Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information File

Ligands with NPNPN-framework and their application in chromium catalyzed ethene Tri-/Tetramerization

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This file includes:

1 General Information

All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. The commercially available amines (Sigma Aldrich) were purified by distillation and stored under argon prior to use.

The following spectrometers were used:

Mass spectra:	Finnigan, MAT 95-XP from Thermo-Electron, CI^+ *Isobutene.*
NMR spectra:	Bruker AV 300 and AV400, ^1H and ^{13}C chemical shifts were referenced to the solvent signals: benzene-d_6 (δ_H 7.15 ppm, δ_C 128.6 ppm)[1], $CDCl_3$ (δ_H 7.26, δ_C 77.4 ppm)[1]
IR spectra:	Bruker Alpha FT-IR.
Melting points:	METTLER-TOLEDO MP 70. Melting points are uncorrected and were measured in sealed capillaries.
Elemental analyses:	Leco Tru Spec elemental analyzer.

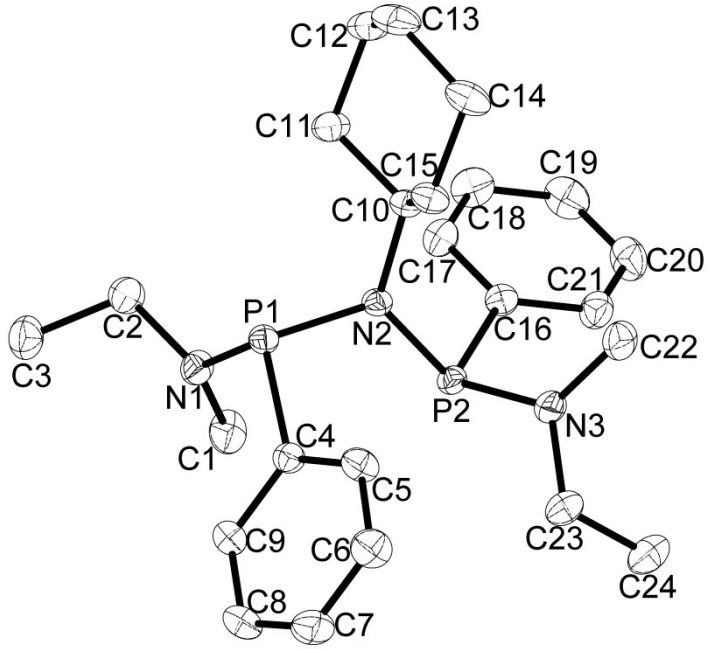
2 Structure Elucidation

Diffraction data for **2, 3, 5, 6, 7, 8** and **11** were collected on a Bruker APEX-II CCD diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[2] All non-hydrogen atoms were refined anisotropically, hydrogen atoms , except H1, H3 in **6** and H1, H3A in **8**, were included in the refinement at calculated positions using a riding model. H1, H3 in **6** and H1, H3A in **8** were found from difference Fourier maps. *XP* in *SHELXTL* (Sheldrick, 2008) and *Diamond* were used for graphical representation.

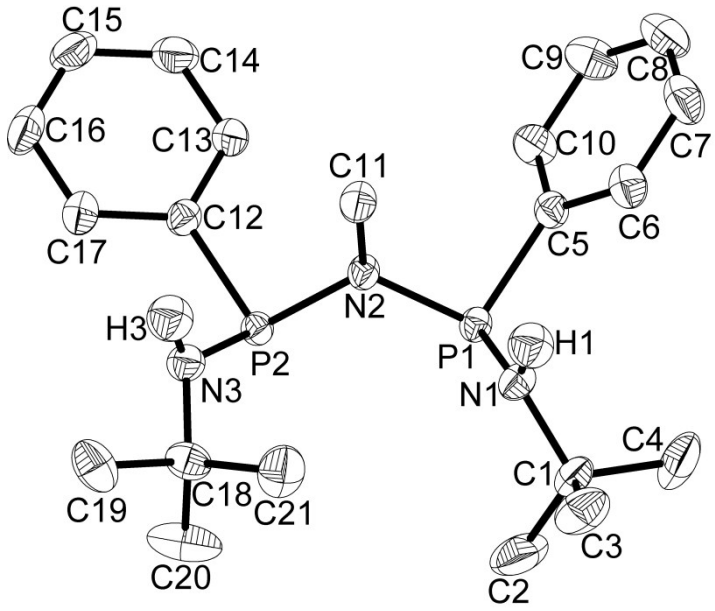
Table S1. Crystallographic Details of

	2	**3**	**5**	**6**	**7**
Chem. Formula	$C_{27}H_{41}N_3P_2$	$C_{31}H_{41}CrN_3O_4P_2$	$C_{24}H_{37}N_3P_2$	$C_{21}H_{33}N_3P_2$	$C_{29}H_{33}N_3O_2P_2$
Form. Weight [g mol^{-1}]	469.57	633.61	429.50	389.44	517.52
Colour	colourless	yellow	colourless	colourless	colourless
Cryst. system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$Pbcn$	$P2_1$
a [Å]	13.1928(5)	10.8808(3)	28.2829(8)	19.6420(4)	9.8140(3)
b [Å]	18.7757(6)	16.6923(4)	9.4907(3)	12.6315(2)	6.7216(2)
c [Å]	11.8910(4)	17.5806(4)	18.7206(5)	18.2652(3)	20.3460(6)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	116.0964(9)	98.4501(7)	107.0550(6)	90.00	99.8118(10)
γ [°]	90.00	90.00	90.00	90.00	90.00
V [Å^3]	2645.17(16)	3158.42(14)	4804.1(2)	4531.74(14)	1322.51(7)
Z	4	4	8	8	2
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
$\rho_{calc.}$ [g cm^{-3}]	1.179	1.332	1.188	1.142	1.300
μ [mm^{-1}]	0.184	0.503	0.196	0.201	0.196
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)
reflections measured	60871	65359	41117	65452	32668
independent reflections	6395	7631	5809	5207	6987
$R_{int.}$	0.0274	0.0392	0.0248	0.0369	0.0249
R_1 ($I > 2\sigma(I)$)	0.0461	0.0305	0.0317	0.0394	0.0300
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1213	0.0732	0.0814	0.0976	0.0741
R_1 (all data)	0.0557	0.0427	0.0373	0.0492	0.0333
$wR_2(F^2)$(all data)	0.1318	0.0802	0.0859	0.1032	0.0760
GOF on F^2	1.023	1.019	1.050	1.152	1.074
Flack parameter	-	-	-	-	0.11
CCDC number	1405811	1405812	1405813	1405814	1405815

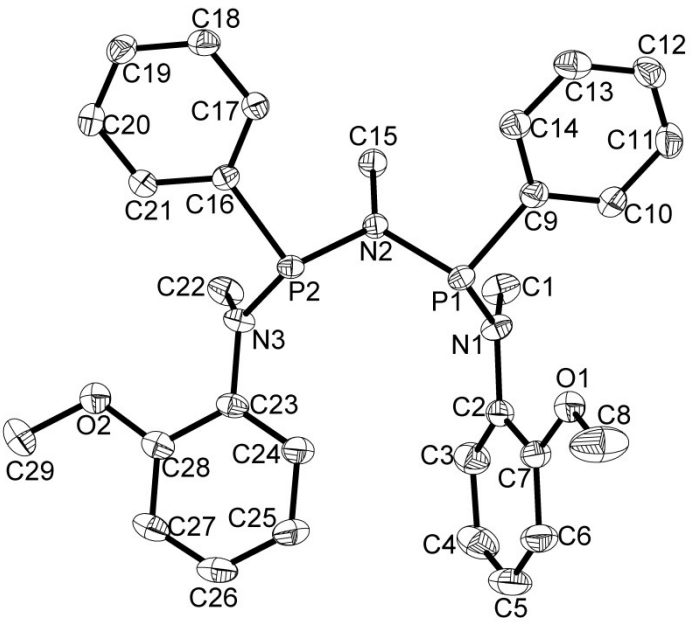
	8	**11**
Chem. Formula	$C_{27}H_{29}N_3O_2P_2$	$C_{26}H_{41}N_3P_2$
Form. Weight [g mol^{-1}]	489.47	457.56
Colour	colourless	colourless
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	14.6955(6)	10.5529(2)
b [Å]	11.8223(5)	14.8073(3)
c [Å]	14.3639(5)	17.6501(3)
α [°]	90.00	90.00
β [°]	94.7107(7)	106.706(1)
γ [°]	90.00	90.00
V [Å^3]	2487.08(17)	2641.59(9)
Z	4	4
Radiation type	MoKα	MoKα
$\rho_{calc.}$ [g cm^{-3}]	1.307	1.151
μ [mm^{-1}]	0.205	0.182
T [K]	150(2)	150(2)
reflections measured	41193	45478
independent reflections	6010	6374
$R_{int.}$	0.0530	0.0317
R_1 ($I > 2\sigma(I)$)	0.0362	0.0324
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0844	0.0866
R_1 (all data)	0.0596	0.0402
$wR_2(F^2)$(all data)	0.0971	0.0944
GOF on F^2	1.024	1.054
Flack parameter	-	-
CCDC number	1405816	1405817



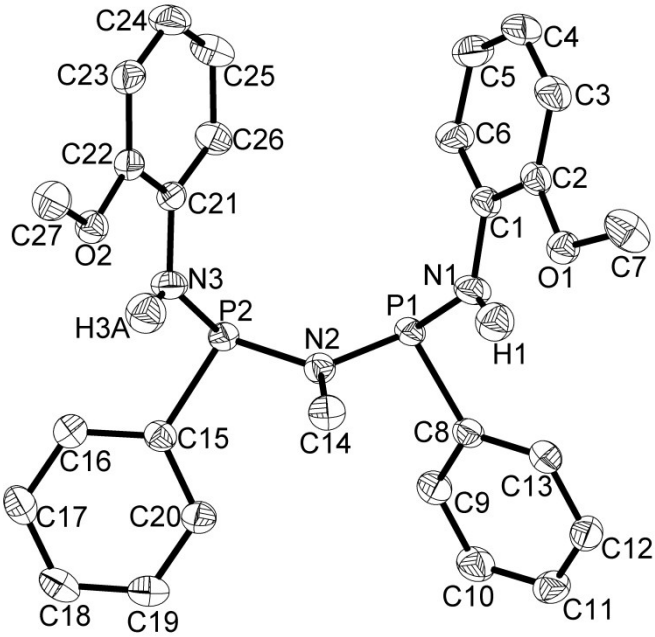
Scheme S 1. Numbering scheme of the molecular structure of (*R/S*) Et(Me)NP(Ph)NcycP(Ph)N(Me)Et (**5**).



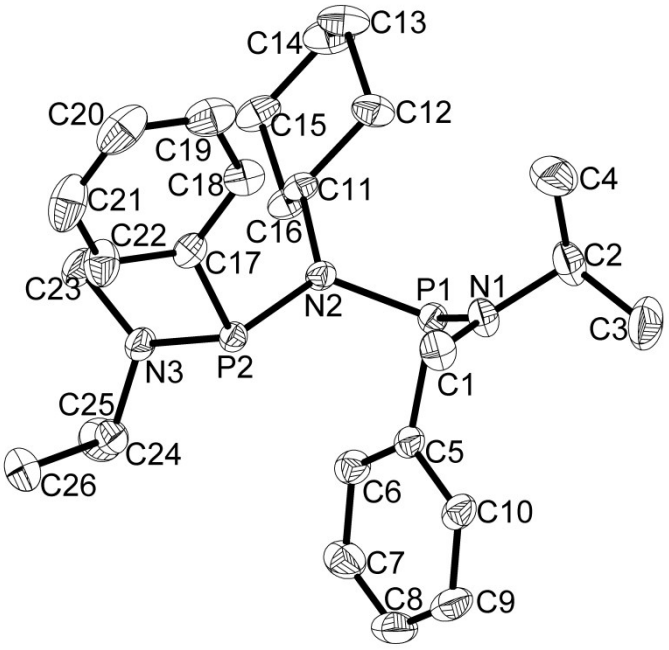
Scheme S 2. Numbering scheme of the molecular structure of (*R/S*) - H(tBu)NP(Ph)NMeP(Ph)N(tBu)H (**6**).



Scheme S 3. Numbering scheme of molecular structure of (*R/S*) -Me(o-MeO-C_6H_4)NP(Ph)NMeP(Ph)N(o-MeO-C_6H_4)Me (**7**).



Scheme S 4. Numbering scheme of the molecular structure of (*R/S*) -H(o-MeO-C_6H_4)NP(Ph)NMeP(Ph)N(o-MeO-C_6H_4)H (**8**).



Scheme S 5. Numbering scheme of Molecular structure of (*R/S*) - iPrN(Me)P(Ph)NcycP(Ph)N(Me)iPr (**11**).

3. Literature

1 G. Fulmer *et al.*, *Organometallics* **2010**, *29*, 2176-2179.

2 G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.