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LiAl(OC(Ph)(CF$_3$)$_2$)$_4$: A Hydrocarbon-Soluble Catalyst for Carbon−Carbon Bond-Forming Reactions

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*Summary: The compound LiAl(OC(Ph)(CF$_3$)$_2$)$_4$ (**1**), prepared from LiAlH$_4$ and HOC(Ph)(CF$_3$)$_2$, is an active Lewis acid catalyst in toluene solution for the 1,4-conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds and for the direct substitution of allylic acetates by silyl ketene acetals. The structure of **1** contains a rare trigonal prismatic coordination sphere around the Li$^+$ cation, with two Li−O(C, Al) bonds and four Li−F(C) bonds.*

One of the most important uses of new weakly coordinating anions (WCAs) is to enhance the catalytic activity of metal cations.[2] Two examples that have received considerable attention recently are metallocene-catalyzed olefin polymerization[3] and lithium-catalyzed Diels−Alder reactions and 1,4-conjugate addition reactions.[4] The best Li$^+$-based catalysts, including LiClO$_4$,[4a,b,d] LiN(O$_2$SCF$_3$)$_2$,[4e,g] and LiCo(C$_2$B$_9$H$_{11}$)$_2$,[4c] exhibit higher activity as the coordinating ability of the solvent decreases from, for example, diethyl ether to 1,2-dichloroethane (DCE). Due to restrictions or hazards associated with DCE and other weakly coordinating halogenated solvents,[5] hydrocarbon-soluble *and hydrocarbon-active* catalysts would be desirable for large-scale industrial use. However, few lithium salts of WCAs are soluble in hydrocarbon solvents, and none that we know of is catalytically active.

We now report that the Li$^+$ salt of a new tetrakis(polyfluoroalkoxy)aluminate shows great promise as a hydrocarbon-active catalyst for 1,4-conjugate addition reactions and the direct substitution of allylic acetates by silyl ketene acetals. The new hydrocarbon-soluble compound LiAl(OC(Ph)(CF$_3$)$_2$)$_4$, **1**, was prepared by adding 4 equiv of HOC(Ph)(CF$_3$)$_2$ to LiAlH$_4$ in toluene solution:[6]

$$4\mathrm{HOC(Ph)(CF_3)_2} + \mathrm{LiAlH_4} \rightarrow \underset{\mathbf{1}}{\mathrm{LiAl(OC(Ph)(CF_3)_2)_4}} + 4\mathrm{H_2}$$

The hygroscopic, volatile, white solid, which was purified by vacuum sublimation at 138 °C, is extremely soluble in hydrocarbon solvents including hexane and toluene. Diffraction-quality crystals were grown by cooling a hexane solution of **1**.[7] The solid-state structure, shown in Figure 1, consists of discrete LiAl(OC(Ph)(CF$_3$)$_2$)$_4$ molecules. The Al atom is tetrahedrally coordinated by four 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxide ligands. The O1−Al−O2 angle of 91.8(1)° is smaller than the five other O−Al−O angles, which range from 105.4(1) to 116.7(1)°. The Al(OC(Ph)(CF$_3$)$_2$)$_4$$^-$ anion is a hexadentate chelating ligand for the Li$^+$ cation. The O1−Al−O2 unit forms a four-membered chelate ring with Li$^+$, with Li−O(Al,C) bond distances of 1.966(8) and 1.978(8) Å. Four C−F bonds from four different CF$_3$ groups form five-membered O−Li−F−C−C chelate rings, with Li−F(C) bond distances of 1.984(9), 2.082(9), 2.098(11), and 2.354 (10) Å. The overall LiO$_2$F$_4$ coordination sphere can best be described

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[2] (a) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (c) Strauss, S. H. *Chemtracts: Inorg. Chem.* **1994**, *6*, 1.

[3] For examples see the following and references therein: (a) Turner, H. W. European Patent Appl. 277,004 (assigned to Exxon), 1988. (b) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265. (c) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755. (d) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Peterson, J. L. *Organometallics* **1995**, *14*, 371.

[4] For examples see the following and references therein: (a) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. (b) Grieco, P. A.; Cooke, R. J.; Henry, K. J.; VanderRoest, J. M. *Tetrahedron Lett.* **1991**, *32*, 4665. (c) DuBay, W. J.; Grieco, P. A.; Todd, L. J. *J. Org. Chem.* **1994**, *59*, 6898. (d) Saidi, M. R.; Heydari, A.; Ipaktschi, J. *Chem. Ber.* **1994**, *127*, 1761. (e) Kobayashi, H.; Nie, J.; Sonoda, T. *Chem. Lett.* **1995**, 307. (f) Arai, T.; Sasai, H.; Aoe, K.; Okamura, K.; Date, T.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 104. (g) Handy, S. T.; Grieco, P. A.; Mineur, C.; Ghosez, L. *Synlett* **1995**, 565.

[5] Kirschner, E. M. Environment, Health Concerns Force Shift in Use of Organic Solvents. *Chem. Eng. News* **1994**, June 20, p 13.

[6] A toluene solution of HOC(Ph)(CF$_3$)$_2$ (5.00 g, 20.5 mmol) was added to a stirred toluene slurry of LiAlH$_4$ (0.180 g, 4.75 mmol). The mixture was slowly heated to reflux, during which time a gas, presumably dihydrogen, was evolved. During 7 h of stirring under reflux, the appearance of the supernatant changed from colorless to blue-green to blue to purple to orange-red, at which point there were no solids present. The volatiles were removed under vacuum to yield a mixture of white and orange solids. The crude product was sublimed at 138 °C. At this temperature, the mixture of solids melted to become a brown liquid. The white solid product **1** collected on the cold finger (yield 1.38 g, 29%). The compound can be further purified by recrystallization from hexanes. Proton, ^{7}Li, ^{13}C, and ^{19}F NMR spectra of **1** in methylcyclohexane-d_{14} were obtained (Supporting Information). The ^{1}H spectrum is unremarkable. The ^{7}Li spectrum shows a single broad resonance at δ −0.35 ppm. The ^{13}C spectrum shows a single type of CF$_3$ group ($J(^{13}\mathrm{C}-^{19}\mathrm{F}) = 289$ Hz), and a single type of phenyl group. The ^{19}F spectrum shows a single environment for all 24 fluorine atoms, indicating rapid exchange of all 24 fluorine atoms. The observed pattern at δ −75.9 is the superposition of a 1:1:1:1 quartet and a broad singlet due to coupling to a single lithium atom ($I = {}^3/_2$ for ^{7}Li, 92.5% NA; $I = 1$ for ^{6}Li, 7.5% NA). The observed separation of the central peaks is 2.4 Hz. Therefore, if the solid-state structure is maintained in solution, then $J(^7\mathrm{Li}-^{19}\mathrm{F}) = 14.4$ Hz ((2.4 Hz)(24 F atoms)/(4 F atoms)). The spectra are consistent with rapid intramolecular exchange of the Li$^+$ ion. Similar spectra were observed in toluene-d_8. Lower temperatures did not result in slow-exchange limit spectra. The solubilities of **1** in benzene-d_6 and methylcyclohexane-d_{14} are at least 41 and 32 mM, respectively.

[7] Crystals of **1** were grown by cooling a hexane solution: C$_{36}$H$_{20}$AlF$_{24}$LiO$_4$, $M_r = 1006.4$, monoclinic, space group *C*2/*c*; $a = 42.297(6)$, $b = 10.641(1)$, $c = 19.132(2)$ Å; $\beta = 114.808(9)°$; $V = 7817(2)$ Å^3, $Z = 8$, $\rho_{\mathrm{calc}} = 1.710$ g cm^{-3}, $F(000) = 4000$, $\lambda(\mathrm{Mo\ K}\alpha) = 0.710\ 73$ Å, $\mu = 2.07$ cm^{-1}, $T = -100$ °C, crystal dimensions 0.60 × 0.46 × 0.12 mm; Siemens *P*4 diffractometer, $\theta-2\theta$ scan technique, 6883 independent reflections measured ($4.2° \le 2\theta \le 50°$); anisotropic refinement (full-matrix least-squares on F^2) for all non-hydrogen atoms; hydrogen atoms in calculated positions; no absorption correction; final $R(I > 2\sigma(I)) = 0.052$, final R(all data) = 0.105; total number of parameters = 596.

S0276-7333(96)00403-7 CCC: $12.00

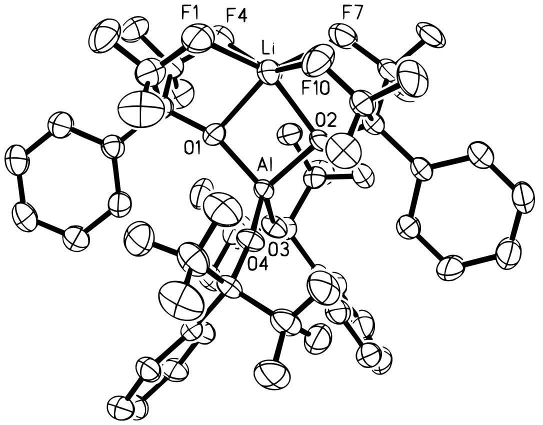
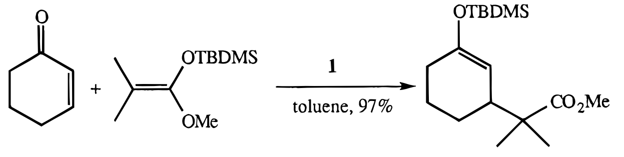


Figure 1. Drawing of the structure of **1**, LiAl(OC(Ph)-$(CF_3)_2)_4$ (hydrogen atoms omitted for clarity). Selected interatomic distances (Å) and angles (deg): Li−O1, 1.978(8); Li−O2, 1.966(8); Li−F1, 1.984(9); Li−F4, 2.354(10); Li−F7, 2.098(11); Li−F10, 2.082(9); O1−Li−O2, 79.9(3); F1−Li−F7, 129.5(4); F4−Li−F10, 149.1(4); C5−F1, 1.376(5); C6−F4, 1.341(5); C7−F7, 1.361(5); C8-F10, 1.384(5); other C−F, 1.298(5)−1.342(5); Al−O1, 1.773(2); Al−O2, 1.755(3); Al−O3, 1.687(3); Al−O4, 1.706(3); O1−Al−O2, 91.8(1); O1−Al−O3, 115.8(1); O1−Al−O4, 112.5(1); O2−Al−O3, 114.8(1); O2−Al−O4, 116.7(1); O3−Al−O4, 105.4(1).

as trigonal prismatic: the $\overline{\mathrm{O1{-}F1{-}F4}}$ and $\overline{\mathrm{O2{-}F7{-}F10}}$ triangular planes make a dihedral angle of only 12°.

There are several unique and noteworthy features about the structural environment of the Li^+ cation in **1**. Lithium(I) is rarely six-coordinate, and on those rare occasions it is generally octahedral (e.g., LiF, $LiClO_4 \cdot 3H_2O$, $LiSbF_6$), not trigonal prismatic. In addition, this is the first example of a compound with more than two Li−F(C) bonds for a given Li^+ ion and the first example in which a majority of atoms coordinated to Li^+ are organofluorine atoms. Furthermore, the 1.984(9) Å Li−F1 distance is shorter than any previously reported Li−F(C) distances.[8,9] For comparison, the Li−F(C) distances in $[Li(FN_2O_3)][ClO_4]$,[8] $Li(2,4,6\text{-}C_6H_2(CF_3)_3)(Et_2O)$,[10] and $Li(C_6F_5NSiF(t\text{-}Bu)_2)(THF)_2$[11] are 2.035(5), 2.25(1) (average of two distances), and 2.27(1) Å, respectively, and the Li−F distance in crystalline LiF is 2.009 Å.[12] The Li−F bonds in **1** cannot be considered secondary bonds: the Li−F1 distance is the same, to within $\pm 3\sigma$, as the two Li−O distances. Finally, the Li−F(C) bonds are sufficiently strong to significantly lengthen the C−F(Li) bonds (1.341(5)−1.384(5) Å) relative to the other C−F bonds (1.298(5)−1.342(5) Å) in **1**. Nevertheless, since carbon−halogen bonds are very poor donor ligands,[9] we anticipated that **1** might function as a hydrocarbon-soluble Lewis acid.

To probe the catalytic activity of **1**, the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl substrates was studied in *toluene* at ambient temperature. Addition of 10 mol % of **1** to a 0.1 M toluene solution of cyclohexenone containing 2.0 equiv of silyl ketene acetal **2** gave rise to a 97% isolated yield of the 1,4-addition product **3** after 4 h (rxn 1). In the absence of catalyst there was no reaction. When 10 mol % lithium trifluoromethanesulfonimide or lithium perchlorate was used instead of **1**, no reaction was observed.[13]



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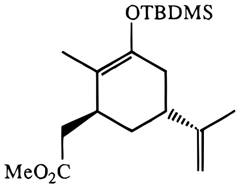
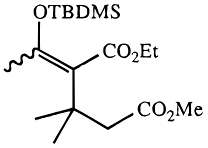
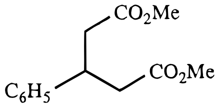
3

A number of other substrates were investigated using 1-methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene (**4**) as the nucleophile (Table 1). In the case of the sterically encumbered substrate **5**, the major product was the result of 1,2-addition: a 0.1 M solution of **5** in toluene containing excess **4** and 10 mol % **1** afforded a 93% isolated yield of a 9:1 mixture of the 1,2- to 1,4-addition products after 40 min. However, addition of 10 mol % *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) gave rise, after 12 h, to a 94% isolated yield of exclusively the 1,4-addition product **6** (rxn 2).[14] Similarly, when a toluene solution of **4** and enone **7** was treated with 10 mol % **1**/TMEDA for 2.5 h, a 93% yield of **8** was isolated

Table 1. $LiAl(OC(Ph)(CF_3)_2)_4$−Catalyzed Conjugate Addition of 1-Methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene to α,β-Unsaturated Carbonyl Compounds[a]

product	time	yield[b]
	30 min	89%
	10 h	93%
	30 min	81%

[a] All reactions were conducted at ambient temperature and pressure employing a 0.1 M solution of substrate in toluene, 10 mol % $LiAl(OC(Ph)(CF_3)_2)_4$, and 2.0 equiv of silyl ketene acetal. [b] Isolated yield.

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(8) Plenio, H.; Diodone, R. *J. Am. Chem. Soc.* **1996**, *118*, 356. FN_2O_3 = 23-fluoro-4,7,20-trioxa-1,10-diazatricyclo[8.7.5.1^{12,16}]tricosa-12,14,-16(23)-triene.

(9) Kulawiec, R. J.; Crabtree R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

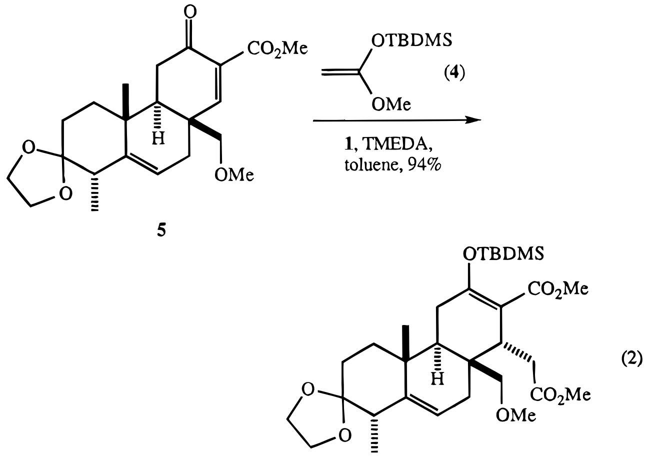
(10) Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1990**, 833.

(11) Stalke, D.; Klingebiel, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1457.

(12) Wells, A. F. *Structural Inorganic Chemistry,* 5th ed.; Oxford University Press: Oxford, England, 1984; p 444.

(13) Shibasaka et al. have recently reported a heterobimetallic catalyst ($LiAl(R\text{-BINOL})_2$) for the 1,4-conjugate addition of malonates to cyclohexenones.[4f] When 10 mol % of $LiAl(R\text{-BINOL})_2$ was employed in the reaction of cyclohexenone with silyl ketene acetal **2** in toluene, no reaction was observed.

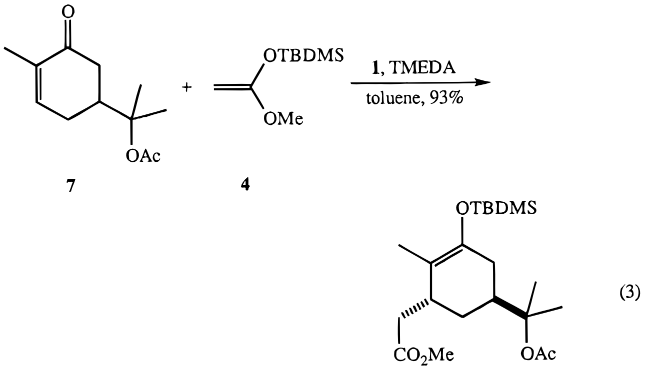
(14) Chelation of Li^+ by TMEDA would produce a sterically more congested lithium Lewis acid. Presumably, 1,4-addition is favored over 1,2-addition when the enone is coordinated to the more congested Lewis acid. As expected, the weaker Lewis acidity of the $Li(TMEDA)^+$ complex results in decreased reaction rates.



5

6

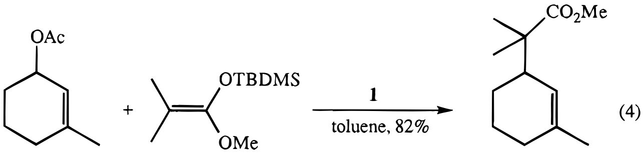
(rxn 3).[15] The ability of **1** to catalyze sterically demanding 1,4-conjugate addition reactions *in toluene* obviates the necessity of using either highly polar media (5.0 M $LiClO_4-Et_2O$)[4b] or ultrahigh pressure.[16]



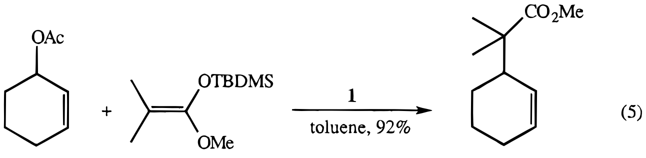
7 **4**

8

During the course of this study, we made the remarkable observation that allylic acetates undergo facile carbon–carbon bond formation when treated with silyl ketene acetals *in toluene* in the presence of **1**. Treatment of a 0.1 M toluene solution of allylic acetate **9** containing 2.0 equiv **2** with 10 mol % **1** afforded an 82% isolated yield of **10** after 2 h (rxn 4). In the absence of catalyst, no reaction was observed. When the unsubstituted silyl ketene acetal **4** was employed in the above reaction, a >90% yield of the corresponding methyl cyclohexenyl acetate was isolated. This type of direct substitution has previously been observed for substrates such as **9** in the presence of **4**, but concentrated solutions of lithium perchlorate in diethyl ether (e.g., 5.0 M $LiClO_4-Et_2O$) were required to effect the transformation.[17] Even more striking was the result with cyclohexenyl acetate **11**. Upon exposure of **11** to **2** in toluene containing 10 mol % **1**, a 92% yield of **12** was isolated after 10 h (rxn 5). The mildness and efficiency of this new carbon–carbon bond-forming reaction will be of considerable interest to those engaged in organic synthesis. Further studies are underway to prepare more effective catalysts and to determine the scope and limitation of this novel process.



9 **2** **10**



11 **2** **12**

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Supporting Information Available: NMR spectra and tables of atomic coordinates, bond distances and angles, thermal parameters, and crystal data and ORTEP diagrams for **1** (16 pages). Ordering information is given on any current masthead page.

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(15) When hexamethylphosphoramide (HMPA) was employed in place of TMEDA in rxns 2 and 3, dramatically lower rates were observed: for example, substrate **5** required *ca.* 50 h in order to realize an 87% yield of **6**.

(16) (a) Matsumoto, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1013. (b) Bunce, R. A.; Schlecht, M. F.; Dauben, W. G.; Heathcock, C. H. *Tetrahedron Lett.* **1983**, *24*, 4943.

(17) (a) Pearson, W. H.; Schkeryantz, J. M. *J. Org. Chem.* **1992**, *57*, 2986. (b) Grieco, P. A.; Collins, J. L.; Henry, K. J. *Tetrahedron Lett.* **1992**, *33*, 4735.