A Novel Concept for Transition-Metal-Catalyzed Reactions: Electron Transfer under Buffered Protic Conditions

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A novel concept for conductingtransition-metal-catalyzed radical reactions that allows highly diastereoselective titanocene-catalyzed pinacol couplings is described.
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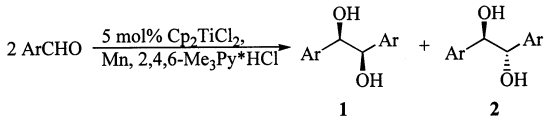
Over the last three years the development of catalytic reactions from stoichiometric processes has attracted increasing attention.[1] The first realization of this concept has been a McMurry coupling catalytic in titanium.[2] Other useful catalytic processes that have been developed are Nozaki-Hiyama reactions,[3] pinacol couplings,[4] and samarium diiodide initiated transformations.[4b][5] Keystep in the catalytic cycle, after the desired initial stoichiometric process, is the silylation of metal oxides or alkoxides to yield chlorides with Me_3SiCl, Me_3SiOTf, or similarily active reagents. Reduction with a cost-efficient stoichiomteric reductant, usually a metal powder, allows for in situ recycling of the initialy stoichiometric reagent. The catalytic cycle is closed. Considering the energy of the overall process, formation of the silicon−oxygen bond, one of the most stable bonds, delivers the energy necessary to regenerate metal chlorides from metal oxides or alkoxides formed in the first step of the catalytic reaction.

However, silylation also poses problems. First, silylation is frequently the slowest step in the catalytic cycle and thus the highly reactive reagents mentioned above have to be employed to exclude uncatalyzed reaction pathways. Functional groups sensitive to these strong Lewis acids are not tolerated. Second, Me_3SiCl promotes electron transfer from metal powders to aldehydes[6] and thus care has to be taken to avoid this undesired uncatalyzed reaction. Third, after hydrolysis hexamethyldisiloxane is formed in stoichiometric amounts that can not be readily recycled and therefore has to be disposed of as waste.

Results and Discussion

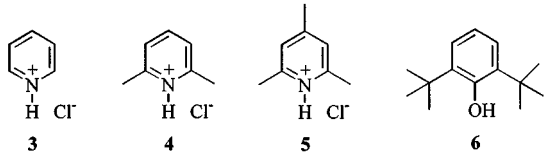
In this paper we address these shortcomings and disclose our results on achieving catalytic turnover in titanocene-catalyzed pinacol couplings[7][8] by protonation of the metal −oxygen bond;[9][10] see Figure 1 for details. Our approach is based on the stability of ketyl radicals under protic conditions and the high free enthalpy of protonation of a metal −oxygen bond.[10]

Figure 1. Titanocene-catalyzed pinacol coupling under buffered protic conditions



Based on the pK_a values of typical alcohols (MeOH: 15.5; EtOH: 15.9; *t*BuOH: 19.2) in water[11] the acid to be utilized should have a pK_a of at most 12.5 in order to ensure complete protonation. The nature of the counterion of the acid is of major importance. Reductions of titanocene(IV) derivatives are well known to proceed best with dihalides and metal powders, e.g. Mg, Zn, Mn, or Al.[12][13] However, alkoxides and triflates are usually inert towards mild reducing reagents. Thus, we decided to use amine hydrochlorides, as buffered derivatives of hydrochloric acid, as acids and Zn and Mn dust as stoichiometric reductants. Pyridine hydrochlorides are especially attractive amines in this respect because both the steric demand and the pK_a value can be changed in a predictable way by alteration of the substitution pattern. A sterically demanding phenol was also investigated. Some of the acids used, and their pK_a values, are depicted in Figure 2.

Figure 2. Acids used in this study and their pK_a values



Mg and Al proved to be unsuitable as stoichiometric reductants because titanocene dichloride is reduced too slowly and thus significant amounts of by-products are

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formed by uncatalyzed processes. Initial experiments were conducted with the combination of benzaldehyde, 3 mol-% of titanocene dichloride as a precatalyst, and manganese as a stoichiometric reductant at 0.1 M concentration in THF with **3**−**6** as proton donors. Table 1 summarizes the results of our investigations.

Table 1. Coupling of benzaldehyde at 0.1 M in THF with 3 mol-% Cp_2TiCl_2 with Mn as reductant

Entry	Acid	Yield [%]	**1/2**[a]
1	**3**	< 5	–
2	**4**	75	82:18
3	**5**	68	95:5
4	**5**	77	78:22[b]
5	**6**	< 5	–

[a] Determined by ^{1}H NMR of the crude mixture after hydrolysis. – [b] Zn used as reductant.

It should be noted that only finely powdered Mn (−325 mesh) leads to the fast reduction of titanocene dichloride, whereas utilization of 50 mesh Mn dust resulted in the failure of the reaction. Phenol **6** did not constitute a reasonable choice in terms of turnover. The effect of substitution on the pyridine hydrochlorides ability to enable catalytic reactions was dramatic. Commercial pyridine hydrochloride (**3**) as acid did not lead to detectable conversion to products. No titanium(III) reagent was formed. 2,6-Lutidine hydrochloride (**4**) gave the 1,2-diol in a yield of 75% but with low diastereoselectivity (78:22) in favor of **1**. Gratifyingly, collidine hydrochloride (**5**) led to a noticeable improvement in diastereoselectivity (95:5), albeit with a reduced yield of 68%. A small amount of benzyl alcohol (ca. 2%) was also formed and about 20% of the benzaldehyde remained unreacted. It seems sensible to assume that the reason for the superiority of **5** in achieving catalytic turnover with high diastereoselectivity is a combination of its low ability to promote electron transfer from Mn to benzaldehyde, and the weak complexation tendency of 2,4,6-collidine with titanium. 2,6-Lutidine hydrochloride (**4**) seems to be a sufficently strong acid to promote electron transfer to benzaldehyde from manganese to levels high enough for reduction of diastereoselectivity. Thus, fine-tuning of the pK_a values of the acid used for protonation of metal alkoxides is essential in order to avoid undesired competing stoichiometric processes. Further optimization studies are summarized in Table 2.

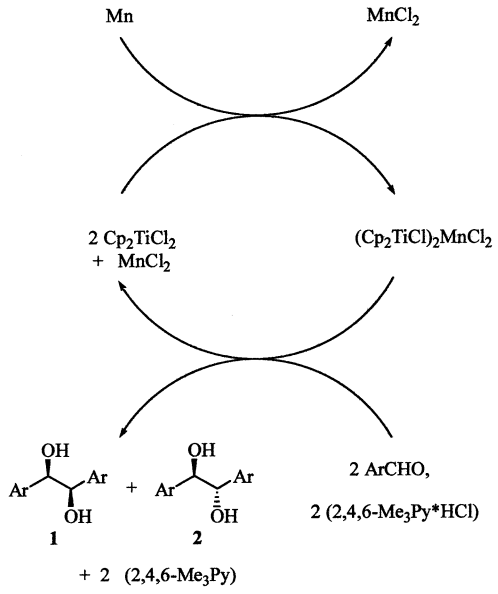
Table 2. Optimization of the coupling conditions with **5** as acid

Entry	cat. [mol-%]	*T* [°C]	Yield [%]	**1/2**[a]
1	0	25	42	72:28
2	0	25	68	63:37[b]
3	3	0	60	92:8
4	3	40	62	87:13
5	5	25	82	98:2

[a] Determined by ^{1}H NMR of the crude mixture after hydrolysis. – [b] Zn used as reductant.

When zinc was used instead of manganese diastereoselectivity decreased dramatically. As demonstrated in control experiments without a catalyst, zinc promoted the uncatalyzed electron transfer significantly faster than manganese. It seems reasonable to assume that $ZnCl_2$, constituting a much stronger Lewis acid than $MnCl_2$, enabled electron transfer to a significantly higher degree than $MnCl_2$. An attractive feature of our reaction conditions is that diastereoselectivity is highest at room temp. Not surprisingly, at higher temperatures selectivity decreased. However, lowering the temperature also led to a deterioration in selectivity. A sensible explanation is that protonation was slowed down and therefore the uncatalyzed coupling occurred to a greater extent. This drop in selectivity is clearly more pronounced in the case of silylation,[4c][4d] indicating that protonation is indeed faster than silylation. Also, collidine can be recycled essentially quantitatively (> 95%) by a simple acid-base extraction, amply demonstrating the economic advantage of protonation over silylation. Gratifyingly, using 5 mol-% of the catalyst results in a further distinct improvement with respect to yield (82%) and diastereoselectivity (98:2 in favor of **1**). Thus Mn/**5** constitutes an ideal system for conducting titanocene-catalyzed pinacol couplings under buffered protic conditions. The catalytic cycle for our reaction is depicted in Figure 3.

Figure 3. Catalytic cycle for titanocene-catalyzed pinacol coupling in the presence of **5** with 5 mol-% catalyst, Mn as reductant, at 20°C at 0.1 M concentration in THF

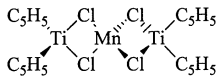


It should be noted that four essential points for achieving catalysis are met by our system: a) **5** is not a strong enough acid to oxidize the metal powder or any titanium(III) species, b) $MnCl_2$ formed after reduction of titanocene dichloride does not activate the aldehyde strongly enough towards electron transfer for interference of uncatalyzed and unselective couplings, c) 2,4,6-collidine formed after protonation of the titanocene alkoxide does not complex and deactivate any titanium species in the catalytic cycle, and d) the diol formed does not bind to any titanium species in the

catalytic cycle and thus does not enable product inhibition.

The redox-active species in our catalytic coupling seems to be a trinuclear complex where the two titanocene(III) units are bridged by manganese dichloride;[13a] see Figure 4 for details.

Figure 4. Likely redox-active trinuclear titanium(III) complex



The optimized conditions were tested for a number of substrates. The results of these investigations are summarized in Table 3.

Table 3. Pinacol coupling of substituted aldehydes under optimized conditions

Entry	Substrate	Yield [%]	**1**/**2**[a]
3a	2-MeC_6H_4CHO	90	97:3
3b	3-MeC_6H_4CHO	85	97:3
3c	4-MeC_6H_4CHO	84	97:3
3d	4-ClC_6H_4CHO	89	97:3
3e	4-BrC_6H_4CHO	82	98:2
3f	4-MeOC_6H_4CHO	91	99:1
3g	4-AcOC_6H_4CHO	85	99:1
3h	4-PhC_6H_4CHO	87	97:3
3i	2-Thienyl-CHO	82	95:5
3j	4-Allyoxy-C_6H_4CHO	91	98:2
3k	4-Homoallyloxy-C_6H_4CHO	94	98:2
3l	4-Cinnamyloxy-C_6H_4CHO	89	96:4

[a] Determined by ^{1}H NMR of the crude mixture after hydrolysis.

A variety of symmetrical 1,2-diols were synthesized with excellent diastereoselectivity and in good yields. An interesting feature of our reaction is that electron-rich and *ortho*-substituted aldehydes are excellent substrates for the reaction but lead to failure of the catalytic reaction with Me_3Si-Cl. In these cases either electron transfer from the catalyst, or binding to the catalyst, seemed to be slow. With silylation this leads to coupling via the uncatalyzed pathway. However, under our buffered protic conditions the uncatalyzed pathway is negligible and the above-mentioned cases are amongst the best examples. These observations amply demonstrate the exceptional mildness of our stoichiometric reductive system and its advantage over other known systems.[4][8] It should be noted that our catalytic coupling not only presents a shortcut of the (existing) two-step sequence, i.e. McMurry coupling[14] and *syn,vic*-dihydroxylation,[15] although we have not yet achieved an enantioselective version of the reaction. More importantly, functional groups being sensitive to either or both of these two reactions are readily tolerated. Thus, double bonds, halides, and phenolate esters are readily tolerated. Our reaction represents a rare example of a transition-metal-catalyzed radical reaction proceeding with reagent control.[9][10] We have convincingly demonstrated that catalytic turnover can indeed be achieved by protonation of a metal−oxygen bond in a buffered protic medium by properly adjusting the pK_a of the acid employed. The application of this concept to other carbon−carbon bond-forming reactions is in progress, and the results of these studies will be reported in due course.

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Experimental Section

General: All reactions were performed in oven-dried (100°C) glassware under N_2. THF was freshly distilled from $LiAlH_4$. Products were purified by flash chromatography[16] on Merck silica gel 50 (eluents given in parentheses). Yields refer to analytically pure samples. Isomer ratios were determined from suitable ^{1}H-NMR integrals of cleanly separated signals. − ^{1}H NMR: Bruker AMX 300 and Varian, integrals in accord with assignments, TMS (δ = 0.00), $CHCl_3$ (δ = 7.26) as internal standard. − ^{13}C NMR: Bruker AMX 300 and Varian, integrals in accord with assignments, TMS (δ = 0.00) or $CDCl_3$ (δ = 77.00) and [D_8]THF (δ = 25.26) as internal standards. − APT ^{13}C-NMR spectra: "+" for CH or CH_3,"−" for CH_2 and C_{quat}. − Combustion analyses: F. Hambloch, Institute of Organic Chemistry, University of Göttingen. − IR spectra: Perkin-Elmer 1600 series FTIR as KBr pellets.

General Procedure for the Coupling with **5** as Acid (Table 2, Entry 5): Dry THF (20 ml) was added to titanocene dichloride (37.4 mg, 0.15 mmol), Mn (165.0 mg, 3.0 mmol), and molecular sieves 4 A (0.5 g) under N_2 and the mixture was stirred until the red colour had faded and turned into lime green. After the addition of 2,4,6-collidine hydrochloride (709 mg, 4.5 mmol), benzaldehyde (310 µl, 3.0 mmol) was added dropwise over 3 h. Stirring was continued for 8 h and the mixture was poured into *t*BuOMe (20 ml) and 2 M HCl (10 ml). The organic layer was washed with 2 M HCl (10 ml), sat. $NaHCO_3$ (10 ml), satd. NaCl (10 ml), and dried (Na_2SO_4). After evaporation of the solvent, the product was purified by chromatography over silica gel (*t*BuOMe/petroleum ether, 20:80 to 80:20) to give 261 mg of 1,2-diphenyl-1,2-ethanediol as 98:2 mixture of **1**/**2** (82%). The minor isomers were identified according to ref.[8b].

(R,R*)-1,2-Bis(2-methylphenyl)-1,2-ethanediol (Table 3, Entry 3a):* After silica gel chromatography (*t*BuOMe/petroleum ether, 25:75 to 50:50) 323 mg of 1,2-bis(2-methylphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (90%). Colorless crystals, m.p. 64°C. − IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1}, 1610, 1490, 1400, 1315, 1250, 1155, 1050. − ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, C*H*$_3$), 2.76 (br. s, O*H*), 4.68 (s, C*H*OH), 6.92 (d, ^3J = 7.6 Hz), 6.98−7.08 (m, 2 H), 7.13 (dd, $^3J_{4',3'} \approx {}^3J_{4',5'} \approx$ 7.6 Hz). − ^{13}C NMR ($CDCl_3$): δ = 21.73, 78.73, 123.95, 127.43, 127.88, 128.50, 137.63, 139.89. − $C_{16}H_{18}O_2$ (242.3): calcd. C 79.31, H 7.49; found C 79.52, H 7.73.

(R,R*)-1,2-Bis(3-methylphenyl)-1,2-ethanediol (Table 3, Entry 3b):*[17] After silica gel chromatography (*t*BuOMe/petroleum ether, 25:75 to 50:50), 307 mg of 1,2-bis(3-methylphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (85%).

(R,R*)-1,2-Bis(4-methylphenyl)-1,2-ethanediol (Table 3, Entry 3c):*[17] After silica gel chromatography (*t*BuOMe/petroleum ether, 20:80 to 80:20), 304 mg of 1,2-bis(4-methylphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (84%).

(R,R*)-1,2-Bis(4-chlorophenyl)-1,2-ethanediol (Table 3, Entry 3e):*[8a] After silica gel chromatography (*t*BuOMe/petroleum ether, 20:80 to 100:0), 376 mg of 1,2-bis(4-chlorophenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (89%).

(R,R*)-1,2-Bis(4-bromophenyl)-1,2-ethanediol (Table 3, Entry 3d):*[18] After silica gel chromatography (*t*BuOMe/petroleum ether,

50:50), 453 mg of 1,2-bis(4-bromophenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (82%).

(R,R*)-1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (Table 3, Entry 3f):*[17] After silica gel chromatography (*t*BuOMe/petroleum ether, 50:50 to 95:5), 371 mg of 1,2-bis(4-methoxyphenyl)-1,2-ethanediol was obtained as a 99:1 mixture of **1**/**2** (91%).

(R,R*)-1,2-Bis(4-acetoxyphenyl)-1,2-ethanediol (Table 3, Entry 3g):*[19] After silica gel chromatography (*t*BuOMe/petroleum ether, 50:50 to *t*BuOMe/ethanol, 50:50), 393 mg of 1,2-bis(4-acetoxyphenyl)-1,2-ethanediol was obtained as a 99:1 mixture of **1**/**2** (85%).

(R,R*)-1,2-Bis(4-phenylphenyl)-1,2-ethanediol (Table 3, Entry 3h):*[20] After silica gel chromatography (*t*BuOMe/petroleum ether, 20:80 to 100:0), 475 mg of 1,2-bis(4-phenylphenyl)-1,2-ethanediol was obtained as a 99:1 mixture of **1**/**2** (87%).

(R,R*)-1,2-Bis(thiophen-2-yl)-1,2-ethanediol (Table 3, Entry 3i):*[17] After silica gel chromatography (*t*BuOMe/petroleum ether, 20:80 to 50:50), 300 mg of 1,2-bis(thiophen-2-yl)-1,2-ethanediol was obtained as a 95:5 mixture of **1**/**2** (82%).

(R,R*)-1,2-Bis(4-allyloxyphenyl)-1,2-ethanediol (Table 3, Entry 3j):* After silica gel chromatography (*t*BuOMe/petroleum ether, 50:50 to *t*BuOMe/ethanol, 90:10), 441 mg of 1,2-bis(4-allyloxyphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (91%). Colorless crystals, m.p. 114°C. − IR (KBr): $\tilde{\nu}$ = 3335 cm^{-1}, 2860, 1610, 1515, 1235, 1020, 995. − ^{1}H NMR ($CDCl_3$): δ = 2.78 (br. s, O*H*), 4.49 (ddd, $^3J'$ = 5.2 Hz, $^4J \approx {}^4J \approx$ 1.5 Hz, CH_2O), 4.62 (s, C*H*OH), 5.27 (dd, ^3J = 10.5 Hz, ^4J = 1.5 Hz, CH^E), 5.39 (dd, ^3J = 17.3 Hz, ^4J = 1.5 Hz, CH^Z), 6.03 (ddt, ^3J = 17.3 Hz, ^3J = 10.4 Hz, ^3J = 5.2 Hz, CH_2CH), AA′BB′ system centred at δ = 6.77 and 7.03. − ^{13}C NMR ($CDCl_3$): δ =“−” 68.67, “+” 78.67, “+” 114.18,“−” 117.59, “+” 128.11,“−” 132.23, “+” 133.13,“−” 158.01. − $C_{20}H_{22}O_4$ (326.4): calcd. C: 73.60, H 6.79; found C: 73.85, H: 6.99.

(R,R*)-1,2-Bis(4-but-3-enyloxyphenyl)-1,2-ethanediol (Table 3, Entry 3k):* After silica gel chromatography (*t*BuOMe/petroleum ether, 50:50 to *t*BuOMe/ethanol, 90:10), 497 mg of 1,2-bis(4-but-3-enyloxyphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1**/**2** (94%). Colorless crystals, m.p. 86°C. − IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1}, 3070, 2920, 2865, 1610, 1515, 1240, 1175, 1040. − ^{1}H NMR ($CDCl_3$): δ = 2.51 (dt, $^3J \approx {}^3J \approx$ 6.8 Hz, $CHCH_2CH_2$), 2.78 (br. s, O*H*), 3.96 (t, ^3J = 6.8 Hz, CH_2O), 4.62 (s, C*H*OH), 5.10 (dd, ^3J = 11.3 Hz, ^4J = 1.9 Hz, CHH^E), 5.15 (dd, ^3J = 16.9 Hz, ^4J = 1.5 Hz, 4′CHH^Z), 5.89 (ddt, $^3J_{trans}$ = 16.9 Hz, ^3J = 10.1 Hz, ^3J = 6.8 Hz, CH_2CHCH_2), AA′BB′ system centred at δ = 6.75 and 7.0. − ^{13}C NMR ($CDCl_3$): δ =“−” 33.56,“−” 67.04, “+” 78.65, “+” 114.01,“−” 116.97, “+” 128.11,“−” 132.10, “+” 134.34,“−” 1158.31. − $C_{22}H_{26}O_4$ (354.5): calcd. C: 74.55, H 7.39; found C 74.65, H 7.19.

(R,R*)-1,2-Bis[4-(3-phenylallyloxy)phenyl]-1,2-ethanediol (Table 3, Entry 3l):* After crystallization from *t*BuOMe, 639 mg of 1,2-bis[4-(3-phenylallyloxy)phenyl]-1,2-ethanediol was obtained as a 99:1 mixture of **1**/**2** (89%). Colorless crystals, m.p. 178°C. − IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1}, 2910, 2870, 1610, 1515, 1245, 1175, 1010, 735, 690. − ^{1}H NMR ($CDCl_3$): δ = 2.77 (br. s), 4.64 (s, C*H*OH), 4.65 (dd, ^3J = 5.7 Hz, ^4J = 1.1 Hz, CH_2O), 6.38 (dt, ^3J = 15.8 Hz, ^3J = 5.8 Hz, $CHCH_2$), 6.70 (d, ^3J = 16.2 Hz, ArC*H*CH), AA′BB′ system centred at δ = 6.81 and 7.04, 7.22−7.44 (m, CH_{Ar}). − ^{13}C NMR ([D_8]THF): δ =“−” 69.07, “+” 79.78, “+” 114.53, “+” 126.03, “+” 127.39, “+” 128.55, “+” 129.25, “+” 129.43, “+” 133.15,“−” 135.20,“−” 137.91,“−” 159.04. − $C_{32}H_{30}O_4$ (478.6): calcd. C 81.31, H 6.32; found C 81.49, H 6.54.

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