SUPPORTING INFORMATION

N-Heterocyclic carbene-phosphino-picolines as precursors of anionic 'pincer' ligands with dearomatised pyridine backbones; transmetallation from potassium to chromium

Thomas Simler,[a] Andreas A. Danopoulos,*[a, b] and Pierre Braunstein*[a]

[a] *Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex (France)*

[b] *Institute for Advanced Study (USIAS), Université de Strasbourg, France*

E-mail: braunstein@unistra.fr, danopoulos@unistra.fr

Contents:

I. General Considerations 2
II. Synthetic procedures for L^R 3
III. Synthetic procedures for KL_{-H}^R 6
IV. Synthetic procedure for $[CrCl(L_{-H}^{t\text{-Bu}})]$ 8
V. Determination of the magnetic susceptibility of $[CrCl(L_{-H}^{t\text{-Bu}})]$ 9
VI. Studies of the solution structures of KL_{-H}^R by NMR spectroscopies 10
VI.1. NOESY structural analysis of KL_{-H}^{Cy} in C_6D_6 solution 10
VI.2. $Z \rightarrow E$ Isomerisation of KL_{-H}^R on dissolution in THF-d_8 11
VI.2.1. KL_{-H}^{Cy} isomerisation 12
VI.2.2. $KL_{-H}^{t\text{-Bu}}$ isomerisation 12
VI.3. Effect of the addition of 18-crown-6 on the *E/Z* equilibrium 15
VI.3.1. Study of KL_{-H}^{Cy} 15
VI.3.2. Study of $KL_{-H}^{t\text{-Bu}}$ 20
VII. X-ray crystallography 25
VII.1. General methods 25
VII.2. Summary of crystal data 26
VII.3. Crystal structure of L^{Cy}·2HBr 27

VII.4. Crystal structure of $KL_{-H}^{Cy}\cdot Et_2O$ 28
VII.5. Crystal structure of $[CrCl(L_{-H}^{t\text{-}Bu})]$ 30
VIII. References 31

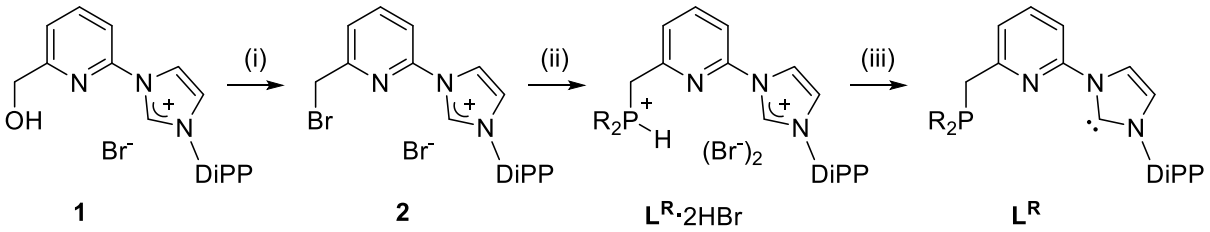
I. GENERAL CONSIDERATIONS

All air- and moisture-sensitive manipulations were performed under dry argon atmosphere using standard Schlenk techniques or in an MBraun glove-box containing an atmosphere of nitrogen. THF and diethyl ether were dried by refluxing over sodium/benzophenone ketyl and distilled under an argon atmosphere prior use. Other solvents (pentane, toluene and acetonitrile) were dried by passing through columns of activated alumina and subsequently purged with argon. The solvents used for the synthesis of the lithium or potassium salts were stored, after drying, over potassium mirror in the glove box until use. C_6D_6 and THF-d_8 were distilled over KH, CD_2Cl_2 and $CDCl_3$ were dried 3 Å or 4 Å molecular sieves and all were degassed by freeze-pump-thaw cycles. The synthesis of 3-(2,6-diisopropylphenyl)-1-(6-(hydroxymethyl)pyridin-2-yl)-1*H*-imidazol-3-ium bromide (**1**) has been described before.[1] Imidazolium salts $\mathbf{L^R}\cdot$2HBr were dried azeotropically with a Dean-Stark apparatus using toluene or benzene under inert-atmosphere. Commercial 18-crown-6 (Aldrich) was recrystallised from acetonitrile and dried under vacuum.[2] $[CrCl_2(THF)_2]$ was prepared by continuous extraction of commercial anhydrous $CrCl_2$ (Aldrich) into dry THF for 3 days, followed by evaporation of the volatiles from the suspension of the extracted complex and drying the light green-gray residue under vacuum for *ca.* 20 min. All other chemicals were obtained from commercial sources and used without further purification.

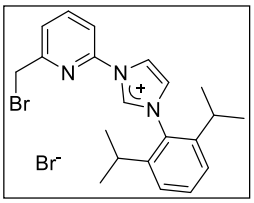
NMR spectra were recorded on Bruker spectrometers (AVANCE I – 300 MHz, AVANCE III – 400 MHz or AVANCE I – 500 MHZ equipped with a cryogenic probe). Downfield shifts are reported as positive and referenced using signals of the residual protio solvent (^{1}H), the solvent (^{13}C) or externally (^{31}P). All NMR spectra were measured at 298 K. The multiplicity of the signals is indicated as s = singlet, d = doublet, t = triplet, q=quartet, sept = septet, m = multiplet and br = broad. Assignments were determined either on the basis of unambiguous chemical shifts, coupling patterns or 2D correlations (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC). Specific NMR experiments are detailed in the corresponding sections.

Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas.

II. SYNTHETIC PROCEDURES FOR L^R



Scheme S1 Synthetic route to $\mathbf{L^R}$·2HBr and its deprotonation to $\mathbf{L^R}$.



Synthesis of 1-(6-(bromomethyl)pyridin-2-yl)-3-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium bromide (2)

To a solution of **1** (3.92 g, 9.41 mmol) in dichloromethane precooled at 0 °C was added dropwise PBr_3 (0.98 mL, 2.80 g, 10.4 mmol) under argon. The resulting solution was stirred at 0 °C for 1 h and allowed to reach room temperature. After 2 h, the reaction mixture was quenched by slow addition of saturated aqueous $NaHCO_3$ and Na_2CO_3 solution until the aqueous phase was basic. The organic layer was separated, washed with water (3 x 10 mL) and dried over anhydrous $MgSO_4$. The solution was concentrated under vacuum to about 2-3 mL and the product was precipitated by addition of diethyl ether. The solid residue was filtered and dried under vacuum to afford a light brown powder. Yield: 4.43 g (9.24 mmol), 98%.

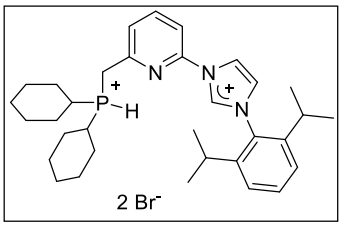
Although the product appeared to be relatively stable at room temperature, it was used immediately after synthesis for the preparation of $\mathbf{L^R}$·2HBr (to avoid quaternisation of the pyridine by reaction with itself).

Anal. Calcd for $C_{21}H_{25}Br_2N_3$ (479.26): C, 52.63; H, 5.26; N, 8.77. Found: C, 52.59; H, 5.26; N, 8.78.

^{1}H NMR (300.17 MHz, $CDCl_3$): δ 11.11 (t, $^4J_{HH}$ = 1.6 Hz, 1H, NC*H*$_{imid.}$N), 9.28 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.7 Hz, 1H, C*H*$_{imid.}$), 9.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C*H*$_{pyr.}$), 8.11 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*$_{pyr.}$), 7.61 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C*H*$_{pyr.}$), 7.56 (t, $^3J_{HH}$ = 7.9 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.39 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.7 Hz, 1H, C*H*$_{imid.}$), 7.34 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-C*H*$_{DiPP}$), 4.55 (s, 2H, C*H*$_2$Br), 2.40 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 156.7 (*C*$_{arom.}$), 145.5 (*C*$_{arom.}$), 145.2 (*C*$_{arom.}$), 142.4 (*C*H$_{arom.}$), 135.9 (*C*H$_{arom.}$), 132.4 (*C*H$_{arom.}$), 130.1 (*C*$_{arom.}$), 125.33 (*C*H$_{arom.}$), 125.29 (*C*H$_{arom.}$), 125.0 (*C*H$_{arom.}$), 121.0 (*C*H$_{arom.}$), 116.1 (*C*H$_{arom.}$), 32.1 (*C*H$_2$Br), 29.0 (*C*H(CH$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$).

HRMS (ESI/[M]$^+$): calcd for $C_{21}H_{25}BrN_3$ 398.1226, found 398.1236.



Synthesis of 1-(6-((dicyclohexylphosphonio)methyl)pyridin-2-yl)-3-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium bromide (L^{Cy}·2HBr)

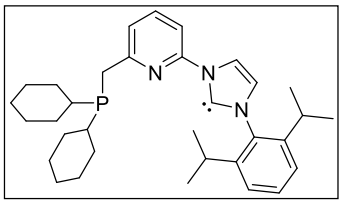
To a solution of **2** (4.43 g, 9.24 mmol) in degassed acetonitrile/THF 5:1 (30 mL) was added with a syringe dicyclohexylphosphine (2.1 mL, 2.05 g, 10.4 mmol). After the light brown solution was stirred for a few hours, a white precipitate appeared and stirring was continued for 2 days. The solid precipitate was filtered, washed with diethyl ether and pentane and dried under vacuum to afford an air-stable white powder. Yield: 4.95 g (7.30 mmol), 79%. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether in a dichloromethane solution of L^{Cy}·2HBr.

Anal. Calcd for $C_{33}H_{48}Br_2N_3P$ (677.55): C, 58.50; H, 7.14; N, 6.20. Found: C, 58.68; H, 7.12; N, 6.11.

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ 12.05 (t, $^4J_{HH}$ = 1.6 Hz, 1H, NC*H*$_{imid.}$N), 9.74 (br d, $^1J_{HP}$ = 519 Hz, 1H, P*H*), 9.71 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.7 Hz, 1H, C*H*$_{imid.}$), 8.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C*H*$_{pyr.}$), 8.16 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*$_{pyr.}$), 7.83 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C*H*$_{pyr.}$), 7.61 (t, $^3J_{HH}$ = 7.9 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.40 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.7 Hz, 1H, C*H*$_{imid.}$), 7.39 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-C*H*$_{DiPP}$), 4.12 (br d, $^2J_{PH}$ = 14.3 Hz, 2H, C*H*$_2$P), 2.56 (br q, *J* = 12.2 Hz, 2H, PC*H*$_{Cy}$), 2.43 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.18-2.00 (m, 4H, Cy), 1.91-1.81 (m, 4H, Cy), 1.77-1.69 (m, 2H, Cy), 1.61-1.44 (m, 4H, Cy), 1.41-1.22 (m, 6H, Cy), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 151.7 (d, $^2J_{PC}$ = 8.2 Hz, *C*$_{pyr.}$), 146.7 (*C*$_{pyr.}$), 145.5 (*o*-*C*$_{DiPP}$), 142.8 (*C*H$_{pyr.}$), 137.9 (NC*H*$_{imid.}$N), 132.3 (*p*-*C*H$_{DiPP}$), 130.7 (N*C*$_{DiPP}$), 126.7 (d, $^3J_{PC}$ = 6.8 Hz, *C*H$_{pyr.}$), 125.9 (*C*H$_{imid.}$), 125.0 (*m*-*C*H$_{DiPP}$), 122.1 (*C*H$_{imid.}$), 115.9 (d, $^5J_{PC}$ = 1.2 Hz, *C*H$_{pyr.}$), 29.3 (*C*H(CH$_3$)$_2$), 29.0 (d, $^1J_{PC}$ = 40.8 Hz, *C*H$_{Cy}$), 27.7 (d, J_{PC} = 3.4 Hz, *C*H$_{2Cy}$), 27.3 (d, J_{PC} = 3.8 Hz, *C*H$_{2Cy}$), 26.5 (d, J_{PC} = 13.1 Hz, *C*H$_{2Cy}$), 26.4 (d, J_{PC} = 12.8 Hz, *C*H$_{2Cy}$), 25.4 (d, J_{PC} = 1.5 Hz, *C*H$_{2Cy}$), 24.4 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.7 (d, $^1J_{PC}$ = 45.1 Hz, *C*H$_2$P).

^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 9.7 (br d, $^1J_{PH}$ = 520 Hz, *P*H).



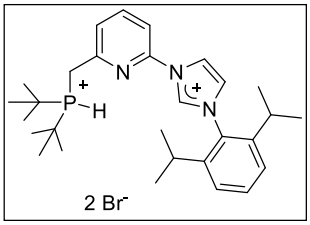
Synthesis of 1-(6-((dicyclohexylphosphanyl)methyl)pyridin-2-yl)-3-(2,6-diisopropylphenyl)-imidazol-2-ylidene (L^{Cy})

To a suspension of L^{Cy}·2HBr (0.271 g, 0.40 mmol) in THF (5 mL) precooled at –78 °C was added a solution of KHMDS (0.164 g, 0.82 mmol) in THF (5 mL). The resulting suspension was allowed to reach room temperature and stirred for 1 h, giving a suspension of KBr in a pale yellow solution. Removal of the volatiles under reduced pressure, extraction of the resulting oil with toluene (5-10 mL), filtration and evaporation of the solvent gave a brown oil. Trituration with cold pentane afforded L^{Cy} as a colourless solid, which can be crystallised from pentane/ether mixtures. Yield: 0.175 g (0.34 mmol), 85%. Satisfactory elemental analysis data could not be obtained due to the air sensitivity of the compound.

^{1}H NMR (500.13 MHz, C_6D_6): δ 8.61 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, C$H_{pyr.}$), 8.49 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H, C$H_{imid.}$), 7.27 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, CH_{DiPP}), 7.17-7.10 (m, 3H, C$H_{pyr.}$ + CH_{DiPP}), 6.91 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, C$H_{pyr.}$), 6.65 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H, C$H_{imid.}$), 2.98 (s, 2H, CH_2P), 2.90 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH_3)$_2$), 1.89-1.78 (m, 4H, Cy), 1.74-1.55 (m, 8H, Cy), 1.39-1.10 (m, 10H, Cy), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.08 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6): δ 219.8 (C_{NHC}), 160.0 (d, J_{PC} = 9.0 Hz, $C_{arom.}$), 153.6 ($C_{arom.}$), 146.3 ($C_{arom.}$), 138.8 ($C_{arom.}$), 138.5 (CH$_{arom.}$), 129.2 (CH$_{arom.}$), 123.8 (CH$_{arom.}$), 122.8 (CH$_{arom.}$), 121.1 (d, J_{PC} = 6.2 Hz, CH$_{arom.}$), 116.4 (CH$_{arom.}$), 111.5 (CH$_{arom.}$), 34.1 (d, $^{1}J_{PC}$ = 16.8 Hz, CH$_{Cy}$), 32.3 (d, $^{1}J_{PC}$ = 23.5 Hz, CH$_2$P), 30.3 (d, J_{PC} = 13.9 Hz, CH$_{2Cy}$), 29.6 (d, J_{PC} = 9.7 Hz, CH$_{2Cy}$), 28.6 (CH(CH_3)$_2$), 27.7 (d, J_{PC} = 10.5 Hz, CH$_{2Cy}$), 27.6 (d, J_{PC} = 7.9 Hz, CH$_{2Cy}$), 26.9 (CH$_{2Cy}$), 24.4 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 3.3.



Synthesis of 1-(6-((di-*tert*-butylphosphonio)methyl)pyridin-2-yl)-3-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium bromide (L$^{t\text{-}Bu}$·2HBr)

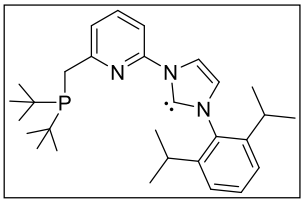
To a solution of **2** (3.73 g, 7.78 mmol) in degassed acetonitrile/THF 5:1 (30 mL) was added with a syringe di-*tert*-butylphosphine (1.6 mL, 1.26 g, 8.65 mmol). After the light brown solution was stirred for a few hours, a white precipitate appeared and stirring was continued for 2 days. The solid residue was collected by filtration, washed with diethyl ether and pentane and dried under vacuum to afford an air-stable white powder. Yield: 4.26 g (6.81 mmol), 87%.

Anal. Calcd for $C_{29}H_{44}Br_2N_3P$ (625.47): C, 55.69; H, 7.09; N, 6.72. Found: C, 55.45; H, 6.97; N, 6.90.

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ 12.03 (t, $^{4}J_{HH}$ = 1.6 Hz, 1H, NC$H_{imid.}$N), 9.80 (dt, $^{1}J_{HP}$ = 508 Hz, $^{3}J_{HH}$ = 4.7 Hz, 1H, PH), 9.59 (t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 1.8 Hz, 1H, C$H_{imid.}$), 8.64 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, C$H_{pyr.}$), 8.15 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, C$H_{pyr.}$), 8.04 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, C$H_{pyr.}$), 7.60 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-CH_{DiPP}), 7.39 (t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 1.8 Hz, 1H, C$H_{imid.}$), 7.37 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-CH_{DiPP}), 4.18 (dd, $^{2}J_{PH}$ = 12.8 Hz, $^{3}J_{HH}$ = 4.7 Hz, 2H, CH_2P), 2.42 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.55 (d, $^{3}J_{PH}$ = 16.3 Hz, 18H, C(CH_3)$_3$), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.18 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 153.3 (d, $^{2}J_{PC}$ = 8.7 Hz, $C_{pyr.}$), 146.6 ($C_{pyr.}$), 145.5 (*o*-C_{DiPP}), 142.4 (CH$_{pyr.}$), 138.0 (NC$H_{imid.}$N), 132.2 (*p*-CH$_{DiPP}$), 130.6 (NC_{DiPP}), 127.1 (d, $^{3}J_{PC}$ = 6.5 Hz, CH$_{pyr.}$), 125.6 (CH$_{imid.}$), 124.9 (*m*-CH$_{DiPP}$), 122.3 (CH$_{imid.}$), 115.7 (CH$_{pyr.}$), 33.5 (d, $^{1}J_{PC}$ = 34.3 Hz, C(CH_3)$_3$), 29.2 (CH(CH_3)$_2$), 27.6 (C(CH$_3$)$_3$), 24.5 (CH(CH$_3$)$_2$), 24.2 (CH(CH$_3$)$_2$), 24.2 (d, $^{1}J_{PC}$ = 41.4 Hz, CH$_2$P, confirmed by DEPT and ^{1}H-^{13}C HSQC).

^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 26.7 (dm, $^{1}J_{PH}$ = 508 Hz, PH).



Synthesis of 1-(6-((di-*tert*-butylphosphanyl)methyl)pyridin-2-yl)-3-(2,6-diisopropylphenyl)-imidazol-2-ylidene ($L^{t\text{-}Bu}$)

To a suspension of $\mathbf{L}^{t\text{-}Bu}\cdot$2HBr (0.282 g, 0.45 mmol) in THF (5 mL) precooled at –78 °C was added a solution of KHMDS (0.184 g, 0.92 mmol) in THF (5 mL). The resulting suspension was allowed to reach room temperature and stirred for 1 h, giving a suspension of KBr in a yellow solution. Removal of the volatiles under reduced pressure, extraction of the resulting solid with diethyl ether (10 mL), filtration and evaporation of the solvent gave $\mathbf{L}^{t\text{-}Bu}$ as a light yellow solid. Yield: 0.188 g (0.41 mmol), 90%. Satisfactory elemental analysis data could not be obtained due to the air sensitivity of the compound.

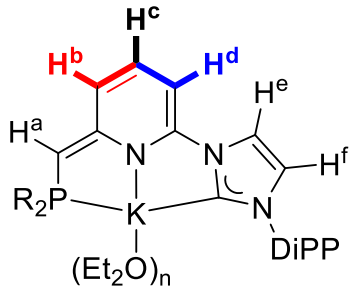
^{1}H NMR (400.13 MHz, C_6D_6): δ 8.60 (br d, $^{3}J_{HH}$ = 8.0 Hz, 1H, *m*-C$H_{pyr.}$), 8.47 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$), 7.27 (dd, $^{3}J_{HH}$ = 8.4, 7.2 Hz, 1H, *p*-CH_{DiPP}), 7.18-7.12 (m, 3H, *p*-C$H_{pyr.}$ + *m*-CH_{DiPP}), 7.07 (ddd, $^{3}J_{HH}$ = 7.6 Hz, J_{PH} = 1.0 Hz, $^{4}J_{HH}$ = 0.7 Hz, 1H, *m*-C$H_{pyr.}$), 6.64 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$), 2.99 (d, $^{2}J_{PH}$ = 2.8 Hz, 2H, CH_2P), 2.91 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, C$H(CH_3)_2$), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.12 (d, $^{3}J_{PH}$ = 10.8 Hz, 18H, C(CH_3)$_3$), 1.08 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6): δ 219.8 (C_{NHC}), 161.1 (d, $^{2}J_{PC}$ = 14.5 Hz, N$C_{pyr.}$), 153.5 (N$C_{pyr.}$), 146.3 (*o*-C_{DiPP}), 138.9 (NC_{DiPP}), 138.4 (*m*-CH$_{DiPP}$), 129.1 (*p*-CH$_{DiPP}$), 123.8 (*p*-CH$_{pyr.}$), 122.7 (CH$_{imid.}$), 121.4 (d, J_{PC} = 8.6 Hz, *m*-CH$_{pyr.}$), 116.4 (CH$_{imid.}$), 111.4 (d, J_{PC} = 1.8 Hz, *m*-CH$_{pyr.}$), 32.0 (d, $^{1}J_{PC}$ = 26.4 Hz, CH$_2$P), 31.9 (d, $^{1}J_{PC}$ = 24.5 Hz, $C(CH_3)_3$), 29.9 (d, $^{2}J_{PC}$ = 14.0 Hz, C(CH$_3$)$_3$), 28.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 35.4.

III. SYNTHETIC PROCEDURES FOR $KL_{\text{-}H}^{R}$

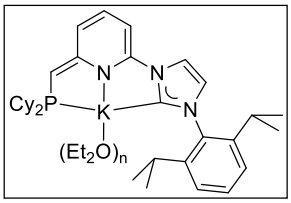
The synthesis of K$\mathbf{L}_{\text{-}H}^{R}$ (R = Cy, *t*-Bu) is described below. Recrystallisation from a mixture of Et_2O and pentane led to etherate complexes, with a loosely coordinated Et_2O molecule. Therefore, a variable amount ($0 \le n \le 1$) of residual coordinated Et_2O was detected in the ^{1}H NMR spectra depending on the drying time of $KL_{\text{-}H}^{R}$ under reduced pressure. In all cases, de-aromatisation of the picoline ring was evidenced by a through-bond $^{3}J_{Hb\text{-}Hc}$ coupling constant in a higher range (8.0 – 9.0 Hz), compared to $^{3}J_{Hc\text{-}Hd}$ (6.5-7.0 Hz). This consideration, togeher with the analysis of 2D correlation spectra (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC), was used for the assignment of the protons, as follows (Figure S1).



$^3J_{Hb\text{-}Hc}$ = 8.0 - 9.0 Hz

$^3J_{Hc\text{-}Hd}$ = 6.5 - 7.0 Hz

Figure S1 Assignment of the protons and selected $^3J_{HH}$ coupling constants in the dearomatised complexes K**L**$_{\text{-H}}^{\text{R}}$.



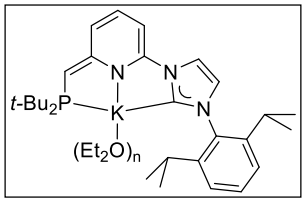
Synthesis of K$\mathbf{L}_{\text{-H}}^{\text{Cy}}$

To a suspension of **L**$^{\text{Cy}}$·2HBr (0.271 g, 0.40 mmol) in diethyl ether (5 mL) precooled at –78 °C was added a solution of KHMDS (0.247 g, 1.24 mmol) in diethyl ether (10 mL). The resulting suspension was allowed to reach room temperature and was stirred for 1 h, giving a suspension of KBr in a pink-red solution. Filtration and evaporation of the solvent gave almost quantitative yields of K$\mathbf{L}_{\text{-H}}^{\text{Cy}}$·n($Et_2O$) ($0 \le n \le 1$) as a pink-red *extremely* air-sensitive solid. Single crystals of K$\mathbf{L}_{\text{-H}}^{\text{Cy}}$·$Et_2O$ suitable for X-ray diffraction were obtained by slow evaporation of a diethyl ether solution of the compound in the glove box at room temperature. Satisfactory elemental analysis data could not be obtained, due to the extreme air sensitivity of the complex and the variable amount of volatile solvent incorporated in the isolated products (see also above).

^{1}H NMR (400.13 MHz, C_6D_6): δ 7.25 (dd, $^3J_{HH}$ = 8.2, 7.2 Hz, 1H, *p*-CH_{DiPP}), 7.14 (overlapping d, $^3J_{HH}$ = 8.2, 7.2 Hz, 2H, *m*-CH_{DiPP}), 7.04 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^e), 6.73 (ddd, $^3J_{HH}$ = 8.6, 6.7 Hz, $^5J_{PH}$ = 1.3 Hz, 1H, C$H_{pyr.}$ H^c), 6.48 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^b), 6.34 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^f), 5.43 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^d), 3.54 (d, $^2J_{PH}$ = 6.9 Hz, 1H, C*H*P H^a), 3.26 (q, $^3J_{HH}$ = 7.0 Hz, 1.3H, CH_2 residual Et_2O), 2.67 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.19-2.09 (m, 2H, Cy), 1.90-1.78 (m, 6H, Cy), 1.77-1.68 (m, 2H, Cy), 1.67-1.57 (m, 2H, Cy), 1.56-1.20 (m, 10H, Cy), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.11 (t, $^3J_{HH}$ = 7.0 Hz, 2.0H, CH_3 residual Et_2O), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 208.0 (C_{NHC}), 167.9 (d, $^2J_{PC}$ = 19.7 Hz, N$C_{pyr.}$), 153.5 (N$C_{pyr.}$), 146.4 (*o*-C_{DiPP}), 139.3 (NC_{DiPP}), 132.9 (d, $^4J_{PC}$ = 2.3 Hz, *C*H$_{pyr.}$ H^c), 129.1 (*p*-*C*H$_{DiPP}$), 123.6 (*m*-*C*H$_{DiPP}$), 120.1 (*C*H$_{imid.}$ H^f), 119.0 (*C*H$_{imid.}$ H^e), 116.7 (d, $^3J_{PC}$ = 8.1 Hz, *C*H$_{pyr.}$ H^b), 87.3 (*C*H$_{pyr.}$ H^d), 64.0 (d, $^1J_{PC}$ = 8.5 Hz, *C*HP), 36.1 (d, J_{PC} = 4.1 Hz, Cy), 32.0 (d, J_{PC} = 15.9 Hz, Cy), 29.5 (d, J_{PC} = 6.0 Hz, Cy), 28.4 (*C*H$(CH_3)_2$), 28.2 (d, J_{PC} = 12.5 Hz, Cy), 28.1 (d, J_{PC} = 6.8 Hz, Cy), 27.5 (Cy), 24.7 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ -15.5.



Synthesis of $KL_{-H}^{t\text{-}Bu}$

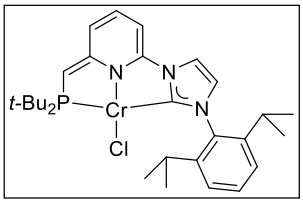
To a suspension of $\mathbf{L}^{t\text{-}Bu}\cdot$2HBr (0.250 g, 0.40 mmol) in diethyl ether (5 mL) precooled at –78 °C was added a solution of KHMDS (0.247 g, 1.24 mmol) in diethyl ether (10 mL). The resulting suspension was allowed to reach room temperature and stirred for 1 h, giving a suspension of KBr in a pink-red solution. Filtration and evaporation of the solvent gave almost quantitative yields of $K\mathbf{L}_{-H}^{t\text{-}Bu}\cdot n(Et_2O)$ ($0 \le n \le 1$) as a pink-red *extremely* air-sensitive solid. Satisfactory elemental analysis data could not be obtained, due to the extreme air sensitivity of the complex and the variable amount of volatile solvent incorporated in the isolated products (see also above).

^{1}H NMR (400.13 MHz, C_6D_6): δ 7.25 (dd, $^3J_{HH}$ = 8.4, 7.0 Hz, 1H, *p*-CH_{DiPP}), 7.13 (two overlapping d, $^3J_{HH}$ = 8.4, 7.0 Hz, 2H, *m*-CH_{DiPP}), 7.05 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^e), 6.76 (ddd, $^3J_{HH}$ = 8.7, 6.7 Hz, $^5J_{PH}$ = 1.4 Hz, 1H, C$H_{pyr.}$ H^c), 6.53 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^b), 6.33 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^f), 5.45 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^d), 3.83 (d, $^2J_{PH}$ = 7.1 Hz, 1H, C*H*P H^a), 3.27 (q, $^3J_{HH}$ = 7.0 Hz, 0.3H, CH_2 residual Et_2O), 2.64 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C$H(CH_3)_2$), 1.32 (d, $^3J_{PH}$ = 10.9 Hz, 18H, C$(CH_3)_3$), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH$(CH_3)_2$), 1.12 (t, $^3J_{HH}$ = 7.0 Hz, 0.5H, CH_3 residual Et_2O), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH$(CH_3)_2$).

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 208.1 (C_{NHC}), 167.5 (d, $^2J_{PC}$ = 21.0 Hz, N$C_{pyr.}$), 153.3 (N$C_{pyr.}$), 146.5 (*o*-C_{DiPP}), 139.4 (NC_{DiPP}), 132.8 (d, $^4J_{PC}$ = 2.7 Hz, *C*H$_{pyr.}$ H^c), 129.1 (*p*-CH_{DiPP}), 123.5 (*m*-CH_{DiPP}), 120.1 (*C*H$_{imid.}$ H^f), 118.9 (*C*H$_{imid.}$ H^e), 116.9 (d, $^3J_{PC}$ = 8.2 Hz, *C*H$_{pyr.}$ H^b), 87.0 (*C*H$_{pyr.}$ H^d), 65.9 (*C*H_2 residual Et_2O), 64.6 (d, $^1J_{PC}$ = 6.9 Hz, *C*HP), 33.4 (d, $^1J_{PC}$ = 12.6 Hz, *C*$(CH_3)_3$), 30.8 (d, $^2J_{PC}$ = 13.1 Hz, C*C*$H_3)_3$), 28.4 (*C*H$(CH_3)_2$), 24.7 (CH(*C*$H_3)_2$), 24.1 (CH(*C*$H_3)_2$), 15.6 (*C*H_3 residual Et_2O).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 14.1.

IV. SYNTHETIC PROCEDURE FOR [CrCl($L_{-H}^{t\text{-}Bu}$)]



To a solution of [$CrCl_2(THF)_2$] (0.053 g, 0.20 mmol) in THF (5 mL) precooled at –78 °C was added a solution of $K\mathbf{L}_{-H}^{t\text{-}Bu}$ (0.100 g, 0.20 mmol) in THF (10 mL). The resulting dark-red purple solution was allowed to reach room temperature and was stirred for 1 h. The volatiles were evaporated under reduced pressure, the residue was washed successively with pentane and toluene and the washings were discarded. The remaining solid was extracted in THF/toluene (*ca.* 7 ml of 4/1 mixture) and the solution was filtered. The intensely coloured red/purple solution was evaporated to dryness and the residue was redissolved in THF (*ca*. 3 ml). Slow evaporation of the THF solution gave dark red/purple

crystals of [CrCl($\mathbf{L}_{\text{-H}}^{t\text{-Bu}}$)]. An additional amount of complex can be obtained by evaporation of the supernatant to dryness.

Anal. Calcd for $C_{29}H_{41}ClCrN_3P$ (550.09): C, 63.32; H, 7.51; N, 7.64. Found: C, 60.68; H, 7.31; N, 7.24.

No better elemental analyses could be obtained due to the extreme air sensitivity of the complex. The values found correspond tentatively to a partially oxidised complex *i.e*. $C_{29}H_{41}ClCrN_3P$ + 3/2 O: C, 60.67; H, 7.20; N, 7.32.

^{1}H NMR (400.13 MHz, THF-d_8): δ 14.2 (br s, *ca.* 16H), 9.4 (s, 4H), 6.5 (s, 3H), 3.4 (s, 1H), 2.4 (br s, *ca.* 8H), 1.3 (s, 1H), 1.1 (s, 1H), 0.9 (s, 1H), 0.1 (s, 1H), -10.6 (s, 1H), -17.0 (s, 1H), -20.9 (s, 1H), -23.5 (s, 1H), -49.1 (s, 1H).

V. DETERMINATION OF THE MAGNETIC SUSCEPTIBILITY OF [CrCl($\mathbf{L}_{\text{-H}}^{t\text{-Bu}}$)]

The determination of the magnetic susceptibility was carried out using Evans' method[3] for a THF solution of [CrCl($\mathbf{L}_{\text{-H}}^{t\text{-Bu}}$)] containing hexamethyldisiloxane (16 % w/w) and using a capillary of THF-d_8 with hexamethyldisiloxane (*ca.* 35 % w/w) as a diamagnetic standard. The solvent correction was not applied[4] and the diamagnetic corrections were calculated using Pascal's constants.[5]

Typical procedure: In a Young NMR tube, 0.013 g (23.6 μmol) of [CrCl($\mathbf{L}_{\text{-H}}^{t\text{-Bu}}$)] was dissolved in a mixture of THF (450 μL) and hexamethyldisiloxane (HMDS, 100 μL). An insert filled with a mixture of THF-d_8 and HMDS in a 3:2 ratio was placed in the tube and the ^{1}H NMR spectrum was recorded at 400.13 MHz and 298 K.

μ_{eff} = 4.47(6) μ_B

VI. STUDIES OF THE SOLUTION STRUCTURES OF KL_{-H}^{R} BY NMR SPECTROSCOPIC METHODS

VI.1. NOESY structural analysis of KL_{-H}^{Cy} in C_6D_6 solution

KL_{-H}^{Cy}, prepared as detailed above, was dissolved in C_6D_6 and the NOESY experiment was performed at room temperature (Figure S2). Only one isomer was detected, the structure of which was assigned as *Z*-syn, confirming that the solid-state structure was retained in C_6D_6 solution. Full 1D ^{1}H-NMR spectral assignment of the *Z*-syn isomer followed.

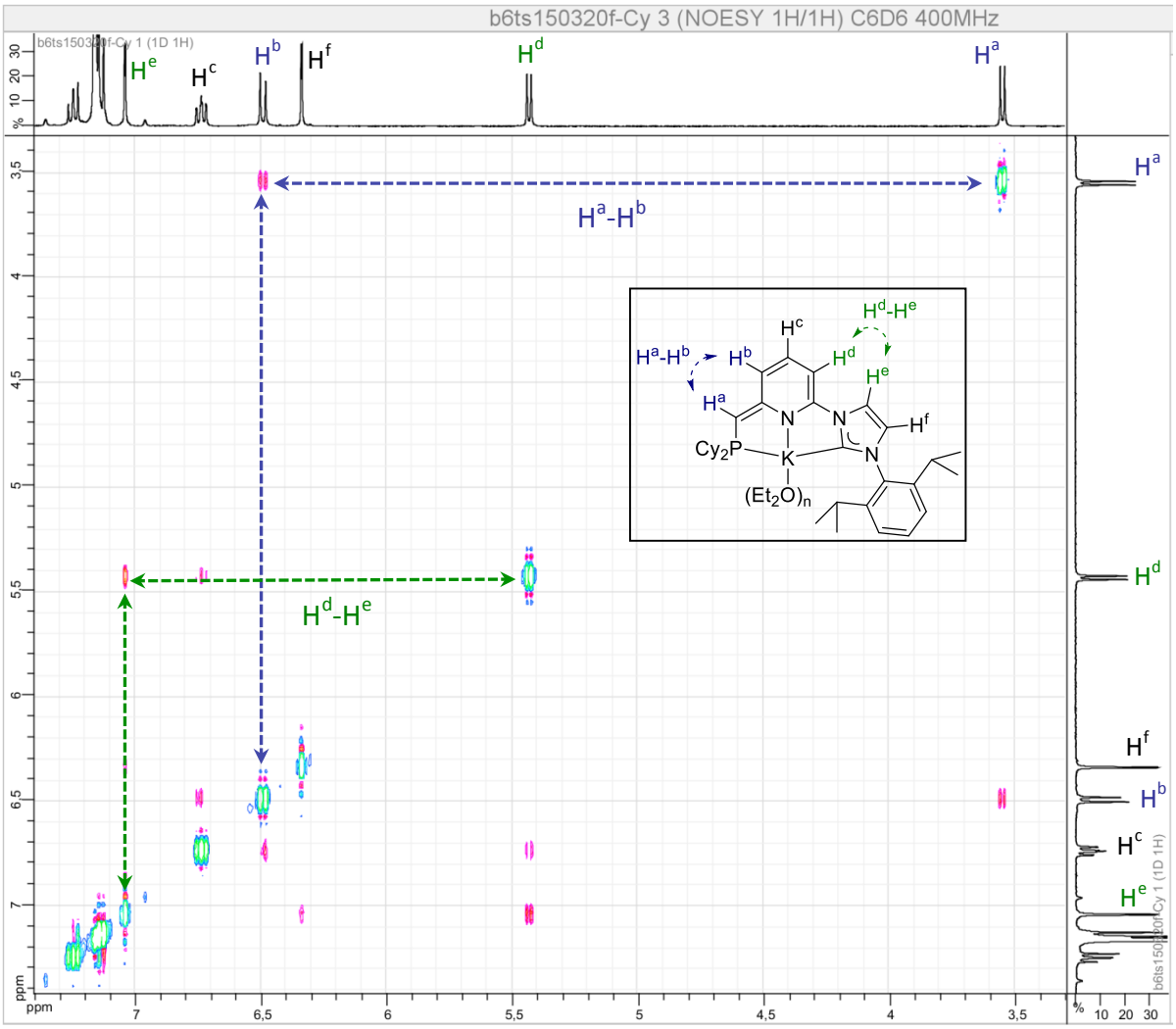
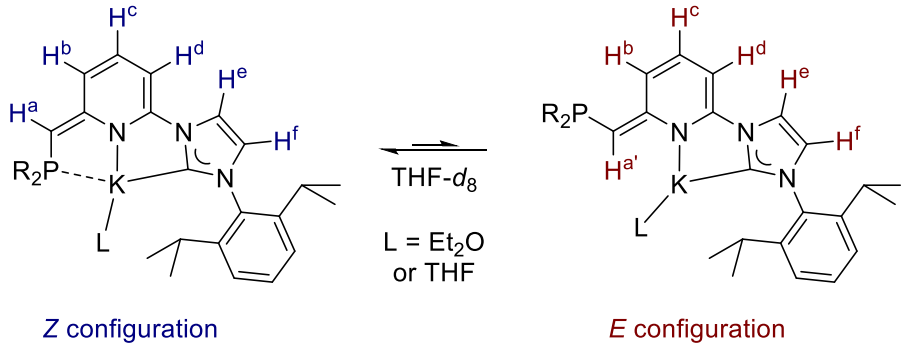


Figure S2 Representative NOESY NMR spectrum of KL_{-H}^{Cy} in C_6D_6. The through-space H^a-H^b and H^d-H^e correlation peaks have been highlighted and indicate retention of the solid-state structure in C_6D_6.

VI.2. *Z* → *E* Isomerisation of KL_{-H}^{R} on dissolution in THF-d_8

Upon dissolution of KL_{-H}^{R} in THF-d_8, isomerisation of the exocyclic double bond was established which leads to a mixture of *Z* and *E* isomers, with a predominance of the *Z* configuration (Scheme S2).



Scheme S2 Isomerisation about the exocyclic double bond upon dissolution in THF-d_8. Note that the conformation of the carbene moiety is retained as indicated by NOESY analyses (Figure S4, *vide infra* and main text).

The assignment of the absolute configuration of the exocyclic double bond was based on J_{HH} and J_{PH} coupling constants (Figure S3) as well as ^{1}H-^{1}H NOESY and ^{31}P-^{1}H HOESY NMR experiments.[6] The distinction between long-range J_{HH} and J_{PH} coupling constants succeeded by recording both standard and phosphorus-decoupled ^{1}H NMR spectra. (The mixing time for the ^{1}H-^{1}H NOESY was set at τ_m = 0.80 s; in the ^{31}P-^{1}H HOESY magnetisation transfer from ^{31}P to ^{1}H *i.e.* ^{1}H detection occurs;[7] τ_m = 0.70 s, relaxation delay D1 = 2.5 s, 14 h of acquisition).

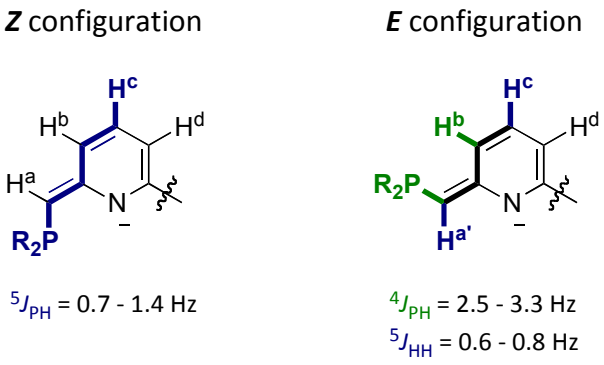


Figure S3 Coupling constants extracted after full spectral assignments. These values were used for the facile quantitative study of *Z*/*E* isomerisation by 1D NMR.

VI.2.1. KL_{-H}^{Cy} isomerisation

KL_{-H}^{Cy} was prepared as detailed above, dissolved in THF-d_8 and the isomerisation was monitored by ^{1}H-NMR spectroscopy. The *E*/*Z* ratio was 1 : 4.5 after the first 10 min and reached the final value of 1 : 1.2 (corresponding to a thermodynamic equilibrium mixture) after 4.5 h.

VI.2.1.1. ^{1}H-NMR spectral assignment of the Z/E equilibrium mixture

Values in bold characters refer to the pathways in Figure S3.

Z isomer (major)

^{1}H NMR (400.13 MHz, THF-d_8): δ 7.44 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^e), 7.34 (dd, $^3J_{HH}$ = 8.4, 7.0 Hz, 1H, *p*-CH_{DiPP}), 7.24 (two overlapping d, $^3J_{HH}$ = 8.4, 7.0 Hz, 2H, *m*-CH_{DiPP}), 6.94 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^f), 6.22 (ddd, $^3J_{HH}$ = 8.5, 6.8 Hz, **$^5J_{PH}$ = 1.3 Hz**, 1H, C$H_{pyr.}$ H^c), 5.74 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^b), 5.16 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^d), 3.38 (q, $^3J_{HH}$ = 7.0 Hz, 0.3H, CH_2 residual Et_2O), 2.91 (d, $^2J_{PH}$ = 7.3 Hz, 1H, C*H*P H^a), 2.68 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.87-1.75 (m, 2H, Cy), 1.70-1.52 (m, 8H, Cy), 1.34-1.12 (m, 12H, Cy), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.10 (t, $^3J_{HH}$ = 7.0 Hz, 0.5H, CH_3 residual Et_2O).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -17.5.

E isomer (minor)

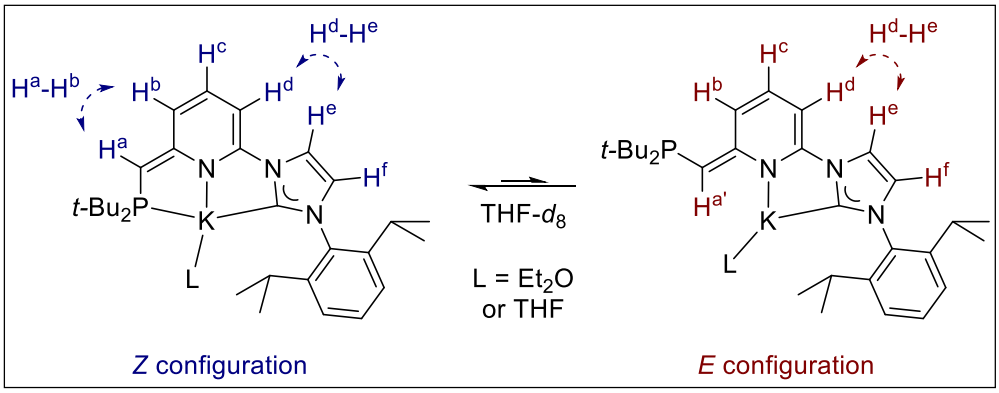
^{1}H NMR (400.13 MHz, THF-d_8): δ 7.44 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^e), 7.34 (dd, $^3J_{HH}$ = 8.4, 7.0 Hz, 1H, *p*-CH_{DiPP}), 7.24 (two overlapping d, $^3J_{HH}$ = 8.4, 7.0 Hz, 2H, *m*-CH_{DiPP}), 6.93 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^f), 6.69 (ddd, $^3J_{HH}$ = 8.9 Hz, **$^4J_{PH}$ = 3.0 Hz**, $^4J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^b), 6.31 (ddd, $^3J_{HH}$ = 8.9, 6.7 Hz, **$^5J_{HH}$ = 0.7 Hz**, 1H, C$H_{pyr.}$ H^c), 5.14 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^d), 3.38 (q, $^3J_{HH}$ = 7.0 Hz, 0.3H, CH_2 residual Et_2O), 2.92 (dd, $^2J_{PH}$ = 7.8 Hz, **$^5J_{HH}$ = 0.7 Hz**, 1H, C*H*P H$^{a'}$), 2.68 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.87-1.75 (m, 2H, Cy), 1.70-1.52 (m, 8H, Cy), 1.34-1.12 (m, 12H, Cy), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.11 (t, $^3J_{HH}$ = 7.0 Hz, 0.5H, CH_3 residual Et_2O), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -16.6.

VI.2.2. $KL_{-H}^{t\text{-}Bu}$ isomerisation

$KL_{-H}^{t\text{-}Bu}$ prepared as detailed above, was dissolved in THF-d_8 and the isomerisation was monitored by ^{1}H-NMR spectroscopy. *The E*/*Z* ratio was 1 : 7 after the first 10 min, 1 : 4 after 1 h and reached the end value of 1 : 2.5 (corresponding to a thermodynamic equilibrium mixture) after 3.5 h (See following Section VI.2.2.1 for the NOESY–based assignment of the isomers).

VI.2.2.1. NOESY structural analysis of the E/Z equilibrium mixture of $KL_{-H}^{t\text{-}Bu}$ in THF-d_8



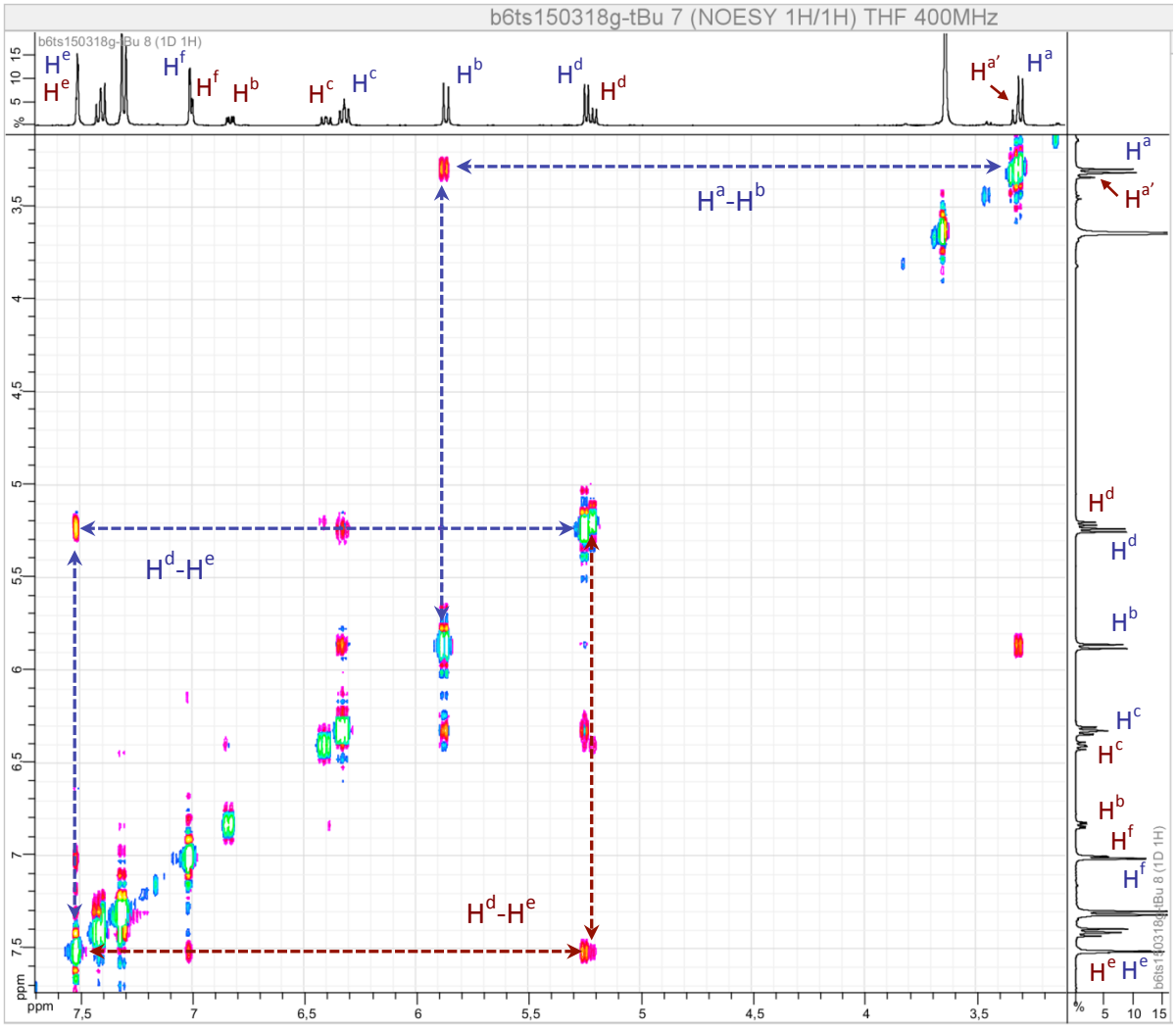


Figure S4 Representative NOESY spectrum of $KL_{-H}^{t\text{-}Bu}$ in THF-d_8. The absence of through-space $H^{a'}$-H^b correlation peaks indicates the formation of the *E* isomer upon dissolution in THF. For both isomers, H^d-H^e correlation peaks suggest conformational retention of the NHC moiety.

VI.2.2.2. ^{1}H-NMR spectral assignment of the Z/E equilibrium mixture

Values in bold characters refer to the pathways in Figure S3.

Z isomer (major)

^{1}H NMR (400.13 MHz, THF-d_8): δ 7.44 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^{e}), 7.34 (dd, $^{3}J_{HH}$ = 8.3, 7.1 Hz, 1H, *p*-CH_{DiPP}), 7.24 (two overlapping d, $^{3}J_{HH}$ = 8.3, 7.1 Hz, 2H, *m*-CH_{DiPP}), 6.94 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^{f}), 6.25 (ddd, $^{3}J_{HH}$ = 8.7, 6.8 Hz, **$^{5}J_{PH}$ = 1.4 Hz**, 1H, C$H_{pyr.}$ H^{c}), 5.80 (dd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^{b}), 5.17 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^{d}), 3.24 (d, $^{2}J_{PH}$ = 7.4 Hz, 1H, C*H*P H^{a}), 2.67 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.12 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.05 (d, $^{3}J_{PH}$ = 10.7 Hz, 18H, C(CH_3)$_3$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 10.5.

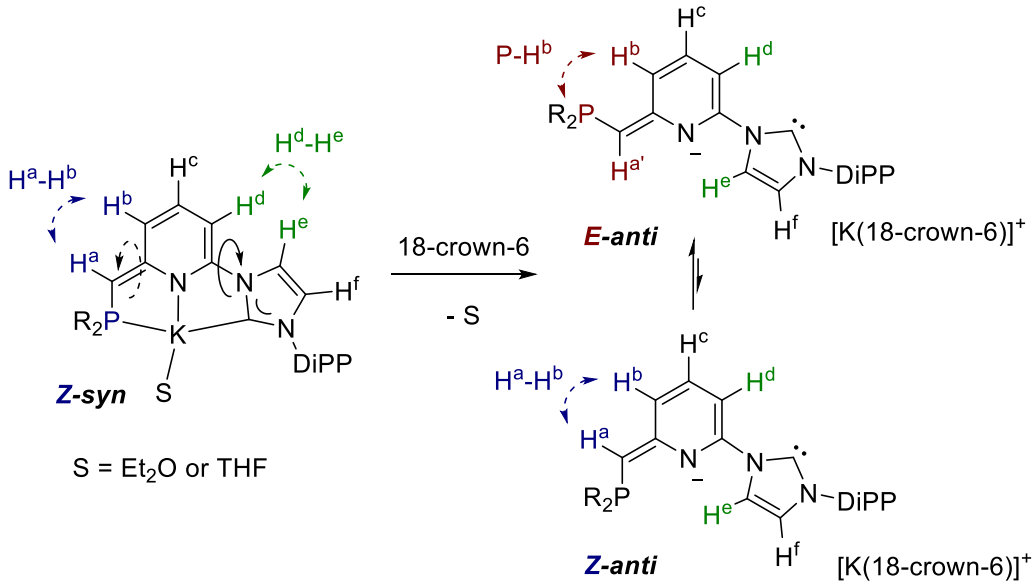
E isomer (minor)

^{1}H NMR (400.13 MHz, THF-d_8): δ 7.45 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^{e}), 7.34 (dd, $^{3}J_{HH}$ = 8.3, 7.1 Hz, 1H, *p*-CH_{DiPP}), 7.24 (two overlapping d, $^{3}J_{HH}$ = 8.3, 7.1 Hz, 2H, *m*-CH_{DiPP}), 6.93 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$ H^{f}), 6.76 (ddd, $^{3}J_{HH}$ = 8.9 Hz, **$^{4}J_{PH}$ = 3.3 Hz**, $^{4}J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^{b}), 6.33 (ddd, $^{3}J_{HH}$ = 8.9, 6.6 Hz, **$^{5}J_{HH}$ = 0.8 Hz**, 1H, C$H_{pyr.}$ H^{c}), 5.14 (dd, $^{3}J_{HH}$ = 6.6 Hz, $^{4}J_{HH}$ = 0.6 Hz, 1H, C$H_{pyr.}$ H^{d}), 3.26 (dd, $^{2}J_{PH}$ = 8.4 Hz, **$^{5}J_{HH}$ = 0.8 Hz**, 1H, C*H*P H$^{a'}$), 2.69 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.13 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.10 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.06 (d, $^{3}J_{PH}$ = 10.3 Hz, 18H, C(CH_3)$_3$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 11.6.

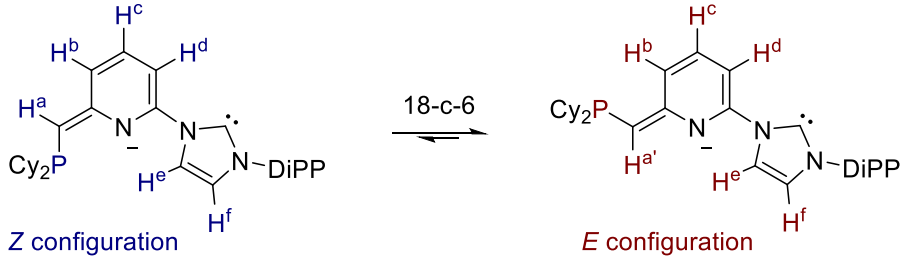
VI.3. Effect of the addition of 18-crown-6 on the *E/Z* equilibrium

To a solution of KL_{-H}^{R} in C_6D_6 or THF-d_8 was added *ca.* 1.2 equiv. of 18-crown-6 (18-c-6). The ^{1}H and ^{31}P NMR spectra were recorded after different evolution times and revealed the disappearance of the added *Z*-syn isomer and the formation of a new equilibrium mixture, the formation of which was rationalised by two simultaneous isomerisation processes: the first originating from the exocyclic double bond and the second from rotation about the $C_{picoline}$-N_{NHC} single bond, as depicted in Scheme S3.



Scheme S3 Selected through-space dipolar interactions extracted from ^{1}H-^{1}H NOESY and ^{31}P-^{1}H HOESY spectra and used for the determination of *Z*/*E* configurations. The conformation of the NHC moiety was established by ^{1}H-^{1}H NOESY.

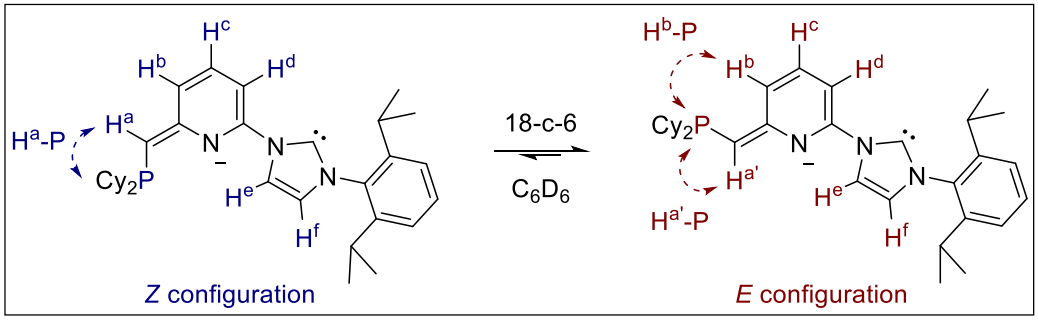
VI.3.1. Study of KL_{-H}^{Cy}



Scheme S4 Equilibrium between the *Z* and *E* configurations for KL_{-H}^{Cy} in the presence of 18-c-6.

VI.3.1.1. HOESY structural analysis of KL-H^{Cy} in C_6D_6 in the presence of 18-c-6.

The assignment of the *E*-geometry to the major isomer in C_6D_6 in the presence of 18-c-6 was established by ^{31}P-^{1}H HOESY as shown in Figure S5.



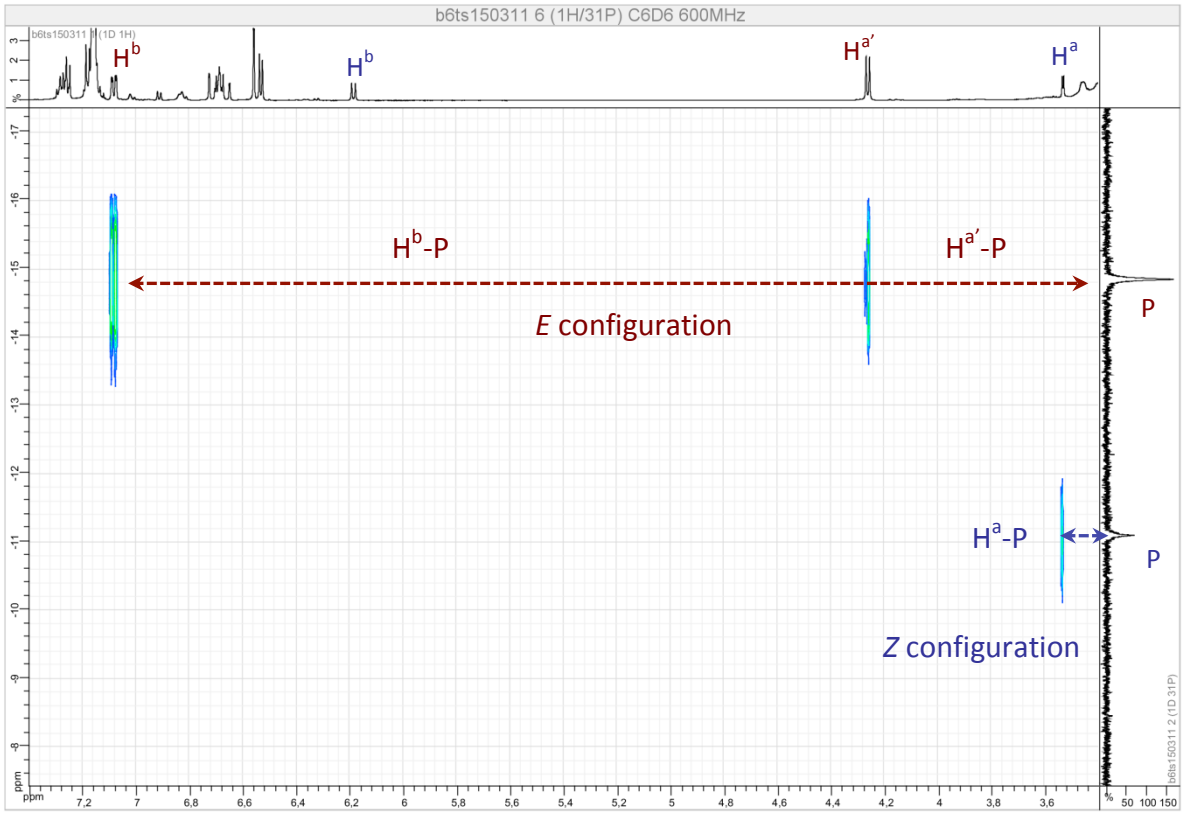


Figure S5 Representative ^{31}P-^{1}H HOESY spectrum in C_6D_6 in the presence of 18-c-6. Through-space H^a-P and $H^{a'}$-P correlation peaks are present for both isomers but only the H^b-P correlation peak exists for the *E* isomer.

VI.3.1.2. NOESY structural analysis of KL$_{-H}^{Cy}$ in C_6D_6 in the presence of 18-c-6.

The assignment *E*-anti geometry to the major isomer in C_6D_6 in the presence of 18-c-6 was established by the NOESY.

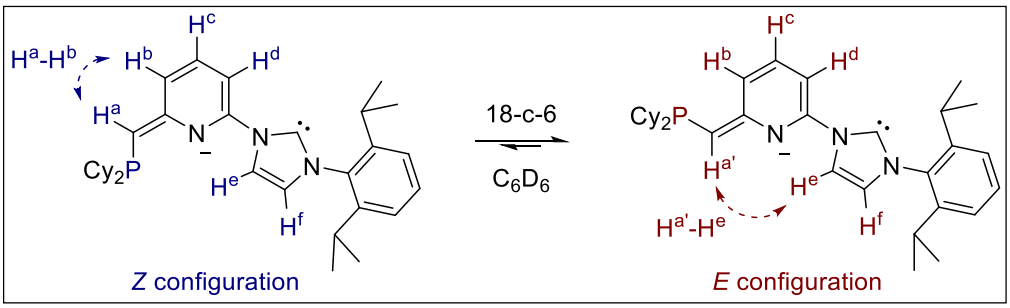
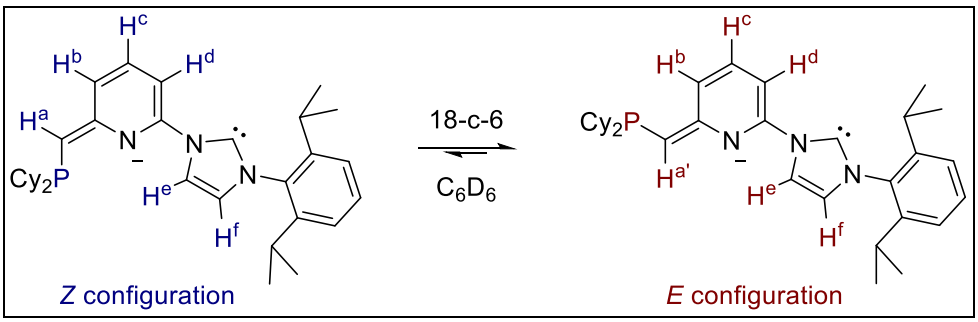


Figure S6 Representative NOESY spectrum of KL$_{-H}^{Cy}$ in C_6D_6 in the presence of 18-c-6. The H^a-H^b correlation peak corresponds to the *Z* isomer, while the absence of through-space H^d-H^e interaction suggests a 180° flip of the NHC ring. A weak $H^{a'}$-H^e correlation peak confirms the rotational conformation of the NHC moiety for the *E* isomer.

VI.3.1.3. NOESY/EXSY detail of the chemical exchange between the two isomers of KL-H^{Cy} in C_6D_6 in the presence of 18-c-6.



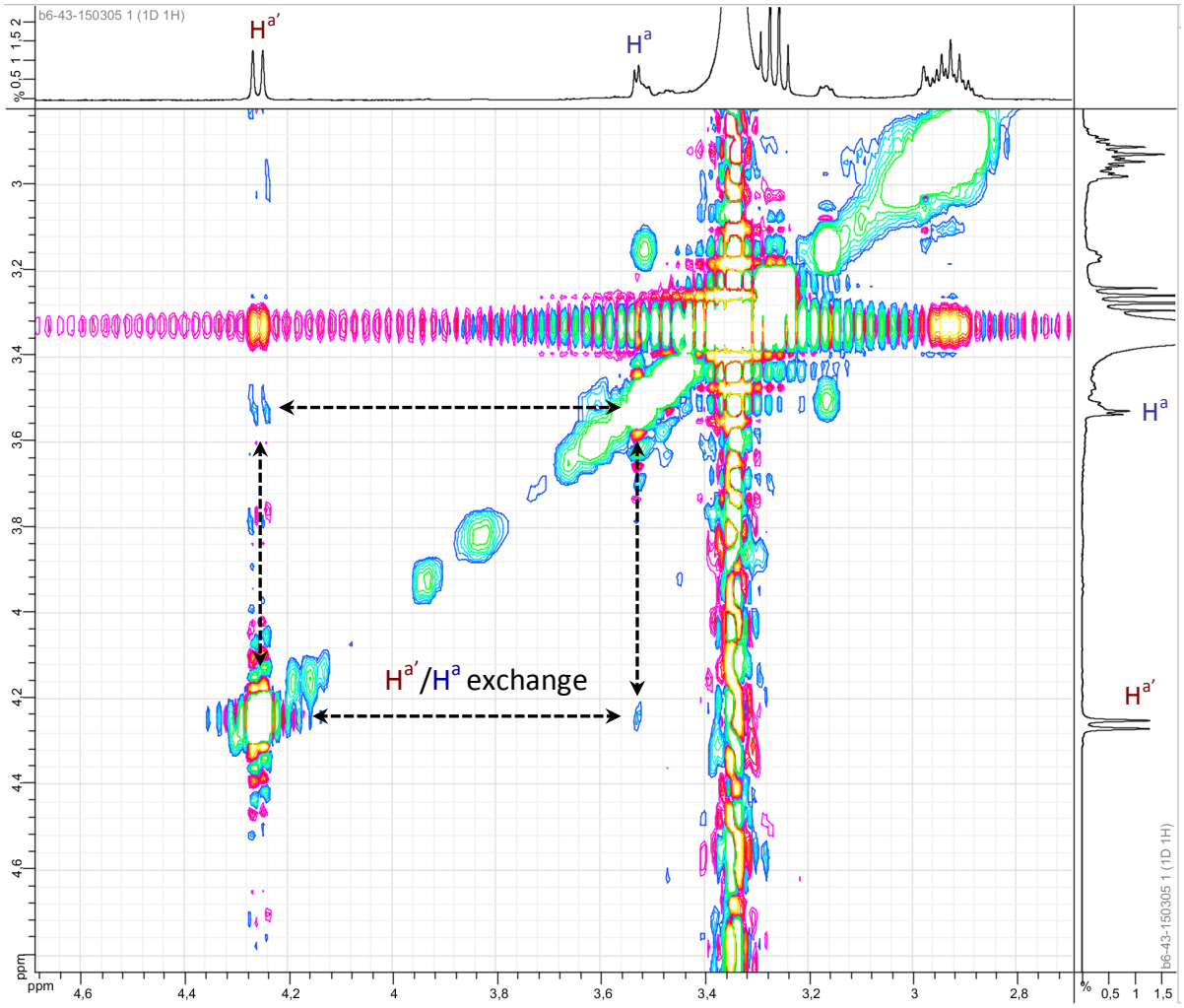


Figure S7 Representative NOESY spectrum of the exchange between H^a (*Z* isomer) and H$^{a'}$ (*E* isomer) of KL-H^{Cy} in C_6D_6 in the presence of 18-c-6. The H$^{a'}$/H^a cross-peaks present the same phase as the diagonal and correspond to exchange (EXSY) peaks.

VI.3.1.4. ^{1}H-NMR spectral assignment of the Z/E equilibrium mixture in C_6D_6 with ca. 1.1 equiv. 18-c-6

A *Z/E* ratio at equilibrium of *ca*. 1 : 2.6 was determined by ^{1}H-NMR spectroscopy. Values in bold characters refer to the pathways in Figure S3.

Z isomer (minor)

^{1}H NMR (400.13 MHz, C_6D_6): δ 8.81 (d, $^3J_{HH}$ = 1.5 Hz, 1H, C*H*$_{imid.}$ H^e), 7.29 (dd, $^3J_{HH}$ = 8.4, 7.1 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.18 (two overlapping d, $^3J_{HH}$ = 8.4, 7.1 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.84 (br d, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*$_{pyr.}$ H^d), 6.73 (d, $^3J_{HH}$ = 1.5 Hz, 1H, C*H*$_{imid.}$ H^f), 6.69 (ddd, $^3J_{HH}$ = 8.4, 6.7 Hz, **$^5J_{PH}$ = 1.0 Hz**, 1H, C*H*$_{pyr.}$ H^c), 6.18 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, C*H*$_{pyr.}$ H^b), 3.53 (d, $^2J_{PH}$ = 3.3 Hz, 1H, C*H*P H^a), 3.34 (s, 18-c-6), 2.94 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.40-2.18 (m, 4H, Cy), 2.01-1.55 (m, 12H, Cy), 1.52-1.24 (m, 6H, Cy), 1.23-1.08 (two overlapping doublets, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -11.0.

E isomer (major)

^{1}H NMR (400.13 MHz, C_6D_6): δ 8.52 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^e), 7.26 (dd, $^3J_{HH}$ = 8.4, 7.1 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.18 (overlapping d, $^3J_{HH}$ = 8.4, 7.1 Hz, 2H, *m*-C*H*$_{DiPP}$), 7.08 (ddd, $^3J_{HH}$ = 8.6 Hz, **$^4J_{PH}$ = 2.6 Hz**, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^b), 6.69 (ddd, $^3J_{HH}$ = 8.6, 6.7 Hz, **$^5J_{HH}$ = 0.6 Hz**, 1H, C*H*$_{pyr.}$ H^c), 6.56 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^f), 6.53 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^d), 4.26 (br d, $^2J_{PH}$ = 7.6 Hz, 1H, C*H*P H$^{a'}$), 3.34 (s, 18-c-6), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.40-2.18 (m, 4H, Cy), 2.01-1.55 (m, 12H, Cy), 1.52-1.24 (m, 6H, Cy), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -14.8.

VI.3.1.5. ^{1}H-NMR spectral assignment of the Z/E equilibrium mixture in THF-d_8 with ca. 1.2 equiv. 18-c-6

A *Z/E* ratio at equilibrium of *ca*. 1 : 5.0 was determined by ^{1}H-NMR spectroscopy.

Values in bold characters refer to the pathways in Figure S3.

Z isomer (minor)

^{1}H NMR (400.13 MHz, THF-d_8): δ 8.41 (d, $^3J_{HH}$ = 1.5 Hz, 1H, C*H*$_{imid.}$ H^e), 7.27 (dd, $^3J_{HH}$ = 8.2, 7.2 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.17 (two overlapping d, $^3J_{HH}$ = 8.2, 7.2 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.72 (br s overlapping with signal of the major isomer, 1H, C*H*$_{imid.}$ H^f), 6.15 (ddd, $^3J_{HH}$ = 8.3, 6.8 Hz, **$^5J_{PH}$ = 0.7 Hz**, 1H, C*H*$_{pyr.}$ H^c), 5.95 (br d, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*$_{pyr.}$ H^d), 5.55 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C*H*$_{pyr.}$ H^b), 3.57 (s, 18-c-6), 3.02 (s, 1H, C*H*P H^a), 2.75 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.94-1.15 (m, 22H, Cy), 1.15-1.07 (overlapping doublets, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$).

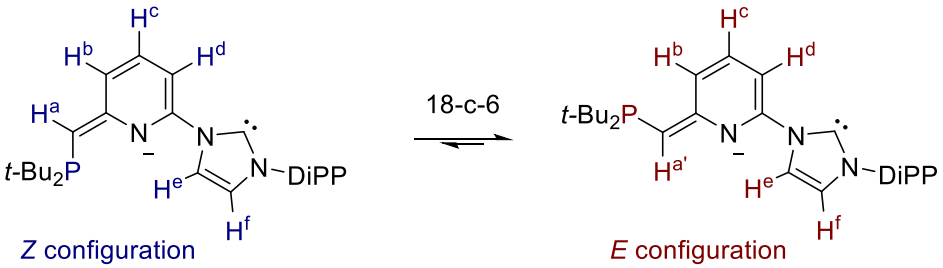
^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -14.0.

E isomer (major)

^{1}H NMR (400.13 MHz, THF-d_8): δ 8.20 (d, $^{3}J_{HH}$ = 1.6 Hz, 1H, C$H_{imid.}$ H^{e}), 7.27 (dd, $^{3}J_{HH}$ = 8.2, 7.2 Hz, 1H, *p*-CH_{DiPP}), 7.17 (two overlapping d, $^{3}J_{HH}$ = 8.2, 7.2 Hz, 2H, *m*-CH_{DiPP}), 6.72 (d, $^{3}J_{HH}$ = 1.6 Hz, 1H, C$H_{imid.}$ H^{f}), 6.44 (ddd, $^{3}J_{HH}$ = 8.6 Hz, **$^{4}J_{PH}$ = 2.5 Hz**, $^{4}J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^{b}), 6.20 (ddd, $^{3}J_{HH}$ = 8.6, 6.8 Hz, **$^{5}J_{HH}$ = 0.5 Hz**, 1H, C$H_{pyr.}$ H^{c}), 5.94 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 0.7 Hz, 1H, C$H_{pyr.}$ H^{d}), 3.57 (s, 18-c-6), 3.20 (d, $^{2}J_{PH}$ = 8.5 Hz, 1H, CHP H$^{a'}$), 2.76 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 1.94-1.15 (m, 22H, Cy), 1.12 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.09 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ -15.1.

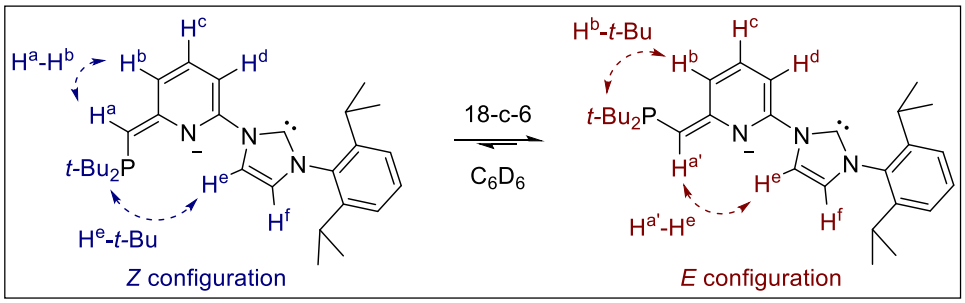
VI.3.2. Study of KL$_{-H}^{t\text{-Bu}}$



Scheme S5 Equilibrium between *Z* and *E* configurations for K**L**$_{-H}^{t\text{-Bu}}$ in the presence of 18-c-6.

VI.3.2.1. NOESY structural analysis of KL$_{-H}^{t\text{-}Bu}$ in C_6D_6 in the presence of 18-c-6.

The assignment of the *E-anti* geometry to the major isomer in the equilibrium established on dissolving K**L**$_{-H}^{t\text{-}Bu}$ in C_6D_6 in the presence of 18-c-6 was established by NOESY experiments.



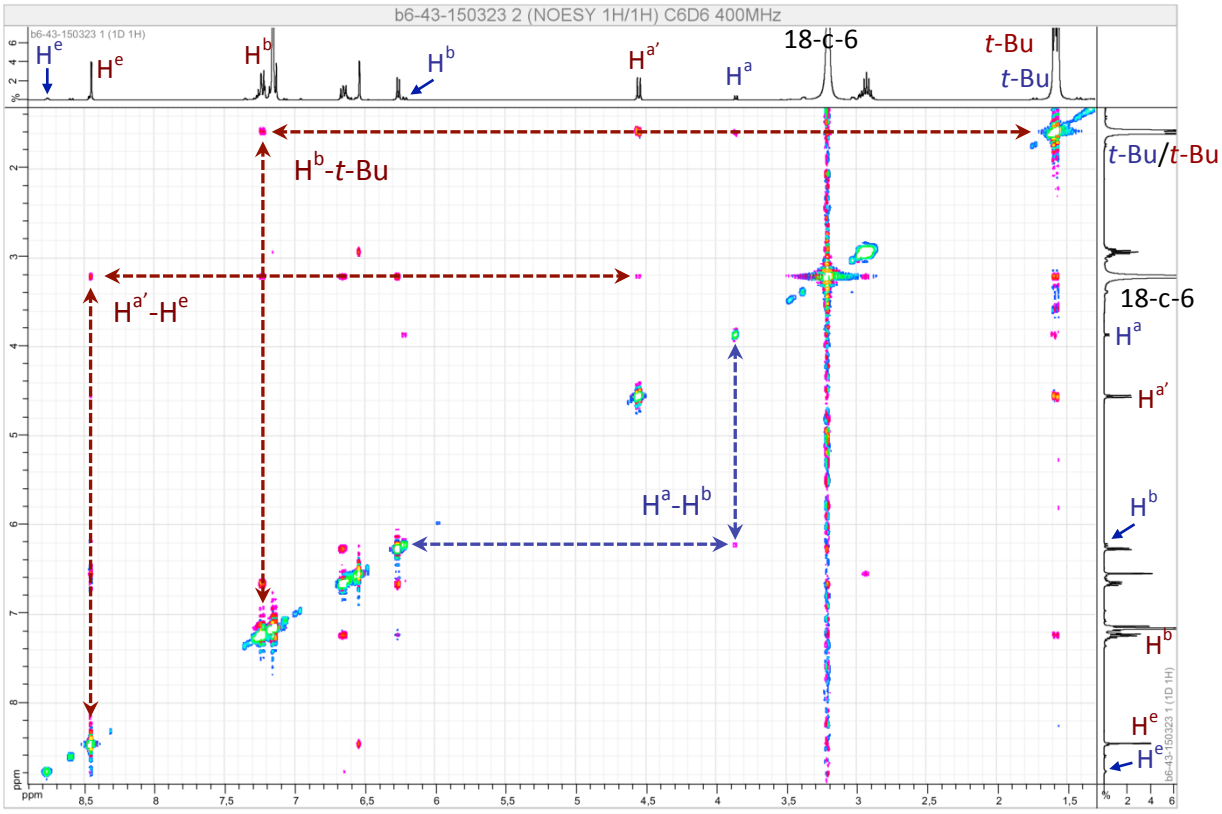
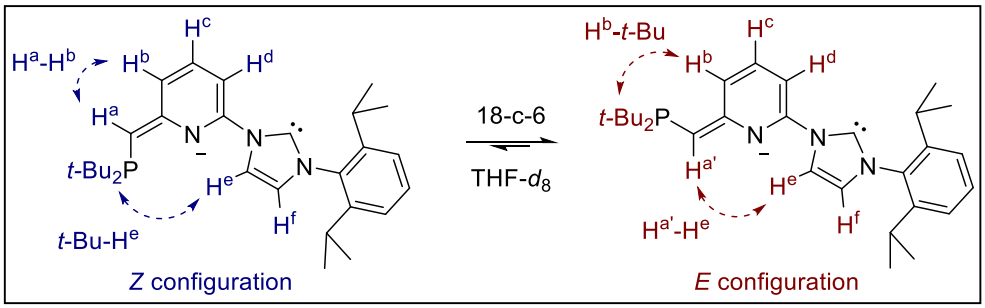


Figure S8 Selection of the NOESY spectrum of K**L**$_{-H}^{t\text{-}Bu}$ in C_6D_6 in the presence of 18-c-6. The H^a-H^b (resp. H^b-*t*-Bu) correlation peak corresponds to the *Z* (resp. *E*) isomer. The absence of through-space H^d-H^e interaction suggests a 180° flip of the NHC, which is confirmed by the weak $H^{a'}$-H^e interaction for the *E* isomer. Due to the low amount of *Z* isomer, the corresponding H^e-*t*-Bu correlation peak cannot be seen here but can be found on a perusal of the NOESY spectrum.

VI.3.2.2. NOESY structural analysis of KL$_{-H}^{t\text{-}Bu}$ in THF-d_8 in the presence of 18-c-6.



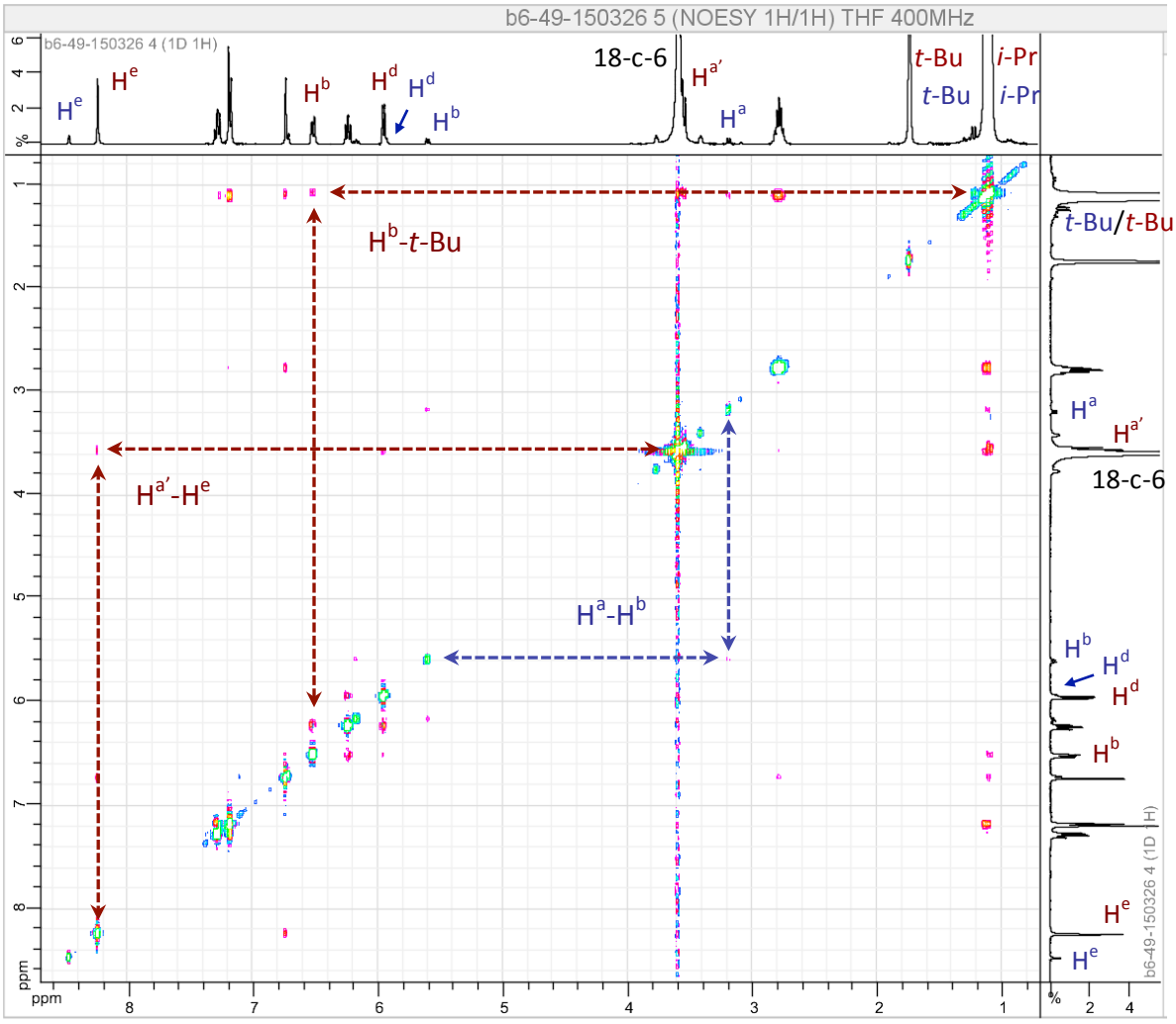


Figure S9 Representative NOESY spectrum of KL$_{-H}^{t\text{-}Bu}$ in THF-d_8 in the presence of 18-c-6. The H^a-H^b (resp. H^b-*t*-Bu) correlation peak corresponds to the *Z* (resp. *E*) isomer. The absence of through-space H^d-H^e interaction suggests a 180° flip of the NHC, which is confirmed by the weak H$^{a'}$-H^e interaction for the *E* isomer. Due to the low amount of *Z* isomer, the corresponding H^e-*t*-Bu correlation peak cannot be seen here but can be found on a perusal of the NOESY spectrum. Note that *iso*-propyl and *tert*-butyl protons are overlapping, as well as H$^{a'}$ and 18-c-6 protons.

VI.3.2.3. ^{1}H-NMR spectral assignment of the *Z/E* equilibrium mixture in C_6D_6, with *ca.* 1.1 equiv. 18-c-6

A *Z/E* ratio at equilibrium of *ca*. 1 : 7.1 was determined by ^{1}H-NMR spectroscopy.

Values in bold characters refer to the pathways in Figure S3.

Z isomer (minor)

^{1}H NMR (400.13 MHz, C_6D_6): δ 8.76 (d, $^3J_{HH}$ = 1.4 Hz, 1H, C*H*$_{imid.}$ H^e), 7.27 (dd, $^3J_{HH}$ = 8.4, 7.1 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.14 (overlapping d, $^3J_{HH}$ = 8.4, 7.1 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.65-6.63 (m, 2H, C*H*$_{pyr.}$ H^d + C*H*$_{imid.}$ H^f), 6.62 (ddd, $^3J_{HH}$ = 8.3, 6.7 Hz, **$^5J_{PH}$ = 1.0 Hz**, 1H, C*H*$_{pyr.}$ H^c), 6.22 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C*H*$_{pyr.}$ H^b), 3.86 (d, $^2J_{PH}$ = 6.8 Hz, 1H, C*H*P H^a), 3.21 (s, 18-c-6), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.60 (d, $^3J_{PH}$ = 10.0 Hz, 18H, C(C*H*$_3$)$_3$), 1.23-1.06 (overlapping doublets, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 15.6.

E isomer (major)

^{1}H NMR (400.13 MHz, C_6D_6): δ 8.45 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^e), 7.24 (dd, $^3J_{HH}$ = 8.4, 7.1 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.23 (ddd, $^3J_{HH}$ = 8.8 Hz, **$^4J_{PH}$ = 2.9 Hz**, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^b), 7.14 (overlapping d, $^3J_{HH}$ = 8.4, 7.1 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.66 (ddd, $^3J_{HH}$ = 8.8, 6.5 Hz, **$^5J_{HH}$ = 0.6 Hz**, 1H, C*H*$_{pyr.}$ H^c), 6.54 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^f), 6.27 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^d), 4.55 (dd, $^2J_{PH}$ = 8.2 Hz, **$^5J_{HH}$ = 0.6 Hz**, 1H, C*H*P H$^{a'}$), 3.21 (s, 18-c-6), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.58 (d, $^3J_{PH}$ = 10.3 Hz, 18H, C(C*H*$_3$)$_3$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 15.3.

VI.3.2.4. ^{1}H-NMR spectral assignment of the Z/E equilibrium mixture in THF-d_8, with ca. 1.1 equiv. 18-c-6

A *Z/E* ratio at equilibrium of *ca*. 1 : 8.5 was determined by ^{1}H-NMR spectroscopy.

Values in bold characters refer to the pathways in Figure S3.

Z isomer (minor)

^{1}H NMR (400.13 MHz, THF-d_8): δ 8.46 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^e), 7.26 (dd, $^3J_{HH}$ = 8.4, 7.0 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.16 (overlapping d, $^3J_{HH}$ = 8.4, 7.0 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.69 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*$_{imid.}$ H^f), 6.15 (ddd, $^3J_{HH}$ = 8.4, 6.8 Hz, **$^5J_{PH}$ = 1.2 Hz**, 1H, C*H*$_{pyr.}$ H^c), 5.92 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^d), 5.58 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$ H^b), 3.57 (s, 18-c-6), 3.17 (d, $^2J_{PH}$ = 8.0 Hz, 1H, C*H*P H^a), 2.77 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.20 (d, $^3J_{PH}$ = 10.7 Hz, 18H, C(C*H*$_3$)$_3$), 1.14-1.07 (overlapping doublets, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 15.3.

E isomer (major)

^{1}H NMR (400.13 MHz, THF-d_8): 8.23 (d, $^{3}J_{HH}$ = 1.6 Hz, 1H, C$H_{imid.}$ H^{e}), 7.26 (dd, $^{3}J_{HH}$ = 8.4, 7.0 Hz, 1H, *p*-CH_{DiPP}), 7.16 (overlapping d, $^{3}J_{HH}$ = 8.4, 7.0 Hz, 2H, *m*-CH_{DiPP}), 6.72 (d, $^{3}J_{HH}$ = 1.6 Hz, 1H, C$H_{imid.}$ H^{f}), 6.50 (ddd, $^{3}J_{HH}$ = 8.7 Hz, **$^{4}J_{PH}$ = 2.8 Hz**, $^{4}J_{HH}$ = 0.8 Hz, 1H, C$H_{pyr.}$ H^{b}), 6.22 (ddd, $^{3}J_{HH}$ = 8.7, 6.7 Hz, **$^{5}J_{HH}$ = 0.7 Hz**, 1H, C$H_{pyr.}$ H^{c}), 5.93 (dd, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1H, C$H_{pyr.}$ H^{d}), 3.57 (s, 18-c-6), 3.53 (dd, $^{2}J_{PH}$ = 8.7 Hz, **$^{5}J_{HH}$ = 0.7 Hz**, 1H, CHP H$^{a'}$), 2.77 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 1.12 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.08 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.07 (d, $^{3}J_{PH}$ = 10.0 Hz, 18H, C(CH_3)$_3$).

^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8): δ 15.6.

VII. X-RAY CRYSTALLOGRAPHY

VII.1. General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Summary of the crystal data, data collection and refinement for compounds are given in Table S1. The crystals were mounted on a glass fiber with grease, from Fomblin vacuum oil. Data sets were collected at 173(2) K on a Bruker APEX-II CCD Duo diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). Specific comments for each data set are given below.

The cell parameters were determined (APEX2 software)[8] from reflections taken from three sets of 12 frames, each at 10 s exposure. The structures were solved by direct methods using the program SHELXS-2013.[9] The refinement and all further calculations were carried out using SHELXL-2013.[9b] The H-atoms were introduced into the geometrically calculated positions (SHELXL-2013 procedures) unless stated otherwise and refined riding on the corresponding parent atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

<u>The following special comments apply to the models of the structures:</u>

The asymmetric unit of $\mathbf{L}^{\mathbf{Cy}}\cdot$2HBr contains one molecule of dichloromethane. Both cyclohexyl groups are disordered over two positions. The hydrogen atom H1P on the phosphorus centre has been located contrary to the other hydrogen atoms placed on calculated positions.

The asymmetric unit of $K\mathbf{L}_{\text{-H}}^{\mathbf{Cy}}\cdot Et_2O$ contains two crystallographically independent $[K\mathbf{L}_{\text{-H}}^{\mathbf{Cy}}\cdot Et_2O]_2$ dimers. Cyclohexyl (C22, C23, C24, C25, C26, C27, C66, C67, C68, C69) and *iso*propyl (C51, C52) carbon atoms are disordered over two positions. The crystal did not diffract very strongly R_{int} = 18% and the ratio observed/unique reflections is low (Alert B).

VII.2. Summary of crystal data

Table S1. Crystal data for compounds $\mathbf{L}^{\mathbf{Cy}}\cdot 2HBr$, $[K\mathbf{L}_{\text{-H}}{}^{\mathbf{Cy}}\cdot Et_2O]_2$, and $[CrCl(\mathbf{L}_{\text{-H}}{}^{t\text{-Bu}})]$.

	$\mathbf{L}^{\mathbf{Cy}}\cdot 2HBr$	$[K\mathbf{L}_{\text{-H}}{}^{\mathbf{Cy}}\cdot Et_2O]_2$	$[CrCl(\mathbf{L}_{\text{-H}}{}^{t\text{-Bu}})]$
Chemical formula	$C_{33}H_{48}N_3PBr \cdot CH_2Cl_2$	$C_{74}H_{110}K_2N_6O_2P_2 \cdot 2(C_{37}H_{55}KN_3OP)$	$C_{29}H_{41}ClCrN_3P$
CCDC Number	1057714	1057715	1057716
Formula Mass	762.46	2511.63	550.07
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	12.1055(4)	12.9906(12)	8.370(2)
b/Å	25.0614(9)	14.5542(13)	23.052(6)
c/Å	14.6620(4)	21.8297(19)	17.180(4)
α/°	90	72.803(2)	90
β/°	123.958(2)	78.663(2)	116.249(10)
γ/°	90	70.389(2)	90
Unit cell volume/Å^3	3689.5(2)	3692.3(6)	2972.9(13)
Temperature/K	173(2)	173(2)	173(2)
Space group	*P*21/*c*	$P\bar{1}$	*P*21/*c*
No. of formula units per unit cell, *Z*	4	1	4
Absorption coefficient, μ/mm	2.412	0.218	0.550
No. of reflections measured	36844	65782	29169
No. of independent reflections	8912	17796	7188
R_{int}	0.0413	0.1848	0.0971
Final R_1 values ($I > 2\,\sigma(I)$)	0.0585	0.0896	0.0636
Final $wR(F^2)$ values ($I > 2\,\sigma(I)$)	0.1313	0.1884	0.1246
Final R_1 values (all data)	0.0934	0.2459	0.1320
Final $wR(F^2)$ values (all data)	0.1487	0.2458	0.1452
Goodness of fit on F^2	1.021	0.944	1.015

VII.3. Crystal structure of L^{Cy}·2HBr

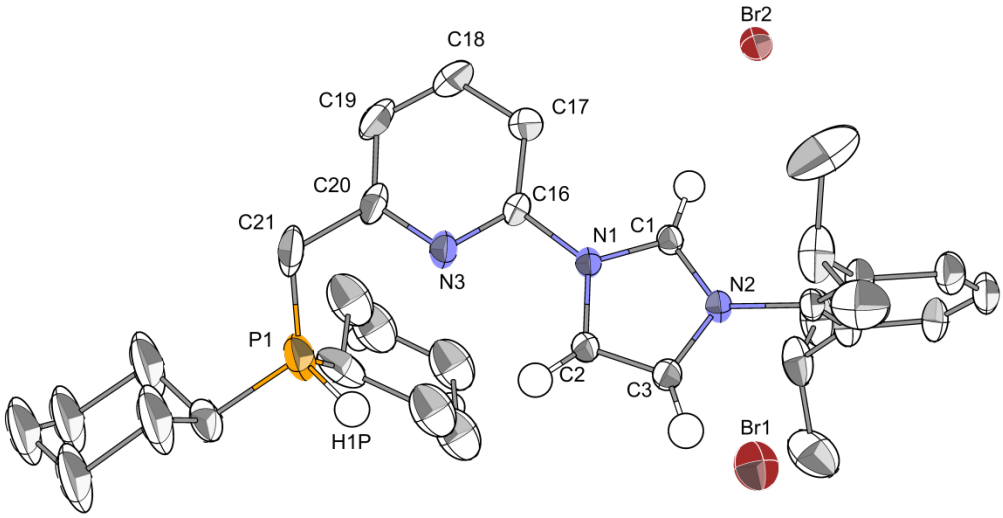


Figure S10 The molecular structure of L^{Cy}·2HBr with thermal ellipsoids represented at the 40% probability level. For clarity, only one disordered cyclohexyl group is displayed. Crystallisation solvent and hydrogen atoms have been omitted except for H1P and the imidazolium protons. Selected bond distances (Å) and angles [°]: P1-H1P 1.38(4), P1-C21 1.796(6), C20-C21 1.515(7), C19-C20 1.369(7), C18-C19 1.375(8), C17-C18 1.384(6), C16-C17 1.374(6), C16-N3 1.328(5), C16-N1 1.435(4), N1-C2 1.391(5), N2-C1 1.327(5), N1-C1 1.340(4); N1-C1-N2 108.4(3), C20-C21-P1 113.9(3); torsion angles P1-C21-C20-N3 -32.6(6), N3-C16-N1-C1 172.2(3).

VII.4. Crystal structure of $KL_{-H}^{Cy}\cdot Et_2O$

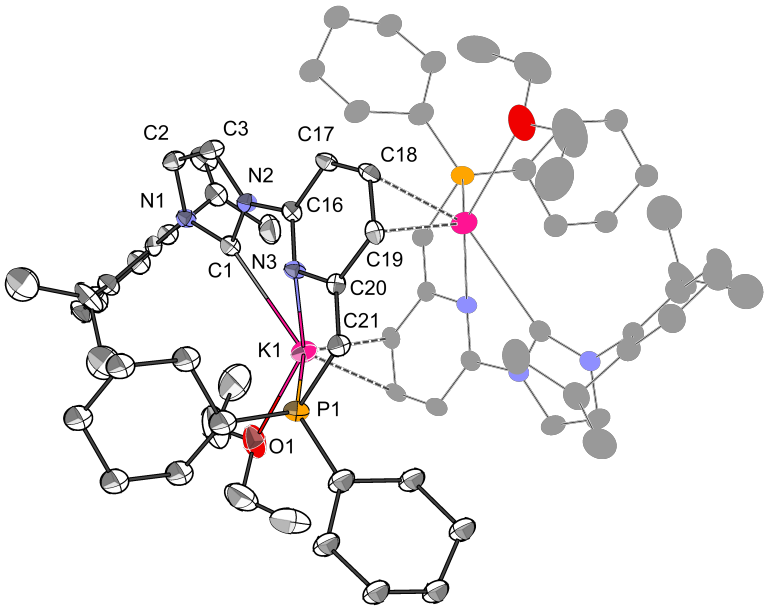


Figure S11 The molecular structure of one of the two crystallographically independent $[KL_{-H}^{Cy}\cdot Et_2O]_2$ dimers with thermal ellipsoids represented at the 30% probability level. For clarity, only one disordered cyclohexyl and *iso*-propyl group are displayed and hydrogen atoms have been omitted. Selected bond distances (Å) and angles [°]: N3-C16 1.333(5), C16-C17 1.379(6), C17-C18 1.403(6), C18-C19 1.357(6), C19-C20 1.451(6), C20-N3 1.393(5), C20-C21 1.383(6), C21-P1 1.777(4), N3-K1 2.792(3), K1-O1 2.822(4), K1-P1 3.258(2), C1-K1 2.887(4), interaction with the second unit: K1-C'18 3.108(4), K1-C'19 3.259(4); C20-C21-P1 124.9(3), N2-C1-N1 101.6(3), N2-C1-K1 109.9(3), C1-K1-N3 59.8(1), N3-K1-P1 61.4(1), P1-K1-O1 102.2 (1), O1-K1-C1 109.5(1). Sum of the angles around K1 *ca*. 332.9°.

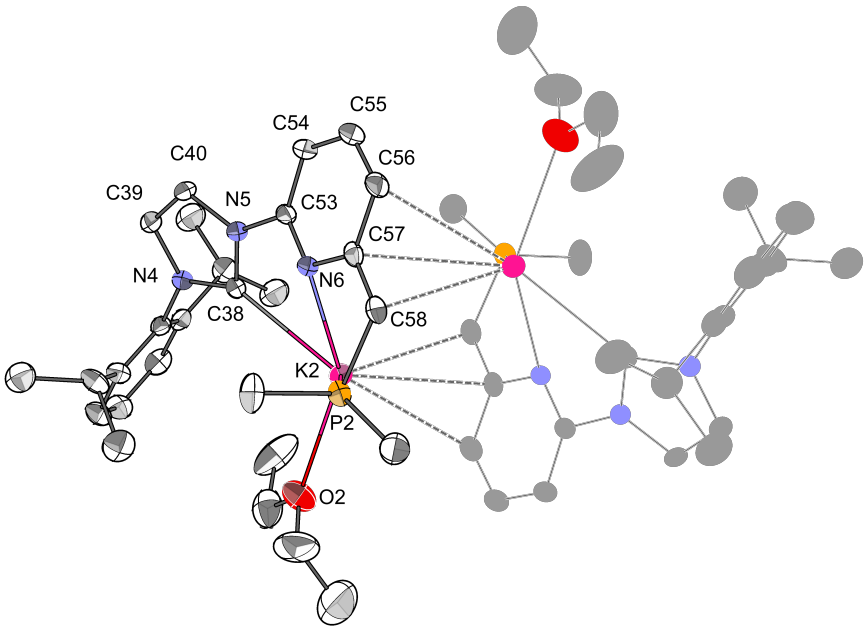


Figure S12 The molecular structure of the second crystallographically independent $[KL_{\text{-H}}^{cy}\cdot Et_2O]_2$ dimer with thermal ellipsoids represented at the 30% probability level. For clarity, only one disordered *iso*-propyl group and one carbon of the cyclohexyl groups are displayed. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles [°]: O2-K2 2.803(4), C38-K2 2.901(4), K2-P2 3.269(2), K2-N6 2.838(4), C58-C57 1.396(6), N6-C57 1.382(5), C57-C56 1.437(6), C56-C55 1.365(7), C55-C54 1.388(7), C54-C53 1.363(6), C53-N6 1.333(5), interaction with the second unit K2-C'56 3.271(5), K2-C'57 3.257(4), K2-C'58 3.225(4); K2-C38-N5 111.2(3), N4-C38-N5 101.7(3), O2-K2-C38 104.7(1), O2-K2-P2 101.8(1), P2-K2-N6 58.7(1), N6-K2-C38 59.7(1). Sum of the angles around K2 *ca.* 324.9°.

VII.5. Crystal structure of [CrCl($L_{-H}^{t\text{-}Bu}$)]

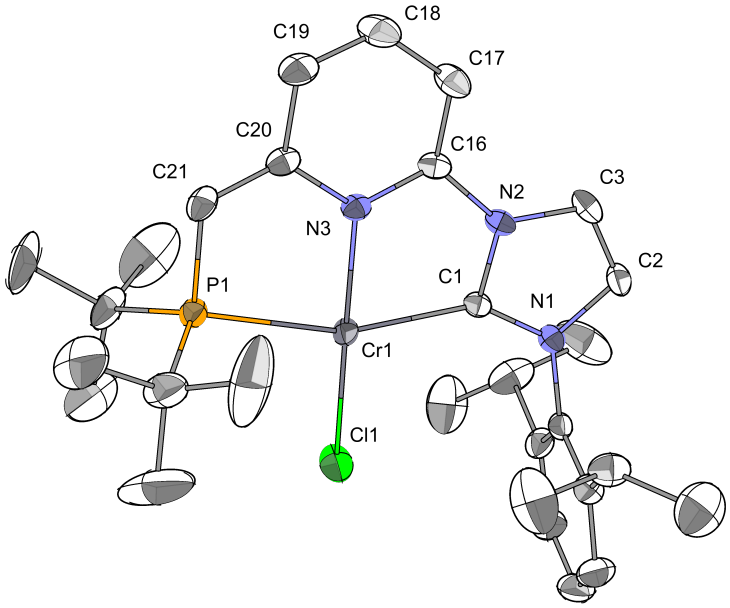


Figure S13 The molecular structure [CrCl($L_{-H}^{t\text{-}Bu}$)] with thermal ellipsoids represented at the 35% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles [°]: N1-C1 1.351(4), C1-N2 1.359(4), C1-Cr1 2.093(3), N2-C16 1.429(4), C16-C17 1.347(4), C17-C18 1.422(5), C18-C19 1.336(5), C19-C20 1.439(4), C16-N3 1.353(4), N3-C20 1.403(4), N3-Cr1 2.047(2), Cr1-Cl1 2.287(1), Cr1-P1 2.462(1), P1-C21 1.757(3), C20-C21 1.370(4); N1-C1-N2 104.2(2), C20-C21-P1 118.8(3), Cr1-C1-N2 112.8(2), Cr1-P1-C21 98.4(1), C1-Cr1-Cl1 101.15(9), Cl1-Cr1-P1 101.00(4), C1-Cr1-N3 77.5(1), N3-Cr1-P1 80.60(8). Sum of the angles around Cr1 *ca*. 360.3°.

VIII. REFERENCES

1. J. A. Wright, A. A. Danopoulos, W. B. Motherwell, R. J. Carroll and S. Ellwood, *J. Organomet. Chem.*, 2006, **691**, 5204.
2. W. L. F. Armarego and D. D. Perrin, eds., *Purification of Laboratory Chemicals (Fourth Edition)*, Butterworth-Heinemann, Oxford, 1996.
3. (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (b) E. M. Schubert, *J. Chem. Edu.*, 1992, **69**, 62.
4. D. H. Grant, *J. Chem. Edu.*, 1995, **72**, 39.
5. G. A. Bain and J. F. Berry, *J. Chem. Edu.*, 2008, **85**, 532.
6. T. D. W. Claridge, ed., *High-Resolution NMR Techniques in Organic Chemistry*, Pergamon, Oxford, 1999.
7. W. Bauer, *Magn. Reson. Chem.*, 1996, **34**, 532.
8. *APEX2*, *SAINT* and *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
9. (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112; (b) G. M. Sheldrick, *SHELX2013*, University of Göttingen, Germany, 2013.