Supporting Information:

C–H Bond Activation by σ-Bond Metathesis as a Versatile Route towards Highly Efficient Initiators for the Catalytic Precision Polymerization of Polar Monomers

*Benedikt S. Soller, Stephan Salzinger, Christian Jandl, Alexander Pöthig, Bernhard Rieger**

WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstraße 4, 85748 Garching

Material and Methods

All reactions were carried out under argon atmosphere using standard Schlenk or glovebox techniques. All glassware was heat dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich, Acros Organics or ABCR and used as received. Toluene, THF and pentane were dried using an MBraun SPS-800 solvent purification system. Hexane was dried over 3 Å molecular sieve. Li(bdsa),[1] the precursor complexes $Ln(bdsa)_3(thf)_2$,[1] $Ln(CH_2TMS)_3(thf)_2$,[2] $Cp_2Ln(bdsa)(thf)$[3] and $Cp_2Ln(CH_2TMS)(thf)$[3] as well as DEVP[4] were prepared according to literature procedures. Monomers were dried over calcium hydride and destilled prior to use. NMR spectra were recorded on a Bruker AVIII-300 or AV-500C spectrometer. ^1H, ^{13}C and ^{29}Si NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. $\delta(^1H)$ is calibrated to the residual proton signal, $\delta(^{13}C)$ to the carbon signal and $\delta(^{29}Si)$ to the deuterium signal of the solvent. ^{31}P NMR spectroscopic chemical shifts are reported in ppm relative to and calibrated to 85% aqueous H_3PO_4. Deuterated solvents were obtained from Eurisotop or Sigma Aldrich and dried over 3Å molecular sieve. Elemental analyses were measured at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at the Technische Universität München. ESI MS analytical measurements were performed with methanol solutions on a Varian 500-MS spectrometer in positive ionization mode.

Complex Synthesis

General procedure for the synthesis of Cp_2LnX:

1 eq of a stem solution of XH in toluene (ca. 5 w%) is added dropwise to a toluene solution of 1 eq of $Cp_2Ln(bdsa)(thf)$ or $Cp_2Ln(CH_2TMS)(thf)$ (ca. 0.1 M) at room temperature. The resulting mixture is stirred for the stated reaction time, the solvent and formed 1,1,3,3-tetramethyldisilazane/$SiMe_4$ are removed *in vacuo.*

$Cp_2Lu(N(SiMe_2O\mathit{i}Pr)(SiMe_2H))$: Following the general procedure, the reaction mixture was stirred over night. Yield: 190 mg white powder (0.39 mmol, quantitative). ^{1}H NMR (C_6D_6, 300 K, 500 MHz): δ = 0.08 (s, 6H, Si(O*i*Pr)(C*H*$_3$)$_2$), 0.27 (d, 6H, 3*J*(H-H) = 3.0 Hz, SiH(C*H*$_3$)$_2$), 0.73 (d, 6H, 3*J*(H-H) = 6.2 Hz, CH(C*H*$_3$)$_2$), 3.50 (sp, 1H, ^{3}*J*(H-H) = 6.2 Hz, O-C*H*(CH$_3$)$_2$), 4.89 (sp, 1H, ^{3}*J*(H-H) = 3.0 Hz, Si-*H*), 6.15 (s, 10H, Cp-*H*). ^{13}C NMR (C_6D_6, 300 K, 125 MHz): δ = 2.5 (s, Si(*C*H$_3$)$_2$), 3.2 (s, Si(*C*H$_3$)$_2$), 24.9 (s, CH(*C*H$_3$)$_2$), 68.7 (s, O*C*H(CH$_3$)$_2$), 111.6 (s, Cp-*C*). ^{29}Si NMR (C_6D_6, 300K, 100 MHz): δ = 24.5 (s), 45.7 (s).

$Cp_2Y(CH_2(C_5H_2Me_2N))$: Following the general procedure, the reaction mixture was stirred for 30 minutes. Yield: 320 mg yellow powder (0.9 mmol, quantitative). ^{1}H NMR (C_6D_6, 292 K, 300 MHz): δ = 1.79 (s, 3H, C*H*$_3$), 2.83 (s, 3H, C*H*$_3$), 2.44 (s, 2H, C*H*$_2$), 5.80 (s, 1H, Pyr-C*H*), 6.05 (s, 10H, Cp-*H*), 6.41 (s, 1H, Pyr-C*H*). ^{13}C NMR (C_6D_6, 298 K, 125 MHz): δ = 21.1 (s, *C*H$_3$), 23.9 (s, *C*H$_3$), 40.7 (d, *C*H$_2$, $^1J_{Y\text{-}C}$ = 12.5 Hz), 111.2 (s, Cp-*C*), 112.3 (s, Pyr-*C*H), 118.5 (s, Pyr-*C*H), 148.0 (s, Pyr-C_{qu}), 155.8 (s, Pyr-C_{qu}), 167.4 (s, Pyr-C_{qu}). Anal. Calcd for $YC_{20}H_{18}N$·0.2thf: C, 63.84; H, 6.16; N, 3.96. Found: C, 63.93; H, 6.08; N, 4.00.

$Cp_2Lu(CH_2(C_5H_2Me_2N))$: Following the general procedure, the reaction mixture was stirred over night. Yield: 174 mg yellow powder (0.4 mmol, 32 %, recrystallized from toluene/pentane). ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ = 1.74 (s, 3H, C*H*$_3$), 1.82 (s, 3H, C*H*$_3$), 2.39 (s, 2H, C*H*$_2$), 5.68 (s, 10H, Pyr-C*H*), 6.04 (s, 1H, Cp-*H*), 6.49 (s, 1H, Pyr-C*H*). ^{13}C NMR (C_6D_6, 298 K, 125 MHz): δ = 20.9 (s, *C*H$_3$), 23.7 (s, *C*H$_3$), 37.8 (s, *C*H$_2$), 110.7 (s, Cp-*C*), 114.7 (s, Pyr-*C*H), 120.2 (s, Pyr-*C*H), 149.5 (s, Pyr-C_{qu}), 156.1 (s, Pyr-C_{qu}), 168.5 (s, Pyr-C_{qu}). Anal. Calcd for $LuC_{20}H_{18}N$: C, 50.83; H, 4.74; N, 3.29. Found: C, 49.18; H, 4.86; N, 2.72.

Oligomerization

5 eq of the respective monomer are added to 1 eq of catalyst in toluene. The resulting mixture is stirred for 2 hours at room temperature and quenched by addition of MeOH. Volatiles were removed under reduced pressure and the residue is extracted with MeOH. For end group analysis, ESI-MS measurements of the methanolic extract are performed.

Activity measurements

For activity measurements, the stated amount of catalyst (15-50 μmol) is dissolved in 20mL of toluene and the reaction mixture is thermostated to the desired temperature. Then, the stated amount of DEVP (3.5-13 mmol) is added. During the course of the measurement, the temperature is monitored with a digital thermometer and aliquots (0.5 mL) are taken and quenched by addition to deuterated methanol (0.2 mL). After the stated reaction time, the reaction is quenched by addition of MeOD (0.5 mL). The reaction is carried out in an MBraun Glovebox under argon atmosphere to take aliquots every 6-10 seconds at the beginning of the measurement. For each aliquot, the conversion is determined by ^{31}P NMR spectroscopy, the molecular weight of the formed polymer by GPC-MALS analysis.

Molecular Weight Determination

GPC was carried out on a Varian LC-920 equipped with two PL Polargel columns. As eluent a mixture of 50% THF, 50% water, and 9 g L^{-1} tetrabutylammonium bromide (TBAB) was used. Absolute molecular weights have been determined online by multiangle light scattering (MALS) analysis using a Wyatt Dawn Heleos II in combination with a Wyatt Optilab rEX as concentration source.

Table S1. Polymerization results for the REM-GTP of 2VP (toluene, 30 °C)[5]

Catalyst	Monomer	$[Mon]_0/[Cat]_0$	Init. period[a]	M_n[b] [kDa]	PDI[b]	I^*_t[b] [%]	I^*[b] [%]	TOF[c] [h^{-1}]	TOF/I^*_t [h^{-1}]
$Cp_2Y(CH_2(C_5H_2Me_2N)$	2VP	100	-[e]	13	1.01	-[e]	80	-[e]	-[e]
$Cp_2Lu(CH_2(C_5H_2Me_2N)$	2VP	100	-[e]	38	1.08	-[e]	28	-[e]	-[e]
$[Cp_2YbMe]_2$	2VP	100	-[e]	14	1.01	-[e]	75	44	-[e]

[a]Initiation period, reaction time until 3% conversion is reached, [b]determined by GPC-MALS, $I^*_t = M_{th}/M_n$, $M_{th} = [Mon]_0/[Cat]_0 \times M_{Mon} \times$ conversion (I^*_t at the maximum rate, I^* at the end of the reaction), [c]determined by ^{31}P (DEVP) or ^1H (IPOx) NMR spectroscopic measurement, [e]not determined.

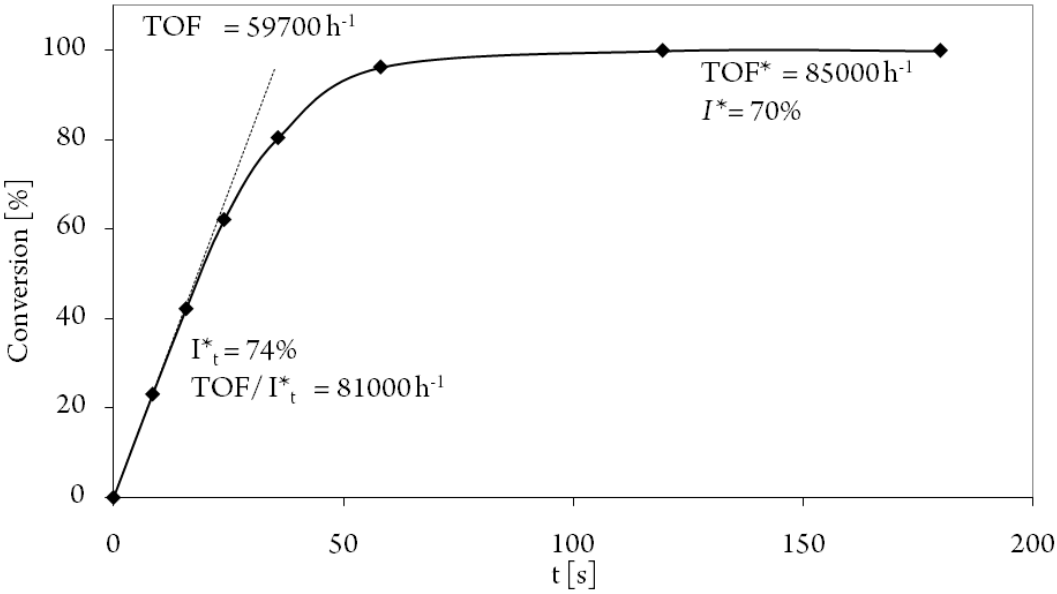

Figure S1: Conversion-reaction time plot for the polymerization of DEVP using *in situ* generated $Cp_2Y(CH_2(C_5H_2Me_2N))$, (7.4 mg catalyst, 10vol% DEVP in 20 mL toluene, 30 °C).

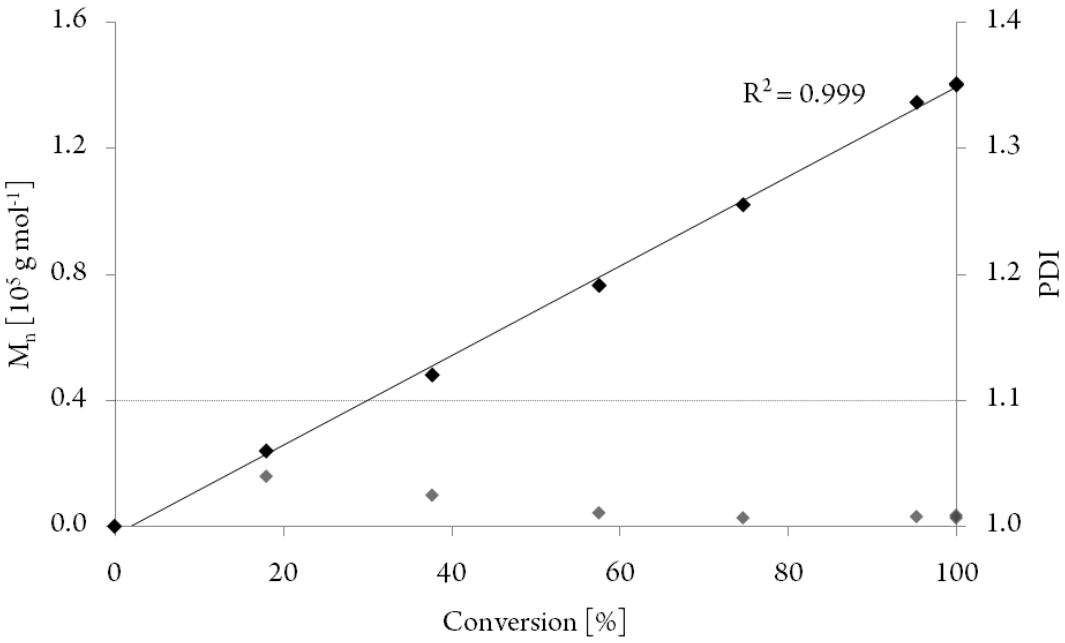

Figure S2: Conversion-reaction time plot for the polymerization of DEVP using *in situ* generated $Cp_2Y(CH_2(C_5H_2Me_2N))$, (7.4 mg catalyst, 10vol% DEVP in 20 mL toluene, 30 °C).

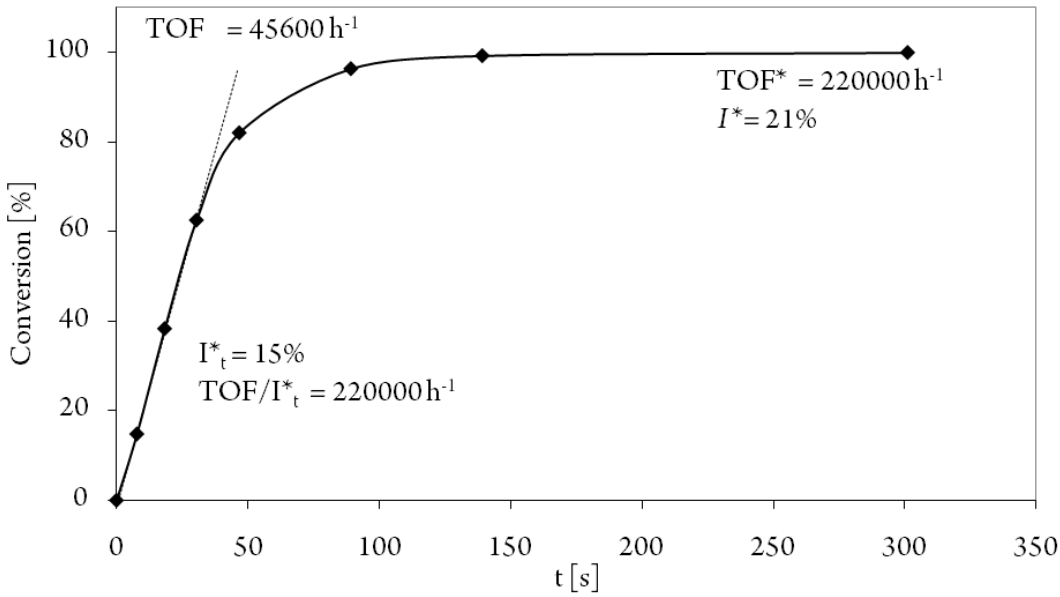

Figure S3. Conversion-reaction time plot for the polymerization of DEVP using $Cp_2Lu(CH_2(C_5H_2Me_2N))$, (9.2 mg catalyst, 10vol% DEVP in 20 mL toluene, 30 °C).

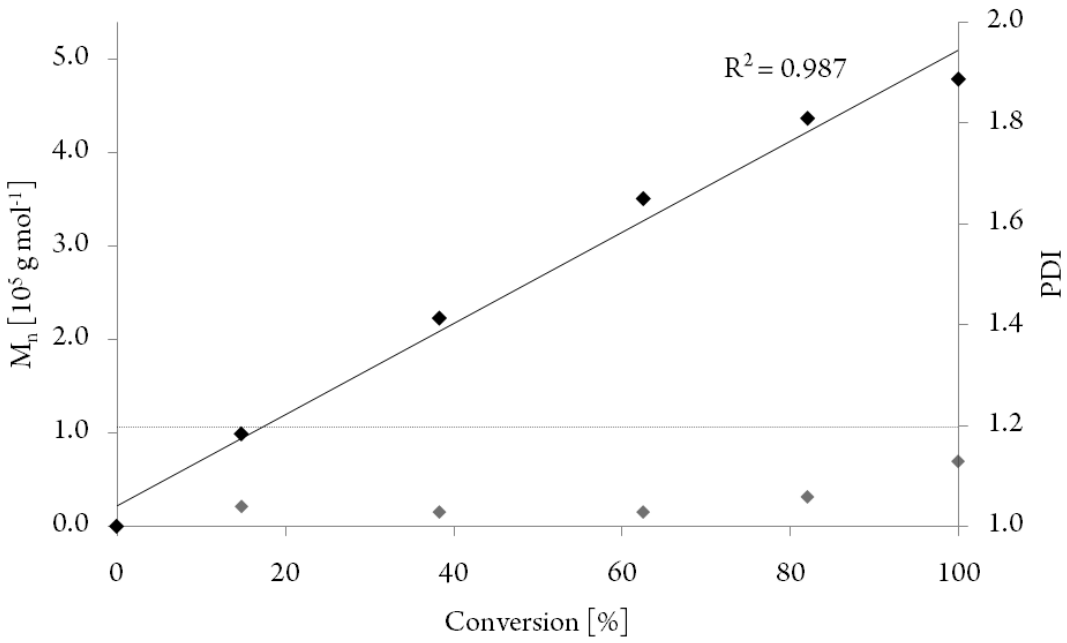

Figure S4: Conversion-reaction time plot for the polymerization of DEVP using $Cp_2Lu(CH_2(C_5H_2Me_2N))$, (9.2 mg catalyst, 10vol% DEVP in 20 mL toluene, 30 °C).

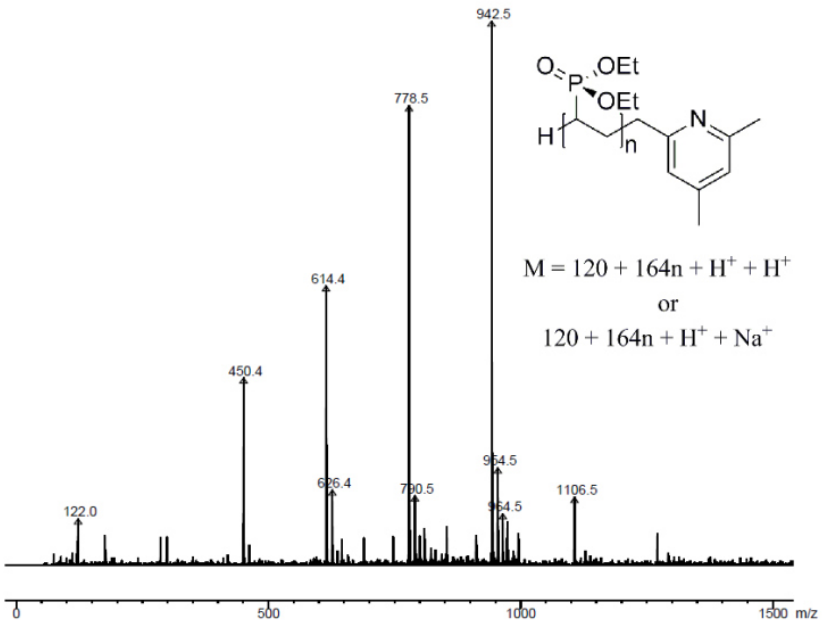

Figure S5. ESI MS spectrum of DEVP oligomers produced with $Cp_2Y(CH_2(C_5H_2Me_2N))$.

SC-XRD determination (CCDC 1031228)

A yellow fragment-like specimen of $C_{36}H_{40}N_2Y_2$, approximate dimensions 0.324 mm x 0.327 mm x 0.405 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo fine-focus tube (λ = 0.71073 Å).

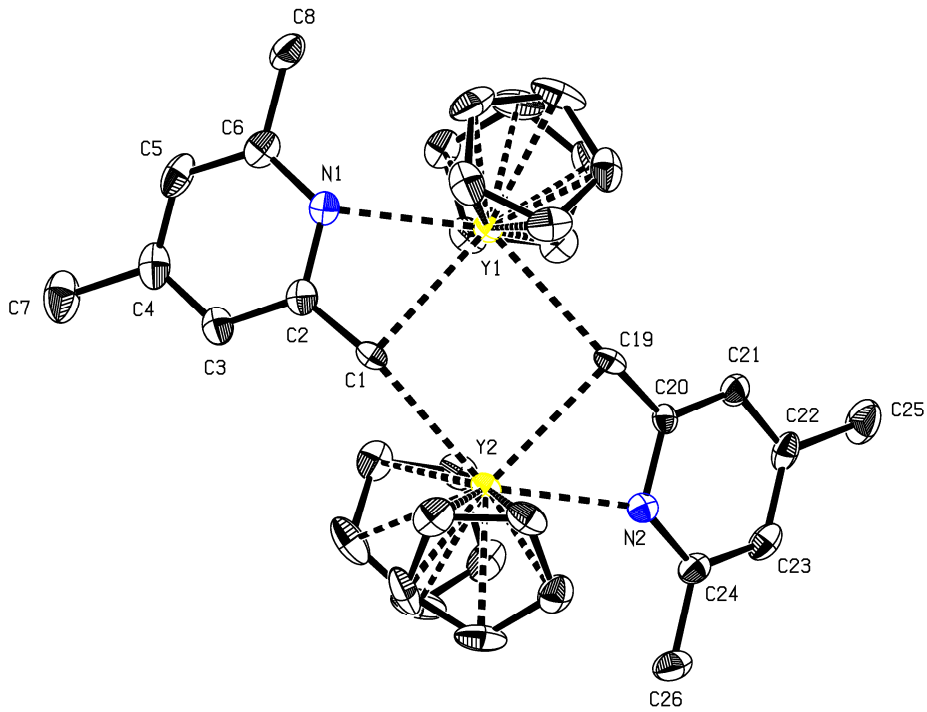

Figure S6. Ortep drawing with 50% ellipsoids for $Cp_2Y(CH_2(C_5H_2Me_2N))$.

A total of 1392 frames were collected. The total exposure time was 23.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34217 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 5737 were independent (average redundancy 5.964, completeness = 100.0%, R_{int} = 10.40%, R_{sig} = 8.18%) and 3937 (68.62%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.9223(4) Å, b = 22.3436(8) Å, c = 12.7820(4) Å, β = 113.273(2)°, volume = 3127.91(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 3701 reflections above 20 σ(I) with 5.032° < 2θ < 46.07°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.643. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3140 and 0.3790.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P 1 21/n 1, with Z = 4 for the formula

unit, $C_{36}H_{40}N_2Y_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 517 variables converged at R1 = 3.83%, for the observed data and wR2 = 7.00% for all data. The goodness-of-fit was 0.997. The largest peak in the final difference electron density synthesis was 0.381 $e^-/Å^3$ and the largest hole was -0.493 $e^-/Å^3$ with an RMS deviation of 0.090 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.441 g/cm^3 and F(000), 1392 e^-.

Chemical formula	$C_{36}H_{40}N_2Y_2$	
Formula weight	678.52	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal size	0.324 x 0.327 x 0.405 mm	
Crystal habit	yellow fragment	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.9223(4) Å	α = 90°
	b = 22.3436(8) Å	β = 113.273(2)°
	c = 12.7820(4) Å	γ = 90°
Volume	3127.91(19) $Å^3$	
Z	4	
Density (calculated)	1.441 g/cm^3	
Absorption coefficient	3.719 mm^{-1}	
F(000)	1392	

Diffractometer	Bruker Kappa APEX II CCD	
Radiation source	fine-focus tube, Mo	
Theta range for data collection	1.82 to 25.35°	
Index ranges	-14<=h<=14, -26<=k<=26, -15<=l<=15	
Reflections collected	34217	
Independent reflections	5737 [R(int) = 0.1040]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.3790 and 0.3140	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008) and SHELXLE (Huebschle. 2011)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5737 / 0 / 517	
Goodness-of-fit on F^2	0.997	
Final R indices	3937 data; I>2σ(I)	R1 = 0.0383, wR2 = 0.0609
	all data	R1 = 0.0802, wR2 = 0.0700
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0251P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.381 and -0.493 $eÅ^{-3}$	
R.M.S. deviation from mean	0.090 $eÅ^{-3}$	

References

[1] J. Eppinger, *PhD Thesis*, Technische Universität München, **1999**.

[2] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228, K. C. Hultzsch, *PhD Thesis*, Universität Mainz, **1999**.

[3] S. Salzinger, B. S. Soller, A. Plikhta, U. B. Seemann, E. Herdtweck, B. Rieger, Journal of the American Chemical Society **2013**, *135*, 13030-13040.

[4] Leute, M. *PhD Thesis*, Universität Ulm, **2007**.

[5] Zhang, N.; Salzinger, S.; Soller, B. S.; Rieger, B. J. Am. Chem. Soc. **2013**, *135*, 8810.