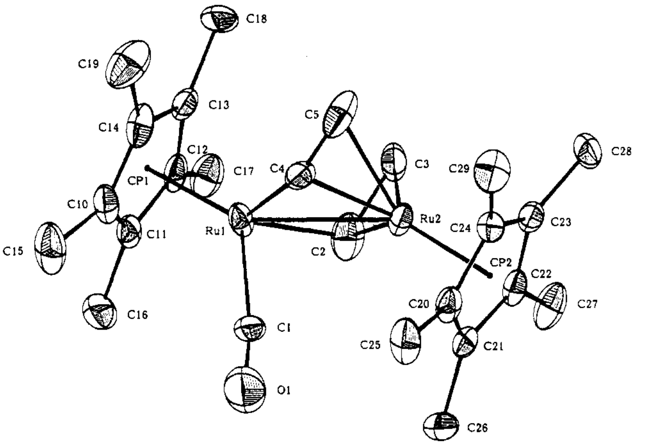

Figure 3. Molecular structure of *trans*-(η^5-C_5Me_5)Ru(CO)($CH{=}CH_2$)$_2$Ru(η^5-C_5Me_5) (**5t**). CP indicates the centroid of a C_5Me_5 ring.

Stirring the solution of **2** in pentane under an atmosphere of hydrogen (1 atm) for 20 h afforded the tetrahydride complex **1** and ethane. No C_2- and C_4-hydrocarbons other than ethane were detected in the volatiles by mass spectrometry.

Evidence of ligand exchange reaction between the coordinated and free ethylene molecules could not be obtained in the magnetization transfer experiment of **2** in the presence of ca. 10-fold excess amount of ethylene in C_6D_6 at 25 °C. However, the ethylene ligand in **2** was smoothly replaced by trimethylphosphine or carbon monoxide (Scheme I).

Treatment of **2** in toluene with 1.2 equiv of trimethylphosphine for 2 h at 50 °C leads to (η^5-C_5Me_5)Ru($CHCH_2$)$_2$(PMe_3)Ru(η^5-C_5Me_5) (**4**) in 91% yield with inversion of the stereochemistry at one of the ruthenium centers.[9] Preliminary results of the X-ray diffraction study of complex **4** show the cis configuration of the C_5Me_5 ligands with respect to the Ru–Ru bond.

Reaction of **2** with carbon monoxide (1 atm) in toluene afforded *trans*-(η^5-C_5Me_5)Ru($CHCH_2$)$_2$(CO)Ru(η^5-C_5Me_5) (**5t**) and its cis isomer **5c** in the 21 and 46% yields, respectively, after purification by column chromatography on Al_2O_3 (Merck Art. 1097).[10] A single-crystal X-ray investigation of **5t** confirmed the proposed structure (Figure 3).[11] A further reactivity study of **2** and a mechanistic study pertaining to the formation of **2** will be reported in due course.

Acknowledgment. Support from the Ministry of Education, Science and Culture of the Japanese Government (No. 63550618) is gratefully acknowledged.

Supplementary Material Available: Tables of mass spectral data, atomic parameters, and bond distances and angles for compounds **2** and **5t** (36 pages); listings of calculated and observed structure factors for compounds **2** and **5t** (49 pages). Ordering information is given on any current masthead page.

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[9] **4**: IR (KBr) 2942, 2896, 2863, 1475, 1417, 1376, 1275, 1259, 1027, 942, 925, 844, 482 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.86 (d, J_{PH} = 8.0 Hz, 9 H, P*Me*$_3$), 1.74 (s, 15 H), 1.76 (s, 15 H), 2.03 (dd, J_{AC} = 10.8 Hz and J_{PC} = 2.7 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.49 (dd, J_{AB} = 6.8 Hz and J_{PB} = 6.7 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.31 (ddd, J_{AB} = 6.8 Hz, J_{AC} = 10.8 Hz and J_{PA} = 4.0 Hz, 2 H, $RuCH_A{=}CH_BH_C$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 10.7 (s, C_5*Me*$_5$), 10.9 (s, C_5*Me*$_5$), 23.0 (d, J_{CP} = 5.2 Hz, P*Me*$_3$), 54.4 (d, J_{CP} = 13.0 Hz, $RuCH{=}CH_2$), 90.1 (s, *C*$_5$Me$_5$), 95.8 (d, J_{CP} = 2.3 Hz, *C*$_5$Me$_5$), 174.2 (d, J_{CP} = 5.2 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, external PPh_3) δ 11.0; mp 178 °C dec. Anal. Calcd for $C_{27}H_{45}PRu_2$: C, 53.81; H, 7.53. Found: C, 53.48; H, 7.91.

[10] **5t**: IR (KBr) 2949, 2941, 1921, 1223, 1022, 904, 759, 479 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.62 (s, 15 H), 1.74 (s, 15 H), 1.93 (dd, J_{AC} = 9.4 Hz and J_{BC} = 1.6 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.55 (dd, J_{AB} = 6.3 Hz and J_{BC} = 1.6 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.50 (dd, J_{AB} = 6.3 Hz and J_{AC} = 9.4 Hz, 2 H, $RuCH_A{=}CH_BH_C$); ^{13}C NMR (C_6D_6) δ 9.6 (q, J_{CH} = 127.2 Hz, C_5*Me*$_5$), 11.1 (q, J_{CH} = 127.0 Hz, C_5*Me*$_5$), 50.0 (dd, J_{CH} = 159.1 and 147.8 Hz, RuCH=*C*H$_2$), 92.1 (s, *C*$_5$Me$_5$), 98.9 (s, *C*$_5$Me$_5$), 177.3 (d, J_{CH} = 162.0 Hz, Ru*C*H=CH$_2$), 202.9 (s, *C*O); mp 172.0 °C dec. Anal. Calcd for $C_{25}H_{36}ORu_2$: C, 54.13; H, 6.54. Found: C, 54.17; H, 6.71. **5c**: IR (KBr) 2941, 2891, 1926, 1237, 1021, 914, 767, 479 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.60 (s, 15 H), 1.68 (s, 15 H), 2.22 (d, J_{AC} = 9.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.58 (d, J_{AB} = 6.4 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.04 (dd, J_{AB} = 6.4 Hz and J_{AC} = 9.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$); ^{13}C NMR (C_6D_6) δ 10.1 (q, J_{CH} = 127.0 Hz, C_5*Me*$_5$), 10.3 (q, J_{CH} = 127.2 Hz, C_5*Me*$_5$), 56.0 (dd, J_{CH} = 143.1 and 160.9 Hz, RuCH=*C*H$_2$), 91.4 (s, *C*$_5$Me$_5$), 98.9 (s, *C*$_5$Me$_5$), 176.6 (d, J_{CH} = 152.2 Hz, Ru*C*H=CH$_2$), 207.4 (s, CO); mp 225.0 °C dec. Anal. Calcd for $C_{25}H_{36}ORu_2$: C, 54.13; H, 6.54. Found: C, 53.74; H, 6.60.

[11] Complex **5t** crystallized from toluene–pentane in the monoclinic system, space group $P2_1/n$, with a = 14.668 (5) Å, b = 16.644 (3) Å, c = 10.087 (4) Å, β = 106.24 (3)°, and Z = 4. Data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the $2° < 2\theta < 60°$ range. The structure was solved by Patterson method and refined by a full-matrix least-squares techniques. The current R value is 0.112 for 4853 independent reflections with $F_o > 5\sigma(F_o)$, and the accuracy of the carbon positions is somewhat low because the intensity data are dominated by the heavy-atom contributions.

Diastereotopic Group Selectivity in the Deprotonation of (η-Arene)$Cr(CO)_3$ Complexes

Joseph A. Heppert,*[†] M. Elizabeth Thomas-Miller,[†] Michael L. Milligan,[†] David Vander Velde,[‡] and Jeffrey Aubé*[‡]

Departments of Chemistry and Medicinal Chemistry
The University of Kansas
Lawrence, Kansas 66045

Received August 12, 1988

Summary: Highly diastereospecific syntheses (de ≥ 94%) of (η-arene)$Cr(CO)_3$ complexes are effected via the group-selective deprotonation of complexes bearing a chiral benzylic directing group. The major diastereomers prepared by this technique are the opposite of those formed in face-selective diastereospecific complexation reactions.

The appeal of transition-metal π-arene reagents in organic synthesis stems from the diverse modifications of arene chemistry exhibited in the metal complexes.[1] Applications of (η-arene)$Cr(CO)_3$ reagents to synthetic problems have included the selective nucleophilic aromatic substitution of arene molecules (deoxyfrenolicin),[1b,2a] regiocontrolled spirocyclization reactions (acorenone-b),[1b,2b] the preparation of highly substituted cyclohexadienone and dihydronaphthalene molecules (daunomycinone and rabelomycin),[2c,d] and the regiospecific substitution of tetralin derivatives at benzylic sites (hydroxycalamene toxins).[2e,f] Recent studies have also demonstrated the potential utility

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[†] Department of Chemistry.

[‡] Department of Medicinal Chemistry.

[1] (a) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Trebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron*, **1981**, *37*, 3957. (b) Semmelhack, M. F. *Pure Appl. Chem.*, **1981**, *53*, 2379. (c) Uemura, M.; Take, K.; Isobe, K.; Minami, T.; Hoyashi, T. *Tetrahedron* **1985**, *41*, 5771. (d) Kundig, E. P. *Pure Appl. Chem.*, **1985**, *57*, 1855.

[2] (a) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.*, **1979**, *101*, 768. (b) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.*, **1980**, *102*, 5926. (c) Uemura, M.; Take, K.; Hayashi, T. *J. Chem. Soc., Chem. Commun.*, 1983, 858. (d) Kundig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.*, **1983**, *105*, 6962. (e) Uemura, M.; Isobe, K.; Hayashi, Y. *Tetrahedron Lett.*, **1985**, *26*, 767. (f) Uemura, M.; Isobe, K.; Hayashi, Y. *Chem. Lett.*, **1985**, 91.

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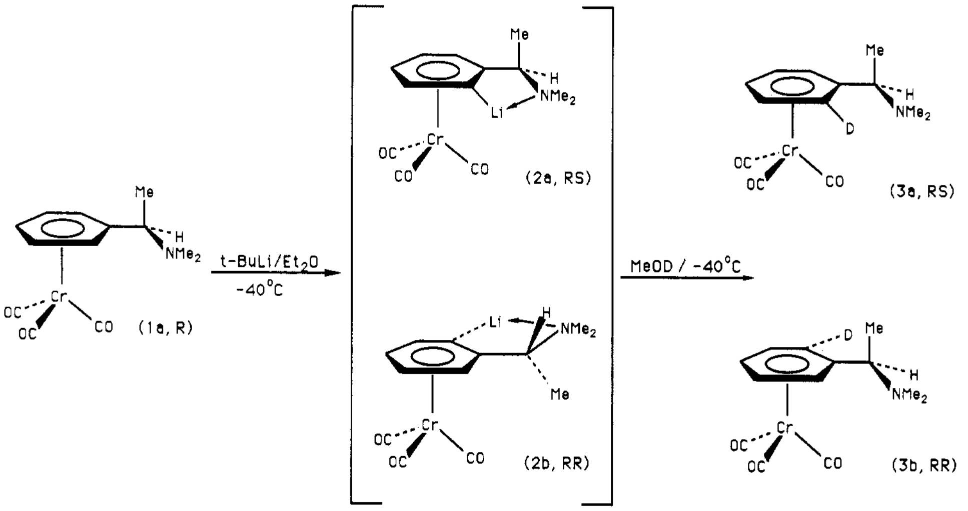
Scheme I



of π-arene chromium complexes as substrates for enantiospecific organic synthesis.[3] Indeed, one of the major obstacles to the further utilization of these reagents in asymmetric synthesis is the relative difficulty of preparing the metal complexes in optically pure form.[4,5] Toward this end, we report a method for the stereoselective introduction of substituents on a complexed arene through the diastereospecific deprotonation of (η-arene)Cr(CO)$_3$ derivatives. There have only been a few reports that describe the synthesis of chiral transition-metal complexes using diastereotopic group selectivity.[6]

In a typical reaction, an ethereal solution of racemic (η-((Me$_2$N)CHMe)C$_6$H$_5$)Cr(CO)$_3$ (**1a**) at -40 °C was treated with 1.2 equiv of *t*-BuLi in hexane (Scheme I). The solution immediately darkened and a yellow-brown precipitate formed. The addition of a small quantity of tetrahydrofuran (THF) to the slurry followed by a single equivalent of methanol-d_1 resulted in the dissolution of the precipitate and the re-formation of a yellow solution. Removal of the solvent in vacuo followed by extraction of the residue with pentanes, and fractional crystallization resulted in the isolation of crystalline (η-((Me$_2$N)CHMe)DC$_6$H$_4$)Cr(CO)$_3$ (**3a**) in 64% yield.[7] A comparison of the ^{1}H NMR spectrum of the starting material (Figure 1a) with the ^{1}H and ^{2}H NMR spectra of the deuteriated product (parts b and c of Figure 1, respectively) indicated that one of the diastereotopic ortho hydrogens had been replaced with a 96% diastereomeric excess (de).

Table I. Product Yields and Diastereotopic Excesses from the Deprotonation of Chiral (η-(XCHMe)C$_6$H$_5$)Cr(CO)$_3$ Complexes (X = NMe$_2$ (a), OCH$_2$OMe (b), OMe (c))

complex	base	electrophile	proposed stereochem[a]	% yield (% de)
1a	*t*-BuLi	MeOD	*R*S**	64 (96)
		MeOSO$_2$F	*R*S**	43 (*b*)
		Me$_3$SiCl	*R*R**[a]	73 (*b*)
		Ph$_2$PCl	*R*R**[a]	50 (*b*)
1b	*sec*-BuLi	MeOD	*R*S**	54 (≥94)
1c	*sec*-BuLi	MeOD	*R*S**	60 (≥96)[c]

[a] This designation represents the proposed stereochemistry of the major product isomer. Changes in the stereochemical notation result solely from changes in the priority of substituents on the product arenes; all of the products are derived by quenching the same mixture of ortholithiated isomers (**2a**) with electrophiles. [b] These yields represent crystalline samples of diastereomerically pure compounds. [c] Complex **1c** exhibited 35% deuterium incorporation into the *pro-S* ortho hydrogen and 65% deuterium incorporation at the benzylic hydrogen.

The complete reaction sequence (Scheme I) proceeds initially to form an insoluble yellow powder that is presumed to be a mixture of the ortholithiated molecules **2a** (*R*S** and *R*R**) in which the former isomer is predominant. These lithiated intermediates are unreactive as a slurry in ether with noncoordinating electrophiles such as Me$_3$SiCl or Ph$_2$PCl but react readily with these reagents either through prior dissolution of the intermediate anion on addition of THF to the slurry, or by isolating the solid by filtration, redissolving it in THF, and adding the desired electrophile. Good yields of crystalline products obtained from the *R*S** ortholithiated isomer were isolated by these methods (Table I).[8] Although no evidence of minor diastereomers was observed in the NMR spectra of the recrystallized products, it is assumed that the limiting purity of the crude product mixture approximates the 96% de

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(3) (a) Uemura, J.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.*, **1986**, *51*, 2859. (b) Uemura, M.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.*, **1987**, *109*, 5277.

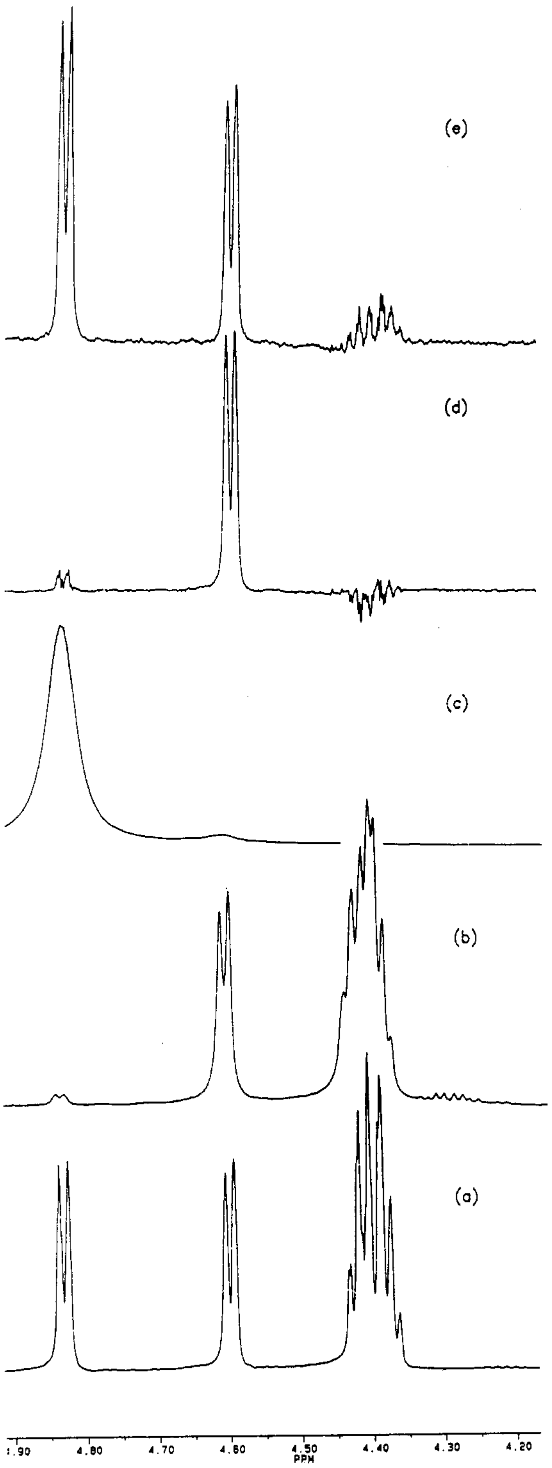
(4) Meyer, A.; Dabaro, R. *J. Organomet. Chem.* **1972**, *36*, C38.

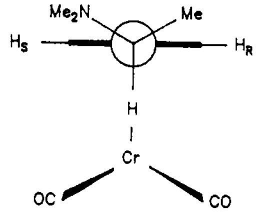
(5) Schloegl, K. *J. Organomet. Chem.* **1986**, *300*, 219.

(6) During the course of our work, a report describing related chemistry appeared: (a) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1805. For related reactions involving chiral ferrocene derivatives, see: (b) Aratani, T.; Gonda, T.; Mozaki, H. *Tetrahedronal Lett.* **1969**, 2265. (c) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffman, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389. (d) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotami, M.; Nagashima, N.; Hamada, Y. Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1151.

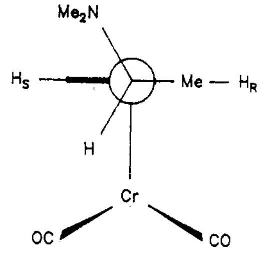
(7) General experimental conditions: *t*-BuLi (0.10 mL of 1.7 *M* in pentane) was added to (η-((Me$_2$N)CHMe)C$_6$H$_5$)Cr(CO)$_3$ (0.300 g) in dry diethyl ether (20 mL) at -40 °C. After 1 h at -40 °C, 5 mL of THF and deaerated MeOD (0.05 mL) were added. The product, primarily (η-(*R*S**)-((Me$_2$N)CHMe)DC$_6$H$_4$)Cr(CO)$_3$ (0.202 g), was isolated by crystallization from hexane and was identified by comparison with ^{1}H NMR and IR spectra of **1a**.

(8) (a) The products and starting materials listed in Table I were identified by ^{1}H, ^{13}C, and ^{31}P (where applicable) NMR spectroscopy, IR spectrophotometry, and mass spectrometry. Satisfactory elemental analysis of the starting reagents and representative products have been obtained. Typical analytical data for (η-(*R*,R**)-*o*-(Me$_2$N)CHMe)-(Ph$_2$P)C$_6$H$_4$)Cr(CO)$_3$: IR (KBr, carbonyl region) 1960 (s), 1883 (s) cm^{-1}; ^{1}H NMR (benzene-d_6, 20 °C) δ 7.55 (t, 2 H), 7.10 (m, 8 H), 4.87 (m, 1 H), 4.65 (t, 1 H), 4.65 (t, 1 H), 4.45 (dq, 1 H), 4.42 (dd, 1 H), 4.20 (t, 1 H), 1.50 (s, 6 H), 0.74 (d, 3 H); ^{13}C {^{1}H} NMR (benzene-d_6, 22 °C) δ 232.9 (s, Cr(CO)$_3$), 137.9, (d, J_{PC} = 103 Hz, i-Ar$_2$P), 138.0 (d, J_{PC} = 81 Hz, i-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, i-Ar), 106.0 (d, J_{PC} = 22 Hz, i-Ar), 100.4, 94.0, 89.3, 87.6 (Ar), 58.8 (d, J_{PC} = 7 Hz, *C*HMe(NMe$_2$)), 37.7 (NMe$_2$), 5.6 (CH*Me*(NMe$_2$)); ^{31}P(^{1}H) NMR (benzene-d_6, 19 °C) δ − 12.11 (s). Anal. Calcd: C, 63.96; H, 5.15; N, 2.98. Found C, 63.73; H, 5.25; N, 2.97. (b) The nomenclature utilized here is that described by Schloegl in ref 5.





(4)



(5)

Figure 1. ^{1}H and ^{2}H NMR and NOE difference spectroscopic study of the deprotonation of **1a**. (a) 500-MHz ^{1}H NMR spectrum of (η-(R*)-(Me_2N)CHMe)C_6H_5)Cr$(CO)_3$ (**1a**). (b) ^{1}H NMR spectrum of (η-(R*S*)-((Me_2N)CHMe)DC_6H_4)Cr$(CO)_3$. (c) 76-MHz ^{2}H NMR spectrum (η-(R*S*)-((Me_2N)CHMe)DC_6H_4)Cr$(CO)_3$. (d) 500-MHz ^{1}H NOE difference spectrum of **1a** irradiating the benzylic methyl resonance. (e) ^{1}H NOE difference spectrum of **1a** irradiating the Me_2N resonance.

of the initial deprotonation reaction.

Arene chromium substrates that utilize an oxygen-containing side chain as a chiral benzylic directing group, such as methoxymethyl 1-phenylethyl ether (**1b**) and methyl 1-phenylethyl ether (**1c**), also exhibit highly diastereospecific deprotonation reactions (Table I). The deprotonation of **1b** with *sec*-BuLi produces 66% deprotonation at the two ortho hydrogen sites, with at least a 94% de favoring the ortho hydrogen similar to that which is removed from **1a**.[8] A significant amount of deprotonation at the benzylic site (22% deuterium incorporation) and at the $-OCH_2O-$ hydrogens was also observed. The treatment of **1b** with *t*-BuLi, in contrast, results principally in substitution at the aromatic ring, with only minor observable products derived from deprotonation reactions at the arene ring or side chain. Significantly, all of the favored diastereoisomers synthesized in this study are the opposite of the isomers produced in Uemura's diastereoselective complexation reactions.[3,9] Thus, it is possible to obtain

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[9] The diastereomeric configuration of (η-(R*R*)-o-(Me_2NCHMe)-(Ph_2P)C_6H_4)Cr$(CO)_3$ has been proved by X-ray analysis. Details will be provided in the full account of this work. We thank Dr. F. Takusagawa for carrying out the X-ray study.

either diastereomeric configuration by simply reversing the order of the aryl ortho substitution and metal complexation reactions.

We anticipated that, by analogy to the previously observed ferrocene deprotonations, the source of the diastereoselectivity observed in these reactions should lie in the existence of a preferred rotamer about the benzylic arene carbon bond in which both the X and methyl groups occupy positions anti to the bulky $Cr(CO)_3$ unit (4). Difference NOE ^1H spectra of **1a** provided clearer evidence for this effect. The irradiation of the α-methyl substituent of **1a** (Figure 1d) caused a 7% NOE enhancement exclusively at the ortho hydrogen that is not removed by *t*-BuLi. Irradiation of the Me_2N group of **1a** (Figure 1e) resulted in 6% and 4% enhancements of the diastereotopic ortho hydrogens, respectively, with the larger effect being evident at the hydrogen which is removed by *t*-BuLi. These results suggest that the preferred conformer of **1a** probably results from a close approach of the benzylic methyl substituent to the plane of the arene ring, placing the Me_2N group approximately 60° above the plane of the arene in a proximate position to both of the ortho hydrogens (5). The closer proximity of the Me_2N unit to the *pro-S* hydrogen should still account for the selective delivery of the complexed lithium reagent to this site over the alternate *pro-R* hydrogen site. Similar correlations of solution conformational preference as determined by NOE difference spectroscopy can be used to account for the formation of the preferred diastereomers from **1b** and **1c**.

We are continuing our investigations on the steric and electronic influences on the selectivity of these deprotonation reactions and are studying potential applications of these procedures to synthetic problems.

Acknowledgment. J.A.H. thanks Research Corp. for a Cottrell Research Grant and the University of Kansas Biomedical Research Fund (#4715-0711) for support of this project.

Additions and Corrections

Eluvathingal D. Jemmis* and A. Chandrasekhar Reddy: Electronic Structure of Triple-Decker Compounds with P_5, P_6, As_5, and C_nH_n as Middle Rings. 1988, *7*, 1561.

In the fifth and sixth lines of the first paragraph, "$C_3B_2H_5$" should be replaced by "$C_2B_3H_5$".

Compound number 8 in Table I should be CpCo($C_2B_3R_5$)CoCp instead of CpCo($C_3B_2R_5$)CoCp.

Reference 9 should include the following: (c) Robinson, W. T.; Grimes, R. N. *Inorg. Chem.* **1975**, *14*, 3056. (d) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10.

Book Reviews

Organometallic Chemistry Reviews. Journal of Organometallic Chemistry Library 20. Edited by A. G. Davies, E. O. Fischer, and O. A. Reutov. Elsevier, Amsterdam. 1988. 365 pp. Dfl. 295; $155.25.

This newest addition to the *Journal of Organometallic Chemistry Library* brings five topical reviews, three of them by Russian authors.

Organic and organometallic carborane chemistry in which the action is at the carbon atoms has been a very active field over the past 25 years. The chemistry thus generated could fill several Gmelin volumes. However, much chemistry can take place at the boron atoms of the C_2B_{10} cage, and the review by Grushin, Bregadze, and Kalinin deals with the interesting area of carboranes containing boron–element bonds. Much of the work reviewed, having been published in Russian in Russian journals, will be unfamiliar to Western readers, and so it is good to have this work summarized in English.

The review on "Pyridine and Quinoline Derivatives of Group IVB Elements" by Lukevics and Segal is so specialized that it will be of interest to only few of our readers, yet this has been a busy field: 142 pages (423 references) are required to summarize it. The next review by Goldberg, Dirnens, and Lukevics on "Phase Transfer Catalysis in Organosilicon Chemistry" will be of greater general interest considering the diversity of organosilicon reactions that can be facilitated by this approach.

If you are into rhenium, then the chapter by C. E. Holloway, on "Rhenium Carbonyl and Organometallic Coumpounds. Analysis and Classification of Crystallographic and Structural Data" with its extensive tables and many figures will be of interest and of some use to you. If not, go on to the last chapter, by J. Klapötke and H. Köpf on metallocenedichalcogenolene complexes. This review (in German) includes and extends the topic of metallocenedithiolene chemistry. It is short (22 pages, 59 references) and brings some useful information for those interested in metal complexes of chalcogen ligands.

The main problem with this book is its price: $155.25 seems rather expensive for a collection of photoreproduced typescripts.

Dietmar Seyferth, *Massachusetts Institute of Technology*