1640, 1450, 1415, 1370, 1310, 1285, 1245, 1210, 1160, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (3 H, s, CH_3), 1.27, 1.35, 1.53 (3 H, 6 H, 3 H, each s, 2 × $C(CH_3)_2$), 3.60 (1 H, d, J = 9 Hz, H-5), 3.78–4.12 (2 H, m, H-2,2′ of the side chain), 4.19 (1 H, d, J = 4 Hz, H-3), 4.62 (1 H, m, H-1 of the side chain), 5.11–5.37 (2 H, m, CH=CH_2), 5.78 (1 H, d, J = 4 Hz, H-2), 6.30 (1 H, ddd, J = 17, 11 and 2 Hz, CH=CH_2). High-resolution mass spectrum, calcd for $C_{14}H_{21}O_5$: m/z 269.1387. Found: M - CH_3, 269.1381.

(2*S*,3*S*,4*S*,5*S*)-5-[(1*R*)-1,2-Dihydroxyethyl]-2,3-(isopropylidenedioxy)-4-methyl-4-vinyltetrahydrofuran (38).[15] A solution of **37** (99 mg, 0.35 mmol) in 50% aqueous trifluoroacetic acid (2 mL) was stirred at ambient temperature for 6 h and evaporated. The residue was chromatographed on silica gel (3 g, ethyl acetate/hexane, 1:3, then 1:2) to afford **38** (79 mg, 93%) as a colorless syrup: $[\alpha]^{22}_D$ -14.6° (c 1.41, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3440, 2990, 2950, 2880, 1640, 1450, 1420, 1375, 1320, 1295, 1250, 1210, 1160, 1140, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (3 H, s, CH_3), 1.28, 1.53 (3 H × 2, each s, $C(CH_3)_2$), 2.47–2.82 (2 H, m, 2 × OH), 3.60 (1 H, d, J = 10 Hz, H-5), 3.69–3.84 (2 H, m, H-2,2′ of the side chain), 4.20 (1 H, d, J = 4 Hz, H-3), 4.09–4.34 (1 H, m, H-1 of the side chain), 5.22–5.50 (2 H, m, CH=CH_2), 5.85 (1 H, d, J = 4 Hz, H-2), 6.40 (1 H, dd, J = 18 and 11 Hz, CH=CH_2). High-resolution mass spectrum, calcd for $C_{11}H_{17}O_5$: m/z 229.1074. Found: M - CH_3, 299.1073.

(2*S*,3*S*,4*S*,5*S*)-5-[(1*R*)-1-Hydroxy-2-(trimethylacetoxy)ethyl]-2,3-(isopropylidenedioxy)-4-methyl-4-vinyltetrahydrofuran (39).[15] Trimethylacetylation of **38** (77 mg, 0.32 mmol) in dichloromethane (3 mL), pyridine (0.3 mL), and triethylamine (0.04 mL) with trimethylacetyl chloride (0.098 mL, 0.8 mmol) for 17 h, then extractive workup (dichloromethane), and chromatographic purification (3 g, ethyl acetate/hexane, 1:10) afforded **39** (93 mg, 90%) as a colorless syrup: TLC R_f 0.57 (ethyl acetate/hexane, 1:10); $[\alpha]^{23}_D$ +4.5° (c 1.39, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3510, 2970, 2940, 2910, 2870, 1725, 1635, 1480, 1455, 1415, 1395, 1370, 1325, 1280, 1265, 1245, 1210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (3 H, s, $OCOC(CH_3)_3$), 1.22 (3 H, s, CH_3), 1.28, 1.52 (3 H × 2, each s, $C(CH_3)_2$), 2.18–2.33 (1 H, br, OH), 3.55 (1 H, d, J = 9 Hz, H-5), 4.18 (1 H, d, J = 4 Hz, H-3), 4.27–4.54 (3 H, m, H-1,2,2′ of the side chain), 5.18–5.44 (2 H, m, CH=CH_2), 5.81 (1 H, d, J = 4 Hz, H-2), 6.38 (1 H, dd, J = 19 and 11 Hz, CH=CH_2). High-resolution mass spectrum, calcd for $C_{16}H_{25}O_6$: m/z 313.1649. Found: M - CH_3, 313.1649.

(1*S*,3*S*,7*S*,8*S*,9*R*,11*R*)-9-Hydroxy-5,5,8-trimethyl-11-[(trimethylacetoxy)methyl]-2,4,6,10-tetraoxatricyclo-[6.3.0^{1,8}.0^{3,7}]undecane (40). Ozonolysis of **39** (38.5 mg, 0.12 mmol), triphenylphosphine treatment, and chromatographic purification of the product (3 g, ethyl acetate/hexane, 1:2) afforded **40** (29.2 mg, 75%) as a colorless syrup: TLC R_f 0.43 (ethyl acetate/hexane, 1:10, then 1:5); $[\alpha]^{21}_D$ -25.8° (c 1.42, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3450, 2970, 2930, 2800, 1725, 1470, 1380, 1370, 1280, 1240, 1210, 1160, 1090, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (12 H, s, CH_3 and $OCOC(CH_3)_3$), 1.30, 1.54 (3 H × 2, each s, $C(CH_3)_2$), 1.83–1.97 (1 H, m, OH), 3.40 (1 H, d, J = 4 Hz, H-1), 4.10–4.42 (4 H, m, H-7,11, $CH_2OCOC(CH_3)_3$), 5.50 (1 H, d, J = 4 Hz, H-9), 5.95 (1 H, d, J = 4 Hz, H-3). High-resolution mass spectrum, calcd for $C_{15}H_{23}O_7$: m/z 315.1442. Found: M - CH_3, 315.1433.

(1*S*,3*S*,7*S*,8*S*,9*R*,11*R*)-9-Acetoxy-5,5,8-trimethyl-11-[(trimethylacetoxy)methyl]-2,4,6,10-tetraoxatricyclo-[6.3.0^{1,8}.0^{3,7}]undecane (41). Acetylation of **40** (10.1 mg, 0.03 mmol) with acetic anhydride (0.5 mL) in pyridine (0.5 mL) for 3 h and chromatographic purification on silica gel (1 g, ethyl acetate/hexane, 1:2) afforded **41** (11.6 mg, quantitatively): TLC R_f 0.50 (ethyl acetate/hexane, 1:2); mp 111.5–113 °C; $[\alpha]^{21.5}_D$ -77.1° (c 0.70, $CHCl_3$); IR ν_{max}^{KBr} 2980, 2960, 2935, 1745, 1730, 1480, 1460, 1400, 1385, 1375, 1360, 1290, 1270, 1250, 1240, 1210, 1170, 1145, 1100, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, s, CH_3), 1.21 (9 H, s, $C(CH_3)_3$), 1.31, 1.54 (3 H × 2, each s, $C(CH_3)_2$), 2.06 (3 H, s, $OCOCH_3$), 4.00–4.50 (5 H, m, H-1,7,11, $CH_2OCOC(CH_3)_3$), 5.93 (1 H, d, J = 4 Hz, H-3), 6.41 (1 H, s, H-9). Anal. Calcd for $C_{18}H_{28}O_8$: C, 58.05; H, 7.58. Found: C, 57.79; H, 7.44.

Rotational Barriers of Bis(2,6-disubstituted-aryl) Ketones and Bis(2,6-disubstituted-aryl)methanes and -ethanes and Their Mono- and Bis(tricarbonylchromium) Complexes†

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Bis(2,6-dialkylphenyl)methanes and -ethanes and bis(2,6-dialkylphenyl) ketones and their mono- and bis(tricarbonylchromium) complexes have been prepared and their variable-temperature NMR spectra recorded. Monocomplexation increases the isomerization barrier of bis(2-ethyl-6-methylphenyl) ketone (**2**) from 51.4 kJ/mol to 83.2/84.4 kJ/mol but does not significantly change the corresponding barriers for bis(2-ethyl-6-methylphenyl)methane (**1**) and 1,1-bis(2-ethyl-6-methylphenyl)ethane (**3**). The barriers of the bis complexes are found to be almost the same as those of the mono complexes. Monocomplexation of bis(2-*tert*-butyl-4,6-dimethylphenyl) ketone (**5**) yields two diastereomers which are stable at room temperature and separable by chromatography. The NMR spectra and possible isomerization pathways of ligands and complexes are discussed.

Compounds with two aryl rings attached to a central unit X, Ar_2X, are the simplest representatives of polyaryl compounds which may undergo correlated rotation,[1,2] the rotation of one ring thus causing rotation of the other. A previous study[3] has shown that in diaryl compounds Ar_2X, depending on the relative size of the aryl rings, the lowest energy pathway for isomerization can be either correlated rotation[4] of the aryl rings or topomerization involving nonflip mechanisms. Variable-temperature proton NMR spectroscopy indicates that the latter mechanism applies for 1-mesityl-1-phenylethane[6,7] and 2,4,6-triisopropyl-

† For a preliminary account of parts of this work, see: Schlögl, K. *J. Organomet. Chem.* **1986**, *300*, 219.

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(4) Correlated and noncorrelated are used in the following sense: Correlated is a motion of both aryl rings as described by flip mechanisms,[3,5] involving helicity reversal of the propeller-shaped diphenyl skeleton. Noncorrelated is a motion described by nonflip mechanisms.
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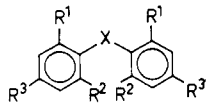
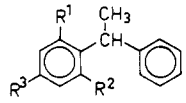
Chart I



	R^1	R^2	R^3	X
1	CH_3	CH_2CH_3	H	CH_2
2	CH_3	CH_2CH_3	H	C=O
3	CH_3	CH_2CH_3	H	CH-CH_3
4	CH_3	CH_2CH_3	H	CH-OH
5	CH_3	$C(CH_3)_3$	CH_3	C=O
6	CH_3	$C(CH_3)_3$	CH_3	CH-OH
7	CH_3	CH_3	OCH_3	C=O
8	CH_3	CH_3	OCH_3	CH-CH_3
9	CH_3	CH_3	OCH_3	CH-OH



	R^1	R^2	R^3
10	CH_3	CH_2CH_3	H

benzophenone[8] and related compounds.[9] In these and similar cases,[3] rotation of a phenyl group is fast on the NMR time scale, but that of a substituted ring is slow.

Using chiroptical methods, Akkerman and Coops investigated the racemization of bis(2,6-disubstituted-aryl)acetic acids[10] and concluded that in these compounds the isomerization mechanism of lowest energy is a disrotatory motion of the phenyl rings,[11] whereas racemization occurs via a conrotatory motion.

Studies of di-, tri-, and tetraaryl compounds have shown that correlated rotation not only affects the number of isomers which are detectable on a particular time scale but also the overall molecular symmetry.[12-17] For example, dimesitylmethane with C_2 symmetry in the ground state is a chiral structure which is racemized by any flip mechanism. However, if one ortho methyl group of each ring is replaced by an ethyl group then the resulting chiral diarylmethane racemizes only by two-ring or zero-ring flips but not by one-ring flips. Because of their importance to reactivity studies of carbenium and carbanion species, tricarbonylchromium complexes of similar compounds have attracted much interest, and some unusually high barriers to arene rotation have been reported.[18,19] In addition, we have found that tricarbonylchromium complexes can serve as intermediates in enantiomeric resolution of torsional isomers,[20,21] but so far relatively little is known about the influence of complexation on arene rotational barriers in such compounds. In order to clarify this situation we now report arene rotational barriers and discuss possible isomerization mechanisms for **1–3** and **10** and for the mono and bis complexes of **1–3**, **5**, **7**, and **8** (Chart I).

Table I. Internal Isomerization of Diarylmethanes and Related Compounds as well as of Mono- and Bis(tricarbonylchromium) Complexes

compd	temp range, °C	solvent	nuclei obsd in signal coalescence	$\Delta G^{\ddagger}$, kJ/mol (temp, K)
1	−30/50	$CDCl_3$	CH_2CH_3	68.6 ± 1.3 (323)
1m	−5/35	$C_6D_5CD_3$	*o*-CH_3	65.6/66.9 ● 1.3 (308)
2	−45/−28	$C_6D_5CD_3$	CH_2CH_3	51.4 ± 3.7 (245)
2m	25/105	$C_6D_5CD_3$	*o*-CH_3	83.2/84.4 ± 1.3 (363)
3	25/65	C_6D_6	*o*-CH_3	69.0 ± 1.3 (323)
3m	−15/45	$C_6D_5CD_3$	$CHCH_3$	64.4/65.6 ± 1.3 (318)
7m	25/107	$C_6D_5CD_3$	*o*-CH_3	83.6 ± 1.3 (376)
7b	25/98	$C_6D_5CD_3$	*o*-CH_3	81.1 ± 1.3 (371)
8m	−30/23	CD_2Cl_2/CS_2[a]	*o*-CH_3	65.2 ± 1.3 (296)
8b	−40/23	CD_2Cl_2/CS_2[a]	*o*-CH_3	63.1 ± 1.3 (296)
10	−60/25	$C_6D_5CD_3$	*o*-CH_3	52.3 ± 1.3 (263)

[a] Ratio 1:1.

Results and Discussion

Compounds **1–9** are expected to undergo correlated rotation. Empirical force-field calculations (EFF) for 2,2′,6,6′-tetramethylbenzophenone (TMB)[3] and bis(2,6-dimethylphenyl)methane (DMM)[22] clearly indicate that correlated rotation is favored as the isomerization pathway of lowest energy, this process giving values of 14.5 kJ/mol (DMM) and 21 kJ/mol (TMB) for idealized one-ring flips[3,12] but 67 kJ/mol for two-ring flips. Our calculations[23] for bis(2-ethyl-6-methylphenyl)methane (**1**) and bis(2-*tert*-butyl-6-methylphenyl)methane (bTBM) also show that all barriers increase with increasing size difference of the ortho substituents but that the disrotatory rotation still remains the lowest energy pathway. Also the calculated barrier of bTBM for a disrotatory rotation (one-ring flip) is 63 kJ/mol which is still lower than the experimental racemization barrier (conrotatory motion) of 95.4 kJ/mol for the structurally similar bis(2-*tert*-butyl-4,6-dimethylphenyl)acetic acid.[10] Hence, according to these calculations the one-ring flip is expected to be the isomerization pathway of lowest energy for compounds **1–9**. Moreover the one-ring flip causes enantiomerization for **7–9** but not for **1–6**.

Variable-Temperature NMR. In principle two different site-exchange processes should be observable: a low-energy process involving disrotatory rotations of the aryl groups and one of higher energy associated with conrotatory rotations.

In the case of **7–9** the room-temperature proton NMR spectrum shows only one singlet for all equivalent ortho methyl groups, and this remains unchanged even at −80 °C. Unlike **10**, the rotation of both aryl rings of **8** is fast on this time scale. The equivalence of all four ortho methyl

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(11) The one-ring flip causes a *disrotatory* motion of both aryl rings but the two-ring and zero-ring flip result in a *conrotatory* motion if both rings are viewed from the central unit X to their ipso carbons.
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Table II. Maximum Number of Tricarbonylchromium Complexes

	no. of isomers[a] correlated rot.		no. of isomers[a] noncorrelated rot.	
compd	mono	bis	mono	bis
1, 2, 5	4	6	2	3
3	8	8	4	4
7	1	2	1	1
8	2	2	2	1

[a] Enantiomers are counted as different isomers.

groups is consistent with either conrotatory or disrotatory motions of both rings; hence no distinction can be made.

Substitution of one ortho CH_3 group on each aryl ring of **8** leads to desymmetrization. Compounds **3**, **4**, and **6** are asymmetric if the rotation is disrotatory but possess bilateral symmetry if the rotation is conrotatory. As with **6**[24] and **4**, the room-temperature spectrum of **3** shows two signals for the ortho-methyl hydrogens. These signals coalesce at higher temperature, and this is consistent with a disrotatory rotation at room temperature and racemization involving conrotatory rotations at higher temperature. The room-temperature spectrum is also consistent with slow rotation of both aryl rings. However, in this case the aryl rotation of **8** would also be slow, since a change from methyl to ethyl has only little effect on the barrier as shown both by EFF calculations[23] and experiment: a slightly higher barrier (5 kJ/mol) was found for 1-phenyl-1-(2-ethyl-6-methylphenyl)ethane (**10**) than for 1-mesityl-1-phenylethane[6] (Table I). Since **8** did not exhibit two ortho methyl signals, this alternative mechanism may be ruled out.

Like **3**, compounds **1**, **2**, and **5** are chiral if the rotation is disrotatory but unlike in **3** the ortho methyl groups are homotopic. The methylene protons of **1** and **2** are diastereotopic with a disrotatory rotation but enantiotopic if racemization occurs. Hence the proton NMR spectra of **1** and **2** show at low temperature (−20/−45 °C) an ABX_3 pattern for both ethyl groups, which collapses to an A_2X_3 system at higher temperature.

Line-shape analysis for two site-exchange processes of these diastereotopic signals gives energies of activation ($\Delta G^{\ddagger}$) for the racemization of **1**–**3** (see Table I) via conrotatory rotations. No other interconversion process was observable for these compounds, indicating a low barrier for the disrotatory rotation of both aryl rings consistent with the EFF calculations. The barriers of **1** and **3** are almost the same, 68.6 and 69.0 kJ/mol, respectively, which indicates that the influence of the methyl group of the central unit X—and by analogy the COOH group in Akkerman's diarylacetic acids—is negligible. The barrier of **2** was found to be 17.2 kJ/mol lower than that of **1**.

Tricarbonylchromium Complexes. Complexation of diaryl compounds may give rise to several different isomers, both enantiomers and diastereomers. The maximum number of possible isomers, detectable on a particular time scale, depends on the symmetry of the ligand and on the possible isomerization pathways.[25] For example, for compounds **7** and **8** in the C_2 and C_1 ground states, respectively, complexation with $Cr(CO)_3$ may result in a maximum of four mono and six bis complexes for **7** and eight mono and eight bis complexes for **8**. With disrotatory rotations the number of isomers changes to one mono and two bis complexes for **7** and two mono and two bis complexes for **8**. Conrotatory rotation changes the number of isomers to one mono and one bis for **7** and to two mono and one bis complex for **8**. Table II summarizes the maximum number of possible isomers resulting from complexation of **1**–**9** either through disrotatory or conrotatory rotations of both aryl rings.

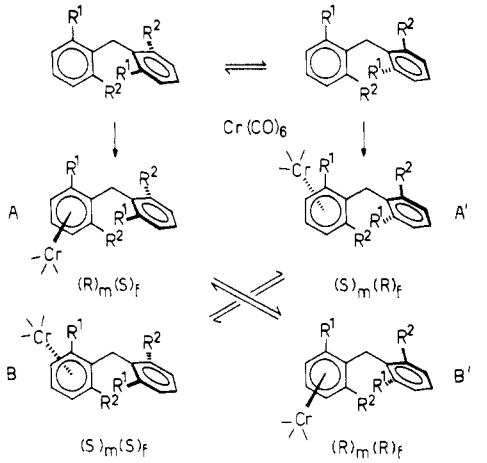

Figure 1. The four monotricarbonylchromium complexes of diarylmethanes and their interconversion paths.

To distinguish these isomers and to clarify the isomerization pathways we use R/S descriptors to denote the configurations of the stereogenic units (Figure 1). Thus the mono complexes of **1** and **2** are named R_mS_f, R_mR_f, S_mS_f, and S_mR_f where the subscripts m and f refer to the stereogenic units (m for metallocene and f for diaryl framework). R's and S's are assigned arbitrarily and no attempt is made to assign configurations to individual isomers on an experimental basis.

Complexation of the diarylmethane of Figure 1 ($R_1 \neq R_2$) and of related compounds yields two pairs of diastereomers A/A′ (R_mS_f/S_mR_f) and B/B′ (S_mS_f/R_mR_f). Conrotatory rotation now interconverts A and B′ as well as B and A′. If this isomerization is fast on a particular time scale only one pair of residual stereoisomers[1,26] (enantiomers) A/B′ and A′/B can be observed. Otherwise A and B′ as well as A′ and B can be detected separately even if the disrotatory rotation is fast.

Variable-Temperature NMR: Mono Complexes. The room-temperature proton NMR spectrum of **7m** and the low-temperature spectrum (−10 °C) of **8m** show great similarity. In both, only one isomer (enantiomers, **8m**) is detectable. The two ortho CH_3 groups of the complexed rings are equivalent in **7m** (Figure 1, $R_1 = R_2$) but are, of course, diastereotopic in **8m**. The ortho-CH_3 hydrogens of the uncomplexed rings are diastereotopic in both **7m** and **8m** as a result of disrotatory rotation or of rigid C_s (**7m**) or C_1 (**8m**) structures. Warming of the solutions of **7m** and **8m** leads to broadening of the signals because of an exchange of the ortho-CH_3 hydrogens of the uncomplexed rings an this is consistent only with a conrotatory rotation. The $\Delta G^{\ddagger}$ values for these processes are listed in Table I.

The ^1H NMR spectra of **1m** and **2m** are also very similar. Separate signals for the methyl groups of the two diastereomers (two pairs of enantiomers) are observed at low temperature (−5/25 °C) in ratios of 3:2 for **1m** and 4:3 for **2m**, and this is again consistent with a disrotatory

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(26) Residual stereoisomers result whenever closed subsets of appropriately substituted interconverting isomers are generated from the full set at a particular time scale of observation and under the operation of a given stereoisomerization mechanism.[1]

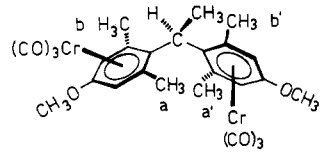

Figure 2. Diastereotopic methyl groups of **8b**.

motion or with rigid C_1 structures. These two diastereomeric pairs, R_mS_f/S_mR_f and S_mS_f/R_mR_f (Figure 1) now isomerize by conrotatory rotations to give two residual stereoisomers R_mS_f/R_mR_f and S_mR_f/S_mS_f, a process which was monitored by the signals of the exchanging ortho CH_3's of **1m** and **2m**. The isomerization barrier of the ketone **2m** is again 18.8 kJ/mol higher than that of **1m** (Table I).

Finally, complexation of **3** yields four diastereomers (again pairs of enantiomers, Table II) identified in the low-temperature ^1H NMR spectrum (−15 °C). However, isomerization by disrotatory rotation now results in two diastereomers which are detectable at 105 °C. Since this isomerization occurs via diastereomeric pathways as well, two different barriers are expected. But due to signal overlap, only one exchange process could be analyzed (Table I).

Monocomplexation of **5**, like **1** and **2**, results in two diastereomers (ratio 1:5),[27] but unlike **1m** and **2m**, these diastereomers are stable at room temperature and are separable by medium-pressure chromatography (see Experimental Section). Both diastereomers are stable in solution ($CDCl_3$) for 24 h at 20 °C and do not interconvert as shown by NMR. This indicates a lower limit of 100 kJ/mol for the isomerization barrier.

Bis Complexes. The low-temperature ^1H NMR spectrum of **7b** shows two signals for the ortho CH_3 group consistent with a rigid C_2 structure or disrotatory rotation. These signals collapse at higher temperature. Unlike **7b** the ground-state symmetry of **8b** as well as the overall symmetry with disrotatory rotation is C_1 (Figure 2). This results in four signals for the ortho CH_3's, which are observed at low temperature (−40 °C). A conrotatory rotation changes the overall symmetry to C_s, and this is monitored by the signals of the exchanging ortho methyls a and a′ as well as b and b′ (Figure 2). However the signals of the methyls a and b (a′ and b′) remain diastereotopic.[28] The rotational barriers of **7b** and **8b** are almost equivalent to those of the corresponding mono complexes (Table I).

Of special interest are the bis complexes **1b** and **2b**, both of which have a room-temperature spectrum that shows only four signals for ortho-methyl hydrogens. This result is compatible with the presence of only two diastereomers of C_1 symmetry. However, assuming similar ground-state energies, three diastereomers (Table II) are expected: A/A′, $R_mR_fR_m/S_mS_fS_m$; B/B′, $S_mR_fS_m/R_mS_fR_m$; C/C′, $R_mR_fS_m/R_mS_fS_m$. In the case of a propeller-like ground-state conformation or disrotatory rotation of the aryl rings, the diastereomers A/A′ and B/B′ have C_2 symmetry but C/C′ has C_1, and this results in four signals for the ortho methyl groups, too. The isomers of **1b** can be distinguished from each other by the methane proton signals, which are singlets for A and B but an AB quartet for C. Furthermore, these singlets coalesce at higher temperature, as expected for the isomerization of A to B′ and B to A′, while the AB pattern of C remains unchanged during the enantiomerization process C/C′. Hence the spectra of **1b** and **2b** are those of a mixture of three diastereomers A, B, and C in a ratio of 1:1:2.

In summary we find that the influence of complexation on the rotational barriers is not uniform but depends strongly on the central unit X (Table I). Monocomplexation of diphenylmethane **1** and -ethane **3** does not change the racemization barriers to a significant degree. The barriers of mono and bis complexes **8a,b** are almost the same, too. We have reported earlier that complexation decreases the inversion barrier of dimethyldihydrophenanthrene by as much as 5.9 kJ/mol.[20] Similarly, a lowering of the rotational barrier of the neopentyl groups in 1,2-dineopentyltetramethylbenzene has been reported.[29] This energy decrease has been attributed to an increase in the ground-state energy in the complexes as compared to the ligands.[29] Obviously such an effect is not present in the case of **1m** and **3m**.

However monocomplexation of **2** increases the racemization barrier to a very significant degree (Table I). The barriers of the mono and bis complexes are again very similar (**7m** and **7b**). This is rather surprising, since the $Cr(CO)_3$ group is a strongly electron-withdrawing group and would be expected to lower the rotational barrier.[30] Trahanovsky and co-workers found the rotational barrier of the mono $Cr(CO)_3$ complex of dimesityl ketone to be 22.2 kJ/mol higher than that of the dimesitylmethane mono complex.[31] They pointed out that the dimesityl ketone mono complex in a C_s conformation, with the central carbonyl and the uncomplexed aryl ring coplanar, might be energetically favored by resonance stabilization. This would cause a decrease in ground-state energy and result in a higher rotational barrier. However this is unlikely for the bis complexes and is not supported by an X-ray structure showing a C_2 symmetrical conformation for (2,2′-difluoro-5,5′-dimethylbenzophenone)bis(tricarbonylchromium(0)).[32]

As already noted, complexation of **5** increases the racemization barrier to such a degree that the diastereomeric mono complexes are separable at room temperature, and this represents an example of stable torsional isomers (residual diastereomers[1]).

Experimental Section

Variable-Temperature NMR Measurements. Variable-temperature proton NMR spectra were recorded with a Bruker WM-250 spectrometer operating at 250.13 MHz. In the case of **7m** and **8m** spectra were determined at 90 MHz with a Jeol FX-90Q spectrometer. Temperatures are considered accurate to ±2 °C. Spectral simulations were performed with the program DNMR3,[33] and satisfactory fits of simulated and observed spectra were judged by visual comparison. Values of $\Delta G^{\ddagger}$ were calculated with the Eyring equation.

Mass spectra were recorded with a Varian MAT-CH7 instrument. Melting points were determined on a Kofler microscope and are uncorrected. Medium-pressure chromatography was carried out at a pressure of 3 bar using silica gel (Merck-60, 0.04–0.0063). The elemental analysis was performed by Dr. J. Zak, Universität Wien. Compounds **5**/**6**,[34] **7**,[35] and **9**[15] were prepared by published procedures.

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Bis(2-ethyl-6-methylphenyl)methane (1). A mixture of 1 g (3.7 mmol) of **4** dissolved in 50 mL of ethanol and 0.5 g of palladium on coal (10%) was hydrogenated for 24 h at room temperature under a hydrogen pressure of 3 bar. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was purified by chromatography (eluent, petroleum ether/2% ethyl acetate) to give 0.6 g (64%) of **1**: mp 40–42 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 6 H), 2.12 (s, 6 H), 2.63 (m, 4 H), 4.18 (s, 2 H), 7.05–7.2 (m, 6 H); mass spectrum, m/e 252 (M^+), 223, 132 (100%), 117. Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.66; H, 9.62.

Bis(2-ethyl-6-methylphenyl)methanone (2). A mixture of 1 g (3.7 mmol) of **4** dissolved in 20 mL of methylene chloride and 1.61 g (7.5 mmol) of pyridinium chlorochromate was stirred at room temperature for two h. Dry ether (100 mL) was added, and the mixture was filtered through a short column of Florisil. Removal of the solvent and chromatography (eluent, petroleum ether/5% ethyl acetate) gave 0.91 g (92%) of **2**: mp 53–59 °C; ^{1}H NMR ($CDCl_3$) δ 1.11 (t, J = 7.0 Hz, 6 H), 2.17 (s, 6 H), 2.53 (q, J = 7 Hz, 4 H), 7.01–7.30 (m, 6 H); mass spectrum, m/e 266 (M^+), 251, 237 (100%), 222. Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.52; H, 8.67.

1,1-Bis(2-ethyl-6-methylphenyl)ethane (3). A Grignard reagent was prepared from 4.5 g (31.6 mmol) of methyl iodide and 0.8 g (3.29 mmol) of Mg in 70 mL of diethyl ether. This mixture was treated dropwise with 2.38 g (6.4 mmol) of **16** dissolved in 20 mL of diethyl ether. The white suspension was heated under reflux for one additional hour and allowed to cool to room temperature. The reaction mixture was quenched by adding ice and acidified with dilute hydrochloric acid. The organic layer was washed with an aqueous NaOH solution (10%) and several times with water and subsequently dried over Na_2SO_4. Evaporation of the solvent and chromatography (eluent, petroleum ether/1% ethyl acetate) yielded 1.02 g (60%) of **3**: mp 36–38 °C; ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 7.4 Hz, 6 H), 1.62 (d, J = 7.7 Hz, 3 H), 2.2 (s, 3 H), 2.28 (s, 3 H), 2.49–2.55 (m, 4 H), 4.6 (q, J = 7.7 Hz, 1 H), 6.88–7.03 (m, 6 H); mass spectrum, m/e 266 (M^+), 251, 237, 146, 131 (100). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.13; H, 9.87.

Bis(2-ethyl-6-methylphenyl)methanol (4). A suspension of 2.7 g (110 mmol) of Mg in 20 mL of dry diethyl ether was treated with 16.93 g (85 mmol) of 2-ethyl-6-methylbromobenzene[36] dissolved in 30 mL of dry ether and heated under reflux for 5 h. A solution of 9 g (61 mmol) of **13** in 20 mL of ether was added to the hot reaction mixture, and heating was continued for 2 h. The solution was allowed to cool to room temperature and was quenched by adding ice–water followed by dilute hydrochloric acid. The organic layer was washed several times with a saturated aqueous solution of sodium chloride and dried on Na_2SO_4. Evaporation of the solvent and chromatography (eluent, petroleum ether/5% ethyl acetate) gave 1.8 g (45%) of **4**: mp 43–47 °C; ^{1}H NMR ($CDCl_3$) δ 1.07 (t, J = 7.0 Hz, 6 H), 1.87 (d, J = 4 Hz, 1 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 2.69 (m, 4 H), 6.50 (d, J = 4 Hz, 1 H), 6.92–7.17 (m, 6 H); mass spectrum, m/e 268 (M^+), 250, 221 (100%), 206, 147. Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01. Found: C, 85.19; H, 9.04.

1,1-Bis(2,6-dimethyl-4-methoxyphenyl)ethane (8). A Grignard reagent was prepared from 10 g (70.4 mmol) of methyl iodide and 1.8 g (75 mmol) of Mg in 90 mL of dry diethyl ether and treated dropwise with 5.48 g (13.5 mmol) of **17**. The white suspension was heated under reflux for 1 h and cooled to room temperature. The reaction mixture was quenched with ice–water and acidified with dilute hydrochloric acid. The organic layer was washed with an aqueous NaOH solution (10%) and water and subsequently dried over sodium sulfate. Evaporation of the solvent and chromatography (eluent, petroleum ether/5% ethyl acetate) gave 1.8 g (45%) of **8**: mp 120 °C; ^{1}H NMR ($CDCl_3$) δ 1.69 (d, J = 8 Hz, 3 H), 2.23 (s, 12 H), 3.75 (s, 6 H), 4.53 (q, J = 8 Hz, 1 H), 6.51 (s, 4 H); mass spectrum, m/e 298 (M^+), 283, 162 (100%). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.42; H, 8.76.

1-Phenyl-1-(2-ethyl-6-methylphenyl)ethane (10). A mixture of 0.5 g (2.25 mmol) of **18**, dissolved in 50 mL of ethanol and 0.2 g of palladium on coal (10%) was hydrogenated for 20 h at room temperature under a hydrogen pressure of 5 bar. The reaction mixture was filtered and the solvent removed. Purification by chromatography (eluent, petroleum ether/2% ethyl acetate) yielded 0.44 g (87%) of **10**: ^{1}H NMR ($CDCl_3$) δ 1.06 (br t, 3 H), 1.67 (d, J = 7.2 Hz, 3 H), 2.02 (br s, 3 H), 2.56 (br m, 2 H), 4.61 (q, J = 7.2 Hz, 1 H), 6.91–7.26 (m, 8 H); mass spectrum, m/e 224 (M^+, 100%), 209, 195, 131, 117.

2-Ethyl-6-methylcarbomethoxybenzene (11). To 38.3 g (1.58 mmol) of Mg in 100 mL of dry ether were added 30 mL of a mixture of 90 g (0.45 mol) of 2-ethyl-6-methylbromobenzene[36] and 98 g (0.9 mol) of ethyl bromide in 200 mL of dry ether. After the solvent started to reflux, the remaining bromide solution was added dropwise. The mixture was heated under reflux for one additional hour, cooled to room temperature, and poured onto 400 g of dry ice. Dry ether (400 mL) was added, and the viscous suspension was stirred vigorously for 20 min. The magnesium salt was hydrolyzed by adding 400 mL of hydrochloric acid (20%), the organic layer was separated and washed twice with water. The ethereal solution was extracted with 270 mL of NaOH (10%), cooled to 0 °C, and acidified with hydrochloric acid (20%). The white precipitate was filtered, washed with cold water, and dried at room temperature under reduced pressure to give 42 g (57%) acid. An analytical sample was recrystallized from n-hexane/acetone: mp 73–74 °C; ^{1}H NMR ($CDCl_3$) δ 1.62 (t, J = 7.2 Hz, 3 H), 2.43 (s, 3 H), 2.77 (q, J = 7.2 Hz, 2 H), 7.0–7.27 (m, 3 H), 10.19 (s, 1 H); mass spectrum, m/e 164 (M^+), 146 (100%), 117. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.22; H, 7.31.

A 1 M solution of diazomethane in ether (500 mL) was added slowly to a suspension of 16.4 g (100 mmol) acid in 100 mL ether. The mixture was stirred at room temperature for one additional hour, washed with 1 N NaOH and water, and then dried over Na_2SO_4. Evaporation of the solvent and chromatographic purification (eluent, petroleum ether/15% ethyl acetate) gave 17.5 g (98%) of **11**: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.0 Hz, 3 H), 2.29 (s, 3 H), 2.60 (q, J = 7.0 Hz, 2 H), 3.89 (s, 3 H), 6.86–7.41 (m, 3 H); mass spectrum, m/e 178 (M^+), 147, 146 (100%). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.16; H, 7.90.

2-Ethyl-6-methyl(hydroxymethyl)benzene (12). To a cooled (0 °C) suspension of 2.5 g (66 mmol) of lithium aluminium hydride was added dropwise a solution of 17 g (95 mmol) of **11** in 20 mL of dry ether. The mixture was stirred for 30 min at room temperature and heated under reflux for 2 h. After the mixture was cooled to 0 °C, 10 mL of water was added and the suspension extracted twice with ether. The combined organic layers were washed with saturated sodium chloride solution, dried (Na_2SO_4), and evaporated. Chromatography (eluent, petroleum ether/15% ethyl acetate) gave 10.8 g (75%) **12**: mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.0 Hz, 3 H), 1.60 (s, 1 H), 2.40 (s, 3 H), 2.74 (m, 2 H), 6.90–7.15 (m, 3 H); mass spectrum, m/e 150 (M^+), 132 (100%), 117, 91. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.96; H, 9.37.

2-Ethyl-6-methylbenzaldehyde (13). To a suspension of 22 g (102 mmol) of pyridinium chlorochromate in 100 mL of methylene chloride was added a solution of 10 g (67 mmol) of **12** in 5 mL of methylene chloride. The mixture was stirred at room temperature for 2 h and diluted with 500 mL of ether. Filtration over Florisil, evaporation of the solvent, and chromatography (eluent, petroleum ether/5% ethyl acetate) yielded 9.7 g (98%) of **13** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7.5 Hz, 3 H), 2.56 (s, 3 H), 2.95 (q, J = 7.5 Hz, 2 H), 7.03–7.41 (m, 3 H), 10.58 (s, 1 H); mass spectrum, m/e 148 (M^+, 100%), 133, 121, 119, 105, 91. Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 78.39; H, 8.05.

Bis(2-ethyl-6-methylphenyl)chloromethane (14). A solution of 4.58 g (17.1 mmol) of **4** in 50 mL of benzene was heated under reflux. Dry HCl was bubbled through this solution for 2 h followed by N_2 for 10 min. The mixture was cooled to room temperature, 200 mg of $KHCO_3$ was added, and the suspension was stirred for 10 min. Filtration and evaporation of the solvent gave 4.57 g (94%) of **14**, which was used without further purification. An analytical sample was purified by chromatography using a short (5-cm) column (eluent, petroleum ether/15% ethyl acetate): ^{1}H NMR ($CDCl_3$) δ 1.03 (t, J = 7.0 Hz, 6 H), 2.34 (s, 6 H), 2.7 (m, 4 H), 6.76 (s, 1 H), 6.86–7.2 (m, 6 H); mass spectrum, m/e 286

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(M^+), 251, 131 (100%). Anal. Calcd for $C_{19}H_{23}Cl$: C, 79.56; H, 8.08; Cl, 12.34. Found: C, 79.41; H, 7.99; Cl, 12.60.

[(Bis(2-ethyl-6-methylphenyl)methoxy)carbonyl]benzene (15). A mixture of 3.05 g (10.6 mmol) of **14** and 5 g of silver benzoate in 70 mL of dry benzene was stirred vigorously for 30 min. The mixture was filtered and evaporated and the residue purified by chromatography (eluent petroleum ether/5% ethyl acetate): yield, 2.38 g (60%); ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 7.6 Hz, 6 H), 2.09 (s, 6 H), 2.63 (q, J = 7.6 Hz, 4 H), 6.85–7.56 (m, 9 H), 8.0–8.15 (m, 2 H); mass spectrum, m/e 372 (M^+), 250, 235, 221, 206, 147 (100%). Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.75; H, 7.56.

Bis(2,6-dimethyl-4-methoxyphenyl)chloromethane (16). Bis(2,6-dimethyl-4-methoxyphenyl)methanol[15] (9 g; 30 mmol) in 50 mL of benzene was reacted with HCl as described for compound **14**. The residue was recrystallized from petroleum ether to give 8.1 g (85%) of **16**: mp 103–105 °C; ^1H NMR ($CDCl_3$) δ 2.21 (s, 12 H), 3.75 (s, 6 H), 6.3 (s, 1 H), 6.5 (s, 4 H); mass spectrum, m/e 318 (M^+), 283 (100%), 267, 253. Anal. Calcd for $C_{19}H_{23}ClO_2$: C, 71.57; H, 7.27; Cl, 11.12. Found: C, 71.94; H, 7.40; Cl, 11.07.

[(Bis(2,6-dimethyl-4-methoxyphenyl)methoxy)carbonyl]benzene (17). A mixture of 8 g (2.5 mmol) of **16** and 10 g of silver benzoate in 150 mL of dry benzene was stirred at room temperature for 30 min and filtered and the solvent evaporated. The residue was recrystallized from methanol: yield, 5.48 g (54%); mp 119–121 °C; ^1H NMR ($CDCl_3$) δ 2.08 (s, 12 H), 3.7 (s, 6 H), 7.18–7.50 (m, 3 H), 7.56 (s, 1 H), 8.00–8.08 (m, 2 H); mass spectrum, m/e 404 (M^+), 283, 267 (100%). Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.14; H, 6.95.

1-Phenyl-1-(2-ethyl-6-methylphenyl)ethylene (18). A Grignard reagent was prepared by heating 18 g (90 mmol) of 2-ethyl-6-methylbromobenzene[36] and 2.9 g (120 mmol) of Mg in 20 mL of dry ether for 3 h. To this mixture was added a solution of 16 g (130 mmol) of acetophenone in 20 mL of dry ether, and resultant mixture was heated for one additional hour. The cooled reaction mixture was poured onto ice, acidified with 2 N HCl, and extracted with ether. The combined organic layers were washed with water, dried over Na_2SO_4, and evaporated. Kugelrohr distillation [191–195 °C (0.1 torr)] of the residue gave 3.3 g (16%) **18** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.07 (t, J = 8.0 Hz, 3 H), 2.14 (s, 3 H), 2.53 (q, J = 8.0 Hz, 2 H), 5.10 (d, J = 2.5 Hz, 1 H), 5.98 (d, J = 2.5 Hz, 1 H), 6.93–7.37 (m, 8 H); mass spectrum, m/e 222 (M^+), 207 (100%), 192, 178, 165. Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.79; H, 8.21.

Complexation of the Ligands 1–3, 5, 7, and 8 to Tricarbonyl(η^6-aryl)chromium Complexes: General Procedure. The ligand was refluxed with a 4-fold molar amount of $Cr(CO)_6$ in dry di-*n*-butyl ether–heptane (2:1) (20 mL for 1 mmol of ligand) for 48 h. The reaction mixture was filtered, the solvent and excess of $Cr(CO)_6$ were removed under reduced pressure, and the residue was purified by chromatography (MPLC) on silica gel.

Complexation of 1. Complexation of 0.5 g (1.98 mmol) of **1** gave 0.5 g (65%) of **1m**, mp 90–91 °C, and 0.042 g (4%) of **1b**, mp 140 °C (chromatography: eluent, petroleum ether/7% ethyl acetate).

1m: mass spectrum, m/e 388 (M^+), 302, 300, 52 (100%). ^1H NMR ($C_6D_5CD_3$; two isomers (ratio 3:2)) [1] δ 0.53 (t, J = 7.1 Hz, 3 H), 1.13 (t, J = 7.5 Hz, 3 H), 1.64 (s, 3 H), 1.69 (s, 3 H), 2.05 (m, 2 H), 2.70 (m, 2 H), 3.72, 3.94 (AB, J = –17.1 Hz, 2 H), 4.29 (d, J = 6.3 Hz, 1 H), 4.38 (d, J = 6.3 Hz, 1 H), 4.56 (dd, J = 6.3 Hz, 1 H), 6.7–7.0 (m, 3 H), [2] 0.56 (t, J = 7.1 Hz, 3 H), 0.77 (t, J = 7.5 Hz, 3 H), 1.71 (s, 3 H), 2.05 (m, 4 H) 2.30 (s, 3 H) 3.65, 3.80 (AB, J = –17.1 Hz, 2 H), 4.29 (d, J = 6.3 Hz, 1 H), 4.38 (d, J = 6.3 Hz, 1 H), 4.56 (dd, J = 6.3 Hz, 1 H), 6.7–7.0 (m, 3 H).

1b: mass spectrum, m/e 524 (M^+), 440, 412, 388, 356, 304, 132 (100%); ^1H NMR (C_6D_6; three isomers (ratio 2:1:1)) δ 0.38 (t, J = 7.5 Hz), 0.48 (t, J = 7.7 Hz), 0.91 (t, J = 7.6 Hz), 0.94 (t, J = 7.5 Hz), 1.35 (s), 1.36 (s), 1.81–1.84 (m), 1.92 (s), 1.94 (s), 1.86–2.05 (m), 2.09–2.22 (m), 2.25–2.40 (m), 3.60 (s), 3.70, 3.75 (AB, J = –17.8 Hz), 3.80 (s), 4.2–4.5 (m).

Complexation of 2. Complexation of 0.85 g (3.19 mmol) of **2** gave 0.32 g (25%) of **2m**, mp 87–90 °C, and 0.93 g (54%) of **2b**, mp 127–130 °C dec (chromatography: eluent, petroleum ether-/15% ethyl acetate).

2m: mass spectrum, m/e 402 (M^+), 318, 52 (100%); ^1H NMR ($C_6D_5CD_3$; two isomers) [1] δ 0.61 (t, J = 7.5 Hz, 3 H), 1.3 (t, J = 7.4 Hz, 3 H), 1.77 (s, 3 H), 1.84 (s, 3 H), 2.24 (m, 2 H), 2.70 (m, 2 H), 4.16–4.30 (m, 2 H), 4.83 (m, 1 H), 6.8–7.0 (m, 3 H) [2] δ 0.64 (t, J = 7.6 Hz, 3 H), 0.76 (t, J = 7.5 Hz, 3 H), 1.87 (s, 3 H), 2.24 (m, 4 H), 2.37 (s, 3 H), 4.16–4.30 (m, 2 H), 4.83 (m, 1 H), 6.8–7.0 (m, 3 H).

2b: mass spectrum, m/e 538 (M^+), 482, 454, 426, 398, 318, 52 (100%); ^1H NMR ($C_6D_5CD_3$; three isomers (ratio 2:1:1)) δ 0.51 (t, J = 7.6 Hz), 0.54 (t, J = 7.5 Hz), 0.92 (t, J = 7.5 Hz), 0.94 (t, J = 7.5 Hz), 1.49 (s), 1.51 (s), 1.92–2.0 (m), 2.07 (s), 2.36 (s), 2.38–2.62 (m), 2.79–3.0 (m), 4.0 (m), 4.13 (m), 4.31 (m), 4.76 (m).

Complexation of 3. Complexation of 1 g (3.75 mmol) of **3** gave 0.36 g (42%) of **3m** (chromatography: eluent, petroleum ether-/15% ethyl acetate): mass spectrum, m/e 402 (M^+), 318 (100%), 198, 172, 159; ^1H NMR ($C_6D_5CD_3$, –15 °C; four isomers) δ 0.21, 0.23, 0.40, 0.54, 0.61, 0.67, 1.14, 1.15 (8 t, J = 7.5 Hz), 1.41, 1.42, 1.57, 1.66 (4 d, J = 7.4 Hz), 1.67, 1.71 (br), 1.80, 2.12, 2.18, 2.20, 2.30 (7 s), 1.9–2.3 (m), 2.4–2.7 (m), 2.9–3.05 (m), 4.1–4.3 (m), 4.55 (q), 4.72 (m), 6.7–7.0 (m).

Complexation of 5. Complexation of 0.5 g (1.43 mmol) of **5** gave two monocomplexes: 0.025 g (4%) of **5m-1**, mp 164–167 °C, and 0.13 g (19%) of **5m-2**, mp 136–139 °C (chromatography: eluent, petroleum ether/15% ethyl acetate): mass spectrum (field desorption), m/e 486 (M^+, 100%), 350, 298; ^1H NMR ($CDCl_3$) [**5m-1**] δ 1.25 (s, 9 H), 1.60 (s, 9 H), 1.81 (s, 3 H), 2.27 (s, 3 H), 2.32 (s, 3 H), 2.56 (s, 3 H), 4.80 (d, J = 1.5 Hz, 1 H), 5.40 (d, J = 1.5 Hz, 1 H), 6.88 (s, 1 H), 7.16 (s, 1 H), [**5m-2**] 1.47 (s, 9 H), 1.52 (s, 9 H), 1.92 (s, 3 H), 2.15 (s, 3 H), 2.25 (s, 3 H), 2.32 (s, 3 H), 4.89 (s, 1 H), 5.54 (s, 1 H), 6.80 (s, 1 H), 7.36 (s, 1 H).

Complexation of 7. Complexation of 1 g (3.35 mmol) of **7** gave 0.49 g (34%) of **7m**, mp 138–140 °C, and 1.09 g (57%) of **7b**, mp 185 °C dec (chromatography: eluent, petroleum ether/50% ethyl acetate).

7m: mass spectrum, m/e 434 (M^+), 378, 350 (100%), 283, 52; ^1H NMR ($C_6D_5CD_3$) δ 1.77 (s, 3 H), 1.92 (s, 6 H), 2.37 (s, 3 H), 3.12 (s, 3 H), 3.32 (s, 3 H), 4.40 (s, 3 H), 6.32 (d, J = 2 Hz, 1 H), 6.43 (d, J = 2 Hz, 1 H).

7b: mass spectrum, m/e 570 (M^+), 514, 486, 458, 430, 402, 350 (100%), 52; ^1H NMR (C_6H_6) δ 1.48 (s, 6 H), 2.14 (s, 6 H), 2.99 (s, 6 H), 4.24 (d, J = 2 Hz, 1 H), 4.27 (d, J = 2 Hz, 1 H).

Complexation of 8. Complexation of 1 g (3.35 mmol) of **8** gave 0.8 g (55%) of **8m**, mp 208–210 °C, and 0.13 g (7%) of **8b**, mp 200 °C (chromatography: eluent, petroleum ether/30% ethyl acetate).

8m: mass spectrum, m/e 434 (M^+), 350 (100%), 285, 214; ^1H NMR [$CDCl_3/CS_2$ (1:1)] δ 1.61 (d, J = 8 Hz, 3 H), 1.93 (s, 3 H), 1.98 (br s, 3 H), 2.41 (br s, 3 H), 2.46 (s, 3 H), 4.24 (q, J = 8 Hz, 1 H), 4.74 (d, J = 2 Hz, 1 H), 4.90 (d, J = 2 Hz, 1 H), 6.41 (br s, 1 H), 6.54 (br s, 1 H).

8b: mass spectrum, m/e 570 (M^+), 486, 434, 402, 350 (100%), 283, 214. ^1H NMR [$CDCl_3/CS_2$ (1:1)] δ 1.65 (d, J = 7.3 Hz, 3 H), 1.93 (br s, 6 H), 2.38 (br s, 3 H), 2.61 (br s, 3 H), 3.68 (s, 6 H), 3.92 (q, J = 7.3 Hz, 1 H), 4.75 (br s, 2 H), 4.90 (br s, 2 H).

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