

Preliminary Communication

Neutral and cationic nickel(II) complexes of phosphino-amines:  
[NiCl<sub>2</sub>(PMe<sub>2</sub>Ph)(PNMe<sub>2</sub>)] and [NiCl(PMe<sub>2</sub>Ph)(PNMe<sub>2</sub>)]PF<sub>6</sub>  
(PNMe<sub>2</sub> = *N,N'*-dimethyl-2-(diphenylphosphino)aniline)

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Abstract

A neutral bidentate P,N-ligand combining a hard dimethylamino nitrogen and a soft phosphine phosphorus donor affords the neutral trigonal bipyramidal as well as the cationic square-planar nickel(II) complexes *cis*-[NiCl<sub>2</sub>(PMe<sub>2</sub>Ph)(PNMe<sub>2</sub>)] and [NiCl(PMe<sub>2</sub>Ph)(PNMe<sub>2</sub>)]PF<sub>6</sub>, respectively. The latter species exhibits an appreciable catalytic activity in propylene oligomerization in the presence of Et<sub>2</sub>AlCl as co-catalyst.

**Keywords:** Crystal structures; Nickel complexes; Phosphino-amine complexes; Chelate complexes

The SHOP process (Shell Higher Olefins Process) makes use of organometallic catalysts on a large commercial scale to manufacture alpha-olefins and internal C<sub>11</sub> through C<sub>14</sub> alkenes in a flexible fashion [1] that can be adjusted to market needs. A typical catalyst is a neutral square-planar Ni(II) compound of the type [Ni(PO)(PR<sub>3</sub>)(R')], where, for example, R is a phenyl, R' a hydrocarbyl ligand and PO is a chelate phosphine functionalized with a carboxylate group. The ligand PR<sub>3</sub> plays essentially the role of stabilizing the catalyst. The anionic ligand R' also cooperates with the putative catalyst stability but it is intended to be the component of the coordination sphere aimed at the formation of an Ni-H entity in the actual catalytic species. On the other hand, the chelate ligand controls the catalytic activity and selectivity [2]. In fact, these complexes become active for ethylene oligomerization at the temperatures needed for nickel hydride formation [2]. More recently, cationic Ni(II) and Pd(II) complexes containing neutral hemilabile P,O-ligands have been proposed for the co-dimerization of ethylene and styrene and co-oligomerization of ethylene and carbon monoxide, respectively [3,4]. In these experiments cationic species appear to be far more efficient than neutral one in terms of

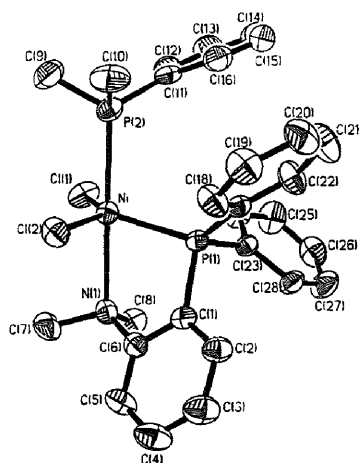
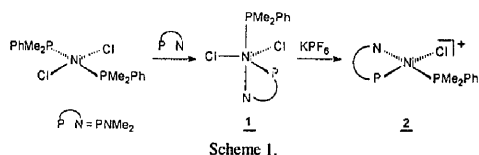


Fig. 1. Molecular structure of 1. Selected bond lengths (pm) and angles (°): Ni–Cl(1) 227.6(2), Ni–Cl(2) 228.4(2), Ni–P(1) 229.0(2), Ni–P(2) 237.2(2), Ni–N(1) 235.3(4); Cl(1)–Ni–Cl(2) 134.8(1), Cl(1)–Ni–P(1) 124.1(1), Cl(2)–Ni–P(1) 99.8(1), P(1)–Ni–P(2) 101.4(1), P(2)–Ni–N(1) 178.8(1), P(1)–Ni–N(1) 77.9(1), Ni–N(1)–C(6) 107.4(3), Ni–P(1)–C(1) 99.9(2).

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catalytic productivity, thanks to the increased hetaillable behavior of the coordinative O–Pd bond which readily generates free coordination sites for catalysis [4]. In this communication we report on the synthesis and full characterization of a new cationic red square-planar Ni(II) complex,  $[\text{NiCl}(\text{PNMe}_2)(\text{PMe}_2\text{Ph})]\text{PF}_6^-$  (**2**), and of its neutral green trigonal bipyramidal precursor,  $[\text{NiCl}_2(\text{PNMe}_2)(\text{PMe}_2\text{Ph})]$  (**1**). Both contain the neutral P,N-ligand  $[N,N'$ -dimethyl-2-(diphenylphosphino)aniline] ( $\text{PNMe}_2$ ) [5].

Compound **1** is prepared upon reacting *trans*- $[\text{NiCl}_2(\text{PMe}_2\text{Ph})_2]$  with  $\text{PNMe}_2$  in 1:1 molar ratio in MeCN at ambient temperature. Complex **2** is easily obtained by action of  $\text{KPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solutions of **1** (Scheme 1). Quite interestingly, complex **1** is a thermally stable five-coordinated species in which Ni(II) is surrounded by a  $\{\text{P}_2\text{NCl}_2\}$  chromophore. Extensive literature produced in the late sixties and seventies [6] showed that, for example,  $\{\text{P}_3(\text{CN})_2\}$  and  $\{\text{P}_3\text{X}_2\}$  ( $\text{X} = \text{halides, NCS}\}$  chromophores [7] are required in order to provide stable five-coordinated Ni(II) species. The molecular structure of **1** demonstrates that other suitable chromophores are effective in this connection and apparently



Scheme 1.

new relevant electronic and/or steric features have to be considered.

The crystal of **1** consists of discrete molecular units (Fig. 1) which are separated by normal van der Waal's distances. Complex **1** represents the first X-ray structure<sup>3</sup> of a five-coordinated, distorted trigonal bipyramidal nickel(II) complex containing the  $\text{Cl}_2\text{NP}_2$  donor set. The N(1) and P(2) atom of the monodentate  $\text{PMe}_2\text{Ph}$  ligand are located at the apices of the bipyramid (P(2)–Ni–N(1) 178.8(1)°, while Cl(1), Cl(2) and P(1) (from the bidentate ligand) atoms define the equatorial plane. The metal deviates by 14 pm from this plane towards P(2), and it is 2 pm from the P(2)–N(1) vector. The five-membered NiP(1)C(1)–C(6)N(1) ring adopts a somewhat envelope conformation. In particular, the ring puckering coordinates [10] are  $q_2 = 0.609(3)$  Å and  $\varphi_2 = -1.00(0.47)^\circ$  and the asymmetry parameters [11] for Ni (0.020; 0.284), P(1) (0.236; 0.212), C(1) (0.360; 0.077), C(6) (0.352; 0.096) and N(1) (0.210; 0.221) represent the displacements from  $C_1$  and  $C_2$  conformations, respectively. A comparison with the data reported in a survey [12], covering inter alia all the Ni(II) complexes, shows in **1** a relevant elongation of Ni–P and Ni–N bonds. This is clearly indicated by the values of Ni–P(1) (229.0 versus 219.2 pm in  $[\text{NiCl}_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})] \cdot \text{C}_6\text{H}_5\text{Me}$  [13], where dppm represents diphenylphosphinomethane, Ni–P(2) (237.2 versus 220.4 in 37 Ni(II)– $\text{PMe}_3$  structures and 222.5 pm in 21 Ni(II)– $\text{PPh}_3$  ones) [12], and Ni–N(1) distances (235.3 pm). This last bond is very long with respect to the mean value found in many Ni(II)–N<sub>tertiary amine</sub> distances (211.2 pm) [12] and it is only shorter than that of a square-pyramidal complex with N in the axial position (242.8 pm) [14]. According to Ref. [14] the Ni–N bond lengthening may be ascribed to both the axial position and the five-membered ring strain. On the contrary, the Ni–Cl distances (227.6 and 228.4 pm) are shorter

<sup>1</sup> Complex **1** was prepared as follows. Solid  $\text{PNMe}_2$  (213 mg, 0.7 mmol) was added to the blood-red solution of  $[\text{NiCl}_2(\text{PMe}_2\text{Ph})_2]$  (310 mg, 0.7 mmol) in MeCN (20 ml) under stirring at room temperature. The solution turned dark-green and after 30 min a light-green solid formed. The mixture was allowed to stir for an additional 45 min and then the solid was filtered off, recrystallized from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , and dried under vacuum (yield 64%). The product is soluble in chlorinated solvents, partially soluble in MeCN and insoluble in  $\text{Et}_2\text{O}$  and hexane. Anal. Calc. for  $\text{C}_{28}\text{H}_{31}\text{N}_2\text{P}_2\text{Cl}_2\text{Ni}$ : C, 60.96; H, 5.46; N, 2.30. Found: C, 59.68; H, 5.45; N, 2.44%. IR (KBr,  $\text{cm}^{-1}$ ): 3045 (w), 1435 (vs), 1101 (s), 907 (s), 748 (vs) and 695 (vs).  $\mu_{\text{eff}} = 3.3$  BM. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): several signals in the region +20.0 to –14.0. Visible band in the solid state (diffuse reflectance):  $\lambda_{\text{max}}$  (nm) 670. UV–Vis bands in  $6 \times 10^{-4}$  M  $\text{CH}_2\text{Cl}_2$  solution:  $\lambda_{\text{max}}$  (nm) 485 ( $\epsilon = 130 \text{ M}^{-1} \text{ cm}^{-1}$ ), 355 ( $\epsilon = 3300 \text{ M}^{-1} \text{ cm}^{-1}$ ), 325 (sh), 255 ( $\epsilon = 7200 \text{ M}^{-1} \text{ cm}^{-1}$ ). Crystals suitable for X-ray analysis were grown from  $\text{CH}_2\text{Cl}_2$ –hexane solutions.

<sup>2</sup> Solid  $\text{KPF}_6$  (46 mg, 0.25 mmol) was added to a solution of **1** (143 mg, 0.25 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (10 ml) under stirring at room temperature. The color of the mixture turned quickly to orange-red and no change was observed after 4 h. The mixture was filtered, the filtrate concentrated via rotavapor and hexane was added to give an orange-red oil, which was separated by decantation. The oil was re-dissolved in  $\text{CH}_2\text{Cl}_2$  and treated with  $\text{Et}_2\text{O}$  to afford a red powder which was filtered off, washed with  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$ , and dried under vacuum (yield 45%). The compound is soluble in  $\text{CH}_2\text{Cl}_2$  without decomposition within 1 h; soluble with decomposition in coordinating solvents such as MeCN and MeOH. Anal. Calc. for  $\text{C}_{28}\text{H}_{31}\text{N}_2\text{P}_2\text{ClF}_6\text{Ni}$ : C, 49.27; H, 4.58; N, 2.05. Found: C, 50.76; H, 4.66; N, 2.00%. IR (KBr,  $\text{cm}^{-1}$ ): 3056 (w), 1436 (s), 1105 (w), 836 (vs.  $\text{PF}_6^-$ ), 557 (s). Visible band in the solid state (diffuse reflectance):  $\lambda_{\text{max}}$  (nm) 480. UV–Vis bands in  $10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solutions:  $\lambda_{\text{max}}$  (nm) 450 ( $\epsilon = 650 \text{ M}^{-1} \text{ cm}^{-1}$ ), 305 ( $\epsilon = 9200 \text{ M}^{-1} \text{ cm}^{-1}$ ), 275 ( $\epsilon = 12100 \text{ M}^{-1} \text{ cm}^{-1}$ ). Molar conductivity in MeCN:  $\Lambda_m = 160.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ M}^{-1}$ . <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , ppm): 8.00–7.05 (19H), 3.22 (s, 6H,  $\text{N}[\text{CH}_3]_2$ ), 1.59 (s, 6H,  $\text{P}[\text{CH}_3]_2$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , ppm): 38.6 (bs), –5.2 (bs), –144.3 (septet)  $J(\text{PF}) = 713$  Hz. Complex **2** can also be prepared in higher yield (72%) in a 'one pot reaction' by mixing equimolar amounts of  $[\text{NiCl}_2(\text{PMe}_2\text{Ph})_2]$  and  $\text{PNMe}_2$ , and a slight excess of  $\text{KPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solutions. The compound is recovered by the same procedure as described above.

<sup>3</sup>  $\text{C}_{28}\text{H}_{31}\text{Cl}_2\text{N}_2\text{P}_2\text{Ni}$ ,  $M = 573.1$ , monoclinic, space group  $P2_1/n$ ,  $a = 939.0(3)$ ,  $b = 1791.4(6)$ ,  $c = 1679.3(6)$  pm,  $\beta = 94.92(3)^\circ$ ,  $U = 2814(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1192$ . Siemens Nicolet R3m/V four-circle diffractometer, Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å), graphite monochromator,  $\omega$ -2 $\theta$  scan mode. 3691 Independent reflections up to  $2\theta > 45^\circ$ , of which 2527 ( $F_o > 4\sigma(F_o)$ ) considered observed and used in the analysis. Heavy-atom method with refinement by standard full-matrix least-squares. In the last cycles of refinement all non-hydrogen atoms were allowed to vibrate anisotropically, and H atoms included in calculated positions ( $U = 0.07$  Å<sup>2</sup>). Quantity minimized  $\sum w(|F_o| - |F_c|)^2$  with  $w^{-1} = \sigma^2(F) + 0.002F^2$ ,  $R = 0.040$ ,  $R_w = 0.051$  (0.056 and 0.060, respectively, for all reflections),  $\text{GOF} = 0.87$  and largest difference peak of  $0.5 \text{ e } \text{Å}^{-3}$ . All calculations were performed using SHELXTL-PLUS [8]. Scattering factors for all the atoms were taken from Ref. [9]. See also Supplementary material.

than the expected value (233.9 pm in 63 Ni(II)–Cl entries) [12].

In spite of the observed moderate distortion from ideal trigonal bipyramidal geometry, for which a diamagnetic ground state would be expected, complex **1** turns out to be paramagnetic in the solid state ( $\mu_{\text{eff}} = 3.3$  BM) at ambient temperature. The unexpected paramagnetic behavior [6,7] is maintained in  $10^{-2}$  M chloroform-d solutions, as evidenced in proton NMR spectra by signals shifting and broadening (see footnote 1, p. 2). It should be pointed out that the visible spectrum of the green solid **1**, recorded in the diffuse reflectance mode ( $\lambda_{\text{max}} = 670$  nm), parallels that obtained in anhydrous  $10^{-2}$  M  $\text{CH}_2\text{Cl}_2$  solutions, thus suggesting an identical structure in solution and in the solid state. However,  $6 \times 10^{-4}$  M  $\text{CH}_2\text{Cl}_2$  solutions of **1** exhibit a remarkably different pattern ( $\lambda_{\text{max}} = 485$  nm,  $\epsilon = 130 \text{ M}^{-1} \text{ cm}^{-1}$ ), indicating a chemical re-arrangement to a non-conducting and still paramagnetic ( $^1\text{H}$  NMR) red species in dilute solutions.

Compound **2** (see footnote 2, p. 2) is proposed to be a cationic (1:1 electrolyte in  $7 \times 10^{-4}$  M MeCN solutions) four-coordinated square-planar Ni(II) complex. Actually,  $\{\text{NiP}_2\text{NCl}\}^+$  complexes are not common, but the average ligand field strength of the  $\{\text{P}_2\text{NCl}\}$  chromophore could justify a planar geometry [15], which fits well with the diamagnetism of **2** both in the solid state and in  $\text{CH}_2\text{Cl}_2$  solution. The  $^{31}\text{P}\{^1\text{H}\}$  spectrum exhibits the septet due to the  $\text{PF}_6^-$  counter ion; in addition, two broad singlets at  $\delta = +38.6$  and  $-5.2$  ppm are attributable to the two magnetically nonequivalent phosphorus donors, mutually *cis*-positioned [16]. Compound **2** has been tested in the oligomerization of propylene in chlorobenzene. In the absence of an alkylating agent, **2** turns out to be catalytically inactive up to 80 °C whereas in the presence of  $\text{Et}_2\text{AlCl}$  added as 1 M toluene solution (Al:Ni = 30:1), >95% dimerization occurs at 0 °C<sup>4</sup>; the maximum activity, obtained after 10 min of operation, is ~40 000 mole propylene/mole Ni/hour (after 10 min activity slowly decreases with time). The product distribution at the end of run is as follows: 16% dimethylbutenes, 71% methylpentenes and 13% hexenes.

### Supplementary material

Atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters and H atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

<sup>4</sup> General conditions: 0.025 mmol of Ni(II) complex dissolved in 50 ml of chlorobenzene;  $p(\text{C}_3\text{H}_6) = 1$  atm; reaction time 26 h.

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### References

- [1] E.F. Lutz, *J. Chem. Educ.*, **63** (1986) 202.
- [2] W. Keim, *Angew. Chem., Int. Ed. Engl.*, **29** (1990) 235.
- [3] M.C. Bonnet, F. Dahan, A. Ecke, W. Keim, R.P. Schulz and I. Tkachenko, *J. Chem. Soc., Chem. Commun.*, (1994) 615.
- [4] G.J. Britovsek, W. Keim, S. Mecking, D. Sainz and T. Wagner, *J. Chem. Soc., Chem. Commun.*, (1993) 1632.
- [5] T.B. Rauchfuss and D.M. Roundhill, *J. Am. Chem. Soc.*, **96** (1974) 3098.
- [6] L. Sacconi, L. Mani and A. Bencini, Nickel, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon, Oxford, 1987, pp. 1–347, and Refs. therein.
- [7] J.W. Dawson, L.M. Venanzi, J.R. Preer, J.E. Hix and H.B. Gray, *Inorg. Chem.*, **9** (1970) 2675; O. Stelzer, *Chem. Ber.*, **107** (1974) 2329; E.J. Lukosius and K.J. Coskran, *Inorg. Chem.*, **14** (1975) 1922; J.W. Dawson, T.J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H.B. Gray, *J. Am. Chem. Soc.*, **96** (1974) 4428.
- [8] G.M. Sheldrick, *SHEXTL-PLUS*, program for crystal structure determination, University of Cambridge, UK, 1990.
- [9] *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974.
- [10] D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, **97** (1975) 1354.
- [11] M. Nardelli, *Acta Crystallogr., Sect. C*, **39** (1983) 1141.
- [12] A. Guy Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.
- [13] L. Manojlovic-Muir, H.A. Mirza, N. Sadiq and R.J. Puddephatt, *Inorg. Chem.*, **32** (1993) 117.
- [14] E.P. Kyba, R.E. Davis, S.-T. Liu, K.A. Hassett and S.B. Larson, *Inorg. Chem.*, **24** (1985) 4629.
- [15] A. Turco, V. Scatturin and G. Giacometti, *Nature (London)*, **183** (1959) 601; P.J. Stone and Z. Dori, *Inorg. Chim. Acta*, **5** (1971) 434; L. Que and L.M. Pignolet, *Inorg. Chem.*, **12** (1973) 156; M.C. Browning, J.R. Mellor, D.J. Morgan, S.A.J. Pratt, L.E. Sutton and L.M. Venanzi, *J. Chem. Soc.*, (1962) 693; R.G. Hayter and F.S. Humic, *Inorg. Chem.*, **4** (1965) 1701; J.T. Wang, C. Udovich, K. Nakamoto, A. Quattrochi and J. Ferraro, *Inorg. Chem.*, **9** (1970) 2675.
- [16] P.S. Pregosin and R.W. Kunz, in P. Diehl, E. Fluck and R. Springer (eds.), *<sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complexes*, Berlin, Heidelberg, 1979.