Electronic Supplementary Information (ESI)

Ln(II) amido complexes coordinated by ring-expanded N-heterocyclic carbenes – promising catalysts for olefin hydrophosphination

Ivan V. Lapshin,[a] Anton V. Cherkasov,[a] Andrey F. Asachenko[b] and Alexander A. Trifonov*[a,b]

[a.] Institute of Organometallic Chemistry of Russian Academy of Sciences, 49 Tropinina str., GSP-445, 630950, Nizhny Novgorod, Russia. E-mail: trif@iomc.ras.ru

[b.] Institute of Organoelement Compounds of Russian Academy of Sciences, 28 Vavilova str., 119334 , Moscow, Russia.

Experimental Procedures

General considerations.

All manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox with rigorous exclusion of traces of moisture and air. All solvents (hexane, THF, diethyl ether, benzene-d_6) were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_2M(THF)_2$ (M = Yb,[1] Sm[2]) and N-heterocyclic carbene (1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-*2*-ylidene (er-NHC),[3] were prepared according to literature procedures. Olefinic substrates (styrene, 1-hexene, 1-heptene, 1-octene, 1-nonene, cyclohexene, norbornene) were purchased from Aldrich and vacuum-distilled over CaH_2 and then were degassed by freeze-pump-thaw methods. Diphenylphosphine, phenylphosphine were donated by Synor Ltd and were vacuum distilled over CaH_2 and then were degassed by freeze-pump-thaw methods. NMR spectra were recorded on a Bruker DPX 200 or Bruker Avance DRX 400 spectrometers. Chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents ($CDCl_3$, C_6D_6) for proton and carbon chemical shifts and to an external 85% H_3PO_4 (δ 0.0) standard for phosphorus chemical shifts. J values are reported in Hz. Lanthanide metal analysis was carried out by complexometric titration.[4] Elemental analysis was performed in the microanalytical laboratory of IOMC.

Synthesis of (er-NHC)Sm[N(SiMe$_3$)$_2$]$_2$ (1). A solution of **er-NHC** (0.320 g, 1.000 mmol) in toluene (10 mL) was added to a solution of $Sm[N(SiMe_3)_2]_2(THF)_2$ (0.615 g, 1.000 mmol) in toluene (10 mL). The reaction mixture was stirred for 30 minutes at room temperature. The volatiles were then removed under reduced pressure and the solid residue was redissolved in toluene. The solution was concentrated and stored at –30 °C for 24 h. The mother liquor was decanted and the obtained crystals were washed with cold toluene and dried in vacuum for 10 min. Complex **1** was isolated in 78 % (0.617 g). IR (Nujol, KBr, ν/cm^{-1}): 475(w), 500(w), 517(m), 529(w), 584(s), 606(m), 661(s), 683(w), 747(w), 759(w), 822(s), 859(w), 870(m), 884(m), 932(w), 972(w), 985(m), 1050(s), 1102(w), 1199(s), 1240(s), 1298(s), 1608(m), 1656(w). Elem. anal. calc. for $C_{34}H_{64}N_4Si_4Sm$ (791.60 g/mol): C 51.59; H 8.15; N 7.08; Sm 18.99. Found: C 51.23; H 8.00; N 7.22; Sm 18.75

Synthesis of (er-NHC)Yb[N(SiMe$_3$)$_2$]$_2$ (2). Protocol similar to that for the preparation of **1** was used: $Yb[N(SiMe_3)_2]_2(THF)_2$ (0.638 g, 1.000 mmol) and **er-NHC** (0.320 g, 1.000 mmol) in toluene (10 mL). Storage of the reaction mixture at –30 °C resulted in the formation of dark red crystals. Yield: 81 % yield (0.660 g). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.23 (s, 36H, Si(CH_3)$_3$), 1.31 (p, $^3J_{HH}$ = 6.1 Hz, 2H, CH_2), 2.14 (s, 6H, para-CH_3), 2.18 (s, 12H, ortho-CH_3), 2.35 (t, $^3J_{HH}$ = 5.9 Hz, 4H, CH_2-N), 6.87 (s, 4H, meta-H, Ar). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 6.0 (Si(CH_3)$_3$), 18.8 (ortho-CH_3, Mes), 20.5 (-CH_2-), 20.9 (para-CH_3, Mes), 44.2 (CH_2-N), 131.3 (para-C, Ar), 135.2 (meta-C, Ar), 138.7 (ortho-C, Ar), 141.4 (ipso-C, Ar). IR (Nujol, KBr, ν/cm^{-1}): 479(w), 500(w), 517(m), 532(w), 589(s), 608(m), 662(s), 689(w), 748(w), 765(w), 826(s), 859(w), 870(m), 885(m), 933(w), 972(w), 988(m), 1035(s), 1102(w), 1200(s), 1239(s), 1296(s), 1608(m), 1656(w). Elem. anal. calc. for $C_{34}H_{64}N_4Si_4Yb$ (814.29g/mol): C 50.15; H 7.92; N 6.88; Yb 21.25. Found: C 49.88; H 7.64; N 6.57; Yb 21.41

Typical hydrophosphinationation experiments: In a typical reaction with neat substrates, the catalyst (10 μmol) was loaded into the NMR tube, and then alkene (0.20*X mmol, X = 1-4) and phosphine (0.20 mmol)) were added. The NMR tube was sealed and shaken vigorously, and the reaction time was started after quick placing the NMR tube into a preheated oil bath at the desired temperature. After certain reaction time, the NMR tube was removed from the oil bath, chloroform-d (0.5 mL) was added under Ar to prevent oxidation of air-sensitive alkylphospine products. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the reaction mixture were recorded. Spectroscopic data are consistent to those reported in the literature for known products.

Spectroscopic data for the hydrophosphination products.

The data for phenethyl(phenyl)phosphine,[5] diphenethyl(phenyl)phosphine,[5] phenethyldiphenylphosphine,[6] hexyl(phenyl)phosphine,[7] heptyl(phenyl)phosphine[8], octyl(phenyl)phosphine,[8] hexyldiphenylphosphine,[9] heptyldiphenylphosphane,[9] octyldiphenylphosphine,[10] cyclohexyl(phenyl)phosphine,[11] cyclohexyldiphenylphosphine,[12] 2-

phenylphosphinonorbornane,[13] 2-diphenylphosphinonorbornane[14] are already reported. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{1H\}$ NMR spectra of two previously uncharacterized n-Nonyl(phenyl)phosphine and n-Nonyldiphenylphosphine are shown in Figures S5-S8.

n-Nonyl(phenyl)phosphine ($CH_3(CH2)_8PHPh$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.20 – 1.38 (m, 12H), 1.40 – 1.56 (m, 2H, CH_2CH_2P), 1.66 – 1.80 (m, 2H, CH_2P), 4.12 (dt, J=209.1, 6.9, 1H), 7.24 – 7.33 (m, 3H, Ph), 7.43 – 7.53 (m, 2H) (m, 2H, Ph). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 14.1 (s, CH_3), 22.7 (s, CH_2CH_3), 23.4 (d, J_{CP} = 10.5 Hz, CH_2P), 28.30 (d, J = 8.0 Hz, $CH_2CH_2CH_2P$), 29.2 (s, CH_2), 29.3 (s, CH_2), 29.4 (s, CH_2), 31.9 (s, CH_2), 35.40 (d, J_{CP} =14.8 Hz, CH_2CH_2P), 128.2(s, meta-C), 128.4(s, para-C), 134.5 (d, $^{2}J_{CP}$ = 15.0 Hz, ortho-C), 134.9 (d, $^{1}J_{CP}$ = 15.4 Hz, ipso-C). $^{31}P\{^{1}H\}$ NMR(162 MHz, $CDCl_3$): δ = -52.0 (s, P, PH).

n-Nonyldiphenylphosphine ($CH_3(CH2)_8PPh_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.90 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.20 – 1.28 (m, 10H, CH_2), 1.38 – 1.46 (m, 4H, $CH_2CH_2CH_2P$), 2.04 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, PCH_2), 7.27–7.33 (m, 6H, Ph), 7.37–7.45 (m, 4H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 14.1 (s, CH_3), 22.6(s, CH_2CH_3), 25.9 (d, $^{2}J_{CP}$ = 16.0 Hz, CH_2CH_2P), 28.1 (d, $^{1}J_{CP}$ = 11.5 Hz), 29.1 (s, CH_2), 29.2 (s, CH_2), 29.4 (s, CH_2), 31.2 (d, $^{3}J_{CP}$ = 12.8 Hz, $CH_2CH_2CH_2P$), 31.8(s, CH_2), 128.2 (d, $^{3}J_{CP}$ = 6.8 Hz, meta-C), 128.4(s, para-C), 132.6 (d, $^{2}J_{CP}$ = 18.4 Hz, ortho-C), 139.1 (d, $^{1}J_{CP}$ = 13.6 Hz, ipso-C). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = -16.1 (s, P).

X-ray crystallography. The X-ray data for **1** and **2** were collected with *Rigaku OD Xcalibur* (**1**) and *Bruker D8 Quest* (**2**) diffractometers ($Mo_{K\alpha}$-radiation, *ω*-scans technique, λ = 0.71073 Å, T = 100(2) K) using *APEX3*[15] and *CrysAlis*^{Pro} [16] software packages. The structures were solved by direct methods and were refined by full-matrix least squares on F^2 for all data using *SHELX* [17]. *SADABS*[18] and scaling algorithms implemented in *CrysAlis*^{Pro} were used to perform absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined isotropically in the "riding" model with $U(H)_{iso}$ = 1.2U_{eq} of their parent atoms ($U(H)_{iso}$ = 1.5U_{eq} for methyl groups).

The crystallographic data and structures refinement details are given in Table S1. CCDC-2021948 (**1**) and 2021947 (**2**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures. The corresponding CIF files are also available in the Supporting Information.

Table S1. Crystal data and structure refinement details for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{34}H_{64}N_4Si_4Sm$	$C_{34}H_{64}N_4Si_4Yb$
Formula weight	791.60	814.29
T, K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 15.5699(3) Å b = 11.4700(2) Å c = 23.5397(5) Å α = 90° β = 94.580(2)° γ = 90°	a = 15.5992(7) Å b = 11.4432(5) Å c = 23.1873(9) Å α = 90° β = 94.693(2)° γ = 90°
V, Å^3	4190.45(14)	4125.2(3)
Z	4	4
d_{calc}, g/cm^3	1.255	1.311
μ, mm^{-1}	1.542	2.410
F_{000}	1656	1688
Crystal size, mm	0.83 x 0.15 x 0.13	0.46 x 0.43 x 0.15
ϑ Range for data collection, deg	3.152 – 27.87	2.42 – 27.88
HKL indices	-19 ≤ h ≤ 20, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30	-20 ≤ h ≤ 20, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30
Reflns collected	67548	50815

Independent reflns (R_{int})	9885 (0.0749)	9840 (0.0538)
Completeness to ϑ, %	98.8	99.9
Data / Restraints / Parameters	9885 / 0 / 406	9840 / 48 / 439
$S(F^2)$	1.073	1.017
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0429$, $wR_2 = 0.0828$	$R_1 = 0.0276$, $wR_2 = 0.0650$
R indices (all data)	$R_1 = 0.0634$ $wR_2 = 0.0891$	$R_1 = 0.0336$, $wR_2 = 0.0678$
Largest diff peak and hole, e/Å^3	1.44 / -0.76	1.63 / -1.60

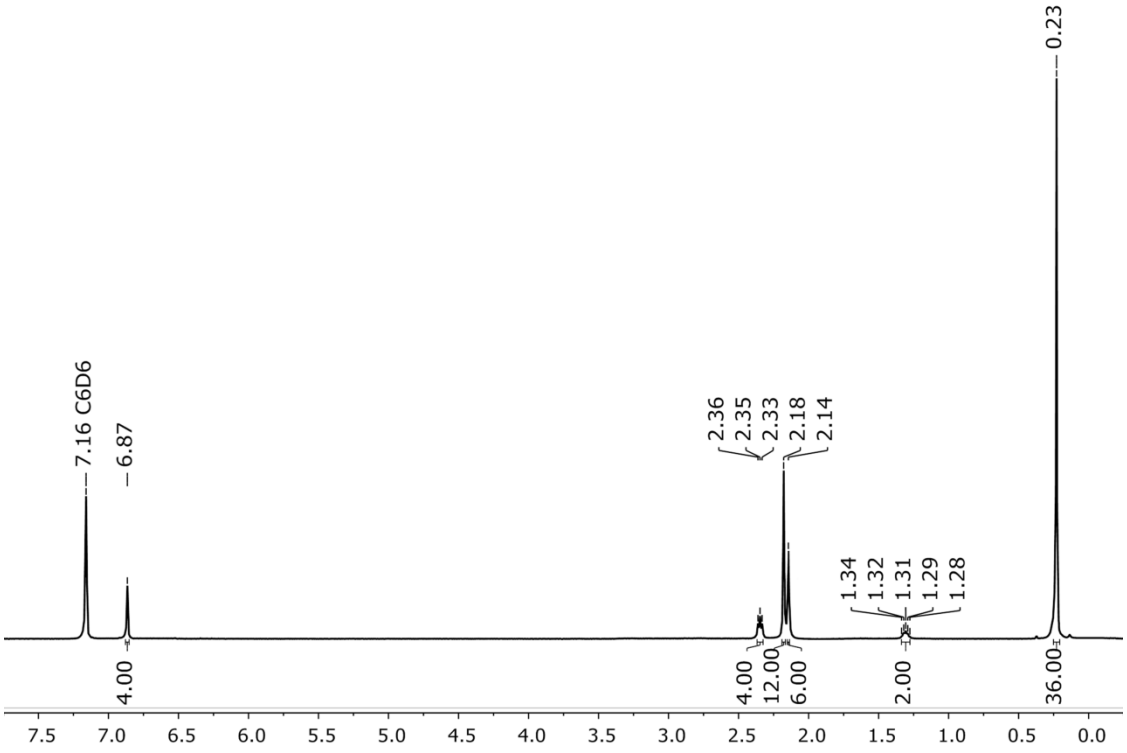


Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6) of **2**.

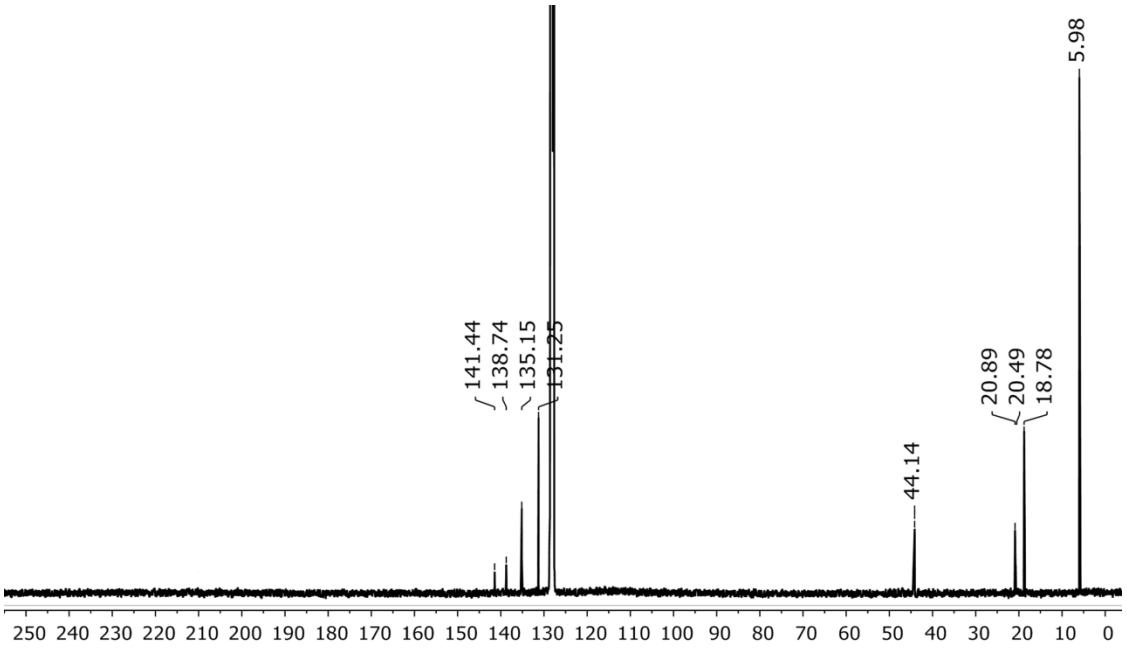


Figure S2. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **2**.

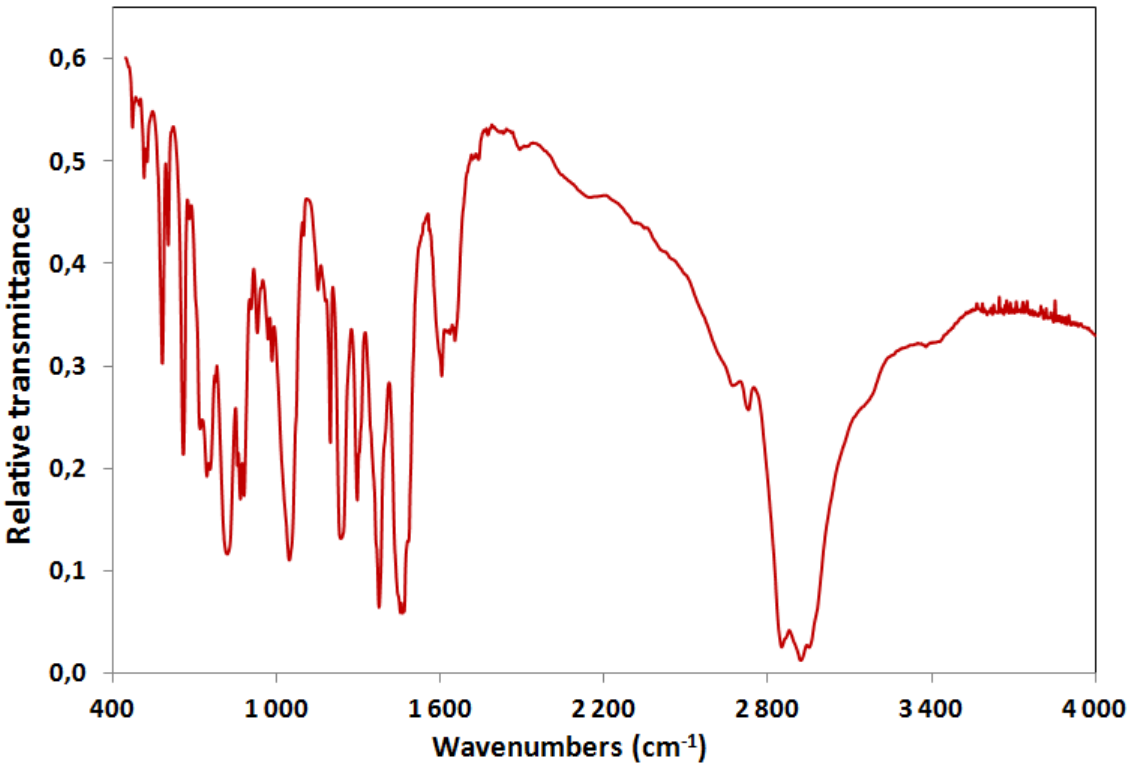


Figure S3. IR spectrum (Nujol, KBr, ν/cm^{-1}) of **1**.

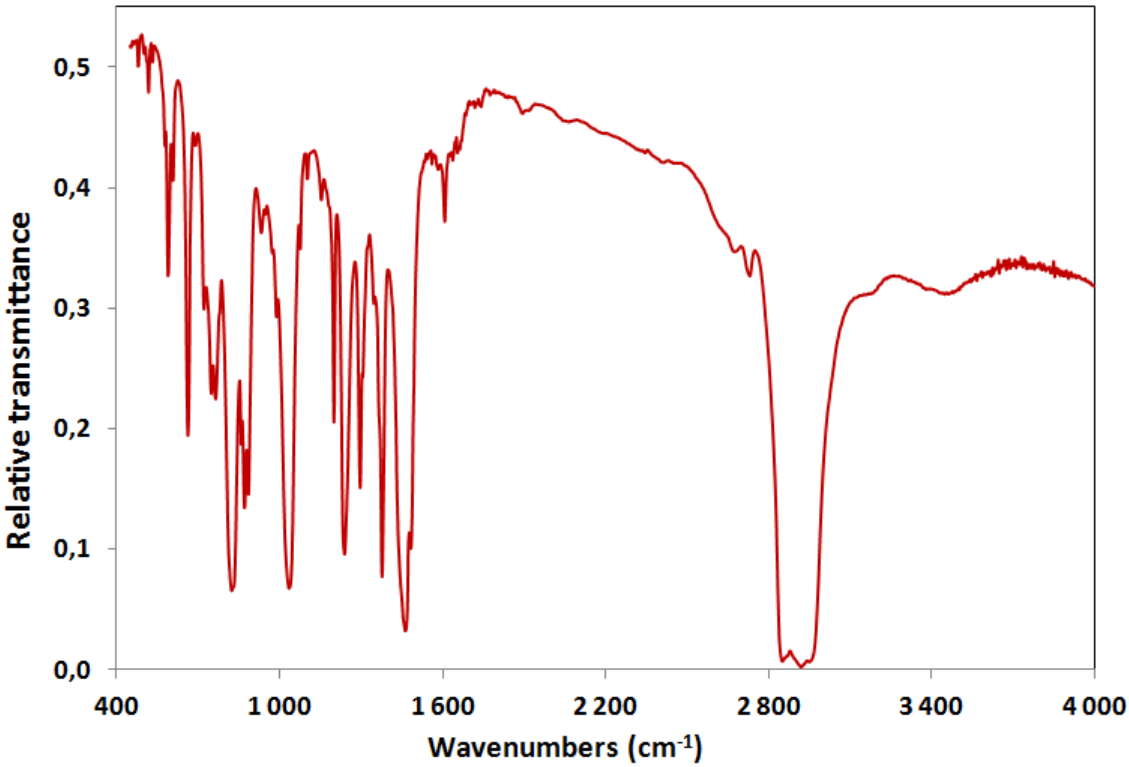


Figure S4. IR spectrum (Nujol, KBr, ν/cm^{-1}) of **2**.

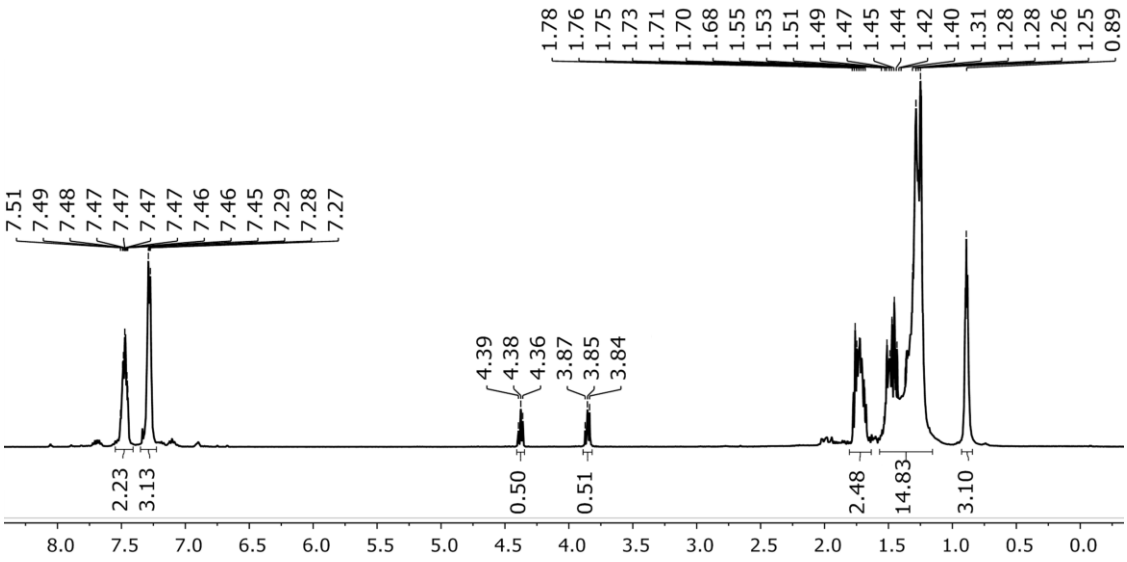


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of n-Nonylphenylphosphine.

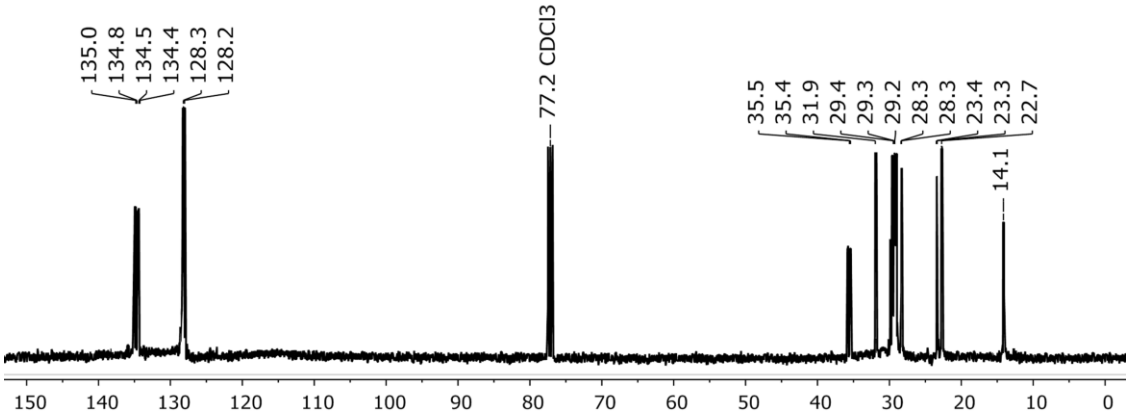


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of n-Nonylphenylphosphine.

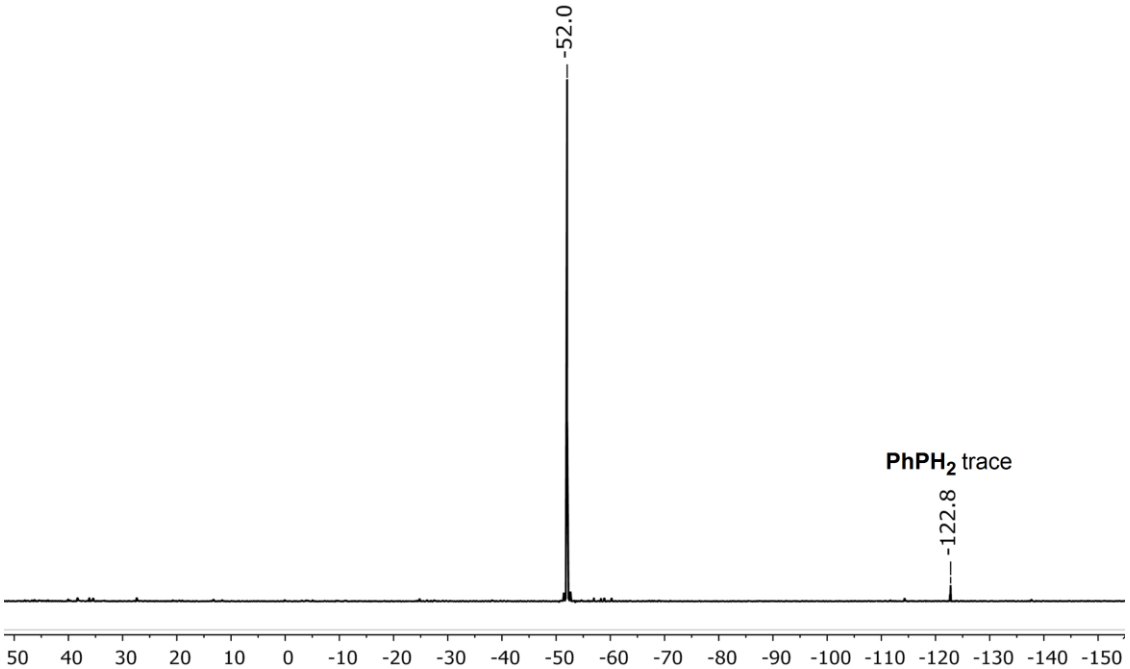


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of n-Nonylphenylphosphine.

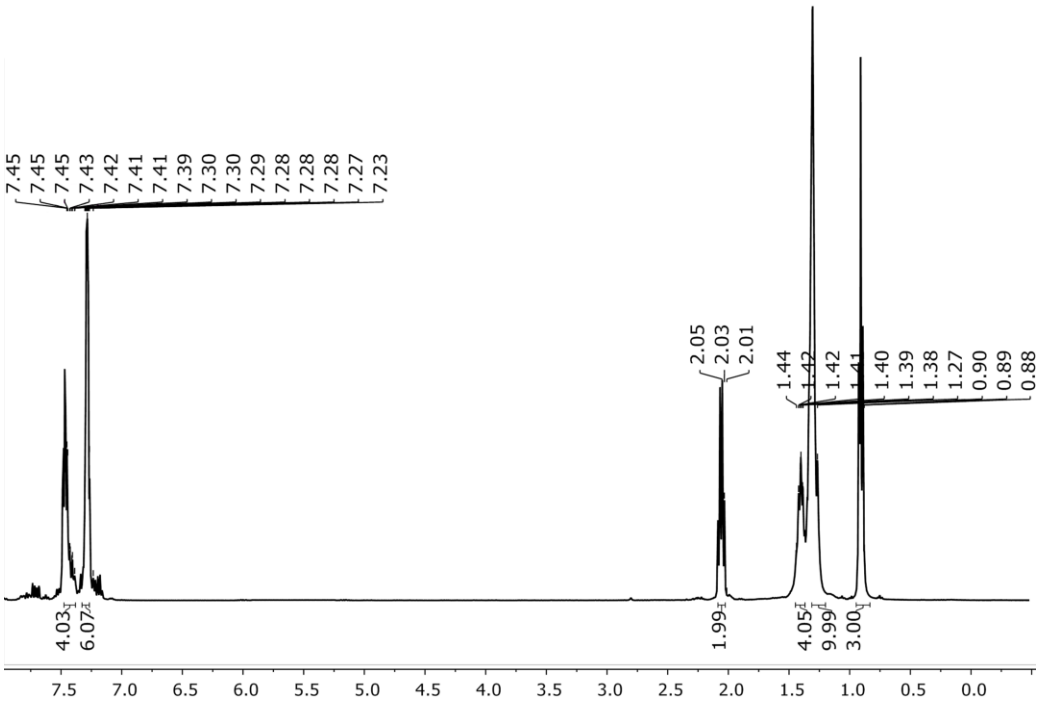


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of n-Nonyldiphenylphosphine.

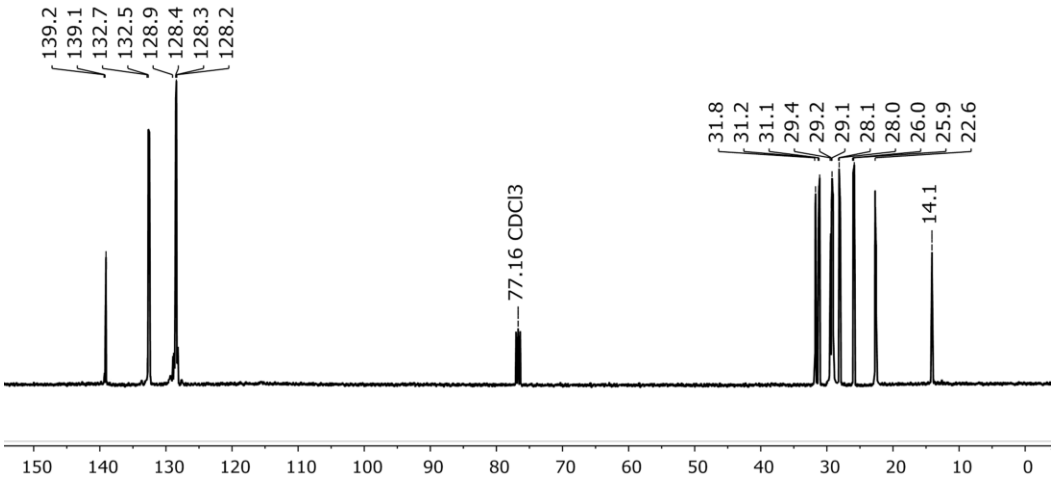


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of n-Nonyldiphenylphosphine.

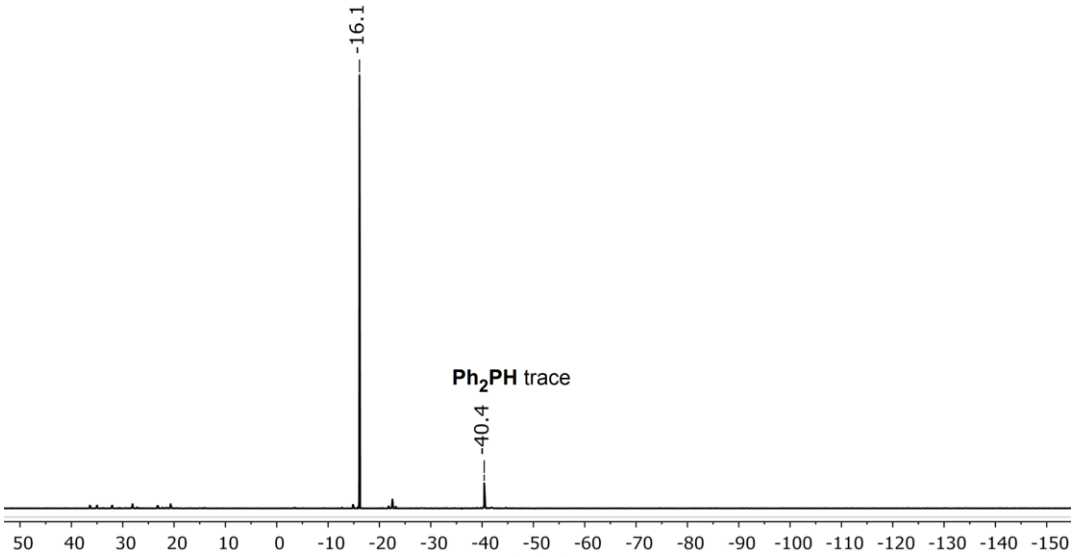


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of n-Nonyldiphenylphosphine.

Typical NMR spectra used for determination of substrates conversion.

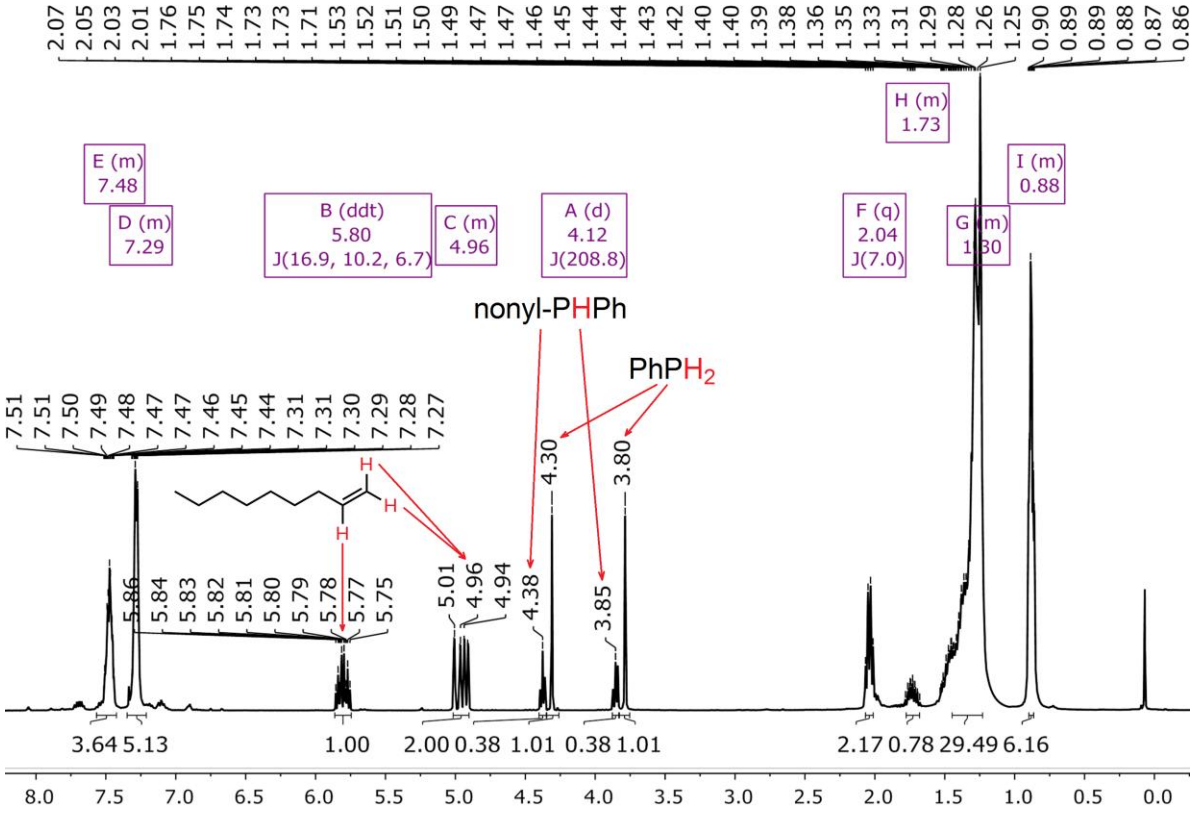


Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction of 1-nonene with Ph_2PH in typical catalytic test (2 mol. % of **1**, neat substrates, 72h, 80 ^{o}C) after addition of $CDCl_3$.

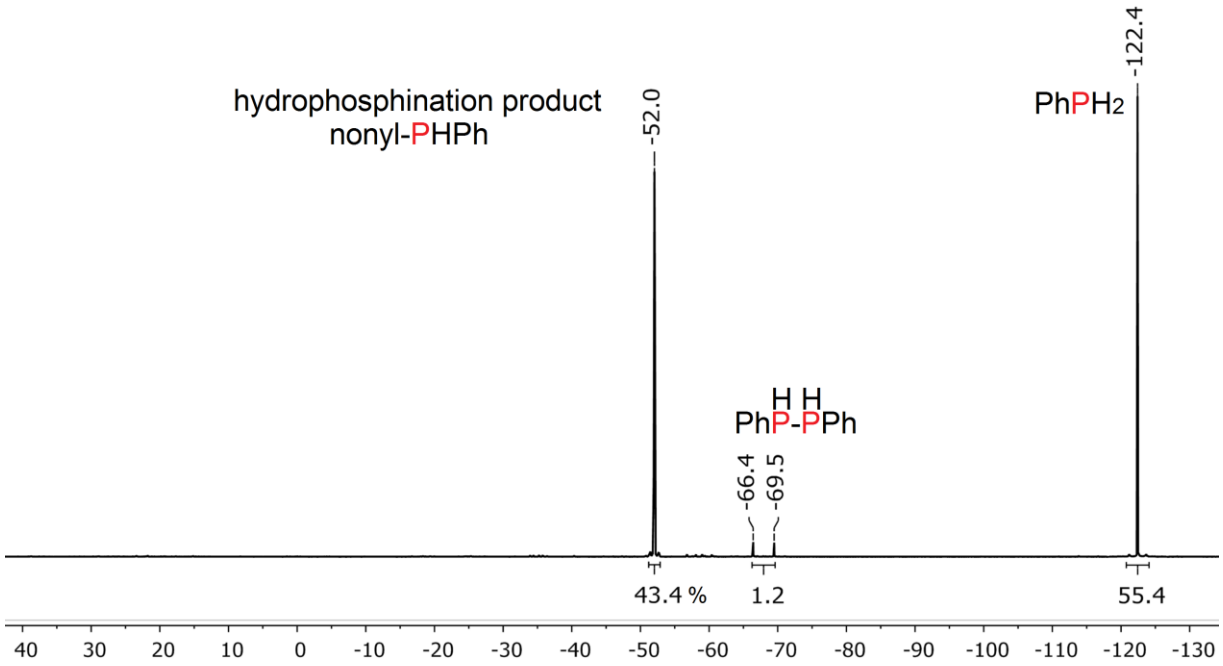
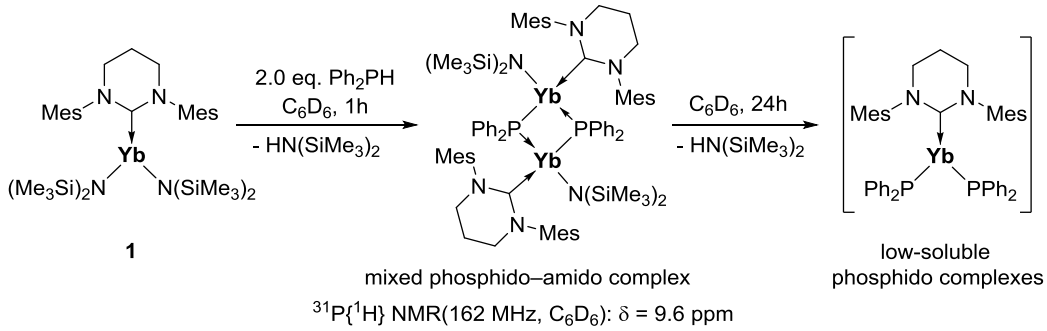


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction of 1-nonene with Ph_2PH in typical catalytic test (2 mol. % of **1**, neat substrates, 72h, 80^{o}C) after addition of $CDCl_3$.

NMR spectra of the stoichiometric reaction of 6MesYb[N(SiMe$_3$)$_2$]$_2$ (2) with 2.0 eq. of Ph$_2$PH



$^{31}P\{^1H\}$ NMR(162 MHz, C_6D_6): δ = 9.6 ppm

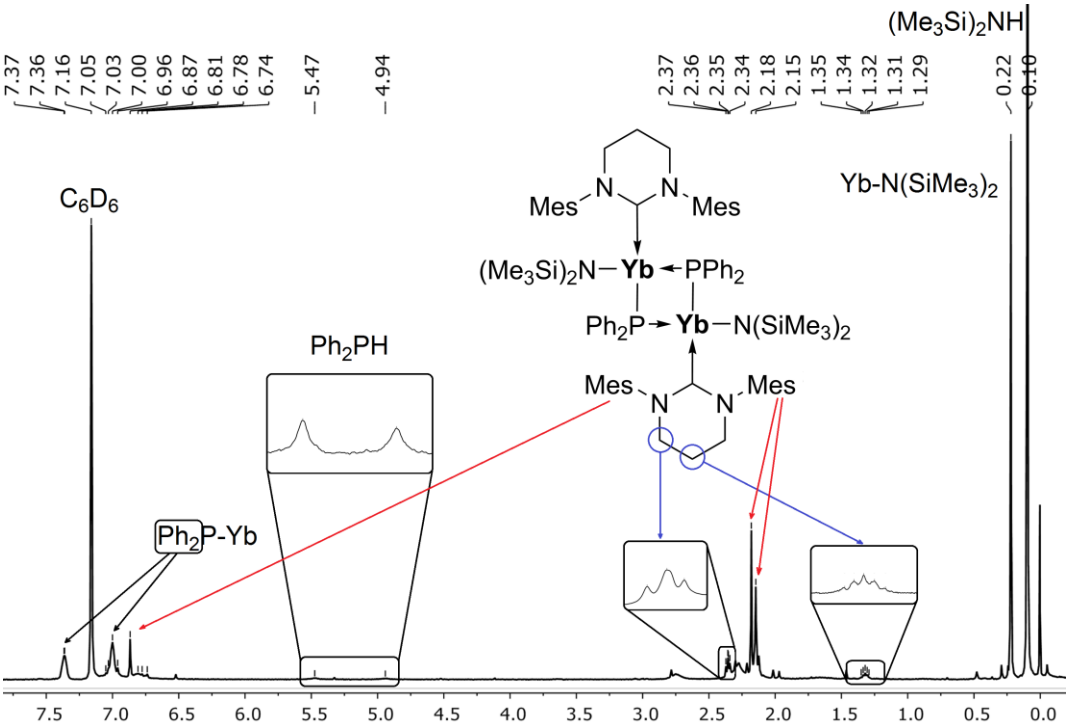


Figure S13. ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between (6Mes)Yb[N(SiMe$_3$)$_2$]$_2$ (**2**) and 2.0 eq. of Ph$_2$PH. Reaction carried out in a J-Young NMR tube at 298 K in C_6D_6, reaction time 1 h.

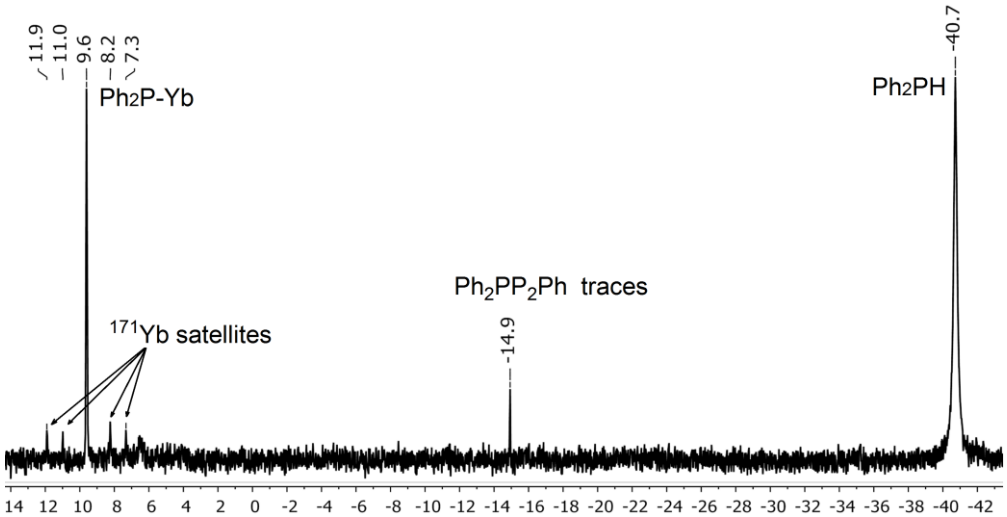


Figure S14. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between (6Mes)Yb[N(SiMe$_3$)$_2$]$_2$ (**2**) and 2.0 eq. of Ph$_2$PH after 1h at 25°C. The putative phosphido-amido complex gives rise to the resonance at 9.6 ppm with ^{171}Yb-^{31}P coupling (dd, J=593.8, 149.5). Residual HPPh$_2$ and Ph$_2$P-PPh$_2$ appear at –40.7 and –14.9 ppm.

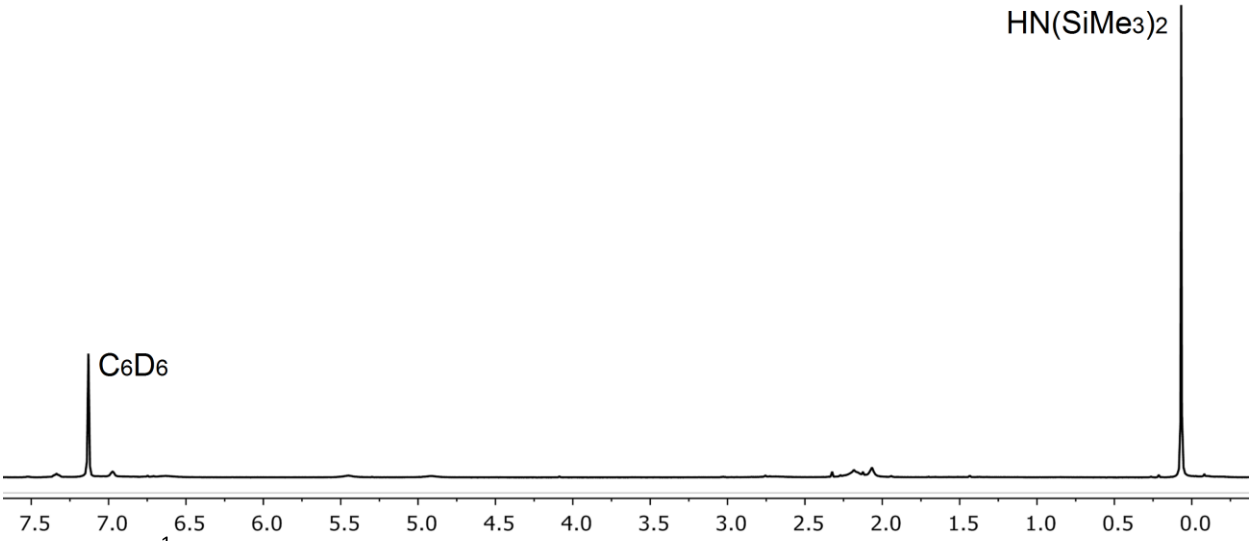


Figure S15. ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between (6Mes)Yb[N(SiMe$_3$)$_2$]$_2$ (**2**) and 2.0 eq. of Ph_2PH after 24h at 25^{o}C.

References

1. T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725-3727.
2. W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575-579.
3. E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.*, 2009, **694**, 2454-2462.
4. S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1183-1187.
5. K. J. Gallagher, M. Espinal-Viguri, M. F. Mahon and R. L. Webster, *Adv. Synth. Catal.*, 2016, **358**, 2460-2468.
6. J. Yuan, H. Hu and C. Cui, *Chem. Eur. J.*, 2016, **22**, 5778-5785.
7. M. B. Ghebreab, C. A. Bange and R. Waterman, *J. Am. Chem. Soc.*, 2014, **136**, 9240-9243.
8. C. A. Bange, M. A. Conger, B. T. Novas, E. R. Young, M. D. Liptak and R. Waterman, *ACS Catalysis*, 2018, **8**, 6230-6238.
9. K. Cao and X. Wang, *Macromol. Rapid Commun.*, 2016, **37**, 246-250.
10. L. de Quadras, J. Stahl, F. Zhuravlev and J. A. Gladysz, *J. Organomet. Chem.*, 2007, **692**, 1859-1870.
11. E. F. Clarke, E. Rafter, H. Müller-Bunz, L. J. Higham and D. G. Gilheany, *J. Organomet. Chem.*, 2011, **696**, 3608-3615.
12. P. Li, R. Wischert and P. Métivier, *Angew. Chem. Int. Ed.*, 2017, **56**, 15989-15992.
13. C. A. Busacca, T. Bartholomeyzik, S. Cheekoori, R. Raju, M. Eriksson, S. Kapadia, A. Saha, X. Zeng and C. H. Senanayake, *Synlett*, 2009, **2009**, 287-291.
14. B. T. Novas, C. A. Bange and R. Waterman, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1640-1643.
15. Bruker (2018). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
16. Rigaku Oxford Diffraction (2018). *CrysAlis^{Pro}* ver. 1.171.38.46, Rigaku Corporation, Wroclaw, Poland
17. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
18. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.