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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With the new chiral phosphine ligand DBUP, obtained from DBU and Ph₂PCl, a remarkable anion effect was observed on the diastereoselective formation of the bischelated complexes $[Ni(DBUP)_2](X)_n$ (X = Cl, Br, n = 2; X = NiCl₄, n = 1), which are active ethylene oligomerization catalyst precursors.

The chemistry and catalytic applications of aminophosphines have generated much attention.¹ In the reaction of 2-methyl-2-oxazoline with Ph₂PCl, in the presence of NEt₃ as HCl scavenger,² the substrate was unexpectedly phosphorylated both on the nitrogen and the exocyclic carbon atoms. We considered that in order to increase the kinetics of the reaction, it would be advantageous to replace NEt₃ by the more basic DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). But unexpectedly, phosphorylation was observed on DBU itself, an unprecedented and particularly surprising feature since DBU is a well-known and much used organic base. In this reaction, DBU behaves as a nucleophile, despite its common definition as "nonnucleophilic" base.³ A P–N bond is initially formed and a 1,3-shift of the P atom follows to form the P–C bond of the resulting new alkyl phosphine (Scheme 1), which was isolated and used as a P,N chelate with Ni(II). Only a few reactions of DBU with phosphorous species have been reported,⁴ but their coordination chemistry has remained unexplored.⁵

The reaction of Ph₂PCl with 2 equiv. DBU in toluene yielded $Ph_2PCH(CH_2)_4N(CH_2)_3N=C$ (DBUP, Scheme 1, Fig. 1) by regioselective phosphorylation at the methylene bonded to the NCN carbon. A yellow paste precipitated immediately when Ph2PCl was added to the DBU solution and was unambiguously characterized as a mixture of $[Ph_2PN(\dots C)(CH_2)_5N(CH_2)_2(CH_2)]Cl$ (intermediate A, Scheme 1, see ESI[†]) and toluene. In contact with the DBU present in solution, A was slowly consumed and colourless DBU-HCl appeared. Consistently, isolated A is rapidly deprotonated by DBU to give DBUP, via the aminophosphine B which was observed by ³¹P NMR. Intra- or inter-molecular phosphoryl migration from N to C occurs, as proposed for a phosphonate derivative.4d When the pale yellow A/toluene paste was left for 24 h under reduced pressure, $[Ph_2PCH(CH_2)_4N(CH_2)_3NH(\cdots C)]Cl$ (DBUP·HCl, Scheme 1) was unexpectedly formed. It is readily converted into DBUP by treatment with additional DBU. The $A \rightarrow DBUP \cdot HCl$ conversion does not take place in homogeneous



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Fig. 1 ORTEP plot of the crystal structure of DBUP. Ellipsoids include 50% of the electron density. Selected distances (Å) and angles (°): P1–C1 1.865(3), C1–C6 1.518(4), N1–C6 1.288(4), N2–C6 1.372(4); N1–C6–N2 125.9(3), N1–C6–C1 117.0(3), N2–C6–C1 117.1(3), C6–N1–C7 115.7(3), C6–N2–C5 123.1(3), C6–N2–C9 119.8(2), C5–N2–C9 114.9(2).

solutions but seems to require the very high concentration existing in the aforementioned paste.

At variance with the 2-methyl-2-thiazoline² and 2-amino-2-thiazoline⁶ cases, no diphosphine ligand was observed. The X-ray structure of DBUP (Fig. 1) confirms that the phosphorus is bonded to the new stereogenic centre C1. The C–N distances suggest that the double bond is localized between C6 and N1. The phosphorus lone pair in DBUP is directed *anti* with respect to the C1 hydrogen [C16–P1–C1–C6 torsion angle: 171.0(1)°]. The N2 atom is slightly pyramidal, the sum of the C–N2–C angles being 357.8(7)°. The P1–C1 bond distance [1.865(3) Å] is typical of alkyl-phosphines.

The reaction of DBUP with [NiCl₂(DME)] (DME = dimethoxyethane) in CH₂Cl₂ afforded a red paramagnetic solution. Its rapid evaporation yielded a red, amorphous solid most likely to be the tetrahedral complex [NiCl₂(DBUP)] (1), but attempts to crystallize it failed. Instead, green crystals of [Ni(DBUP)₂](NiCl₄) (2), a formula isomer of 1, were obtained from MeOH, acetone (Fig. 2) or CH₂Cl₂. The metal centre in the dication of $2 \cdot 3C_3H_6O$ is P,N-chelated by two mutually *cis* DBUP ligands. It adopts a tetrahedrally distorted square planar geometry [angle between the P1,Ni1,N1 and P2,Ni1,N3 planes: 15.14(7)°]. A NiCl₄²⁻ group acts as a counterion.



Fig. 2 ORTEP plot of the crystal structure of $[Ni(DBUP)_2]^{2+}$ in 2·3C₃H₆O. Only one of the two disorder images, representing the *S*,*R* diastereoisomer, is depicted. Hydrogen atoms and solvent molecules omitted for clarity. The NiCl₄ dianion (omitted) is located far from the cationic metal centre. Ellipsoids include 50% of the electron density. Selected distances (Å) and angles (°): Ni1–P1 2.1337(8), Ni1–P2 2.1454(9), Ni1–N1 1.953(3), Ni1–N3 1.938(2), N1–Ni1–P1 80.41(7), N3–Ni1–P2 83.11(8).

The two possible diastereoisomers of **2** co-crystallized in a 1:1 ratio and are present as two resolved disordered images in the main residue, as also observed for $4.6H_2O$ (see Fig. 3 and below for details). Dissolution of the green crystals of **2** in chlorinated solvents or MeCN reforms a red solution of **1**,§ as confirmed by IR spectroscopy. Crystallization of **2** from solutions containing **1** is quantitative and can be explained by the Le Chatelier's principle, implying an equilibrium between the two species in solution (Scheme 2). Although bischelated Ni(II) complexes featuring NiCl₄²⁻ as counterion have been reported in the literature, equilibria with the parent monochelated NiCl₂L₂ complex have



Fig. 3 Diagrams of the crystal structure of $4.6H_2O$. The red and green C–C bonds depict the two figures of the disorder (see text). Only the *ipso* phenyl atoms are shown. Solvent and hydrogen atoms omitted for clarity. A complete ORTEP plot is provided in the ESI.[†]



never been described, to the best of our knowledge.7 In EtOH, MeOH or water, 2 forms yellow solutions, as the result of $NiCl_4^{2-1}$ solvation,⁸ and the metal remains bischelated, as confirmed by comparison of its NMR and IR data with those of [Ni(DBUP)₂]Cl₂ (3). The latter was independently prepared by a 2:1 reaction of DBUP with [NiCl₂(DME)]. Single crystals of 3.4CHCl₃.Et₂O (see below) and of the related dibromide $[Ni(DBUP)_2]Br_2$ (4, in 4.6H₂O) were obtained (Fig. 3). The structure of the cation $[Ni(DBUP)_2]^{2+}$ in 4.6H₂O is similar to that in 2. A disorder affects the ligands (green and red images in Fig. 3) which display two opposite configurations for the carbon bonded to P1. The two possible diastereoisomers thus co-crystallized in a 0.7:0.3 ratio (S, S/R, S and their enantiomers, respectively). A second disorder involves the seven-membered cycle of phosphine P2 but it does not affect the configuration of the CH carbon. In contrast to the situation in the S,S/R,R-diastereoisomer, which displays a C_2 pseudosymmetry (Fig. 3, bottom left), the phosphines are not equivalent in the R, S/S, R diastereoisomer.

The ${}^{31}P{}^{1}H$ NMR spectrum of **4** (Fig. 4) is consistent with what is observed in the solid state. At 298 K, the spectrum shows

 Table 1
 Comparative catalytic data in ethylene oligomerization with AlEtCl₂ as cocatalyst^a

	Quantity based on Ni mol	AlEtCl ₂ (equiv.)	C_4	C ₆	C ₈	TOF (mol C_2H_4)/(mol Ni h)	1–butene (%) ^c
1 ^b	4.07×10^{-5}	10	69	28	3	79900	5.8
1 ^{<i>a</i>}	4.71×10^{-5}	10	68	28	4	51200	5.0
2 ^{<i>a</i>}	4.07×10^{-5}	10	60	34	5	67200	8.7
2 ^b	4.00×10^{-5}	10	63	32	4	60256	7.4
3 ^{<i>a</i>}	4.48×10^{-5}	10	78	20	2	54300	14.4
$[Et_4N]_2[NiCl_4]^{a,d}$	4.12×10^{-5}	10	72	26	3	40700	8.5

^{*a*} Ext. temp. = 20 °C, C_2H_4 pressure = 10 bar, solvent = toluene (10 mL), cocatalyst: AlEtCl₂ (5 mL toluene solution). [NEt₄][PF₆] alone was confirmed to be inactive. Minute amounts of C₁₀ oligomers were typically detected. ^{*b*} In chlorobenzene (10 mL). ^{*c*} Within the C₄ fraction. ^{*d*} A negligible activity was observed in chlorobenzene.



a sharp peak (SS/RR 65.0 ppm) and a very broad one (RS/SR ca. 55 ppm, see ESI[†]), which splits into two doublets at 233 K (one of which is partially masked) with a typical $cis {}^{2}J_{P-P}$ value. This can be explained as the result of a concerted movement that exchanges the equatorial and axial positions of the C-C bond (Fig. 3, bottom right). At 213 K, one of the doublets further splits, consistent with the disorder involving the P2 phosphine (Fig. 3). In the crystal 3.4 CHCl₃·Et₂O, only the S,S/R,R diastereoisomer is present and no trace of the R,S/S,R diastereoisomer was detected in the crude product, at variance with the case of the analogous dibromide 4. This suggests a remarkable anion effect on the diastereoselective formation of the bischelate complexes. In 3, the smaller chloride anion is significantly closer to the metal centre than the bromide in 4 [Ni \cdots Cl distances: 3.623(2) and 4.127(2) Å; Ni…Br distances: 4.102(1) and 4.401(1)], resulting also in closer H1/H22...halogen contacts, which are the shortest found in 3.4CHCl₃·Et₂O (see Fig. 5). These non-classical hydrogen bonds involve the stereogenic CH centre and, although of low energetic nature, their contribution may be sufficient for the stabilization of the S, S/R, R diastereoisomer.

Our results provide a further example (complex 1) of the remarkable structural diversity, in solution and in the solid state, shown by $[NiX_2(P,N)]$ (X = halogen, P,N = phosphinoamine) complexes.⁹ This has consequences in their reactivity, *e.g.* in the catalytic oligomerization of ethylene. Preliminary catalytic results (Table 1) indicate that 1 and 2 lead to similar activities and selectivities, suggesting the involvement of a similar active species. In chlorobenzene, the most soluble isomer 1, present mainly in the monochelated [NiCl₂(DBUP)] form, shows enhanced activity but the selectivity remains similar to that observed for a toluene suspension. Complex 3 is also active and gives results similar or slightly higher than those found for a range of Ni(II) complexes with P,N chelates¹⁰ and *ca.* 10 times higher than an interesting Ni(II) complex with a *N*-phosphinoguanidine P,N ligand related



Fig. 5 Diagram of the ion pairing observed in $3 \cdot 4$ CHCl₃·Et₂O. The red dashed lines represent the shortest H \cdots Cl contacts between the cation and the chlorides. The H1 and H22 atoms were constrained in calculated positions with respect to the parent atoms (C–H distance: 0.98 Å).

to DBUP.¹¹ Since $[Et_4N]_2[NiCl_4]$ also displays catalytic activity (Table 1), the equilibria shown in Scheme 2 emphasize the caution to be exerted when trying to establish structure–properties relationships.

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Notes and references

§X-Ray diffraction data (173 K, Mo Kα): DBUP: C₂₁H₂₅N₂P, *M* = 336.40, *P*2₁/*c*, *a* = 8.6126(5), *b* = 15.514(1), *c* = 14.403(1) Å, β = 109.505(4)°, *V* = 1814.0(2) Å³, *Z* = 4, *D_c* = 1.231 g cm⁻³, μ = 0.156 mm⁻¹, *F*(000) = 720, *R*_{int} = 0.051, *R*₁ (*I* > 2σ) = 0.056, w*R*₂ (*I* > 2σ) = 0.137 (217 param., 2218 obs. refl., 3755 unique); **2**·3C₃H₆O: C₅₁H₆₈Cl₄N₄Ni₂O₃P₂, *M* = 1106.25, *P*-1, *a* = 10.6254(3), *b* = 13.0726(5), *c* = 19.4149(7) Å, α = 82.882(2), β = 82.801(2), γ = 86.872(2)°, V = 2652.79(16) Å³, *Z* = 2, *D_c* = 1.385 g cm⁻³, μ = 1.016 mm⁻¹, *F*(000) = 1160, *R*_{int} = 0.045, *R*₁ (*I* > 2σ) = 0.052, w*R*₂ (*I* > 2σ) = 0.111 (665 param., 8595 obs. refl., 12083 unique); **3**·4CHCl₃·Et₂O: C₅₀H₆₄Cl₁₄N₄NiOP₂, *M* = 1354.00, *P*-1, *a* = 14.4443(5), *b* = 15.8472(6), *c* = 15.9016(4) Å, α = 116.871(2), β = 95.778(2), γ = 97.478(2)°, V = 3166.5(2) Å³, *Z* = 2, *D_c* = 1.420 g cm⁻³, μ = 0.986 mm⁻¹, *F*(000) = 1392, $\begin{array}{l} R_{\rm int} = 0.050, R_1 \ (I > 2\sigma) = 0.058, wR_2 \ (I > 2\sigma) = 0.148 \ (678 \ {\rm param.}, \\ 7846 \ {\rm obs. refl.}, 13080 \ {\rm unique}); {\bf 4.6H_2O: } C_{42}H_{62}{\rm Br_2N_4NiO_6P_2}, M = 999.43, \\ P2_1/c, a = 11.9492(3), b = 15.0496(5), c = 25.3293(5) \ {\rm \AA}, \beta = 90.227(2)^\circ, \\ V = 4554.9(2) \ {\rm \AA}^3, Z = 4, D_c = 1.457 \ {\rm g \ cm^{-3}}, \mu = 2.299 \ {\rm mm^{-1}}, F(000) = \\ 2072, R_{\rm int} = 0.053, R_1 \ (I > 2\sigma) = 0.064, wR_2 \ (I > 2\sigma) = 0.157 \ (538 \ {\rm param.}, \\ 6827 \ {\rm obs. refl.}, 10110 \ {\rm unique}). \end{array}$

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