



$[(\text{CH}_2=\text{CH})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$: a vinylalane reagent suitable for conjugate additions to α,β -unsaturated ketones

Herbert Schumann,^{a,*} Jens Kaufmann,^a Sebastian Dechert,^a Hans-Günter Schmalz^b and Janna Velder^b

^aInstitut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

^bInstitut für Organische Chemie, Universität Köln, Greinstraße 4, D-50939 Cologne, Germany

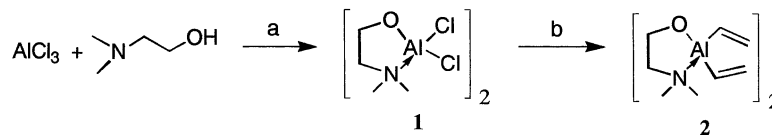
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Abstract—The reaction of AlCl_3 with 2-dimethylaminoethanol in a 1:1 mole ratio yields $[\text{Cl}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**1**), which further reacts with two equivalents of vinylmagnesium chloride to give the divinylalane $[(\text{CH}_2=\text{CH})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**2**). Compound **2** was characterized by elemental analysis, ^1H , ^{13}C , and ^{27}Al NMR spectra, mass spectrum and by X-ray structural analysis. Compound **2** was found to be a useful reagent for the transfer of a vinyl group to 1,3-diphenyl-2-propene-1-one (*trans*-chalcone). The 1,4-addition product is formed regioselectively, both in a non-catalyzed as well as in a nickel-catalyzed reaction. © 2001 Elsevier Science Ltd. All rights reserved.

In recent years, the 1,4-addition of organometallic reagents to α,β -unsaturated carbonyl compounds has become a commonly applied method for C–C bond formation.¹ Conjugate reactions of organoaluminium compounds were used to transfer the methyl group² and various alkyl³ or alkynyl groups⁴ to enones. Also, a number of methods have been developed which allow access to γ,δ -unsaturated ketones, e.g. the nickel catalyzed 1,4-addition of alkenylzirconium species,⁵ the conjugate vinyl group transfer using Grignard or lithium reagents in the presence of copper(I) compounds,⁶ or the copper-catalyzed reactions of alkenylalanes.⁷ However, the alkenylalanes used in these reactions were usually generated only in situ. Solely, Bartocha et al.⁸ were successful in isolating THF,

trimethylamine, and pyridine adducts of the unstable trivinylaluminium. The pyridine adduct, the only solid adduct, appears to be considerably more stable against polymerization than the other two. Here we report on the isolation and characterization of the divinylalane $[(\text{CH}_2=\text{CH})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ and its ability to transfer the vinyl group to 1,3-diphenyl-2-propen-1-one (chalcone) in a conjugate fashion.

Aluminium chloride reacts with equimolar amounts of 2-dimethylaminoethanol in ether at room temperature with vigorous evolution of HCl and precipitation of dimeric dichloroaluminium-2-*N,N*-dimethylaminoethanolate $[\text{Cl}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**1**) (Scheme 1). The colorless amorphous crude **1** decomposes on expo-



Scheme 1. (a) AlCl_3 (5.53 g, 41.48 mmol) solved in ether (50 mL) at 0°C , addition of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$ (3.69 g, 41.48 mmol) in ether (50 mL) at 20°C , vigorous evolution of HCl and precipitation of **1**, stirring for 12 h at 20°C , decantation of the solvent, drying of the residue in vacuum: yield: Crude **1** (7.34 g, 95%). (b) **1** (0.59 g, 3.2 mmol) in THF (30 mL), addition of $\text{CH}_2=\text{CHMgCl}$ in THF (10 mL, 1 M) at -78°C , stirring for 12 h at 20°C , removal of the solvent in vacuum, washing of the residue with hexane (70 mL), separation, filtration and concentration of the hexane solution, precipitation of **2**, recrystallization from hexane: yield. Pure **2** (0.19 g, 30%).

Keywords: aluminium; ketones; 1,4-addition; regioselectivity; vinyl complexes.

* Corresponding author. Tel.: +49-30-31423984; fax: +49-30-314221658; e-mail: schumann@chem.tu-berlin.de

sure to air and moisture and is soluble only in polar solvents like THF or pyridine. Treatment of crude **1** with an excess of vinylmagnesium chloride in THF at -78°C to room temperature results in the formation of the new intramolecular stabilized dimeric divinylaluminum-2-dimethylaminoethanolate $[(\text{CH}_2=\text{CH})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$ (**2**)⁹ with a yield of 30% (Scheme 1). The dimer **2** which melts at 114°C is sensitive to oxygen and moisture, but can be stored in a nitrogen atmosphere for a long period without polymerization.

Crystals of **2** suitable for X-ray diffraction¹⁰ were obtained from hexane solution at room temperature. An ORTEP¹¹ diagram of the molecular structure is shown in Fig. 1. Compound **2** exists as an oxygen bridged dimer in the solid state. Both aluminium

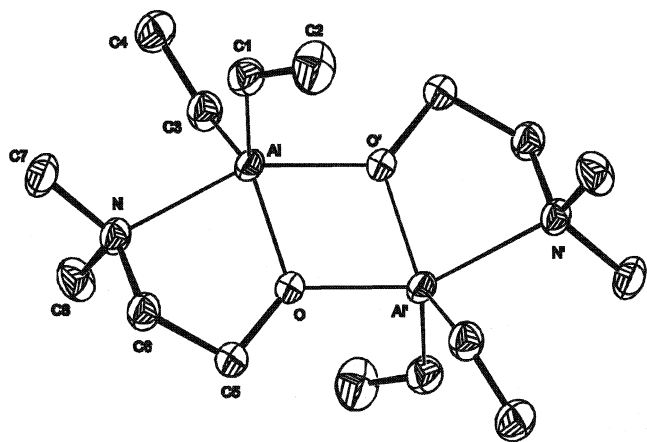
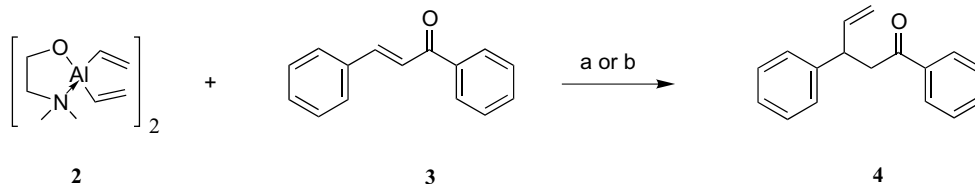


Figure 1. ORTEP¹¹ diagram of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Al–O 1.8452(11), Al–O' 1.9240(11), Al–N 2.1974(13), Al–C(1) 1.9868(16), Al–C(3) 1.9847(16), C(1)–C(2) 1.320(2), C(3)–C(4) 1.323(2); N–Al–O' 153.15(5), O–Al–O' 74.38(5), O–Al–N 79.33(5), O–Al–C(1) 117.50(6), O–Al–C(3) 126.60(6), O'–Al–C(1) 100.05(6), O'–Al–C(3) 97.76(6), C(1)–Al–C(3) 115.89(7), C(1)–Al–N 96.75(6), C(3)–Al–N 93.51(6). Symmetry transformation used to generate equivalent atoms: (') $-x+1, -y+1, -z+1$.

atoms are five-coordinated. The coordination geometry around each aluminium atom corresponds to a distorted trigonal bipyramid with the coordinating nitrogen and oxygen atoms in the axial positions. The equatorial positions are occupied by the two vinyl groups and the respective bridging alkoxide oxygen. The central Al_2O_2 ring is perfectly planar. As it is typical for five-coordinated aluminium alkoxides,¹² the Al–O_{axial} distances (1.92 Å) are slightly longer than the Al–O_{equat.} (1.85 Å) distances. The Al–N distance (2.20 Å) is longer than that reported for $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$ (2.13 Å), but shorter than that in $[\text{t-Bu}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$ (2.34 Å).¹³ This is consistent with the increase in bulkiness of the hydrocarbon groups at the aluminium atoms. The axial N–Al–O' angle (153.1°) is comparable to the values estimated for other five-coordinate aluminium 2-(dimethylamino)alkoxides.¹²

In order to test the usability of **2** in organic synthesis, we treated it with 1,3-diphenyl-2-propene-1-one PhCH=CHCOPh (*trans*-chalcone) (**3**) as a representative substrate. The reaction conducted in toluene at temperatures above 100°C for a period of 2 days resulted in the transfer of the vinylic group to give the 1,4-addition product PhCH(CH=CH₂)CH₂COPh (**4**)⁹ as a colorless oil (Scheme 2). Whereas no reaction occurs at temperatures below 100°C , the addition of a nickel catalyst allows more gentle reaction conditions. Thus, the reaction of **2** with **3** in the presence of $\text{Ni}(\text{acac})_2$ affords the addition product **4** already at room temperature in a yield of 50%. In the high temperature reaction, as well as in the catalyzed low temperature reaction not even traces of the 1,2-addition product can be observed in the crude reaction mixture. Only some of the reactant **3** was recovered.

Concluding, it can be stated that compound **2** represents the first example of a new type of stable vinyl aluminium reagent which is of potential use in organic synthesis. The regioselective transfer of the vinyl group of **2** to an enone by way of a 1,4-addition, which is catalyzed by nickel compounds may be regarded as the starting point of the development of a new synthetic methodology based on intramolecularly stabilized alkenylaluminium reagents.



Scheme 2. (a) **2** (0.11 g, 0.65 mmol) solved in toluene (5 mL), addition of *trans*-chalcone (0.14 g, 0.65 mmol) in toluene (5 mL), heating to 100°C for 2 days, quenching with aqueous NaCl (20 mL) and HCl (10%, 2 mL), extraction with CH_2Cl_2 (30 mL), separation, drying (Na_2SO_4), and concentration of the organic phase, purification by LC (hexane/ethylacetate, 20/1): yield. **4** (0.07 g, 46%); (b) dropwise addition of **2** in toluene to a solution of **3** and $\text{Ni}(\text{acac})_2$ (10 mol% in toluene), stirring for 12 h at 20°C , work-up similar to (a), isolation of **4** (50%).

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- Analytical and spectroscopic data (^1H NMR, 200 MHz, C_6D_6 ; ^{13}C NMR, 50.32 MHz, C_6D_6 ; ^{27}Al NMR, 104.29 MHz, C_6D_6 ; 70 eV EI mass spectra; IR, KBr). Compound **2**: ^1H NMR: δ 1.85 (s, 6H, NCH_3), 1.94 (t, 2H, $J=5.9$ Hz, NCH_2), 3.50 (t, 2H, $J=5.9$ Hz, OCH_2), 6.07 (dd, 2H, $J=20.7$, 7.3 Hz, CHCHH'), 6.55 (dd, 2H, $J=16.5$, 7.3 Hz, AlCH), 6.65 (dd, 2H, $J=20.7$, 16.5 Hz, CHCHH'). ^{13}C NMR: δ 44.7 (NCH_3), 55.7 (NCH_2), 58.5 (OCH_2), 131.2 (CHCH_2), 152.0 (AlCH). ^{27}Al NMR: δ 123.34 ($h_{1/2}=2205.9$ Hz). Anal. calcd for $\text{C}_8\text{H}_{16}\text{AlNO}$: C, 56.79; H, 9.53. Found C, 56.33; H, 8.43. MS: m/z (%): 311 (100) $[\text{M}-\text{C}_2\text{H}_3]^+$, 142 (15) $[\text{C}_4\text{H}_{13}\text{AlNO}]^+$, 72 (64) $[\text{C}_4\text{H}_{10}\text{N}]^+$, 58 (18) $[\text{AlO}_2]^+$. Compound **4**: ^1H NMR: δ 3.40 (dd, 1H, $J=5.4$, 15.4 Hz, CHH'), 3.46 (dd, 1H, $J=8.0$, 15.4 Hz, CHH'), 4.19 (dddd, 1H, $J=1.0$, 1.1, 5.4, 6.8, 8.0 Hz, CH), 5.08 (ddd, 1H, $J=1.1$, 1.2, 17.4 Hz, CHCHH'), 5.11 (ddd, 1H, $J=1.0$, 1.2, 10.4 Hz, CHCHH'), 6.09 (ddd, 1H, $J=6.8$, 10.4, 17.4 Hz, CHCH_2), 7.33, 7.53, 7.96 (m, 10 H, C_{arom}). ^{13}C NMR: δ 43.96 (CH), 44.48 (CH), 114.67 (CHCH_2), 126.50, 127.70, 128.00, 128.53, 132.99 (C_{arom}), 140.61 (CHCH_2), 198.23 (CO). Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.41; H, 6.82. Found C, 85.43; H, 6.39. IR (cm^{-1}): 3083 (m), 2855 (s), 1895 (s), 1639 (m), 1580 (m), 1539 (s), 847 (s). MS: m/z (%): 236.2 (10) $[\text{M}]^+$, 131.3 (4) $[\text{C}_{10}\text{H}_{11}]^+$, 105.1 (100) $[\text{C}_7\text{H}_5\text{O}]^+$, 77.2 (23) $[\text{C}_6\text{H}_5]^+$, 39.2 (5) $[\text{C}_3\text{H}_4]^+$.
- Data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo $\text{K}\alpha$ radiation, $\lambda=0.71073$ Å) with area-detector at 173 K. The structure was solved by direct methods using SHELXS-97 [Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Solution*, Universität Göttingen, 1990] and refined on F^2 using all reflections with SHELXL-97 [Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Refinement*, Universität Göttingen, 1997]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned an isotropic displacement parameter of 0.08 Å². SADABS [Sheldrick, G. M. *SADABS Empirical Absorption Correction Program*, Universität Göttingen, 1996] was used to perform area-detector scaling and absorption corrections ($T_{\text{max}}=0.9653$, $T_{\text{min}}=0.6549$). Crystal data for $\text{C}_{16}\text{H}_{32}\text{Al}_2\text{N}_2\text{O}_2$ (**1**): fw=338.40, crystal dimensions $0.50\times 0.48\times 0.28$ mm, monoclinic, space group $P2_1/n$, $a=7.3511(2)$ Å, $b=11.0441(3)$ Å, $c=12.1568(3)$ Å, $\beta=90.310(1)^\circ$, $V=986.95(5)$ Å³, $Z=2$, $\rho_{\text{calcd}}=1.139\times 10^3$ kg m^{-3} , $\mu=0.155$ mm⁻¹, $F(000)=368$, $5.0\leq 2\theta\leq 55.0^\circ$, $-9\leq h\leq 9$, $-14\leq k\leq 14$, $-9\leq l\leq 15$, 7220 data collected, 2253 unique data ($R_{\text{int}}=0.0416$), 1822 data with $I>2\sigma(I)$, 102 refined parameters, $\text{GOF}(F^2)=1.045$, final R indices ($R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1=0.0376$, $wR_2=0.1030$, max/min residual electron density $0.307/-0.224$ e Å⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-163265 (**1**). 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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