$CH_2NH + NH_2^- \rightarrow CH_2N^- + NH_3$ (9a)
($\Delta H = 15$ kcal mol^{-1})
$CH_2N^- + NH_3 \rightarrow HCN + H_2 + NH_2$ (9b)
($\Delta H = -15$ kcal mol^{-1})
An acid-catalyzed sequence like that in reaction (10) is also conceivable.
$CH_2NH + NH_4^+ \rightarrow HCNH^+ + H_2 + NH_3$ (10a)
($\Delta H = 32$ kcal mol^{-1})
$HCNH^+ + NH_3 \rightarrow HCN + NH_4^+$ (10b)
($\Delta H = -32$ kcal mol^{-1})
($\Delta H = +32$ kcal mol^{-1})
$HCNH^+ + NH_3 \rightarrow HCN + NH_4^+$ (10b)
($\Delta H = -32$ cal mol^{-1})

[13] Product distribution for $[PtCD_2]^+ + NH_3$: $[Pt,C,N,H_2,D]^+ + HD$ (20%), $CD_2NH_2^+ + PtH$ (70%), $NH_3D^+ + [PtCD]$ (10%).
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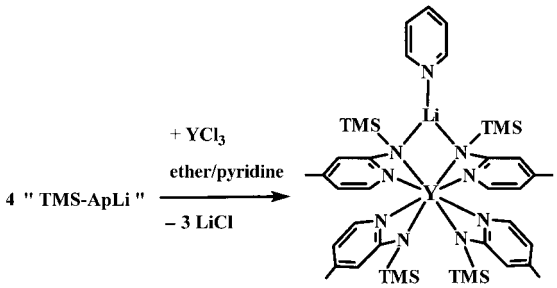
Yttrate-Mediated Ligand Transfer and Direct Synthesis as a Route to Amidopalladium Complexes**

Anke Spannenberg, Perdita Arndt, and Rhett Kempe*

In the wide range of applications of palladium compounds,[1] amidometal complexes[2] have played only a secondary role to date.[3] Only a few examples of this reactive class of compounds have been reported.[3, 4] This could be due to difficulties in the synthesis or to the instability of these compounds which arise from the "unfortunate" combination of a soft metal with the hard amido ligand.[5] The development of new synthetic routes could help solve this problem. We report here on an yttrate-mediated ligand transfer as well as the direct synthesis as efficient routes to amido complexes of late transition metals.

The in situ reaction of lithiated 4-methyl-2-(trimethylsilylamino)pyridine (TMS-ApH) with dry YCl_3 in ether in the presence of pyridine gave the colorless yttrate complex **1** in good yields [Eq. (a)].



(a)

1

Aminopyridinato complexes of the early transition metals are rare,[6] and compounds with Group 3 metals, as well as the corresponding lanthanide complexes, have not yet been reported. The two sets of signals observed for the aminopyridinato ligands in the ^{1}H NMR spectrum of **1** (see Table 1) is explained by coordination to lithium. This was confirmed by X-ray structural analysis[7] (Figure 1). The lithium atom is sterically shielded and has trigonal planar coordination (sum of the angles 360°).[8] Because of the bridging function of the amido nitrogen atom, the $Y-N_{pyridine}$ bond in the Li-coordinated TMS-Ap ligands is significantly shorter than the $Y-N_{amido}$ bond. The yttrium–nitrogen bond lengths of the other two aminopyridinato ligands are equally long and indicate a delocalized bonding mode.[9] In the reaction of **1** with $ZrCl_4$ the complexed lithium is displaced by a $ZrCl_3$ unit to form the extremely unstable Y-Zr heterobimetallic complex **2**, which is also colorless [Eq. (b)]. Complex **2** acts as an intermediate in

[*] Dr. R. Kempe, Dr. A. Spannenberg, Dr. P. Arndt
Abt. Komplexkatalyse, IfOK an der Universität Rostock
Buchbinderstrasse 5–6, D-18055 Rostock (Germany)
Fax: (+49) 381-466-9374
E-mail: rkempe@chemie1.uni-rostock.de

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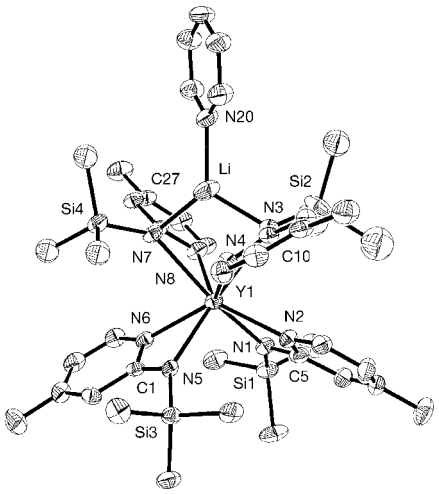
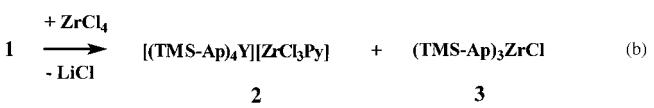
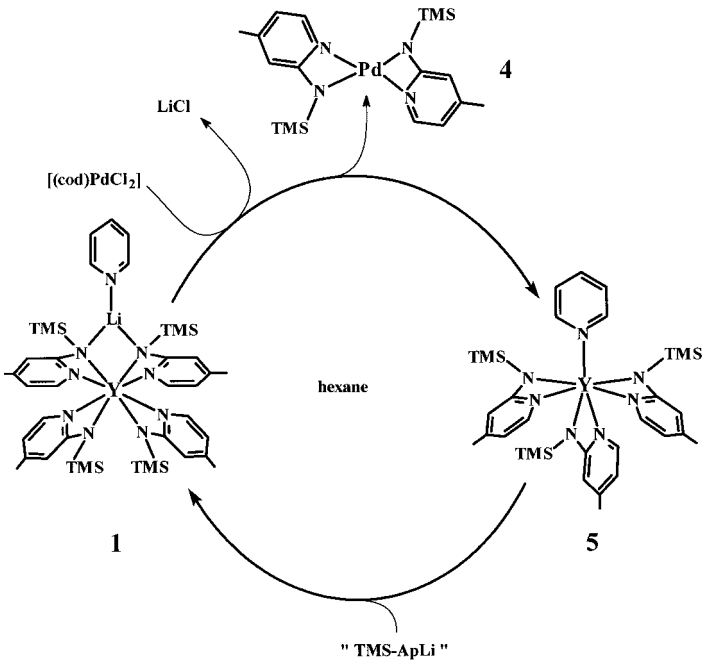


Figure 1. Crystal structure of **1** (thermal ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: N1–Y 2.448(5), N2–Y 2.448(5), N3–Li 2.057(14), N3–Y 2.620(6), N4–Y 2.572(6), N5–Y 2.442(5), N6–Y 2.497(6), N7–Li 2.03(2), N7–Y 2.569(5), N8–Y 2.508(6), N20–Li 2.01(2); N1-Y-N2 56.3(2), N5-Y-N6 55.9(2), N8-Y-N7 54.5(2), N4-Y-N3 52.9(2), N20-Li-N7 129.0(7), N20-Li-N3 119.7(8), N7-Li-N3 111.1(7).

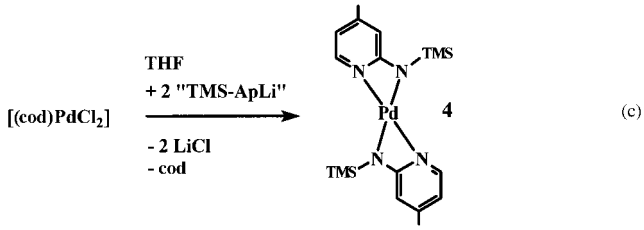


the transfer of ligands from yttrium to zirconium to produce $[(TMS\text{-}Ap)_3ZrCl]$ (**3**) as a side or decomposition product. An analogous ligand-transfer reaction also allows access to palladium complexes: the treatment of **1** with $[(cod)PdCl_2]$ in hexane (Scheme 1, top half) gave $[(TMS\text{-}Ap)_2Pd]$ (**4**) and $[(TMS\text{-}Ap)_3YPy]$ (**5**). This reaction seems laborious in comparison to a direct synthesis [Eq. (c)]; however, it can



Scheme 1. Yttrate-mediated synthesis of $[(TMS\text{-}Ap)_2Pd]$ (**4**).

be made more efficient, because compound **5**, in the presence of "TMS-ApLi", reacts to give **1** (Scheme 1, bottom half).[10] The latter can be explained by the coordinative unsaturation



of **5**.[11] Complex **1** can now participate in a further ligand-transfer reaction so that a cyclic reaction is possible. In order to test this premise, **1** was treated with an equimolar amount of $[(cod)PdCl_2]$ in hexane at temperatures below 0 °C, after 12 hours one equivalent of "TMS-ApLi" was added, and after a further 12 hours one equivalent of $[(cod)PdCl_2]$ was added. The last two steps were each repeated twice to give 1.25 equivalents of **4** after work-up. This corresponds to a turnover number (TON) of 2.5 with regard to the ligand transfer reaction. The sequential addition of the starting materials and excess $[(cod)PdCl_2]$ are essential in order to produce **4** catalytically. We explain this prerequisite by assuming that the reduction of $[(cod)PdCl_2]$ in the presence of "TMS-ApLi", which takes place even at low temperatures in hexane, can thus be suppressed. A control experiment, without **1** as the catalyst, produced no **4**; the treatment of "TMS-ApLi" and $[(cod)PdCl_2]$ in hexane at low temperatures (−78 to 0 °C) gave only the starting materials along with colloidal palladium after work-up, and mainly colloidal palladium was obtained at temperatures above 10 °C. In THF **4** can be obtained in 48% yield at a temperature of −30 °C by direct synthesis [Eq. (c)].[12]

Complex **4** is an orange, crystalline compound that exhibits a ^1H NMR spectrum with one simple set of signals, typical of TMS-Ap ligands (Table 1). The molecular structure, obtained by X-ray structural analysis[7] (Figure 2), shows two transoid-coordinated aminopyridinato ligands and a planar coordination geometry at the palladium center. The two, drastically different N-Pd-N angles [114.55(9)° and 65.45(9)°] confirm

Table 1. Selected analytical data of **1**, **2**, **4**, and **5**.

1: $C_{41}H_{65}LiN_9Si_4Y \cdot 0.5\,C_4H_{10}O$ (929.28): calcd C 55.58, H 7.59, N 13.57; found C 55.53, H 7.58, N 13.42; ^1H NMR ([D$_8$]toluene, 298 K): $\delta = 8.19$ (d, 2H, *o*-H, Py), 7.65 (br, 2H, Ap), 6.79 (t, 1H, *p*-H, Py), 6.46 (m, 2H, *m*-H, Py), 6.3–6.5 (br, 5H, Ap), 1.8 (br, 12H, Me), 0.06 (br, 36H, $SiMe_3$, Ap).

2: $C_{41}H_{65}Cl_3N_9Si_4YZr$ (1082.85): calcd C 45.48, H 6.05, N 11.64, Zr 8.42; found C 45.52, H 6.07, N 11.51, Zr 9.07. Since compound **2** does not dissolve without decomposition, an unambiguous characterization by NMR spectroscopy was not possible.

4: $C_{18}H_{30}N_4PdSi_2$ (465.05): calcd C 46.49, H 6.50, N 12.05; found C 46.78, H 6.56, N 12.09; ^1H NMR (C_6D_6, 303 K): (δ) = 7.50 (d, $J = 5.6$ Hz, 1H, H-6, Ap), 5.75 (s, 1H, H-3, Ap), 5.57 (d, $J = 5.6$ Hz, 1H, H-5, Ap), 1.72 (s, 3H, Me), 0.32 (s, 9H, $SiMe_3$).

5: $C_{32}H_{50}N_7Si_3Y$ (705.96): calcd C 54.44, H 7.14, N 13.89; found C 54.92, H 7.15, N 13.31; ^1H NMR (C_6D_6, 303 K): $\delta = 8.75$ (d, $J = 4.5$ Hz, 2H, *o*-H, Py), 7.74 (s, 3H, Ap), 6.82 (m, 1H, *p*-H, Py), 6.52 (m, 2H, *m*-H, Py), 6.35 (s, 3H, Ap), 5.98 (d, $J = 1.2$ Hz, 3H, Ap), 1.82 (s, 9H, Me), 0.28 (s, 27H, $SiMe_3$).

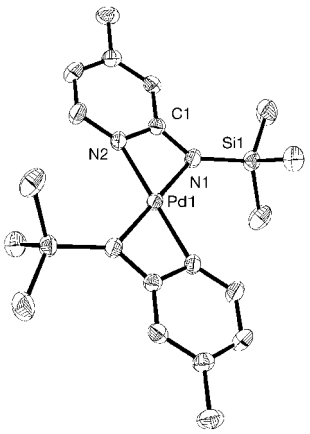


Figure 2. Crystal structure of **4** (thermal ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: N1 – Pd 2.054(2), N2 – Pd 2.017(3); N2′-Pd-N1 114.55(9), N2-Pd-N1 65.45(9). Labeled and corresponding nonlabeled atoms are related by the following symmetry operators: $-x, -y, -z$.

the severe strain in the complex. The $Pd-N_{pyridine}$ bond length (2.017(3) Å) is shorter than that of $Pd-N_{amido}$ (2.054(2) Å), which verifies the delocalized bonding mode. Complex **5** is a colorless crystalline compound and its elemental analysis agrees with the composition of the structure depicted in Scheme 1. The ^{1}H NMR spectrum shows, along with the resonances of coordinated pyridine, a single simple set of signals typical of aminopyridinato ligands in trisaminopyridinato complexes[6b,f] (Table 1). Scheme 1 presents the probable mechanism of the yttrate-catalyzed ligand-transfer reaction. We also assume, in analogy to the reaction of compound **1** with $ZrCl_4$, that an intermediate Y-Pd complex is unstable and could not be isolated.

Currently we are investigating whether the yttrate-mediated transfer is the best method for the synthesis of amido complexes of the later transition metals in those cases in which the direct synthesis failed. Furthermore, we are trying to discover how the ligand-transfer reaction can be deliberately suppressed in order to obtain stable, heterodinuclear complexes.

Experimental Section

All work was performed under the exclusion of oxygen and moisture in an argon atmosphere.

1: A solution of 4-methyl-2-(trimethylsilylamino)pyridine[6a] (2.86 mL, 13.44 mmol) in ether (40 mL) at $-40\,^\circ$C was slowly treated with a solution of *n*BuLi in hexane (2.5 M, 5.4 mL, 13.44 mmol) and then stirred at room temperature for 2 h. The resulting "TMS-ApLi" solution was added to a suspension of YCl_3 (656 mg, 3.36 mmol) in ether (20 mL) containing pyridine (407 µL, 5.04 mmol). Since **1** is sensitive to light, the reaction must take place in the dark. After stirring for 48 h at room temperature, the reaction mixture was filtered, the solvent removed in vacuo, and the residue taken up in ether/hexane. Crystallization at $-30\,^\circ$C gave a colorless crystalline solid (1.92 g, 64%). M.p.: 109 °C.

2: A suspension of $ZrCl_4$ (141 mg, 0.6 mmol) in ether (5 mL) was treated with a solution of **1** (540 mg, 0.6 mmol) in ether (10 mL). The solution turned yellowish very quickly. It was filtered, the residue washed, and the volume of the filtrate greatly reduced in vacuo. The addition of hexane precipitated compound **2** (400 mg, 61%) as a white powder. M.p. (decomp.): 178 °C. [(TMS-Ap)$_3$ZrCl] **3** (30 mg, 22%) crystallized from the mother liquor (hexane/ether). M.p.: 268 °C.

Synthesis of **4** by yttrate-mediated ligand transfer: A solution of **1** (892 mg, 1 mmol) in hexane (10 mL) at 0 °C was added to a suspension of [(cod)$PdCl_2$] (285 mg, 1 mmol) in hexane (10 mL). The reaction mixture was kept in the dark between 0 and $-78\,^\circ$C until work-up. The reaction solution was stirred for 12 h and then treated with "TMS-ApLi" (1 mmol, prepared as described for **1**) and after a further 12 h further [(cod)$PdCl_2$] (285 mg, 1 mmol) was added. The last two steps were both repeated twice. After stirring for a further 12 h the LiCl formed was filtered off, the residue extracted three times with hexane, and the filtrate concentrated. Crystallization at $-30\,^\circ$C afforded orange needles of **4** (580 mg, 1.25 mmol).

Direct synthesis of **4**: A solution of "TMS-ApLi" (prepared as described for **1** from TMS-ApH (425 µL, 2 mmol), *n*BuLi (0.8 mL) in hexane (2.5 M, 2 mmol), and THF (20 mL)) was added at $-30\,^\circ$C to [(cod)$PdCl_2$] (286 mg, 1 mmol) in THF (20 mL). After 12 h at $-30\,^\circ$C, the solvent was removed in vacuo and the residue washed several times with hexane. LiCl was filtered off, and the combined filtrates concentrated in vacuo. Crystallization at $-30\,^\circ$C afforded **4** (226 mg, 48%).

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Keywords: amido complexes · N ligands · palladium · synthetic methods · yttrium

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[7] X-ray structural analyses of **1** and **4**: STOE-IPDS diffractometer, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, structure solved by direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.), and refined with the full-matrix least-squares method against F^2 (SHELXL-93: G. M. Sheldrick, still unpublished), structural representation: XP (Siemens), compound **1**: $0.7 \times 0.4 \times 0.3$ mm, colorless prisms, space group $P2_1/n$, monoclinic, $a = 12.195(2)$, $b = 22.055(3)$, $c = 22.071(3)$ Å, $\beta = 97.60(2)^\circ$, $V = 5884(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.104$ g cm^{-3}, 16848 measured, 8683 were independent of symmetry, of which 3876 were observed ($I \geq 2\sigma(I)$), $R = 0.066$, wR^2 (all data) = 0.176, 499 parameters. Compound **4**: $0.3 \times 0.15 \times 0.15$ mm, orange prisms, space group $P2_1/c$, monoclinic, $a = 7.773(11)$, $b = 11.644(2)$, $c = 12.372(2)$ Å, $\beta = 91.360(11)^\circ$, $V = 1119.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.380$ g cm^{-3}, 3289 measured reflections, 1714 were independent of symmetry, of which 1366 were observed ($I \geq 2\sigma(I)$), $R = 0.026$, wR^2 (all data) = 0.066, 175 parameters. Crys-

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tallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-100685. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] The negative charge of the aminopyridinato ligand is not localized on the amido nitrogen atom.

[10] Compound **5** is not accessible by transmetalation with YCl_3 and three equivalents "TMS-ApLi" (ether/pyridine); this procedure affords compound **1** instead.

[11] The "ate" complexes are very often observed for lanthanide ions: a) H. Schumann, *Angew. Chem.* **1984**, *96*, 475–493; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 474–492; b) R. D. Köhn, G. Kociok-Köhn, H. Schumann in *Encyclopedia of Inorganic Chemistry* (Ed.: R. B. King), Wiley, New York, **1994**; c) C. J. Schaverien, *Adv. Organomet. Chem.* **1994**, *36*, 283–362; d) F. T. Edelmann in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford **1995**; e) H. Schumann, J. A. Meerse-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986.

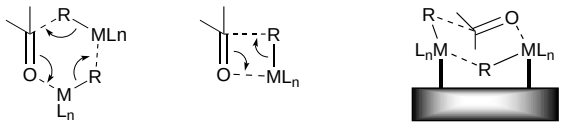
[12] Sincere thanks are due to the referee who provided this information.

Rate Acceleration in Nucleophilic Alkylation of Carbonyl Compounds with a New Template Containing Two Metallic Centers**

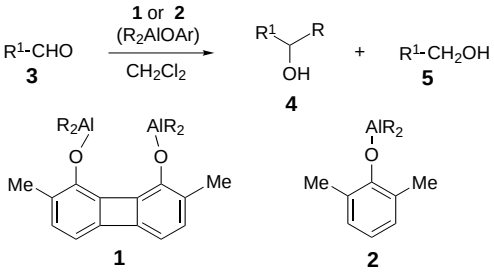
Takashi Ooi, Makoto Takahashi, and Keiji Maruoka*

The nucleophilic addition of reactive organometallic reagents to carbonyl compounds is undoubtedly one of the most thoroughly investigated of all organic transformations because of sustained interest in its mechanism and selectivity, as well as numerous applications to a variety of syntheses in the fields of natural products, pharmacology, and material science.[1]

The preferred transition state for addition of Grignard and organoaluminum reagents is often a cyclic six-membered array (**A**) that contains a carbonyl group and two molecules of organometallic reagent.[2] With the same reactants in a 1:1 ratio, a four-centered transition state (**B**) is also conceivable, although alkylation proceeds more slowly by this route. Hence, facilitation of the six-membered transition state **A** is



crucial in order to achieve high reactivity, particularly in the case of less reactive organometallic reagents. In this context, we became interested in designing new molecules of type **C** with two metallic centers that would permit simple alkylation of carbonyl compounds with otherwise less reactive alkylmetal species.[3] Here we report initial results with the modified bis(dialkylaluminum) reagent **1**, an efficient alkyl-transfer system for aldehydes (Scheme 1).[4]



Scheme 1. Alkylation of aldehydes with dialkylaluminum reagents.

Treatment of benzaldehyde (**3**; $R^1 = Ph$) with one equivalent of Me_3Al in CH_2Cl_2 at $-78\,^\circ C$ gave a long-lived monomeric 1:1 complex that gradually decomposed to 1-phenylethanol (**4**; $R^1 = Ph$, $R = Me$) on warming to $-20\,^\circ C$.[5] Use of (2,6-dimethoxyphenyloxy)dimethylaluminum (**2**, $R_2 = Me$) instead of Me_3Al significantly retarded the rate of alkylation under similar reaction conditions. Even use of excess **2** (2 equiv) failed to yield methylation product **4** at $-20\,^\circ C$. In marked contrast, however, methylation of benzaldehyde proceeded quite smoothly with one equivalent of 2,7-dimethyl-1,8-biphenylenedioxybis(dimethylaluminum) (**1**; $R = Me$) at $-20\,^\circ C$ to furnish after 4 h 1-phenylethanol (**4**; $R^1 = Ph$, $R = Me$) in 84% yield.[6] With higher alkyl derivatives of **1** ($R = Et$, Hex), alkylation was accompanied by concomitant formation of reduction product **5**, and different aldehydes gave equally good results (Table 1).

Table 1. Alkylation of aldehyde **3** with dialkylaluminum reagents.[a]

Entry	R^1	R	Reaction conditions [°C, h][a]	Yield of **4** and **5** [%][b] Use of **1**	Use of **2**
1	Ph	Me	−20,4	84	0
2	Ph	Et	−78,1; −40,2	71 (11)	10 (2)
3	Ph	Hex	−78,1; −40,1.5	60 (36)	6 (5)
4	*c*Hex	Me	−78,1; −40,3; −20,3	63	4[c]
5	*c*Hex	Et	−78,2; −40,3	52 (22)	10 (9)
6	*c*Hex	Et	−78,2; −40,3[d]	50 (20)	3 (2)
7	C_9H_{19}	Me	−20,4.5	86	< 1

[a] Alkylation was carried out under the reaction conditions cited with **1** (1 equiv) or **2** (2 equiv) in CH_2Cl_2. [b] Yield of **5** in parentheses. [c] Aldol product through self-condensation. [d] Use of dilute CH_2Cl_2 solution.[7]

[*] Prof. K. Maruoka, M. Takahashi, Dr. T. Ooi
Department of Chemistry, Graduate School of Science
Hokkaido University
Sapporo, 060 (Japan)
Fax: (+81) 11-746-2557
E-mail: maruoka@sci.hokudai.ac.jp

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