Electronic Supporting Information

Thermally stable Ln(II) and Ca(II) bis(benzhydryl) complexes – excellent pre-catalysts for intermolecular hydrophosphination of C-C multiple bonds

Alexander N. Selikhov,^{a,b} Gleb S. Plankin,^a Anton V. Cherkasov,^a Georgy K. Fukin,^a Andrey S.

Shavyrin,^a Elisa Louyriac,^c Laurent Maron,^c Alexander A. Trifonov^{*,b,a}

^a G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603137, 49 Tropinina str., Nizhny Novgorod, Russia GSP-445, Fax: + 007-831-462-74-97 E-mail: trif@iomc.ras.ru.
^b A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 28 Vavilova str., 119991, Moscow, GSP-1, Russia
^cLaboratoire de Physique et Chimie des Nanoobjets, LPCNO, CNRS & INSA, Université Paul Sabatier, 135 Avenue de Rangueil, 31077 Toulouse, France

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Synthesis of (1,2-diphenylethyl)(phenyl)phosphane :



(1,2-diphenylethyl)(phenyl)phosphane

Trans-stylbene (0.07g, 0.38 mmol), PhPH₂ (0.042g, 0.38 mmol), complex **3** (0.013 g, 1.5 μmol %) were loaded in a NMR tube in the glovebox and the reaction mixture was heated at 90 °C during 100 h. After the desired reaction time, the NMR tube was opened in the glovebox and C₆D₆ was added. ¹H NMR (400 MHz, C₆D₆, 293 K): δ 2.97-3.12 (compl m, 4 H, two -CH₂- of both disastereomers), 3.35-3.46 (compl m, 2 H, two -CH- of both diastereomers), 4.25 (dd, $J_{PH} = 210$ Hz, ${}^{3}J_{HH} = 5.7$ Hz, 1 H, PH), 4.36 (dd, $J_{PH} = 206$ Hz, ${}^{3}J_{HH} = 5.5$ Hz, 1 H, PH), 6.90-7.33 (compl m, 30 H, C₆H₅ of both diastereomers). ¹³C{¹H} NMR (100 MHz, C₆D₆, 293 K): δ 40.0 (d, $J_{CP} = 21.1$ Hz, CH₂), 41.2 (d, $J_{CP} = 14.0$ Hz, CH₂), 45.2 (d, $J_{CP} = 13.8$ Hz, CH), 45.6 (d, $J_{CP} = 13.6$ Hz, CH), 126.2 (s), 126.4 (d, $J_{CP} = 12.0$ Hz), 126.5 (d, $J_{CP} = 2.2$ Hz), 127.0 (s), 128.2 (d, $J_{CP} = 4.9$ Hz), 128.4 (s), 128.5 (s), 128.6 (d, $J_{CP} = 3.4$ Hz), 128.7 (s), 128.8 (d, $J_{CP} = 5.9$ Hz), 128.9 (s), 129.1 (d, $J_{CP} = 6.8$ Hz), 129.2 (d, $J_{CP} = 2.5$ Hz), 134.7 (s), 134.8 (d, $J_{CP} = -9.9$ Hz), 140.6 (d, $J_{CP} = 3.3$ Hz), 142.0 (s), 142.4 (d, $J_{CP} = 7.3$ Hz), 143.0 (d, $J_{CP} = 2.2$ Hz). ³¹P {¹H} NMR (162 MHz, C₆D₆, 293 K) δ -30.3 (s, PH), -25.6 (s, PH).

	1	2	3	4
Empirical	C ₅₀ H ₇₄ O ₄ Sm,	C48H70N2Sm	C48H70N2Yb	C48H70N2Ca
formula	$^{1}/_{2}C_{6}H_{14}$			
Formula Weight	932.52	825.41	848.10	715.14
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_{1}/c$	<i>C2/c</i>	<i>C2/c</i>	C2/c
<i>a</i> , Å	17.1749(6)	34.5518(11)	34.8610(9)	34.9207(7)
b, Å	17.3174(3)	15.6134(5)	15.6061(4)	15.6370(2)
<i>c</i> , Å	18.1145(4)	17.6080(5)	17.5569(5)	17.5764(3)
α, °	90	90	90	90
β , °	112.148(3)	113.9620(10)	115.0220(10)	115.231(2)
γ, °	90	90	90	90
<i>V</i> , Å ³	4990.2(2)	8680.3(5)	8655.3(4)	8682.0(3)
Ζ	4	8	8	8
d_{calc} , Mg/m ³	1.241	1.263	1.302	1.094
μ , mm ⁻¹	1.218	1.386	2.194	0.177
F^{000}	1972	3472	3536	3136
Crystal Size,	0.80 imes 0.60 imes	$0.34 \times 0.20 \times$	0.30 imes 0.10 imes	0.41 × 0.35 ×
mm	0.03	0.14	0.10	0.23
θ Range for Data	3.03-26.02	2.25–28.72	2.23–28.73	2.91-28.69
Collection, °				
Index Ranges	$-21 \le h \le 21$	$-46 \le h \le 46$	$-34 \le h \le 47$	$-47 \le h \le 47$
	$-21 \le k \le 21$	$-21 \le k \le 21$	$-21 \le k \le 21$	$-21 \le k \le 21$
	$-22 \le l \le 22$	$-23 \le l \le 23$	$-23 \le l \le 21$	$-23 \le l \le 22$
Reflns Collected	79943	47818	37360	24439

Table S1. Crystal Data and Structure Refinement Details for Complexes 1–4

Independent	9814 (0.0647)	11228 (0.0349)	11198 (0.0176)	11200 (0.0261)
Reflns (R _{int})				
Completeness to	99.8	99.9	99.7	99.7
θ, %				
Data / Restraints	9814 / 34 / 596	11228 / 12 / 528	11198 / 0 / 516	11200 / 0 / 516
/ Parameters				
$S(F^2)$	1.064	1.018	1.054	1.026
Final <i>R</i> Indices	$R_1 = 0.0356$	$R_1 = 0.0228$	$R_1 = 0.0181$	$R_1 = 0.0420$
(<i>I</i> >2σ(<i>I</i>))	$wR_2 = 0.0890$	$wR_2 = 0.0490$	$wR_2 = 0.0426$	$wR_2=0.1010$
R Indices (all	$R_1 = 0.0463$	$R_1 = 0.0326$	$R_1 = 0.0213$	$R_1 = 0.0582$
data)	$wR_2 = 0.0973$	$wR_2=0.0524$	$wR_2 = 0.0443$	$wR_2 = 0.1097$
Largest Diff.	1.23 / -1.00	0.66 / -0.46	0.48 / -0.91	0.38 / -0.26
Peak and Hole,				
e/Å ³				

Electronic energies (a.u.) and optimized geometries:

Complex 1

-			
E:	-2278.976	346	
С	6.708692	9.904737	10.534084
С	7.816164	9.177301	11.067962
С	7.556041	8.563589	12.330326
С	6.319219	8.648002	12.952736
С	5.228501	9.355763	12.409313
С	5.469174	9.970889	11.174363
С	9.047769	9.127671	10.325345
С	10.265759	8.403327	10.623162
С	11.121554	8.021331	9.552644
С	12.310669	7.336982	9.748801
С	12.762465	6.963349	11.030105
С	11.940383	7.347009	12.094880
С	10.744148	8.045585	11.908733
С	14.058433	6.162295	11.198558
С	3.872291	9.367069	13.123817
Sm	9.208220	11.896151	10.738044
0	10.026995	14.539082	11.509680
С	11.360376	15.013639	11.630940
С	8.948341	13.284137	8.326095
С	7.730142	12.674097	7.834505
С	6.484980	13.299221	8.133465
С	5.267865	12.805392	7.691661
С	5.170611	11.636577	6.912072
С	6.384844	11.012682	6.608031
С	7.617532	11.499904	7.047798
С	3.808665	11.140500	6.414239
0	9.537825	11.423590	13.451765
С	10.799337	11.818722	13.966735
С	11 880/36	11 268763	13 079131
	11.009430	11.200705	15.077151
0	11.722347	11.757029	11.754164

O 7.415978 13.655172 11.984675

С	7.696170	15.028287	11.743684
С	9.097584	15.354401	12.198797
С	10.315714	12.980783	7.987076
С	10.832867	11.702803	7.622263
С	12.169964	11.514407	7.273475
С	13.115446	12.548879	7.292448
С	12.635698	13.798767	7.726918
С	11.304784	14.004498	8.065808
С	14.555893	12.305304	6.825438
С	15.425060	13.565801	6.943392
С	15.211383	11.193627	7.669093
С	14.543416	11.869248	5.345258
С	8.484057	11.517755	14.400846
С	6.014041	13.387378	12.003489
Н	8.808344	14.324162	8.629060
Н	10.180181	10.837588	7.584892
Н	12.472815	10.512528	6.975896
Н	13.307804	14.651028	7.778594
Н	10.984399	15.006467	8.346765
Η	15.274114	11.487780	8.722832
Н	14.648013	10.256883	7.616104
Η	15.564424	11.691192	4.984929
Η	14.087474	12.641599	4.716492
Η	13.971845	10.946365	5.204108
Н	15.490394	13.920667	7.978439
Η	15.042476	14.384366	6.323799
Н	6.498154	14.232213	8.696593
Η	4.366488	13.359493	7.948316
Н	6.395354	10.115797	5.995502
Η	8.506861	10.976505	6.718753
Н	8.897867	9.291368	9.253898
Н	10.815613	8.260011	8.535632
Η	12.895551	7.069776	8.870573
Н	12.222679	7.098634	13.114844
Н	10.182824	8.326420	12.793120

Н	8.315200	7.944270	12.792347	Η	3.063957	9.931113	15.074281
Η	6.194778	8.112596	13.892929	Η	4.737415	9.361422	15.143588
Н	4.674343	10.507361	10.663698	Η	4.382033	10.978236	14.514560
Η	6.788686	10.335826	9.534173	С	14.374333	5.872302	12.672760
Н	7.588491	11.109846	13.929813	С	13.927528	4.811574	10.464045
Η	8.311813	12.560384	14.699306	С	15.245102	6.945334	10.600999
Η	11.858439	10.171334	13.070003	Η	15.307776	5.302819	12.746286
Η	13.739478	11.603763	11.275694	Η	14.503267	6.794965	13.250270
Н	12.600739	11.744038	9.906576	Η	13.586243	5.277863	13.148069
Н	12.728027	10.198329	10.796408	Η	14.847203	4.222751	10.570806
Η	5.533947	13.954266	12.812397	Η	13.096312	4.226557	10.872219
Н	5.889257	12.317897	12.175464	Η	13.741684	4.950898	9.394298
Н	5.552576	13.647798	11.043717	Η	16.173403	6.367330	10.690277
Н	6.993971	15.657776	12.310050	Η	15.091383	7.165662	9.539933
Η	7.577192	15.250843	10.674248	Η	15.386587	7.898791	11.122447
Н	9.290533	16.416866	11.983925	С	3.927737	9.847523	5.594642
Η	9.196486	15.203069	13.285514	С	2.878376	10.862868	7.612378
Η	11.450155	16.018048	11.195894	С	3.164039	12.218340	5.517527
Н	12.001430	14.323337	11.085005	Η	1.893367	10.525929	7.266006
Н	11.671916	15.050037	12.684735	Η	3.297655	10.083683	8.257969
Η	8.717978	10.916402	15.289219	Η	2.726649	11.759913	8.222095
Н	10.939382	11.410363	14.978629	Η	2.933067	9.523975	5.267358
Н	10.852949	12.916465	14.030335	Η	4.539910	9.990879	4.697457
Н	12.865929	11.592149	13.472251	Η	4.365524	9.032916	6.182046
Н	16.229517	10.990192	7.314769	Η	2.187838	11.879773	5.148219
Н	16.443651	13.344961	6.604739	Η	3.008226	13.156092	6.061091
С	2.831434	10.214762	12.378977	Η	3.800547	12.436634	4.653237
С	3.331343	7.925181	13.223345				
С	4.025975	9.941766	14.547050	Sm-	CH-diph-2,7	<i>t</i> Bu (compl	ex 2)
Н	2.360156	7.909686	13.733896				
Η	3.202179	7.490721	12.226419	E:	-2009.09760	00	
Η	4.013554	7.276539	13.782273	С	6.529742	5.831463	6.222697
Н	1.884750	10.209570	12.930962	С	6.472397	5.424568	7.589991
Н	3.150259	11.258860	12.279883	С	6.990446	6.389228	8.504408
Н	2.630163	9.824636	11.375791	С	7.440877	7.644612	8.083718

С	7.447142	8.041430	6.743399	С	6.773641	2.400840	4.235189
С	6.984314	7.078873	5.824601	С	5.982678	1.305226	4.594052
С	6.031664	4.093169	7.899377	С	6.536257	0.442875	5.560751
С	5.674263	3.484835	9.152985	С	7.778749	0.671853	6.129811
С	5.295194	2.104855	9.146616	С	14.026759	6.098771	6.134151
С	4.883965	1.436168	10.286180	С	15.057125	5.623126	5.088422
С	4.835164	2.057075	11.553037	С	4.610398	1.008301	3.979580
С	5.237046	3.395140	11.582713	С	4.649365	-0.360440	3.268789
С	5.652984	4.089504	10.440583	С	13.514480	7.480435	5.704458
С	4.310192	1.295969	12.775403	С	14.730377	6.253059	7.497854
С	2.834878	0.909730	12.538313	С	4.196335	2.069180	2.949636
С	7.890596	9.453310	6.342358	С	3.537837	0.972039	5.087122
С	7.894128	9.647938	4.818964	Н	10.286490	1.009847	6.814962
С	5.132553	0.010754	13.000557	Н	12.484611	1.744871	6.952924
С	4.383715	2.135869	14.058522	Н	14.191107	3.456670	6.892565
С	6.922455	10.486293	6.956475	Н	11.270115	6.334262	5.603506
С	9.315894	9.731439	6.860314	Н	9.571167	4.656422	5.620849
Sm	8.667657	3.554053	8.295385	Н	13.044141	7.450160	4.715674
Ν	9.587072	1.779730	10.317596	Н	12.787996	7.885576	6.417722
С	8.469648	1.577973	11.248611	Н	14.351859	8.184937	5.649635
С	10.736504	2.414707	10.980425	Н	15.140501	5.302218	7.853618
С	10.480155	3.836239	11.461014	Н	15.560651	6.965910	7.424357
Ν	10.193776	4.801897	10.389127	Н	14.033048	6.624099	8.257441
С	11.413314	5.142360	9.643945	Н	14.589577	5.514981	4.103865
С	9.640586	6.025006	10.981757	Н	15.879498	6.343860	5.000007
С	10.006597	0.477890	9.787527	Н	15.489748	4.654362	5.358831
С	10.839410	2.999612	6.302077	Н	8.601338	3.480458	4.415103
С	12.200292	2.759171	6.676335	Н	6.425594	3.095721	3.476168
С	13.172566	3.739223	6.632134	Н	5.985041	-0.440887	5.876001
С	12.895982	5.069357	6.236818	Н	8.165912	-0.046446	6.851747
С	11.565627	5.336767	5.916066	Н	4.898315	2.118053	2.109760
С	10.562147	4.356093	5.952569	Н	3.210221	1.821597	2.541246
С	9.882573	1.939490	6.414988	Н	4.126585	3.066261	3.398293
С	8.593279	1.785560	5.773938	Н	5.757723	3.501413	7.025730
С	8.027539	2.645304	4.800910	Н	5.287882	1.580038	8.193117

Η	4.575312	0.397383	10.182220]	Η	9.176228	0.010011	9.252394
Η	5.207863	3.949081	12.517230	J	Η	10.836883	0.607399	9.089246
Η	5.851154	5.148973	10.550974]	H	8.780257	0.993072	12.131816
Η	5.104491	-0.650159	12.128053]	H	8.050971	2.529106	11.584069
Η	6.181868	0.248243	13.208874]	H	7.662309	1.044033	10.742369
Η	4.737999	-0.552943	13.854787]	H	2.552810	0.747739	4.659746
Η	3.769437	3.040235	13.989897]	H	3.755774	0.204610	5.837180
Η	4.011590	1.550000	14.906438]	H	3.473329	1.935766	5.603497
Η	5.412056	2.436947	14.289541]	H	3.673461	-0.589843	2.823517
Η	2.722575	0.273986	11.654049]	H	5.399573	-0.363934	2.470593
Η	2.435506	0.360321	13.399915]	H	4.897204	-1.170308	3.962651
Η	2.219225	1.802594	12.385452]	H	11.050468	1.815100	11.855176
Η	6.981732	6.196909	9.570492					
Η	7.775272	8.341125	8.851158	У	'b-	CH-diph-2,7	- <i>t</i> Bu (compl	ex 3)
Η	6.964328	7.307084	4.762805					
Η	6.168914	5.136103	5.468826	E	E: -2	2013.182213		
Η	6.909937	10.424644	8.049723	(С	20.621552	8.818783	-1.352277
Η	7.218028	11.506239	6.680510	(С	21.674097	7.889967	-1.545950
Η	5.899465	10.318788	6.602770	(С	21.309345	6.533038	-1.335799
Η	10.031417	9.019278	6.435420	(С	20.023465	6.160835	-0.950850
Η	9.636452	10.742760	6.581405	(С	18.993224	7.092937	-0.753678
Η	9.374988	9.656812	7.951156	(С	19.338322	8.435692	-0.976859
Η	8.570019	8.944231	4.320166	(С	22.971038	8.350172	-2.005054
Η	6.893850	9.524850	4.389849	(С	24.254589	7.716466	-1.787631
Η	8.233048	10.661431	4.576957	(С	25.413901	8.221252	-2.451826
Η	10.342513	6.481208	11.701167	(С	26.671906	7.636477	-2.322831
Η	9.429592	6.752749	10.195149	(С	26.891231	6.504041	-1.522357
Η	8.705953	5.799384	11.503091	(С	25.764127	6.015710	-0.840501
Η	12.184034	5.573810	10.305525	(С	24.499596	6.582593	-0.968461
Η	11.836497	4.266438	9.145283	Y	ľb	23.362180	7.987389	-4.613097
Η	11.178943	5.873801	8.866250	I	N	23.999360	5.462552	-5.253660
Η	11.359981	4.162802	12.045064	(С	24.297879	4.763084	-3.994744
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С	29.762933	10.323687	-5.659776	Н	26.047626	8.255707	-7.722489
С	22.878360	10.372790	-6.200905	Н	23.035710	9.437239	-2.112523
С	21.744187	10.542204	-7.051056	Н	25.351117	9.158214	-3.013562
С	20.604506	11.217805	-6.652738	Н	27.499532	8.101250	-2.853845
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Η	17.851050	11.269622	-6.140215	Н	21.454000	5.097685	-4.296706
Η	17.052929	12.206281	-4.870233	Н	22.907374	5.089802	-6.997658

Η	25.468536	4.394329	-6.382833	E: -	2657.767746	5	
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Н	24.997039	5.985912	-7.038216	C	7.846579	6.894684	8.483882
Н	24.575054	3.711712	-4.180095	С	7.842922	7.275783	9.850586
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Η	16.725802	5.618811	1.427282	С	2.256349	1.668397	8.840387
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С	30.122707	11.775877	-6.036825	С	2.442482	2.532913	11.169410
С	30.116252	10.088052	-4.177608	С	8.211658	11.581542	10.548078
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Η	29.885251	11.975197	-7.087336	Ca	8.954346	3.571937	8.309015
Η	29.573095	12.500570	-5.427772	Ν	8.911691	2.634385	10.715825
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Η	31.688935	9.580830	-6.316778	Ν	11.031483	4.469515	9.532571
Η	30.440510	8.330246	-6.277693	С	12.240939	3.680795	9.256445
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Η	21.806501	10.163666	-8.070053	C	10.336511	2.732735	6.022871
				C	11.742093	2.914325	5.866171
Ca-	CH-diph-2,7-	tBu (comple	ex 4)	С	12.285777	3.984550	5.177336

Ca-CH-diph-2,7-*t*Bu (complex 4)

C 11.488795 4.988498 4.584818

С	10.110943	4.838224	4.740704	Н	4.963645	-1.395750	3.560502
С	9.547274	3.760085	5.437162	Н	3.651153	-2.290847	4.333325
С	9.822647	1.639482	6.826124	Н	3.945144	-0.604472	4.780054
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С	7.722214	1.045663	5.477799	Н	6.656566	3.174463	7.029306
С	6.674935	0.161262	5.207802	Н	5.054324	1.641142	7.923370
С	6.485510	-1.023536	5.926638	Н	3.867178	4.572787	10.838957
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С	12.137884	6.131420	3.796782	Н	4.573642	0.816602	11.289710
С	12.915804	5.548680	2.598420	Н	3.131586	-0.072699	10.765635
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Η	10.621140	1.060093	7.297241	Н	7.456432	6.591967	10.601385
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Η	13.600647	7.714288	4.142778	Н	10.109909	10.008465	11.825884
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Η	7.831492	1.909650	4.830595	Н	11.516843	5.922455	8.086626
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Η	7.350970	-2.187855	7.533445	Н	13.080044	4.000384	9.897030
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Η	9.890292	5.149058	11.142251
Η	10.930061	2.263809	11.132511
Η	8.754590	0.731489	11.680564
Η	7.839849	0.908126	10.161556
Η	9.599972	0.735105	10.107112
Η	7.711201	2.820488	12.466529
Η	7.835625	4.295144	11.474804
Η	6.833486	2.956267	10.917034
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Η	5.141485	-2.694861	7.700305
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Η	6.623963	-3.206913	4.251422
Η	6.666459	-3.790134	5.920417
Η	10.058093	2.992096	12.473428



Figure S1. ¹H NMR spectrum of $\{[Ph(p-tBu)]_2CH\}_2Sm(DME)_2$ (1). (400 MHz, THF-*d*₈, 293 K).



Figure S2. ${}^{13}C{}^{1}H$ NMR spectrum of {[Ph(*p*-*t*Bu)]₂CH}₂Sm(DME)₂ (1). (400 MHz, THF-*d*₈, 293 K).



Figure S3. ¹H NMR spectrum of {[Ph(*p*-*t*Bu)]₂CH}₂Sm(TMEDA) (**2**). (200 MHz, C₆D₆, 293 K).



Figure S4. ¹H NMR spectrum of $\{[Ph(p-tBu)]_2CH\}_2Yb(TMEDA)$ (3). (400 MHz, C₆D₆, 293 K).



Figure S5. ${}^{13}C{}^{1}H$ NMR spectrum of {[Ph(*p*-*t*Bu)]₂CH}₂Yb(TMEDA) (**3**). (400 MHz, C₆D₆, 293 K).



Figure S6. ¹⁷¹Yb-¹H 2D *ge*-HMBC NMR spectrum of {[Ph(*p*-*t*Bu)]₂CH}₂Yb(TMEDA) (**3**). (400 MHz, C₆D₆, 293 K).



Figure S7. ¹H NMR spectrum of $\{[Ph(p-tBu)]_2CH\}_2Ca(TMEDA)$ (4). (400 MHz, C₆D₆, 293 K).



Figure S8. ${}^{13}C{}^{1}H$ NMR spectrum of {[Ph(*p*-*t*Bu)]₂CH}₂Ca(TMEDA) (**4**). (400 MHz, C₆D₆, 293 K).



Figure S9. ¹H NMR spectrum of [Ph(*p*-*t*Bu)]₂CHMe (200 MHz, CDCl₃, 293 K).



Figure S10. ¹³C{¹H} NMR spectrum of [Ph(*p*-*t*Bu)]₂CHMe (50 MHz, CDCl₃, 293 K).



Figure S11. ¹H NMR spectrum of **6**. (400 MHz, C₆D₆, 293 K).



Figure S12. ¹³C{¹H} NMR spectrum of **6**. (100 MHz, C₆D₆, 293 K).



Figure S13. ³¹P{¹H} NMR spectrum of **6**. (162 MHz, C₆D₆, 293 K).



Figure S14. ³¹P-¹H 2D *ge*-HSQC NMR spectrum of **6**. (100 MHz, C₆D₆, 293 K).



Number of detected peaks: 2

Apex RT	Start RT	End RT Area	%Area	
24.93	24.87	25.00	29116532.494	55.69
25.13	25.06	25.23	23168910.019	44.31

Figure S15. Thermal decomposition GC/MS spectrum of complex 1.





Figure S16. IR (KBr) spectrum of complex {[Ph(*p*-*t*Bu)]₂CH}₂Sm(DME)₂(1).

Figure S17. IR (KBr) spectrum of complex {[Ph(*p*-*t*Bu)]₂CH}₂Sm(TMEDA) (2).



Figure S18. IR (KBr) spectrum of complex {[Ph(*p*-*t*Bu)]₂CH}₂Yb(TMEDA) (3).



Figure S19. IR (KBr) spectrum of complex {[Ph(*p-t*Bu)]₂CH}₂Ca(TMEDA) (4).



Figure S20. . IR (KBr) spectrum of [Ph(*p*-*t*Bu)]₂CHMe.