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Diastereotopic group selective reactions at .pi.-arene chromium derivatives: deprotonation and nucleophilic addition reactions of substrates bearing benzylic chiral centers

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compound were chosen from samples recrystallized from the solvents indicated in the preparations. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction with the program TRACER revealed primative crystal systems. Data were collected on the crystal in accord with the parameters in Table X. The space group was uniquely assigned on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the rhodium atom. The Molecular Structure Corp. TEXSAN programs were used for solution and refinement of the structure.[27] Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms, with positional and thermal parameters of the hydrogens "riding" with the atom to which they were attached.

Acknowledgment is made to the the U.S. Department of Energy (DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Alfred P. Sloan and Camille and Henry Dreyfus Foundations for Awards.

Supplementary Material Available: Listings of anisotropic thermal parameters and bond distances and angles for $RhCl(CNCH_2CMe_3)(P\text{-}i\text{-}Pr_3)_2$, $RhCl(CN\text{-}2,6\text{-xylyl})(P\text{-}i\text{-}Pr_3)_2$, and $[Rh(CNCH_2CMe_3)_2(P\text{-}i\text{-}Pr_3)_2]Cl$ (30 pages); listings of calculated and observed structure factors for these compounds (51 pages). Ordering information is given on any current masthead page.

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(27) $R_1 = \{\sum||F_o| - |F_c||/\}\sum|F_o|\}$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum wF_o^2\}$, where $w = \{\sigma^2(F_o) + [\rho F_o^2]^2\}^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B and 2.3.1.

Diastereotopic Group-Selective Reactions at π-Arene Chromium Derivatives: Deprotonation and Nucleophilic Addition Reactions of Substrates Bearing Benzylic Chiral Centers

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$(\eta^6\text{-}(MeHXC)C_6H_5)Cr(CO)_3$ ($X = NMe_2$ or OR) substrates undergo deprotonation by alkyllithium bases to produce, after quenching with electrophiles (E^+), high diastereomeric excesses (de) of $(\eta^6\text{-}o\text{-}E\text{-}(MeHXC)C_6H_4)Cr(CO)_3$ products. The *N*,*N*-dimethylamino substrate shows excellent chemoselectivity for ortho metalation, in addition to having ≥96% de in the formation of the product isomers. The propensity for ether derivatives to undergo benzylic deprotonation interferes with chemoselectivity in these substrates, although the selectivity for ortho substitution can be improved by employing chelating ether substituents and reduced reaction temperatures. The stereochemistry of deprotonation is evidently controlled by the tendency of the heteroatom side chain to adopt a conformation that minimizes steric interactions with the $Cr(CO)_3$ moiety and promotes the delivery of the ligated base to a specific ortho hydrogen. NOEDS studies indicate that the conformation of the benzylic side chain in the solutions containing only $(\eta^6\text{-}(MeHXC)C_6H_5)Cr(CO)_3$ probably closely mirrors those involved in the delivery of the alkyllithium reagent. Reactions between $(\eta^6\text{-}(MeH(RO)C)C_6H_5)Cr(CO)_3$ and *tert*-butyllithium in diethyl ether produced significant quantities of $(\eta^4,\eta^2\text{-}2\text{-}tert\text{-butylcyclohexadienylidene-}exo\text{-ethane})Cr(CO)_3$ after the mixture is quenched with a proton donor. The reaction displayed a peculiar temperature dependence, with an approximate 1:1 ratio of the S^*,S^*,R^* and S^*,S^*,S^* diastereomers being produced if the quench is performed below -40 °C and a 10:1 ratio of the S^*,S^*,R^* and S^*,S^*,S^* isomers, respectively, being produced by quenching the reaction at an ambient temperature. An X-ray crystallographic study unambiguously identified the molecule formed in predominance at elevated temperatures as the S^*,S^*,R^* *exo*-ethane *Z* isomer. Crystal data for $(\eta^6\text{-}(R^*,R^*)\text{-}o\text{-}(Ph_2P)(MeH(Me_2N)C)C_6H_4)Cr(CO)_3$ at 20 °C: $a = 14.056$ (4) Å, $b = 9.730$ (3) Å, $c = 17.736$ (5) Å, $\alpha = 105.78$ (2)°, $Z = 4$, $D_{calc} = 1.30$, space group $P2_1/c$ and $R(F) = 0.044$, $R_w(F) = 0.051$ for 1434 reflections. Crystal data for $(\eta^4,\eta^2\text{-}S^*,S^*,R^*\text{-}2\text{-}tert\text{-butylcyclohexadienylidene-}exo\text{-ethane})Cr(CO)_3$ at 23 °C: $a = 13.457$ (4) Å, $b = 8.505$ (2) Å, $c = 14.350$ (2) Å, $\alpha = 112.92$ (2)°, $Z = 4$, $D_{calc} = 1.31$, space group $P2_1/c$ and $R(F) = 0.038$, $R_w(F) = 0.050$ for 1496 reflections.

Introduction

It is a matter of consensus that organometallic complexes play a major role in the development of new methodology in organic synthesis.[4] π-Arene chromium complexes have been particularly prominent in such endeavors, primarily due to the wide variety of useful organic molecules that can be obtained easily from modification

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(1) Department of Chemistry.

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(3) X-ray Crystallographic Facility, Department of Chemistry.

(4) A variety of texts and monographs chronicle interest in these areas. For examples, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Synthesis*; Pergamon Press: Oxford, 1982.

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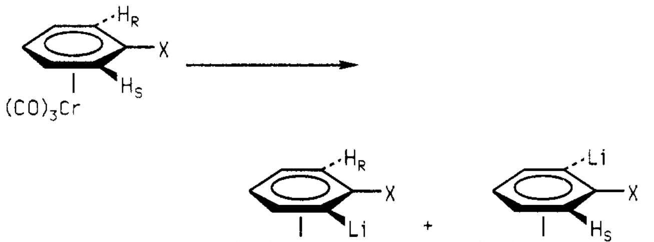
Scheme I



of the complexed substrate and subsequent removal of the chromium moiety.[5] For example, formation of benzylic cations or anions are each rendered more facile relative to those in uncomplexed arenes,[6] as is the ability to engender ortho deprotonation/alkylation or ring addition processes.[7] A number of important groups of natural products and substrate types have been obtained through this chemistry, including highly functionalized cyclohexenone, tetralones, and spirocyclic terpenes.[8]

The chromium tricarbonyl moiety can also function as a useful stereochemical template.[9] This results from the restriction of the approach of nucleophilic or electrophilic reagents to pendant functional groups such that predominantly or exclusively anti attack (relative to the chromium tricarbonyl moiety) is observed. The level of stereoselectivity in substrate arene complexes containing acyclic side chains is, of course, dependent on the relative populations and reactivities of the side-chain rotamers. An ortho substituent often suffices to restrict the rotamer populations so that only one prochiral face of a proximal functional group, such as a ketone, undergoes attack by external reagents.[10]

It is desirable to take advantage of such diastereoselectivity in the context of the synthesis of chiral, nonracemic compounds. However, this requires the preparation of the original π-arene complex in optically pure form, a challenge that has been only incompletely met.[9b] Traditionally, optically active π-arene complexes have been obtained through resolution procedures.[9b,11,12] More recently, Uemura and co-workers have investigated syntheses of such compounds via stereospecific complexation chemistry.[13]

In addition to the development of new methods of asymmetric synthesis, the investigation of the regio- and stereochemical details of lithiation reactions are of fundamental interest to organic and organometallic chemists.[14] For example, the products of ortho-lithiation reactions belong to the general class of dipole-stabilized anions, i.e., anions that are stabilized by coordination of the lithium counterion to proximal Lewis base sites in the substrate.[14a,b] Such anions have become increasingly useful in asymmetric synthesis, as exemplified by the outstanding work of Meyers and others in the utilization of chiral formamidine-stabilized species for the asymmetric synthesis of a number of important alkaloid systems.[15] Of special relevance to the present paper are reactions featuring transfer of asymmetry from an arene-substituted chiral auxiliary to an axially dissymmetric core during the preparation of a number of systems bearing chiral diaryl linkages.[15b]

This strategy is applicable to the problem of chiral π-arene synthesis. To wit, in a monosubstituted η^6-arene chromium complex (Scheme I), it is apparent that the ortho protons H_S and H_R are diastereotopic if the side chain X is chiral. If means could be found to stereoselectively lithiate one of these positions, a potentially general route to a wide variety of ortho-substituted π-arene chromium complexes would be realized. Furthermore, it was felt that the most efficient means of carrying out such a reaction would be via an anion that could enjoy dipole stabilization by a heteroatom-bearing side chain. In this scenario, following an initial precomplexation step, the organolithium base could be regiospecifically delivered in an intramolecular fashion.

Such reactions had been previously reported in ferrocene complexes bearring an 1-(dimethylamino)ethyl side chain, notably by Ugi and co-workers.[16] We felt that the ap-

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plication of this chemistry to chromium/arene substrates would be significant for several reasons. First, π-arene chromium complexes have found wider use in organic synthesis than ferrocenes.[5-8] Second, with respect to the potential use of derivatives of either complex as ligands for potential asymmetric catalysts, it is of practical import that the starting material for the chromium analogue is a common and commercially available chiral amine, which is not the case for the ferrocene derivative. Finally, we hoped to gain some insight into the features that contribute to the stereoselectivity of such reactions.

During the course of our work,[17] a publication detailing the same approach to this important problem emanated from the laboratory of Davies,[18] and the reader is encouraged to also consult this prior publication. In this full account of our own efforts, we disclose (1) the highly stereospecific deprotonation and alkylation chemistry of a series of chiral π-arene chromium complexes, (2) isolation and characterization of the ortho-deuterated complexes, (3) NMR spectroscopic investigations of the starting complexes and their deuterio derivatives that may bear on the source of the observed stereoselectivities, (4) an X-ray crystallographic analysis of the one of the key adducts obtained using this procedure, (5) the synthesis of the alternative diastereomeric complex via a diastereoselective complexation reaction, and (6) preliminary results from our investigations of the effect of side-chain chirality on the addition reactions of *tert*-butyllithium to phenethyl alcohol derived complexes, leading to chiral chromium-complexed cyclohexadienyl units bearing an exocyclic olefin moiety.

Results and Discussion

Ortho Metalation of *N*,*N*-Dimethyl-α-phenylethylamine Complexes. For our initial studies, we chose to study the π-arene complex 1 derived from racemic *N*,*N*-dimethyl-α-phenylethylamine, readily prepared in 30% yield (Scheme II).[19] Upon treatment of the complex with *tert*-butyllithium in anhydrous diethyl ether at −40 °C, a yellow-brown precipitate formed, which was presumed to be the ortho-lithiated species. Dissolution of this slurry by the addition of anhydrous tetrahydrofuran (THF) resulted in a homogeneous solution, which was reacted with 1.1 equiv of methanol-d_1. Removal of solvent, extraction of the residue with benzene, and recrystallization from hexane afforded a 64% yield of an isomerically enriched sample of (η^6-((Me$_2$N)CHMe)DC$_6$H$_4$)Cr(CO)$_3$ (Scheme II).

We turned to a series of nuclear magnetic resonance studies to assess the diastereomeric purity and relative configuration of the deuterated species and, by inference, the lithiated intermediates. Removal of one of the ortho protons of the starting complex affords the R^*,S^* complex **2a**, whereas the removal of the other ortho proton affords the complementary R^*,R^* isomer **2b**. The two protons in the starting complex appear as clean doublets at 4.60 and 4.83 ppm, respectively, in the 300-MHz ^{1}H NMR spectrum. Upon deuteration, the downfield signal largely disappears, whereas the integration of the upfield doublet remains nearly intact (Figure 1). It was a priori unclear whether the small doublet remaining at 4.83 ppm was due to the other stereochemical isomer or undeprotonated starting material. Thus, the diastereomeric purity of the deprotonation reaction was assayed by the examination of the ^{2}H NMR spectrum, which is shown in Figure 1c. The major deuterium signal appeared at 4.83 ppm, corresponding to the downfield ortho proton in the starting material, whereas a small signal corresponding to the minor isomer appeared at 4.60 ppm, as expected. Integration of the deuterium spectrum results in a ratio of 98:2. Thus, the deprotonation reaction occurred with very high diastereoselectivity (≥95:5).

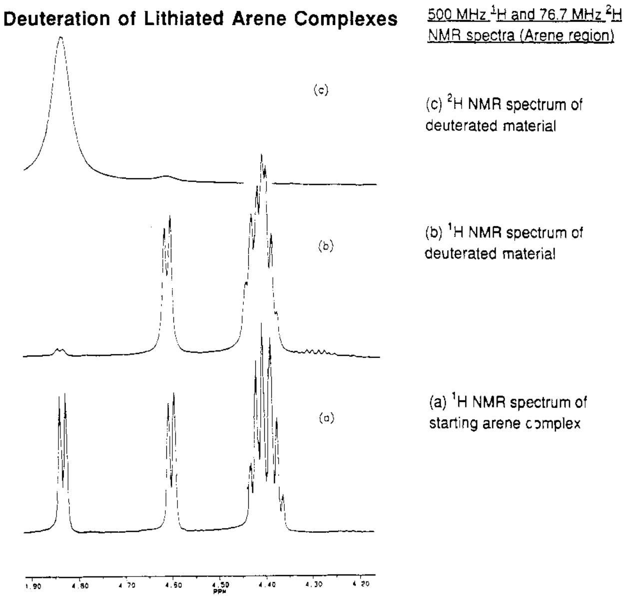

Figure 1. The 500-MHz ^{1}H and 76.7-MHz ^{2}H NMR spectra of (η^6-o-(R^*,S^*)-{(Me$_2$N)CHMe}DC$_6$H$_4$)Cr(CO)$_3$ (**2a**) showing (a) the ^{1}H NMR spectrum of the precursor amine complex (1), (b) the ^{1}H NMR spectrum of **2a**, and (c) the ^{2}H NMR spectrum of **2a**.

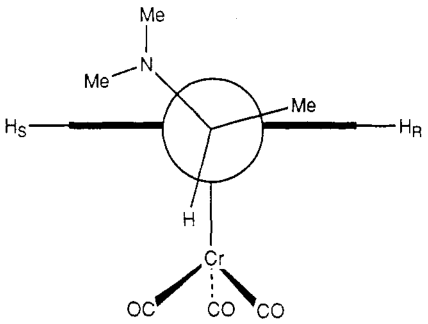

Figure 2. Hypothetical average solution-state conformation of the benzylic side chain in 1 as inferred from NOEDS.

Several nuclear Overhauser enhancement difference spectroscopy (NOEDS) studies (500 MHz) were also carried out on 1. Irradiation of the doublet at 0.74 ppm corresponding to the benzylic methyl substituent results in the exclusive enhancement of the upfield ortho proton, i.e., that which is *not* removed by the organolithium base. Irradiation of the methyl singlet resulting from the benzylic dimethylamino substituent results in enhancement of both ortho protons, with the downfield proton being more highly enhanced.

The NMR results are consistent with an average solution-state conformation such as that depicted in Figure 2. If the benzylic hydrogen atom preferentially occupies a site adjacent to the bulky chromium tricarbonyl moiety, as has been observed in similar systems, the enhancement of both ortho protons (albeit to differing extents) by irradiation of the dimethylamino protons suggest that this group can obtain a reasonably close approach to both sides of the

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[17] Preliminary communication: Heppert, J. A.; Thomas-Miller, M. E.; Milligan, M. L.; Takusagawa, F.; Aubé, J. *Organometallics* **1988**, *7*, 2581.

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[19] Davies and co-workers reported[18] a 50% yield for this reaction. Recent results obtained by drying the *N*,*N*-dimethyl-α-phenethylamine reactant over 150 mesh activated neutral alumina led to an increase in the yields of 31–67%.

Scheme II

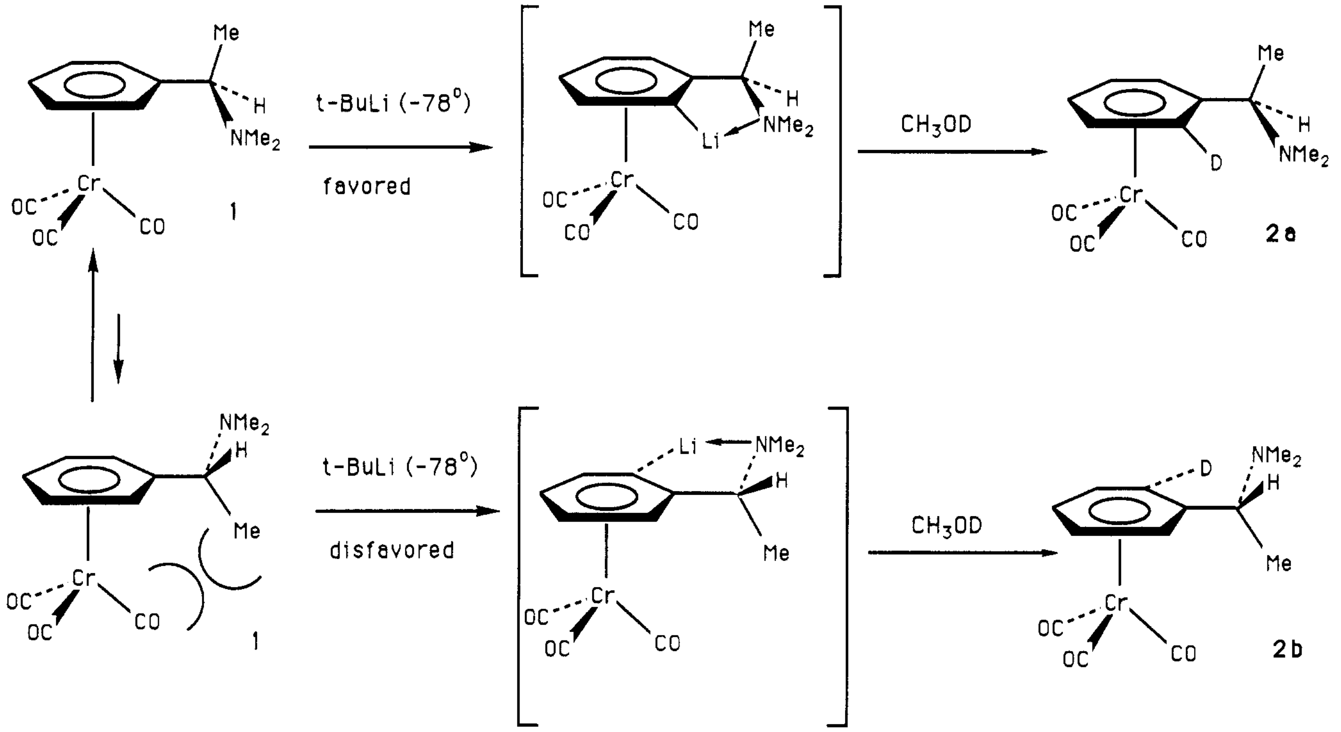

Table I. Summary of Products from the Lithiation of $(\eta\text{-}\{(Me_2N)CHMe\}C_6H_5)Cr(CO)_3$ (1)

entry	electrophile (compd no.)	proposed stereochemistry[a]	% yield[b]	% de[c]
1	D (**2a**)	*R**,*S**	64	96
2	Me (**3a**)	*R**,*S**	43	98
3	Me_3Si (**4a**)	*R**,*R**	73	98
4	Ph_2P (**5a**)	*R**,*R**	55	98
5	PhS (**6a**)	*R**,*R**	79	98

[a] Changes in configuration are due solely to changes in substituent priority designations. [b] Isolated yield of crystalline products. [c] Corresponds to observable de as determined by ^2H NMR (entry 1) or ^1H NMR spectroscopic examination of the crude reaction mixtures. A value of ≥98% de indicates that only a single diastereomer was detected.

Table II. Crystallographic Coordinates and *B*(eq) Values for $(\eta^6\text{-}[R^*,R^*]\text{-}o\text{-}(Ph_2P)\{(Me_2N)CHMe\}C_6H_4)Cr(CO)_3$ (5a)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Cr	0.57007 (9)	0.1352 (1)	0.34963 (7)	3.63 (5)
P	0.8222 (1)	0.0699 (2)	0.4821 (1)	3.44 (9)
O1	0.6727 (5)	-0.0070 (8)	0.2446 (4)	8.4 (4)
O2	0.3940 (5)	0.1834 (6)	0.2136 (4)	7.5 (3)
O3	0.4732 (5)	-0.1266 (7)	0.3750 (3)	6.5 (3)
N	0.8754 (5)	0.3181 (6)	0.4158 (3)	4.1 (3)
C1	0.7022 (5)	0.2702 (7)	0.3847 (4)	3.1 (3)
C2	0.6179 (6)	0.3507 (8)	0.3600 (4)	4.0 (3)
C3	0.5379 (6)	0.3366 (9)	0.3928 (5)	4.6 (4)
C4	0.5429 (5)	0.241 (1)	0.4522 (4)	4.4 (4)
C5	0.6273 (5)	0.1582 (8)	0.4767 (4)	3.7 (3)
C6	0.7086 (5)	0.1728 (8)	0.4453 (4)	3.2 (3)
C7	0.7899 (5)	0.2833 (8)	0.3502 (4)	3.7 (4)
C8	0.7730 (6)	0.382 (1)	0.2804 (5)	5.8 (4)
C9	0.8745 (6)	0.454 (1)	0.4494 (5)	6.0 (5)
C10	0.9709 (6)	0.288 (1)	0.4013 (5)	5.7 (4)
C11	0.6303 (7)	0.047 (1)	0.2851 (5)	5.4 (5)
C12	0.4639 (7)	0.1647 (8)	0.2655 (5)	5.1 (4)
C13	0.5120 (6)	-0.027 (1)	0.3655 (5)	4.6 (4)
C14	0.8857 (5)	0.1661 (8)	0.5704 (4)	3.6 (4)
C15	0.9845 (6)	0.135 (1)	0.6028 (5)	5.5 (4)
C16	1.0389 (7)	0.207 (1)	0.6675 (6)	7.0 (5)
C17	0.9973 (9)	0.308 (1)	0.7006 (5)	6.6 (6)
C18	0.8993 (7)	0.339 (1)	0.6690 (5)	6.1 (5)
C19	0.8439 (6)	0.267 (1)	0.6043 (5)	5.2 (4)
C20	0.7745 (5)	-0.0803 (8)	0.5237 (4)	3.7 (4)
C21	0.7811 (6)	-0.1016 (9)	0.6006 (5)	4.6 (4)
C22	0.7503 (7)	-0.222 (1)	0.6274 (5)	5.6 (5)
C23	0.7118 (6)	-0.325 (1)	0.5756 (6)	5.3 (5)
C24	0.7022 (7)	-0.306 (1)	0.4975 (6)	5.5 (5)
C25	0.7356 (6)	-0.186 (1)	0.4727 (5)	4.8 (4)

arene moiety. A plausible conformation consistent with this notion places the dimethylamino group at approximately a 60° angle with respect to the arene plane. This requires that the benzylic methyl group be nearly coplanar with the arene, despite the possibility for nonbonded interactions with the ortho substituent on the aromatic ring.[20] This latter feature is also borne out by the NOEDS studies, since only one proton is substantially enhanced by irradiation of the benzylic methyl doublet.

It was expected on the basis of previously enunciated principles[14a,b,16] that the benzylic dimethylamino group would deliver a precomplexed organolithium base to a proximal ortho proton. Thus, if a conformation similar to that shown in Figure 2 is operative in the transition state, deprotonation should occur selectively at H_S. Alternatively, removal of the proton adjacent to the benzylic methyl group in Figure 2 (i.e., H_R) would engender an unfavorable steric interaction between the benzylic methyl substituent and the chromium tricarbonyl moiety.

The ortho-lithiated intermediate was functionalized by several additional electrophiles, as summarized in Table I. In each case, only a single diastereoisomer could be detected in the 300-MHz ^1H NMR spectrum of crude product mixtures, and the diastereomeric ratios of the isomers formed are presumed to closely parallel the selectivity of the deprotonation step as probed by the deuteration studies above (i.e., ca. 96% diastereomeric excess (de)). An X-ray crystallographic study was carried out on compound **5a** to unambiguously confirm the stereochemical assignment.

Crystal Structure of $(\eta^6\text{-}[R^*,R^*]\text{-}o\text{-}(Ph_2P)\{(Me_2N)CHMe\}C_6H_4)Cr(CO)_3$ (5a). A ball-and-stick

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(20) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

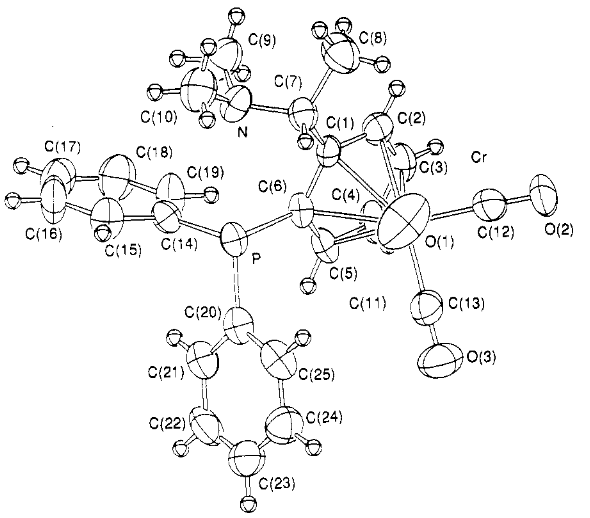

Figure 3. ORTEP-like representation of the molecular structure of (η^6-*o*-(R^*,R^*)-(Ph_2P){(Me_2N)CHMe}C_6H_4)Cr(CO)$_3$ (**5a**) showing 50% thermal ellipsoids. The numbering of atoms is arbitrary.

Table III. Selected Bond Distances and Angles for (η^6-[R^*,R^*]-*o*-(Ph_2P){(Me_2N)CHMe}C_6H_4)Cr(CO)$_3$ (5a)

atom	atom	dist, Å	atom	atom	atom	angle, deg
C	C(CO)	1.82 (1)	C(11)	Cr	C(12)	88.6 (4)
Cr	C(5)	2.189 (6)	C(11)	Cr	C(13)	89.7 (4)
Cr	C(2)	2.195 (8)	C(12)	Cr	C(13)	87.8 (3)
Cr	C(3)	2.195 (8)	C(13)	Cr	C(5)	89.1 (3)
Cr	C(4)	2.209 (7)	C(13)	Cr	C(4)	95.2 (3)
Cr	C(1)	2.221 (7)	C(13)	Cr	C(6)	100.9 (3)
Cr	C(6)	2.237 (7)	C(14)	P	C(20)	102.0 (3)
P	C(14)	1.835 (8)	C(14)	P	C(6)	101.5 (3)
P	C(20)	1.844 (8)	C(20)	P	C(6)	101.4 (3)
P	C(6)	1.847 (7)	C(9)	N	C(10)	111.4 (7)
C	O(CO)	1.16 (1) av	C(9)	N	C(7)	116.0 (6)
N	C	1.46 (1) av	C(10)	N	C(7)	114.1 (6)
C	C(Ar)	1.40 (1) av				

representation of the structure of **5a** is shown in Figure 3, and lists of the crystallographic coordinates and selected bond distances and angles are collected in Tables II and III. In accord with the structure of (η^6-[R^*,S^*)-*o*-Me-{(Me_2N)MeHC}C_6H_4)Cr(CO)$_3$ (**3a**) previously published by Davies,[18] this structure confirms the relative stereochemistry of deprotonation inferred above. The (η-arene)Cr(CO)$_3$ fragment shows close conformity to an octahedral coordination environment. The only deviation from the indistinguishability of arene C–C bonding interactions common to most structurally characterized π-arene chromium complexes is found in the Cr–C(arene) distances to aromatic carbons bearing the diphenylphosphino (Ph_2P) and 1-(dimethylamino)ethyl ((Me_2N)CHMe) groups.[21] These distances are, respectively, 0.012 and 0.032 Å longer than the remaining Cr–C(arene) bond distances. A slightly lengthened π-bonding interaction between the Cr and "1,2-disubstituted vinyl" units has been observed in other ortho-functionalized arene complexes.[22] Like many disubstituted π-arene derivatives,[21] the conformation of the Cr(CO)$_3$ moiety is apparently determined more by a tendency to avoid steric contact between the CO ligands and the substituents on the aromatic ring than by electronic considerations. In this molecule (as it would be viewed from above the plane of the arene), the CO ligands are displaced by 15° clockwise from eclipsing the C(1), C(3), and C(5) carbon atoms. This conformation allows the Cr(CO)$_3$ unit to straddle the PPh_2 unit, thereby relieving interactions between the endo Ph substituent and the Cr(CO)$_3$ moiety and avoiding an eclipsing interaction between a CO moiety and the ((Me_2N)CHMe) substituent on the C(1) carbon.

The conformation of the substituents with respect to the π-arene plane bears some comment. One of the phenyl groups of the Ph_2P unit is essentially anti to the Cr(CO)$_3$ fragment, having a 98.3° dihedral angle with respect to the carbon bearing the (Me_2N)CHMe group. This conformation forces the remaining phenyl substituent to lie 24.0° below the plane of the π-arene ring, although in an apparent effort to avoid steric contact with the adjacent carbonyl ligand, this phenyl group adopts an orientation virtually perpendicular to the π-arene moiety. Interestingly, the dihedral angle between the C(8) methyl group and the adjacent ortho proton is 6°; apparently, 1,3-allylic strain[20] between the benzylic methyl group and the C(2) ortho hydrogen is not a compelling factor in determining the conformation of this side chain. The X-ray structure of the methyl derivative **3a** is similar in an overall sense to that reported here but shows a higher dihedral angle between the benzylic methyl group and the arene plane (25°).[18] On the whole, the close proximity of the Ph_2P and Me_2N subunits strongly suggest that ortho-substituted derivatives of the *N*,*N*-dimethyl-1-phenylethyl complexes that contain an α heteroatom may be useful asymmetric ligands for the synthesis of complexes similar to those derived from chiral bidentate ferrocenyl derivatives.[23] Investigations along these lines are currently in progress.

Diastereoselective Complexation Reactions. We were interested to see whether we could obtain the alternate diastereomer by carrying out a stereospecific complexation reaction on an ortho-substituted π-arene chromium complex in the style of Uemura.[13] It was expected that such should be the case, due to the stereochemically divergent natures of the "delivery" steps involved in these deprotonation and complexation processes (Scheme III). In the former, the reactive rotamer must be one that brings the ligation site into the general zone occupied by one or another ortho-hydrogen atom, while simultaneously avoiding steric interactions with the chromium tricarbonyl moiety. For a diastereomeric complexation reaction to occur, the reactive rotamer of the uncomplexed arene should be that which minimizes steric interactions between the benzylic methyl group and ortho substituent. The ortho lithiation and alkylation of the uncomplexed arenes is a known and practical process. In synthetic terms, the two protocols are complementary because they allow the synthesis of either diastereomeric complex merely by reversing the order of the complexation and lithiation steps.

The silylation of *N*,*N*-dimethyl-α-phenethylamine was effected by treatment with *tert*-butyllithium in THF followed by quenching the anion thus formed with chlorotrimethylsilane.[24] The silylated arene was then reacted with Cr(CO)$_6$ in dibutyl ether at reflux overnight. Concentration, followed by examination of the crude ^{1}H NMR spectrum, revealed an approximately 1:4 mixture of the two diastereomeric complexes **4a** and **4b**, with the (R^*,S^*)-**4b** isomer clearly predominating. The analogous reaction, when it was carried out with use of (naphthalene)Cr(CO)$_3$ as a chromium-transfer reagent, resulted in the formation of **4b** as the sole diastereomer.

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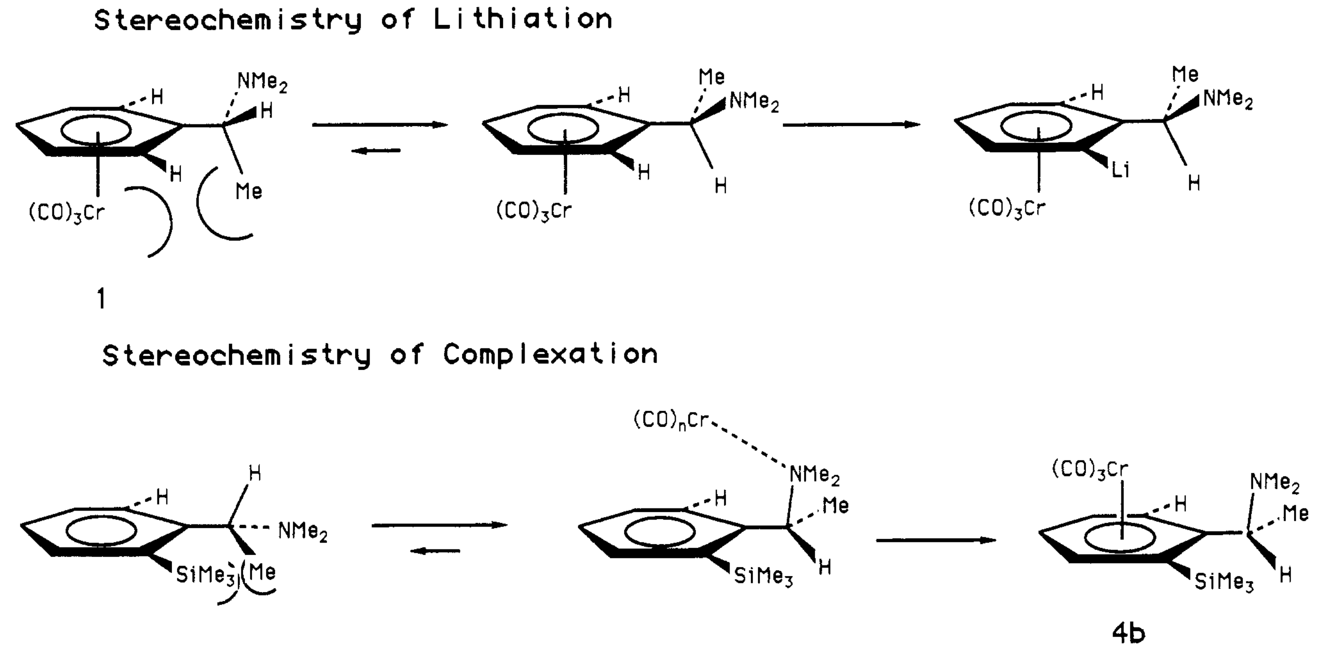
(21) Watts, W. E. In *Comprehensive Organometallics Chemistry*; Wilkinson, G., Ed.; Pergammon Press: London, 1985; Vol. 3, p 1001.

(22) Heppert, J. A.; Thomas-Miller, M. E.; Swepston, R. N.; Extine, M. W. *J. Chem. Soc., Chem. Commun.* **1988**, 280.

(23) (a) Kumada, M.; Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138. (b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395.

(24) Rahman, M.; Mohammed, R. *Acta Chem. Scand. B* **1977**, *31*, 516.

Scheme III



Scheme IV

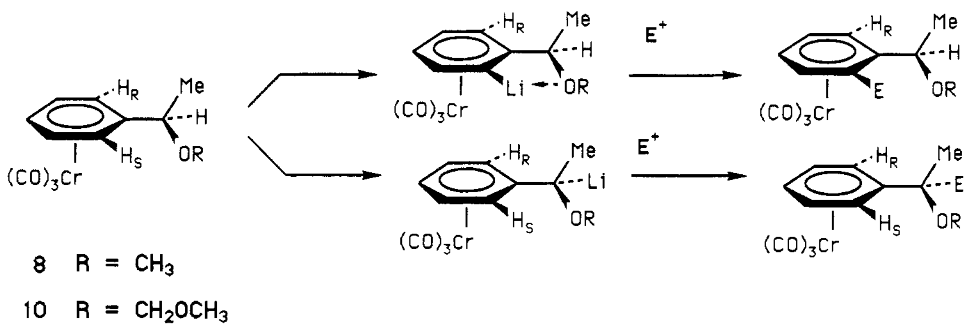
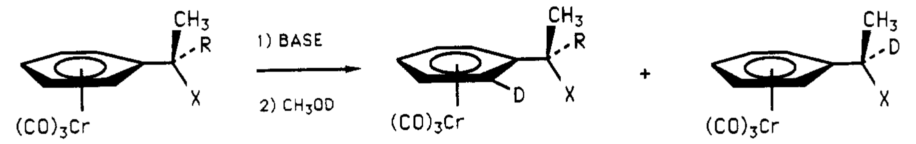


Table IV. Product Distribution from the Lithiation/Deuteration of π-1-Phenylethyl Ether Complexes



entry	substrate	R	X	base (T, °C)	product distribution and addition products	de, %
1	1	H	NMe_2	t-BuLi (-78)	ortho (98%)	96
2	8	H	OMe	t-BuLi (-78)	ortho and benzylic (20%), arene addition (80%)	
3	8	H	OMe	s-BuLi (-40)	ortho (35%), benzylic (65%)	≥94
4	10	H	OCH_2OMe	s-BuLi (-40)	ortho (66%), benzylic (22%), other (12%)	≥96
5	10	H	OCH_2OMe	s-BuLi (-78)	ortho (75%), benzylic (25%)	≥96
6	13	Me	OMe	s-BuLi (-78)	homobenzylic (≥98%)	
7	20	H	$OSiPh_3$	s-BuLi (-40)	meta and para (≥96%)	
8	17	H	$CH_2NMe(CHMe_2)$	s-BuLi (-40)	no reaction	
9	17	H	$CH_2NMe(CHMe_2)$	t-BuLi (-40)	ortho (9%), benzylic (24%), other (67%)	

Deprotonation of Benzylic Ether Derivatives. (η^6-1-Phenylethyl ether)$Cr(CO)_3$ complexes are readily deprotonated by *sec*-butyllithium, producing mixtures of ortho- and benzylic-substitution products after quenching with electrophiles (Scheme IV).[25] Unlike the reactions of (η^6-{(Me_2N)CHMe}C_6H_5)$Cr(CO)_3$ in diethyl ether, the *sec*-phenylethyl ether derivatives form homogeneous orange-brown solutions of lithiated intermediates. Table IV contains a list of π-arene substrates and distributions of the products produced via the deuteration of the deprotonated intermediates. Four general trends in the reactivity of the substrates are evident from these data: (1) Despite a significant lack of chemoselectivity in many of the metalation reactions, the relative ratios of the two ortho-substituted diastereomers always approach that observed in the deprotonation of the amine complex (≥95:5). (2) Increases in the steric bulk of substituents adjacent to the benzylic and ortho protons (as with the

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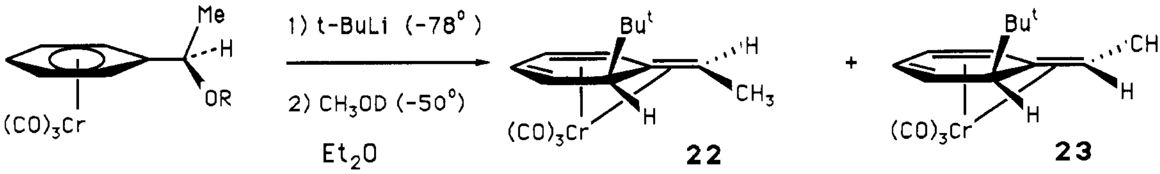
[25] Also see a related study: (a) Davies, S. G.; Holman, J. J.; Laughton, C. A.; Nobbs, B. E. *J. Chem. Soc., Chem. Commun.* **1983**, 1316. (b) Blagg, J.; Davies, S. G.; Holman, N. J.; Laughton, C. A.; Hobbs, B. E. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1581. (c) Brocard, J.; Mahmoudi, M.; Pelinski, L.; Maciejewski, L. *Tetrahedron Lett.* **1989**, *30*, 2549. (d) Davies, S. G.; Goodfellow, C. L. *J. Organomet. Chem.* **1989**, *370*, C5. (e) For benzylic deprotonation of an uncomplexed benzylic ether, see: Engler, T. A.; Schechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715.

Scheme V



triarylsilyl ether derivative **20**) result in the nonselective deprotonation of hydrogens that are remote from the heteroatom substituent (i.e., meta and para hydrogens). (3) Under identical reaction conditions, the use of a chelating ether substituent on the benzylic side chain increases the chemoselectivity specificity of ortho deprotonation. (4) Reducing the reaction temperature also enhances the chemoselectivity of the deprotonation reactions. Another noteworthy feature of this study is the tendency of homobenzylic hydrogens in **13** to become the favored site for metalation in the absence of a benzylic hydrogen.

Based on the available body of data, it is not possible to draw firm conclusions regarding the origins of the chemoselectivity of the deprotonation. The concept that ortho deprotonation is both ether-assisted and a kinetic process gains support from previous studies of toluene metalation.[26] These studies demonstrated that kinetic bases preferentially deprotonate at positions meta and para to the methyl substituent and that thermodynamic bases lead to benzylic metallation. Furthermore, ^{1}H NOEDS spectra of the methyl (**8**) and methoxymethyl (**10**) ether derivatives are consistent with the proximity of the ether group and the ortho proton that is preferentially deuterated. So it seems that the average solution-state structures of the side chains also closely reflect the conformations that assist in base delivery to a specific ortho proton in the transition state for deprotonation.

Davies argued that the preferential benzylic metalation of the *sec*-phenylethyl ether substrates by *tert*-butyllithium in THF reflected a tendency of *tert*-butyllithium to remove the most kinetically acidic proton without prior precomplexation.[18,25] This explanation might provide a rationale for the enhanced chemoselectivity observed in the deprotonation by *sec*-butyllithium of the methoxymethyl ether derivative **10** over that observed for the methyl ether complex **8**. In this scenario, the increased ligating ability of the difunctional ether would facilitate the delivery of *sec*-butyllithium to an ortho proton at the expense of the benzylic metalation process. We should caution against more detailed comparisons of our observations and Davies's results,[17,18] because the difference in the solvent systems employed may influence the nuclearity of the alkyllithium bases, the ligating ability of the ether side chain, and the propensity of the lithium reagents to react through electron-transfer pathways. These factors can and apparently do (vide infra) result in significant changes in the observed chemistry.

Nucleophilic Addition to Benzylic Ether Complexes. The treatment of (η^6-1-phenylethyl ether)Cr(CO)$_3$ derivatives (both methyl and methoxymethyl ethers have been employed) with 1.1 equiv of *tert*-butyllithium in diethyl ether at −78 °C followed by slow warming to −50 °C produces a brown solution that rapidly converts to a homogeneous dark burgundy solution on quenching with 1.1 equiv of ethanol. Removal of solvent from the former in vacuo, followed by extraction with hexanes, separates a red soluble fraction from a pale yellow powdery residue. Removal of solvent from the former leaves a red oily residue, which on the basis of ^{1}H and ^{13}C NMR spectroscopy was identified as an approximate 1:1 mixture of the two diastereomers of (η^4,η^2-2-*tert*-butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (**22** and **23**, Scheme V). A similar reaction employing PhLi results in substantially lower yields of the (η^4,η^2-2-phenylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ isomers. The spectroscopic characteristics of the molecules prepared in this study clearly differentiate them from ordinary (η^6-arene)Cr(CO)$_3$ complexes.[21] ^{1}H NMR spectra of the products show five distinct resonances associated with the ring protons over the range 1.3–5.0 ppm, whose connectivity can be enumerated by selective decoupling experiments. The ^{13}C NMR spectra display two unique features: (1) resonances near 55 and 85 ppm representing the new *exo*-alkane unit; (2) three distinct carbonyl resonances, differentiated by a loss of free rotation about the Cr–Ar$_{\text{centroid}}$ vector.

The nature of this reaction is strikingly different from any we had thus far observed between lithium alkyls and heteroatom-substituted π-arene complexes. This chemistry is, in fact, closely related to the heteroatom-assisted synthesis of (η^6-2-R-cyclohexadienylidene-*exo*-methane)Cr(CO)$_3$ from (η^6-benzyl alcohol)Cr(CO)$_3$.[27] The scope of the nucleophiles that participate in the addition to π-*sec*-phenylethyl ether complexes is severely limited. For example, while substantial quantities of addition products are observed with both *tert*-butyllithium and phenyllithium, reactions between *sec*-butyllithium and the ether complexes result exclusively (≥95%) in deprotonation, while (NC)Me$_2$CLi fails to react with these arene complexes.

Factors that may distinguish Davies's deprotonation of **8** with *tert*-butyllithium[18,25] from our nucleophilic addition reactions include (a) a change in the solvent used for the reaction, (b) an increase in the ligating ability of the ether substituent (the quantity of observed nucleophilic addition products increase as MeO < MeOCH$_2$O), and (c) a variation of the electrophile from Davies study (MeI) to our study (EtOH or H$_2$O). With respect to this latter concern, it is noteworthy that no organometallic products were recovered from attempts to quench the brown intermediate mixture formed in our reactions with chlorotrimethylsilane.

Literature precedents suggest the following mechanistic model for this nucleophilic addition/alkoxide elimination process (Scheme VI).[26,27] Addition of the organolithium reagent to ortho positions on the π-arene substrate is assisted by the ether substituent, resulting in the formation of the π-cyclohexadienide intermediates **26** and **27**. These species suffer elimination of the benzylic ether substituent upon protonation, affording the observed products **22** and **23**. The latter step might be expected to be stereoselective on the basis of the proposed tendency for the benzylic leaving group to undergo elimination anti to the Cr(CO)$_3$

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[26] (a) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2556, 2560. (b) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *107*, 768. (c) Jaouen, G.; Meyer, A.; Simmonneaux, G. *J. Chem. Soc., Chem. Commun.* **1975**, 813.

[27] Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1283.

Scheme VI

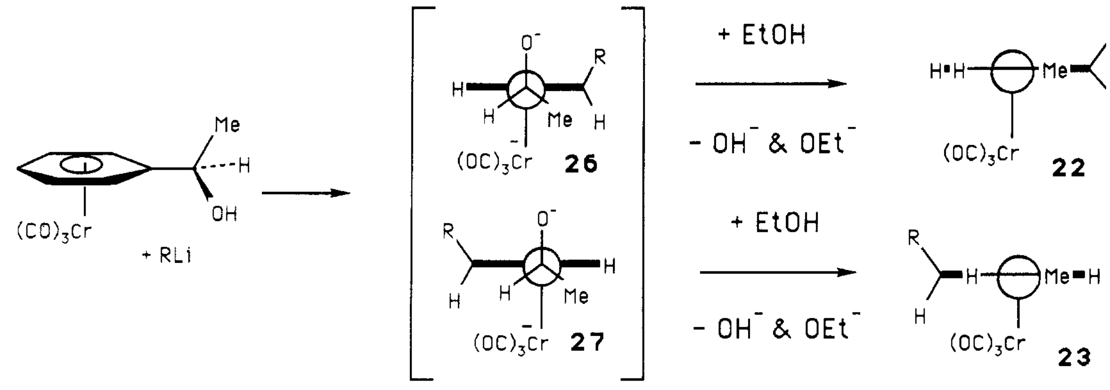

Table V. Crystallographic Coordinates and B(eq) Values for (η^4,η^2-[S^*,S^*,R^*]-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (22)

atom	x	y	z	B(eq), Å^2
Cr	0.30074 (5)	0.36600 (6)	0.07324 (4)	3.06 (3)
O(9)	0.4068 (3)	0.3718 (4)	−0.0754 (3)	6.3 (2)
O(10)	0.3558 (3)	0.0242 (4)	0.0764 (3)	6.9 (2)
O(11)	0.0872 (3)	0.3586 (5)	−0.1016 (3)	8.1 (2)
C(1)	0.2649 (3)	0.4043 (4)	0.2066 (3)	3.2 (2)
C(2)	0.3806 (3)	0.3877 (4)	0.2355 (3)	3.6 (2)
C(3)	0.4311 (3)	0.4923 (4)	0.1938 (3)	3.7 (2)
C(4)	0.3671 (3)	0.6051 (4)	0.1239 (3)	3.7 (2)
C(5)	0.2614 (3)	0.6246 (4)	0.1073 (3)	3.5 (2)
C(6)	0.2155 (3)	0.5664 (4)	0.1814 (3)	3.1 (1)
C(7)	0.2043 (3)	0.2689 (4)	0.1776 (3)	4.3 (2)
C(8)	0.0854 (4)	0.2551 (5)	0.1400 (4)	6.2 (2)
C(9)	0.3664 (3)	0.3747 (5)	−0.0182 (3)	4.2 (2)
C(10)	0.3322 (3)	0.1546 (5)	0.0758 (3)	4.2 (2)
C(11)	0.1697 (4)	0.3592 (5)	−0.0343 (3)	4.6 (2)
C(12)	0.2290 (3)	0.6738 (5)	0.2734 (3)	4.2 (2)
C(13)	0.3462 (4)	0.7005 (7)	0.3448 (4)	6.4 (2)
C(14)	0.1750 (5)	0.8309 (6)	0.2313 (5)	7.2 (3)
C(15)	0.1697 (4)	0.5954 (6)	0.3323 (3)	5.5 (2)

moiety. However, the ratios of the S^*,S^*,R^* (**22**) and S^*,S^*,S^* (**23**) products exhibit a curious temperature dependence. Annealing an unquenched mixture of addition products at temperatures exceeding −20 °C generates **22** and **23** in a 10:1 ratio, while adding alcohol to the reaction mixture below −40 °C produces a virtually equimolar product mixture. We have not, as yet, successfully characterized the cause of these variations in the product distributions. Possible explanations include (1) a nonstereospecific addition process, (2) a nonstereospecific elimination reaction, (3) equilibration processes that occur under some reaction conditions, or (4) some combination of the above mechanisms. The isomer **22**, isolated as the principle product in the room-temperature quench, was isolated as red blocks and subjected to a crystallographic study.

Crystal Structure of (η^2,η^4-[S^*,S^*,R^*]-2-*tert*-butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (22). A ball-and-stick representation of **22** showing a view perpendicular to and along the Cr–cyclohexadiene vector is shown in Figures 4 and 5 and lists of crystallographic coordinates and selected bond distances and angles are collected in Tables V and VI. The structure confirms that the regiochemistry of attack by the *t*-Bu nucleophile is anti to the Cr(CO)$_3$ subunit. The hydrocarbyl fragment displays C–C bond distances consistent with the localized cyclohexadienylidene-*exo*-ane valence structure suggested by Davies,[26] with the C=C distances varying between 1.358 (5) and 1.389 (5) Å. All six of the sp^2-hybridized carbon centers are within bonding distance of the Cr(CO)$_3$ frag-

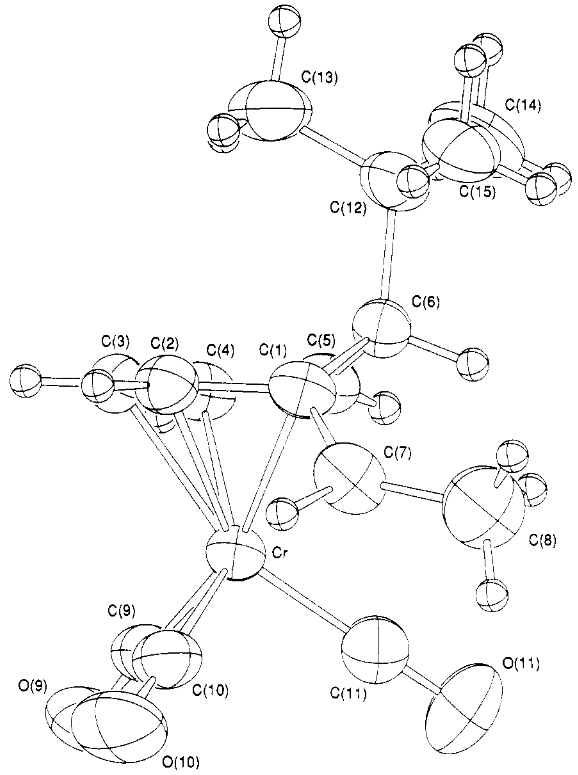

Figure 4. ORTEP-like representation of the molecular structure of (η^2,η^4-(S^*,S^*,R^*)-2-*tert*-butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (**22**) viewed perpendicular to the Cr–cyclohexadiene vector showing 50% thermal ellipsoids. Note that the Cr–C(7) and Cr–C(5) attachments have been omitted for clarity. Numbering of atoms is arbitrary.

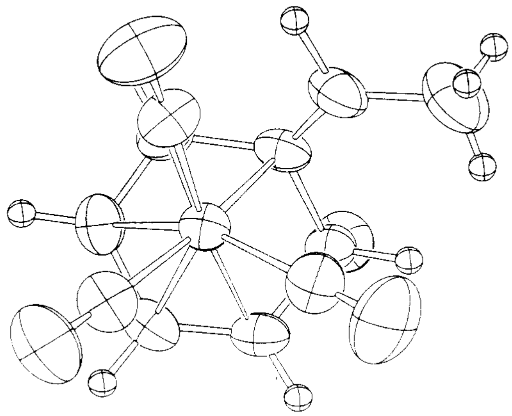

Figure 5. ORTEP-like representation of **22** viewed down the Cr–cyclohexadiene vector. The Cr–C(7) attachment and the C(13), C(14), and C(15) atoms have been omitted for clarity.

Table VI. Selected Bond Distances and Angles for (η^4,η^2-[S*,S*,R*]-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (22)

atom	atom	dist, Å	atom	atom	atom	angle, deg
Cr	C(11)	1.837 (5)	C(11)	Cr	C(10)	91.1 (2)
Cr	C(10)	1.844 (4)	C(11)	Cr	C(9)	88.5 (2)
Cr	C(9)	1.846 (4)	C(10)	Cr	C(9)	83.3 (2)
Cr	C(2)	2.160 (4)	C(7)	C(1)	C(2)	116.6 (3)
Cr	C(1)	2.173 (4)	C(7)	C(1)	C(6)	122.4 (3)
Cr	C(3)	2.205 (4)	C(7)	C(1)	Cr	85.2 (2)
Cr	C(4)	2.226 (4)	C(2)	C(1)	C(6)	118.7 (3)
Cr	C(5)	2.358 (4)	C(3)	C(2)	C(1)	117.6 (3)
Cr	C(7)	2.474 (4)	C(3)	C(2)	Cr	73.2 (2)
C(1)	C(7)	1.378 (5)	C(2)	C(3)	C(4)	118.4 (3)
C(1)	C(2)	1.454 (5)	C(5)	C(4)	C(3)	121.0 (3)
C(1)	C(6)	1.512 (5)	C(5)	C(4)	Cr	78.2 (2)
C(2)	C(3)	1.389 (5)	C(4)	C(5)	C(6)	121.7 (3)
C(3)	C(4)	1.412 (5)	C(5)	C(6)	C(1)	101.8 (3)
C(4)	C(5)	1.358 (5)	C(5)	C(6)	C(12)	117.4 (3)
C(5)	C(6)	1.507 (5)	C(1)	C(6)	C(12)	115.9 (3)
C(6)	C(12)	1.557 (5)	C(1)	C(7)	C(8)	127.2 (4)
C(7)	C(8)	1.481 (6)				

ment. The C(5) and C(7) atoms, representing the termini of the triene framework, display the longest Cr–C bonds at 2.358 (4) and 2.474 (4) Å, respectively. The C(1)–C(7) *exo*-alkane unit dips below the plane of the diene unit (toward the Cr(CO)$_3$ fragment) by approximately 50° to allow the *exo*-C(7) carbon to approach within bonding distance of the metal. The perpendicular between the Cr and hexadiene plane is significantly shifted away from the hexadiene "centroid" along the C(1)–C(4) vector toward the *exo*-ethane unit. This distortion from the habitually centric (η^6-arene)Cr(CO)$_3$ geometry[21] evidently promotes more efficient π-bonding between the chromium and the *exo*-ethane unit. In an occurrence that is seldom observed for (η^6-arene)Cr(CO)$_3$ complexes,[21] the Cr(CO)$_3$ fragment shows a marked distortion from idealized octahedral geometry. The C–Cr–C angles in this fragment vary between 97.1 (2) and 83.3 (2)°, with the most obtuse angle being formed by the carbonyl ligands that straddle the *exo*-ethane unit. Moreover, although each carbonyl ligand should attempt to maximize π-back acceptance from the metal by orienting itself trans to an olefinic unit, the carbonyl ligands fall short of this goal, adopting C(CO)–Cr–alkane(cent) angles between 154.10 and 160.58°. While some of this distortion is undoubtedly generated by the presence of the new unsymmetrical triene framework, a significant contribution also stems from the angular distortions of the Cr(CO)$_3$ tripod. From these observations, we infer that the intrusion of the *exo*-ethane unit into the ligand environment of the metal center largely determines the rotational conformation of the Cr(CO)$_3$ fragment.

Summary

A useful route to diastereomerically pure 1,2-disubstituted η-arene chromium in optically active form has been demonstrated. This technique has been shown to specifically afford an isomer that is not readily accessible using previously reported techniques (e.g., diastereoselective complexation processes). In addition, various structural aspects of the reactants and products have been investigated via NMR and X-ray methodology. The scope of the synthetic method has been addressed with respect to side-chain structure. These reactions have also yielded structurally interesting methylenecyclohexadienyl products under certain conditions.

Experimental Section

All reactions were carried out with the exclusion of air and moisture through modified Schlenk techniques. Although the compounds isolated were generally stable in air for long periods in a crystalline state, many of the products were found to decompose in alkane solutions on exposure to air under laboratory light. Consequently, chromatographic and NMR spectroscopic samples and metalation reactions were always protected from exposure to oxygen. Solvents were dried over sodium benzophenone ketyl except for di-*n*-butyl ether, which was dried over Na/K alloy. NMR solvents were dried over 5-Å molecular sieves and purged with dry nitrogen gas to remove oxygen. *N*,*N*-Dimethyl-2-phenylethylamine was purchased from Alpha, and (η^6-naphthalene)Cr(CO)$_3$ and 2-(trimethylsilyl)-*N*,*N*-dimethyl-1-phenylethylamine were prepared according to published procedures.[23,28] Products were chromatographed on a 5 cm × 6 cm alumina column (15 mol % H_2O) with Et_2O eluent.

^{1}H, ^{2}H, ^{13}C, and ^{31}P NMR spectra were acquired on Varian FX 300 and Brucker GM 500 spectrometers. ^{1}H NMR spectra were referenced against the residual ^{1}H impurity in benzene-d_6 or toluene-d_8 (methyl), and ^{13}C NMR spectra were referenced against the ^{13}C resonances of benzene-d_6 or toluene-d_8 (methyl). ^{2}H spectra were referenced against an internal benzene-d_6 spike. ^{31}P NMR spectra were referenced against an external 70% H_3PO_4 sample. IR spectra were acquired on an IBM FT/IR 30, with KBr pellets. Mass spectra were obtained on a Ribermag MS 10, with a direct insert source, and high-resolution mass spectra (HRMS) were acquired on a VG Analytical ZAB high-resolution mass spectrometer. Elemental analysis were performed by Desert Analytics, Tuscon, AZ, and Microanalytical Laboratories, Engelskiechen, FRG.

(η^6-*N*,*N*-Dimethyl-α-phenylethylamine)Cr(CO)$_3$ (1). In a Schlenk flask (250 mL), Cr(CO)$_6$ (5.0 g, 22.7 mmol), di-*n*-butyl ether (60 mL), THF (6 mL), and *N*,*N*-dimethylphenylethylamine (18.9 mmol, 3.1 mL) were heated to reflux for 24 h. After cooling, the solution was filtered to remove crystallized Cr(CO)$_6$, and the solvent was removed in vacuo. The product was extracted from the red, oily residue with three portions of pentane (50 mL each), and the combined pentane solution was filtered through a thin pad of silica on a glass frit. Recrystallization from pentane produced yellow needles of **1** (1.94 g, 6.81 mmol, 30%): IR (KBr, carbonyl region, cm^{-1}), 1963 (s), 1871 (s); ^{1}H NMR (C_6D_6) δ 4.83 (d, 1 H, J = 5.7 H, ortho), 4.29 (d, 1 H, J = 6.0 Hz, ortho), 4.40 (m, 3 H, meta and para), 3.11 (q, 1 H, J = 6.9 Hz, C*H*Me(NMe$_2$)), 1.82 (s, 6 H, N*Me*$_2$), 0.94 (d, 3 H, J = 6.9 Hz, CH*Me*(NMe$_2$)); ^{13}C {^{1}H} (C_6D_6) δ 233.6 (Cr(*C*O)$_3$), 112.4 (ipso), 95.7, 92.3, 91.9, 91.4 (*o*,*m*,*p*), 61.4 (*C*HMe(NMe$_2$)), 40.5 (N(*C*H$_3$)$_2$), 12.1(CH(*C*H$_3$)-(NMe$_2$)). Anal. Calcd for $C_{13}H_{15}CrNO_3$: C, 54.74; H, 5.30; N, 4.91. Found: C, 54.55; H, 5.24; N, 4.84.

(η^6-(*R,*S**)-*o*-{(Me$_2$N)CHMe}DC$_6$H$_4$)Cr(CO)$_3$ (2).** In a Schlenk flask (50 mL), **1** (0.300 g, 1.1 mmol) was dissolved in diethyl ether (20 mL). The solution was cooled to −40 °C, and *tert*-butyllithium (1.7 M in pentane, 0.71 mL, 1.2 mmol) was added dropwise by syringe. After stirring at −40 °C for 45 min, THF (5 mL) was added to dissolve the yellow precipitate. CH_3OD (49 μL, 1.2 mmol) was added, and the solution was allowed to warm to room temperature over several hours. The solvent was removed in vacuo, and the residue was taken up in benzene and filtered through Celite. Recrystallization from hexane produced yellow crystals of **2** (0.200 g, 0.70 mmol, 64% yield). The minor *R**,*R** diastereomer accounted for 2% of the product (96% de); ^{1}H NMR (C_6D_6) δ 4.60 (d, 1 H, J = 6.0 Hz, Ar), 4.40 (m, 3 H, Ar), 3.11 (q, 1 H, J = 6.9 Hz, C*H*(Me)(NMe$_2$)), 1.82 (5, 6 H, N*Me*$_2$), 0.94 (d, 3 H, J = 6.9 Hz); ^{2}H NMR (C_6H_6 spiked w/C_6D_6) δ 4.84 (major), 4.60 (minor); IR (KBr, carbonyl region, cm^{-1}) 1962 (s), 1877 (s).

(η^6-(*R,*S**)-*o*-{(Me$_2$N)CHMe}(Me)C$_6$H$_4$)Cr(CO)$_3$ (3).** The experimental conditions were identical with those used for the synthesis of **2**. Reagents and amounts used are as follows: **1** (0.300 g, 1.05 mmol), *t*-BuLi (1.7 M in pentane, 0.68 mL, 1.2 mmol), $MeOSO_2F$ (95 μL, 1.2 mmol). Yield of **3**, 43% (0.135 g, 0.45 mmol as yellow crystals); IR (KBr, carbonyl region, cm^{-1}) 1948 (s), 1861 (s); ^{1}H NMR (C_6D_6) δ 4.81 (d, 1 H, J = 60 Hz, Ar), 4.54 (t, 1 H, J = 6.3 Hz, Ar), 4.33 (m, 2 H, Ar), 3.34 (q, 1 H, J = 6.6 Hz,

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C*H*(Me(NMe$_2$)), 1.88 (s, 3 H, Ar–C*H*$_3$), 1.79 (s, 6 H, N*Me*$_2$), 0.90 (d, 3 H, J = 7.2 Hz, CH*Me*(NMe$_2$)); ^{13}C NMR (C$_6$D$_6$) δ 233.9 (Cr(*C*O)$_3$), 111.9, 110.9 (ipso Ar), 93.9, 93.7, 92.8, 89.1 (Ar) 57.8 (*C*H(Me)(NMe$_2$)), 39.9 (N(*C*H$_3$)$_2$), 18.5, 8.5 (CH$_3$); MS, m/e 299 (M$^+$), 242 (M$^+$ – 2CO), 215 (M$^+$ – 3CO), 172 (M$^+$ – 3CO – N(C$_2$H$_5$)); HRMS m/e calcd for $\mathrm{C_{14}H_{17}\,CrNO_3}$ M$^+$ = 299.0608, found M$^+$ = 299.0609.

(η^6-(R^*,R^*)-o-{(Me$_2$N)CHMe}(SiMe$_3$)C$_6$H$_4$)Cr(CO)$_3$ (4a). The experimental conditions were identical with those used for the synthesis of **2**. Reagents and amounts used are as follows: **1** (0.300 g, 1.05 mmol), *t*-BuLi (1.7 M in pentane, 0.68 mL, 1.2 mmol), Me$_3$SiCl (0.15 mL, 1.2 mmol). Yield of **4** = 73% 0.275 g, 0.77 mmol, as yellow crystals; IR (KBr, carbonyl region, cm^{-1}) 1950 (s), 1877 (s); ^{1}H NMR (C$_6$D$_6$) δ 3.08 (d, 1 H, J = 6.3 Hz, Ar), 4.79 (t, 1 H, J = 6.3 Hz, Ar), 4.51 (d, 1 H, 6.9 Hz, Ar), 4.38 (t, 1 H, 6.3 Hz, Ar) 3.70 (q, 1 H, J = 6.9 Hz, C*H*(Me)(NMe$_2$)), 1.72 (s, 6 H, N*Me*$_2$), 0.75 (d, 3 H, J = 6.6 Hz, CH(*Me*)(NMe$_2$)), 0.26 (s, 9 H, Si(C*H*$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) δ 233.9 (Cr(CO)$_3$), 120.2, 101.0 (ipso Ar), 101.5, 94.5, 90.4, 89.4 (Ar), 59.3 (*C*H(Me)(NMe$_2$), 39.3 (N(CH$_3$)$_2$), 6.9 (CH(*Me*)(NMe$_2$), 0.64 (Si(*C*H$_3$)$_3$); MS, m/e 357 (M$^+$), 301 (M$^+$ – 2CO), 273 (M$^+$ – 3CO), 230, (M$^+$ – 3CO – N(C$_2$H$_5$)); HRMS m/e calcd for $\mathrm{C_{16}H_{23}CrNO_3Si}$ M$^+$ = 357.0857, found M$^+$ = 357.0861.

(η^6-(R^*,S^*)-o-{(NMe$_2$)CHMe}(SiMe$_3$)C$_6$H$_4$)Cr(CO)$_3$ (4b). Preparation by Carbonyl-Exchange Reactions. 2-(Trimethylsilyl)-*N*,*N*-dimethylphenylethylamine (0.28 mL, 1.13 mmol), Cr(CO)$_6$ (0.25 g, 1.13 mmol), dibutyl ether (16 mL), and THF (1.6 mL) were placed in a Schlenk flask and heated to a gentle reflux for 24 h. The solution was cooled, and the solvent was removed in vacuo. The mixture was left under vacuum for a few more hours after the solvent was removed to sublime off any remaining Cr(CO)$_6$. The ^{1}H NMR of the crude reaction mixture showed a ratio of 83:17 for the R^*,S^* and R^*,R^* diastereomers, respectively. Successive crystallizations from hexane yielded the pure diastereomer R^*,S^* of **4b**, yield 22% (0.090 g, 0.25 mmol, as yellow needles).

Preparation by Arene Exchange. (η^6-naphthalene)Cr(CO)$_3$ (0.30 g, 1.13 mmol) was dissolved in dibutyl ether (16 mL) and THF (2 mL). 2-(Trimethylsilyl)-*N*,*N*-dimethylphenylethylamine (0.28 mL, 1.13 mmol) was added. The solution was heated to 70 °C for 19 h. The cooled solution was filtered through Celite. The solvent was removed in vacuo, and the residue was taken up in hot hexane and filtered through Celite. Recrystallization from hexane gave the pure R^*,S^* diastereomer, yield 30% (0.120 g, 0.336 mmol); IR (KBr, carbonyl region, cm^{-1}) 1950 (s), 1877 (s); ^{1}H NMR (C$_6$D$_6$) δ 5.47 (d, 1 H, J = 7.5 Hz, Ar), 4.72 (m, 2 H, Ar), 4.52 (t, 1 H, J = 6.3 Hz), 3.09 (q, 1 H, J = 6.9 Hz, C*H*Me(NMe$_2$)), 2.18 (s, 6 H, N*Me*$_2$), 0.92 (d, 3 H, 6.9 Hz, CH(C*H*$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) δ 233.9 (Cr(*C*O)$_3$), 125.0, 98.4 (ipso Ar), 98.0, 93.4, 92.6, 91.4 (Ar), 61.9 (*C*HMe(NMe$_2$)), 44.1 (N(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)(NMe$_2$), 1.28 (Si(*C*H$_3$)$_3$). Anal. Calcd for $\mathrm{C_{16}H_{23}CrNO_3Si}$: C, 53.76; H, 6.49; N, 3.92. Found: C, 53.50; H, 6.46; N, 3.78.

(η^6-(R^*,R^*)-o-{(Me$_2$N)CHMe}(Ph$_2$P)C$_6$H$_4$)Cr(CO)$_3$ (5). In a Schlenk flask (50 mL) **1** (0.300 g, 1.05 mmol) was dissolved in diethyl ether (20 mL). The solution was cooled to –40 °C, and *tert*-butyllithium (1.7 M in pentane, 0.71 mL, 1.20 mmol) was added dropwise by syringe. After this was stirred for 45 min at –40 °C, THF (5 mL) was added to dissolve the yellow precipitate. Next, chlorodiphenylphosphine (0.21 mL, 1.20 mmol) was added dropwise. The solution was allowed to warm slowly to room temperature, and the solvent was removed in vacuo. The residue was taken up in toluene and filtered through Celite on a glass frit. The product was recrystallized by layering pentane onto a toluene solution of the crude product. Yellow needles of **5** were collected by filtration and dried in vacuo, yield = 50% (0.246 g, 0.523 mmol); IR (KBr, carbonyl region, cm^{-1}) 1960 (s), 1883 (s); ^{1}H NMR (C$_6$D$_6$) δ 7.55 (t, 2 H), 7.10 (m, 8 H), 4.87 (d, 1 H, J = 6.3 Hz, Ar) 4.65 (t, 1 H, J = 6.9 Hz, Ar), 4.55 (dq, 1 H, J_{HH} = 6.9 and J_{PH} = 6.9, C*H*Me(NMe$_2$)), 4.42 (dd, 1 H, Ar), 4.20 (t, 1 H, J = 6.3 HZ, Ar), 1.50 (s, 6 H, NMe$_2$), 0.74 (d, 3 H, J = 6.9 Hz, CH*Me*(NMe$_2$)); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 232.9 (s, Cr(*C*O)s$_3$), 137.9 (d, J_{PC} = 103 Hz, ipso Ar$_2$P) 138.0 (d, J_{PC} = 81 Hz ipso Ar$_2$P), 135.1 (d, J_{PC} = 18 Hz, *o*-Ar$_2$P), 132.3 (d, J_{PC} = 20 Hz, *o*-Ar$_2$P), 129.2, 128.8, 128.6 (*m*,*p*-Ar$_2$P), 120.0 (d, J_{PC} = 20 Hz, ipso Ar), 106.0 (d, J_{PC} = 22 Hz, ipso Ar), 100.4, 94.0, 89.3, 87.6 (Ar), 58.8 (d, J_{PC} = 7 Hz, CHMe(NMe$_2$)), 37.7 (N(*ME*)$_2$), 5.6 (CH(*Me*)(NMe$_2$)); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ –12.11 (s). Anal. Calcd for $\mathrm{C_{25}H_{24}CrNO_3P}$: C, 63.96; H, 5.15; N, 2.98. Found: C, 63.73; H, 5.25; N, 2.97.

(η^6-(R^*,R^*)-o-{(Me$_2$N)CHMe}(SPh)C$_6$H$_4$)Cr(CO)$_3$ (6). The experimental conditions were identical with those for **2**. Reagents and amounts used are as follows: **1** (0.139 g, 0.487 mmol), *t*-BuLi (1.7 M in pentane, 0.31 mL, 0.536 mmol), Ph–S–S–Ph (0.117 g, 0.536 mmol), yield 79% (0.152 g, 0.386 mmol, as yellow crystals); IR (KBr, carbonyl region, cm^{-1}) 1949 (s), 1859 (s); ^{1}H NMR (C$_6$D$_6$) δ 7.60 (d, 2 H, S*Ph*), 7.03 (m, 3 H, S*Ph*), 4.72 (d, 1 H, J = 6.9 Hz, Ar), 4.53 (d, 1 H, J = 6.3 Hz, Ar), 4.34 (t, 1 H, J = 6.3 Hz, Ar), 4.25 (t, 1 H, J = 6.3 Hz, Ar), 4.0 (q, 1 H, J = 6.9 Hz, (C*H*MeNMe$_2$)), 1.95 (s, 6 H, N(CH$_2$)$_2$), 0.94 (d, 3 H, J = 6.0 Hz, (CH(C*H*$_3$)NMe$_2$)); ^{13}C NMR (C$_6$D$_6$) δ 233.4 (Cr(*C*O)$_3$), 135.4, 129.8, 129.4 (SC$_6$H$_5$), 117.0, 113.2 (ipso Ar), 92.0, 91.7, 90.1, 90.0 (Ar), 59.0 (*C*HMeN(Me)$_2$), 39.6 (N(*C*H$_3$)$_2$), 8.0 (CH(*C*H$_3$)(NMe$_2$)); MS, m/e 393 (M$^+$), 337 (M$^+$ – 2CO), 309 (M$^+$ – 3CO), 266 (M$^+$ – 3CO – N(C$_2$H$_5$)); HRMS m/e calcd for $\mathrm{C_{19}H_{19}CrNO_3S}$ M$^+$ = 393.0496, found M$^+$ = 393.0510.

(η^6-1-Phenylethanol)Cr(CO)$_3$ (7). In a Schlenk flask (100 mL), Cr(CO)$_6$ (5.0 g, 22.7 mmol), dioxane (50 mL), THF (5 mL), and 1-phenyl ethanol (2.0 mL, 16.6 mmol) were heated to reflux for 72 h. After cooling, the solution was filtered to separate crystallized Cr(CO)$_6$, and the solvent was removed in vacuo to yield **7** as a crude yellow semisolid, yield 42.4% (1.82 g, 7.05 mmol); ^{1}H NMR (C$_6$D$_6$) δ 4.95 (d, 1 H, J = 6.8 Hz, *o*-Ar), 4.47 (d, 1 H, J = 7.2 Hz C*H*CH$_3$), 1.02 (d, 3 H, J = 6.3 Hz, CHC*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 233.52 (Cr(*C*O)$_3$), 117.31 (ipso Ar), 29.51, 45.14, 39.06, 51.22, 65.10 (Ar), 34.72 (*C*H(OH)CH$_3$), 54.69 (CH(OH)*C*H$_3$).

(η^6-1-Phenylethyl methyl ether)Cr(CO)$_3$ (8). In a Schlenk flask (50 mL) was added 50% NaH/mineral oil (0.368 g, 766 mol) that was washed with 3 × 5 mL of hexane to remove the mineral oil. To the NaH was added THF (20 mL) and a solution of **7** (1.82 g, 7.05 mmol) in THF (10 mL). The suspension was stirred until H$_2$ evolution ceased (ca. 1 h) followed by quenching with CH$_3$I (0.54 mL, 8.67 mmol). The mixture was stirred for 12 h and filtered to remove any unreacted solids, and the solvent removed in vacuo. The residue was recrystallized from hexane to yield yellow crystals of **8** (0.882 g, 3.0 mmol, 43%); ^{1}H NMR (C$_6$D$_6$) δ 4.98 (d, 1 H, J = 6.0 Hz, *o*-Ar), 4.49 (d, 1 H, J = 6.0 Hz, *o*-Ar′), 4.29–4.45 (m, 3 H, *m*,*p*-Ar), 3.49 (q, 1 H, J = 6.5 Hz, C*H*(CH$_3$)OCH$_3$), 3.10 (s, 3 H, CH(CH$_3$)OC*H*$_3$), 1.03 (d, 3 H, J = 6.5 Hz, CH(C*H*$_3$)OCH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 233.52 (Cr(*C*O)$_3$), 114.01 (ipso Ar), 92.25 (Ar), 91.82 (Ar), 91.31 (Ar), 90.75 (Ar), 83.92 (Ar), 76.71 (*C*(CH$_3$)H), 56.93 (O*C*H$_3$), 22.27 (C(*C*H$_3$)). Anal. Calcd for $\mathrm{C_{12}H_{12}CrO_4}$: C, 52.95; H, 4.44. Found: C, 52.62; H, 4.32.

(η^6-{MeOCHMe}C$_6$H$_5$)Cr(CO)$_3$-d_1 (9). In a Schlenk flask (30 mL), **8** (0.155 g, 0.569 mmol) was dissolved in diethyl ether (20 mL). The solution was cooled to –78 °C, and *sec*-butyllithium (1.3 M solution in cyclohexane, 0.48 mL, 0.626 mmol) was added dropwise by syringe. After stirring for 1 h at –78 °C, the solution was warmed to –40 °C followed by quenching with CH$_3$OD (35 μL, 0.854 mmol). The solution was warmed to 25 °C and the solvent removed in vacuo. The residue was taken up in toluene and filtered through a pad of Celite on a glass frit. Recrystallization from hexane produced yellow crystals of **9** (0.93 g, 0.34 mmol, 60%). Deuterium incorporation: ^{1}H NMR δ 3.49 (benzylic, 65%), 4.98 (R^*,S^* isomer, ortho, 35%), 4.49 (R^*,R^* isomer, ortho, ≤2%); ^{2}H NMR (C$_6$H$_6$ spiked with C$_6$D$_6$) δ 4.96 (s, 1 D, *o*-Ar), 3.42 (s, 1 D, CDCH$_3$OCH$_3$). The synthesis was repeated using **8** (0.300 g, 1.102 mmol), *tert*-butyllithium (1.7 M solution in pentane, 0.72 mL, 1.22 mmol), at –40 °C, and CH$_3$OD (60 μL, 1.65 mmol), yield 18.4% (0.0555 g, 0.203 mmol). Deuterium incorporation: ^{1}H NMR δ 3.48 (benzylic, 57%), 4.97 (R^*,S^* isomer, ortho, 43%), 4.46 (R^*,R^* isomer, ortho, ≤2%); ^{2}H NMR (C$_6$H$_6$ spiked with C$_6$D$_6$) δ 4.96 (s, 1 D, o-Ar), 3.42 (s, 1 D, C*D*(CH$_3$)OCH$_3$).

(η^6-1-Phenylethyl methoxymethyl ether)Cr(CO)$_3$ (10). The experimental conditions were identical with those used for the synthesis of 8. Reagents and amounts used are as follows: **7** (0.961 g, 3.72 mmol), NaH (50%, 0.467 g, 9.70 mmol), ClCH$_2$OCH$_3$ (0.75 mL, 9.70 mmol), yield of **10** 74% (0.84 g, 2.72 mmol as yellow crystals); IR (KBr, carbonyl region, cm^{-1}) 1958 (s), 1892 (s); ^{1}H NMR (C$_6$D$_6$) δ 5.02 (d, 1 H, J = 4.8 Hz, *o*-Ar), 4.50 (AB$_\mathrm{q}$, 2 H, J_{AB} = 6.9 Hz, $\Delta\nu$ = 40.0 Hz, OC*H*$_2$O), 4.53 (d, 1 H, J = 5.40 Hz, *o*-Ar′), 4.27–4.38 (m, 3 H, *m*,*p*-Ar), 4.04 (q, 1 H, J = 6.30 Hz,

$CH(CH_3)OCH_2$), 3.13 (s, 3 H, CH_2OCH_3), 1.11 (d, 3 H, $J = 5.70$ Hz, $CH(CH_3)CH_2$); ^{13}C NMR (C_6D_6) δ 233.4 ($Cr(CO)_3$), 113.6 (ipso Ar), 95.4 (Ar), 92.7 (Ar), 92.0 (OCH_2O), 91.35 (Ar), 91.0 (Ar), 72.6 ($CH(CH_3)O$), 55.3 (OCH_2O), 23.0 ($CH(CH_3)O$). Anal. Calcd for $C_{13}H_{14}CrO_5$: C, 51.66; H, 4.67. Found: C, 51.61; H, 4.57.

(η^6-(*R,*S**)-*o*-{$MeOCH_2OCHMe$}C_6H_5)$Cr(CO)_3$-*d*$_1$ (11).** The experimental conditions were similar to those used in the synthesis of **9**. Reagents, amounts, and special conditions used are as follows: **10** (0.163 g, 0.536 mmol), *sec*-butyllithium (0.45 mL, 0.59 mmol) at −78 °C, CH_3OD (26.3 μL, 0.648 mmol) at −78 °C, yield of **11** 51% (0.083 g, 0.272 mmol). Deuterium incorporation: ^1H NMR δ 4.04 (benzylic, 75%), 5.02 (*R**,*S** isomer, ortho, 25%), 4.53 (*R**,*R** isomer, ortho, ≤2%); ^2H NMR (C_6H_6 spiked with C_6D_6) δ 5.02 (s, 1 D, ortho), 4.04 (s, 1 D, $CD(CH_3)OCH_2$). The synthesis was repeated using 11 (0.280 g, 0.920 mmol), *sec*-butyllithium (0.45 mL, 0.59 mmol) at −40 °C, and CH_3OD (26.3 μL, 0.648 mmol) at −40 °C, yield 60% (0.168 g, 0.552 mmol as yellow crystals). Deuterium incorporation: ^1H NMR δ 4.04 (benzylic, 22%), δ 5.02 (*R**,*S** isomer, ortho 66%), (other sites 12%); ^2H NMR (C_6H_6 spiked with C_6D_6) δ 5.0 (s, 1 D, ortho), 4.0 (s, 1 D, $CD(CH_3)OCH_2$).

(η^6-2-Phenylpropan-2-ol)$Cr(CO)_3$ (12). The experimental conditions were identical with those used for the synthesis of **7**. Reagents and amounts used are as follows: 2-phenylpropan-2-ol (1.1 mL, 8.3 mmol), $Cr(CO)_6$ (1.8 g, 8.1 mmol), dioxane (50 mL), and THF (5 mL), yield of **12** 28% (0.63 g, 2.3 mmol as yellow crystals); IR (KBr, carbonyl region, cm^{-1}) 1950 (s), 1860 (s); ^1H NMR (C_6D_6) δ 4.94 (d, 2 H, $J = 6.90$ Hz, *o*-Ar), 4.43 (t, 1 H, $J = 6.90$ Hz, *p*-Ar), 4.31 (t, 2 H, $J = 6.90$ Hz, *m*-Ar); ^{13}C NMR (C_6D_6) δ 233.87 ($Cr(CO)_3$), 93.29 (Ar), 91.61 (Ar), 90.91 (Ar), 83.86 (ipso Ar), 70.28 ($C(CH_3)_2$), 31.32 ($C(CH_3)_2$); MS, *m*/*e* 272 (M^+), 188 ($M^+ - 3CO$), 170 ($M^+ - 3CO - H_2O$), 91 (tropylium$^+$), 77 ($M^+ - Cr(CO)_3 - CH_3C(OH)CH_3$; HRMS *m*/*e* calcd for $C_{12}H_{12}CrO_4$ $M^+ = 272.0136$, found; $M^+ = 272.0147$.

(η^6-2-Phenyl-2-propyl methyl ether)$Cr(CO)_3$ (13). The experimental conditions were identical with those used for the synthesis of **8**. Reagents and amounts used are as follows: **12** (0.63 g, 2.3 mmol), NaH (50%, 0.155 g, 3.23 mmol) THF (30 mL), and CH_3I (0.20 mL, 3.23 mmol), yield of **13** 61% (0.404 g, 1.41 mmol); IR (KBr, carbonyl region, cm^{-1}) 1950 (s), 1860 (s); ^1H NMR (C_6D_6) δ 4.98 (d, 2 H, $J = 6.9$ Hz, *o*-Ar), 4.49 (dd, 1 H, $J = 6.90$ Hz, $J = 6.00$ Hz, *p*-Ar), 4.32 (dd, 2 H, $J = 6.9$ Hz, $J = 6.0$ Hz, *m*-Ar), 2.93 (s, 3 H, $C(CH_3)_2OCH_3$), 1.11 (s, 6 H, $C(CH_3)_2OCH_3$); ^{13}C NMR (C_6D_6) δ 233.60 ($Cr(CO)_3$), 93.61 (Ar), 92.32 (Ar), 89.86 (Ar), 83.88 (ipso Ar), 49.84 (OCH_3), 26.92 (CH_3); MS, *m*/*e* 286 (M^+), 255 ($M^+ - OCH_3$), 230 ($M^+ - 2CO$), 170 ($M^+ - HOCH_3 - 3CO$); HRMS *m*/*e* calcd for $C_{13}H_{14}CrO_4$ $M^+ = 286.0292$, found $M^+ = 286.0289$.

(η^6-{$(MeO)C(Me)(CH_2D)$}C_6H_5)$Cr(CO)_3$ (14). The experimental conditions were similar to those used in the synthesis of **9**. Reagents, amounts, and special conditions used are as follows: **13** (0.200 g, 0.698 mmol), *sec*-butyllithium (0.59 mL, 0.77 mmol) at −40 °C, and CH_3OD (34 μL, 0.845 mmol) at −40 °C, yield of **14** 25% (0.050 g, 0.17 mmol as yellow crystals). Deuterium incorporation: ^1H NMR δ 1.1 (homobenzylic position, ≥98%); ^2H NMR (C_6H_6 spiked with C_6D_6), δ 1.1 (s, 1 D, $C(CH_3)CH_2D)OCH_3$).

(η^6-2-Phenyl-2-propyl methoxymethyl ether)$Cr(CO)_6$ (15). The experimental conditions were identical with those used for synthesis of **10**. Reagents and amounts used are as follows: **12** (0.885 g, 3.25 mmol), NaH (50%, 0.17 g, 3.54 mmol), $ClCH_2OCH_3$ (0.27 mL, 3.58 mmol), yield of **15** 36% (0.366 g, 1.16 mmol as yellow crystals); IR (KBr, carbonyl region, cm^{-1}) 1940 (s), 1855 (s); ^1H NMR (C_6D_6) δ 5.00 (d, 2 H, $J = 6.42$ Hz, *o*-Ar), 4.55 (s, 2 H, *m*-Ar), 3.14 (s, 3 H, OCH_3), 1.23 (s, 6 H, $C(CH_3)_2O$); ^{13}C NMR δ 233.55 ($Cr(CO)_3$), 118.42 (ipso Ar), 93.58 (Ar), 92.24 (OCH_2O), 91.40 (Ar), 89.76 (Ar), 75.28 ($C(CH_3)_2$), 55.19 (OCH_3), 28.23 $(CCH_3)_2$; MS, *m*/*e* = 316 (M^+), 255 ($M^+ - OCH_2OCH_3$), 170 ($M^+ - 3CO - HOCH_2OCH_3$), 91 (tropylium ion); HRMS *m*/*e* calcd for $C_{14}H_{16}CrO_5$ $M^+ = 316.0398$, found $M^+ = 316.0387$.

(η^6-{$(MeOCH_2O)C(CH_3)_2$}C_6H_5)$Cr(CO)_3$-*d*$_1$ (16). The experimental conditions were similar to those used for synthesis of **9**. Reagents, amounts, and special conditions used are as follows: **15** (0.368 g, 1.16 mmol), *sec*-butyllithium (0.98 mL, 1.28 mmol) at −40 °C, CH_3OD (18.5 μL, 1.28 mmol) at 40 °C, yield of **16** 30% (0.112 g, 0.353 mmol). Deuterium incorporation: ^1H NMR δ = 5.0 (ortho sites ≥98%); ^2H NMR (C_6H_6 spiked with C_6D_6) δ = 5.0 (s, 2 D, *o*-Ar).

***N*-Methyl-*N*-isopropyl-2-phenylpropylamine (17).** In a Schlenk flask (100 mL), 2-phenylpropylamine (6.0 mL, 0.164 mmol), glacial acetic acid (95 mL), and acetone (12.0 mL, 0.164 mmol) were stirred for 1 h at 25 °C. The solution was cooled to 0 °C followed by slow addition of $NaBH_4$ (3.13 g, 0.083 mmol) and then stirred for 1.5 h. The resulting solution was dissolved in 300 mL of distilled water, rendered alkaline by slow addition of solid NaOH, extracted with 5 × 60 mL of diethyl ether, and dried over Na_2SO_4. The etheral solution was concentrated in vacuo to yield a slightly yellow oil, *N*-isopropyl-2-phenylpropylamine, which was immediately used in the synthesis of **17**. No yield was determined; ^1H NMR (C_6D_6) δ 7.30–7.20 (m, 5 H, Ar), 2.78 (dq, 1 H, $J = 5.40$ Hz, $CH(CH_3)CH_2N$), 2.67 (AB, 2 H, $J_{AB} = 4.95$ Hz, $\Delta\nu = 6.45$ Hz, $CH(CH_3)CH_2N$), 2.60 (sep, 1 H, $J = 6.3$ Hz, $NCH(CH_3)_2$), 1.19 (d, 3 H, $J = 7.20$ Hz, $CH(CH_3)CH_2$), 0.92 (d, 3 H, $J = 5.40$ Hz, $N(CH_3)_2$), 0.87 (d, 3 H, $J = 6.89$ Hz, $N(CH_3)_2$. The procedure used by Clarke et al.[30] was adopted in the synthesis of **17**. The reagents and amounts used are as follows: *N*-isopropyl-2-phenethylamine from previous synthesis, formic acid (90%) 9.97 g, 0.195 mol), and formaldehyde (37%, 6.4 mL, 0.986 mmol, yield of **17** 87.3% after distillation by Kugelrohr apparatus, 75 °C at 5 Torr (6.85 g, 0.036 mmol as a colorless oil); ^1H NMR (C_6D_6) δ 7.09–7.25 (m, 5 H, Ar), 2.78 (dq, 1, $CH(CH_3CH_2)$, 2.68 (sep, 1 H, $J = 6.1$ Hz, $NCH(CH_3)_2$), 2.34 (AB, 2 H, $J_{AB} = 4.95$ Hz, $\Delta\nu$ 6.43 Hz, CH_2N), 2.10 (s, 3 H, $N(CH_3)$) 1.28 (d, 3 H, $J = 8.10$ Hz, $CH(CH_3)CH_2$), 0.89 (d, 3 H, $J = 6.00$ Hz, $N(CH_3)_2$), 0.85 (d, 3 H, $J = 6.00$ Hz, $N(CH_3)_2$); ^{13}C NMR (C_6D_6) δ 146.82 (ipso Ar), 128.52, 127.67, 126.26 (Ar), 61.52 (CH_2N), 54.26 ($C_6H_5CH(CH_3)$), 38.95 ($C_6H_5CH(CH_3)$), 37.32 (NCH_3), 19.68 ($NCH(CH_3)_2$), 17.68, 18.12 $(NCH(CH_3)_2$.

(η^6-*N*-Methyl-*N*-isopropyl-β-phenylpropylamine)$Cr(CO)_3$ (18). The experimental conditions were identical with those used for the synthesis of **7**. Reagents and amounts used are as follows: **17** (3.0 g, 15.7 mmol), $Cr(CO)_6$ (4.0 g, 18.2 mmol), and dioxane (100 mL), THF (10 mL), yield of **19** 10% (0.510 g, 1.59 mmol as yellow crystals that melt at room temperature); ^1H NMR (C_6D_6) δ 4.72 (d, 1 H, $J = 6.00$ Hz, *o*-Ar), 4.60 (d, 1 H, $J = 6.00$ Hz, *o*-Ar), 4.55–4.40 (m, 3 H, *m*,*p*-Ar), 2.45 (sep, 1 H, $J = 6.00$ Hz, $NCH(CH_3)_2$), 2.21 (dq, 1 H, $CH(CH_3)CH_2$), 2.0 (d, 2 H, $J = 6.30$ Hz, CH_2N), 1.01 (d, 3 H, $J = 6.90$ Hz, $CH(CH_3)CH_2$), 0.75 (d, 3 H, $J = 6.00$ Hz, $NCH(CH_3)_2$), 0.70 (d, 3 H, $J = 6.90$ Hz, $NCH(CH_3)_2$).

(η^6-{$(CH_3)(Pr)NCH_2CH(CH_3)$}C_6H_5)$Cr(CO)_3$-*d*$_1$ (19). The experimental conditions were similar to those used for the synthesis of **9**. Reagents and amounts used are as follows: **18** (0.160 g, 0.489 mmol), *tert*-butyllithium (0.32 mL, 0.54 mmol) at −40 °C, CH_3OD (30 μL, 0.73 mmol) at −40 °C. Deuterium incorporation: ^1H NMR δ 4.72 (ortho, 9.1%), 4.55–4.40 (meta and para, 67.2%), 2.21 (benzylic, 23.7%); ^2H NMR (C_6H_6 spiked with C_6D_6) δ = 4.95 (s 1 H, $CD(CH_3)CH_2$).

18 (0.150 g, 0.458 mmol), *sec*-butyllithium (0.40 mL 0.53 mmol) at −78 °C, and CH_3OD (28 μL, 0.69 mmol) at −50 °C; no deuterium incorporation was observed. ^2H NMR (C_6H_6 spiked with C_6D_6): no resonances were detected.

(η^6-1-Phenylethyl triphenylsilyl ether)$Cr(CO)_3$ (20). The experimental conditions were identical with those used for synthesis of **10**. Reagents and amounts used are as follows: **7** (1.95 g, 7.55 mmol), NaH (50%, 0.40 g, 8.33 mmol), $(Ph)_3SiCl$ (2.45 g, 8.30 mmol), yield of **20** 13% (0.500 g, 0.97 mmol as yellow crystals); ^1H NMR (C_6D_6) δ 7.77 (d, 6 H, Si(*o*-Ar)), 7.22 (t, 9 H, Si(*m*,*p*-Ar)), 5.06 (d, 2 H, $J = 6.3$ Hz, *o*-Ar), 4.50 (q, 1 H, $J = 6.3$ Hz, $CH(CH_3)$), 4.46–4.32 (m, 4 H, *m*,*p*-Ar), 1.15 (d, 3 H, $J = 6.3$ Hz, $CH(CH_3)$); ^{13}C NMR (C_6D_6) δ 233.4 ($Cr(CO)_3$) 136.0 (Ar), 134.4 (ipso-Ar), 130.6 (Ar), 128.3 (Ar), 116.4 (ipso Ar), 91.7, 90.6, 90.5 (Ar), 26.3 (CH_3). Anal. Calcd for $C_{29}H_{24}CrO_4Si$: C, 67.43; H, 4.68. Found: C, 66.72; H, 4.53.

(η^6-*m*-{$Ph_3SiOCHMe$}C_6H_5)$Cr(CO)_3$-*d*$_1$ (21). The experimental conditions were similar to those used in the synthesis of **9**. Reagents, amounts, and special conditions used are as follows: **20** (0.434 g, 0.840 mmol), *sec*-butyllithium (0.88 mL, 1.15 mmol) at −40 °C, and CH_3OD (14 μL, 0.97 mmol) at −40 °C, yield of **22** 65% (0.260 g, 0.504 mmol as yellow crystals). Deuterium incorporation: ^2H NMR (C_6H_6 spiked with C_6D_6) δ 4.46–4.32 (meta and para ≥98%).

(η^4,η^2-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)$Cr(CO)_3$ (22 and 23). Typical procedure for a reaction at room temperature: In a Schlenk flask (50 mL), 7 (0.401 g, 1.55 mmol) in THF (25 mL) was cooled to −78 °C, followed by addition of *tert*-butyllithium with stirring (1.56 M in pentane, 2.5 mL, 3.0 mmol). The solution darkened as it warmed to 25 °C. After 10 h, the solution was quenched with an excess amount of 2-propanol. Stirring for an additional 10 h at 25 °C yielded a crimson solution. The solvent was removed in vacuo, and the crimson residue was taken up in toluene, filtered through a fine glass frit, and concentrated to yield a crude product (diastereomeric excess was determined at this point by ^{1}H NMR). Typical diastereomer ratios [S^*,S^*,R^*]:[S^*,S^*,S^*] (**22**:**23**) averaged 10:1.0, while yields averaged 27% (highest yield = 31%). Chromatography on a deactivated alumina column (2.5 cm × 15 cm) using diethyl ether as eluent and crystallization from hexane (−60 °C) yielded crimson needles of **22**, yield = 24% (0.111 g, 0.372 mmol); IR (KBr carbonyl region, cm^{-1}) 1955 (s), 1868 (s); ^{1}H NMR (C_6D_6, 22 °C) δ 4.85 (dd, 1 H, J_{34} = 4.80 Hz, J_{32} = 6.00 Hz, H(3)), 4.67 (dd, 1 H, J_{45} = 6.90 Hz, J_{43} = 4.80 Hz, H(4)), 4.09 (q, 1 H, $J_{\text{Bz-Me}}$ = 6.90 Hz, H(Bz)), 3.62 (d, 1 H, J_{23} = 6.00 Hz, H(2)), 2.43 (dd, 1 H, J_{56} = 6.60 Hz, J_{54} = 6.90 Hz, H(5)), 1.74 (d, 1 H, J_{65} = 6.60 Hz, H(6)), 1.53 (d, 3 H, $J_{\text{Me}-\text{Bz}}$ = 6.90 Hz, Me), 0.44 (s, 9 H, CMe$_3$); ^{13}C NMR (C_6D_6) δ 239.0 (s, Cr(*C*O)$_3$), 235.5 (s, Cr(CO)$_3$), 235.2 (s, Cr(*C*O$_3$), 102.9, 96.0, 94.6, 94.6 (d, J = 181 Hz (Ar), C(2)–C(5)), 85.1 (s, C(1)), 54 (d, J = 172 Hz, *C*HMe), 41.47 (d, J = 134 Hz, *C*H-*t*-Bu), 37.10 (s, *C*(CH$_3$)$_3$), 26.02 (q, J = 130 Hz, C(*C*H$_3$)$_3$), 13.94 (q, J = 128 Hz, Me). Anal. Calcd for $C_{15}H_{18}CrO_3$: C, 60.40; H, 6.08. Found: C, 60.17; H, 6.21. MS, *m/e* 298 (M$^+$), 270 (M$^+$ − CO), 242 (M$^+$ − 2CO), 214 (M$^+$ − 3CO), 157 (M$^+$ = 3CO − Bu^t), 129 (M$^+$ − 3CO − Bu^t − C_2H_4); HRMS calcd M$^+$ = 298.0660, found M$^+$ = 298.0669.

Typical procedure for low-temperature reaction: In a Schlenk flask (25 mL), **10** (524 mg, 1.72 mmol) in Et_2O (15 mL) was cooled to −78 °C, followed by addition of *tert*-butyllithium (1.56 M in pentane, 1.18 mL, 2.06 mmol) with stirring. The solution immediately darkened. The solution was allowed to warm to −50 °C and stirred for 1 h followed by quenching with methyl alcohol (0.63 mL, 15.5 mmol). The solution was allowed to warm slowly to 25 °C over 1 h, resulting in a crimson solution. The solvent was removed in vacuo, and the crimson residue was take up in toluene, filtered through a fine glass frit, and concentrated to yield a crimson oil. Typical diasteromeric ratios [S^*,S^*,R]:[S^*,S^*,S^*] (**22**:**23**) averaged 0.84:1.0, while yields averaged 35% (highest yield 37%).

(η^4,η^2-2-Phenylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (24 and 25). The experimental conditions were identical with those used for the synthesis of **22** and **23**. Reagents and amounts used are as follows: **7** (0.513 g, 1.99 mmol) and phenyllithium (1.98 M in a solution of cyclohexane/diethyl ether, 2.6 mL, 5.1 mmol), yield of **24** and **25** 20% (0.142 g, 0.394 mmol as a semisolid crimson material); ^{1}H NMR indicated a diastereomeric ratio of 2.3:1.0% ^{1}H NMR major isomer (C_6D_6, 22 °C) δ 7.45 (d, 2 H, *o*-Ar), 7.21 (dd, 2 H, *m*-Ar), 7.18 (dd, 1 H, *p*-Ar), 5.38 (d, 1 H, H(3)), 4.74 (dd, 1 H, H(4)), 4.27 (q, 1 H, H(7)), 3.08 (d, 1 H, H(2)), 2.07 (dd, 1 H, H(5)), 1.86 (d, 1 H, H(6)), 1.53 (d, 3 H, CH_3); ^{1}H NMR minor isomer (C_6D_6, 22 °C) δ 7.45 (d, 2 H, *o*-Ar), 7.21 (dd, 2 H, *m*-Ar), 7.18 (dd, 1 H, *p*-Ar), 5.52 (d, 1 H, H(3)), 4.80 (dd, 1 H, H(4)), 4.17 (q, 1 H, H(7)), 3.63 (d, 1 H, H(2)), 2.58 (dd, 1 H, H(5)), 1.90 (d, 1 H, H(6)), 1.54 (d, 3 H, CH_3).

Crystallographic Studies. The general procedures for both structure characterizations are outlined here: Suitably sized crystals of the two compounds were mounted on glass fibers by using epoxy glue. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 45.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.37°, with a takeoff angle of 6.0°. Scans of (1.63 ± 0.30 tan θ)° were made at a speed of 4.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans), and the counts were accumulated to assure good counting statistics. The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{\text{C-H}}$ = 0.95 Å) and were assigned isotopic thermal parameters that were 20% greater than the B_{equ} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was converged with unweighted and weighted agreement factors of $R = \sum||F_o - |F_c||/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]$. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. Details of the structure refinements are outlined below and in Tables VII and VIII.

Table VII. Summary of Crystal Data for (η^6-[R^*,R^*]-*o*-(Ph_2P){(Me_2N)CHMe}C_6H_4)Cr(CO)$_3$ (5a)

empirical formula	$CrPO_3NC_{24}H_{24}$
formula wt	457.43
cryst syst	monoclinic
lattice params	
a, Å	14.056 (4)
b, Å	9.730 (3)
c, Å	17.736 (5)
α, deg	105.78 (2)
V, Å^3	2334 (1)
space group	$P2_1/c$ (no. 14)
Z	4
D_{calc}, g/cm^3	1.30
F_{000}	952
$\mu_{\text{Mo K}\alpha}$, cm^{-1}	5.67
diffractometer	Rigaku AFC5R
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromated
temp, °C	23
$2\theta_{\max}$, deg	45.0
no. of observns ($I > 3\sigma(I)$)	1434
no. variables	280
residuals R, R_w	0.044, 0.051
GOF indicator	1.10
max shift in final cycle	0.01
largest peak in final diff map, e^2/Å^3	0.25

Table VIII. Summary of Crystal Data for (η^4,η^2-[S^*,S^*,R^*]-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (22)

empirical formula	$CrO_3C_{15}H_{18}$
formula wt	298.30
cryst syst	monoclinic
lattice params	
a, Å	13.457 (4)
b, Å	8.505 (2)
c, Å	14.350 (2)
α, deg	112.92 (2)
V, Å^3	1512.9 (7)
space group	$P2_1/c$ (no. 14)
Z	4
D_{calc}, g/cm^3	1.31
F_{000}	624
$\mu_{\text{Mo K}\alpha}$, cm^{-1}	7.37
diffractometer	Rigaku AFC5R
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromated
temp, °C	23
$2\theta_{\max}$, deg	45.0
no. of observns ($I > 3\sigma(I)$)	1496
no. variables	172
residuals R, R_w	0.038, 0.050
GOF indicator	1.49
max shift in final cycle	0.00
largest peak in final diff map, e^2/Å^3	0.48

(η-{Ph_2P}{(Me_2N)MeHC}C_6H_4)Cr(CO)$_3$ (5a). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 23 carefully centered reflections in the range 9.04 < 2θ < 19.27°, corresponded to a monoclinic cell. On the basis of the systematic absences $h0l$ for $l \neq 2n + 1$ and $0k0$ for $k \neq 2n + 1$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (no. 14). Of the 3430 reflections that were collected, 3274 were unique (R_{int} = 0.045). The intensities of three representative reflections that were measured after every 150 reflections and remained constant throughout the data collection, indicating that no decay correction was necessary. The linear absorption coefficient for Mo Kα is 4.3 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. This resulted in transmission factors ranging from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects. For a final refinement based on 1434 observed reflections ($I > 3.00r(I)$) and 280 variable parameters, the weighted and unweighted agreement factors were $R = 0.044$ and $R_w = 0.051$. The largest parameter shift in the final cycle was 0.01 times its esd. The standard deviation of an observation of unit weight was 0.93. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to down weight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum peak in the final difference Fourier map corresponded to 0.25 $e^-/Å^3$.

(η^2,η^4-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ (22). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 14 carefully centered reflections in the range $39.73 < 2\theta < 39.98°$, corresponded to a monoclinic cell. On the basis of the systematic absences $h0l$ for $l \neq 2n + 1$ and $0k0$ for $k \neq 2n + 1$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (no. 14). Of the 2239 reflections that were collected, 2135 were unique ($R_{int} = 0.040$). The intensities of three representative reflections that were measured after every 150 reflections and remained constant throughout the data collection, indicating that no decay correction was necessary. The linear absorption coefficient for Mo Kα is 7.4 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. This resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarization effects. For a final refinement based on 1496 observed reflections ($I > 3.00r(I)$) and 172 variable parameters, the weighted and unweighted agreement factors were $R = 0.038$ and $R_w = 0.050$. The largest parameter shift in the final cycle was 0.00 times its esd. The standard deviation of an observation of unit weight was 1.49. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to down weight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.48, and -0.16 $e^-/Å^3$, respectively.

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Supplementary Material Available: Complete tables of X-ray crystallographic data for **5a** and **22**, including fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (18 pages); tables of observed and calculated structure factors for **5a** and **22** (24 pages). Ordering information is given on any current masthead page.

α-Elimination of Carbon Induced by Manganese

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Unlike the case for the α-methoxycyclobutyl complex of dicarbonyl(η^5-cyclopentadienyl)iron, photolysis of the α-methoxycyclobutyl complex of Mn(CO)$_5$ does not lead to the ring-expanded metallacyclopentenes **27** (from α-elimination of carbon); the dominant products are simply methoxycyclobutene and α-methoxycyclobutanecarboxaldehyde (along with traces of methoxycyclobutane). The same results are found when reaction is induced by either heat or trimethylamine oxide. From the available evidence, these reactions are better explained by CO loss followed by β-hydrogen elimination than by homolysis of the carbon–metal bond followed by radical reactions. In contrast, α-elimination of carbon occurs smoothly when strain relief is increased and methoxycyclobutene formation is retarded by benzannelation. This rearrangement gives the two isomeric cyclic carbene complexes **34** and **35**. The latter does not isomerize to **34** upon heating to 72 °C for 36 h.

Rearrangement of an alkyl or aryl group from a saturated carbon to an electron-deficient iron (α-elimination of carbon)[1,2] appears to normally be thermodynamically unfavorable. However, we have recently found that if the carbene is stabilized by an electron-donating group and if sufficient ring strain is relieved during the rearrangement, the equilibrium between the 16-electron iron and its corresponding alkyl-substituted carbene can be induced to favor the carbene; for example, photolysis of **1**[5,7] or **4**[6] leads cleanly to **3** and **7**, respectively.

The purpose of the work reported herein was to determine if a metal other than iron would induce α-elimination of carbon. For these studies, pentacarbonylmanganese(I) (and derivatives) was selected as the metal system because, when this work was begun, the only published[8] theoretical

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(1) Cf.: Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. For one example of a reaction where the published data are consistent with α-elimination of carbon as one step in the mechanism, see: Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

(2) The reverse of this reaction (carbene migratory insertion) is well documented[3] as are both α-elimination of hydrogen (insertion of electron-deficient transition metal into α-C–H) and its reverse.[4]

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