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[7] Crystal data for **3**: $C_{16}H_{14}B_2Cl_2Mn_2O_4$, $M_r = 472.67$, crystal dimensions $0.32 \times 0.20 \times 0.02$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.5756(18)$, $b = 7.9087(9)$, $c = 15.034(3)$ Å, $\beta = 102.045(13)^\circ$, $V = 1811.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.733$ g cm^{-3}, $2\theta_{max} = 52^\circ$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\omega/2\theta$ scans, $T = 213(2)$ K, $\mu = 1.708$ mm^{-1}. Of 4338 collected reflections, 3556 were unique ($R_{int} = 0.0455$). LP and empirical (psi scans) absorption corrections were applied. The structure was solved by direct methods and refined using SHELXTL.[17] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions (C–H = 0.98 Å and included as riding with $U_{iso}(H) = 1.3\,U_{eq}$ (non-H). $R = 0.0526$ ($I > 2\sigma(I)$), $R_w = 0.0983$ (F^2, all data), 235 parameters, final difference map extremes 0.509 and -0.480 e Å^{-3}. CCDC-173229 (**1**) and -173230 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] Considering the t_{2g} orbital set the d^6ML_5 fragment (η^5-$C_5H_4CH_3$)Mn(CO)$_2$ is isolobal to CH_2 and the four vertex *nido*-cluster **3** shows the required total of six electron pairs in its skeleton. For isolobal analogy see: R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 725.

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Enantioselective C–C Bond Formation with Titanium(IV) Alkoxides—an Unusual Alkylation**

Rainer Mahrwald*

Recently we described an enantioselective aldol reaction of aldehydes with unactivated ketones mediated by titanium(IV) alkoxide ligand exchange.[1] In attempts to optimize this reaction further by catalytic control, metal salts, among other things, have been used as additives in the aldol reactions. In particular the use of lithium salts has been described by a number of authors in different C–C bond formation processes,[2] and the use of lithium perchlorate in the Mukaiyama reaction has been known for some time.[3] Lithium perchlorate is also used in enantioselective aldol reactions. Here a weakening or a cleavage of the metal alkoxide – aldolate bond is assumed. The aldols formed are thus continuously released from the catalyst,[4] and in this way catalytic control of the reaction is achieved in many cases.[5]

In our investigations on catalytic aldol addition we observed an activation of the aldehyde in the absence of the ene component (ketone): under the reaction conditions described ($LiClO_4$, Ti(O*t*Bu)$_4$, α-hydroxy acids, RT) the aldehydes themselves react with the ligands of the Ti(O*t*Bu)$_4$ in an alkylation-type reaction. After the initial conversion of benzaldehyde and Ti(O*t*Bu)$_4$ the *meso* compound **1a**, the *anti* triol **2a**, and the monoaddition product **3a** (Scheme 1) were isolated. The structure of the compounds was determined by nuclear Overhauser enhancement (NOE) difference measurements.[6] By the addition of D-mandelic acid in this experiment the *anti*-triol **2a** was obtained in enantiomeric excesses of $>85\,\%$,[7] whereas in contrast the diol **3a** was isolated as the racemate. (The *meso* compound **1a** is optically inactive.)

The formation of compounds **1a**, **2a**, and **3a** is dependent upon the amount of D-mandelic acid used. With one

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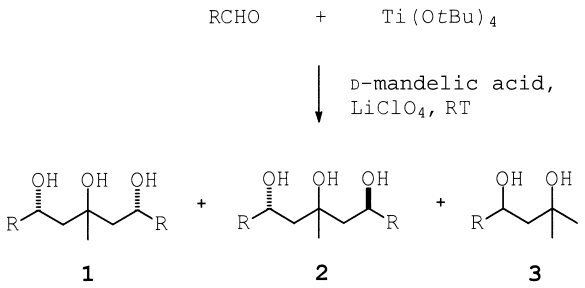


a: R = Ph
b: R = Me
c: R = C≡CPh

Scheme 1. Reaction of aldehydes with $Ti(OtBu)_4$ in the presence of $LiClO_4$ and D-mandelic acid.

equivalent of D-mandelic acid relative to $Ti(OtBu)_4$ the *meso, syn* triol **1a** is formed as the main product (kinetic control). After subsequent equilibration[8] (2 days, RT) the optically active *anti* triol **2a** is formed as the main product. With four equivalents of D-mandelic acid the diol **3a** is isolated as the main product (Table 1).

Table 1. Reactions of aldehydes with $Ti(OtBu)_4$ in the presence of D-mandelic acid.

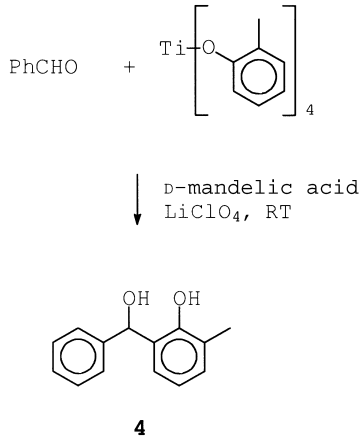
	Aldehyde	Product	Yields [%] [a]	[b]	[c]	*ee* [%] [b]
1	Ph–CHO	**1a**	65	5	7	
2		**2a**	12	68	13	84
3		**3a**	5	7	64	
4	Me–CHO	**1b**	43	15	–	
5		**2b**	8	36	8	65
6		**3b**	2	–	51	
7	Ph–≡–CHO	**1c**	55	25	–	
8		**2c**	11	28	11	78
9		**3c**	4	5	53	

[a] Procedure A (see Supporting Information): freshly distilled aldehyde (10.0 mmol) under argon was added at room temperature to a solution of $LiClO_4$ (10.0 mmol) in $Ti(OtBu)_4$ (10.0 mmol). After 15 min D-mandelic acid (10.0 mmol) was added; stir for 24 h. [b] Equilibration, 2 days, RT.[8] [c] Procedure B (see Supporting Information): as procedure A, only 40.0 mmol D-mandelic acid; stir for 24 h. The ratios of compounds **1**, **2**, and **3** were determined by integration of suitable signals in the ^1H NMR spectra (e.g. RC*H*(OH)CH_2).

These surprising results were investigated for their general applicability. Both aromatic and aliphatic aldehydes react according to Scheme 1, and the reaction is dependent upon the carbonyl activity of the aldehyde used. Longer reaction times and lower yields were observed with α-branched aldehydes (R = *t*Bu, 8 days, RT, yield 10%).

Not all the metal salts used were able to induce this reaction. $LiClO_4$ was the most efficient. No consistent reactions were observed with the use of $Ba(ClO_4)_2$, $LiCF_3SO_3$, and $Mg(ClO_4)_2$. The use of $NaClO_4$, $Mg(CF_3SO_3)_2$, $MgBr_2$, Na_2SO_4, LiCl, LiF, and NEt_4ClO_4 gave no reaction. These results indicate the selective involvement of hard cations (e.g. Li^+). Similar results were obtained by Evans et al in enantioselective aldol reactions.[5]

After the reaction of the aldehydes with $Ti(OiPr)_4$ the expected products (secondary alcohols) were only obtained in very low yields. The main products here were the corresponding alcohols formed by reduction. This result is attributed to the pronounced tendency of the secondary titanium(IV) alkoxides to undergo Meerwein–Ponndorf–Verley reduction. Other titanium(IV) alkoxides containing a quaternary carbon atom are more suitable for this reaction. The reaction of benzaldehyde with titanium(IV) *o*-methylphenolate in the presence of D-mandelic acid and $LiClO_4$ affords the diol **4** (yield 62%) in enantiomeric excesses >88% (Scheme 2). This method thus provides simple and rapid access to optically active saligenol derivatives.[9]



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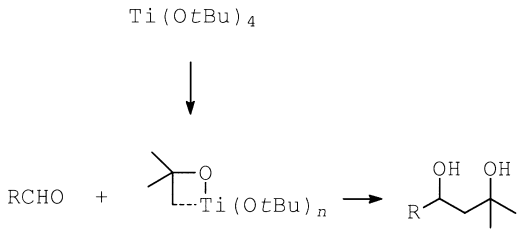
Scheme 2. Reaction of benzaldehyde with titanium(IV)-*o*-methylphenolate in the presence of $LiClO_4$ and D-mandelic acid at room temperature.

The reaction mechanism is still unexplained. Enol structures cannot be involved in these reactions as the conversions with $Ti(OtBu)_4$ show. A C–H activation occurring under the mild reactions conditions described could induce this reaction. Scheme 3 illustrates a proposed mechanism. The C–H activations of *tert*-butyl groups by palladium catalysis have already been described.[10]



Scheme 3. Proposed mechanism for the reaction of aldehydes with $Ti(OtBu)_4$ in the presence of $LiClO_4$ and D-mandelic acid at room temperature. Oxa-2-titana-cyclobutanes were assumed to be the reactive species.

Because of the considerable preparative value and utility of the reactions described here, which must operate for similar C–H activation processes, these results are of great significance.[11] Investigations aimed at understanding the mechanism and extending this reaction are underway.

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A Defined N-Heterocyclic Carbene Complex for the Palladium-Catalyzed Suzuki Cross-Coupling of Aryl Chlorides at Ambient Temperatures**

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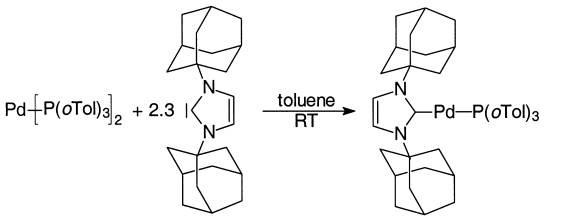
Dedicated to Prof. Dr. Gottfried Huttner on the occasion of his 65th birthday

The Suzuki cross-coupling reaction, which involves the coupling of aryl boronic acid with an organohalide, has proven to be a versatile tool in organic synthesis.[1] Recent developments have led to catalysts based on sterically demanding, basic phosphanes allowing even the conversion of unreactive aryl chlorides.[2] Nevertheless, these reactions still proceed very slowly at room temperature.[3] As N-heterocyclic carbenes (NHC) are sometimes better ligands than phosphanes in homogeneous catalysis,[4] they were also tested in cross-coupling chemistry.[5–7] However, for the effective activation of aryl chlorides the known NHC-based catalysts require temperatures above 80 °C to yield reasonable activities. We now report on palladium(0) catalysts for the Suzuki cross-coupling at *ambient temperatures.*

Recently we established a synthetic procedure for homoleptic bis(NHC)-complexes of palladium(0) by ligand exchange in bis(tri-*ortho*-tolylphosphane)palladium(0) (**1a**).[6] The catalytic activity of these complexes strongly depends on the steric bulk of the NHC ligand. 1,3-Bisadamantylimidazolin-2-ylidene (**2**), as one of the most bulky NHC ligands,[8] represents a good candidate for palladium(0) catalysts of high activities in the Suzuki cross-coupling. However, even in presence of an excess of **2** only one phosphane ligand of **1a** was exchanged, which resulted in the formation of complex **3a** [Eq. (1)].



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