# Nickel Complexes with Heterofunctionalized Phosphine Ligands. Catalytic Oligomerization of Ethylene with $[Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)Ph\}]$ *

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Reaction of $[Ni(C_5Ph_5)Br(CO)]$ with $Ph_2PCH_2C(O)Ph$ in the presence of 1,8-bis(dimethylamino)naphthalene (proton sponge) gives the chelate complex $[Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)Ph\}]$ **1**. The complexes $[Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)(C_5H_4)Fe(C_5H_5)\}]$ **2**, $[Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)(1,3\text{-}C_6H_4)C(O){=}HCPPh_2\}Ni(C_5Ph_5)]$ **3**, $[Ni(C_5H_5)\{Ph_2PCH{=}C(O)Ph\}]$ **4** and $[Ni(C_5H_5)\{Ph_2PCH{=}C(O)(C_5H_4)Fe(C_5H_5)\}]$ **5** have been synthesised using the appropriate phosphine ligand and applying a procedure similar to that for **1**. Complex **1**, activated with $NaBH_4$, exhibits catalytic activity in the low-pressure oligomerization of ethylene. At 130 °C, under 38 bar of ethylene, selectivities of up to 98% towards linear α-olefins were achieved. Protonation of the bimetallic complex **2** with $HBF_4$ gave the cationic complex $[Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]BF_4$ **6**. Crystals of **6** belong to the orthorhombic space group *Pbca* with $a = 19.427(6)$, $b = 38.595(11)$, $c = 13.001(4)$ Å and $Z = 8$. The structure was refined to $R = 0.049$ ($R' = 0.067$). The bonding of $C_5Ph_5$ contrasts with the bonding modes usually found for cyclopentadienyl ligands. The ring contains two short [1.384(8) and 1.389(8)], two medium [1.444(8) and 1.443(8)], and one long [1.474(8) Å] C–C bonds so that the $C_5Ph_5$ may be viewed as an (alkyl, diene) ligand. This unusual bonding is likely to result from the 'chemical' dissymmetry of the *P,O* ligand and the low *trans* influence of the oxygen atom. The extremely low ν(C=O) frequency of the co-ordinated ketone (1525 $cm^{-1}$) reflects the strong electron-withdrawing effect of the $Ni(C_5Ph_5)^+$ moiety.

The current interest in the preparation of transition-metal complexes containing hybrid, *i.e.* heterofunctionalized, phosphine ligands is largely motivated by their potential applications in homogeneous catalysis.[1] In the seventies, methods for the preparation of nickel catalysts of the type $[NiPh\{Ph_2PCR^1{=}C(O)R^2\}L]$ (L = phosphine) suitable for the polymerization and selective oligomerization of ethylene were patented by Shell.[2] One such complex, $[NiPh\{Ph_2PCH{=}C(O)Ph\}(PPh_3)]$, models the large-scale industrial process for the production of α-olefins by giving high yields and excellent selectivities when used as a catalyst for the oligomerization of ethylene.[3] Complexes of this type were obtained by oxidative addition of α-keto phosphorus ylides, $Ph_3P{=}CR^1C(O)R^2$, on $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) in the presence of a two-electron donor ligand. In the course of this reaction a P–Ph bond of the keto-ylide is cleaved, thus generating the crucial $[Ph_2PCR^1{=}C(O)R^2]^-$ ligand. Although leading to very efficient catalysts, this synthetic principle does not enable the preparation and study of new types of catalyst precursors, notably systems for which the induction and initiation steps of the catalytic cycle may be better tuned. In view of the industrial relevance of three-electron *P,O* systems, we aimed at developing a new and convenient route to nickel(II) complexes containing a single chelating *P,O* ligand. For this purpose we considered acylmethylphosphines, $Ph_2PCH_2C(O)R$, a class of ligands which are readily enolizable. The use of such phosphines as precursors instead of ylides provides a great potential for variation.

We also aimed at investigating the catalytic potential of such complexes carrying other organic ligands than those usually employed for ethylene oligomerization. Despite the ease of obtaining of cyclopentadienyl complexes, the number of reports on the use of $[Ni(C_5R_5)(P\text{–}O)]$ complexes for oligomerization is rather low. In a recent publication, the complex $[Ni(C_5H_5)\{Ph_2PCH{=}C(O)Ph\}]$ was reported to display poor activity and selectivity for ethylene oligomerization.[4] This may be due to the fact that the $C_5H_5$ ligand cannot be readily displaced, therefore inhibiting the formation of a vacant site. We focused our efforts on another $C_5R_5$ ligand, namely the pentaphenylcyclopentadienyl anion. The co-ordination chemistry of this ligand has been examined by various research groups in the last decade.[5] Reactions resulting in a rapid and sometimes surprising displacement of this ligand are well known, leaving the residual framework of the molecule intact.[5d,e] The conditions leading to this reactivity are not clear. Possible reaction paths are the displacement of the ligand as a $C_5Ph_5$ radical or as $C_5Ph_5H$. Taking into account this known reactivity, we prepared some $[Ni(C_5Ph_5)(P\text{–}O)]$ complexes and tested their reactivity towards ethylene oligomerization.

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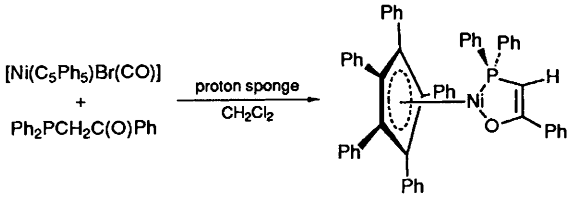
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

## Results and Discussion

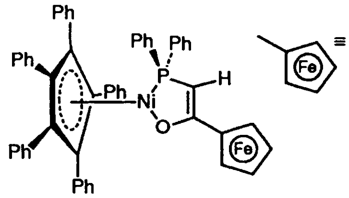
When a dichloromethane solution of [Ni(C$_5$Ph$_5$)Br(CO)] was treated with equimolar amounts of Ph$_2$PCH$_2$C(O)Ph and proton sponge, the dark red enolato complex **1** was obtained in nearly quantitative yield [equation (1)]. The IR spectrum of **1** displays notably a strong absorption band at 1521 cm$^{-1}$ (KBr) due to the enolate function. The $^1$H and $^{31}$P NMR spectra unambiguously confirm the presence of a co-ordinated three-electron *P,O* ligand (see Experimental section). When this reaction was performed without addition of 1,8-bis(dimethylamino)naphthalene (proton sponge) a dark green compound **1′** was formed, characterized by a strong $\nu(\mathrm{C{=}O})_{\mathrm{ketone}}$ absorption band at 1674 cm$^{-1}$. Attempts to isolate pure **1′** have failed, the complex being readily converted into **1**. The absence of any $\nu(\mathrm{C{\equiv}O})$ absorption band in the IR spectrum of **1′** suggests that this complex is the substitution product [Ni(C$_5$Ph$_5$){Ph$_2$PCH$_2$C(O)Ph}Br]. The route leading to **1** is a general method for the preparation of (enolatophosphine)nickel complexes starting from methylacylphosphines. Thus, using a procedure similar to that described above, complexes **2** and **3** were conveniently prepared in 80 and 69% yield, respectively. The method could be extended to the cyclopentadienyl complexes **4** and **5**, by employing [Ni(C$_5$H$_5$)(cod)]BF$_4$ as precursor. Work-up details are given in the Experimental section.



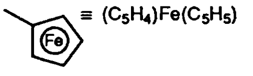
(1)

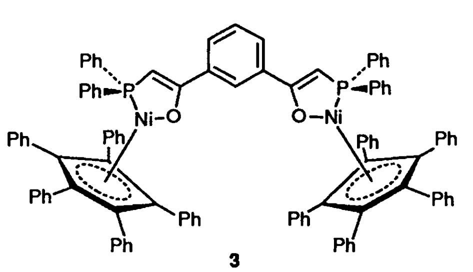
**1**

Complex **1**, when associated with a stoichiometric amount of NaBH$_4$, catalyses the low-pressure oligomerization of ethylene. The presence of NaBH$_4$ is *required* to induce catalytic activity for ethylene pressures below 40 bar (with a temperature maintained at 130 °C). In a typical run [100 cm$^3$ steel autoclave, 188 mmol ethylene, 130 °C, 38 bar, ethylene:Ni = 3030:1, solvent 5 cm$^3$ tetrahydrofuran (thf) + 25 cm$^3$ toluene)] ethylene was converted into linear α-olefins with a selectivity of *ca.* 98%. An induction period of 40 min was necessary before the pressure decreased in the autoclave. The formation of a nickel hydride, a prerequisite for catalytic activity, is likely to result under the conditions described above from reaction of NaBH$_4$ with **1** and not *via* insertion of ethylene into the Ni–C$_5$Ph$_5$ moiety. Under similar conditions, complex **4** also leads to α-olefins; in contrast to the reaction with **1**, the catalytic run with **4** led to the formation of high proportions of polyethylene ($M_n$ = 479). This suggests that the nickel hydride is more easily formed, *i.e.* is formed at lower temperatures, with the 'Ni(C$_5$H$_5$)' complex than with the 'Ni(C$_5$Ph$_5$)' complex. It is noteworthy that, according to a recent publication,[4] ethylene pressures of 70 bar are required to observe activity of complex **4** in the absence of any additive. Even under these conditions, however, the activity of **4** was low.

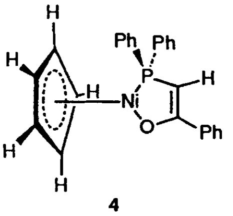


**2**

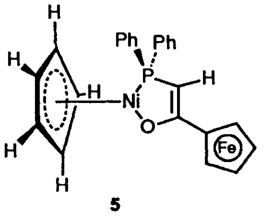




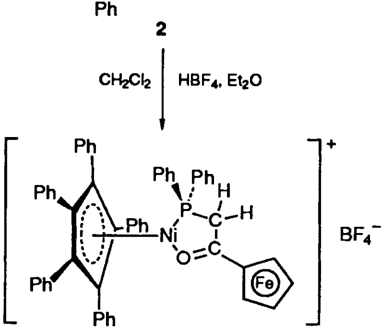
**3**



**4**



**5**



BF$_4^-$ (2)

Nickel catalysts with three-electron *P,O* chelates which have been employed for carbon–carbon linkage of monoolefins are regarded as bearing chemically inert (*P,O*) moieties; these latter are sometimes called 'spectator' ligands since they do not participate directly in the catalytic cycle. To obtain insight concerning the stability of such ligands, we tested the reactivity of a *P,O* complex toward protonation. On treating the heterobimetallic compound **2** with HBF$_4$–Et$_2$O in dichloromethane an instantaneous change in colour to intense bright blood-red occurred. The protonation gave the cationic complex [Ni(C$_5$Ph$_5$){Ph$_2$PCH$_2$C(O)(C$_5$H$_4$)Fe(C$_5$H$_5$)}]BF$_4$ **6** which could be isolated as dark red crystals [equation (2)]. In the $^1$H NMR (1,1,2,2-C$_2$D$_2$Cl$_4$, 60 °C) spectrum of **6** the PCH$_2$ protons appear as a doublet at δ 4.26 with a typical $^2J$(PH) coupling constant of 10 Hz. Consistent with the formation of a cationic species, the $^{31}$P chemical shift varies from δ 21.1 for **2** to 27.6 for **6**. We also obtained compound **6** in a somewhat surprising way. Having measured the cyclic voltammogramm of complex **2**, which displays two reversible oxidation waves, at 0.46 and 0.68 V *vs.* SCE respectively,[6] we tried to oxidize **2** chemically. On treating [Ni(C$_5$Ph$_5$){Ph$_2$PCH=C(O)(C$_5$H$_4$)Fe(C$_5$H$_5$)}] **2** with 1 equivalent of AgBF$_4$ [$E_{\frac{1}{2}}$(Ag$^+$–Ag) = *ca.* 0.97 V *vs.* SCE] in dichloromethane a change in colour from dark red to red-brown and a precipitation of silver metal were observed. After separation of the silver, we attempted to grow crystals from the filtered solution. In the course of crystallization, a further slowly occurring colour change was observed. An X-ray diffraction analysis of the thus obtained crystals revealed the formation of the nickel complex **6** described above. The formation of **6** in the reaction of **2** with AgBF$_4$ results from a complex redox process. In view of the lower Fe$^{\mathrm{II}}$–Fe$^{\mathrm{III}}$ *vs.* Ni$^{\mathrm{II}}$–Ni$^{\mathrm{III}}$ oxidation potential, an iron(III) radical cationic species should be formed first. As recently shown,[7] enolate-substituted ferrocenium species undergo intramolecular redox processes in which an electron is

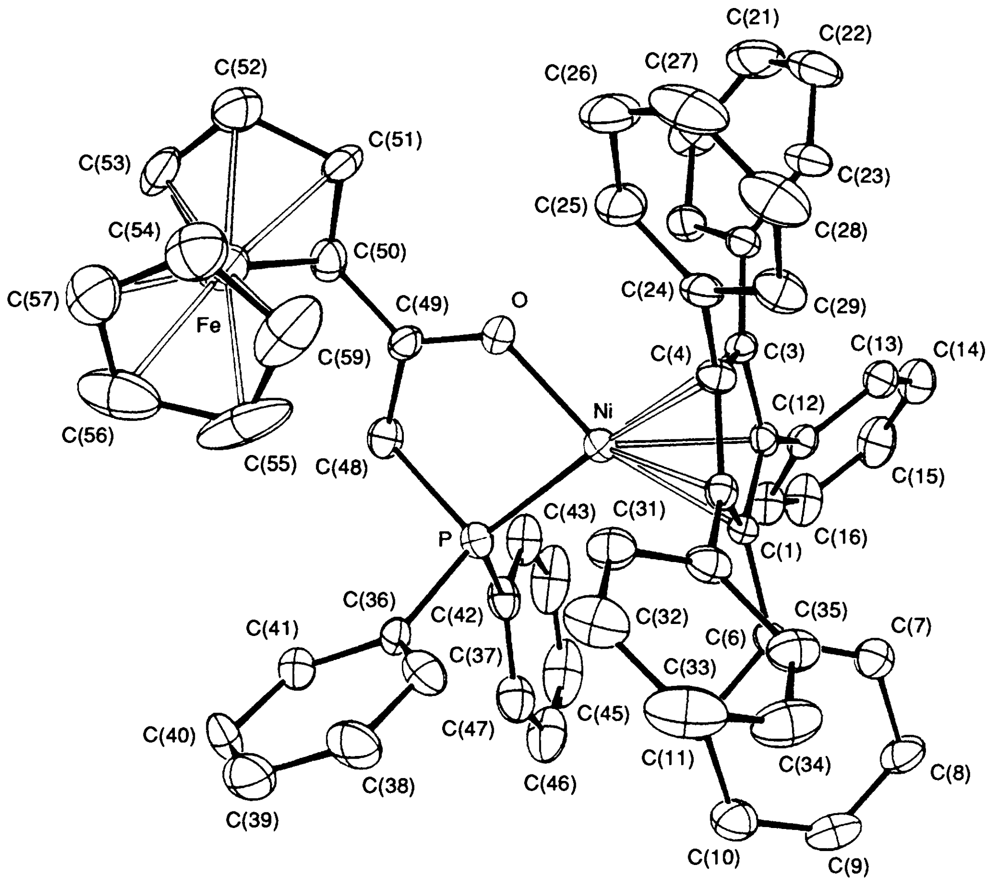
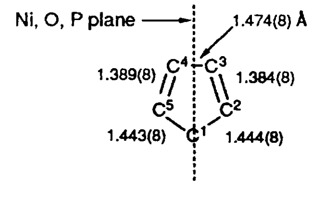


**Fig. 1** An ORTEP[8] plot of the cation $[Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]^+$ showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted



given to the iron centre from the *P,O* ligand. In the course of this process, a further reduction including protonation of the enolate may occur, possibly involving the solvent. Although we were able to detect by ESR spectroscopy, the formation of paramagnetic species in the reaction with $Ag^+$, all attempts to isolate a pure, paramagnetic species have failed. Only the protonated complex **6** could be characterized.

The molecular structure of complex **6** is shown in Fig. 1. Positional parameters are given in Table 1, selected bond distances and angles in Table 2. The geometry around the nickel atom may be viewed as square planar, the co-ordination positions being occupied by the atoms P, O and C(1) and the centre of the C(3)–C(4) bond. The least-squares $C_5$ (of $C_5Ph_5$) plane and the O,Ni,P plane are perpendicular [91.1(2)°] and the latter plane may be regarded as a mirror plane of the $C_5Ph_5$ ring. The structure of **6** displays a particular bonding mode of the $C_5Ph_5$ ligand. The Ni–C(1) distance [2.072(6) Å] is significantly shorter than the other Ni–C bond lengths which lie in the range 2.140(6)–2.177(6) Å. Since C(1) lies in the O–Ni–P plane, it appears likely that the shortening of the Ni–C(1) bond length is due to the influence of the oxygen atom *trans* to C(1). The dissymmetry of the $C_5Ph_5$ bonding mode thus could reflect the intrinsic dissymmetry of the *P,O* chelate. The C–C bond lengths in the $C_5Ph_5$ ring also display remarkable features (see Table 1). There are two short [C(2)–C(3), C(4)–C(5)], two medium [C(1)–C(2), C(1)–C(5)] and one long [C(3)–C(4)] bond lengths so that the cyclopentadienyl ligand could be viewed as a diene–alkyl ligand. The $\sigma,\eta^4$-bonding mode found clearly contrasts with the metal–cyclopentadienyl interactions usually found or proposed, *i.e.* for example $\eta^5$, $\eta^3$-allyl, $\eta^2$-ene or $\eta^4$.[9] Note however that an analogous situation was found in the solid-state structure of the complex $[Pd(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(PPr^i_3)]$ where the $\eta^5$-$C_5H_5$ ligand displays the same alternating C–C distances in the ring as that found for **6**. Extended Hückel molecular-orbital calculations by Hofmann and co-workers[10] for $[Pd(\eta^5\text{-}C_5H_5)Me(PH_3)]$ indicate that in this model system the observed distortions are to be expected. The calculations predict a shorter M–C($C_5H_5$) bond *trans* to the weaker σ donor, *i.e.* the oxygen atom in our case.

The $C_5Ph_5$ ligand shows the usual propeller-like arrangement for the five phenyl rings,[5d–f] the torsion angles of the phenyl groups around the $C_5Ph_5$ plane lying in the range 48–61°. As shown in Fig. 2, the five-membered *P,O* chelate ring is not planar, the envelope shape being a result of the $sp^3$ geometry of the $CH_2$ carbon atom [C(48)]. The deviation of C(48) from the Ni–O–P plane is 0.372(7) Å. The small dihedral angle O–C(49)–C(50)–C(51) of 6° shows a high degree of conjugation between the C=O bond and the $C_5H_4$ ring. The Ni–O distance of 1.877(4) Å is close to the sum of the covalent radii for nickel and oxygen (1.91 Å).[11] Interestingly the ν(C=O) IR absorption band at 1525 $cm^{-1}$ is rather low for a co-ordinated ketone, *cf.* 1554 $cm^{-1}$ for the cationic chelate complex *cis*-$[\{Pd[Ph_2PCH_2C(O)Ph]_2\}_2]^{2+}$.[12] This indicates a strong ketone binding in **6**. This strong interaction likely originates from the ability of the $[Ni(C_5Ph_5)]^+$ d orbitals to accept electron density from ligands with free electron pairs of π symmetry.[13]

To summarize, this report describes a new and convenient synthesis of nickel-based oligomerization catalysts, starting

**Table 1** Positional parameters with their estimated standard deviations (e.s.d.s) for $[Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]BF_4$ **6**

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Ni | −0.008 10(5) | 0.117 92(2) | 0.496 71(7) | C(31) | 0.033 7(3) | 0.090 4(2) | 0.768 2(5) |
| Fe | 0.172 48(6) | 0.210 27(3) | 0.581 51(8) | C(32) | 0.034 7(4) | 0.087 4(2) | 0.873 4(5) |
| P | −0.067 20(8) | 0.165 04(4) | 0.517 3(1) | C(33) | −0.005 0(4) | 0.062 8(2) | 0.921 5(5) |
| O | 0.066 2(2) | 0.146 56(9) | 0.461 1(3) | C(34) | −0.045 9(4) | 0.041 6(2) | 0.863 4(5) |
| C(1) | −0.066 0(3) | 0.074 0(1) | 0.526 0(4) | C(35) | −0.048 5(3) | 0.044 6(2) | 0.757 3(5) |
| C(2) | −0.042 4(3) | 0.070 7(1) | 0.421 1(4) | C(36) | −0.080 3(3) | 0.182 9(2) | 0.645 1(5) |
| C(3) | 0.028 8(3) | 0.072 0(1) | 0.422 7(5) | C(37) | −0.066 9(3) | 0.163 2(2) | 0.731 9(5) |
| C(4) | 0.051 1(3) | 0.071 9(1) | 0.531 1(4) | C(38) | −0.069 9(4) | 0.177 6(2) | 0.829 3(5) |
| C(5) | −0.007 1(3) | 0.072 0(1) | 0.593 3(4) | C(39) | −0.085 8(4) | 0.212 1(2) | 0.840 2(6) |
| C(6) | −0.139 7(3) | 0.069 5(1) | 0.556 2(4) | C(40) | −0.099 7(4) | 0.232 1(2) | 0.755 0(6) |
| C(7) | −0.173 5(3) | 0.039 1(2) | 0.525 8(5) | C(41) | −0.096 7(4) | 0.217 7(2) | 0.659 1(6) |
| C(8) | −0.240 9(3) | 0.033 4(2) | 0.550 5(5) | C(42) | −0.147 3(3) | 0.170 7(2) | 0.448 7(5) |
| C(9) | −0.275 5(4) | 0.057 3(2) | 0.605 8(5) | C(43) | −0.146 7(4) | 0.172 2(2) | 0.342 1(5) |
| C(10) | −0.244 7(4) | 0.087 0(2) | 0.638 1(6) | C(44) | −0.207 5(5) | 0.173 5(2) | 0.287 8(6) |
| C(11) | −0.175 6(3) | 0.092 8(2) | 0.614 4(5) | C(45) | −0.269 2(5) | 0.171 3(2) | 0.338 0(7) |
| C(12) | −0.085 2(3) | 0.065 4(1) | 0.328 0(5) | C(46) | −0.271 5(4) | 0.169 6(2) | 0.443 7(7) |
| C(13) | −0.067 0(3) | 0.039 4(2) | 0.258 9(5) | C(47) | −0.209 7(4) | 0.169 8(2) | 0.500 0(6) |
| C(14) | −0.105 2(4) | 0.032 6(2) | 0.172 8(5) | C(48) | −0.005 9(4) | 0.195 2(2) | 0.457 7(5) |
| C(15) | −0.162 9(4) | 0.052 2(2) | 0.153 9(6) | C(49) | 0.064 1(3) | 0.178 7(2) | 0.456 7(4) |
| C(16) | −0.181 5(4) | 0.078 3(2) | 0.218 8(6) | C(50) | 0.126 2(4) | 0.198 4(2) | 0.446 7(5) |
| C(17) | −0.144 0(3) | 0.084 3(2) | 0.306 8(5) | C(51) | 0.194 2(4) | 0.184 0(2) | 0.450 5(5) |
| C(18) | 0.073 3(3) | 0.072 4(1) | 0.330 7(4) | C(52) | 0.241 6(4) | 0.211 2(2) | 0.460 3(6) |
| C(19) | 0.065 0(3) | 0.096 7(2) | 0.254 9(4) | C(53) | 0.205 4(4) | 0.241 9(2) | 0.465 2(6) |
| C(20) | 0.103 7(4) | 0.095 6(2) | 0.167 4(5) | C(54) | 0.134 5(4) | 0.235 2(2) | 0.457 8(5) |
| C(21) | 0.151 7(4) | 0.070 4(2) | 0.154 9(6) | C(55) | 0.107 9(4) | 0.200 3(3) | 0.703 3(6) |
| C(22) | 0.161 0(4) | 0.045 9(2) | 0.228 6(6) | C(56) | 0.138 2(5) | 0.234 1(3) | 0.710 5(6) |
| C(23) | 0.123 0(3) | 0.047 0(2) | 0.317 2(5) | C(57) | 0.206 5(4) | 0.230 3(2) | 0.715 8(6) |
| C(24) | 0.123 4(3) | 0.067 6(2) | 0.563 8(4) | C(58) | 0.225 8(4) | 0.196 0(2) | 0.710 0(6) |
| C(25) | 0.173 7(3) | 0.089 7(2) | 0.532 3(6) | C(59) | 0.166 5(5) | 0.177 6(3) | 0.702 0(6) |
| C(26) | 0.242 3(4) | 0.083 9(2) | 0.562 6(6) | B | —0.000 9(7) | 0.189 8(3) | 0.117 3(9) |
| C(27) | 0.258 5(4) | 0.055 9(2) | 0.622 4(6) | F(1) | 0.027 4(4) | 0.168 0(2) | 0.057 3(5) |
| C(28) | 0.208 0(4) | 0.034 3(2) | 0.653 0(6) | F(2) | 0.002 6(4) | 0.220 2(2) | 0.071 8(5) |
| C(29) | 0.140 8(3) | 0.039 6(2) | 0.626 3(5) | F(3) | 0.014 8(4) | 0.189 4(2) | 0.212 2(4) |
| C(30) | −0.008 2(3) | 0.069 3(2) | 0.707 7(5) | F(4) | −0.069 9(4) | 0.185 1(3) | 0.104 3(5) |

**Table 2** Selected bond distances (Å) and angles (°) for $[Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]BF_4$ **6**

| | | | |
|---|---|---|---|
| Ni–C(1) | 2.072(6) | B–F(2) | 1.32(1) |
| Ni–C(2) | 2.177(6) | B–F(3) | 1.27(2) |
| Ni–C(3) | 2.140(6) | B–F(4) | 1.36(2) |
| Ni–C(4) | 2.163(6) | C(1)–C(2) | 1.444(8) |
| Ni–C(5) | 2.171(6) | C(1)–C(5) | 1.443(8) |
| Ni–cp(centroid) | 1.770(1) | C(2)–C(3) | 1.384(8) |
| Ni–O | 1.877(4) | C(3)–C(4) | 1.474(8) |
| Ni–P | 2.167(2) | C(4)–C(5) | 1.389(8) |
| B–F(1) | 1.27(2) | C(49)–O | 1.241(8) |
| | | | |
| Ni–O–C(49) | 125.0(5) | Ni–P–C(48) | 97.9(2) |
| P–C(48)–C(49) | 108.7(5) | C(1)–Ni–O | 161.1(2) |

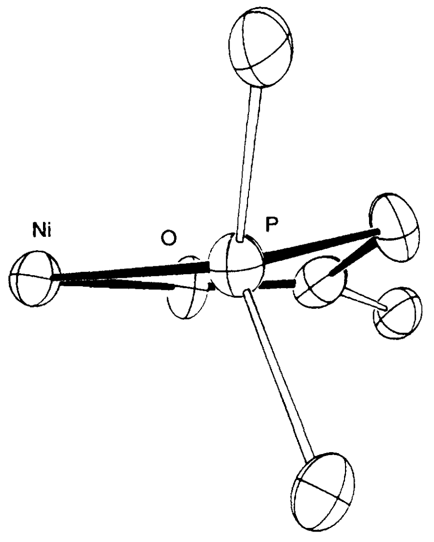


Fig. 2 View showing the puckering of the chelate ring of complex **6**

from methylacylphosphines. An efficient activation of the complexes **1** and **4** could be achieved by addition of $NaBH_4$. Protonation of the nickel enolate **2** selectively yields the cationic complex **6** containing the [2 + 2] electron-donor ligand $[Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)]$.

## Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk-tube techniques. Dichloromethane was dried over phosphorus pentaoxide and pentane over sodium–potassium alloy; all solvents were stored under an argon atmosphere before use. The ligands $Ph_2PCH_2C(O)Ph$,[14] $[Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)]$[14] and $C_6H_4[C(O)CH_2PPh_2]_2$-*m*[15] and the complexes $[Ni(C_5Ph_5)(CO)]$[16] and $[Ni(C_5H_5)(cod)]BF_4$[17] were prepared according to published procedures. The salt $AgBF_4$ and 1,8-bis(dimethylamino)naphthalene were purchased from Aldrich Chemicals. Silica gel 60 was a product from Merck, Germany. Infrared spectra were recorded on a IFS 66 Bruker spectrophotometer and measured as KBr pellets, NMR spectra on a Bruker WP 200 SY at 200 ($^1H$ NMR) or 80 MHz ($^{31}P$ NMR) or on a FT Bruker AM 400 instrument ($^1H$ NMR, 400 MHz). Proton chemical shifts are given in ppm with respect to $SiMe_4$; those of the $^{31}P$ signals are relative to external 85% $H_3PO_4$. Elemental analyses were performed by the Service de Microanalyse de l'Université Louis Pasteur. The catalytic runs were performed in a glass-lined stainless-steel autoclave (100 $cm^3$) containing a magnetic stirring bar. In a typical run, a given quantity of the catalyst precursor was introduced under argon (possibly with additional $NaBH_4$). After two argon-vacuum cycles, the solvent was added (30 $cm^3$). The autoclave was then pressurized with ethylene and heated to 130 °C. The stirring speed was 600 revolutions $\mathrm{min^{-1}}$. At the end of the catalytic run the autoclave was cooled and the remaining ethylene was slowly vented. The liquid phase was analysed by GC. The solid was washed with toluene and dried *in vacuo*.

*Syntheses*.—$[\mathrm{Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)Ph\}}]$ **1**. To a solution of $[\mathrm{Ni(C_5Ph_5)Br(CO)}]$ (0.306 g, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (30 $\mathrm{cm^3}$) was added a solution of $\mathrm{Ph_2PCH_2C(O)Ph}$ (0.152 g, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (10 $\mathrm{cm^3}$). The solution turned dark green with evolution of CO and after 15 min the reaction was complete. The solution was then treated with 1,8-bis(dimethylamino)-naphthalene (proton sponge) (0.112 g, 0.52 mmol) and the colour of the reaction mixture immediately changed to deep red. After stirring for 1 h the solvent was evaporated to dryness, and the dark red residue chromatographed through a short column of silica gel 60 using toluene as eluent. The resulting solution was evaporated to dryness and the product, after drying *in vacuo* for about 30 min, redissolved in $\mathrm{CH_2Cl_2}$. A layer of pentane was carefully added and, after diffusion at room temperature, dark red crystals of $[\mathrm{Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)Ph\}}]$ were obtained, washed with pentane and dried *in vacuo* (0.290 g, 72%). IR (KBr): 1521s [$\nu$(C–O) + $\nu$(C=C)] $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1$H, $\delta$ 4.95 [d, 1 H, PCH, $^2J$(PH) = 1.9 Hz] and 6.85–7.58 (40 H, aromatic H); $^{31}$P, $\delta$ 21.5 (s) (Found: C, 78.60; H, 5.20. Calc. for $\mathrm{C_{55}H_{41}NiOP{\cdot}0.5CH_2Cl_2}$: C, 78.40; H, 5.00%).

$[\mathrm{Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)(C_5H_4)Fe(C_5H_5)\}}]$ **2**. Using a procedure similar to that described above for the synthesis of complex **1**, $[\mathrm{Ni(C_5Ph_5)Br(CO)}]$ (0.306 g, 0.50 mmol) was treated with $[\mathrm{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)}]$ (0.208 g, 0.505 mmol) and proton sponge (0.112 g, 0.52 mmol) in $\mathrm{CH_2Cl_2}$ (30 $\mathrm{cm^3}$). The complex was obtained as dark red crystals (0.366 g, 80%). IR (KBr): 1523s [$\nu$(C–O) + $\nu$(C=C)] $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1$H, $\delta$ 4.07 (s, 5 H, $\mathrm{C_5H_5}$), 4.11 and 4.37 (two t, AA′BB′ spin system, 4 H, $\mathrm{C_5H_4}$), 4.46 [d, 1 H, PCH, $^2J$(PH) = 2.2 Hz] and 6.86–7.56 (35 H, aromatic H); $^{31}$P, $\delta$ 21.1 (s) (Found: C, 75.20; H, 4.85. Calc. for $\mathrm{C_{59}H_{45}FeNiOP{\cdot}0.5CH_2Cl_2}$: C, 74.60; H, 4.85%).

$[\mathrm{Ni(C_5Ph_5)\{Ph_2PCH{=}C(O)(1,3\text{-}C_6H_4)C(O){=}HCPPh_2\}Ni(C_5Ph_5)}]$ **3**. Using a procedure similar to that described above for complex **1**, $[\mathrm{Ni(C_5Ph_5)Br(CO)}]$ (0.612 g, 1.00 mmol) was treated with $\mathrm{C_6H_4[(O)CCH_2PPh_2]_2}$-*m* (0.265 g, 0.50 mmol) and proton sponge (0.224 g, 1.04 mmol) in $\mathrm{CH_2Cl_2}$ (60 $\mathrm{cm^3}$). The complex was recovered as purple-red crystals (0.530 g, 69%). IR (KBr): 1523s [$\nu$(C–O) + $\nu$(C=O)] $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1$H, $\delta$ 4.74 [d, 2 H, PCH, $^2J$(PH) = 2.0 Hz] and 6.81–7.52 (74 H, aromatic H); $^{31}$P, $\delta$ 21.3 (s) (Found: C, 80.25; H, 4.95. Calc. for $\mathrm{C_{104}H_{76}Ni_2O_2P_2{\cdot}0.25CH_2Cl_2}$: C, 80.35; H, 4.95%).

$[\mathrm{Ni(C_5H_5)\{Ph_2PCH{=}C(O)Ph\}}]$ **4**. To a solution of $[\mathrm{Ni(C_5H_5)(cod)]BF_4}$ (0.159 g, 0.5 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) was added $\mathrm{Ph_2PCH_2C(O)Ph}$ (0.152 g, 0.5 mmol) and proton sponge (0.112 g, 0.52 mmol). The colour changed from green to orange; after 1 h the solution was filtered over a short silica column with $\mathrm{CH_2Cl_2}$. The solution was evaporated to dryness, the residue was dissolved in $\mathrm{CH_2Cl_2}$, and analytically pure crystals were obtained by diffusion of pentane into this solution (0.170 g, 80%). In the work-up of this complex, the use of thf should be avoided since decomposition reactions were sometimes observed when the products was filtered over silica gel. IR (KBr): 1511s [$\nu$(C–O) + $\nu$(C=O)] $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1$H, $\delta$ 4.93 [d, 1 H, PCH, $^2J$(PH) = 0.8 Hz], 5.35 (s, 5 H, $\mathrm{C_5H_5}$) and 7.22–7.78 (18 H, aromatic H); $^{31}$P, $\delta$ 33.8 (s) (Found: C, 70.10; H, 4.95. Calc. for $\mathrm{C_{25}H_{21}NiOP}$: C, 70.30; H, 4.95%).

$[\mathrm{Ni(C_5H_5)\{Ph_2PCH{=}C(O)(C_5H_4)Fe(C_5H_5)\}}]$ **5**. Using a procedure similar to that described above for complex **4**, $[\mathrm{Ni(C_5H_5)(cod)]BF_4}$ (0.159 g, 0.50 mmol) was treated with $[\mathrm{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)}]$ (0.208 g, 0.50 mmol) and proton sponge (0.112 g, 0.52 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$). The colour turned from green to red. Analytically pure crystals were obtained, after work-up, by recrystallization from dichloromethane–pentane (0.230 g, 86%). As for **4**, thf should be avoided. IR (KBr): 1516s [$\nu$(C–O) + $\nu$(C=C)] $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1$H, $\delta$ 4.07 (s, 5 H, $\mathrm{C_5H_5Fe}$), 4.12 and 4.47 (two t, AA′BB′ system, 4 H, $\mathrm{C_5H_4}$), 4.51 [d, 1 H, PCH, $^2J$(PH) = 0.8 Hz], 5.30 (s, 5 H, $\mathrm{C_5H_5Ni}$) and 7.43–7.78 (12 H, aromatic H); $^{31}$P, $\delta$ 33.4 (s) (Found: C, 64.85; H, 4.85. Calc. for $\mathrm{C_{29}H_{25}NiOP}$: C, 65.10; H, 4.70%).

$[\mathrm{Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]BF_4}$ **6**. *Method* (*a*). To a solution of complex **2** (0.183 g, 0.2 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) were added 5 drops of a 54% solution of $\mathrm{HBF_4}$ in diethyl ether. The colour of the solution changed instantaneously from red-brown to blood-red. Stirring was continued for 0.5 h. Then the solvent was evaporated to dryness and the residue dried carefully *in vacuo*. Black-red crystals of **6** were obtained by slow diffusion of pentane into a dichloromethane solution.

*Method* (*b*). The salt $\mathrm{AgBF_4}$ (0.025 g, 0.13 mmol) was added to a solution of complex **2** (0.114 g, 0.13 mmol) in $\mathrm{CH_2Cl_2}$ (5 $\mathrm{cm^3}$). After stirring for 3 h the dark solution was filtered in order to remove the precipitated silver. Pentane was added slowly to the filtered solution; after several days, black crystals of **6** were collected and washed with pentane (0.104 g, 80%). IR (KBr): 1525s [$\nu$(C–O) + $\nu$(C=C)], *ca.* 1060(br) ($\mathrm{BF_4}$) $\mathrm{cm^{-1}}$. NMR (1,1,2,2-$\mathrm{C_2D_2Cl_4}$): $^1$H (60 °C), $\delta$ 4.10 (s, 5 H, $\mathrm{C_5H_5}$), 4.26 [2 H, $\mathrm{PCH_2}$, $^2J$(PH) = 10 Hz], 4.80 (br s, 2 H, $\mathrm{C_5H_4}$), 4.96 (br s, 2 H, $\mathrm{C_5H_4}$) and 6.89–7.80 (35 H, aromatic H); in the range 25–100 °C, the chemical shifts of most signals exhibit unexplained variations, the highest displacement being *ca.* 0.3 ppm for one of the $\mathrm{C_5H_4}$ signals; $^{31}$P, $\delta$ 27.6 (s) (Found: C, 70.60; H, 4.70. Calc. for $\mathrm{C_{59}H_{46}BF_4FeNiOP}$: C, 70.65; H, 4.60%).

*Catalytic Run with Complex* **1**.—To a steel autoclave (100 $\mathrm{cm^3}$) containing complex **1** (0.50 g, 0.06 mmol) and $\mathrm{NaBH_4}$ (0.003 g, 0.06 mmol) was added thf (5 $\mathrm{cm^3}$), then toluene (20 $\mathrm{cm^3}$). The reactor was pressurized with ethylene (5.28 g, 188 mmol; 22 bar at 25 °C) and the temperature raised to 130 °C. After 4 h the autoclave was cooled to room temperature (at this stage the pressure was 9 bar) and the content analysed by GC. This revealed exclusively the presence of $\alpha$-olefins of which *ca.* 98% were linear. The amount of insoluble polyethylene was 1.7 g. The extent of ethylene conversion was 80%.

*Crystal Structure Determination*.—Suitable single crystals of complex **6** were obtained according to the procedure described above. A crystal of approximate size 0.38 × 0.20 × 0.20 mm was cut from a cluster and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **6** belong to the orthorhombic system. Quantitative data were obtained at −100 °C by using a locally built gas-flow device. Precise cell parameters were obtained from 25 carefully centred reflections and refined by least squares. All experimental parameters used are given in Table 3. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius MOLEN package was used[18] with the exception of a local data-reduction program. Three standard reflections measured every hour during the entire data collection period showed no significant decay. The raw step-scan data were converted into intensities using the Lehman–Larsen method[19] and then corrected for Lorentz and polarization factors. The structure was solved using the heavy-atom method. After refinement of the heavy atoms, a Fourier-difference map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced in structure-factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic thermal parameters such as $B(\mathrm{H}) = 1.3\,B_{\mathrm{eq}}(\mathrm{C})\ \text{Å}^2$ but not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart[20] since face indexation was not possible under the cold gas stream. Full-matrix least-squares refinements minimizing $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$, where $w = 1/\sigma^2$ and $\sigma^2(F^2) = \sigma^2{}_{\mathrm{counts}} +$

**Table 3** Crystal data and details of data collection for $[Ni(C_5Ph_5)\{Ph_2PCH_2C(O)(C_5H_4)Fe(C_5H_5)\}]BF_4$ **6**

| | |
|---|---|
| Formula | $C_{59}H_{46}BF_4FeNiOP$ |
| $M$ | 1003.3 |
| Colour | Black |
| Crystal system | Orthorhombic |
| Space group | *Pbca* |
| $a$/Å | 19.427(6) |
| $b$/Å | 38.595(11) |
| $c$/Å | 13.001(4) |
| $U$/Å$^3$ | 9748(1) |
| $Z$ | 8 |
| $F$(000) | 4144 |
| $D_c$/g cm$^{-3}$ | 1.367 |
| μ/cm$^{-1}$ | 36.358 |
| Radiation | Cu-Kα graphite monochromated |
| λ/Å | 1.5418 |
| Mode | θ–2θ flying step-scan |
| Scan speed/°s$^{-1}$ | 0.024 |
| Step width/° | 0.04 |
| Scan width/° | $0.90 + 0.14 \tan\theta$ |
| Octants | $+h + k + l$ |
| θ range/° | 3–52 |
| Number of data collected | 6090 |
| Number of data with $I > 3\sigma(I)$ | 3097 |
| Minimum, maximum absorption | 0.68, 1.34 |
| $R$[a] | 0.049 |
| $R'$[b] | 0.067 |
| Goodness of fit[c] | 1.450 |

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [c] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, $N_o$ and $N_p$ are the number of observations and parameters.

$(0.08I)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients were from ref. 21(*a*) and 21(*b*) respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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