was added at −78 °C to a solution of sodium iodoacetate (624 mg, 3 mmol) in THF (10 mL). Workup by method b gave 2-cyclopropylsuccinic acid (**36**) (440 mg, 93%) as a white solid, mp 135–137 °C. No olefinic protons were detected in the crude ^{1}H NMR spectrum. ^{1}H NMR (360 MHz, $CDCl_3$/DMSO-d_6): −0.02 (m, 1 H), 0.22 (m, 1 H), 0.30 (m, 2 H), 0.70 (m, 1 H), 1.80 (dt, J = 5.0 and 10.0 Hz, 1 H), 2.29 (dd, J = 5.0 and 16.3 Hz, 1 H), 2.57 (dd, J = 10.0 and 16.3 Hz, 1 H), 8.0 (br). High resolution MS calcd for $C_7H_8O_3$ ($M^+ - H_2O$), 140.0473; found, 140.0472.

The reaction was repeated with lithium 1-iodocyclobutanecarboxylic acid (prepared in situ by treatment of the free acid with 1 equiv LDA at −78 °C). No ring-opened product could be detected in the ^{1}H NMR spectrum of the crude product.

Electrolysis of Dilithiated Phenylacetic Acid in the Presence of Diisopropylamine. The electrolyses were carried out exactly as described previously (eq 3). Before the electrolysis, diisopropylamine (1 to 5 equiv) was added to the anodic compartment. The composition of the crude product was determined by ^{1}H NMR. Dimer **12** was formed in 30 to 40% yield, irrespective of the amount of amine present.

Reaction of Dilithiated Phenylacetic Acid Generated with LiHMDS with Iodine. Phenylacetic acid (4 mmol, 545 mg) in THF (3 mL) was added at 0 °C to a solution of lithium hexamethyldisilazide [prepared at 0 °C from 1,1,1,3,3,3-hexamethyldisilazane (8 mmol) and butyllithium (8 mmol) in THF (16 mL)]. After 2 h of stirring at room temperature, the clear yellow solution was treated with iodine (508 mg, 2 mmol) by method b. The mixture was allowed to warm up to room temperature overnight before workup. The crude product consisted only of the dimer **12**; less than 2% of phenylacetic acid could be detected in the ^{1}H NMR spectrum of the crude product.

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Meerwein–Ponndorf–Verley-Type Reduction of Dicarbonyl Compounds to Hydroxy Carbonyl Compounds and α,β-Unsaturated Carbonyl Compounds to Allylic Alcohols Catalyzed by Zirconocene and Hafnocene Complexes

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Group IVA metallocene complexes such as bis(η^5-cyclopentadienyl)zirconium dihydrides, Cp_2ZrH_2 (**1**), and hafnium dihydrides, Cp_2HfH_2 (**8**), catalyze the chemoselective reduction of polycarbonyl compounds to hydroxy carbonyl compounds. For instance, the reduction of keto aldehydes 3-ketobutanal (**2g**) and 2-phenyl-2-ketoethanal (**2h**) proceeded selectively at aldehyde group to provide the corresponding hydroxy ketones **3g** and **3h** in 91% and 93% yields, respectively. Under similar conditions, however, cyclohexanediones were easily aromatized to benzenediols. On the other hand, **1** and **8** also catalyze the selective 1,2-reduction of various types of α,β-unsaturated carbonyl compounds, giving the corresponding allylic alcohols in good to excellent yields. Thus, steroidal dicarbonyl compounds, having an enone framework in their molecules Δ^4-androstene-3,17-dione (**11a**) and Δ^4-progestene-3,20-dione (**11b**) were reduced by **1** to 17-hydroxy-Δ^4-androsten-3-one (**12a**) and 20-hydroxy-Δ^4-progest-3-one (**12b**), which are essential human hormones, in 80% and 67% yields, respectively.

Recently we reported that bis(η^5-cyclopentadienyl)zirconium dihydride, Cp_2ZrH_2 (**1**), catalyzed the hydrogen-transfer reaction of alcohols to carbonyl compounds.[1-4] Thus, the Meerwein–Ponndorf–Verley-type (MPV-type) reduction of carbonyl compounds and the Oppenauer-type (OPP-type) oxidation of alcohols proceed simultaneously under the influence of catalytic amount of **1**. Simple carbonyl compounds can be readily reduced by **1** in 2-propanol to give the corresponding alcohols in good yields.[1] In the above reduction, the ease with which zirconocene catalyzed MPV-type reduction occurred decreased in the order aldehydes > aromatic > alicyclic > aliphatic ketones. Therefore, in the reduction of compounds containing multiple carbonyl groups, a particular carbonyl group will be expected to be reduced preferentially by this method.

Hydroxy carbonyl derivatives derived from the reduction of dicarbonyl compounds are often used as valuable precursors in synthetic organic chemistry.[5,6] Usually the selective reduction of dicarbonyl compounds to hydroxy carbonyl compounds has been achieved by using special reducing agents.[7] Therefore, the preferential reduction to hydroxy carbonyl compounds of dicarbonyl compounds **2** and **4** catalyzed by zirconocene complexes offer an attractive route to the valuable products **3** and **5** (eq 1 and 2).

Table I. Reduction of 3-Ketobutanal (2g) in 2-Propanol Catalyzed by Some Group IVA Metallocene Complexes[a]

run	catalyst	**3g**, %[b]	others, %[c]
1	Cp_2ZrH_2	94 (56)	trace
2	Cp_2HfH_2	91 (95)	trace
3	Cp_2TiCl_2	11 (7)	38
4	Cp_2ZrCl_2	43 (32)	26
5	Cp_2HfCl_2	92 (90)	4
6	$Cp_2Ti(O\text{-}i\text{-}Pr)_2$	42 (26)	25
7	$Cp_2Zr(O\text{-}i\text{-}Pr)_2$	94 (95)	trace
8	$Cp_2Hf(O\text{-}i\text{-}Pr)_2$	93 (84)	trace

[a] A mixture of **2i** (10 mmol) and 2-propanol (50 mL) was allowed to react in the presence of catalyst (0.2 mmol) at 130 °C for 8 h. [b] Determined by VPC. Parentheses indicate the yield at 80 °C. [c] Condensation products were included.

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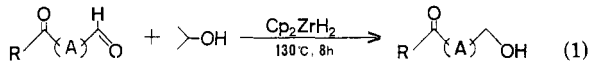
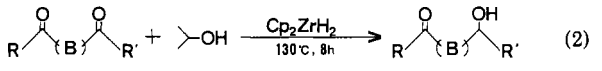


(1)

2 3

2a, 3a: R = H, A = $(CH_2)_3$
2b, 3b: R = H, A = $(CH_2)_4$
2c, 3c: R = H, A =
2d, 3d: R = H, A =
2e, 3e: R = CH_3, A = none
2f, 3f: R = CH_2CH_3, A = none
2g, 3g: R = CH_3, A = CH_2
2h, 3h: R = C_6H_5, A = none

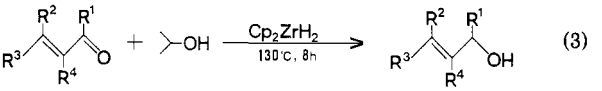


(2)

4 5

4a, 5a: R = Ch_3, R′ = CH_3, B = none
4b, 5b: R = C_6H_5, R′ = C_6H_5, B = none
4c, 5c: R = CH_3, R′ = CH_3, B = CH_2
4d, 5d: R = CH_3, R′ = CH_3, B = $CH(CH_3)$
4e, 5e: R = CH_3, R′ = CH_3, B = $(Ch_2)_2$
4f, 5f: R = C_6H_5, R′ = CH_3, B = CH_2
4g, 5g: R = C_6H_5, R′ = CH_3, B = $CH(CH_3)$
4h, 5h: R,R′ = CH=CH, B = CH=CH
4i, 5i: R,R′ = $(CH_2)_4$, B = none
4j, 5j: R,R′ = $(CH_2)_3$, B = CH_2
4k, 5k: R,R′ = $(CH_2)_3$, B = $CH(CH_3)$
4l, 5l: R,R′ = $CH_2C(CH_3)_2CH_2$, B = CH_2
4m, 5m: R,R′ = $CH_2C(CH_3)_2CH_2$, B = $CH(CH_3)$

Furthermore, we have also studied the regioselective 1,2-reduction of various α,β-unsaturated carbonyl compounds, **6**, to allylic alcohols, **7** (eq 3). An improved re-



(3)

6 7

6a, 7a: R^1 = H, R^2 = H, R^3 = CH_3, R^4 = H
6b, 7b: R^1 = CH_3, R^2 = H, R^3 = CH_3, R^4 = H
6c, 7c: R^1 = H, R^2 = H, R^3 = $(CH_2)_2CH_3$, R^4 = H
6d, 7d: R^1 = H, R^2 = H, R^3 = C_6H_5, R^4 = H
6e, 7e: R^1 = CH_3, R^2 = H, R^3 = C_6H_5, R^4 = H
6f, 7f: R^1 = H, R^2 = H, R^3 = H, R^4 = H
6g, 7g: R^1 = CH_3, R^2 = H, R^3 = H, R^4 = H
6h, 7h: R^1 = H, R^2 = H, R^3 = $(CH_2)_2CH_3$, R^4 = CH_2CH_3
6i, 7i: R^1 = H, R^2 = H, R^3 = $(CH_2)_6CH_3$, R^4 = $(CH_2)_5CH_3$
6j, 7j: R^1 = CH_3, R^2 = CH_3, R^3 = CH_3, R^4 = H
6k, 7k: R^1 = CH_3, R^2 = H, R^3 = C_6H_5, R^4 = CH_3
6l, 7l: R^1,R^2 = $(CH_2)_2$, R^3 = H, R^4 = H
6m, 7m: R^1,R^2 = $(CH_2)_3$, R^3 = H, R^4 = H
6n, 7n: R^1,R^2 = $CH_2C(CH_3)_2CH_2$, R^3 = CH_3, R^4 = H

duction of the carbonyl group of α,β-unsaturated carbonyl copounds to allylic alcohols has long been a desired synthetic transformation, since this transformation frequently results in undesired 1,4-reduction products.[8] Several methods known to bring about such a conversion have been explored,[9-11] but these methods call for the use of excess or stoichiometric amount of reagents and sometimes result in overreduction products.

In addition, selective reduction of some steroidal polycarbonyl compounds to steroidal hydroxy carbonyl compounds, which are of valuable precursors in medical and pharmaceutical chemistry, will be described.[12]

Table II. Cp_2HfH_2 (8) Catalyzed Reduction of Dicarbonyl Compounds Involving Aldehyde Groups 2a–h[a]

run	dicarbonyl compound	product	yield, %[b]	others, %[c]
1	**2a**	**3a**	52 (60)	35
2	**2b**	**3b**	54 (61)	31
3	**2c**	**3c**	66 (71)	28
4	**2d**	**3d**	91 (88)	4
5	**2e**	**3e**	93 (85)	trace
6	**2f**	**3f**	91 (90)	5
7	**2g**	**3g**	95 (93)	trace
8	**2h**	**3h**	93 (88)	4

[a] A mixture of **2** (10 mmol) and 2-propanol (50 mL) was allowed to react in the presence of 8 (0.2 mmol) at 80 °C for 8 h. [b] Isolated yield. Parentheses indicate the yield when 1 (0.2 mmol) was used at 130 °C. [c] Condensation products were included.

Table III. Cp_2HfH_2 (8) Catalyzed Reduction of Various Diketones (4a–m)[a]

run	diketone	product	yield, %[b]	others, %[c]
1	**4a**	**5a**	98	trace
2	**4b**	**5b**	91	4
3	**4c**	**5c**	88	8
4	**4d**	**5d**	87	8
5	**4e**	**5e**	72	23[d]
6	**4f**	**5f**	88	6
7	**4g**	**5g**	91	trace
8	**4h**	**5h**	0	59[e]
9	**4i**	**5i**	62	36[e]
10	**4j**	**5j**	61	37[e]
11	**4k**	**5k**	52	44[e]
12	**4l**	**5l**	84	7
13	**4m**	**5m**	87	6

[a] A mixture of **4** (10 mmol) and 2-propanol (50 mL) was allowed to react in the presence of 8 (0.2 mmol) at 80 °C for 8 h. [b] Isolated yield. [c] Condensation products were included. [d] 3-Methyl-2-cyclopenten-1-one (**9**) was included. [e] Benzenediols were included.

Results and Discussion

(A) Reduction of Various Dicarbonyl Compounds, 2 and 4, Catalyzed by Metallocene Complexes of Zr and Hf. In order to test the catlytic activity of several group IVA metallocene complexes, the MPV-type reduction of 3-ketobutanal (**2g**) to 1-hydroxy-3-butanone (**3g**) was chosen as a model reaction. These results are summarized in Table I.

Among the complexes examined, hafnocene complexes Cp_2HfH_2 (8), $Cp_2Hf(O\text{-}i\text{-}Pr)_2$, and Cp_2HfCl_2 showed high activity for the reduction of **2g** to **3g**. The catalytic activity of zirconocene complexes **1** and $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ was comparable to the activity of hafnocene complexes in the reduction at higher temperature(130 °C). However, hafnocene complexes were superior than the corresponding zirconocene complexes in the reduction of **2g** in refluxing 2-propanol. Cp_2ZrCl_2 and Cp_2TiCl_2 showed poor activity in the above reduction. It is interesting to note that Cp_2HfCl_2 had a high activity comparable to that of 8 de-

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spite the fact that the corresponding zirconocene and titanocene homologues Cp_2ZrCl_2 and Cp_2TiCl_2 had no catalytic activity (runs 3–5). The difference of catalytic activity among IVA metallocene chlorides may be attributed to the bond strength between the metal and the chlorine in those complexes. Recently, Bercaw has reported that the hafnium–chlorine bond was appreciably weaker than zirconium– and titanium–chlorine bonds.[13] The fact that $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ at lower temperature, i.e., in refluxing 2-propanol, exhibited a higher activity than **1** for the reduction of **2g** to **3g** suggests that the present reduction proceeds via a pathway in which an alkoxy complex is the key intermediate (runs 4 and 7). A similar suggestion could be made in the reduction by Cp_2TiCl_2 and $Cp_2Ti(O\text{-}i\text{-}Pr)_2$, although the catalytic activity of titanocene complexes was lower than that of the corresponding zirconocene complexes (runs 3 and 6).

On the basis of these results, a variety of dicarbonyl compounds were reduced in a fivefold excess of 2-propanol under the influence of catalytic amount (0.02 equiv) of **1** or **8**. All of the dicarbonyl compounds used were reduced to hydroxy carbonyl compounds in satisfactory yields. The reduction of dicarbonyl compounds **2a–h** having an aldehyde group are shown in Table II.

Dialdehydes **2a–c** were reduced to monohydroxy aldehydes **3a–c**, which are valuable intermediates in synthetic organic chemistry,[14] in fair yields along with aldol condensation products (runs 1–3). Terephthalaldehyde (**2d**) was converted to *p*-(hydroxymethyl)benzaldehyde (**3d**) in 91% yield (run 4) without the formation of any byproduct such as 1,4-benzenedimethanol which is often the product of the overreduction[5] of **3d**.

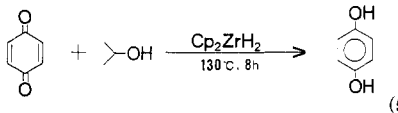
The reduction of dicarbonyl compounds 2-ketopropanal (**2e**), 2-ketobutanal (**2f**), 3-ketobutanal (**2g**), and 2-phenyl-2-ketoethanal (**2h**), involving both the aldehyde and the ketone groups in the molecules, occurred chemoselectively at the aldehyde groups, giving hydroxy ketones **3e–h** in 91–95% yields (runs 5–8).

Simple diketones **4a–m** were reduced with ease in Zr- or Hf-catalyzed MPV-type reductions (Table III).

Symmetrical diketones 2,3-butanedione (**4a**), diphenylethanedione (**4b**), and 2,4-pentanedione (**4c**) were converted to 3-hydroxy-2-butanone (**5a**), 2-hydroxy-1,2-diphenylethanone (**5b**), and 4-hydroxy-2-pentanone (**5c**) in 98%, 91%, and 88% yields, respectively (runs 1–3). However, 2,5-hexanedione (**4e**) was reduced in competition with intramolecular ring closure of **4e** to form 5-hydroxy-2-hexanone (**5e**) and 3-methyl-2-cyclopenten-1-one (**9**) in 72% and 23% yields, respectively.

Although 3-methyl-2,4-pentanedione (**4d**) and 1-phenyl-2-methyl-1,3-butanedione (**4g**) were reduced in good yields, these reductions gave a diastereomeric mixture of threo and erythro isomers in a ratio of about 6:4 (runs 4 and 7). The reduction of 1-phenyl-1,3-butanedione (**4f**) could be achieved regioselectively, providing 1-phenyl-3-hydroxybutan-1-one (**5f**) in 88% yield, in which the carbonyl group adjacent to the methyl group of **4f** was reduced (run 6).

The reduction of cyclic diketones such as *p*-benzoquinone (**4h**), 1,2-cyclohexanedione (**4i**), 1,3-cyclohexanedione (**4j**), and 2-methyl-1,3-cyclohexanedione (**4k**) afforded the corresponding cyclic hydroxy ketones **5h–k**, but the yields somewhat decreased due to the aromatization to benzenediols. Compound **4h**, which tends to aromatize under the mild condition of refluxing 2-propanol-,[7d,15] gave exclusively hydroquinone, but the yield was low (run 8) (eq 4). On the other hand, 5,5-dimethyl-1,3-



(4)

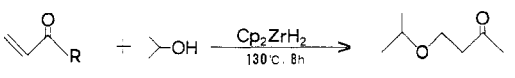
4h

cyclohexanedione (**4l**) and 2,5,5-trimethyl-1,3-cyclohexanedione (**4m**), which have skeletons that resist aromatization, were reduced in good yields to cyclic hydroxy ketones **5l** and **5m**, respectively, without the formation of undesirable benzenediols (runs 12 and 13).

(B) Reduction of α,β-Unsaturated Carbonyl Compounds 6 Catalyzed by Metallocene Complexes of Zr and Hf. α,β-Unsaturated carbonyl compounds **6** were reduced by zirconocene or hafnocene complexes in 2-propanol, giving 1,2-reduction products, allylic alcohols **7**, in satisfactory yields.

Representative results were obtained when **6** (10 mmol) was allowed to react in 2-propanol (50 mmol) under the influence of **1** or **8** (0.2 mmol) at 130 °C for 8 h (Table IV).

α,β-Unsaturated linear aldehydes and ketones such as *trans*-2-butenal (**6a**), *trans*-3-penten-2-one (**6b**), *trans*-2-hexenal (**6c**), cinnamaldehyde (**6d**) and 4-phenyl-3-buten-2-one (**6e**) were readily reduced to the corresponding allylic alcohols **7a–e** in 89–96% yields with only small amounts of saturated carbonyl and alcohol byproducts (runs 1–5). However, in the reduction of 2-propenal (**6f**) and 3-buten-2-one (**6g**), both possessing a terminal double bond, no formation of a 1,2-reduction product was detected. Instead, 3-(2-propoxy)propanal (**10a**) and 4-(2-propoxy)-2-butanone (**10b**) were obtained as the sole products in 90% and 66% yields, respectively (runs 6 and 7). The formation of **10** is attributed to Michael addition of 2-propanol to the carbon–carbon double bond of **6** (eq 5). It has been reported that this type of addition easily



(5)

6 10

6f, 10a: R = H
6g, 10b: R = CH_3

Table IV. Group IVA Metallocene Complex Catalyzed Reduction of α,β-Unsaturated Carbonyl Compounds 6a–n[a]

run	diketone	product	yield, %[b]	others, %[c]
1	**6a**	**7a**	92 (91)	3
2	**6b**	**7b**	96 (94)	trace
3	**6c**	**7c**	90 (93)	6
4	**6d**	**7d**	90 (91)	4
5	**6e**	**7e**	89 (90)	5
6	**6f**	**7f**	0 (0)	90[d]
7	**6g**	**7g**	0 (0)	66[d]
8	**6h**	**7h**	88 (84)	trace
9	**6i**	**7i**	91 (88)	trace
10	**6j**	**7j**	86 (86)	7
11	**6k**	**7k**	68 (72)	0
12	**6l**	**7l**	82 (80)	4
13	**6m**	**7m**	88 (84)	2
14	**6n**	**7n**	66 (73)	trace

[a] A mixture of **6** (10 mmol) and 2-propanol (50 mL) was allowed to react in the presence of Cp_2HfH_2 (**8**) (0.2 mmol) at 130 °C for 8 h. [b] Isolated yields. Parentheses indicate the yield when Cp_2ZrH_2 (**1**) was used. [c] Overreduction product and 1,4-adduct were included. [d] β-Alkoxy carbonyl compound was included.

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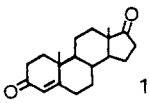
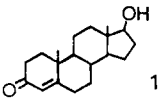
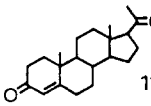
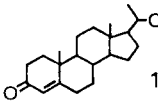
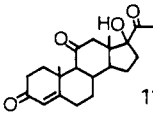
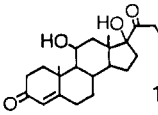
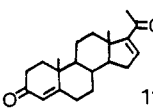
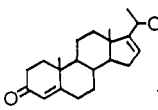
Table V. Cp_2HfH_2 (8) Catalyzed Reduction of Steroidal Diketones 11a–d[a]

run	diketone	product	yield, %[b]	others, %[c]
1	 11a	 12a	80	5
2	 11b	 12b	67	11
3	 11c	 12c	44	18
4	 11d	 12d	20	10
5[d]	**11d**	**12d**	35	16

[a] A mixture of **11** (10 mmol) and 2-propanol (50 mL) was allowed to react in the presence of **8** (0.2 mmol) at 80 °C for 8 h. [b] Isolated yield. [c] Condensation products were included. [d] At 130 °C.

takes place under acidic or basic conditions.[16]

On the other hand, α,β-unsaturated carbonyl compounds having alkyl and aromatic substituents at the α- and/or β-positions such as *trans*-2-ethyl-2-hexanal (**6h**), *trans*-2-hexyl-2-decenal (**6i**), mesityl oxide (**6j**) and *trans*-3-methyl-4-phenyl-3-buten-2-one (**6k**), were reduced to the corresponding allylic alcohols **7h–k** (runs 8–11). Similarly, α,β-unsaturated cyclic ketones **6l** and **6m** gave cyclic allylic alcohols in good yields except for the case of sterically hindered isophorone (**6n**). Thus, 2-cyclopenten-1-one (**6l**) and 2-cyclohexen-1-one (**6m**) were converted to 2-cyclopenten-1-ol (**7l**) and 2-cyclohexen-1-ol (**7m**) in 82% and 88% yields, respectively (runs 12 and 13). In the reduction of **6l** and **6m** with simple metal hydrides such as $LiAlH_4$ and $NaBH_4$, 1,4-reduction took place as well as 1,2-reduction to give a mixture of cyclopentanone + **7l** and cyclohexanone + **7m**, respectively.[9c,10c,11b,12a] In contrast, Krishnamurthy has reported that satisfactory yields of **7l** and **7m** can be obtained by using excess 9-borabicyclo-[3.3.1]nonane (9-BBN), which is one of the efficient reagents for regioselective 1,2-reduction of α,β-unsaturated carbonyl compounds.[17]

(C) Reduction of Steroidal Carbonyl Compounds 11 Catalyzed by Metallocene Complexes of Zr and Hf. Since the hafnocene complex was found to be the best catalyst for the MPV-type reduction of dicarbonyl compounds, some steroidal compounds with polycarbonyl groups (**11a–d**) were allowed to react in 2-propanol under the influence of **8** (Table V).

The simple steroidal diketone Δ^4-androsten-3,17-dione (**11a**) was reduced with high chemoselectivity at the refluxing temperature of 2-propanol to the hydroxy enone **12a**, an essential human hormone, in 80% yield (run 1). The reduction of Δ^4-progestene-3,20-dione (**11b**) gave 20-hydroxy-Δ^4-progest-3-one (**12b**), in which the carbonyl group anchoring the side chain on D-ring was exclusively hydrogenated. Menawhile, Δ^4-cortin-3,11,17-trione 20-acetate (**11c**) containing four carbonyl groups in the molecule was converted to 11-hydroxy-Δ^4-cortin-3,17-dione 20-acetate (**12c**) in 44% yield while 16-dehydro-Δ^4-progestene-3,20-dione (**11d**) was resistant to the reduction, giving 16-dehydro-20-hydroxy-Δ^4-progesten-3-one (**12d**) in low yield (20%) even after 98 h. Although the yield of **12d** at higher temperature (130 °C) increased to 35%, an undesirable overreduction product was also formed.

In conclusion, group IVA metallocene complexes, particularly zirconocene and hafnocene, showed high chemoselectivity for the reduction of dicarbonyl compounds to hydroxy carbonyl compounds and α,β-unsaturated carbonyl compounds to allylic alcohols. With the present MPV-type reduction, a wide variety of hydroxy carbonyl compounds were obtained in good yields. In comparison to more difficult conventional methods, these valuable intermediates, especially the hydroxy aldehydes, were easily obtained by this new method. Furthermore, steroidal ketones with polycarbonyl groups or enone framework were also reduced chemoselectively to provide the corresponding monohydroxy compounds.

Experimental Section

The melting points were determined with a Yanaco MP52032 melting point apparatus and are corrected. IR spectra were taken with a JASCO A202 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL pmx-60 spectrometer and a Hitachi R-90H, respectively. Tetramethylsilane was used as the internal standard. The GLC analyses were performed with a Yanaco G-1800 instrument using a 3 m × 2.5 mm column packed with 5% Silicon OV-7 and PEG-20M on Chromosorb W.

Compounds were commercial grade, and solvents were used after drying by conventional methods.

Group IVA Metallocene Complexes. Cp_2ZrH_2 (**1**), Cp_2ZrCl_2, Cp_2HfH_2 (**8**), Cp_2HfCl_2, Cp_2TiCl_2, and $Cp_2Ti(O^iPr)_2$ were prepared by a procedure similar to that described by Wailes[18] and by Lappert.[19] $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ and $Cp_2Hf(O\text{-}i\text{-}Pr)_2$ were prepared by the addition of 2 mol of acetone to 1 mol of **1** and **8**, respectively.[20]

1: mp 304–305 °C (lit.[18] mp 305 °C); IR (KBr) 3100, 1520, 1300, 1020, 840 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.49 (s, 10 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 108.2 (s).

8: IR (KBr) 3400, 1570, 1400, 1380, 1020, 820, 600 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.30 (s, 10 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 112.2 (s).

$Cp_2Ti(O\text{-}i\text{-}Pr)_2$: IR (KBr) 3100, 1020, 850, 770 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.28 (s, 10 H) 2.1–1.3 (m, 14 H); ^{13}C NMR

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(C_6D_6/Me_4Si) δ 112.7 (s), 65.7 (d), 25.1 (q).

$Cp_2Zr(O\text{-}i\text{-}Pr)_2$: IR (KBr) 3100, 1015, 840, 770 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.22 (s, 10 H), 2.2–1.4 (m, 14 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 113.3 (s), 66.6 (d), 25.3 (q).

$Cp_2Hf(O\text{-}i\text{-}Pr)_2$: IR (KBr) 3040, 1600, 1300, 1230, 1150, 1000, 840 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.35 (s, 10 H), 2.2 (m, 14 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 113.1 (s), 68.1 (d), 30.8 (q).

Cp_2ZrCl_2: IR (KBr) 3070, 1440, 1010, 800 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.18 (s, 10 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 115.9 (s).

Cp_2HfCl_2: IR (KBr) 3110, 1440, 1020, 830 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.30 (s, 10 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 114.4 (s).

Cp_2TiCl_2: IR (KBr) 3100, 1440, 1010, 830 cm^{-1}; ^1H NMR (C_6D_6/Me_4Si) δ 6.07 (s, 10 H); ^{13}C NMR (C_6D_6/Me_4Si) δ 116.7 (s).

Dicarbonyl Compounds and α,β-Unsaturated Carbonyl Compounds. Commercially available dicarbonyl compounds **2d–j**, **4a–c,e–f,h–l**, and **11a–d** and α,β-unsaturated carbonyl compounds **6a–h,6j–n** were used directly without additional purification. The other dicarbonyl compounds and α,β-unsaturated carbonyl compounds were prepared according to the general method described below.

1,5-Pentanedial (**2a**), 1,6-hexanedial (**2b**), and 1,3-cyclopentanedicarboxaldehyde (**2c**) were prepared by oxidative cleavage of the corresponding cyclic olefins cyclopentene, cyclohexene, and bicyclo[2.2.1]hept-2-ene with potassium permanganate followed by treatment with buffer solution (pH 3–4).[21] 3-Methyl-2,4-pentanedione (**4d**) and 1-phenyl-2-methyl-1,3-butanedione (**4g**) were prepared by methylation of 2,4-pentanedione (**4c**) and 1-phenyl-1,3-butanedione (**4f**) with TlOEt–MeI, respectively.[22]

trans-2-Hexyl-2-decenal (**6i**) was prepared by self-aldol condensation of octanal in the presence of 0.1 equiv of $CuCl_2$ as catalyst. These analytical data are in agreement with those of authentic samples and literature values.[23]

2a: [M^+], *m/e* 100; IR (NaCl) 2950, 2750, 1710, 1480–1330, 1100, 1000, 740 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 10.0 (t, 2 H) 2.8–1.7 (m, 4 H), 1.5–1.0 (m, 2 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 206.5 (d), 40.6 (t), 27.1 (t).

2b: [M^+], *m/e* 114; IR (NaCl) 2950, 2850, 2750, 1720, 1480–1330, 1130, 1020, 740 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.7 (d, 2 H), 2.7–2.3 (m, 4 H), 1.9–1.4 (m, 4 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 207.1 (d), 40.1 (t), 24.5 (t).

2c: [M^+], *m/e* 126; IR (NaCl) 2950, 2850, 2700, 1730, 1380–1030, 950, 920, 880, 840, 770 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.7 (d, 2 H), 2.9–2.5 (m, 2 H), 2.0–1.4 (m, 6 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 205.8 (d), 46.6 (d), 25.1 (t), 24.3 (t).

4d: [M^+], *m/e* 114; IR (NaCl) 2950, 2900, 2700–2550, 1600, 1450, 1380–1100, 1080–950, 880 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 2.5 (m, 1 H), 2.3 (s, 6 H), 1.4 (d, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 203.7 (s), 59.1 (d), 29.5 (q), 20.7 (q).

4g: [M^+], *m/e* 172; IR (NaCl) 2950, 2850, 1660, 1600, 1450, 1280–1110, 760 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 7.4–6.9 (m, 5 H), 2.7 (m, 1 H), 2.4 (s, 3 H), 2.1 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 209.9 (s), 206.8 (s), 134.3 (s), 129.3 (d), 128.6 (d), 126.9 (d), 58.8 (d), 50.7 (t), 29.3 (q), 21.1 (q).

6i: [M^+], *m/e* 238; IR (NaCl) 2970, 2900, 1760, 1700, 1640, 1470, 1380, 1260, 1180, 1090, 910, 870, 750 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.5 (d, 1 H), 6.2 (t, 1 H), 2.9–1.5 (m, 22 H), 1.9 (t, 3 H), 0.9 (t, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 193.5 (d), 153.5 (d), 142.8 (s), 44.4 (t), 31.7 (d), 29.3 (t), 29.0 (t), 28.8 (t), 28.6 (t), 28.2 (t), 26.3 (t), 22.8 (t), 22.6 (t), 20.7 (t), 13.9 (q), 13.7 (q).

General Method for Reduction of Dicarbonyl Compounds 2 and 4 Catalyzed by Cp_2HfH_2 (8). A mixture of **8** (0.2 mmol) and **2** or **4** (10 mmol) in 2-propanol (20 mL) was allowed to react at 80 °C under a nitrogen stream. After the reaction, the catalyst was removed by centrifugation of filtration. The solutions were distilled under reduced pressure and the products **3** and **5** isolated by MPLC on silica gel (hexane/chloroform, 1–5:1, eluent). Spectral data were compared with those of authentic samples and the literature values.[3a,7,10–13,22–28] The analytical data of compounds **3a–c,e–j** and **5h–i,l** are as follows.

5-Hydroxypentanal (3a): [M^+], *m/e* 102; IR (NaCl) 3300–3100, 2950, 2800, 1710, 1440–1260, 1120–980, 740 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.7 (t, 1 H), 3.7–3.5 (m, 2 H), 2.4–2.2 (m, 2 H), 2.3 (s, 1 H), 2.1–1.6 (m, 4 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 202.8 (d), 63.1 (t), 40.7 (t), 31.3 (t), 16.7 (t).

6-Hydroxyhexanal (3b): [M^+], *m/e* 116; IR (NaCl) 3300–3100, 2950, 2800, 1720, 1450–1240, 1130–980, 770 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.8 (t, 1 H), 3.4–3.2 (m, 2 H), 2.3–1.0 (m, 8, H), 2.2 (s, 1 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 202.5 (d), 63.3 (t), 45.3 (t), 32.7 (t), 16.6 (t), 14.8 (t).

3-(Hydroxymethyl)cyclopentanecarboxaldehyde (3c): [M^+], *m/e* 128; IR (NaCl) 3300–3100, 2950, 2850, 1710, 1450–1280, 1200–1100, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 9.5 (d, 1 H), 3.4–2.8 (m, 3 H), 2.6 (s, 1 H), 2.4–1.1 (m, 7 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 204.1 (d), 66.8 (t), 47.6 (d), 34.1 (d), 27.3 (t), 24.4 (t), 22.1 (t).

3-Hydroxy-5-methyl-1-cyclohexanone (5j): [M^+], *m/e* 128; IR (NaCl) 3500–3300, 2900, 1660, 1460–1030, 1010–900, 800, 750 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 3.9 (s, 1 H), 3.9–3.3 (m, 1 H), 2.3 (d, 2 H), 2.2 (d, 2 H), 1.8 (d, 2 H), 1.6 (m, 1 H), 1.2 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 211.7 (s), 66.0 (d), 45.8 (t), 32.2 (t), 29.7 (t), 28.8 (d), 15.2 (q).

3-Hydroxy-5,5-dimethyl-1-cyclohexanone (5k): [M^+], *m/e* 128; IR (NaCl) 3500–3300, 2900, 1670, 1480–1050, 1020–880, 810, 760 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 3.95 (s, 1 H), 3.9–3.4 (m, 1 H), 2.4 (s, 2 H), 2.2 (d, 2 H), 1.8 (d, 2 H), 1.2 (s, 6 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 212.2 (s), 66.3 (d), 47.1 (t), 39.7 (t), 35.4 (s), 32.6 (t), 17.3 (q).

Reduction of 2,5-Hexanedione (4e) in 2-Propanol Catalyzed by Cp_2HfH_2 (8). A mixture of **8** (0.2 mmol) and **4e** (10 mmol) in dry 2-propanol (20 mmol) was allowed to react under nitrogen stream at 80 °C for 8 h. After the reaction, the catalyst was removed by filtration. 5-Hydroxy-2-hexanone (**5e**) was isolated by distillation under reduced pressure in 72% yield, and then 3-methyl-2-cyclopenten-1-one was separated from the distillation residue by MPLC on silica gel (ethyl acetate/hexane, 1:5, eluent) in 23% yield. Spectral data were compared with the literature values.[29]

3-Methyl-2-cyclopenten-1-one (9): [M^+], *m/e* 96; IR (NaCl) 3000, 1670, 1640, 1350, 1060, 870, 750 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) 6.22 (s, 1 H), 2.2–1.4 (m, 4 H), 0.9 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 204.8 (d), 148.2 (s), 131.9 (d), 35.3 (t), 26.7 (t), 22.0 (q).

Reduction of 2,5-Cyclohexadiene-1,4-dione (4h), 1,3-Cyclohexanedione (4j), and 5-Methyl-1,3-cyclohexanedione (4k) in 2-Propanol Catalyzed by Cp_2HfH_2 (8). A mixture of **8** (0.2 mmol) and **4j** (10 mmol) in dry 2-propanol (20 mL) was allowed to react under nitrogen at 80 °C for 8 h. After removal of the catalyst by filtration, 3-hydroxycyclohexanone (**5j**) was isolated by vacuum distillation in 62% yield. The residue was cooled overnight in a refrigerator and the 1,3-benzenediol separated as a white crystalline solid in 36% yield. In the reduction of **4h** and **4k**, 1,4-benzenediol and 2-methyl-1,3-benzenediol were obtained in 59% and 39% yield, respectively, in the same manner as above. Spectral data were compared with the literature values.[10,30,31]

1,3-Benzenediol: [M^+], *m/e* 110; IR (NaCl) 3700–3200, 2900, 2800, 1620–1140, 1100, 1050, 850, 760–720 cm^{-1}; ^1H NMR ($CDCl_3$/Me_4Si) δ 8.5 (s, 1 H), 7.2–6.8 (m, 1 H), 6.5–6.2 (m, 2 H), 6.4 (s, 2 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 150.2 (s), 126.1 (d), 122.6 (d), 115.3 (d).

1,4-Benzenediol: [M^+], *m/e* 110; IR (NaCl) 3700–3000, 2950,

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2800, 1570–1450, 1400, 1280–1140, 1100, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 7.9 (s, 2 H), 6.7 (s, 4 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 148.7 (s), 123.7 (d).

2-Methyl-1,3-benzenediol: [M^+], m/e 110; IR (NaCl) 3700–3200, 2900, 2800, 1600–1150, 1100, 1030, 860, 740–720 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 8.4 (s, 1 H), 7.3–6.7 (m, 2 H), 6.5–6.1 (m, 2 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 152.2 (s), 126.5 (d), 120.6 (d), 114.1 (d), 22.6 (q).

General Method for the Cp_2HfH_2 (8) Catalyzed Reduction of α,β-Unsaturated Carbonyl Compounds 6. A mixture of 8 (0.2 mmol) and **6** (10 mmol) in 2-propanol (20 mL) was allowed to react under nitrogen stream at 80 °C. After removal of catalyst by centrifugation or filtration, the products were isolated by distillation in vacuo or by MPLC on silica gel (hexane/chloroform, 3–5:1, eluent). Spectral data of each product were compared with those of authentic samples and the literature values. The analytical data of the compound **7i** are as follows.

***trans*-2-Hexyl-2-decen-1-ol (7i)**: [M^+], m/e 240; IR (NaCl) 3350, 3000, 2900, 1450, 1400–1200, 1100–930, 890 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.3 (t, 1 H), 2.7–1.2 (m, 24 H), 2.5 (s, 1 H), 1.1 (t, 1 H), 1.0 (t, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 139.1 (s), 122.2 (d), 55.1 (d), 38.0 (t), 29.1 (t), 27.7 (t), 26.0 (t), 25.3 (t), 25.1 (t), 24.7 (t), 23.3 (t), 22.5 (t), 21.9 (t), 20.8 (t), 14.3 (q), 13.9 (q).

Reduction of 2-Propenal (6f) and 3-Buten-2-one (6g) Catalyzed by Cp_2HfH_2 (8). A mixture of 8 (0.2 mmol) and **6f** or **6g** (10 mmol) in 2-propanol (20 mL) was allowed to react under nitrogen stream at 80 °C. After the reaction, the catalyst was removed by filtration, and 3-(2-propoxy)propanal (**10a**) or 4-(2-propoxy)-2-butanone (**10b**) was isolated from the filtrate by distillation under reduced pressure in 90% and 66% yields, respectively. Spectral data of **10a,b** are as follows.

3-(2-Propoxy)propanal (10a): [M^+], m/e 106; IR (NaCl) 2900, 1710, 1360, 1110 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 10.9 (d, 1 H), 4.3–3.7 (m, 3 H), 1.2 (d, 6 H), 1.1 (t, 2 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 190.3 (d), 73.6 (d), 68.1 (d), 32.8 (t), 14.1 (q).

4-(2-Propoxy)-2-butanone (10b): [M^+], m/e 120; IR (NaCl) 2950, 1730, 1380, 1140 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 4.1–3.3 (m, 3 H), 1.5 (s, 3 H), 1.2 (d, 6 H), 1.1 (t, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 214.1 (s), 71.2 (d), 66.1 (d), 34.0 (t), 26.1 (s), 14.3 (q).

General Method for the Cp_2HfH_2 (8) Catalyzed Reduction of Steroidal Carbonyl Compounds 11. A mixture of 8 (0.2 mmol) and **11** (10 mmol) in 2-propanol (20 mL) was allowed to react under nitrogen stream at 80 °C. After the reaction, the catalyst was removed by centrifugation or filtration. The solvent was removed under reduced presure and then the products **12** were isolated by MPLC on silica gel (hexane/chloroform or ethyl acetate, 1–5:1, eluent). Spectral data were compared with the literature values.[22-28] The analytical data of compounds **12a–d** are as follows.

17-Hydroxy-Δ^4-androsten-3-one (12a): [M^+], m/e 288; IR (NaCl) 3600–3200, 2900, 2800, 1660, 1450, 1330, 1260–1100, 1060, 950, 870 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.7 (s, 1 H), 3.9–3.5 (m, 1 H), 2.6–0.8 (m, 19 H), 2.15 (s, 1 H), 1.2 (s, 3 H), 0.8 (s, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 199.3 (s), 171.2 (s), 123.7 (d), 81.2 (d), 53.9 (d), 50.5 (d), 42.8 (s), 38.6 (s), 36.4 (t), 35.7 (t), 35.6 (d), 33.8 (t), 32.8 (t), 31.5 (t), 30.3 (t), 23.3 (t), 20.7 (t), 17.4 (q), 11.1 (q).

20-Hydroxy-Δ^4-progest-3-one (12b): [M^+], m/e 316; IR (NaCl) 3600–3400, 2950, 2850, 1660, 1450, 1330, 1250–1080, 1150, 950, 870 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.7 (s, 1 H), 4.1–3.9 (m, 1 H), 2.4–0.8 (m, 20 H), 2.1 (s, 1 H), 1.2 (d, 3 H), 1.0 (s, 3 H), 0.8 (s, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 98.9 (s), 170.6 (s), 123.8 (d), 70.0 (d), 63.4 (d), 55.9 (d), 53.6 (d), 43.8 (s), 38.6 (t), 38.5 (s), 35.7 (t), 35.5 (t), 33.9 (d), 32.7 (t), 31.9 (t), 31.4 (t), 24.3 (q), 22.8 (t), 21.0 (t), 17.3 (q), 13.3 (q).

11-Hydroxy-Δ^4-cortin-3,17-dione 20-acetate (12c): [M^+], m/e 404; IR (NaCl) 3600–3400, 2950, 2850, 1700, 1650, 1600, 1480, 1380–1280, 1260–1150, 950, 880 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.7 (s, 1 H), 4.2–3.8 (m, 1 H), 4.2 (s, 2 H), 2.8–0.9 (m, 17 H), 2.4 (s, 1 H), 2.3 (s, 3 H), 2.15 (s, 1 H), 1.35 (s, 3 H), 0.7 (s, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 204.7 (s), 199.9 (s), 170.4 (s), 169.3 (s), 124.3 (d), 88.6 (s), 67.8 (t), 64.2 (t), 62.5 (d), 51.1 (s), 50.0 (d), 49.9 (t), 38.2 (s), 36.5 (d), 35.0 (t), 34.6 (t), 33.4 (t), 32.5 (t), 32.3 (t), 23.2 (t), 20.5 (q), 17.2 (q), 15.3 (q).

16-Dehydro-20-hydroxy-Δ^4-progesten-3-one (12d): [M^+], m/e 314; IR (NaCl) 3500–3200, 2950, 2850, 1660, 1450, 1320, 1250–1120, 950, 860 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 6.7 (t, 1 H), 5.7 (s, 1 H), 4.0–3.8 (m, 1 H), 2.6–0.9 (m, 17 H), 2.3 (s, 1 H), 1.4 (d, 3 H), 1.0 (s, 3 H), 0.65 (s, 3 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 198.9 (s), 170.5 (s), 155.0 (d), 143.9 (s), 123.8 (d), 63.1 (d), 55.6 (d), 54.0 (d), 46.0 (s), 38.6 (s), 35.5 (t), 34.4 (t), 33.8 (t), 33.7 (d), 32.6 (t), 32.0 (t), 31.7 (t), 27.0 (q), 20.6 (t), 17.1 (q), 15.7 (q).

Registry No. **1**, 37342-98-6; **2a**, 111-30-8; **2b**, 1072-21-5; **2c**, 4750-17-8; **2d**, 623-27-8; **2e**, 78-98-8; **2f**, 4417-81-6; **2g**, 625-34-3; **2h**, 1074-12-0; **3a**, 4221-03-8; **3b**, 34067-76-0; **3c**, 114764-46-4; **3d**, 52010-97-6; **3e**, 116-09-6; **3f**, 5077-67-8; **3g**, 590-90-9; **3h**, 582-24-1; **4a**, 431-03-8; **4b**, 134-81-6; **4c**, 123-54-6; **4d**, 815-57-6; **4e**, 110-13-4; **4f**, 93-91-4; **4g**, 114764-47-5; **4h**, 166-54-1; **4i**, 765-87-7; **4j**, 504-02-9; **4k**, 1193-55-1; **4l**, 126-81-8; **4m**, 1125-11-7; (±)-**5a**, 52217-02-4; (±)-**5b**, 579-44-2; (±)-**5c**, 74339-90-5; (±)-(*R**,*R**)-**5d**, 114764-52-2; (±)-(*R**,*S**)-**5d**, 114789-63-8; (±)-**5e**, 114818-69-8; (±)-**5f**, 105927-50-2; (±)-(*R**,*R**)-**5g**, 79963-28-3; (±)-(*R**,*S**)-**5g**, 114764-48-6; (±)-**5i**, 114818-70-1; (±)-**5j**, 114764-49-7; **5k**, 102547-88-6; (±)-**5l**, 114764-50-0; **5m**, 114764-51-1; **6a**, 123-73-9; **6b**, 3102-33-8; **6c**, 6728-26-3; **6d**, 14371-10-9; **6e**, 1896-62-4; **6f**, 107-02-8; **6g**, 78-94-4; **6h**, 64344-45-2; **6i**, 64935-39-3; **6j**, 141-79-7; **6k**, 42968-14-9; **6l**, 930-30-3; **6m**, 930-68-7; **6n**, 78-59-1; **7a**, 504-61-0; (±)-**7b**, 60102-79-6; **7c**, 928-95-0; **7d**, 4407-36-7; (±)-**7e**, 84519-62-0; **7h**, 38384-38-2; **7i**, 74612-63-8; (±)-**7j**, 53177-37-0; **7k**, 87422-10-4; (±)-**7l**, 62894-08-0; (±)-**7m**, 62860-38-2; (±)-**7n**, 114818-71-2; **8**, 68183-87-9; **9**, 2758-18-1; **10a**, 39563-51-4; **10b**, 32541-58-5; **11a**, 63-05-8; **11b**, 57-83-0; **11c**, 50-04-4; **11d**, 1096-38-4; **12a**, 58-22-0; **12b**, 145-14-2; **12c**, 50-03-3; **12d**, 972-43-0; Cp_2TiCl_2, 1271-19-8; Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $Cp_2Ti(O\text{-}i\text{-}Pr)_2$, 52445-46-2; $Cp_2Zr(O\text{-}i\text{-}Pr)_2$, 78091-18-6; $Cp_2Hf(O\text{-}i\text{-}Pr)_2$, 114764-53-3; *i*-PrOH, 67-63-0; *n*-$C_7H_{15}CHO$, 124-13-0; 1,4-$C_6H_4(OH)_2$, 123-31-9; 1,2-$CoH_4(OH)_2$, 120-80-9; 1,3-$C_6H_4(OH)_2$, 108-46-3; 1,3,2-$CoH(OH)_2Me$, 608-25-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8; bicyclo[2.2.1]hept-2-ene, 498-66-8.