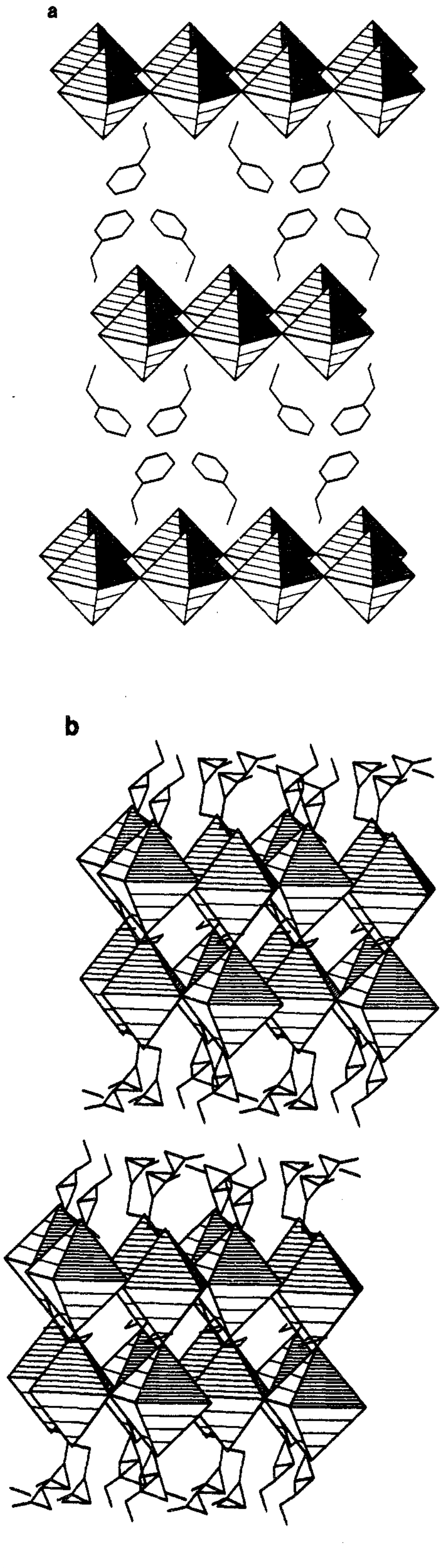

Figure 2. Representations of the layered structures $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$. Only one set of disordered iodide ions is shown for each structure, and a single component of the disordered phenethylammonium cation is shown in Figure 2a. Selected distances (Å) and angles (deg) are given. (a) Compound **1**, $n = 1$, "monolayer": $Pb-I_{bridge}$, 3.158 (1), 3.178 (1); $Pb-I_{terminal}$, 3.204 (1); $I_{terminal}-Pb-I_{terminal}$, 180; $I_{bridge}-Pb-I_{bridge}$, 89.45 (3), 180; $I_{terminal}-Pb-I_{bridge}$, 88.65 (1), 90.91 (2); $I_{bridge}-Pb-I'_{bridge}$, 26.67 (4), 27.79 (3); Pb–I–Pb, 152.21 (4), 153.33 (4). (b) Compound **2**, $n = 2$, "bilayer": $Pb-I_{terminal}$, 3.130 (3), 3.138 (3); $Pb-I_{bridge,interplane}$, 3.263 (3), 3.272 (3); $Pb-I_{bridge,intraplane}$, 3.161 (2)–3.189 (2); $I_{terminal}-Pb-I_{interplane}$, 177.0 (1), 177.2 (1); $I_{terminal}-Pb-I_{intraplane}$, 89.07 (7)–93.86 (7); $Pb-I_{interplane}-Pb$, 180 (1); $Pb-I_{intraplane}-Pb$, 154.9 (1)–156.9 (1).

perovskite structure of $(MeNH_3)PbX_3$, providing a possible means of stabilizing colloidal "perovskite-type" lead halo complexes, which we will pursue elsewhere.

Registry No. 1, 131457-08-4; **2**, 131457-10-8; $[Me(CH_2)_8NH_3]_2PbI_4$, 102190-35-2; $[Me(CH_2)_9NH_3]_2PbI_4$, 121718-82-9; $[Me(CH_2)_8NH_3]_2(MeNH_3)Pb_2I_7$, 131457-11-9; $[Me(CH_2)_9NH_3]_2(MeNH_3)Pb_2I_7$, 131457-12-0; $[Me(CH_2)_8NH_3]_2PbBr_4$, 131457-13-1; $[Me(CH_2)_8NH_3]_2(MeNH_3)Pb_2Br_7$, 131489-29-7; $[Me(CH_2)_8NH_3]_2(MeNH_3)Pb_3Br_{10}$, 131457-15-3; $[Ph(CH_2)_2NH_3]_2PbBr_4$, 131457-16-4; $[Me(CH_2)_8NH_3]_2PbCl_4$, 131457-17-5; $[Ph(CH_2)_2NH_3]_2PbCl_4$, 131457-18-6.

Supplementary Material Available: Tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles and alternative views of the structures of compounds **1** and **2** (9 pages); tables of F_{obsd} and F_{calcd} for compounds **1** and **2** (15 pages). Ordering information is given on any current masthead page.

Developing Molecular Fischer–Tropsch Type Chemistry: The Triethylboron-Catalyzed Oligomerization of CO-Derived Methylene Groups from a (η^2-Formaldehyde)zirconocene Dimer

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The search for alternative routes to petrochemical products has remained a great challenge over the years. Investigations toward developing variations of the Fischer–Tropsch reaction for, e.g., selectively producing hydrocarbons from CO and hydrogen have been of great interest in this respect.[1] There is convincing evidence that the essential carbon–carbon coupling steps can be described as a chemistry of methylene units at the heterogeneous Fischer–Tropsch catalyst surface.[2] We have recently begun to develop the chemistry of homogeneous model systems which mimic some important aspects of this "CH_2-on-a-surface chemistry" using metallaoxirane complexes containing $[Cp_2\overline{ZrOC}H_2]$ units.[3] These molecular entities contain carbon monoxide derived CH_2 groups which often behave as methylene units being attached to a supporting metal oxide framework. We here report a novel reaction whereby these CO-derived methylene groups are catalytically removed from the metal oxide type carrier and oligomerized in a homogeneous system similar to what may be taking

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(1) (a) E. L. Muetterties noted that "a so-called selective Fischer–Tropsch synthesis, an unknown element today (with the possible exception of polymethylene synthesis) but a desirable technological achievement, will be mechanistically differentiable from the Fischer–Tropsch synthesis and should receive a distinctive name when discovered". Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) For selected reviews, see: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. Rofer-De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 441. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. See also: Henrici-Olivé, G.; Olivé, S. *Angew. Chem.* **1976**, *88*, 144; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(2) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97; *Chem. Ber.* **1926**, *59*, 830. Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181; **1981**, *103*, 1287.

(3) (a) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447. Review: Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. See also: Erker, G.; Czisch, P.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem.* **1986**, *98*, 356; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 364. Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (b) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (c) Erker, G.; Hoffmann, U.; Zwettler, R.; Betz, P.; Krüger, C. *Angew. Chem.* **1989**, *101*, 644; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630. Erker, G.; Hoffmann, U.; Zwettler, R.; Krüger, C. *J. Organomet. Chem.* **1989**, *367*, C15. Erker, G.; Sosna, F.; Hoffmann, U. *J. Organomet. Chem.* **1989**, *372*, 41.

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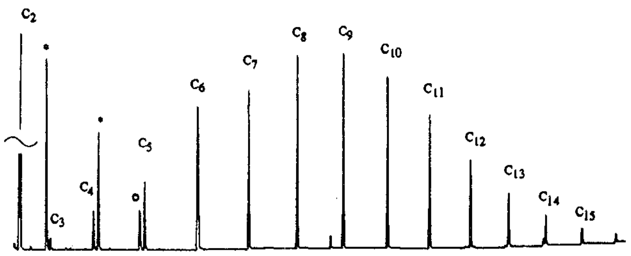
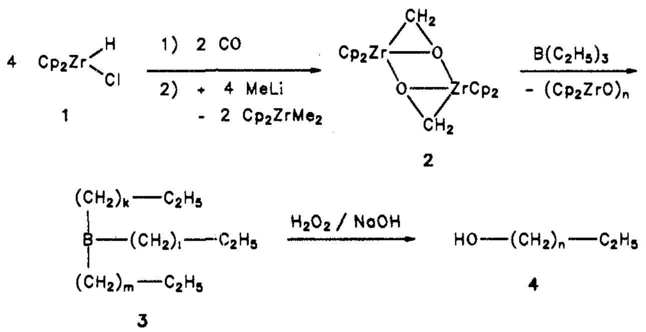


Figure 1. Gas chromatogram (Carbowax 20 M capillary column, temperature programmed: 4 °C/min) of the mixture of primary alcohols [ethanol (C_2) and propanol (**4a**) (C_3) to pentadecanol (**4m**) (C_{15})] obtained from the reaction between **2** and BEt_3 (conditions similar to those of experiment VII) and subsequent oxidative workup; (O) is cyclopentadiene; (*) denotes unidentified additional stoichiometric reaction products.

place during poly(methylene) formation[4] at heterogeneous Fischer–Tropsch contacts.

In the (η^2-formaldehyde)zirconocene dimer **2**, two CO-derived methylene groups are attached edge-bridging to a central four-membered Zr_2O_2 metal oxide framework which is stabilized and solubilized by saturating the remaining valence positions at zirconium with η^5-Cp ligands. Complex **2** was prepared in a simple two-step reaction sequence by hydrozirconation of carbon monoxide, followed by treatment with methyllithium as previously described.[3c]



Complex **2** was reacted with substoichiometric quantities of triethylboron (Figure 1). In a typical experiment (experiment IV) a solution of 0.4 mmol of BEt_3 in 2 mL of tetrahydrofuran was added to 1.1 g (2.1 mmol) of **2** in tetrahydrofuran at −70 °C and the mixture was then allowed to warm to ambient temperature. A yellowish precipitate, which presumably consisted of the insoluble oligomeric zirconocene oxide $[Cp_2ZrO]_x$,[5] was isolated by filtration. The filtrate contained a very complicated mixture of trialkylboron products (**3**), which was oxidatively degraded by treatment with alkaline hydrogen peroxide to give a series of linear primary alcohols $HO(CH_2)_nC_2H_5$ (**4**). GLC analysis revealed the formation of a mixture of alkanols **4** ranging from 1-propanol (**4a**) to 1-undecanol (**4i**) for this specific experiment.[6]

Some ethanol was also found (here ca. 17%) indicating the presence of a fraction of unreacted BC_2H_5 groups in the primary product mixture. In this experiment, the products 1-propanol to 1-undecanol (**4a–i**) were formed in an approximate ratio of 4:10:15:18:17:15:11:6:3. This sequence can be described by a Poisson distribution for the product mole fractions $N_x/N_0 = e^{-\upsilon}\upsilon^{x-1}/(x-1)!$ (with $x = n + 1$ and υ indicating the number of monomers consumed per active catalyst center)[7a] (Figure 2). A good correlation is found for $\upsilon = 4.9$ (the calculated **4a–i** ratio is 3.8:9.3:15.1:18.6:18.2:14.9:10.4:6.4:3.5), which corresponds nicely with the molar ratio of the two starting components $[Cp_2Zr(CH_2O)]_2$ (**2**) and BEt_3 which were employed in this reaction in an approximate ratio of 5:1.

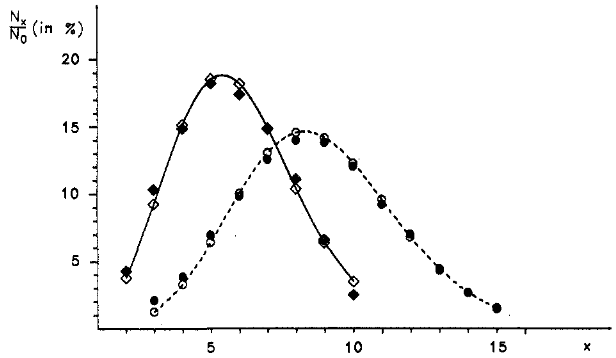
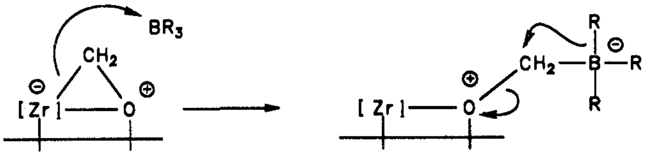


Figure 2. 1-Alkanol distributions [1-propanol (**4a**, $x = 2$) to 1-hexadecanol (**4n**)] obtained from experiments IV (◆) and VII (●). The open symbols ◇ and ○ denote N_x/N_0 values calculated for Poisson distributions with $\upsilon = 4.9$ and 7.8, respectively.

With a decreasing **2**:BEt_3 ratio (experiments III to I) the N_x/N_0 maximum of the Poisson function shifts considerably to lower x numbers. With increasing **2**:BEt_3 ratios (experiments V to VII) the N_x/N_0 vs x distribution curve gets broader and has its maximum ordinate values shifted to the right. In all cases the calculated υ values seem to qualitatively parallel the initial molar (formaldehyde)zirconocene dimer to catalyst concentration ratios.[8] This indicates living oligomerization behavior with most boron centers being active right from the beginning of the reaction. Accordingly, the ratio of the molecular weight to number averages [calculated as $M_w/M_n = 1 + \upsilon/(\upsilon + 1)^2$][7] decreases with an increasing degree of oligomerization (DO = υ + 1) and appears to converge to a limiting value of unity.[7b]

We assume that the methylene insertion into the boron–carbon bond requires a precoordination of complex **2** to the BEt_3 catalyst. An oxonium ylide type reactivity of the zirconium oxide bound methylene unit may explain this reaction pattern.[9]



The described reactions indicate that it may be worthwhile to investigate the potential role of electrophilic catalyst components in controlling selectivity in the heterogeneous Fischer–Tropsch reaction as well. Especially the features of boron-containing contacts seem to have been looked at only superficially.[10] In

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(4) Falbe, J., Ed. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980. Kugler, E. L., Steffgen, F. W., Eds. Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen. *Adv. Chem. Ser.* **1979**, *178*.

(5) The C,H elemental analysis of the insoluble precipitate (in ca. 95% yield isolated) corresponds with oligomeric zirconocene oxide (calcd for $C_{10}H_{10}OZr$ C 50.59, H 4.25; found C 50.89, H 4.51).

(6) 1-Alkanols **4** were identified by GLC retention time. From experiment V (see text and ref 8) the main products 1-hexanol and 1-heptanol were isolated by preparative GLC (SE 10 column) and identified by their ^1H and ^{13}C NMR spectra.

(7) (a) Flory, P. *J. Am. Chem. Soc.* **1940**, *62*, 1561. Billingham, N. C. *Comprehensive Polymer Science*; Pergamon Press: New York, 1989; Vol. 3, p 43. (b) The M_w/M_n values observed in experiments I–VII are as follows: 1.25 (I); 1.22 (II); 1.19 (III); 1.14 (IV); 1.13 (V); 1.11 (VI); 1.10 (VII).

(8) Observed (calculated) 1-alkanol product distributions (1-propanol, 1-butanol, etc.) obtained from experiments with varying initial **2**:BEt_3 ratios are as follows (approximate starting **2**:BEt_3 ratios are given in square brackets). Experiment I [1:1]: 57 (58.3), 30 (29.1), 9 (9.7), 4 (2.4); υ(calcd) = 1.0. Experiment II [2:1]: 31 (31.9), 33 (31.9), 20 (21.3), 12 (10.6), 4 (4.3); υ(calcd) = 2.0. Experiment III [3:1]: 20 (18.2), 24 (25.5), 23 (23.8), 17 (16.6), 9 (9.3), 4 (4.3), 2 (1.7), 1 (0.6); υ(calcd) = 2.8. Experiment IV: see text. Experiment V [7:1]: 7 (6.9), 12 (12.5), 15 (16.9), 16 (18.2), 14 (16.4), 11 (12.7), 8 (8.5), 5 (5.1), 3 (2.8); υ(calcd) = 5.4. Experiment VI [8:1]: 3 (2.0), 6 (4.7), 9 (8.5), 12 (12.2), 13 (14.6), 14 (15.1), 13 (13.6), 10 (10.8), 8 (7.8), 6 (5.1), 3 (3.1), 2 (1.7), 1 (0.9); υ(calcd) = 7.2. Experiment VII [10:1]: <1 (<1), 2 (1.3), 4 (3.3), 7 (6.4), 10 (10.0), 13 (13.1), 14 (14.5), 14 (14.2), 12 (12.3), 9 (9.6), 7 (6.8), 4 (4.4), 3 (2.6), 2 (1.5); υ(calcd) = 7.8.

(9) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, 2251. Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. Erker, G.; Schlund, R.; Albrecht, M.; Sarter, C. *J. Organomet. Chem.* **1988**, *353*, C27.

(10) Anderson, R. B. *The Fischer–Tropsch Synthesis*; Academic Press: New York, 1984.

addition, our results suggest that Fischer–Tropsch methylene coupling may lead to new ways of making close to monodisperse poly(ethylene).[11] We are currently checking to see if such a merging interest of the objectives of Fischer–Tropsch and Ziegler–Natta type chemistry can be experimentally realized.

Acknowledgment. Financial support by the Fonds der Chemischen Industrie and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

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(11) See for a comparison: Shapiro, P. J.; Bund, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

Evidence for Gated Stereodynamics in [1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]chromium Tricarbonyl

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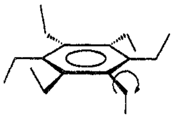
Networks of cooperative nonbonded interactions often lead to restricted motions in molecules.[2] Cascades of such networks in which the stereodynamics of one network gate that of another present especially tough stereochemical problems; unique observation of gated behavior among several processes in the same system places strong constraints on the allowable relationships between the static and dynamic symmetries of the molecule. One molecule in which this type of gated stereochemistry has been disputed for some time is (hexaethylbenzene)chromium tricarbonyl (**1**-Cr).[3] We now present clear evidence for a cascade of processes in **2**-Cr, a system analogous to **1**-Cr.



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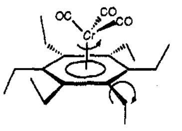
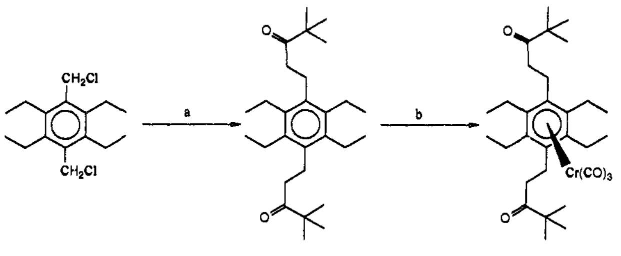


1-Cr

Shortly after the use of metal complexation had been shown to be an effective method for desymmetrizing hexaethylbenzene (**1**), in order to study the ethyl group dynamics,[4] speculations appeared suggesting that the barrier to ethyl group rotation was interrelated with the rotational barrier for the chromium tricarbonyl tripod.[5] Recently, McGlinchey[6] and others[7] showed that the tripod rotation was hindered in sterically encumbered alkyl aromatics. **2**-Cr represents the first system designed to allow the observation of both processes concomitantly and thereby uniquely answer this question of gated dynamics.

Scheme I[a]



2 **2-Cr**

[a] (a) $TiCl_4$, $(CH_3)_3CCH{=}CHOTMS$, −45 °C, CH_2Cl_2, 30 min. (b) $Cr(NH_3)_3(CO)_3$, dioxane, reflux, 5 h.

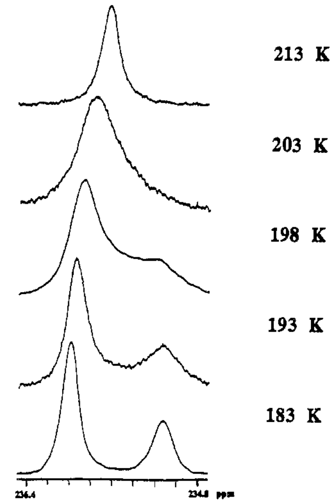


Figure 1. Variable-temperature ^{13}C NMR spectra of **2**-Cr in the region of the carbon monoxide (bound) carbons. The exchange barrier for the carbon monoxide carbons (chromium tripod rotation) is 9.5 kcal/mol.

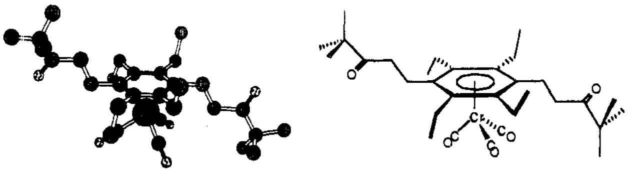


Figure 2. Structure of **2**-Cr as predicted from empirical force field calculations (MXX): (a) picture from Chem-3D and (b) ChemDraw.

Synthesis of **2** is effected by the Reetz reaction[8] of the trimethylsilyl enol ether of pinacolone[9] and 1,4-bis(chloromethyl)-2,3,5,6-tetraethylbenzene[10] with titanium tetrachloride in dichloromethane.[11,12] The reaction of **2** with triamminetricarbonylchromium[13] in refluxing dioxane produced **2**-Cr in 35% yield[11,14] (Scheme I).

The static symmetry of **2**-Cr is C_s and should give rise to two types of carbon monoxide sites in a ratio of 2:1 as well as two ketone carbon sites in a ratio of 1:1. Tripod rotation produces

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(1) American Cancer Society Junior Faculty Fellow, 1990–1993; NSF-PYI, 1988–1993.

(2) (a) Siegel, J.; Gutièrrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569. (b) Berg, U.; Liljefors, T.; Roussel, C.; Sandstrom, J. *Acc. Chem. Res.* **1985**, *18*, 80.

(3) Although Mislow and co-workers[4] believed the barrier to chromium tricarbonyl rotation to be no greater than ca. 5 kcal/mol, McGlinchey and co-workers[5] estimated the barrier to rotation of the chromium tripod at ca. 11 kcal/mol, which would rival the ethyl group rotational barrier.

(4) (a) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (b) Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1633. (c) Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 172.

(5) (a) McGlinchey, M. J.; Fletcher, J. L.; Sayer, B. G.; Bougeard, P.; Faggiani, R.; Lock, C. J. L.; Bain, A. D.; Rodger, C.; Kündig, E. P.; Astruc, D.; Hamon, J.-R.; Le Maux, P.; Top, S.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1983**, 634. (b) McGlinchey, M. J.; Bougeard, P.; Sayer, B. G.; Hofer, R.; Lock, C. J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 789.

(6) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27.

(7) (a) Chudek, J. A.; Hunter, G.; MacKay, R. L.; Färber, G.; Weissensteiner, W. *J. Organomet. Chem.* **1989**, *377*, C69. (b) Kremminger, P.; Weissensteiner, W.; Kratky, C.; Hunter, G.; MacKay, R. L. *Monatsh. Chem.* **1989**, *120*, 1175.

(8) (a) Reetz, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 96. (b) Reetz, M. T.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 48.

(9) (a) Cazeau, P.; Moulines, F.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C9. (b) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(10) Kilway, K. V.; Siegel, J. S., submitted for publication.

(11) Full experimental details are in the supplementary material.

(12) Spectral data on **2**: mp 151–153 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.17 (18 H, s), 1.19 (12 H, t, $J = 7.6$ Hz), 2.58 (8 H, q, $J = 7.6$ Hz), 2.77 (4 H, m), 2.85 (4 H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 15.7, 22.4, 23.5, 26.4, 38.0, 44.1, 135.6, 138.4, 215.6; IR (KBr) 1690 cm^{-1}; FABMS (high resolution) found 414.3462 (calcd for $C_{28}H_{46}O_2$ (M^+) 414.3498).

(13) (a) Moser, G. A.; Rausch, M. D. *Synth. React. Met.-Org. Chem.* **1974**, *4*, 37. (b) Razuvaev, G. A.; Artemov, A. N.; Aladjin, A. A.; Sirotkin, N. I. *J. Organomet. Chem.* **1976**, *111*, 131.

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