Anion effect in the diastereoselective formation of bischelated Ni(II) complexes with a novel, chiral phosphine derived from 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

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Experimental

Synthesis data

General Considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.48 and 121.49 MHz, respectively, using TMS, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. Elemental C, H, N analyses were performed by the "Service de microanalyses", Université de Strasbourg. $[NiCl_2(DME)_2]$ (DME = dimethoxyethane) was prepared according to published procedures.[S-1] All other chemicals were purchased and used as received. The solvents were distilled and degassed prior to use.

Synthesis of diphenylphosphino-1,8-diaza-6-bicyclo(5.4.0)undec-7-ene (DBUP). Liquid Ph_2PCl (4.0 mL, 4.9 g, 22.2 mmol) was added dropwise to a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (6.7 mL, 6.80 g, 44.4 mmol) in toluene (200 mL), whereupon a pale yellow precipitate formed. The suspension was stirred for two days, during which the yellow precipitate dissolved and a colourless microcrystalline solid precipitated. The solution

was filtered, and the filtrate collected and the volatiles were removed under reduced pressure to give a viscous oil. The latter was redissolved in a minimum amount of toluene. This solution was added dropwise to stirred cold pentane (200 mL, -78 °C) to form a microcrystalline solid, which was collected by filtration *via* a cannula. The volatiles were removed under reduced pressure, giving DBUP as a colourless crystalline solid. Yield: 4.74 g, 63% based on Ph_2PCl. Crystals suitable for X-ray diffraction were obtained by layering pentane on a saturated Et_2O solution of DBUP. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = -12.3 (s) ppm; ^1H NMR ($CDCl_3$): δ = 1.24-1.85 (m, 8H; H8, H2, H3, and H4; see Figure 1 in the manuscript for labeling scheme), 3.10-3.32 (m, 6H, H5, H7 and H9), 3.58 (ddd, 1H, $^2J(H,^{31}P)$ = 9.9 Hz, $^3J(H,H)$ = 1 Hz, $^3J(H, H)$ = 15 Hz, simulated, H1), 7.14-7.54 (m, 10H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.6 (s, C8), 28.1 (s, C4), 28.5 (d, $^3J(^{13}C\text{-}^{31}P)$ = 9.9 Hz, C3), 28.9 (d, $^2J(^{13}C\text{-}^{31}P)$ = 16.6 Hz; C2), 44.4 (d, $^4J(^{13}C\text{-}^{31}P)$ = 2.6 Hz; C7), 44.8 (d, $^1J(^{13}C, P)$ = 4.8 Hz; C1), 48.8 (s, C5), 52.1 (d, $^4J(^{13}C\text{-}^{31}P)$ = 3.6 Hz; C9), 127.4-140.5 (Ph), 159.8 (d, $^2J(^{13}C, ^{31}P)$ = 7.3 Hz; C6) ppm. Anal. Calcd. for $C_{21}H_{25}N_2P$ (336.41): C, 74.98; H, 7.49; N, 8.33. Found: C, 74.63; H, 7.44; N, 7.98.

Isolation of [*N*-diphenylphosphino-1,8-diaza-6-bicyclo(5.4.0)undec-7-ene]·HCl (Intermediate A).

Following the same procedure reported above for DBUP, the yellow precipitate which formed immediately after addition of Ph_2PCl was collected and washed twice with Et_2O (2 x 20 mL). Even after multiple washings with Et_2O/pentane, residual toluene was found in the samples. Treatment of the paste under vacuum gave intermediate C (see below). For these reasons, satisfactory elemental analyses were not obtained for intermediate A. When toluene is not considered, the sample was found to be spectroscopically pure by NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 71.7 (s) ppm; ^1H NMR ($CDCl_3$): δ = 1.50-1.90 (m, 8H, H8, H2, H3, and H4; see Figure 1 in the manuscript for labeling scheme), 3.15-3.95 (m, 6H, H5, H7, and H9), 7.20-7.50 (m, 10H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.9 (s, C8), 23.0 (s, C2), 25.6 (s, C3), 27.9 (s, C4), 31.6 (d, $^3J(^{13}C\text{-}^{31}P)$ = 35.2 Hz, C1), 44.3 (d, $^2J(^{13}C\text{-}^{31}P)$ = 6.1 Hz, C7), 50.4 (s, C5), 56.4 (s, C9), 129.5-137.7 (Ph), 173.2 (d, $^2J(^{13}C, ^{31}P)$ = 26.6 Hz, C6) ppm. In the $^{13}C\{^1H\}$ DEPT spectrum, no CH signals were detected in the region 0-129 ppm, confirming that the phosphoryl group is bound to the nitrogen atom.

Isolation of [C1-diphenylphosphino-1,8-diaza-6-bicyclo(5.4.0)undec-7-ene]·HCl (Intermediate C). Intermediate A was left under vacuum for 24 h. The conversion is accompanied by the decomposition of intermediate A in DBU·HCl and $Ph_2P(O)PPh_2$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = -17.7 (s) ppm; selected ^1H NMR data: δ = 4.90 (m, br, 1H, H1), 11.19 (br, 1H, NH) ppm; selected $^{13}C\{^1H\}$ NMR data: 41.9 (d, ^1J(H, ^{31}P) = 20.4 Hz, C1), 164.9 (d, ^2J(H, ^{31}P), C6).

Synthesis of $[NiCl_2(DBUP)]$ (1) and $[Ni(DBUP)_2][NiCl_4]$ (2). Solid DBUP (0.46 g, 1.37 mmol) was added to a solution of anhydrous $[NiCl_2(DME)]$ (0.30 g, 1.37 mmol) in CH_2Cl_2 (200 mL). The reaction mixture was stirred overnight to form a red solution. The volatiles were removed under vacuum, giving **1** as a red powder. Precipitation of a CH_2Cl_2 or $CHCl_3$ solution containing **1** with pentane afforded **2** as a green powder. Layering a MeOH solution of **1** with Et_2O gave green crystals of **2**·MeOH. Green crystals of **2**·CH_2Cl_2 were obtained by layering a CH_2Cl_2 solution containing **1** with pentane. Evaporation at atmospheric pressure of a red acetone solution of **1** gave green crystals of **2**·3Me_2CO. Solutions of complex **1** can be obtained from **2** by redissolution of the latter in CH_2Cl_2, chlorobenzene, MeCN, $CHCl_3$ or acetone. Yield of **2**·CH_2Cl_2: 0.51 g, 73% based on nickel. Both **1** and **2** give rise to paramagnetic solutions, e.g. in $CDCl_3$ and CD_3OD. $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 62.7 (very broad) ppm. Anal. Calcd. for $C_{42}H_{50}N_4P_2Ni_2Cl_4$·($CH_2Cl_2$) (1016.95): C, 50.79; H, 5.15; N, 5.51. Found: C, 50.02; H, 5.22; N, 5.94. ESI-MS (MeOH): 429.0924 $\{(DBUP)NiCl\}^+$ and 765.2709 $\{[(DBUP)_2Ni]Cl\}^+$. ESI-MS (MeCN): 337.1933 $\{DBUPH\}^+$, 429.0928 $\{(DBUP)NiCl\}^+$, 765.2700 $\{[(DBUP)_2Ni]Cl\}^+$.

Synthesis of (*SS,RR*)-$[(DBUP)_2Ni]Cl_2$ (3). Anhydrous $[NiCl_2(DME)]$ (0.16 g, 0.73 mmol) was added to a solution of DBUP (0.49 g, 1.46 mmol) in CH_2Cl_2 (90 mL) to form a reddish-brown solution. After the mixture was stirred for 4 h, hexane was added to precipitate a brown powder, which was collected by filtration and redissolved in a minimum amount of $CDCl_3$ (10 mL). The insoluble residue was removed by centrifugation and the solution layered with Et_2O, giving orange crystals of **3**·4$CDCl_3$·Et_2O. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 64.9 (s) ppm; ^1H NMR ($CDCl_3$): δ = 1.25-2.10 (m, 7H, H2a, H3, H4, and H8; see Figure 1 in the manuscript for the labeling scheme), 2.33 (br, 1H, H2b), 2.80-3.65 (m, 5H, H5, H9, and H7a), 4.86 (d, 1H, ^2J(H.H) = 12.4 Hz, H7b), 6.77 (br, 1H, H1), 6.90-8.70 (m, 10H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.0 (s, C8),

24.6/24.7/25.2 (m, C2, C3, C4), 48.6 (s, C7), 50.6 (s, C9), 50.8 (d, $^{1}J(^{13}C\text{-}^{31}P)$ = 12 Hz, C1), 52.6 (s, C5), 120.2-137.8 (Ph), 165.2 (br, C6) ppm. Anal. Calcd. for $C_{42}H_{50}N_4P_2NiCl_2$ (802.42): C, 62.87; H, 6.28; N, 6.98. Found: C, 62.38; H, 5.67; N, 6.40.

Synthesis of [Ni(DBUP)$_2$]Br$_2$. Anhydrous $NiBr_2$ (0.30 g, 1.37 mmol) was added to a solution of DBUP (0.46 g, 1.37 mmol) in EtOH (60 mL). The brown reaction mixture was stirred for 24 h and the volume of the solvent was reduced to 15 mL under vacuum. Addition of diethyl ether (50 mL) resulted in the precipitation of a brown solid, which was collected by filtration, dried under vacuum and redissolved in water. Slow evaporation of this orange solution gave orange-red crystals of **[Ni(DBUP)$_2$]Br$_2$**·6H_2O (Yield: 0.59 g, 43%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 298 K): δ = 65.2 (s, *SS/RR* enantiomers), ca. 55 (very broad, *SR/RS* enantiomers) ppm; $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 213 K): δ = 65.2 (s, *SS/RR* enantiomers), 44.8 (d, $^{2}J(^{31}P,^{31}P)$ = 68.2 Hz, *SR/RS* enantiomers), 65.1 (d, $^{2}J(^{31}P,^{31}P)$ = 68.2 Hz, *SR/RS* enantiomers) ppm (see Figure S-1 for the VT-NMR); ^{1}H NMR (CD_2Cl_2, 298 K; assignments correspond to the major *SS/RR* enantiomers): δ = 1.30-2.15 (m, 7H; H2a, H3, H4 and H8; see figure 1 in the manuscript for labeling scheme), 2.32 (br, 1H; H2b), 2.80-3.50 (m, 5H; H5, H9, and H7a), 4.60 (d, 1H, ^{2}J(H.H) = 12.9 Hz; H7b), 6.53 (br, 1H; H1), 6.90-8.50 (m, 10H; Ph) ppm; a broad signal was detected for the *RS/SR* enantiomers at 5.23 ppm. This signal splits at 213 K into two broad multiplets at 6.4 and 4.0 ppm, see Figure S-2; $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 298 K): δ = 22.7 (s, C8), 24.6/25.1/26.0 (m, C2, C3, C4), 48.8 (s, C7), 50.5 (s, C9), 51.4 (m, C1), 52.5 (s, C5), 119.3-139.3 (Ph), 165.2 (br, C6) ppm. Anal. Calcd. for $C_{42}H_{50}Br_2N_4NiP_2$·6H_2O (999.41): C, 50.47; H, 6.25; N, 5.61. Found: C, 50.10; H, 6.49; N, 5.65.

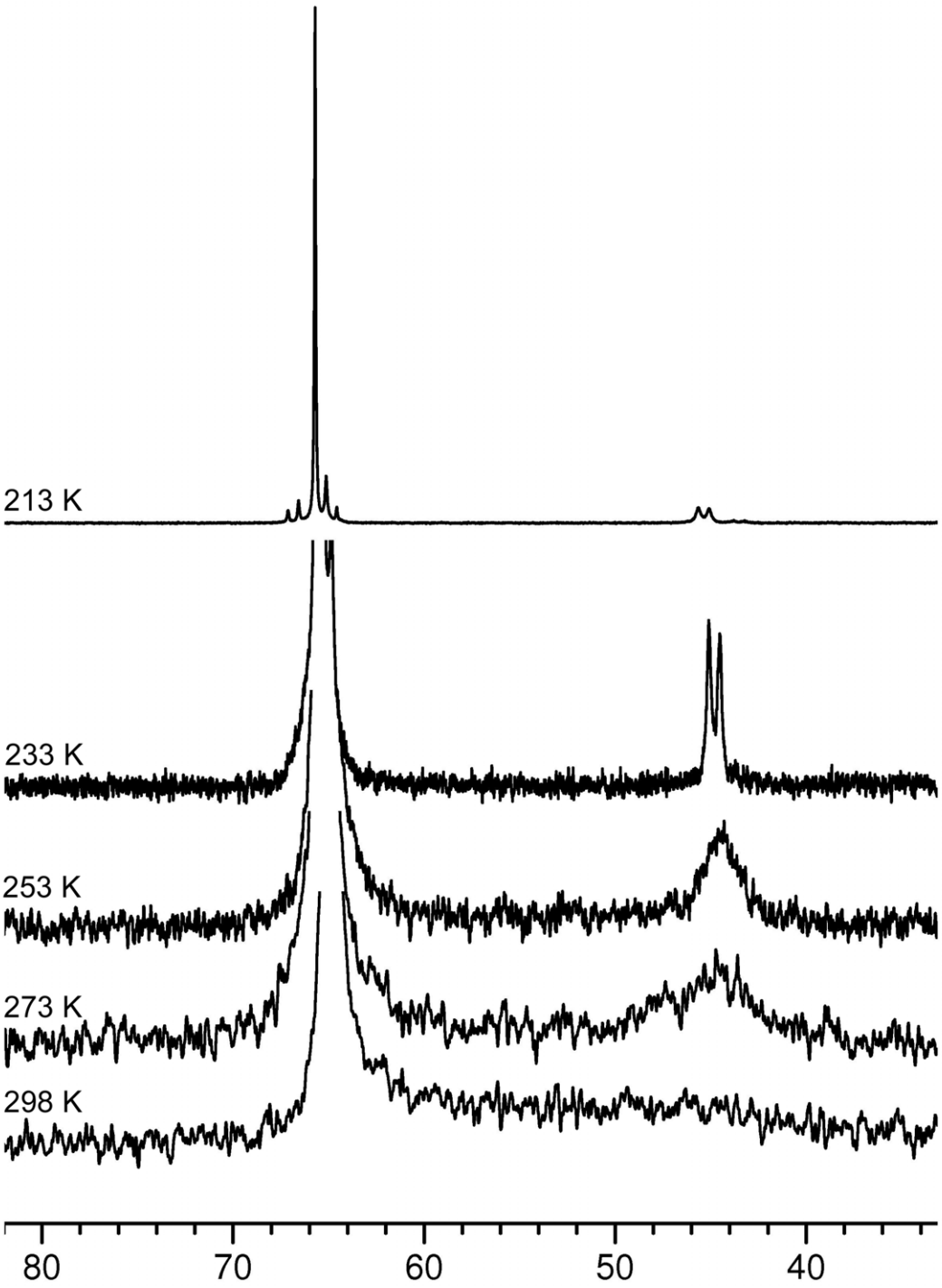


Figure S-1: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **4** in CD_2Cl_2. For sake of clarity, the upper spectrum has been scaled down.

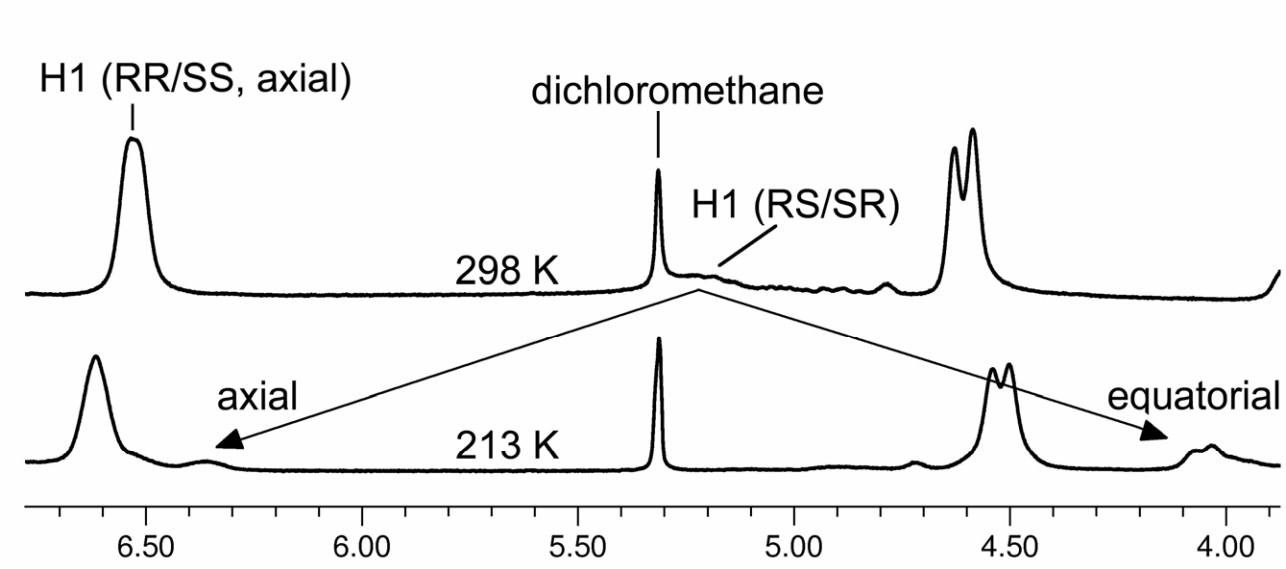
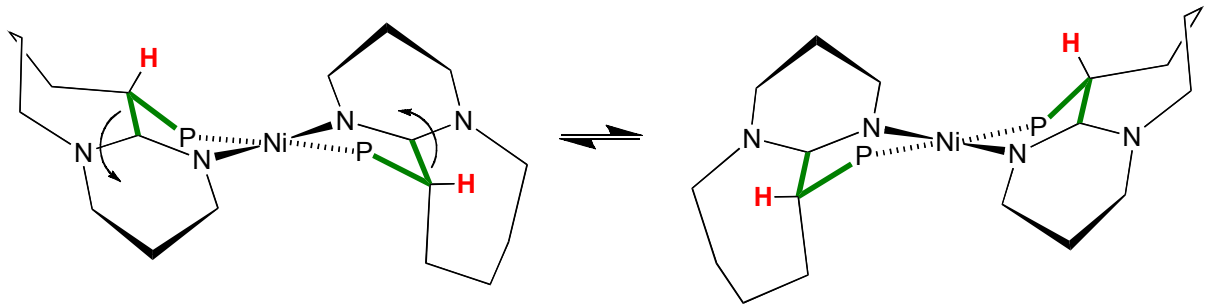


Figure S-2: Variable temperature ^{1}H NMR spectra of **4** in CD_2Cl_2.



Scheme S-1: Proposed solution equilibrium for RS/SR-$[Ni(DBUP)_2]Cl_2$, based on the VT $^{31}P\{^{1}H\}$ and ^{1}H NMR data (phenyls omitted for clarity). The dynamic behaviour can be explained as a concerted inversion of the envelope-like five-membered chelation cycles. This brings the axial methylene proton to an equatorial position and *vice versa*, consistently with the spectra reported in Figures S-1 and S-2. Hypothetical conformations in which both protons occupy axial or equatorial positions is probably avoided by the mutual steric hindrance of the six membered cycles. Note that

this situation is reversed in the case of the *SS/RR* enantiomers in which only the axial-axial conformation is observed.

Catalytic Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The Ni complex ($4x10^{-2}$ mmol based on Ni) was dissolved in 10 mL of solvent and injected into the reactor under an ethylene flux. Then 5 mL of a $EtAlCl_2$ solution, corresponding to 10 equivalents, was added to form a total volume of 15 mL with the precatalyst solution.

All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 min.) a dry ice bath was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC, the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The amount of unreacted ethylene was thus determined. Although this method is of limited accuracy, it was used throughout and gave satisfactory reproducibility. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product.

Crystallographic data

X-ray data collection, structure solution and refinement for all compounds

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S- 2] (graphite

monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Crystallographic and experimental details for the structures are summarized in Table S1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-3] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. In **2**·$3C_3H_6O$, four carbons of one of the seven membered cycles were found disordered in two position with equal occupancy factors. The two images were refined anisotropically, except C22A, C22B, C26A and C26B which were refined isotropically. Distances C26B-N4, C26A-N4, C25-C26A and C25-C26B were restrained to match the appropriate geometry. One of the acetone molecules was found disordered in two positions with no atom in common and with equal occupancy factors. In **3**·$4CHCl_3$·Et_2O, one of the chloroform molecules was found disordered over three positions with unequal occupancy factors. The six chlorine positions were located, while the carbon atom was refined as occupying one position, although probably disordered. This resulted in C-Cl distances and Cl-C-Cl angles deviating from the ideal ones. The chlorine atoms of the solvent were refined anisotropically with thermal parameters restrained to isotropic ones. The ether molecule was as well found disordered and was isotropically refined with restrained geometrical parameters. In **4**·$6H_2O$, a severe disorder involved both phosphines. The P1 seven-membered cycle was disordered in two positions with occupancy factors 0.3/0.7. The P2 seven-membered cycle was disordered in two positions having equal occupancy factors. Atoms C1A, C1B, C3A, C3B, C24A and C24B were refined isotropically. Several distances in the disordered moieties were restrained to match the appropriate geometry, namely distances C23-C24A, C23-C24B, C26B-C25B, C24B-C25B and C24A-C25A and angular distances C3A···C5 and C3B···C5. The deviation of the N4-C26(A and B) distances from the ideal ones is probably due to an additional disorder concerning the C7-C8-C9-N2 atoms (see ellipsoids in Figure S-5), which could not be resolved. Although several of the water hydrogens were found in the density maps, the H_2O hydrogens were omitted in the refinement. A MULTISCAN[4] absorption correction was applied for **4**·$6H_2O$, which had an absorption coefficient larger than those of the other compounds. CCDC 724933 (DBUP) and 724930 (**2**·$3C_3H_6O$) and 724931 (**3**·$4CHCl_3$·Et_2O) and 724932 (**4**·$6H_2O$) contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S-1. Data collection and refinement parameters for all compounds.

	DBUP	**2**·3C_3H_6O	**3**·4$CHCl_3$·Et_2O	**4**·6H_2O
Chemical formula	$C_{21}H_{25}N_2P$	$C_{42}H_{50}N_4NiP_2.Cl_4Ni$ ·3(C_3H_6O)	$C_{42}H_{50}N_4NiP_2$·$C_4H_{10}O$ ·4($CHCl_3$)·(Cl)$_2$	$C_{42}H_{50}Cl_2N_4NiP_2$. 2(Br).6(H_2O)
M_r	336.40	1106.25	1354.00	999.43
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, P-1	Triclinic, P-1	Monoclinic, $P2_1/c$
a, b, c (Å)	8.6126(5), 15.5139(14), 14.4029(10)	10.6254(3), 13.0726(5), 19.4149(7)	14.4443(5), 15.8472(6), 15.9016(4)	11.9492(3), 15.0496(5), 25.3293(5)
α, β, γ (°)	90.00, 109.505(4), 90.00	82.882(2), 82.801(2), 86.872(2)	116.871(2), 95.778(2), 97.478(2)	90.00, 90.227(2), 90.00
V (Å^3)	1814.0(2)	2652.79(16)	3166.49(18)	4554.9(2)
Z	4	2	2	4
D_x (Mg m^{-3})	1.231	1.385	1.420	1.457
μ (mm^{-1})	0.16	1.02	0.99	2.30
Crystal size (mm)	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.13 × 0.11 × 0.08	0.14 × 0.12 × 0.12
meas., indep. and obsvd. Refl.	6624, 3755, 2218	25907, 12083, 8595	30223, 13080, 7849	24227, 10110, 6827
R_{int}	0.051	0.045	0.050	0.053
θ_{max} (°)	26.5	27.5	26.5	27.5
$R[I>2\sigma(I)]$,$wR(F^2)$, S	0.056, 0.194, 1.05	0.052, 0.133, 1.07	0.058, 0.181, 0.98	0.064, 0.178, 1.02
No. of parameters	217	655	678	538
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, –0.45	0.68, –0.82	1.49, –0.83	1.68, –2.09

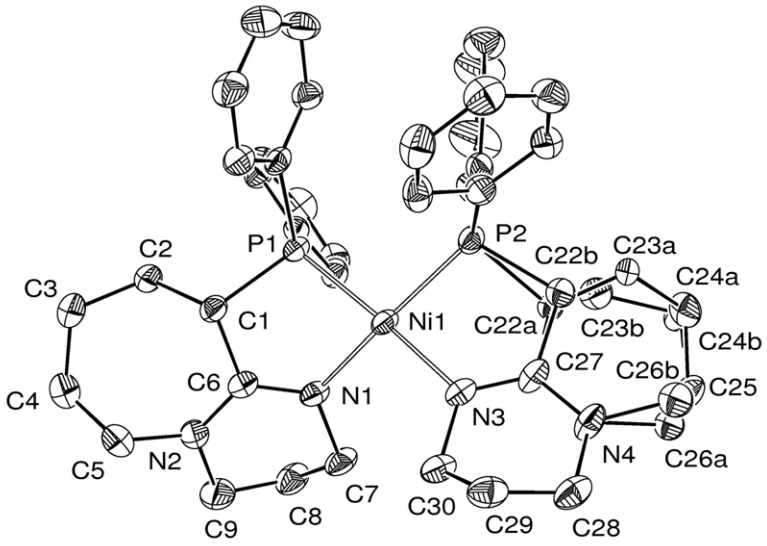


Figure S-3: ORTEP plot of the cation in **2**·3C_3H_6O, including the disorder. Ellipsoids at 50% probablility level, hydrogen atoms omitted.

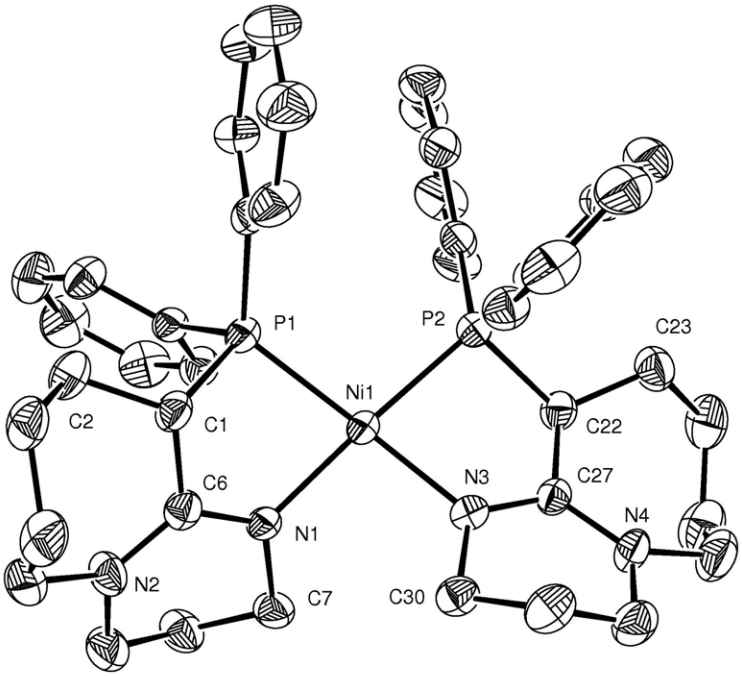


Figure S-4: ORTEP plot of the cation in **3**·4$CHCl_3$·Et_2O. Ellipsoids at 50% probablility level,

hydrogen atoms omitted.

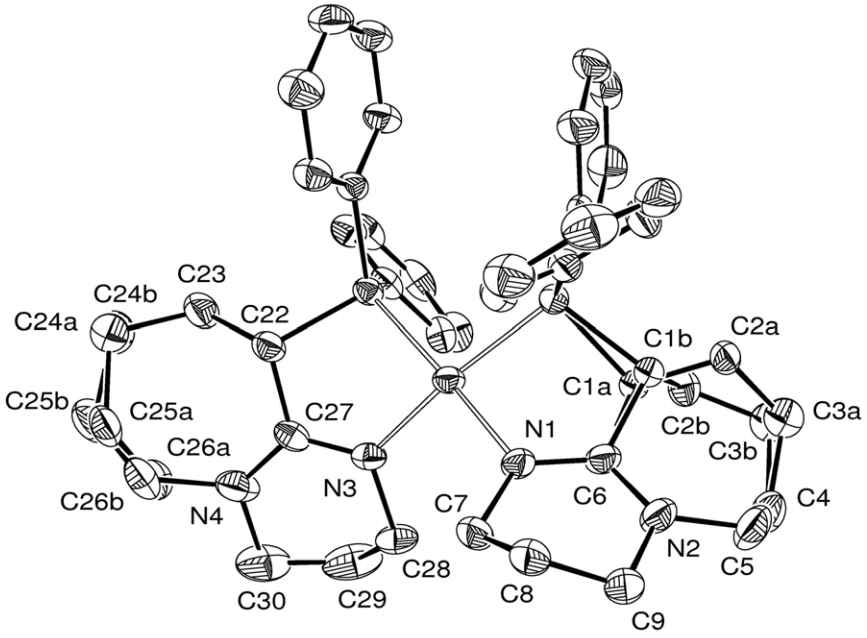


Figure S-5: ORTEP plot of the cation in **4**·6H_2O, including the disorder. Ellipsoids at 50% probablility level, hydrogen atoms omitted.

References

[S-1] L. G. L. Ward, *Inorg. Synth.* **1971**, *13*, 154–164**.**

[S-2] Bruker-Nonius, *Kappa CCD Reference Manual,* Nonius BV, The Netherlands, **1998**.

[S-3] Sheldrick., M; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.

[S-4] MULABS, PLATON; L. Spek, *J. Appl.Cryst*. **2003**, *36*, 7-13; B. Blessing, *Acta Cryst*, **1995**, A51, 33-38