Supporting Informations

A Highly Efficient Large Bite Angle Diphosphine Substituted Molybdenum Catalyst for Hydrosilylation

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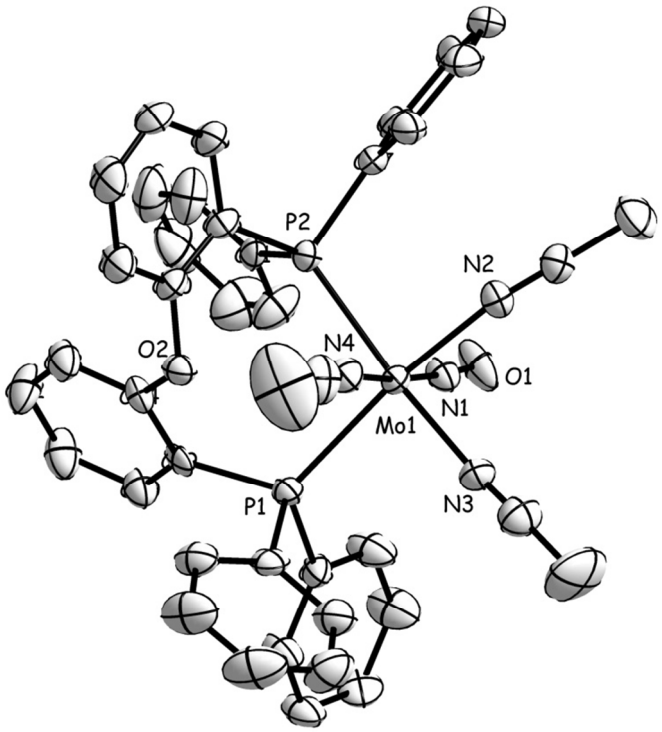


Figure S1. Molecular structure of the cationic part of $[Mo(NO)(P\cap P)(NCMe)_3]$ $[Zn_2Cl_6]_{1/2}$ **(2)**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms, solvent molecule and $[Zn_2Cl_6]_{1/2}$ counter ion are omitted for clarity. Selected bond distances (Å) and bond angles

(°): Mo1-N1 1.769(4), Mo1-N2 2.151(5), Mo1-N3 2.149(5), Mo1-N4 2.220(5) Mo1-P1 2.4919(14) Mo1-P2 2.4660(14) N1-O1 1.210(5) N1-Mo1-N4 174.04(18), N2-Mo1-N3 80.60(16), P1-Mo1-P2 96.76(5) P1-Mo1-N2 169.43(12) P1-Mo1-N3 89.72(12)

Table S1. Reaction conditions for kinetic measurements for the hydrosilylations of acetophenone catalysed by **3** at room temperature.

Runs	1	2	3	4
$PhCOCH_3$(mmol)	0.62	0.62	1.24	0.62
3 (mmol)	0.0006	0.0006	0.0006	0.0003
C_6D_5Cl (mL)	0.3	0.3	0.3	0.3
$PhMeSiH_2$(mmol)	0.73	1.46	0.73	0.73

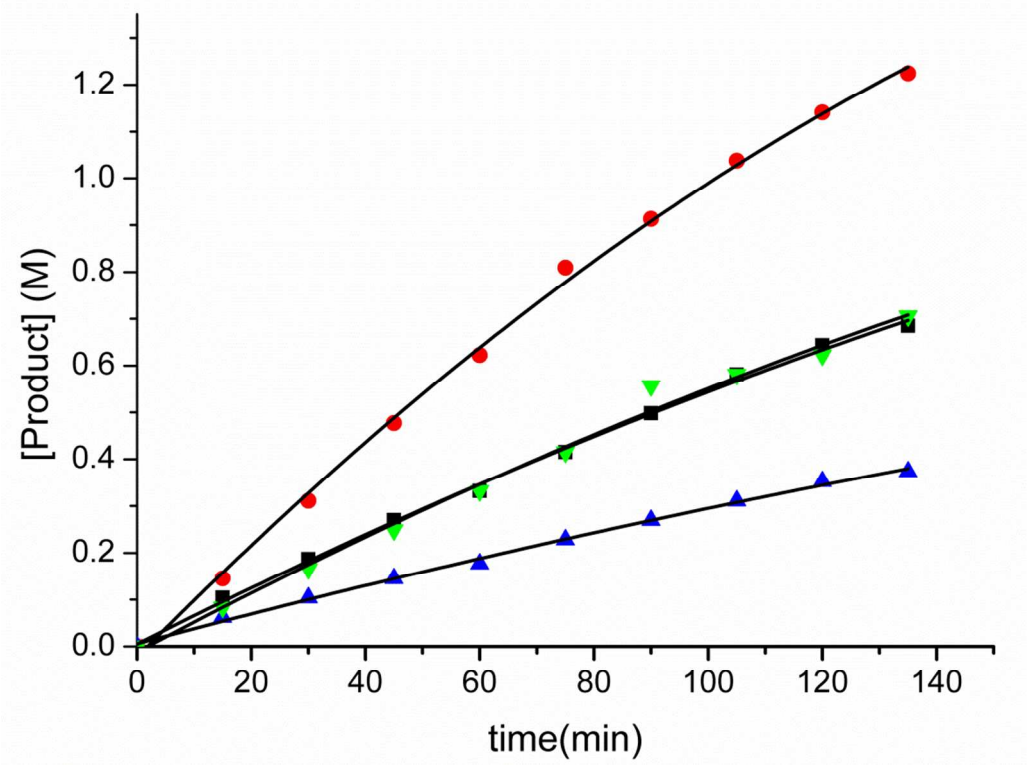
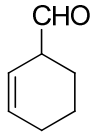
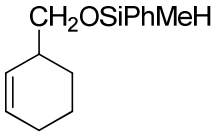
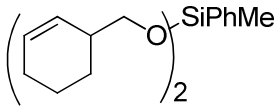
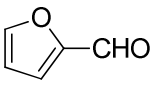
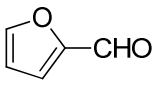
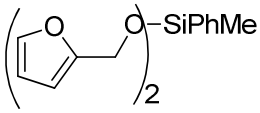
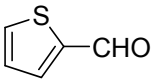
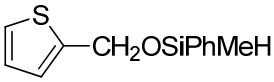
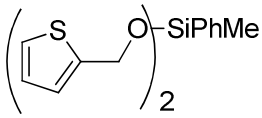
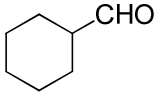
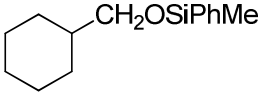
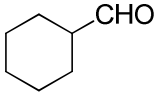
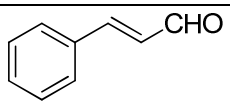
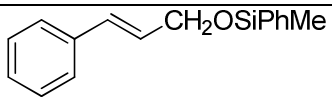
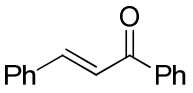
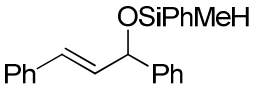
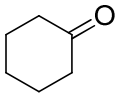
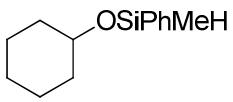
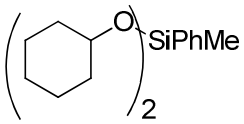
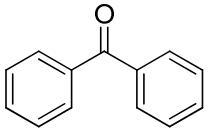
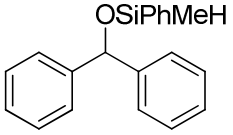
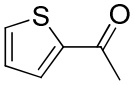
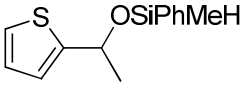
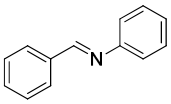
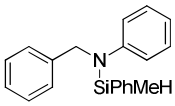
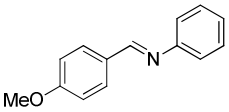
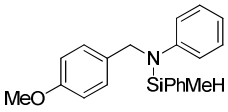


Figure S2. Kinetic plot of product concentrations over time. Blue triangles: $[PhC(O)CH_3]$ = 2.075 M, [cat] = 0.001 M, $[PhMeSiH_2]$ = 2.43 M; Black Squares: $[PhC(O)CH_3]$ = 2.075 M, [cat] = 0.002 M, $[PhMeSiH_2]$ = 2.43 M; Green triangles: $[PhC(O)CH_3]$ = 4.14 M, [cat] = 0.002 M,

[$PhMeSiH_2$] = 2.43 M; Red circles: [$PhC(O)CH_3$] = 2.075 M, [cat] = 0.002 M, [$PhMeSiH_2$] = 4.86 M.

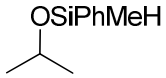
Table S2. GC/MS data for various hydrosilylated products of aldehydes and ketones:

Entry[a]	**substrates**	**Product a**	**Product b**
1	 rt = 3.624 min m/z = 110	 rt = 8.692 min m/z = 231	 rt =13.662 min m/z = 342
2	 rt = 2.759 min m/z 96	 rt = 7.581 min m/z 217	 rt = 10.901min m/z 315
3	 rt = 4.035 min m/z 112	 rt = 8.847 min m/z 234	 rt = 14.486 min m/z 346
4	 rt = 3.562 min m/z = 113	 rt = 8.598 min m/z = 233	 rt = 13.281 min m/z = 346
5	 rt = 6.266 min m/z 131	 rt = 10.584 min m/z 254	-

6	 rt = 11.230 min m/z 15.234	 rt =15.234 min m/z 331	-
7	 rt = 3.101 min m/z = 99	 rt = 7.738 min m/z = 219	 rt = 11.266 min m/z = 318
8	 rt = 8.884 min m/z = 182	 rt = 12.095 min m/z = 8.884	-
9	 rt = 4.660 min m/z = 126	 rt = 8.666, 8.741 min m/z = 248	-
10	 rt = 9.173 min m/z = 181	 rt = 13.070 min m/z = 303	-
11	 rt = 11.131min m/z 211	 rt = 16.173 min m/z 333	-

[a]rt = retention time, **a** = monosilylated products, **b** = disilylated products.

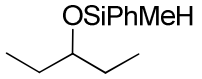
^{1}H and ^{13}C NMR data for the hydrosilylation reactions between acetone and phenylmethylsilane catalysed by 3.



^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ 7.64 (m, Ph), 7.44- 7.42 (m, Ph), 5.1 (q, 1H, -OSiPhMeH), 4.1 (CH), 1.25 - 1.12(6H, CH_3), 0.49 (d, 3H, -OSiPhMeH)

^{13}C NMR data: $^{13}C\{^{1}H\}$ NMR (75.45 MHz, $CDCl_3$, 300K): δ = 137 (s, Ph), 133.8 (s, Ph), 129.9 (s, Ph), 127.9 (s, Ph), 66.8 (s, CH), 25.3 (d, Ph), -2 (s, OSiPhMeH)

^{1}H and ^{13}C NMR data for the hydrosilylation reactions between 3-pentanone and phenylmethylsilane catalysed by 3.



^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ 7.64 (m, Ph), 7.5-7.45 (m, Ph), 5.2 (q, 1H, -OSiPhMeH), 3.6 (pent, 1H, CH), 1.65- 1.55 (m, 4H, CH_2), 1.1- 0.94, (m, CH_3), 0.57 (d, 3H, -OSiPhMeH).

^{13}C NMR data: $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 300K): δ = 136 (s, Ph), 134 (s, Ph), 130 (s, Ph), 128 (s, Ph), 77 (s, CH), 29.4(d, CH_3), 10.03(d, CH_2), -1.92(s, OSiPhMeH).

Table S3. Crystallographic data for **2**, and **3**.

	2	**3**
CCDC	921393	921394
empirical formula	$C_{42}H_{37}MoN_4O_2P_2$, $0.5(Cl_6Zn_2)$, C_7H_8	$2(C_{42}H_{37}MoN_4O_2P_2)$, $2(C_{32}H_{12}BF_{24})$, C_5H_{12}
formula weight ($g \cdot mol^{-1}$)	1051.51	3373.87
temperature (K)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073
crystal system, space group	monoclinic, $P\,2_1/c$	triclinic, P -1
a (Å)	20.0576(4)	12.4979(2)
b (Å)	14.3652(3)	15.4233(3)
c (Å)	17.2290(4)	19.7740(4)

α (deg)	90	88.382(2)
β(deg)	95.415(2)	81.163(2)
γ(deg)	90	87.527(1)
volume ($Å^3$)	4942.06(18)	3761.96(12)
Z, density (calcd) ($Mg·m^{-3}$)	4, 1.413	1, 1.489
abs coefficient (mm^{-1})	1.008	0.325
F(000)	2144	1702
crystal size (mm^3)	0.26 x 0.21 x 0.03	0.38 x 0.32 x 0.23
θ range (deg)	2.48 to 25.68	2.64 to 30.51
reflections collected	36864	66387
reflections unique	9379 / R_{int} = 0.0898	22919 / R_{int} = 0.0268
completeness to θ (%)	99.9	99.9
absorption correction	analytical	analytical
max/min transmission	0.974 and 0.812	0.941 and 0.908
data / restraints / parameters	5081 / 85 / 602	17440 / 184 / 1025
goodness-of-fit on F^2	0.916	1.115
final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0620, 0.0893	0.0480, 0.1423
R_1 and wR_2 indices (all data)	0.1531, 0.1070	0.0637, 0.1478
largest diff. peak and hole ($e·Å^{-3}$)	1.101 and -0.624	1.143 and -0.855

The unweighted R-factor is $R_1 = \sum(Fo - Fc)/\sum Fo$ and the weighted R-factor is $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$