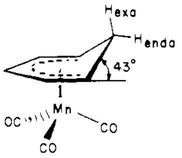


(1)

as **2**, supported by kinetic evidence and analogy with the mechanism of nucleophilic substitution in halonitroarenes.[4] The $Cr(CO)_3$ group serves as a stabilizing substituent for the negative charge, like nitro groups in the well-known anionic σ complexes (Meisenheimer intermediates).[4] But neither direct observation nor the general reactivity of **2** has been reported.

The addition of nucleophiles to cationic arene–metal complexes often produces stable, well-characterized η^5-cyclohexadienyl derivatives, either uncharged or cationic.[5] For example, addition of hydride to η^6-benzenetricarbonylmanganese cation (**4**) produces η^5-cyclohexadienyltricarbonylmanganese (**5**) which is isoelectronic with the postulated intermediate, **2**.[6] In this reaction, in the addition of other nucleophiles to **4**,[7] and in general for addition of nucleophiles to π ligands in 18-electron metal complexes, the addition is exo, from the face of the π ligand opposite from the metal.[8] Also isoelectronic with **2** is the cationic iron complex **6**, obtained by hydride abstraction from a cyclohexa-1,3-diene iron tricarbonyl derivative.[9] The structures of **5** and **6** have been determined by X-ray diffraction analysis.[9,10] Attention has been drawn to the deformation from planarity of the cyclohexadienyl ligand in complexes such as **5** (43°) and **6** (40°)[11] and to the conformational preference (as shown in **5** and **6**) of the $M(CO)_3$ unit with respect to the cyclohexadienyl ligand.[12]



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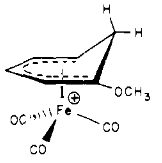


6

In the exploration of preparative applications of the reaction in eq 1, we have undertaken a systematic study of addition of carbon nucleophiles to arene chromium tricarbonyl complexes.[13] With sufficiently reactive carbanions, adducts are observed which display structural and chemical features of interest for organometallic theory and for organic synthesis methodology. In this paper, we describe adducts with η^6-benzenetricarbonylchromium(0) (**7**), which we have characterized with spectral and chemical data and, in one case, with an X-ray diffraction analysis.

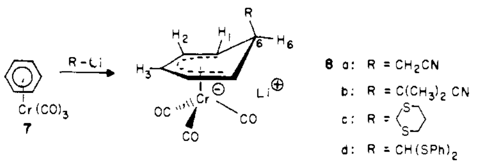
Results

A. Preparation. The lithium salts of simple ester enolates react with η^6-benzenetricarbonylchromium (**7**) rapidly below 0 °C in a medium of tetrahydrofuran (THF)/hexamethylphosphoric triamide (HMPA) with volume ratio 10:1 to 1:1. No obvious change is observed in the appearance of the solution (homogeneous yellow), but ^1H NMR can be used to monitor disappearance of **7** (singlet at δ 5.45, THF-d_8). Similarly, the lithium salts of carbanions from alkyl nitriles and from 1,3-dithiane react rapidly with **7** in THF alone. The adducts are stable for long periods of 0 °C but decompose rapidly in the presence of oxidizing agents or electrophilic reagents. Cooling, evaporation of solvent, and/or addition of hexane cause crystallization or precipitation of yellow salts. Characterization by combustion analysis or by melting point was not generally satisfactory owing to inclusion of variable amounts of solvent in the solids.

B. Solution Spectroscopy. Reaction of lithiocyanomethane with **7** produced a solution which was evaporated at 0.001 Torr (25 °C) and then dissolved in THF-d_8 for ^1H NMR studies. Except for residual signals from traces of hydrogen in the THF-d_8, all observed signals were consistent with the adduct, assuming the cyclohexadienyl structure, **8a:** δ 4.92 (br, t, 1 H, H_4 in **8a**), 4.22 (m, 2 H, H_3), 2.6 (m, 3 H, H_2 and H_1), and 1.48 (d, $J = 6$ Hz, 2 H, $-CH_2CN$). Irradiation at δ 2.6 (H_2 and H_1) provided a triplet at δ 4.92 ($J_{4,3} = 6$ Hz), a broad doublet at 4.22 ($J_{4,3} = 6$ Hz), and a singlet at 1.48. Irradiation at δ 4.92 converted the absorption at δ 4.22 to a broad singlet with small unresolved couplings (apparently $J_{4,2}$ or $J_{4,1}$ is between 0 and 2 Hz) and left the other absorptions essentially unchanged. Irradiation at δ 4.22 provides a broad singlet at δ 4.92 and no other significant changes. Irradiation at δ 1.48 had no significant effect on the spectrum. The adducts of **7** with three other carbanions were studied by NMR and the assignments are displayed in Table I.

Table I. ^1H NMR Data for Adducts **8a–d**

entry	adduct	H_3	$H_{2,4}$	$H_{1,5}$	H_6	H in R
1	**8a**	4.92	4.22	2.6	2.6	1.48 (d, $J \simeq 6$ Hz, $-CH_2$)
2	**8b**	4.87	4.61	2.7	2.6	1.00 (s, $-CH_3$)
3	**8c**	4.82	4.35	[—3.1–1.4 (~10 H)—]		
4	**8d**	4.92	4.41	2.8	2.4	3.40 (d, $J \simeq 10$ Hz, $-CH$) 7.20 (m, $-C_6H_5$)



Significant absorptions in the infrared spectra of **8d** include the CO stretching bands at 5.26, 5.55, and 5.84 μ of similar intensity. Also significant is the absence of a band in the region 4.15–4.35 μ, where a weak absorption is usually observed for an exo C–H stretching vibration (e.g., if R = H in **8**) in complexes related to **8** with other metals.[14] The spectra were recorded in THF-d_8 (transparent at 4.15–4.35 μ) at high concentration.

C. X-ray Diffraction Analysis. Reaction of 2-lithio-1,3-dithiane with **7** in THF at −30 °C produced a yellow, crystalline solid (**8c**). Although well-formed crystals were obtainable from THF at temperatures between −30 and −80 °C, they turned to an amorphous semisolid above 0 °C, due to THF bound to the complex. Attempts to remove excess THF by pumping at low temperature resulted in crystals which were stable at 25 °C but of poor quality. Crystallization of the anionic complex (Li counterion) from less coordinating solvents or with the PPN cation[15] in place of Li failed to give useful crystals. However, the complex produced stable, regular crystals incorporating solvent when crystallized from 1,4-dioxane at 50 °C. Spectral data were collected on the crystals which were identical with data obtained from a sample before treatment with hot 1,4-dioxane.

The two independent molecules in the asymmetric unit have the same conformation, within experimental error, for the $C_{13}H_{13}O_3S_2Cr$ anions; Figure 1 shows a computer-generated perspective drawing of only one anion. In the following discussion averaged bonding parameters are used. All bonds to C(6) appear to be normal. The sp^2-sp^3 bonds [C(6)–C(1) and C(6)–C(5)] are 1.49 Å and the sp^3-sp^3 [C(6)–C(7)] bond is 1.53 Å. The remaining bonds in the pentadienyl fragment are 1.41 Å. The Cr atom is situated roughly equidistant from C(1), C(2), C(3), C(4), and C(5) at an average distance of 2.22 Å. The pentadienyl fragment is coplanar within 0.028 Å and C(6) is 0.59 Å from this plane. The Cr atom is 1.746 Å from the plane. The interplanar angle between the pentadienyl plane and the C(1)–C(6)–C(5) plane is 38.6°. The $Cr(CO)_3$ fragment is rotated to give the anion approximate mirror symmetry with one carbonyl oriented under C(6).

Table II. Oxidation of Adduct **8b**

entry	oxidant (molar equiv)	conditions^a	yield of **9**,^{b} %
1	I_2 (4)	3 h	94
2	O_2 (excess)	2 h, 0 °C	$34^{c,d}$
3	$FeCl_3$ (7)	18 h	81
4	Fe-DMF (4)^f	3 h	99
5	benzoquinone (4)	2.5 h	59
6	$Co(acac)_3$ (6)	3 h	13^e
7	$Fe(acac)_3$ (8)	3 h	13^e
8	$CuCl_2$-DMF (8)	3 h	74
9	$SnCl_4$ (8)	3 h	<5
10	Ce(IV)	0.5 h	71^g

[a] All reactions were carried out in THF or 1:1 THF-HMPA at 25 °C. [b] The yield is based on distilled, pure samples of **9** unless otherwise noted. [c] This yield was determined by GLC using an internal standard. [d] The starting complex (**7**) was detected in the crude product. [e] This yield is based on integration of the ^1H NMR spectrum of the product, weighed and distilled, but <95% pure. [f] This oxidant is the complex of ferric chloride and DMF (see Experimental Section). [g] The oxidant is a solution of ceric ammonium nitrate in acetonitrile (see Experimental Section).

Table III. Reaction of Adduct **8b** with Electrophiles

entry	electrophile	products (yield)
1	CH_3I (25 °C, 1 h)	$(CH_3)_3CN$ (high), **7** (high)
2	PhCOPh (0 °C, 0.5 h)	$(Ph)_2C(OH)C(CH_3)_2CN$ (93%), **7** (79%)
3	$Ph_3C^+\ ^-BF_4$ (25 °C, 0.5 h)	**7** (>90%)
4	Et_3B (25 °C, 2 h)	**7** (>90%)

Only the Li^+ atom is involved in intermolecular contacts less than van der Waals distances. Li(1) is coordinated by one carbonyl oxygen (1.90 Å) and two dioxane oxygens (1.91 and 1.98 Å) while Li(2) is coordinated by one carbonyl oxygen (1.93 Å) and one dioxane oxygen (1.93 Å).

D. Chemical Properties. The reactivity of the adducts is generally consistent with the cyclohexadienyl structure, but with some unanticipated features. The adduct (**8b**) from 2-lithio-2-methylpropionitrile and η^6-benzenetricarbonylchromium (**7**) was studied most thoroughly.

Oxidation of **8b** with a variety of oxidizing agents led to formation of 2-methyl-2-phenylpropionitrile (**9**, see Table II). Conversion of **8b** to η^6-[(2-cyano-2-methylethyl)benzene]tricarbonylchromium (**10**) by selective oxidation has not yet been accomplished. A series of experiments involving oxidation with controlled amounts of iodine established that approximately 2.5 molar equiv of I_2 is required for complete conversion of **8b** to **9**; smaller amounts of iodine led to mixtures of products, including **7** and **9**, but **10** was not detected.

Attempts to convert **8b** to **10** using electrophilic reagents which can function as hydride acceptors (removing H^- from C-6 in **8b**) also failed (Table III). The favorable reaction in these cases appears to be abstraction of the original carbanion [$^-C(CH_3)_2CN$] to give the adduct **11** (generalized electrophile E) and regeneration of the starting arene complex, **7** (Scheme I).

Reaction of *tert*-butyllithium with **7** generated an adduct (presumably **12**) which reacts with iodine to produce *tert*-butylbenzene. In contrast to **8b**, adduct **12** showed no tendency to react with electrophiles via cleavage of the exo carbon-carbon bond at C-6. Instead, reaction with methyl iodide, benzophenone, and triphenylmethyl fluoroborate produced complex product mixtures containing no more than a trace of **7** (Scheme II). Treatment of a solution of adduct **12** with methyl iodide (25 °C, 1 h) followed by oxidation with excess iodine led to formation of *tert*-butylbenzene as the major product, suggesting no significant reaction between methyl iodide and **12** under these conditions.

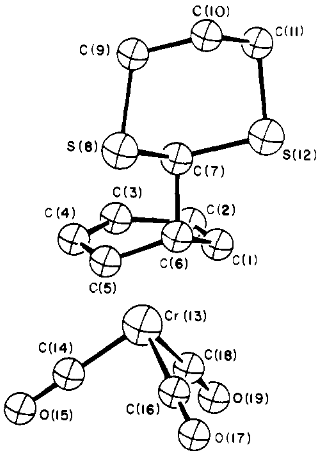
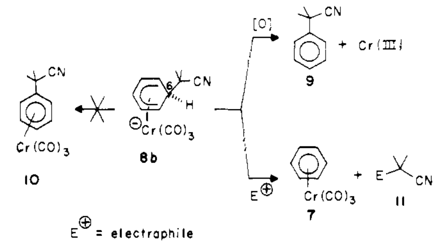


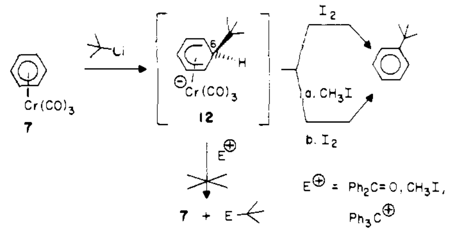
Figure 1. ORTEP drawing of adduct **8c**.

Samples of **8a** and **8b** reacted with proton donors via two main pathways, depending on the strength and quantity of the added acid (Scheme III). When water, acetic acid, or 2,2,2-trifluoroethanol (1 molar equiv or large excess) or trifluoroacetic acid (1 molar equiv) is added to a solution of **8a** or **8b** at 0 °C, the starting complex (**7**) and the protonated carbanion [CH_3CN or $CH(CH_3)_2CN$] appeared rapidly. Complex **7** was recovered to the extent of 70-90%. Addition of excess D_2O to a solution of **8b** produced **7** with no significant deuterium incorporation (<1.0% by mass spectral analysis) and produced 2-methylpropionitrile-*2-d* with >90% deuterium at C-2 (^1H NMR). Addition of water to a solution of **8a** in THF-d_8 at −60 °C in a sample tube for ^1H NMR observation led to severe broadening of the characteristic signals of **8a** and no significant new signal was observed. As the sample was warmed to −30

Scheme I



Scheme II



Scheme III

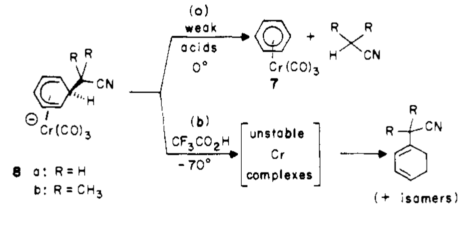
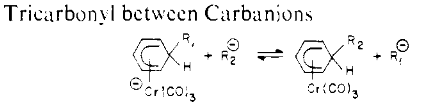
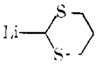
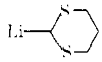
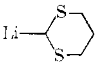
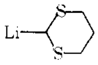
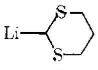
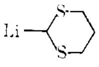
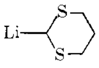


Table IV. Exchange of Benzenechromium Tricarbonyl between Carbanions

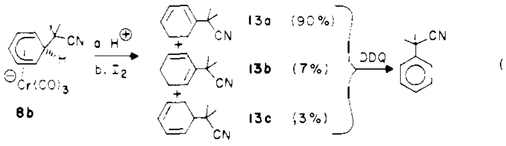


entry	R_1	R_2	reaction condition[b]	product ratio[a] % R_1Ph	product ratio[a] % R_2Ph
1	$LiCH(CH_3)CO_2$-*t*-Bu		0 °C, 15 min, THF-HMPA	100	0
2		$LiC(CH_3)_2CN$	25 °C, 52 h	100	0
3	$LiC(CH_3)_2CN$		0 °C, 0.25 h, THF	97	3
4	$LiC(CH_3)_2CN$		0 °C, 0.5 h, THF	91	9
5	$LiC(CH_3)_2CN$		24 °C, 5 h, THF	76	24
6	$LiC(CH_3)_2CN$		24 °C, 11.3 h, THF	61	39
7	$LiC(CH_3)_2CN$		24 °C, 52 h, THF	43	57

[a] The products were obtained together by short-path distillation and analyzed by quantitative GLC; the absolute yields of R_1Ph and R_2Ph ranged from 63 to 86% for examples in this table. [b] See Experimental Section.

°C, the signals changed position and sharpened until, after 0.5 h at −30 °C, only two singlets remained, at δ 5.45 (complex 7) and 2.00 (CH_3CN).

Addition of trifluoroacetic acid (5 molar equiv) at −70 °C to a solution of **8b** in THF followed by warming slowly to 25 °C produced a deep red solution. Attempts to isolate organochromium complexes from this solution failed owing to serious thermal and oxidative sensitivity; however, oxidative detachment [I_2, Ce(IV)] and ligand displacement (NH_4OH, Ph_3P) were effective in freeing the organic ligands. The product mixture was identified as the isomeric 1,3-cyclohexadienes, **13a–c**, in the ratio indicated in eq 2. Proof of structure rested primarily on characterization of the Diels–Alder adducts (**14a,b**) of **13a–c** with *N*-phenyl-1,2,4-triazoline-3,5-dione, where integration of vinylic hydrogens vs. bridgehead hydrogens provided the key distinguishing feature. Treatment of the mixture **13a–c** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in benzene at reflux for 0.5 h gave a single product, 2-methyl-2-phenylpropionitrile, in 86% yield, thus verifying the skeletal relationships of **13a–c** (eq 2).



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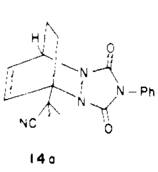
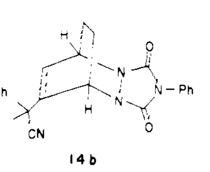
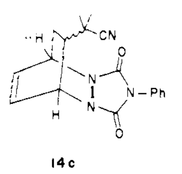


14a

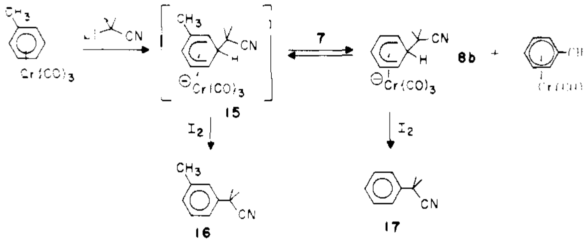


14b

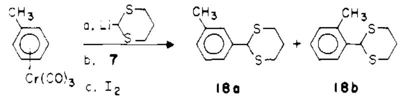


14c

The transfer of the carbanion unit [$^-C(CH_3)_2CN$ in **8b**] from the arene ring to an electrophile (Scheme I) also applies when another η^6-arenetricarbonylchromium complex acts as the electrophile. For example, reaction of $LiC(CH_3)_2CN$ with η^6-(toluene)tricarbonylchromium produced an adduct (presumably mainly **15**) which was not fully characterized. Addition of η^6-benzenetricarbonylchromium to this solution (0.25 h, 0 °C) followed by oxidative quenching (I_2) produced a mixture of the toluene derivative (**16**, 17%) and the benzene derivative (**17**, 69%), as depicted in eq 3. In a similar set of steps, 2-lithio-1,3-dithiane was allowed to add to η^6-(toluene)tricarbonylchromium and later η^6-benzenetricarbonylchromium was added. As outlined in eq 4, toluene derivatives (**18a,b**) were the major products (>95%). After 0.25 h at 0 °C, the ratio **a**:**b** was 50:50 (72% yield), and after 1.0 h at 22 °C, **a**:**b** = 50:50 (53% yield). In both cases, the yield of 2-phenyl-1,3-dithiane was <5%.

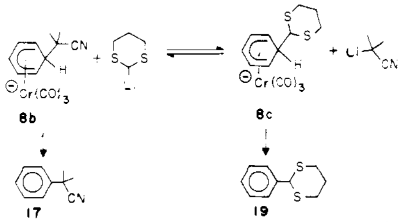


(3)



(4)

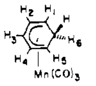
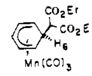
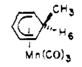
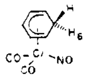
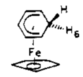
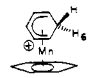
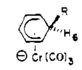
Exchange of carbanion units in adducts such as **8b** is a slow process. For example, treatment of **8b** with 2-lithio-1,3-dithiane in THF gave a mixture of cyclohexadienyl complexes (**8b,8c**) which was analyzed after oxidative quenching. Two products are possible, **17** and 2-phenyl-1,3-dithiane (**19**). The amount of each depends on the reaction time and temperature (Table IV). Single experiments were also carried out starting from **8c** and adding 2-lithio-2-methylpropionitrile (entry 2), and starting from the adduct of **7** with the lithium enolate of *tert*-butyl acetate and adding 2-lithio-1,3-dithiane (entry 1).



Discussion

The ^1H NMR spectra of **8a–d** are consistent with the pres-

Table V. ^{1}H NMR Chemical Shift Assignments for Representative η^5-Cyclohexadienyl Complexes

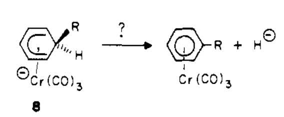
	Chemical Shifts H_3	$H_{2,4}$	$H_{1,5}$	H_6	Ref.
	5.20(tt) J_{23} = 5.1 Hz J_{13} = 1.2 Hz	4.16(br.t) J_{23} = 6.5 Hz J_{12} = 5.1 Hz	2.35(m)	2.3(m)	20
	5.82(t) J_{23} = 5.5 Hz	4.89(dd) J_{23} = 5.5 Hz J_{12} = 5.5 Hz	⟵ 3.0-3.4 ⟶		21
	5.66(t) J_{23} = 5.4 Hz	4.69(br.t) J_{23} = 5.4 Hz J_{12} = 6.0 Hz	3.15(br.t) J_{12} = 6.0 Hz J_{16} = 6.0 Hz	2.58(sextup.) J_{H_6,CH_3} = 6.5 Hz J_{16} = 6.0 Hz	22
	5.00(m)	—	—	2.00(m)	23
	5.87(tt) J_{23} = 6 Hz J_{13} = 1.5 Hz	4.07	⟵ 1.56-2.59 ⟶		24
	4.0(t) J_{23} = 5 Hz	3.50(t) J_{23} = 5 Hz J_{12} = 5 Hz	2.4(m)	1.05(m)	25
	4.82-4.92(br.t) J_{23} = 6 Hz	4.22-4.61(br.t) J_{12} = 6 Hz J_{23} = 6 Hz	2.6-2.8(m)	2.4-2.6(t,q, or pentup.) $J_{H_6,R}$ = 6 Hz J_{16} = 6 Hz	26

ence of a 6-substituted η^5-cyclohexadienyl ligand. The peak assignments are parallel with those for closely related manganese,[16] iron,[17] and chromium(I)[18] η^5-cyclohexadienyl complexes, as presented in Table V. The most downfield signal is assigned to the hydrogen at C-3 (para to the site of carbanion attack), with strong coupling to the C_2 and C_4 hydrogens and additional broadening due to coupling with the hydrogens at C_1 and C_5. The signal due to the hydrogen at C-6 appears upfield, often partially overlapping with the hydrogens at C_1 and C_5. The coupling constant (~6 Hz) between H_1 and H_6 is appropriate for a dihedral angle of 30-40°, consistent with an out-of-plane position for C-6 as revealed in the X-ray structure (see below).

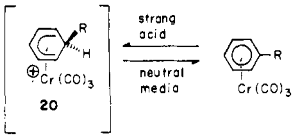
The detailed structure determined by X-ray diffraction contains no surprises. Consistent with predictions[11,12] and in line with uncharged and cationic isoelectronic analogues,[9,10] the chromium tricarbonyl unit resides in a conformation with a Cr–CO bond eclipsed with C-6, and C-6 is bent away from the plane of C-1 to C-5 by 38.6°. While the exo C-C bond at C-6 appears to be labile in these complexes (especially **8a** and **8b**, see below), there is no evidence for unfavorable nonbonded interactions or unusual bond distances in **8c**. The association of the Li cation with a CO ligand is consistent with a strong concentration of negative charge on the carbon monoxide oxygen atoms, as predicted.[19]

The formation of adducts such as **8a–d** involves the attachment of a nucleophilic carbon to an aromatic ring carbon, and appears to be quite general for reactive carbanions.[13a] Formation of carbon bonds to aromatic rings by nucleophilic attack is not often used for complex molecular synthesis, perhaps for lack of general and selective methodology. Therefore, we are particularly interested in the chemical reactivity of **8** with respect to manipulating the cyclohexadienyl ligand into useful types of organic products and eventually removing the chromium unit.

A survey of oxidizing agents and potential hydride abstracting agents was carried out in order to find optimum conditions for the removal of the endo hydrogen at C-6 (eq 5). This conversion would give nucleophilic substitution at a ring position and maintain the activating substituent [$Cr(CO)_3$] for further substitutions or other manipulations of the arene ligand. At the end, mild oxidation[27] and irradiation[28] are known to cleave arene–chromium bonds cleanly. We anticipated two general mechanisms for the reaction in eq 5: direct bonding of electrophilic atoms with the endo hydrogen (hydride abstraction) or two-electron transfer to generate the 16-electron complex **20**. Complex **20** is of a type invoked to explain arene ring proton exchange of arene–chromium complexes in strong acid[29] and clearly would suffer rapid loss of a proton in neutral media (eq 6).

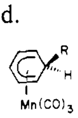


(5)



(6)

Other η^5-cyclohexadienyl metal species have been oxidized, with some of the same questions in mind. The manganese analogues (i.e., **21**) resulting from addition of cyanide anion, malonate anion, and other carbanions are oxidized with cerium(IV)/sulfuric acid to remove the hydrogen at C-6 *and* detach the metal.[30] Electrophilic agents such as triphenylmethyl cation preferentially remove the (exo) carbanion unit, to regenerate the unsubstituted benzenemanganese tricarbonyl. Similarly, the adducts (e.g., **22**) of bis(mesitylene)iron dication and alkyllithium reagents can be oxidatively decomposed to a 2-alkylmesitylene derivative (loss of Fe).[31] The yields for a variety of anions ($^-CH_2NO_2$, $^-CH_2CO_2R$, etc.) range from 50 to 80%. Reaction with hydride-abstracting agents has not been reported.



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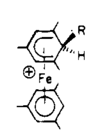

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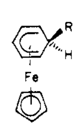

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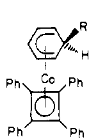
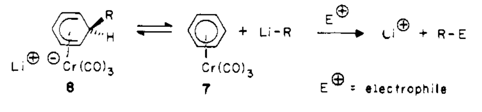


24

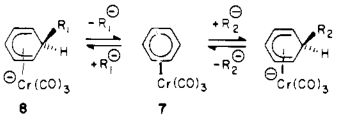
A systematic study of reactions of η^5-cyclohexadienyl-η^5-cyclopentadienyliron complexes (e.g., **23**) has appeared.[32,33] It was reported that, with R = CH_3 or R = Ph in **23**, reaction with *N*-bromosuccinimide led to the *substituted* (i.e., η^6-toluene or η^6-biphenyl) η^6-arene-η^5-cyclopentadienyliron(II) cations in yields of 60%.[32] With triphenylmethyl cation, hydride abstraction occurred for complexes of type **23** only when R = H.[32] A few years later, a series of complexes of type **23** (R = CH_3, CH_2CH_3, CH_2Ph, C_5H_5) was studied in reaction with *N*-bromosuccinimide and triphenylmethyl cation.[33] With either reagent, **23** (R = CH_3) gave only endo-H abstraction to produce η^6-toluene-η^5-cyclopentadienyliron cation. However, **23** (R = CH_2CH_3 or C_5H_5) gave a mixture of abstraction of exo-R and abstraction of endo-H. With **23** (R = CH_2Ph) reaction with either reagent gave only exo-R abstraction, formation of η^6-benzene-η^5-cyclopentadienyliron cation.[33] Corresponding cobalt complexes (**24**, R = C_4H_9 and Ph) are converted very efficiently to the substituted arene derivatives by endo-H abstraction with *N*-bromosuccinimide in methyl alcohol.[34]

From these data and many earlier examples, it is clear that abstraction of the exo substituent at C-6 in η^5-cyclohexadienyl complexes with an electrophilic reagent is a favorable process, and endo-hydrogen abstraction is not. Even exo-carbon units such as -CN, -CH(CO_2Et)$_2$, and -CH_2Ph can be cleaved, although -CH_3 is not generally abstracted. In the chromium series, especially for **8a** and **8b**, we have failed to find an electrophilic reagent which will remove the endo hydrogen at C-6, although many oxidizing agents will induce loss of the hydrogen at C-6 *and* detachment of the arene ligand from the chromium. This is a conversion of some potential for organic synthesis, but lacks the control implicit in the still elusive conversion in eq 5. Complex **8b** is reactive toward simple electrophiles such as ketones, transferring the carbanion unit [$^-C(CH_3)_2CN$] via nucleophilic addition to the ketone carbonyl. It is also reactive toward protons above −30 °C by a similar process which detaches the $-C(CH_3)_2CN$ unit and regenerates the η^6-benzene complex, **7**. The reactions with protons and other electrophiles can be interpreted as electrophilic trapping of the carbanion [$LiC(CH_3)_2CN$] from a mobile equilibrium, as outlined in eq 7. But evidence against



(7)

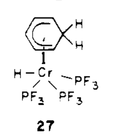
an equilibrium between **7** and **8** (which is established rapidly at below 0 °C) comes from the experiments in Table IV. The exchange of anions (eq 8) R_1^- and R_2^- occurs slowly at 24 °C



(8)

($t_{1/2} \sim 40$ h), ruling out rapid generation of R_1^- from **8** at −30 °C. These results indicate that, in general, electrophiles react *directly* with **8** rather than with R^- as indicated in eq 7. It is interesting to note that rapid transfer of anion units between arene ligands (reaction 3) occurs under conditions where formation of free R^- is expected to be slow. Presumably, this transfer occurs by a bimolecular mechanism such as direct transfer of the exo unit of **8** to the exo face of η^6-arenetricarbonylchromium. When the exo substituent is 1,3-dithian-2-yl, this type of transfer reaction is very slow; anion interchange is not observed. This adduct (**8c**) appears to be less labile with respect to electrophilic attack and to simple dissociation to starting arene complex (**7**) and 2-lithio-1,3-dithiane. Similarly, the adduct (**12**) with *tert*-butyllithium shows no tendency to transfer the *tert*-butyl group to electrophiles.

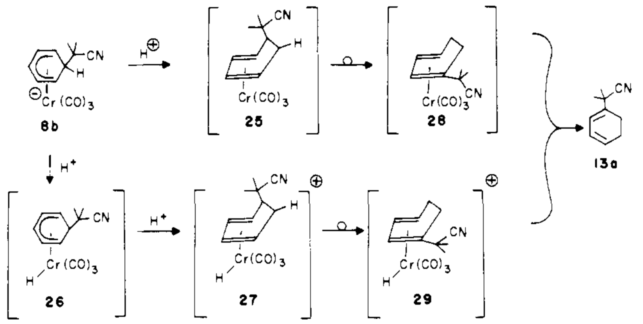
The addition of excess trifluoroacetic acid at −70 °C results in addition of a proton to the η^5-cyclohexadienyl ligand (see eq 2), presumably forming an η^4-diene complex (e.g., **25**). Complex **25** was not detected, but simple analogues of **25** such as η^4-(1,3-butadiene)tetracarbonylchromium are known and are rather labile toward detachment of the 1,3-diene unit. Alternative intermediates may be derived from initial protonation at chromium to give complex **26**, with a chromium-hydrogen bond. A close analogue (**27**) is known, although it



27

is obtained by an entirely different pathway, and shows a signal at δ −4.00 in the ^{1}H NMR spectrum.[35] No signal in this region was observed during protonation studies with **8a** and **8b**, but serious line broadening observed may have made the signal too weak to detect under our conditions. The major isomer observed after decomplexation is **13a**, which is unlikely to represent the first-formed isomer during protonation. We postulate rapid hydrogen rearrangement in a η^4-diene intermediate (**25** or **27**), with the configuration in **13a** providing the more stable complex (**28** or **29**).

From the standpoint of applications in organic synthesis, it is important to recognize that reactive, useful carbanions will form carbon-carbon bonds with η^6-arenetricarbonylchromium complexes, and the intermediate η^5-cyclohexadienyl anion species can be oxidized under mild conditions and in high yield



to give the free arene resulting from formal nucleophilic substitution for hydride. It can also be protonated to give a substituted 1,3-cyclohexadiene, a conversion involving formal addition of R-H across a benzene π bond.

Experimental Section

General. Tetrahydrofuran (THF) and dioxane were freshly distilled from sodium-benzophenone ketyl under argon immediately before use. THF-d_6 (Merck, Canada) was dried and purified by repeated vacuum transfer from sodium-potassium alloy. Diisopropylamine, hexamethylphosphoric triamide, acetonitrile, and 2-methylpropionitrile were distilled from calcium hydride under argon and stored under argon over Linde Type 4A molecular sieves. All other solvents were ACS reagent grade and were not further purified unless otherwise noted. All reactions involving organochromium complexes were carried out under an atmosphere of argon achieved by alternately evacuating and filling the reaction vessel three times with argon. All organic extracts were dried over anhydrous magnesium sulfate. *n*-Butyllithium was obtained from Lithium Corporation of America, filtered through dry Celite under argon, and stored under argon at 25 °C. The solutions were titrated periodically using a standard solution of 2-butanol in toluene with 1,10-phenanthroline as indicator.[36] Most ^{1}H NMR spectra were obtained on a Hitachi Perkin-Elmer R-24 or R-24B 60-MHz spectrometer using deuteriochloroform and tetramethylsilane as internal reference.

Analytical GLC was performed on a Perkin-Elmer Model 3920 gas chromatograph equipped with flame ionization detectors using 0.125-in. o.d. stainless steel columns with N_2 carrier. For quantitative analyses, a weighed amount of a standard was added to the sample and relative peak areas of the sample components and standard were measured with a disk integrator. The relative detector response factors were determined independently using pure samples of each component mixed with the standard, using carrier flow rates and instrument conditions as close as possible to identical for all determinations.

Preparation of η^5-(6-Cyanomethylcyclohexadienyl)tricarbonylchromium(0) Lithium Salt (8a). Lithium diisopropylamide (1.0 mmol) was prepared from diisopropylamine (0.10 g, 1.0 mmol) and *n*-butyllithium (0.48 mL of 2.1 M in *n*-hexane, 1.0 mmol) at 0 °C in 5.0 mL of THF. After the solution was stirred for 0.3 h, acetonitrile (41 mg, 1.0 mmol) was added rapidly dropwise via syringe. After 1.0 h at 0 °C, the volatile materials were removed (0.01 Torr 25 °C, 2 h) to leave a colorless powder. Then 0.7 mL of THF-d_8 was introduced and a sample (0.2 mL) of the resulting solution was studied by ^{1}H NMR: δ 0.4 (br s, $LiCH_2CN$) and small signals at δ 1.00 [d, J = 7 Hz, $(CH_3)_2CHN$, trace of residual diisopropylamine]. To the NMR sample at −78 °C was added via syringe a solution of η^6-benzenetricarbonylchromium (**7**, 32 mg, 0.15 mmol)[37] in 0.4 mL of THF-d_8. The ^{1}H NMR spectrum of the yellow solution was recorded at −60 °C, and is presented in Table I. Double irradiation experiments (see Results) were carried out on a Bruker HX-90 spectrometer. Attempts to crystallize **8a** at low temperature gave yellow microcrystals which softened or melted above 0 °C. The complex is insoluble in hexane and toluene at 25 °C, and very soluble in polar solvents. Deliberate addition of air to a solution of **8a** in THF at 25 °C gave immediate green coloration and a precipitate.

Preparation of η^5-[6-(2-Cyano-2-methylethyl)cyclohexadienyl]tricarbonylchromium(0) Lithium Salt (8b). Exactly according to the procedure immediately above, 2-lithio-2-methylpropionitrile was prepared as a colorless powder. The salt (1.0 mmol) was dissolved in 0.7 mL of THF-d_8 and a sample was removed for ^{1}H NMR analysis: δ 1.56 (s). A solution of η^6-benzenetricarbonylchromium (**7**, 46 mg, 0.22 mmol) in 0.2 mL of THF-d_8 was added via syringe to the NMR sample at −78 °C. The sample tube was shaken well at −78 °C and the ^{1}H NMR was measured at −35 °C and recorded in Table I.

Preparation of η^5-[6-(1,3-Dithian-2-yl)cyclohexadienyl]tricarbonylchromium(0) Lithium Salt (8c). A solution of 2-lithio-1,3-dithiane[38] was prepared in 10 mL of THF from 1,3-dithiane (240 mg, 2.50 mmol) and *n*-butyllithium (0.95 mL of 2.1 M solution in *n*-hexane). With the mixture at −78 °C, a solution of η^6-benzenetricarbonylchromium (428 mg, 2.00 mmol) in 4.0 mL of THF was added dropwise via syringe. No reaction was apparent from the appearance of the mixture (homogeneous yellow), but, upon warming slowly to 0 °C, yellow crystals appeared (first at −45 °C and nearly complete after 0.5 h at −30 °C). At 0 °C, the solution was again homogeneous. Cooling and/or addition of toluene caused formation of yellow solid, which contained large amounts of THF (^{1}H NMR) and melted below 25 °C. After evacuation at 0.001 Torr and 0 °C, a yellow, amorphous solid was obtained; the ^{1}H NMR spectrum in THF-d_8 is recorded in Table I.

In order to obtain suitable crystals for an X-ray diffraction study, a number of solvents were tested for recrystallization. Complex **8c** was very soluble in 1,2-dimethoxyethane and acetonitrile and insoluble in toluene and dichloromethane. It was sparingly soluble in dioxane at 25 °C, and dissolved easily above 50 °C. A sample of **8c** (after pumping away the THF) was dissolved in dioxane to saturation at 90 °C; then the solution was maintained at 50 °C while yellow crystals appeared slowly. These were submitted to X-ray diffraction analysis (see below).

Preparation of η^5-[6-(Bis(phenylthio)methyl)cyclohexadienyl]tricarbonylchromium(0) Lithium Salt (8d). In a Schlenk reaction vessel equipped with a side arm fused to an NMR sample tube was placed bis(phenylthio)methane (29 mg, 0.13 mmol) and 0.5 mL of THF-d_8 was added. With the solution at −78 °C, *n*-butyllithium (0.13 mmol of a 2 M solution in hexane) was added dropwise over 5 min via syringe. The solution was warmed to 0 °C and stirred for 0.2 h, then cooled to −78 °C and evacuated (0.001 Torr, 4 h, −78 °C) to provide a pale yellow solid. A solution of η^6-benzenetricarbonylchromium (**77**, 26.8 mg, 0.13 mmol) in 0.5 mL of THF-d_8 was added via syringe to the solid at −78 °C. The yellow solution thus obtained was transferred (tilting the vessel) to the NMR tube, and the tube was sealed. The ^{1}H NMR spectrum was recorded at −60, −30, and 0 °C, revealing no significant temperature effect. A sample of **8d** in THF was treated with toluene at 0 °C to induce precipitation of an amorphous, yellow solid. After the solid was exposed to 0.01 Torr, 25 °C, 24 h, it was sealed in a capilliary under vacuum and gave mp 111–114 °C: IR (THF-d_8 vs. THF-d_8 reference) 5.26 (s), 5.55 (s), 5.84 (s), 6.41 (w), 6.82 (w), 7.00 (w), 7.36 (m), 8.10 (m) μ.

General Procedure for Preparation of Complex 8b in Situ for Preparative Experiments. A solution of lithium diisopropylamide (1.1 mmol in 5 mL of THF) was prepared as before in a 50-mL three-necked round-bottom flask fitted with a serum stopper, a gas adapter attached to a vacuum/argon double manifold, and a solid addition tube charged with the crystalline complex **7** (214 mg, 1.0 mmol). To the clear, colorless solution at −78 °C was added 2-methylpropionitrile (98 μL, 1.1 mmol) over 1 min via syringe. After 0.5 h, the solid addition tube was rotated to allow complex **7** to drop into the clear, colorless solution. Stirring was continued at −78 °C until the complex had dissolved. As determined by NMR spectroscopy and the oxidation experiments below, the reaction to form **8b** was complete within 0.5 h at −78 °C with no obvious change in the appearance of the solution.

Oxidation of 8b with Iodine. A solution of iodine (7–10 mg-atoms) in THF (10 mL) was added rapidly via syringe to the solution of **8b** at −78 °C. The resulting mixture was warmed to 20–25 °C for 3–6 h (gas evolution). The crude mixture was diluted with ether (equal volume) and washed sequentially with a 10-mL portion of saturated aqueous sodium bisulfite solution, three 10-mL portions of 1 M hydrochloric acid, and one 10-mL portion of saturated aqueous sodium chloride solution. The ether phase was dried and diluted to 100.0 mL in a volumetric flask. Exactly 5.00 mL was transferred onto 5.6 mg of biphenyl (GLC internal standard) and analyzed on a 6-ft column of 5% OV-17 at 130 °C: retention time of 2-methyl-2-phenylpropionitrile was 5.2 min, and of biphenyl was 13.2 min. The yield was 96%. The remainder of the ether solution was concentrated in vacuo and flash distilled at 0.01 Torr (50 °C). The GLC retention time and ^{1}H NMR spectrum of the distillates were identical with parallel data on a sample of 2-methyl-2-phenylpropionitrile prepared from commercial phenylacetonitrile by dimethylation. ^{1}H NMR (CDCl$_3$): δ 7.2–7.5 (m, 5 H, aryl) and 1.67 (s, 6 H, -CH$_3$). The weight of distillate was 136 mg (94% yield).

Oxidation of 8b with Oxygen. Complex **8b** (1.0 mmol) was prepared in situ as before at −30 °C and dry oxygen was introduced into the solution by means of a syringe needle beneath the surface of the solution. During 0.3 h at −30 °C, a brown solid appeared. Oxygen addition was maintained for 2 h at 0 °C, and the mixture was filtered through a pad of Florisil (in air) using 50 mL of ether. Aqueous extraction procedures as before left an ether solution which was diluted to 100.0 mL with ether and treated as above, GLC yield 34%. The crude product appeared by ^{1}H NMR analysis and TLC to consist of 2-methyl-2-phenylpropionitrile and complex **7**.

Oxidation with Ferric Chloride. Exactly as before, a solution of **8b** (1.0 mmol) was prepared at −30 °C and a solution of anhydrous ferric chloride in THF (7.0 mL of a 1.0 M solution) was added via syringe. After 18 h at 25 °C, aqueous extraction led to an ether solution which was concentrated by rotary evaporation and the residue was flash distilled (0.001 Torr, 40 °C) to give a colorless distillate (117 mg, 81% yield) whose ^{1}H NMR spectrum and GLC retention time matched exactly those of pure 2-methyl-2-phenylpropionitrile.

Oxidation with Tris(*N*,*N*-dimethylformamide)dichloroferric Tetrachloroferrate (Fe–DMF).[39] As before, reaction of **8b** with Fe–DMF (4.0 mmol in 10 mL of THF) was carried out for 3 h at 25 °C. The mixture was processed as before to afford a colorless distillate of pure 2-methyl-2-phenylpropionitrile (143 mg, 99%).

Oxidation with *p*-Benzoquinone. A solution of *p*-benzoquinone (432 mg, 4.0 mmol) in 6 mL of THF was added to a THF solution of **8b** at −78 °C. The mixture turned black immediately. It was stirred for 2.5 h at 25 °C and then processed as before. Flash distillation produced 85 mg (59%) of 2-methyl-2-phenylpropionitrile. The residue was estimated to contain complex **7** corresponding to about 25% recovery, based on ^{1}H NMR integration.

Oxidation with Tris(acetylacetonato)cobalt(III). As before, a solution of **8b** was treated with tris(acetylacetonato)cobalt(III) (2.14 g, 6.0 mmol, 15 mL of THF) at −78 °C. There was no evidence of reaction. After being stirred for 3 h at 25 °C, the mixture was processed as before to afford a green, semisolid residue. Flash distillation (0.001 Torr, 25 °C) provided a pale yellow distillate (44 mg) which contained 2-methyl-2-phenylpropionitrile and olefinic products. The relative areas of ^{1}H NMR signals applied to the weight of distillate allowed the yield of 2-methyl-2-phenylpropionitrile to be determined (13%).

Oxidation with Tris(acetylacetonato)iron(III). As before, reaction with tris(acetylacetonato)iron(III) (2.83 g, 8.0 mmol, 3.0 h, 25 °C) led to a pale yellow distillate (54 mg) similar by ^{1}H NMR spectroscopy to the product from Co(III). Approximate quantitative analysis by ^{1}H NMR integration suggested a yield of 13% for 2-methyl-2-phenylpropionitrile.

Oxidation with Cupric Chloride. As before, a solution of **8b** was treated with a solution of anhydrous cupric chloride (Fisher, 1.08 g, 8.0 mmol) in 10 mL of *N*,*N*-dimethylformamide. After 3.0 h at 25 °C, the olive-green solution was processed to give a colorless distillate of pure 2-methyl-2-phenylpropionitrile (108 mg, 74%). The residue appeared to contain complex **7** (10% recovery, ^{1}H NMR signal at δ 5.45).

Oxidation with Stannic Chloride. As before, a solution of **8b** was treated with stannic chloride (468 μL, 8.0 mmol) added via syringe. After 3.0 h at 25 °C, processing as usual gave crude product which was complex **7** (>95% by ^{1}H NMR, 179 mg, 83% recovery).

Oxidation with Cerium(IV). As before, a solution of **8b** was treated with a solution of ceric ammonium nitrate (3.0 g) in 20 mL of acetonitrile. The mixture turned brown, then green during 0.5 h at −78 °C. It was allowed to warm to 25 °C over 0.5 h, then processed as before to give a colorless distillate of pure 2-methyl-2-phenylpropionitrile (102 mg, 71%).

Reaction of 8b with Methyl Iodide. To a sample of **8b** (0.22 mmol) in an NMR sample tube was added methyl iodide (0.22 mmol, 13 μL) at −78 °C. The mixture was warmed to 25 °C over 0.5 h and observed at 35 °C in the ^{1}H NMR spectrometer. The spectrum consisted of two singlets: δ 5.43 for complex **7** and δ 1.33 for 2,2-dimethylpropionitrile. The identity of the products was supported by TLC (**7**) and GLC (for 2,2-dimethylpropionitrile) elution behavior.

Reaction of 8b with Benzophenone. To a solution of **8b** (0.96 mmol) in THF (5 mL) at −78 °C was added a solution of benzophenone (1.00 mmol, 182 mg) in 2.0 mL of THF. The mixture turned orange and, after it was warmed at 0 °C for 0.5 h, crystals appeared. The solvent was removed at 0.01 Torr and the residue was chromatographed on Florisil. Elution with a mixture of hexane and dichloromethane gave complex **7** (162 mg, 0.76 mmol, 78% recovery) and 3-hydroxy-2,2-dimethyl-3,3-diphenylpropionitrile (225 mg, 0.90 mmol, 93% yield): ^{1}H NMR ($CDCl_3$) δ 7.7–7.1 (m, 10 H, aryl H), 2.5 (s, 1 H, -OH), 1.44 (s, 6 H, $-CH_3$); IR ($CHCl_3$) 4.18 μ ($C{\equiv}N$); mass spectra peak at highest mass *m/e* 234 (parent -OH); crystallization from ether, mp 161–162 °C. Reaction of 2-lithio-2-methylpropionitrile (prepared as usual from lithium diisopropylamide) with benzophenone (−78 to 25 °C) led to the same product (100% yield), which was identical in ^{1}H NMR and melting point and had an undepressed mixture melting point.

Reaction of 8b with Triphenylmethyl Fluoroborate. To a solution of **8b** (1.0 mmol) at −78 °C was added a solution of triphenylmethyl fluoroborate (Cationics, 330 mg) in 5 mL of THF. The mixture became dark red after 3 h at 25 °C It was then diluted with ether, washed with water, and dried. Concentration by rotary evaporation gave a yellow residue which was chromatographed (Florisil, hexane/dichloromethane) to provide complex **7** (210 mg, 96% recovery).

Reaction of 8b with Triethylborane. To a solution of **8b** (1.0 mmol) at −78 °C was added a solution of triethylborane (1.0 mmol) in tetrahydropyran. After being stirred at 25 °C for 1.0 h, the mixture was processed as before through column chromatography. Complex **7** was isolated (211 mg, 90% recovery).

Reaction of η^6-Benzenetricarbonylchromium (7) with *tert*-Butyllithium Followed by Reaction with Iodine and Other Electrophiles. A. With Iodine. A solution of *tert*-butyllithium (1.0 mL of a 2.1 M solution in *n*-pentane, 4.2 mmol) was mixed with THF (5 mL) at −78 °C under argon. Into the mixture was added a solution of **7** (434 mg, 2.03 mmol) in 5 mL of THF dropwise over a few minutes at −78 °C. After being stirred at −78 °C for 1.5 h, the solution was warmed at 0 °C for 1.0 h and then cooled to −78 °C again. A solution of iodine (2.0 g, 7.9 mg-atoms) in 5 mL of THF was added rapidly via syringe. After 3 h at 25 °C, the mixture was diluted with ether, washed successively with aqueous solutions of sodium bisulfite and sodium chloride, dried, and analyzed for *tert*-butylbenzene by GLC using *p*-xylene as internal standard. The yield was 185 mg (68%). In a separate experiment, the ether solution was concentrated and flash distilled (0.001 Torr, 25 °C) to yield a colorless liquid: ^{1}H NMR (CCl_4) δ 7.5–7.0 (m, 5 H, aryl H), 1.30 (s, 9 H, CH_3-), identical with that of a commercial sample.

B. With Water. The solution resulting from addition of *tert*-butyllithium to **7** was prepared as above and cooled to −78 °C. Then water (0.50 mL, 28 mmol) was added and stirring was continued for 0.5 h at −78 °C and 1.0 h at 25 °C. Removal of volatile material (0.01 Torr, 25 °C) left a greenish-yellow oil which was analyzed for **7** by ^{1}H NMR (appearance of a singlet at δ 5.3–5.5). This region of the spectrum was blank, indicating <5% recovered **7**. No attempt was made to identify the products.

C. With Methyl Iodide. To a solution of the adduct (1.0 mmol) of *tert*-butyllithium with **7**, prepared as before in THF at −78 °C, was added methyl iodide (160 mg, 1.1 mmol). The solution was allowed to warm to 25 °C in an NMR sample tube; a complex series of broadened signals was observed, but the characteristic singlet of **7** at δ 5.3–5.4 was completely absent. The mixture was cooled to −78 °C and excess iodine was added as before. After processing as above, GLC analysis indicated the presence of *tert*-butylbenzene in >50% yield.

D. With Triphenylmethyl Fluoroborate. The procedure was exactly as in B, except using excess solid triphenylmethyl fluoroborate in THF instead of water. Removal of volatile material (0.01 Torr, 25 °C) gave a dark residue; TLC and ^{1}H NMR analysis indicated the absence of **7**.

Reaction of 8b with D_2O. Adduct **8b** (1.0 mmol) was prepared as before, in situ, in THF solution at −78 °C. Deuterium oxide (0.10 mL, 5.0 mmol) was added all at once. The mixture was stirred at 0 °C for 2 h, then evaporated (25 °C, 0.01 Torr) to leave a yellow, crystalline residue. The product (complex **7**) was isolated by silica gel column chromatography (hexane/dichloromethane). Repeated scanning of the parent ion region of the mass spectrum showed average ratio of *m/e* 215/214 = 0.207 (σ = 0.012). Using a sample of pure **7**, repeated scanning of the mass spectrum showed average ratio of *m/e* 215/214 = 0.202 (σ = 0.011) (calculated for **7** with 1% excess deuterium (above natural abundance): *m/e* 215/214 = 0.212). In a separate experiment carried out under identical conditions in THF-d_8, the yellow solution after addition of D_2O at 25 °C for 1 h was examined by ^{1}H NMR. The signal attributable to $(CH_3)_2CHCN$ appeared as a singlet, δ 1.30 [$(CH_3)_2CDCN$].

Reaction of 8b with Excess Trifluoroacetic Acid. Formation and Characterization of 13a, 13b, and 13c. A solution of **8b** (2.0 mmol) in THF (20 mL) at −78 °C was prepared. Then trifluoroacetic acid (1.0 mL, 13 mmol) was added dropwise rapidly. The color changed from yellow to deep red. The mixture was warmed to 20 °C over 15 min, diluted with ether, and washed with water. Excess iodine (10 mg-atoms) was added to the ether solution, and the mixture was stirred for 3 h at 25 °C, then shaken with aqueous sodium bisulfite solution and finally with water. The ether layer was concentrated by rotary evaporation and flash distilled to give a pale yellow oil, 250 mg (90% based on $C_{10}H_{13}N$). GLC analysis (12-ft 5% DEGS on Chromosorb P, 120 °C) showed three peaks with the following retention times (rel area): A, 2.70 min (7%); B, 2.90 min (94%); C 3.4 min (3%). Preparative GLC (0.375 in. × 12 ft, FFAP on Chromosorb P, 180 °C) allowed separation of the product into three fractions. The first was a mixture of A and B, the second was pure B, and the third was pure C. Identification as outlined below gives A = **13b**, B = **13a**, and C = **13c**.

Compound **13a**: ^{1}H NMR ($CDCl_3$) δ 5.6–6.1 (m, 3 H, vinyl H), 2.23 (br s, 4 H, $C{=}CCH_2$), 1.48 (s, 6 H, $-CH_3$); IR (neat) 4.41 μ ($C{\equiv}N$); mass spectrum parent at *m/e* 147 (calcd for $C_{10}H_{13}N$, *m/e* 147). Reaction with *N*-phenyl-1,2,4-triazoline-3,5-dione (prepared from 4-phenylurazole and nitrogen dioxide)[40] in dichloromethane at 0 °C led to immediate decoloration of the dienophile. The solvent was removed by rotary evaporation and the product (**14a**) was recrystallized from ether: mp 180–181.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 5 H, C_6H_5-), 6.68 and 6.75 (main peaks of AB q, 2 H, $HC{=}CH$), 5.1 (br s, 1 H, bridgehead), 1.5–2.5 (m, 4 H, $-CH_2CH_2-$), 1.84 (s, 3 H, $-CH_3$), 1.70 (s, 3 H, CH_3). Anal. Found for $C_{18}H_{18}N_4O_2$: C, 67.11; H, 5.61; N, 17.38.

Compound **13c**: ^{1}H NMR ($CDCl_3$) δ 5.7–6.2 (m, 4 H, vinyl H), 2.2–2.3 (br s, 3 H, $C{=}CCH_2$), 1.33 (s, 6 H, $-CH_3$); IR (neat) 4.41 μ ($C{\equiv}N$); mass spectrum parent at *m/e* 147 (calcd for $C_{10}H_{13}N$, *m/e* 147). Adduct **14c** with *N*-phenyl-1,2,4-triazoline-3,5-dione had mp 215–218 °C (ether); ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5 H, aryl H), 6.5 (m, 2 H, $HC{=}CH$), 5.0 (br s, 2 H, bridgehead), 1.7–2.8 (m, 3 H, $-CHCH_2-$), 1.45 (s, 3 H, $-CH_3$), 1.35 (s, 3H, $-CH_3$); mass spectral mol wt 322.1441 (calcd for $C_{18}H_{18}N_4O_2$, 322.1430).

Compound 13b. This compound could not be separated from the mixture with **13a**. However, the mixture reacted with *N*-phenyl-1,2,4-triazoline-3,5-dione to give two adducts (**14a** and **14b**) which were separated by preparative TLC. Adduct **14c** showed mp 199–201 °C; ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5 H, aryl H), 6.5 (m, 1 H, vinyl H), 5.0 (br s, 2 H, bridgehead), 1.5–2.5 (m, 4 H, $-CH_2CH_2-$); mass spectral mol wt 322.1436 (calcd for $C_{18}H_{18}N_4O_2$, 322.1430).

Reaction of 13a, 13b, and 13c with DDQ. To a mixture of **13a**, **13b**, and **13c** (flash distillate from reaction immediately above, 50 mg, 0.34 mmol) in 10 mL of benzene was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (200 mg, 0.84 mmol). The solution was heated at reflux for 1.0 h, cooled, and added to 25 mL of 15% aqueous sodium hydroxide solution. The layers were separated and the organic layer was washed successively with 5% aqueous sodium hydroxide, water, and saturated salt solution. After the organic solution was dried, the volatile material was removed by rotary evaporation and the residue was flash distilled to give a colorless liquid (43 mg, 86%) with GLC and ^{1}H NMR spectral properties identical with those of 2-methyl-2-phenylpropionitrile.

Detection of Exchange of 2-Lithio-2-methylpropionitrile from η^6-Toluene- to η^6-Benzenetricarbonylchromium. A solution of 2-lithio-2-methylpropionitrile (2.0 mmol) was prepared as usual in THF at −78 °C. A solution of η^6-toluenetricarbonylchromium (456 mg, 2.00 mmol) in 3.5 mL of THF was added, and the mixture was stirred at 0 °C for 10 min. After the mixture was cooled to −78 °C, a solution of complex **7** (428 mg, 2.00 mmol) in 3.0 mL of THF was added rapidly dropwise. The resulting yellow solution was warmed to 0 °C for 15 min and cooled to −78 °C, and then a solution of iodine (4.38 g, 17.3 mg-atoms) in 5 mL of THF was added rapidly dropwise. The mixture was allowed to stir at 25 °C for 3.75 h and then processed through aqueous extraction, flash distillation, and quantitative GLC analysis (0.125 in. × 6 ft, 5% of 1:1 DEGS:Bentone 34 at 120 °C) with *p*-methylacetophenone as internal standard. The order of elution of products is *p*-methylacetophenone, 2-methyl-2-phenylpropionitrile, 2-methyl-2-(*o*-tolyl)propionitrile, 2-methyl-2-(*m*-tolyl)propionitrile, and 2-methyl-2-(*p*-tolyl)propionitrile. The products were identified by comparison of GLC retention times with samples prepared by an independent route (see below). The yields of the products follow: 2-methyl-2-(*m*-tolyl)propionitrile, 17%; 2-methyl-2-phenylpropionitrile, 69%.

Attempted Exchange of 2-Lithio-1,3-dithiane from η^6-Toluene- to η^6-Benzenetricarbonylchromium. To a solution of 2-lithio-1,3-dithiane (2.0 mmol) in 7 mL of THF, prepared as before, at −78 °C was added a solution of η^6-toluenetricarbonylchromium (502 mg, 2.20 mmol) in 3 mL of THF rapidly dropwise. After the mixture was warmed at 0 °C for 15 min, it was cooled to −78 °C, and a solution of complex **7** (428 mg, 2.00 mmol) in 3 mL of THF was added. After the mixture was warmed at 0 °C for 15 min, it was cooled to −78 °C and a solution of iodine (4.0 g, 16 mg-atoms) in 5 mL of THF was added rapidly dropwise. The solution was stirred at 25 °C for 3 h, then processed as usual. The crude product was analyzed by quantitative GLC (0.125 in. × 12 ft, 5% DEGS at 120 °C) with the order of elution being 2-phenyl-1,3-dithiane, 2-(*o*-tolyl)-1,3-dithiane, 2-(*m*-tolyl)-1,3-dithiane, and 2-(*p*-tolyl)-1,3-dithiane. These products were identified by comparison with samples prepared according to procedures below. The yields are recorded in eq 4 (Results). This experiment was repeated with longer time and higher temperature allowed for exchange (see eq 4).

Exchange of η^6-Benzenetricarbonylchromium (7) between Carbanions. General Procedure. In a 25-mL two-neck round-bottom flask was generated 2.5 mmol of the first carbanion (see Table IV, Results), either *tert*-butyl 2-lithiopropionate,[41] 2-lithio-1,3-dithiane (as before), or 2-lithio-2-methylpropionitrile (as before), in 5.0 mL of THF at −78 °C. Then complex **7** (2.5 mmol) was added as a solid and the mixture was warmed to 0 °C for 15 min. With *tert*-butyl 2-lithiopropionate, 5.0 mL of HMPA was also added. Then a solution of the second anion (2.5 mmol, either 2-lithio-2-methylpropionitrile or 2-lithio-1,3-dithiane) in 5 mL of THF was added rapidly via syringe. After a period at 0 or 24 °C, the mixture was cooled to −78 °C and a solution of iodine (2.5 g, 25 mg-atoms) in 10 mL of THF was added rapidly. The mixture was brought to 25 °C and stirred until evolution of gas ceased. After the usual aqueous extraction procedures, the crude organic product was analyzed by quantitative GLC for *tert*-butyl 2-phenylpropionate, 2-methyl-2-phenylpropionitrile, and 2-phenyl-1,3-dithiane, with an internal standard (2-methylnaphthalene). The reaction conditions and results are presented in Table IV.

Preparation of Standard Comparison Compounds. General Procedures. A. Products from 2-Lithio-2-methylpropionitrile. The products from arylation of 2-lithio-2-methylpropionitrile were prepared by dimethylation of the corresponding arylacetonitrile (commercially available). A 50-mL three-necked round-bottom flask fitted with a serum stopper, a glass stopper, a gas adapter attached to a vacuum/argon manifold, and a magnetic stirring bar was placed under argon. THF (15 mL) and diisopropylamine (2.20 g, 3.10 mL, 22 mmol) were added via syringe. The solution was cooled to 0 °C for 5 min, and *n*-butyllithium (6.18 mL of 3.4 M solution in *n*-hexane, 21 mmol) was added via syringe at the rate of 1 drop/s. The solution was stirred for 15 min at 0 °C, then cooled to −78 °C. After 5 min, the arylacetonitrile (phenyl-, *o*-tolyl-, *m*-tolyl-, or *p*-tolyl-, Aldrich Chemical Co., 10 mmol) was added (1 drop/s via syringe), and the solution was stirred at −78 °C for 5 min. Then HMPA (3.83 mL, 3.94 g, 22 mmol) was added rapidly via syringe, and the mixture was stirred until homogeneous. Methyl iodide (1.37 mL, 3.194 g, 22 mmol) was added rapidly via syringe, and the solution was allowed to warm to 24 °C for 0.5 h, then diluted with ether (30 mL). The organic layer was washed successively with 30-mL portions of 1 M aqueous hydrochloric acid, 10% aqueous sodium bisulfite, water, and saturated aqueous sodium chloride solution. The organic layer was dried and concentrated by rotary evaporation to produce 1.2–1.3 g of a colorless oil. Short-path distillation (35 °C, 0.001 Torr) afforded the pure product (GLC analysis).

2-Methyl-2-(*o*-tolyl)propionitrile: ^{1}H NMR (CCl_4) δ 1.70 (s, 6 H), 2.60 (s, 3 H), 7.15 (br s, 4 H); IR (neat) 4.45 μ (m, C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 144 (100), 159 (37), 161 (0.2). Anal. Found for $C_{11}H_{13}N$: C, 82.83; H, 8.16; N, 8.79. Yield: 1.300 g (82%).

2-Methyl-2-(*m*-tolyl)propionitrile: ^{1}H NMR (CCl_4) δ 1.66 (s, 6 H), 2.35 (s, 3 H), 6.7–7.3 (br m, 4 H); IR (neat) 4.48 μ (m, C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 144 (100), 159 (37), 160 (5.6). Anal. Found for $C_{11}H_{13}N$: C, 82.85; H, 8.23; N, 8.94. Yield: 1.38 g (87%).

2-Methyl-2-(*p*-tolyl)propionitrile: ^{1}H NMR (CCl_4) δ 1.73 (s, 6 H), 2.30 (s, 3 H), 7.23 (dd, 4 H); IR (neat) 4.45 μ (m, C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 144 (100), 159 (27), 160 (3.3). Anal. Found for $C_{11}H_{13}N$: C, 83.04; H, 8.14; N, 9.02.

2-Methyl-2-phenylpropionitrile: ^{1}H NMR (CCl_4) δ 1.73 (s, 6 H), 7.23 (br s, 5 H); IR (neat) 4.45 μ (m, C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 130 (100), 145 (26), 146 (3).

B. Products from 2-Lithio-1,3-dithiane. The products from arylation of 2-lithio-1,3-dithiane were prepared from the corresponding aldehyde and 1,3-propanedithiol using chloroform and boron trifluoride etherate as the medium.

2-(*o*-Tolyl)-1,3-dithiane: ^{1}H NMR (CCl_4) δ 1.7–2.27 (br m, 2 H), 2.42 (s, 3 H), 2.76–3.09 (br m, 4 H), 5.22 (s, 1 H), and 6.97–7.70 (br m, 4 H); IR (CS_2) 3.42 (m), 7.07 (m), 7.84 (s), 8.45 (m), 10.93 (m), 11.31 (m), 13.40 (s) μ; mass spectrum (70 eV) *m/e* (rel abundance) 31 (100), 135 (50), 136 (63), 145 (19), 210 (50), 211 (7), 212 (6), 213 (1). Anal. Found for $C_{11}H_{14}S_2$: C, 62.71; H, 6.76; S, 30.26. Yield 46%; mp 92–93 °C (methyl alcohol).

2-(*m*-Tolyl)-1,3-dithiane: ^{1}H NMR (CCl_4) δ 1.74–2.22 (br m, 2 H), 2.35 (s, 3 H), 2.73–3.09 (br m, 4 H), 5.00 (s, 1 H), 6.95–7.31 (br m, 4 H); IR (CS_2) 3.36 (m), 6.18 (w), 7.03 (m), 7.81 (m), 8.49 (m), 9.09 (w), 10.86 (m), 11.42 (w), 13.30 (s), 14.31 (m) μ; mass spectrum (70 eV) *m/e* (rel abundance) 91 (11), 135 (100), 136 (32), 137 (10), 210 (65), 211 (11), 212 (7). Anal. Found for $C_{11}H_{14}S_2$: C, 62.71; H, 6.72; S, 30.22. Yield 49%; mp 66.5–67.0 °C (methyl alcohol).

2-(*p*-Tolyl)-1,3-dithiane: ^{1}H NMR (CCl_4) δ 1.66–2.16 (br m, 2 H), 2.32 (s, 3 H), 2.71–3.08 (br m, 4 H), 5.01 (s, 1 H), 7.17 (dd, 4 H); IR (CS_2) 3.49 (m), 7.19 (m), 7.93 (s), 8.59 (m), 9.07 (w), 10.98 (m), 11.35 (m), 11.85 (w), 12.32 (m), 13.20 (s) μ; mass spectrum (70 eV) *m/e* (rel abundance) 91 (17), 135 (56), 136 (85), 137 (17), 145 (24), 210 (100), 211 (14), 212 (10), 213 (1). Anal. Found for $C_{11}H_{14}S_2$, C, 62.84; H, 6.65; S, 30.67. Yield 41%; mp 91.5–92.5 °C (methyl alcohol).

X-ray Crystallographic Study of Complex 8c. Pale yellow crystals of **8c** were grown from dioxane at 50 °C. A crystal was carefully sealed in a Lindemann capillary in an argon atmosphere to avoid decomposition. Preliminary Weissenberg and precession photographs indicated that the crystals were triclinic. An approximately equidimensional crystal, 0.15 mm on an edge, was used to determine accurate cell constants and record intensity data. The cell constants, determined by a least-squares fit of 15 2θ values, were $a = 10.866$ (5) Å, $b = 14.595$ (5) Å, $c = 19.684$ (9) Å, $\alpha = 93.73$ (3)°, $\beta = 104.58$ (3)°, and $\gamma = 106.41$ (4)°. The instability of the compound prevented a density measurement but a physically reasonable value was calculated assuming four units of composition $C_{13}H_{13}O_3S_2Cr{\cdot}Li(C_4H_8O_2)_3$. Cell constants and intensity data were obtained at ~ -120 °C. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using graphite monochromatic Cu Kα (1.541 78 Å) X-rays and a variable speed ω-scan technique. Of the 7781 reflections surveyed in this manner, 4797 (62%) were judged observed $(I \geq 2\,\sigma(I)]$ after correction for Lorentz, polarization, and background effects. The structure was solved by the usual heavy-atom procedure, deconvolution of the Patterson to reveal the Cr positions and location of the nonhydrogen atoms in a subsequent electron density synthesis. The space group was assumed to be $P\bar{1}$ with two independent molecules in the asymmetric unit. One of the six dioxane molecules was disordered and only four atoms were eventually located. These four atoms were refined isotropically as carbon atoms. All of the remaining nonhydrogen atoms were refined anisotropically. All hydrogen atoms, except those bonded to the disordered dioxane, were included at calculated positions but not refined. Hydrogens were assigned the final isotropic temperature factors of the nonhydrogen atom to which they were bonded. Full-matrix least-squares refinements have converged to a conventional crystallographic residual of 0.093. The supplementary material available for this paper contains tables of fractional coordinates and thermal parameters, bond distances, bond angles, and observed and calculated structure factors.[42]

Acknowledgments. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for financial support of this work. Important contributions in early experiments relating to the work described here were carried out by Christine Carter and Joel Belasco, and later by Ed Arnold, to whom we are indebted.

Supplementary Material Available: A list of (1) fractional and temperature factors, (2) bond distances, (3) bond angles, and (4) observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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