Intramolecular O–H···O–Ni and N–H···O–Ni Hydrogen Bonding in Nickel Diphenylphosphinoenolate Phenyl Complexes: Role in Catalytic Ethene Oligomerisation; Crystal Structure of $[\overline{\mathrm{NiPh}\{\mathrm{Ph_2PCH}{\cdots}\mathrm{C}(\cdots\mathrm{O}})(o\text{-}\mathrm{C_6H_4NHPh})\}(\mathrm{PPh_3})]$

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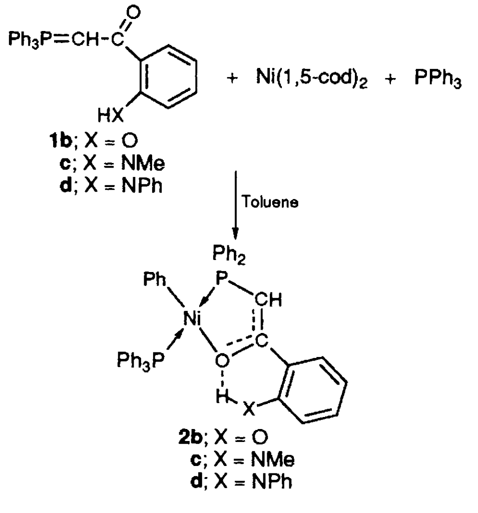
Nickel diphenylphosphinoenolate complexes are prepared from *ortho*-HX-substituted phenacylidenetriphenylphosphoranes (X = O, NMe, NPh) which display strong intramolecular hydrogen bonding between the enolate oxygen and the H–X function; this feature dramatically influences the molecular mass distribution of the oligomers obtained by catalytic oligomerisation of ethene.

Nickel complexes containing specific three electron donor phosphorus–oxygen chelating ligands are very efficient catalysts for the oligomerization of ethylene to linear α-olefins. The combined soft-hard properties of the chelating P,O ligand have been shown by Keim *et al.* to play a key role in the properties of these catalyst and this concept has led to the industrialization of the Shell Higher Olefin Process (SHOP), which is one of the largest applications of homogeneous catalysis.[1] The complex $[\overline{\mathrm{Ni(Ph)}\{\mathrm{Ph_2PCH}{\cdots}\mathrm{C}(\cdots\mathrm{O}})\mathrm{Ph}\}(\mathrm{PPh_3})]$ **2a** has been structurally characterised and regarded as a suitable model for the organometallic active species present in the industrial process.[2a] Allyl nickel complexes with P,O-type ligands have also been recently studied.[2b]

Many attempts have been made to modify the molecular mass distribution of oligomers by changing the structure of the phosphinoenolate ligand and/or the ancillary phosphine.[3] With the aim of facilitating the β-hydrogen elimination step during the growing step and thus favouring low molecular mass products, which represent an important market, we have tried to decrease the electronic density at the nickel centre by forming an additional intramolecular bonding with the enolate oxygen atom.

Reaction of the *ortho*-substituted phenacylidenetriphenylphosphoranes **1b–d**, prepared by modified literature methods,[4] with 1 equiv. of $[\mathrm{Ni(1,5\text{-}cod)_2}]$ and 1 equiv. of triarylphosphine in toluene, afforded complexes **2b–d** under similar conditions to those described previously for complex **2a** [eqn. (1)].[2a] The new, yellow complexes were isolated analytically pure by precipitation with pentane.† The *trans* arrangement of the P atoms gives rise in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum to an AB pattern with typical coupling constants (Table 1).



The crystal structure of complex **2d** has been determined by X-ray diffraction (Fig. 1).‡ The square-planar coordination around nickel is only slightly distorted and the five-membered $\overline{\mathrm{Ni{-}P{-}C{-}C{-}O}}$ cycle is nearly planar, owing to electron delocalisation within the enolate moiety. The relatively short Ni–Ph distance is consistent with the electron affinity of the P,O chelate. Since the first step in the catalytic cycle is the insertion of ethylene into the Ni–Ph bond, which is followed by ß-H elimination, the strength of this bond influences the catalyst activation temperature.[5] The most notable feature in

Table 1 Selected ^{1}H and ^{31}P NMR (81 MHz C_6D_6) spectroscopic data of the phosphoranes and the phosphinoenolate complexes.

	1b	**2b**	**1c**	**2c**	**1d**	**2d**
^{1}H (XH)	13.88	11.35	8.35	6.4–7.7[a]	10.05	8.95
$^{31}\mathrm{P}\{^1\mathrm{H}\}$ (PPh$_3$)		16.2		16.4		15.02
$^{31}\mathrm{P}\{^1\mathrm{H}\}$ (P, O)		20.1		19.5		19.9
$^2J_{\mathrm{PP}}$ (Hz)		279		280		270

[a] masked by aromatic protons.

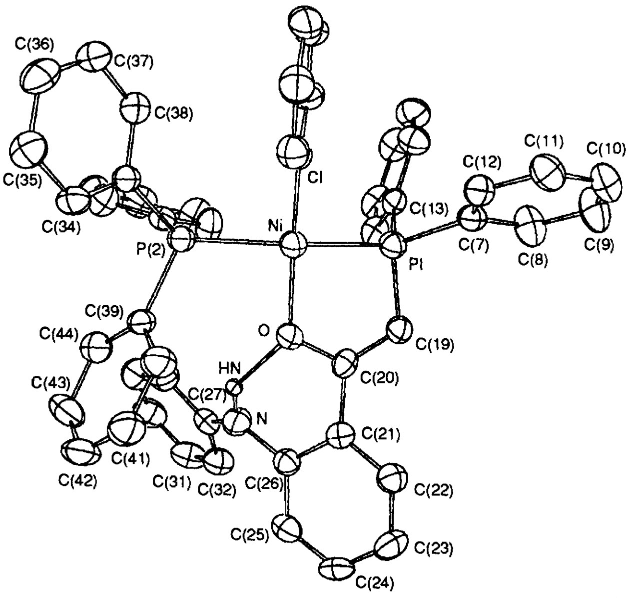


Fig. 1 Molecular structure of complex **2d**. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.886(3), Ni–O 1.923(2), Ni–P(1) 2.180(1), Ni–P(2) 2.214(1), P(1)–C(19) 1.766(4), C(19)–C(20) 1.345(4), C(20)–O 1.332(4), C(20)–C(21) 1.498(5), C(21)–C(26) 1.413(4), C(26)–N 1.396(5), N–C(27) 1.400(4), N–H_N 0.87(3), O–H_N 2.06(3); C(1)–Ni–O 170.1(1), P(1)–Ni–P(2) 159.78(4), P(1)–Ni–O 86.20(6), P(1)–C(19)–C(20) 113.6(2), C(19)–C(20)–O 122.4(3), C(20)–O–Ni 117.9(2), C(20)–O–H_N 93.4(8), C(26)–N–H_N 112(2), C(26)–N–C(27) 128.3(3), C(27)–N–H_N 118(2).

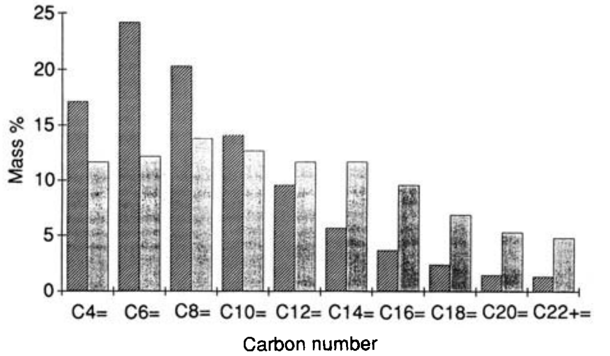


Fig. 2 Catalytic ethene oligomerisation. Olefin distribution using complexes **2a** (▒) and **2d** (▨).

the structures of **2b–d**, which is absent in that of **2a**, is the strong intramolecular N–H···O hydrogen bonding: the distance between the NH hydrogen atom and the oxygen atom of the enolate ligand is rather short [2.06(3) Å in **2d**].[6] However, this value is larger than that found for the intermolecular O–H···O distance (1.60 Å) for free phenol in the phenoxo complex [NiMe(OPh)(HOPh)(PMe$_3$)$_2$].[7]

Remarkably, the nitrogen atom has practically planar coordination in **2d** with the sum of its valency angles being 358.3°. This is probably due to the combined influence of electronic and steric interactions resulting from the hydrogen bonding and this leads to a stabilised, nearly planar six-membered ring. The ^{1}H NMR data (Table 1) are typical for OH···O, resp. NH···O protons in complexes **2b–d**[8] and it is noteworthy that these resonances are more shielded than in the corresponding free phosphoranes. Structural results for **2c** parallel those for **2d**.[9]

Complexes **2b–d** display high activity and selectivity in ethene oligomerisation to linear α-olefins (toluene, 0.10 mmol catalyst, 60–95 °C, 6 MPa ethylene, 90–300 min), with a marked shift of the product distribution to lower molecular masses. We compare in Fig. 2 the composition of the olefin mixtures obtained with catalysts **2a** and **2d** under similar experimental conditions (50–80 °C; 6 MPa; toluene as solvent). The intramolecular hydrogen bonding in these new catalytic precursors allows a fine tuning of their selectivity; it favours β-hydrogen elimination and thus the formation of C_4–C_8 olefins, of which 95–97% are linear α-olefins.

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Footnotes

† *Selected data* for **2b**: IR (KBr): 1585w, 1565w, 1520s, 1480w. ^{1}H NMR (200 MHz, C_6D_6) δ: 5.15 (s, 1H, PCH). For **2c**: IR (KBr): 1600w, 1580w, 1510s, 1470w. ^{1}H NMR (200 MHz, C_6D_6) δ: 1.90 (s, 3H, NMe), 5.05 (s, 1H, PCH). For **2d**: IR (KBr): 1575w, 1500s, 1460w. ^{1}H NMR (200 MHz, C_6D_6) δ: 5.09 (s, 1H, PCH).

‡ Yellow crystals of **2d** from toluene–pentane. *Crystal data* for **2d**: $C_{50}H_{41}NOP_2Ni$, M = 792.5; monoclinic; space group $P2_1/n$; a = 18.774(6), b = 19.725(6), c = 10.808(3) Å, β = 103.04(2)°, U = 3899.2 Å^3, Z = 4, D_c = 1.350 g cm^{-3}, μ = 17.852 cm^{-1}. Measurements: Philips PW1100/16, θ/2θ flying step-scan, radiation: Cu-Kα graphite monochromated (λ = 1.5418 Å), T = 173 K; solution: Molen/Vax programs. 4525 unique reflections (θ = 3–51°), of which 2907 with $I > 3\sigma(I)$ were used for structure solution (direct methods) and refinement (full-matrix least squares analysis); R = 0.029, R_w = 0.040. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions (d_{C-H} = 0.95 Å, $B_H = 1.3B_{equiv}$ for the carbon to which it was attached), except for the NH proton which was located in the difference Fourier map and refined with a fixed isotropic B = 4 Å^2.

Atomic coordinates, bond lengths and angles, and thermal parameters of **2c** and **2d** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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