Supporting Information

Development of zinc alkyl/air systems as radical initiators for organic reactions

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Experimental Section

General Remarks

Syntheses of organometallic initiators were conducted under a nitrogen atmosphere using standard Schlenk techniques. All reagents were of commercial grade and obtained from Sigma-Aldrich Co.. Solvents and the propionic acid used for the preparation of initiators were carefully dried and distilled under nitrogen atmosphere prior to use. TEMPO was sublimated and stored under nitrogen atmosphere. NMR spectra were acquired on a Varian Mercury 400 Spectrometer IR spectra were measured on Perkin-Elmer System 2000 FT-IR spectrophotometer. GC-MS analysis was performed on Agilent 6890N chromatograph coupled with Agilent 5973N MS detector.

Synthesis and characterization of new alkylzinc complexes

Ethylzinc propionate EtZn(O_2CEt)

Et_2Zn (0.247 g, 2.00 mmol) was added dropwise to a stirred suspension of propionic acid (0.148 g, 2.00 mmol) in hexane (10 mL) at –78 °C. After the addition was completed the resulting white slurry was allowed to warm up to RT and stirred for further 2h. The solvent was removed under vacuum until a dry paste remained, giving a crude material in quantitative yield, which was used in the next step without purification. δ_H(400 MHz, C_6D_6) ppm: 0.26 (q, 2H, $CH_3C\mathit{H_2}$-Zn), 1.11 (t, 3H, $C\mathit{H_3}CH_2$-Zn), 1.18 (t, 3H, $C\mathit{H_3}CH_2$-), 2.39 (q, 2H, $CH_3C\mathit{H_2}$-). ν_{max}/cm^{-1} (Nujol): 1568(s), 1557(s), 1463(s), 1422(s), 1379(m), 1296(m), 1081(w), 988(w), 952(w), 920(w), 893(w), 812(w), 683(w), 609(m); ν_{max}/cm^{-1} (CH_2Cl_2): 1620(s), 1464(m), 1409(s), 1372(m), 1291(m), 1085(w), 988(w), 954(w), 923(w), 899(w), 815(w), 618(w).

Methylzinc benzoate MeZn(O_2CPh)

A solution of Me_2Zn (0.191 g, 2.00 mmol) in THF (2 mL) was added to a stirred solution of benzoic acid (0.244 g, 2.00 mmol) in THF (6 mL) at –78 °C. The reaction mixture was allowed to warm up to RT and stirred until gas evolution had ceased and the solid dissolved completely. The resulting colourless solution was used in the next step without further purification. δ_H(400 MHz, C_6D_6) ppm: -0.46 (s, 3H, $C\mathit{H_3}$-Zn), 6.96 (m, 2H, $C\mathit{H}_{Ar}$), 7.07 (m, 1H, $C\mathit{H}_{Ar}$), 8.10 (m, 2H, $C\mathit{H}_{Ar}$).

Methylzinc propionate $MeZn(O_2CEt)$

An analogous practice as that for methylzinc benzoate was applied, starting from THF solutions of Me_2Zn (0.191 g, 2.00 mmol) and propionic acid (0.148 g, 2.00 mmol). δ_H(400 MHz, THF-D_8) ppm: 0.99 (s, 3H, CH_3-Zn), 0.96 (t, 3H, CH_3CH_2-), 2.16 (q, 2H, CH_3CH_2-).

Tert-butylzinc propionate $tBuZn(O_2CEt)$

To a stirred solution of propionic acid (0.148 g, 2.00 mmol) in toluene (6 mL) was added 1.4 M solution of $t\mathrm{Bu}_2Zn$ (1.43 mL, 2.00 mmol) in toluene (4 mL) at –78 °C. The reaction mixture was allowed to warm up to RT and stirred for 2 h. All volatile material was removed under vacuum and white polycrystalline solid of *tert*-butylzinc propionate was obtained with quantitative yield and used in the model reaction without further purification. δ_H(400 MHz, C_6D_6) ppm: 0.88 (t, 3H, CH_3CH_2-); 1.07 (s, 9H, $(CH_3)_3C$-Zn); 2.13 (q, 2H, CH_3CH_2-); elemental analysis (%) found: C 43.05, H 7.15, calcd for $C_7H_{14}O_2Zn$: C 42.99, H 7.22; ν_{max}/cm^{-1} (Nujol): 1596(s), 1464(s), 1411(s), 1379(m), 1357(w), 1290(s), 1167(w), 1082(w), 1009(w), 936(w), 893(w), 814(w), 721(w), 684(w).

Procedures used in the model reaction mediated by $Me_2Zn(t\mathrm{BuDAB})$, TEMPO/Et_2Zn and $[(EtZn)_2Zn(OAr)_4]/O_2$ systems

*Addition of THF to **1a** in the presence of $Me_2Zn(tBuDAB)$*

To a stirred solution of *t*BuDAB (0.673 g, 4.00 mmol) in toluene (2 mL) a 2 M solution of Me_2Zn in toluene (2.00 mL, 4.00 mmol) was added at –78 °C. Reaction mixture was allowed to warm up to 0 °C and a solution of **1a** (0.220 g, 1.00 mmol) in THF (14 mL) was added and the reaction mixture was warmed up to 30 °C and stirred for 48 h. The post-reaction mixture was analyzed by ^1H NMR without hydrolysis. Spectrum did not show any signals associated with **2a** or any other product of a reaction of **1a**.

*Addition of THF to **1a** in the presence of TEMPO and Et_2Zn*

To a stirred solution of Et_2Zn (0.492 g, 4.00 mmol) and **1a** (0.220 g, 1.00 mmol) in THF (7 mL) was added a dark-orange solution of TEMPO (0.624 g, 4.00 mmol) in THF (7 mL) at –78 °C. Reaction mixture was allowed to slowly warm up to room temperature (decolouration was observed) and was further stirred for 48 h. The post-reaction mixture was analyzed by ^1H NMR without hydrolysis. Spectrum did not show any signals associated with **2a** or any other product of a reaction of **1a**.

*Addition of THF to **1a** in the presence of TEMPO and Et_2Zn (dropwise addition of TEMPO)*

To a stirred solution of Et_2Zn (0.492 g, 4.00 mmol) and **1a** (0.220 g, 1.00 mmol) in THF (7 mL) a solution of TEMPO (0.624 g, 4.00 mmol) in bezene (2 mL) was added dropwise over 10 minutes at room temperature. Mixture was further stirred for 48 h. The post-reaction mixture was analyzed by ^1H NMR without hydrolysis. Spectrum did not show any signals associated with **2a** or any other product of a reaction of **1a**.

*Addition of THF to **1a** in the presence of the $[(EtZn)_2Zn(OAr)_4]/O_2$ system*

To a stirred solution of the $[(EtZn)_2Zn(OAr)_4]$ complex (4.32 g, 4.00 mmol) in THF (7 mL) a solution of **1a** (0.220 g, 1.00 mmol) in THF (7 mL) was added at 0 °C. The reaction mixture was exposed to an excess of dry air for 48 h at room temperature. The post-reaction mixture was analyzed by ^1H NMR without hydrolysis. Spectrum did not show any signals associated with **2a** or any other product of a reaction of **1a**.

Table 1S. Conversion ratios of **1a** in the reaction of addition THF radical initiated by the tested initiating systems.

	Reaction time (min)								
Mediating system	**1.5**	**5**	**15**	**60**	**120**	**240**	**1440**	**2880**	**Isolated yield of 2a after 24 h, [%]**
	Conversion								
Me_2Zn(*t*BuDAB)	0	0	0	0	0	0	0	0	0
TEMPO $ZnEt_2$	0	0	0	0	0	0	0	0	0
$[(EtZn)_2Zn(OAr)_4]/O_2$	0	0	0	0	0	0	0	0	0
$EtZn(O_2CPh)$/air	0.11	0.38	0.68	0.90	0.97	0.99	0.99	-	95
$MeZn(O_2CPh)$/air	0.12	0.21	0.62	0.93	0.98	0.99	0.99	-	92
$EtZn(O_2CEt)$/air	0.07	0.21	0.52	0.87	0.95	0.99	0.99	-	96
$MeZn(O_2CEt)$/air	0.11	0.32	0.71	0.90	0.98	0.99	0.99	-	95
t$BuZn(O_2CEt)$/air	0.01	0.02	0.05	0.07	0.08	0.10	0.10	-	6
Me_2Zn/air	0.12	0.26	0.43	0.66	0.75	0.76	0.76	-	72

X-ray Structure Determination

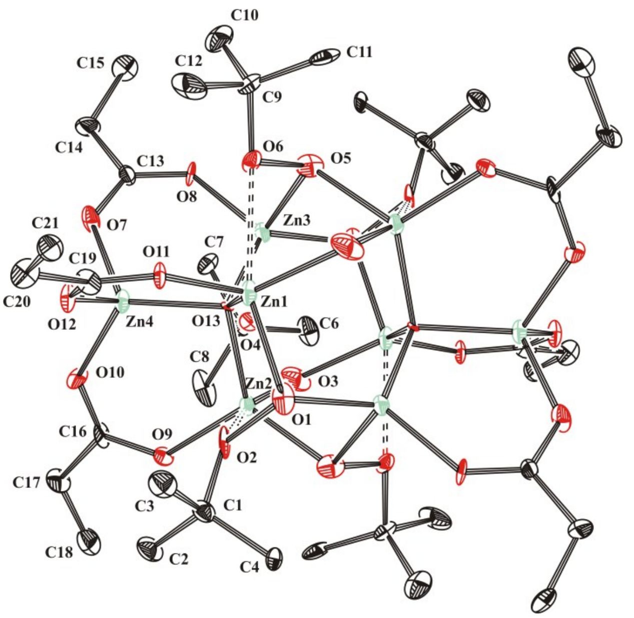

Figure 1S. Molecular structure of **3** with thermal ellipsoids set at 30% probability.

Table 2S. Selected bond lengths (Å) and angles (deg) for compound **3**.

Zn1 – O1	1.970(3)	Zn4 – O9	1.993(3)
Zn1 – O7	1.974(3)	Zn4 – O11	1.960(3)
Zn1 – O12	1.945(3)	Zn4 – O13	2.441(3)
Zn1 – O11	1.929(3)		
Zn2 – O2	1.957(3)	Zn1 – O12 – C16	115.7(2)
Zn2 – O3	1.953(3)	Zn1 – O11 – Zn2	107.89(14)
Zn2 – O10	1.955(3)	Zn1 – O11 – Zn3	116.56(14)
Zn2 – O11	1.948(3)	Zn1 – O11 – Zn4	113.26(14)
Zn3 – O4	1.996(3)	O10 – Zn2 – O11	111.09(12)
Zn3 – O5	1.953(3)	O3 – Zn2 – O11	110.59(13)
Zn3 – O12	1.937(3)	O2 – Zn2 – O10	106.14(13)
Zn3 – O11	1.951(3)	Zn4 – O13 – C16	120.5(3)
Zn4 – O6	2.079(3)	Zn4 – O13 – C19	129.6(3)
Zn4 – O8	1.990(3)	Zn3 – O11 – Zn4	104.94(13)

Crystal data for **3**, **$[Zn_4(\mu_3\text{-OO}t\text{Bu})_3(\mu_4\text{-O})(O_2CEt)_3]_2$**, $C_{42}H_{84}O_{26}Zn_8$: M = 1528.05, crystal dimensions 0.42 × 0.28 × 0.22 mm^3, monoclinic, space group C 2/c (no. 15), a = 22.502(2) Å, b = 12.8820(12) Å, c = 21.7730(14) Å, β = 98.995(5) °, U = 6233.7(9) Å^3, Z = 4, F(000) = 3136, D_c = 1.628 g cm^{-3}, T = 100(2)K, μ(Mo-Kα) = 3.097 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 21.97°, 3779 unique reflections. The structure was solved by direct methods using the SHELXS97[1] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.1605, $wR2$ = 0.2492 for all data and 343 parameters ($R1$ = 0.0956, $wR2$ = 0.1910 for 2200 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.132. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2\ )/3$ was used in the final stage of refinement. The residual electron density = +1.01/-0.93eÅ^{-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 746458. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

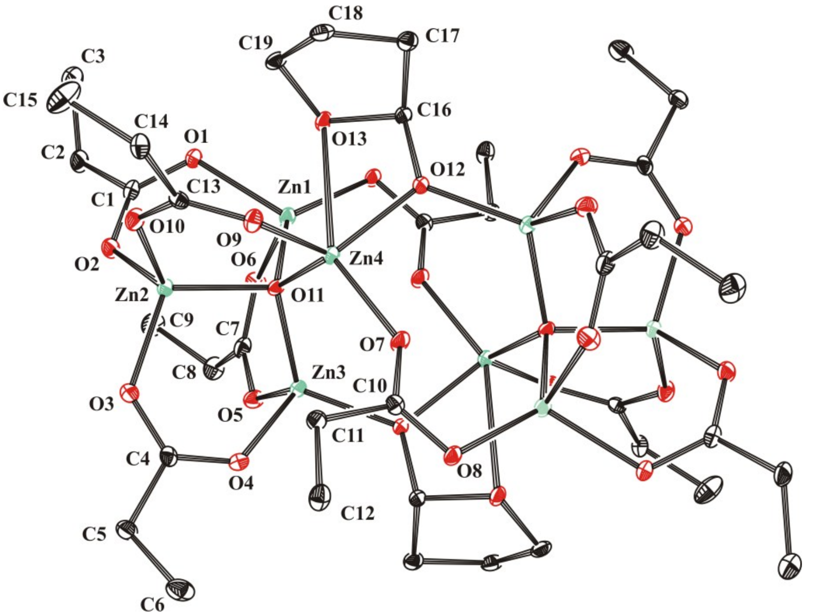

Figure 2S. Molecular structure of **4** with thermal ellipsoids set at 30% probability.

Table 3S. Selected bond lengths (Å) and angles (deg) for compound **4**.

O1 – O2	1.48(2)	Zn4 – O12	1.950(15)
O3 – O4	1.53(2)	Zn4 – O13	1.955(12)
O5 – O6	1.51(2)	C1 – O2	1.45(3)
Zn1 – O1	2.001(17)	C5 – O4	1.43(3)
Zn1 – O3	1.994(16)	C9 – O6	1.46(3)
Zn1 – O6	2.454(14)		
Zn1 – O13	1.995(14)	Zn1 – O1 – O2	101.2(10)
Zn2 – O2	2.428(16)	Zn1 – O1 – Zn3	103.3(8)
Zn2 – O3	1.986(19)	C1 – O2 – O1	110.7(14)
Zn2 – O5	2.009(15)	Zn1 – O3 – O4	108.9(11)
Zn2 – O13	2.000(13)	Zn1 – O3 – Zn2	104.0(8)
Zn3 – O1	2.037(15)	Zn1 – O13 – Zn3	114.9(6)
Zn3 – O4	2.415(15)	Zn2 – O3 – O4	99.7(12)
Zn3 – O5	1.998(14)	O3 – O4 – C5	109.5(15)
Zn3 – O13	1.934(14)	Zn2 – O5 – O6	108.7(10)
Zn4 – O7	1.957(15)	Zn3 – O5 – O6	100.7(10)
Zn4 – O10	1.943(14)	O5 – O6 – C9	107.9(15)

Crystal data for **4**, **$[Zn_4(\mu_4\text{-}O)(\mu_3\text{-}2\text{-}OTHF)(O_2CEt)_5]_2$**, $C_{38}H_{64}O_{26}Zn_8$: M = 1460.01, crystal dimensions 0.52 × 0.45 × 0.38 mm^3, triclinic, space group P -1 (no. 2), a = 9.5731(4) Å, b = 10.8542(6) Å, c = 13.0771(7) Å, α = 77.371(2) °, β = 83.044(3) °, γ = 80.914(3) °, U = 1304.01(12) Å^3, Z = 1, F(000) = 740, D_c = 1.859 g cm^{-3}, T = 100(2)K, μ(Mo-Kα) = 3.696 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 24.71 °, 4450 unique reflections. The structure was solved by direct methods using the SHELXS97[5] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[6] H-atoms were included in idealized positions and refined isotropically. Refinement converged at $R1$ = 0.0535, $wR2$ = 0.0831 for all data and 330 parameters ($R1$ = 0.0391, $wR2$ = 0.0774 for 3685 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.134 A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.51/-0.56 eÅ^{-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 753795. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

References:

1 SHELXS-97, Program for Structure Solution: G.M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467-473.
2 G. M. Sheldrick, SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.