Preparation and Reactivity of Five-membered Phosphonickelocycles†

Guillermo Muller,*,[a] David Panyella,[a] Mercè Rocamora,*,[a] Joaquim Sales,[a] Mercè Font-Bardía[b] and Xavier Solans[b]
[a] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[b] *Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain*

The complexes *trans*-[NiCl(P–C)L] [L = PMe_2Ph **1a**, PEt_3 **1b**, $P(CH_2Ph)_3$ **1c** or PPh_3 **1d**], and [{NiCl(P–C)}$_2$] containing the bidentate anionic ligand *o*-$C_6H_4CH_2PPh_2$ (P–C) have been prepared. The molecular structure of **1c** has been determined by single-crystal X-ray crystallographic methods: space group $P2_1/c$, $a = 20.641(6)$, $b = 9.794(3)$, $c = 17.047(5)$ Å, $\beta = 102.05(3)°$ and $Z = 4$. Complexes **1** showed a conformational interconversion of the metallocyclic ring. Different amounts of *cis* and *trans* isomers were observed in the solutions of [NiX(P–C)L] compounds by NMR spectroscopy, depending on the size of the phosphine and the anionic ligands. With [Ni($C_6H_2Me_3$-2,4,6)(P–C){$P(CH_2Ph)_3$}] only the *cis* product is obtained. The ionic compounds [Ni(P–C)$(PMe_2Ph)_2$]BF_4 and [Ni(P–C)(MeCN){$P(CH_2Ph)_3$}]BF_4 were synthesised by reaction of [NiCl(P–C)L] with 1 equivalent of $TlBF_4$ in the presence of free ligand. The five-co-ordinate compound [NiCl(P–C)$(PMe_2Ph)_2$] was obtained from **1a** and PMe_2Ph. The reactivity of the Ni–C bond of compounds **1** in the presence of CO, SO_2, CS_2, CO_2, alkynes and olefins was studied. Acyl or S-sulfinate compounds containing six-membered rings [NiCl(*o*-$COC_6H_4CH_2PPh_2$)L] [L = PEt_3 or $P(CH_2Ph)_3$] and [NiCl(*o*-$SO_2C_6H_4CH_2PPh_2$){$P(CH_2Ph)_3$}] were obtained from the reactions with CO and SO_2. The reaction with diphenylacetylene or ethyl phenylpropiolate of compounds **1a** and **1c** gave one isomer of [NiCl{*cis*-(CPh=CPh)($C_6H_4CH_2PPh_2$}L] [L = PEt_3 or $P(CH_2Ph)_3$] and [NiCl{2-(CPh=CCO_2Et)$C_6H_4CH_2PPh_2$}{$P(CH_2Ph)_3$}], with the alkenyl fragment *cis* with respect to the substituents of the alkyne. The geometry of the latter was confirmed by single-crystal X-ray structure determination: space group $P2_1/c$, $a = 11.386(3)$, $b = 14.715(3)$, $c = 26.000(5)$ Å, $\beta = 90.03(4)°$ and $Z = 4$. Decomposition products after insertion of ethylene under pressure in **1c** and [Ni($C_6H_2Me_3$-2,4,6)(P–C){$P(CH_2Ph)_3$}] were also observed. No evidence of insertion reactions was obtained with CS_2 and CO_2 even under pressure.

The preparation and study of metal complexes containing polydentate ligands has become a field of increasing interest. The selection of the number and type of co-ordinating atoms of the ligand, the size of the ring formed on complexation, and the neutral or ionic nature of the ligand allow a very wide modulation of the steric and electronic properties of this type of ligand.[1,2] Polydentate ligands are able to stabilize species not accessible with simple monodentate ligands and show particular reactivity related to the ring itself or induced in the ancillary co-ordination positions.[3,4] Examples of this behaviour are the nickel complexes with anionic P,O-donor ligands, *e.g.* $Ph_2PCH_2CO_2$, which are active catalysts in the oligomerization of ethylene as discovered by Keim,[5] and the ring contraction from a six- to a five-membered ring observed by Yamamoto *et al.*[6] with dianionic C,O-donor ligands in [Ni(C–O)L_n] complexes.

We are interested in the preparation of nickel compounds containing anionic P,C chelates because of their potential applications in catalytic systems when preservation of the chelate part Ni(P–C) is possible. These compounds also could be useful to study stoichiometric insertions in the Ni–C bond, taking advantage of the stability of the rings obtained. Another aspect to be considered is the accessibility of the fifth co-ordination position in square-planar d^8 complexes, probably very different with bi- or mono-dentate ligands, having consequences in nickel-catalysed reactions like the oligomerization of ethylene, where compounds containing monodentate phosphines lead to dimerization products, but ethylene oligomers or polymers are obtained with bidentate anionic P,O ligands. However, little is known about nickel complexes containing anionic P,C chelates. Compounds [Ni(P–C)$_2$] with $P–C^-$ = *o*-$CH_2C_6H_4PPh_2$ or *o*-$C_6H_4CH_2PPh_2$, derivatives of diphenyl(*o*-tolyl)phosphine[7] and benzyldiphenylphosphine,[8] have scarcely been reported; [Ni(P–C)(η^5-C_5H_5)] complexes[9] where $P–C^-$ = $PPh_2(CH_2)_n{}^-$ (n = 2–4) have been obtained and their reactivity towards CO or SO_2 investigated.

The reactions of $PPh_2(CH_2C_6H_4Cl$-*o*) and [Ni$(cod)_2$] (cod = *cis,cis*-cycloocta-1,5-diene) alone or in the presence of different phosphines to give a group of nickelocycles [NiCl(P–C)L] (P–C = *o*-$C_6H_4CH_2PPh_2$) are reported in the present study. The reactivity related to halide abstraction and the insertion of small molecules such as CO, SO_2, CS_2, CO_2, and alkynes into the Ni–C bond have been investigated. Insertion of diphenylacetylene in the nickelocycle was carefully studied, since the final cyclic compound was stable in an excess of alkyne and did not undergo the isomerization process observed when the insertion was studied with simple alkyl[10] or aryl[11] ligands. The stereochemistry of the addition has been confirmed by X-ray diffraction analysis of

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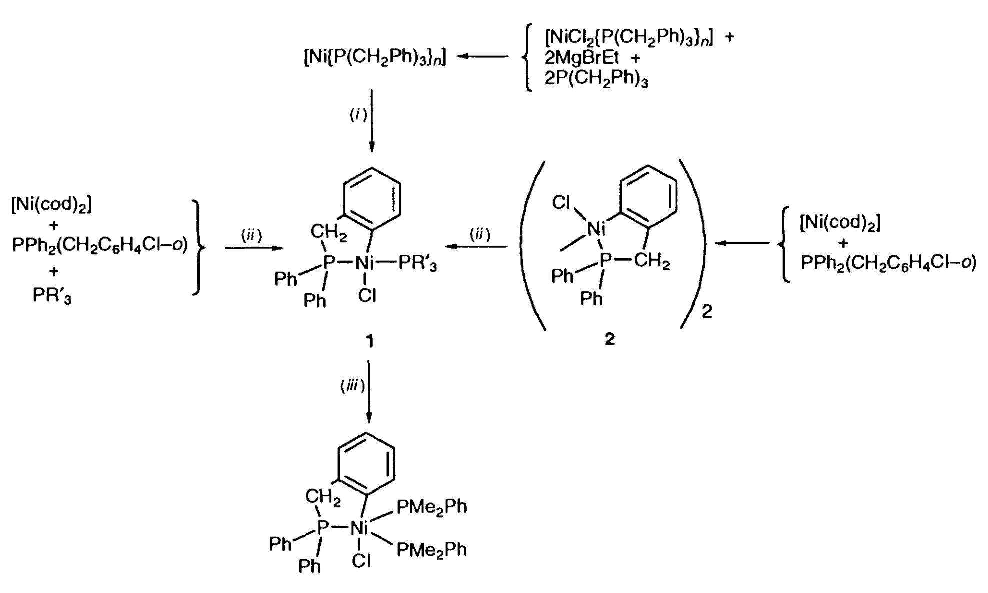
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) $PPh_2(CH_2C_6H_4Cl$-*o*); (*ii*) $PR'_3 = PMe_2Ph$ **1a**, PEt_3 **1b**, $P(CH_2Ph)_3$ **1c** or PPh_3 **1d**; (*iii*) PMe_2Ph

the starting complex [$NiCl$(*o*-$C_6H_4CH_2PPh_2$){$P(CH_2Ph)_3$}] and the *cis*-insertion of ethyl phenylpropiolate [$NiCl${(*E*)-2-($CPh{=}C(CO_2Et)C_6H_4CH_2PPh_2$}{$P(CH_2Ph)_3$}].

Results and Discussion

Synthesis of Nickelocycles.—To prepare stable phosphonickelocycles the benzyl group was selected as a convenient bridge since the well known five-membered ring can be formed. The ligand precursors (*o*-chlorobenzyl)diphenylphosphine and benzyldiphenylphosphine were obtained by one-pot synthesis from PPh_2Cl, Mg and *o*-chlorobenzyl or benzyl chlorides. From these precursors, formation of the cyclic product involves activation of a C–H or C–Cl bond.

Reactions involving C–H bond activation were unsuccessful. From a mixture of [$Ni(cod)_2$] with $PPh_2(CH_2Ph)$ only partial substitution of cod by phosphine was observed. However, formal activation of a C–H bond in methacrylamide by [$Ni(cod)_2$] leading to a nickelocyclic amide has been described.[12] Elimination reactions directly from nickel(II) complexes also failed. Dehydrohalogenation in [$NiCl_2\{PPh_2(CH_2Ph)\}_2$] was not observed when the complex was boiled in toluene, in the presence of free phosphine, and only decomposition products were recovered. The same reaction performed with [$NiBr(2\text{-}MeC_6H_4)\{PPh_2(CH_2Ph)\}_2$] in toluene led to decomposition products containing $(2\text{-}MeC_6H_4)_2$. Activation of the C–H bond by nickel(II) compounds involving the formation of a ring together with the evolution of hydrogen halide or a previously co-ordinated organic group has also been described.[13,14]

The activation of the C–Cl bond allowed us to obtain the desired compounds. The reaction of [$Ni(cod)_2$] with $PPh_2(CH_2C_6H_4Cl$-*o*) in the presence of free phosphines gave the compounds [$NiCl$(*o*-$C_6H_4CH_2PPh_2$)(PR'_3)] [$PR'_3 = PMe_2Ph$ **1a**, PEt_3 **1b**, $P(CH_2Ph)_3$ **1c** or PPh_3 **1d**] (Scheme 1) in good yields. In the absence of free phosphine it was possible to obtain the dinuclear complex [{$NiCl$(*o*-$C_6H_4CH_2PPh_2$)}$_2$] **2**. Addition of phosphine to solutions of **2** led to cleavage of the chloride bridge giving compounds **1**. The oxidative addition of $PPh_2(CH_2C_6H_4Cl$-*o*) to [$Ni\{P(CH_2Ph)_3\}_n$] was also observed but at slower rate and giving poorer yields of **1c** than that observed in the reaction with [$Ni(cod)_2$].

Elemental analyses of compounds **1** and **2** were satisfactory except for **1d**; both decompose in solution in air but are stable as dry solids or in solution under N_2. An X-ray diffraction study on a single crystal of **1c** and the ^{31}P-{^1H} NMR spectra showed a *trans* arrangement of the products **1**; however, complex **2** may be a mixture of the *cis* and *trans* isomers since the ^{31}P NMR signal is broad and complex (Table 1).

Dynamic behaviour was present in compounds **1** because the ^{31}P NMR spectra must be taken at low temperatures to observe well defined signals; only with **1c** was it observed at room temperature. The process responsible for this dynamic behaviour may be related to a ring twist around the methylene and phosphorus atoms. At 220 K free dissociated phosphine was not observed and addition of free phosphine PEt_3 or $P(CH_2Ph)_3$ (Ni:P = 1:0.5) led to slight broadening in the signal of the co-ordinated PR'_3. A rapid equilibrium between free and co-ordinated phosphine is unlikely since the rate of the dynamic process decreased with increasing size of the phosphine. So, only the spectra of compound **1c** containing the biggest phosphine $P(CH_2Ph)_3$ can be recorded at room temperature because of the slow dynamic behaviour when the complex is crowded. However, slow phosphine exchange took place in complex **1c** because in the ^{31}P NMR spectra at low temperature (220 K) in toluene a second doublet of doublets can also be distinguished (δ 57.3, 15.2, J_{PP} = 38 Hz). The small coupling constant indicated the presence of the *cis*-[$NiCl$(*o*-$C_6H_4CH_2PPh_2$){$P(CH_2Ph)_3$}] (⩽10% of the whole compound).

The ring effect in the ^{31}P NMR spectra of organometallic compounds has been observed for four- to six-membered rings.[15] This important contribution to the chemical shift gives information about changes in the ring size. The spectra of type **1** compounds showed a signal corresponding to the phosphonickelocycle between δ 41.8 and 43.6, the free ligand $PPh_2(CH_2Ph)$ at δ −10.7 and the complex [$NiBr(2\text{-}MeC_6H_4)\{PPh_2(CH_2Ph)\}_2$] containing the monodentate organic and phosphine ligands similar to that found for the phosphonickelocycle at δ 18.2. So the value of the ring contribution is about 24.5 ppm to lower field for the PPh_2 end, in the range observed for five-membered rings.[15]

In the ^1H NMR spectra (Table 2) the methylene protons of the bridge occur as a single doublet, $^2J_{PH}$ = 7.9 (**1b**) or 9.0 (**1c**) Hz, and the signals of the monodentate phosphine are coupled with only one phosphorus atom. The signals are broad. Variable-temperature ^1H NMR spectra of compound **1a** between 220 and 305 K were recorded; **1a** contains the methylene group of the bidentate phosphine (P–C) and

Table 1 Phosphorus-31 NMR data for complexes $[NiX(C-P_a)P_b]$ in toluene and $[Ni(C-P_a)P_b(P_L)]BF_4$ in thf; $P(OMe)_3$ as internal reference (δ 140.1)

Compound	δ(P_a)	δ(P_b)	$J(P_a-P_b)$/Hz	T/K
1a	43.2	−6.35	356	223
1b	42.15	11.85	351	223
1c	41.8	12.75	352	308
1d	43.6	22.05	341	223
2	50–51			223
3a	62.2 −	3.7 −7.3[δ(P_L)]	290.5 44.5,[a] 38.25[b]	223
3c	55.55	21.8	281	223
4c	41.4	1.6	5.9	308
5a	20.0	−6.12	240	223
5b	22.9	15.5	239	223
5c[c]	24.9	15.25	220	223
6c	38.15	15.05	296	308
7a	30.5	−13.7	339	308
7b	27.9	4.9	320	308
7c	30.65	2.25	324	308
7c′	28.35	0.9	315	308
8a	−4.35	−14.75	179.6	223

[a] $J(P_a-P_L)$. [b] $J(P_b-P_L)$. [c] In thf–toluene.

Table 2 Proton NMR data[a] for non-aromatic protons of selected complexes

Compd.	Bridge $Ph_2PCH_2C_6H_4$	Monodentate phosphine	T/K
1a	3.6	PCH_3, 1.46	273
1b	4.0 (d, 7.9)	PCH_2CH_3, 1.96 (m) PCH_2CH_3, 1.46 (dt, J_{HH} = 7.25, J_{PH} = 6.5)	273
1c	3.55 (d, 9.0)	PCH_2Ph, 3.18 (d, 8.5)	308
4c[b]	3.46 (d, 6.0)	PCH_2Ph, 2.75 (s)	308
5b	3.12 (s)	PCH_2CH_3, 1.98 (m) PCH_2CH_3, 1.5 (m)	273
5c	2.85 (d, 7.7)	PCH_2Ph, 3.23 (d, 7.4)	308
7a	3.71 (t, ≈8) 2.91 (t, ≈8)	PCH_3, 1.61 (d, 8.78), 1.43 (d, 8.32)	308
7c	3.88 (t, ≈10.3)	PCH_2Ph, 3.51 (dd, J_{PH} = 7.6, J_{HH} = 14.2)	308
	2.91 (t, ≈9.2)	3.26 (dd, J_{PH} = 7.3, J_{HH} = 14.2)	
7c′[c]	4.07 (dd, 12, 8)	PCH_2Ph, 3.34 (dd, J_{PH} = 7.2, J_{HH} = 14.6 Hz)	308
	2.86 (t, ≈12)	3.21 (dd, J_{PH} = 8.3, J_{HH} = 14.6 Hz)	308

[a] δ in ppm relative to $SiMe_4$ (J in Hz), in C_6D_6 or $[^2H_8]$toluene. [b] The three methyl groups of the mesitylene ligand are inequivalent: δ 2.15; 2.6 and 1.95. [c] δ 3.84 (dq, J_{HH} = 7, $J_{HH'}$ = 6, $CO_2CH_2CH_3$) and 0.66 (t, J_{HH} = 7 Hz, $CO_2CH_2CH_3$).

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for the compound *trans*-$[NiCl(o\text{-}C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}]$ **1c**

Ni–P(1)	2.163(3)	Cl–Ni–P(1)	96.5(1)
Ni–P(2)	2.236(3)	Cl–Ni–P(2)	89.9(1)
Ni–Cl	2.219(3)	P(1)–Ni–C(123)	81.7(2)
Ni–C(123)	1.936(6)	C(123)–Ni–P(2)	96.8(2)
P(1)–C(121)	1.871(10)	P(1)–Ni–P(2)	158.0(1)
C(121)–C(122)	1.502(12)	Cl–Ni–C(123)	166.3(2)
C(122)–C(123)	1.395	Ni–P(1)–C(121)	101.3(4)

PMe_2Ph which could be sensitive to the loss of the plane of symmetry of the co-ordination sphere (NiClPP′C) (*i.e.* the two methyl groups would become inequivalent) in the complex by the arrangement of the bridge. However the spectra are not definitive because at 220 K both signals are slightly split into two bands; it is not possible to rule out coupling with the phosphorus atom of each *trans* phosphine as the main reason for this splitting. So, the conformational interconversion of the metallocyclic ring is still rapid at 220 K. Similar results were obtained by van Koten and co-workers[16] for compounds with tridentate NCN ligands.

Addition of an excess of PMe_2Ph to an orange toluene solution of complex **1a** gave a violet solution containing the five-co-ordinated species $[NiCl(o\text{-}C_6H_4CH_2PPh_2)(PMe_2Ph)_2]$ **8a** according to the ^{31}P NMR spectra. Eight signals were observed corresponding to a second-order AB_2 system (δ_P −4.35 for P–C, −14.75 for PMe_2Ph; J_{PP} = 179.6 Hz), with three phosphorus atoms in the equatorial co-ordination plane of a trigonal-bipyramidal geometry. The signal of the P–C ligand appears in a completely unexpected position for a five-membered-ring complex (see Table 1). The existence of this ring was confirmed by addition of $TlBF_4$ to a tetrahydrofuran (thf) solution of **8a** which led to the ionic compound $[Ni(o\text{-}C_6H_4CH_2PPh_2)(PMe_2Ph)_2]BF_4$ **3a** (see below). However, when $P(CH_2Ph)_3$ was added to solutions of **1c** no reaction was observed. Furthermore, the addition of an excess of this phosphine to a solution of **1a** led to substitution of PMe_2Ph, giving **1c** and the five-co-ordinate complex **8a** in a 1 : 1 ratio according to the ^{31}P NMR spectra. This demonstrates the inertness of the saturated complex **8a** and the capacity of the bidentate (P–C) ligand to stabilize five-co-ordinate species.

Molecular Structure of Complex **1c**.—The molecular and crystal structures of *trans*-$[NiCl(o\text{-}C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}]$ **1c** were determined by X-ray diffraction. The crystal structure consists of discrete molecules (Fig. 1). Selected bond lengths and angles are listed in Table 3 and atomic coordinates in Table 4. The complex exhibits a distorted square-planar geometry. The following displacements (Å) are observed from the least-squares plane of the co-ordination sphere: Ni, −0.072(3); P(1), 0.358(4); Cl, −0.265(4); C(123), −0.329(6); P(2), 0.318(3).

The tetrahedral distortion also reflected in the P(1)–Ni–P(2) and C(123)–Ni–Cl angles of 158.0(1) and 166.3(2)° may be associated with the steric requirements for the accommodation of the five-membered ring containing two sp^2 carbon atoms and the $P(CH_2Ph)_3$. The angle P(1)–Ni–C(123) of 81.7(2)° has the lowest value of the angles P–Ni–X (X = C, N or O) of five-membered nickelocycles which range from 82.22 to 90.53° (mean 86.48° from 39 molecular structures) excluding one compound containing a P_2N_2 macrocycle.[17] The angle between the plane of the co-ordination sphere Ni–P(1)–P(2)–C(123)–Cl and that defined by the benzyl bridge Ni–C(123)–C(122)–C(121) is 38.1°, so the ideal plane of symmetry of the co-ordination sphere is broken by the bridge. Consequently, the two protons of the methylene group in the bridge are inequivalent and could be observed separately by ^1H NMR spectroscopy in the absence of fluxional processes involving the five-membered cyclometallated ring.

Halide Substitution on $[NiCl(P-C)(PR_3)]$ **1**.—When $MgBr(C_6H_2Me_3\text{-}2,4,6)$ in thf was added to complex **1c** the yellow compound $[Ni(C_6H_2Me_3\text{-}2,4,6)(o\text{-}C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}]$ **4c** was obtained (Scheme 2). The ^{31}P NMR spectrum (Table 1) at room temperature showed the presence of one group of signals assigned to the *cis* isomer. In the ^1H NMR spectrum at room temperature the methylene protons of $P(CH_2Ph)_3$ occurred as a singlet. The methyl substituents of the mesitylene ligand appear as three independent signals showing the strong steric crowding in the complex and lack of a plane of symmetry defined by the square-planar co-ordination sphere. However the CH_2 group of the bridge still appears as a single doublet with coupling to one phosphorus atom. To test the

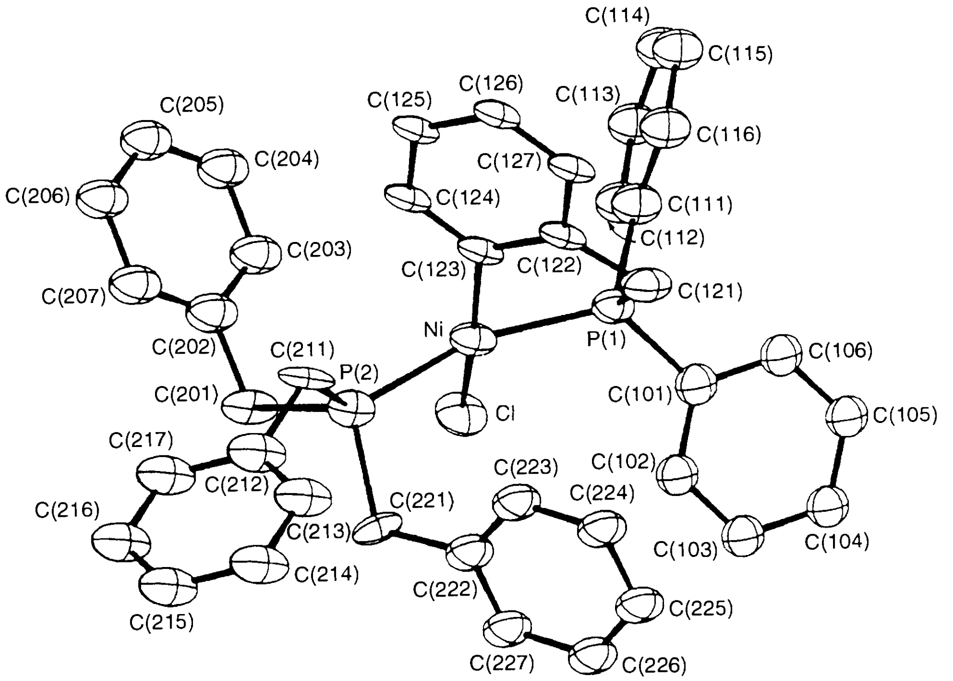


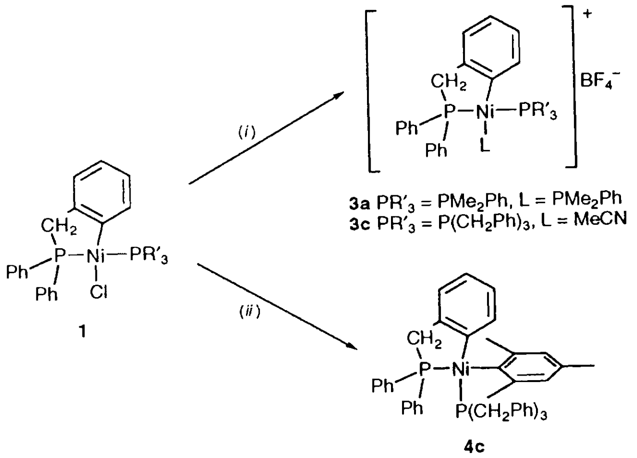
Fig. 1 View of the structure of complex **1c** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity

Table 4 Final atomic coordinates (× 10^4) of *trans*-[$NiCl(o-C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}$] **1c**

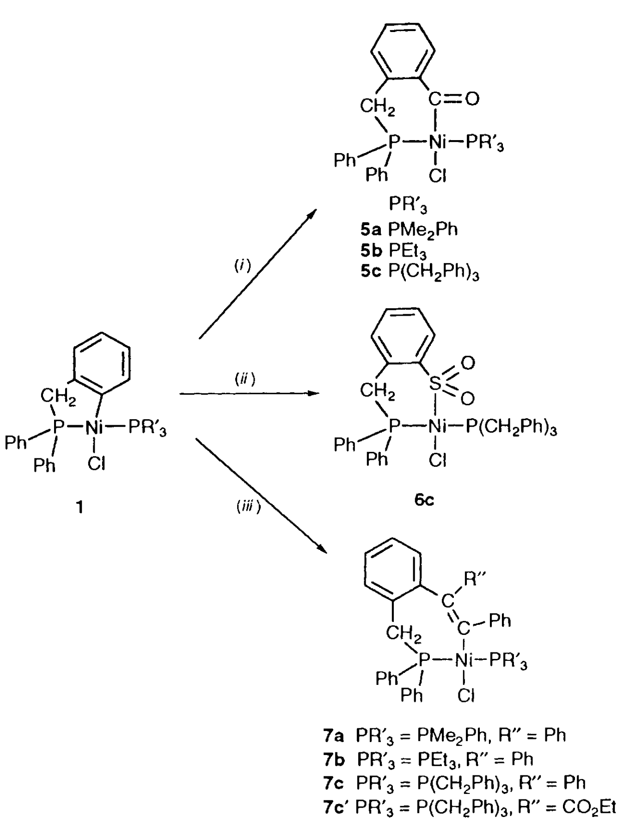
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	72 105(5)	376(12)	18 546(9)	C(124)	6 510(3)	−1 993(7)	703(3)
P(1)	7 174(1)	−906(3)	2 992(2)	C(125)	6 262(3)	−3 224(7)	457(3)
Cl	7 294(1)	2 174(3)	2 297(2)	C(126)	6 420(3)	−4 341(7)	969(3)
C(121)	7 440(5)	−2 691(10)	2 824(8)	C(127)	6 825(3)	−4 168(7)	1 727(3)
P(2)	7 634(1)	664(3)	803(2)	C(202)	6 541(3)	1 811(7)	−207(4)
C(201)	7 247(4)	2 148(7)	225(7)	C(203)	6 040(3)	1 812(7)	229(4)
C(211)	7 719(4)	−665(10)	17(7)	C(204)	5 391(3)	1 500(7)	−151(4)
C(221)	8 474(4)	1 331(10)	1 196(6)	C(205)	5 243(3)	1 186(7)	−967(4)
C(101)	7 698(3)	−369(7)	3 930(3)	C(206)	5 745(3)	1 184(7)	−1 403(4)
C(102)	8 276(3)	363(7)	3 917(3)	C(207)	6 394(3)	1 497(7)	−1 023(4)
C(103)	8 715(3)	674(7)	4 634(3)	C(212)	8 279(3)	−403(8)	−423(5)
C(104)	8 577(3)	252(7)	5 364(3)	C(213)	8 855(3)	−1 179(8)	−206(5)
C(105)	7 999(3)	−481(7)	5 376(3)	C(214)	9 377(3)	−985(8)	−598(5)
C(106)	7 560(3)	−792(7)	4 659(3)	C(215)	9 323(3)	−14(8)	−1 208(5)
C(111)	6 342(3)	−1 062(7)	3 201(4)	C(216)	8 746(3)	762(8)	−1 424(5)
C(112)	6 025(3)	127(7)	3 371(4)	C(217)	8 224(3)	568(8)	−1 032(5)
C(113)	5 381(3)	63(7)	3 503(4)	C(222)	8 895(3)	488(7)	1 881(4)
C(114)	5 054(3)	−1 189(7)	3 464(4)	C(223)	8 830(3)	−913(7)	1 983(4)
C(115)	5 371(3)	−2 378(7)	3 294(4)	C(224)	9 228(3)	−1 576(7)	2 634(4)
C(116)	6 015(3)	−2 314(7)	3 162(4)	C(225)	9 691(3)	−834(7)	3 184(4)
C(122)	7 073(3)	−2 877(7)	1 972(3)	C(226)	9 756(3)	569(7)	3 082(4)
C(123)	6 916(3)	−1 760(7)	1 461(3)	C(227)	9 358(3)	1 230(7)	2 431(4)

dependence of the geometry of the complex on the size of the ligands two reactions were performed in a NMR tube. Substitution of the chloride using KNCS in acetone gave the isothiocyanate complex [$Ni(NCS)(o-C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}$]. The ^{31}P NMR spectrum at 220 K in toluene contains two groups of doublets of doublets assigned to the *trans* and *cis* isomers (δ_{trans} 47.3, 18.0, $J_{PP} = 321$; δ_{cis} 54.74, 15.98, $J_{PP} = 39$ Hz) in a ratio *trans*:*cis* = 8:2. Further, a solution of $MgBr(C_6H_2Me_3-2,4,6)$ in thf was added to **1a** containing the smaller phosphine PMe_2Ph. The ^{31}P NMR spectrum of the hydrolysed solution showed at 220 K two groups of signals that can be assigned to *trans*- and *cis*-[$Ni(C_6H_2Me_3-2,4,6)(o-C_6H_4CH_2PPh_2)(PMe_2Ph)$] ($\delta_{trans}$ 47.0, 3.2, $J_{PP} = 293$; $\delta_{cis} = 49.0$, 0.2, $J_{PP} = 16$ Hz). At this temperature the ratio of the *cis*:*trans* isomers is 1:1; at 308 K the same pattern is observed with a slight increase in the *cis* isomer. The substitution of the chloride ligand by the most basic and biggest mesitylene ligand that would increase the lability of the phosphine ligand does not increase the rate of the dynamic process of the complexes. This suggests that the dynamic behaviour observed in the NMR spectra of complexes **1** is independent of a rapid exchange of phosphine and confirms the non-rigidity of the five-membered phosphonickelocycle.

The complexes [$Ni(o-C_6H_4CH_2PPh_2)(PMe_2Ph)_2$]$BF_4$ **3a** or [$Ni(o-C_6H_4CH_2PPh_2)(MeCN)\{P(CH_2Ph)_3\}$]$BF_4$ **3c** can be prepared from the consecutive reaction of **1a** or **1c** with $TlBF_4$ in toluene followed, after separation of the $TlBF_4$, by the addition of the neutral ligand PMe_2Ph or MeCN respectively. The former cannot be obtained as an analytically pure solid but all the NMR data obtained are in accord with the structure proposed. Only the *trans* isomer was detected in solutions of **3c**.



Scheme 2 (*i*) $TlBF_4$, thf, L; (*ii*) $MgBr(C_6H_2Me_3$-2,4,6)



Scheme 3 (*i*) Toluene, room temperature (r.t.), P_{CO} = 1 atm (101 325 Pa), 1 min; (*ii*) toluene, r.t., P_{SO_2} = 1 atm, 15 min; (*iii*) thf, r.t., PhCCR″ (1 : 1), 60 min

Reactions of the Nickel–Carbon Bond.—The insertion of small molecules into transition metal–carbon bonds is the fundamental step in a number of stoichiometric and catalytic processes. Thus the reactions of [NiCl(P–C)L] **1** compounds with a group of small and unsaturated organic molecules CO, CO_2, SO_2, CS_2, olefins and alkynes have been studied to test the stability of the Ni–C bond, since preservation of the chelate part Ni(P–C) of the complex as a stable unit in the presence of these molecules is a condition for the use of these complexes as precursors of catalytic species.

When CO, SO_2, dry CO_2, or $CH_2{=}CH_2$ was bubbled at atmospheric pressure through orange solutions of complexes **1** the formation of new compounds was only observed with CO and SO_2 (Scheme 3). The reactions were completed in about 5 min with CO or 15 min with SO_2. The new species decompose quickly in an excess of CO but are moderately stable in an excess of SO_2. No intermediates were observed in the reactions followed by ^{31}P NMR spectroscopy. The compounds [NiCl(*o*-$COC_6H_4CH_2PPh_2$)L] [L = PEt_3 **5b** or $P(CH_2Ph)_3$ **5c**] and [NiCl(*o*-$SO_2C_6H_4CH_2PPh_2$){$P(CH_2Ph)_3$}] **6c** were obtained and characterized as solids, but **5a** (L = PMe_2Ph) was obtained only in solution. The IR spectra of compounds **5** show a band at 1600 cm^{-1} assigned to the acyl CO stretch. Bands associated with a S-sulfinate insertion compound[18] at 1180(ν_{asym}) and 1080(ν_{sym}) cm^{-1} were exhibited by **6c**. The ^{31}P NMR spectra show a *trans* geometry for the insertion products (Table 1) and the expected upfield change of chemical shift because of the increase in the ring size by one atom. However, the molecules inserted have very different new co-ordinating atoms and the precise evaluation of the ring contribution is impossible since compounds with monodentate ligands analogous to those of complexes **5** and **6** are not available. The values of the chemical shift of the monodentate phosphine and phosphorus–phosphorus coupling constants also change simultaneously with the change in ring size (see Table 1).

Evolution of a small amount of but-1-ene was observed when a toluene solution of complex **1a** was kept under a pressure of 40 bar (4 × 10^6 Pa) of ethylene for 2 h. The reaction begins when the solution is heated to 60 °C; the turnover (butene formed per Ni) is about 20. Only decomposition products were recovered; mass spectra of the phosphine oxide formed from the chelate phosphine showed incorporation of one or two ethylene molecules. Solutions of **1a** and **1b** with *trans*-stilbene and methyl acrylate in ratios Ni:olefin ≈ 1:4 remain unchanged up to 70 °C; at this temperature the organometallic compounds decompose but phosphine oxides are recovered without incorporation of olefin. So, insertion of olefin prior to decomposition of the organometallic species takes place only with ethylene. Furthermore, the formation of small amounts of butenes (90% but-1-ene) was observed at 40 °C when a toluene solution of **4c** was placed in the reactor vessel under 20 bar of ethylene. 2,4,6-Trimethylstyrene, $OP(CH_2Ph)_3$ and $OPPh_2(CH_2Ph)$ were detected showing that the decomposition of the organometallic complex takes place by insertion of ethylene in the nickel–mesitylene bond followed by the β elimination of 2,4,6-trimethylstyrene. The unstable hydride obtained gives small amounts of butenes decomposing by reductive elimination to $PPh_2(CH_2Ph)$.

Only slight decomposition of the organometallic complex was observed when a tetrahydrofuran solution of **1c** was placed under 6 bar of CO_2. Furthermore, mixtures of toluene solutions of **1a** and **1c** with CS_2 at room temperature remain unaltered and only slow decomposition of the organometallic compound could be observed. However, the reactivity of nickelabenzocyclopentene complexes towards CO_2[19] and CS_2[20] is completely different, giving insertion of the small molecules in the nickel–aryl bond in both cases. This different reactivity may be related to the lability of the organic ligand since these reactions take place at −78 °C.

The insertion of alkynes into a transition metal–carbon bond is a widely observed general reaction but still lacking a clear mechanistic model supported by kinetic studies. Definition of this model presents considerable difficulties, since the results of the reactions are variable; *cis* or *trans* insertion products are obtained depending on the transition-metal complex and alkyne.[10,11] These results have been interpreted as a concerted *cis* insertion of the alkyne into the nickel–carbon bond with an independent isomerization step. Moreover, the instability of the alkenyl organometallic products of the insertion reaction in the presence of large amounts of alkynes usually precludes a careful kinetic study of the reaction. Only Samsel and Norton[21] have studied kinetically a clean intramolecular insertion with palladium complexes.

The reaction of compounds **1** in toluene solutions with alkynes such as diphenylacetylene or ethyl phenylpropiolate

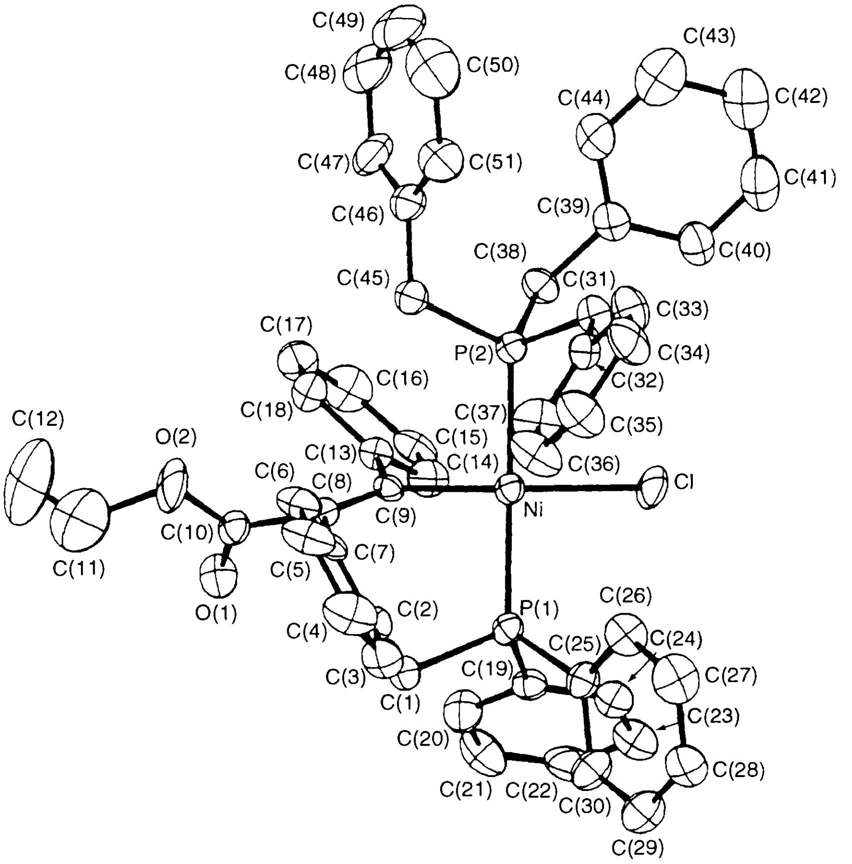


Fig. 2 View of the structure of complex **7c′** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity

Table 5 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[\overline{NiCl\{(E)\text{-}2\text{-}(CPh{=}CCO_2Et)C_6H_4CH_2P}Ph_2)\text{-}\{P(CH_2Ph)_3\}]$ **7c′**

Cl–Ni	2.217(2)	C(25)–P(1)	1.855(6)
P(2)–Ni	2.216(1)	C(2)–C(1)	1.479(7)
P(1)–Ni	2.204(1)	C(7)–C(2)	1.409(8)
C(9)–Ni	1.896(6)	C(8)–C(7)	1.523(8)
C(1)–P(1)	1.826(6)	C(9)–C(8)	1.316(8)
C(19)–P(1)	1.816(5)		
P(2)–Ni–Cl	89.8(1)	C(1)–P(1)–Ni	114.5(2)
P(1)–Ni–Cl	92.2(1)	C(2)–C(1)–P(1)	110.4(4)
P(1)–Ni–P(2)	167.0(1)	C(7)–C(2)–C(1)	119.8(5)
C(9)–Ni–Cl	160.1(2)	C(8)–C(7)–C(2)	116.8(5)
C(9)–Ni–P(2)	92.3(2)	C(9)–C(8)–C(7)	124.7(6)
C(9)–Ni–P(1)	90.1(2)	Ni–C(9)–C(8)	129.7(5)

takes place at room temperature and, depending on the excess of alkyne, 1 or 2 h for a ratio Ni:alkyne = 1:2 are enough to complete the reaction. Only one cyclic alkenyl isomer was obtained (Scheme 3). Compounds **7a**, **7c** and **7c′** were isolated as solids and **7b** was obtained in solution. The insertion of only one molecule of alkyne into the Ni–C bond was observed, further molecules being blocked by the bulky substituents of the alkenyl derivative. With ethyl phenylpropiolate only the regioisomer resulting upon migration from the organic end of the ring to the least-hindered alkyne carbon is observed, as confirmed by a crystal structure determination of **7c′**. No isomerization of the alkenyl complex was observed. The mechanism proposed for this process[10] is disfavoured since it includes a rotation about the C_α–C_β bond, which involves a twist of the whole ring. The ^{31}P NMR spectra of compounds **7** (Table 1) revealed their *trans* geometry and loss of the dynamic behaviour of the ring, allowing the spectra to be recorded at room temperature. The ^1H NMR spectra (Table 2) showed two signals for the protons of the methylene group of the ring, according to their diastereotopic character. These signals appear as apparent triplets because $^2J_{PH} \approx {}^2J_{HH}$. The same pattern was observed for the signals of the protons of the remaining CH_2 groups of the $P(CH_2Ph)_3$ in **7c** and **7c′** or the ethyl ether fragment in **7c′**. The phosphine methyls of **7a** were also different, giving two doublets with coupling to a phosphorus atom.

The conversion of complexes **1a** and **1c** into **7a** and **7c** can be monitored by ^{31}P NMR spectroscopy. The reactions were performed in a closed NMR tube with a ratio Ni:alkyne: 1:2 at room temperature but the spectra were recorded at 220 K. A small signal of free phosphine [δ −11.1, $P(CH_2Ph)_3$] or phosphine oxide [δ 35.8, $OP(CH_2Ph)_3$; 30.0, $OPMe_2Ph$] was detected and a small new common signal at δ 36.8 was observed. This last signal may be associated with the common intermediate '$\overline{NiCl(o\text{-}C_6H_4CH_2P}Ph_2)(PhCCPh)$'. The stereochemistry of the reaction can be considered as a *cis* 2,3 addition of the nickel–carbon bond to the alkyne, in good agreement with the proposal of Bergman[10] and other results,[11,22] but not with the results of Bochmann *et al.*[23] The insertion of diphenylacetylene or ethyl phenylpropiolate into the nickel–carbon bond of the ring in compounds **1** led to a unique cyclic alkenyl isomer when either symmetric or asymmetric alkynes were employed. However, the contribution of electronic factors, polarity of the triple bond or the presence of a secondary co-ordination centre, in the reaction with ethyl phenylpropiolate, cannot be ruled out.

Molecular Structure of Complex **7c′**.—In order to establish unambiguously the conformation of the insertion products, the molecular and crystal structures of *trans*-$[\overline{NiCl\{(E)\text{-}2\text{-}(CPh{=}CCO_2Et)C_6H_4CH_2P}Ph_2)\}\{P(CH_2Ph)_3\}]$

Table 6 Final atomic coordinates (× 10^4; Ni, Cl and P, × 10^5) of $[\overline{\mathrm{NiCl\{(}E\mathrm{)\text{-}2\text{-}(CPh{=}CCO_2Et)C_6H_4CH_2P}}\mathrm{Ph_2)\{P(CH_2Ph)_3\}}]$ **7c′**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni	31 576(7)	29 483(4)	62 427(3)	C(24)	4 233(8)	5 394(4)	6 806(3)
Cl	31 304(17)	31 016(10)	70 909(6)	C(25)	5 944(5)	3 748(3)	6 556(2)
P(2)	20 228(13)	17 307(8)	63 086(5)	C(26)	6 149(7)	2 947(4)	6 810(3)
P(1)	46 074(13)	39 304(8)	61 617(5)	C(27)	7 230(7)	2 827(4)	7 058(4)
O(1)	2 968(5)	4 101(3)	4 511(2)	C(28)	8 037(6)	3 504(5)	7 085(3)
O(2)	3 009(7)	2 661(3)	4 243(2)	C(29)	7 840(6)	4 299(4)	6 831(3)
C(1)	5 274(5)	3 961(3)	5 523(2)	C(30)	6 796(6)	4 422(4)	6 567(3)
C(2)	5 509(6)	3 028(4)	5 338(3)	C(31)	2 570(6)	915(4)	6 785(2)
C(3)	6 645(6)	2 645(5)	5 337(3)	C(32)	3 780(6)	498(3)	6 676(2)
C(4)	6 838(8)	1 792(5)	5 143(4)	C(33)	4 055(8)	−297(4)	6 941(3)
C(5)	5 930(8)	1 304(5)	4 936(5)	C(34)	5 168(9)	−683(5)	6 885(4)
C(6)	4 816(7)	1 653(4)	4 927(3)	C(35)	6 003(8)	−298(6)	6 562(4)
C(7)	4 592(5)	2 511(3)	5 123(2)	C(36)	5 697(8)	477(6)	6 306(4)
C(8)	3 373(5)	2 937(3)	5 125(2)	C(37)	4 607(8)	872(4)	6 367(5)
C(9)	2 758(5)	3 116(3)	5 541(2)	C(38)	514(6)	2 014(4)	6 544(2)
C(10)	3 071(6)	3 313(3)	4 604(2)	C(39)	25(6)	1 492(4)	6 990(3)
C(11)	3 132(13)	2 987(6)	3 702(4)	C(40)	159(8)	1 806(5)	7 489(3)
C(12)	2 522(14)	2 839(9)	3 434(6)	C(41)	−307(8)	1 338(7)	7 893(3)
C(13)	1 549(5)	3 530(3)	5 515(2)	C(42)	−965(9)	574(6)	7 838(4)
C(14)	1 210(6)	4 215(4)	5 834(3)	C(43)	−1 069(9)	226(6)	7 334(4)
C(15)	110(7)	4 608(5)	5 803(3)	C(44)	−617(7)	709(5)	6 927(3)
C(16)	−701(7)	4 283(5)	5 435(4)	C(45)	1 797(6)	1 049(3)	5 728(2)
C(17)	−405(6)	3 593(5)	5 131(3)	C(46)	950(6)	281(4)	5 748(3)
C(18)	711(5)	3 191(4)	5 154(3)	C(47)	−219(7)	438(5)	5 587(3)
C(19)	4 210(6)	5 100(3)	6 303(2)	C(48)	−1 039(11)	−220(7)	5 594(4)
C(20)	3 848(7)	5 697(4)	5 917(3)	C(49)	−794(11)	−995(8)	5 775(4)
C(21)	3 531(9)	6 579(5)	6 046(4)	C(50)	407(14)	−1 274(6)	5 927(4)
C(22)	3 520(11)	6 861(5)	6 572(5)	C(51)	1 264(9)	−560(4)	5 934(3)
C(23)	3 901(9)	6 269(5)	6 940(4)				

7c′ were determined by X-ray diffraction. The crystal structure consists of discrete molecules (Fig. 2) separated by van der Waals distances. Selected bond lengths and angles are listed in Table 5 and atomic coordinates in Table 6. The bond distances are in the range expected. The complex exhibits a distorted square-planar geometry. The following displacements (Å) are observed from the least-squares plane (A) of the co-ordination sphere: Ni, −0.0402; P(1), −0.2908; Cl, 0.2843; C(9), 0.3365; P(2), −0.2897. The angles between the atoms of the co-ordination sphere showed less deviation than those in the five-membered ring compound **1c**. The atoms C(7), C(8), C(9), C(10), C(13) showed very low deviations from the alkenyl plane (B), but the nickel atom directly bonded to C(9) is displaced by 0.3761 Å. The benzyl group of the phosphine included in the seven-membered ring, C(2)–C(8), also forms a well defined plane (C); the angles between the normals to the planes AB, AC and BC are respectively 73.66, 94.43 and 105.64°, showing the perpendicular arrangement of the benzyl bridge with respect to the co-ordination sphere.

Conclusion

Compounds **1** containing bidentate ligands with different co-ordinating atoms $[\overline{\mathrm{NiX(P\text{–}C}}\mathrm{)L}]$ showed at least two dynamic processes, a fast ring twist and a slow equilibrium between *cis* and *trans* geometries on the NMR time-scale according to their ^1H and ^{31}P NMR spectra, showing their extreme sensitivity to steric factors in solution. Furthermore, an increase in the ring size or the size of the ligands in these compounds results in a parallel decrease in the ring twist rate. The distortion of the square-planar co-ordination sphere is bigger in compound **1c** containing a five-membered nickelocycle than in **7c′** with a seven-membered ring.

The presence of bidentate ligands favoured the formation of five-co-ordinate complexes. Neutral complexes with monodentate ligands of this type are rare, only $[NiMe_2L_3]$ (L = PMe_3[24] or PMe_2Ph[25]) have been described; with bidentate ligands some ionic complexes have also been obtained.[26,27] The accessibility of the fifth co-ordination position did not allow the detection of five-co-ordinate intermediates in the insertion reactions with CO, SO_2, or alkynes. However, the regioselectivity of the reaction with alkynes is confirmed as a *cis*-addition process in a system that greatly hinders concurrent or posterior isomerizations.

The nickel–carbon bond of the chelate part $\overline{\mathrm{Ni(P\text{–}C}}\mathrm{)}$ of compounds prepared for use as catalytic precursors must be stronger than those obtained in this work with the benzyl bridge.

Experimental

All manipulations of the organonickel compounds were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran was distilled over sodium–benzophenone under nitrogen before use. Phosphines were obtained commercially or prepared according to procedure described.[28] The complex $[Ni(cod)_2]$ was prepared by the method reported[29] with small modifications.

^1H NMR spectra were recorded on a Varian XL 200 or a Bruker WP80SY instrument, ^{31}P spectra at different temperatures on a Bruker WP80SY instrument (32.38 MHz). The references used were tetramethylsilane and 85% H_3PO_4 for ^1H and ^{31}P respectively; all chemical shifts are reported in downfield from standards. Solvents used were C_6D_6 and $[^2H_8]$toluene for ^1H NMR, and toluene and thf with a 5 mm coaxial insert tube containing $[^2H_6]$acetone–$P(OMe)_3$ for ^{31}P spectra. Infrared spectra were recorded on a Perkin Elmer 1330 instrument. Gas chromatography (GC) was performed on a Hewlett-Packard 5890 chromatograph connected to a HP 3396A integrator equipped with a 50 m ultra-2 cross-linked 5% phenyl–methyl silicone capillary column. Mass spectra were obtained with a Hewlett-Packard 5971A mass-selective detector coupled to a Hewlett-Packard 5890 chromatograph. Helium was used as the carrier gas. Insertion reactions under pressure were carried out in a Berghof reactor equipped with a Teflon liner of 75 cm^3 capacity. Analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona (Consejo Superior de Investigacines Cientificas).

Crystallographic Studies.—Crystals of complex **1c** were grown from a dichloromethane–ethanol mixture by cooling to −20 °C. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($6 \leqslant \theta \leqslant 12°$) and refined by the least-squares method.

Crystal data. $\mathrm{C_{40}H_{37}ClNiP_2}$, M = 673.85, monoclinic, space group $P2_1/c$, a = 20.641(6), b = 9.794(3), c = 17.047(5) Å, β = 102.05(3)°, U = 3370(3) Å^3, Z = 4, D_c = 1.328 g cm^{-3}, $F(000)$ = 1408.0, μ(Mo-Kα) = 7.77 cm^{-1}.

Intensities were collected with graphite-monochromatized Mo-Kα radiation, by the ω-scan technique (scan width 0.8°, scan speed 0.03° s^{-1}). A total of 3808 reflections were measured in the range $2 \leqslant \theta \leqslant 24°$, 1308 of which were assumed as observed by applying the condition $I \geqslant 2.5\sigma(I)$; R_{int} on F was 0.052. Three reflections were measured every 2 h as orientation control; significant intensity decay was not observed. Lorentz-polarization, but not absorption, corrections were made.

The structure was solved by Patterson synthesis, using the SHELXS computer program and refined by full-matrix least-squares with SHELX 76.[30] The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = \sigma^2(F_o)$; f, f' and f'' were taken from ref. 31. In order to reduce the number of refined parameters the phenyl rings were refined with constrained geometry (planar, bond lengths 1.395 Å, bond angles 120°). All atoms of the same phenyl ring were refined with overall isotropic coefficients. The final R factor was 0.040 (R' = 0.044) for all observed reflections. Number of refined parameters 150. Maximum shift/e.s.d. = 0.01; maximum and minimum peaks in the final difference synthesis 0.4 and −0.2 e Å^{-3} respectively.

Crystals of complex **7c′** were grown from a mixture of dichloromethane and methanol at room temperature. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 \leqslant \theta \leqslant 22°$) and refined by the least-squares method.

Crystal data. $\mathrm{C_{51}H_{47}ClNiO_2P_2}$, M = 848.05, monoclinic, space group $P2_1/c$, a = 11.386(3), b = 14.715(3), c = 26.000(5) Å, β = 90.03(4)°, U = 4356(3) Å^3, Z = 4, D_c = 1.293 g cm^{-3}, $F(000)$ = 1776.0, μ(Mo-Kα) = 6.21 cm^{-1}.

Intensities were collected as above. A total of 7064 reflections were measured in the range $2 \leqslant \theta \leqslant 30°$, 3584 of which were assumed as observed by applying the condition $I \geqslant 2.5\sigma(I)$; R_{int} on F was 0.023. Three reflections were monitored but no significant intensity decay was observed. Intensities corrected as before.

The structure was solved and refined as for complex **1c**, except that $w = [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$. The positions of all H atoms were computed and refined with an overall isotropic thermal parameter. The final R factor was 0.050 (R' = 0.055) for all observed reflections. Number of refined parameters 607. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.3 and −0.3 e Å^{-3} respectively.

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

Preparations.—*trans*-[NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)L] [L = $\mathrm{PMe_2Ph}$ **1a**, $\mathrm{PEt_3}$ **1b** *or* $\mathrm{P(CH_2Ph)_3}$ **1c**]. To a suspension of [Ni(cod)$_2$] (1.32 g, 4.80 mmol) in thf (30 cm^3) at −78 °C was added L ($\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{PEt_3}$, or $\mathrm{P(CH_2Ph)_3}$; 4.80 mmol) and (*o*-chlorobenzyl)diphenylphosphine (1.5 g, 4.80 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 30 min under these conditions. The initial yellow mixture became darker. The solvent was partially removed under vacuum. The orange complexes [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)L] were precipitated on adding absolute ethanol (**1a**, 1.6 g, 60%; **1b** 1.4 g, 55%; **1c**, 2.6 g, 75%) (Found: C, 63.55; H, 5.40. Calc. for $\mathrm{C_{27}H_{27}ClNiP_2}$ **1a**: C, 63.90; H, 5.35. Found: C, 59.00; H, 6.20. Calc. for $\mathrm{C_{25}H_{31}ClNiP_2}$ **1b**: C, 61.60; H, 6.40. Found: C, 71.3; H, 5.50. Calc. for $\mathrm{C_{40}H_{37}ClNiP_2}$ **1c**: C, 71.3; H, 5.55%).

[{NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)}$_2$] **2**. To a suspension of [Ni(cod)$_2$] (1.32 g, 4.80 mmol) in toluene (10 cm^3) at −78 °C was added (*o*-chlorobenzyl)diphenylphosphine (1.5 g, 4.80 mmol). The reaction mixture was allowed to warm at 0 °C and maintained overnight under these conditions. Then the mixture was filtered to separate the nickel(0) impurities formed. The clear solution was concentrated and hexane was added. On cooling at −10 °C the dimeric orange compound **2** was obtained (1.05 g, 60%) (Found: C, 62.70; H, 4.80. Calc. for $\mathrm{C_{38}H_{32}Cl_2Ni_2P_2}$: C, 61.80; H, 4.35%).

[Ni(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)(MeCN){$\mathrm{P(CH_2Ph)_3}$}]$\mathrm{BF_4}$ **3c**. To a solution of [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$){$\mathrm{P(CH_2Ph)_3}$}] (0.5 g, 0.742 mmol) in thf–toluene (1 : 1, 60 cm^3), acetonitrile (0.061 g, 1.5 mmol) and $\mathrm{TlBF_4}$ (0.25 g, 0.8 mmol) were added. The mixture was stirred for 24 h, and the TlCl formed was filtered off under nitrogen. The thf was removed under reduced pressure and compound **3c** was precipitated from the toluene solution (0.39 g, 70%) (Found: C, 64.50; H, 4.90. Calc. for $\mathrm{C_{42}H_{40}BF_4NNiP_2}$: C, 65.85; H, 5.25%).

cis-[Ni($\mathrm{C_6H_2Me_3}$-2,4,6)(*o*-$\mathrm{C_6H_4CH_2PPh_2}$){$\mathrm{P(CH_2Ph)_3}$}] **4c**. The stoichiometric amount of mesitylmagnesium bromide obtained from 1-bromo-2,4,6-trimethylbenzene (2.0 g, 10 mmol) and magnesium (0.48 g, 20 mmol) in thf (15 cm^3) was added to a suspension of [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$){$\mathrm{P(CH_2Ph)_3}$}] (0.5 g, 0.742 mmol) in toluene (10 cm^3) at room temperature. In a few minutes the precipitate was dissolved. The solvent was reduced to half its volume under reduced pressure and on cooling the solution at −78 °C for several hours the product **4c** was precipitated. Recrystallization from ethanol–toluene gave 0.19 g (30%) of the pure product (Found: C, 77.60; H, 5.80. Calc. for $\mathrm{C_{49}H_{48}NiP_2}$: C, 77.70; H, 5.40%).

Reaction of [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)L] *with* CO; [NiCl(*o*-$\mathrm{COC_6H_4CH_2PPh_2}$)L] [L = $\mathrm{PEt_3}$ **5b** *or* $\mathrm{P(CH_2Ph)_3}$ **5c**]. Carbon monoxide was bubbled into a suspension containing [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)L] (1 mmol) in toluene (60 cm^3) under nitrogen at room temperature. When the solid was completely dissolved the CO current was stopped. The solvent was reduced in volume by evaporation under vacuum and the complex [NiCl(*o*-$\mathrm{COC_6H_4CH_2PPh_2}$)L] was precipitated after the addition of ethanol (**5b**, 0.33 g, 60%; **5c**, 0.49 g, 65%). The formation of **5a** was followed by ^{31}P NMR spectroscopy in toluene solution but it was not separated as a solid (Found: C, 58.45; H, 6.00. Calc. for $\mathrm{C_{26}H_{31}ClNiOP_2}$ **5b**: C, 60.55; H, 6.05. Found: C, 70.75; H, 5.60. Calc. for $\mathrm{C_{41}H_{37}ClNiOP_2}$ **5c**: C, 70.15; H, 5.30%).

[NiCl(*o*-$\mathrm{SO_2C_6H_4CH_2PPh_2}$){$\mathrm{P(CH_2Ph)_3}$}] **6c**. Sulfur dioxide was bubbled through a suspension of [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$){$\mathrm{P(CH_2Ph)_3}$}] (0.5 g, 0.7 mmol) in toluene (20 cm^3) at room temperature. When the solid was completely dissolved and the solution became red the gas current was stopped. After the addition of hexane, yellow solid **6c** was obtained (0.38 g, 80%) (Found: C, 65.60; H, 5.10. Calc. for $\mathrm{C_{40}H_{37}ClNiO_2P_2S}$: C, 65.10; H, 5.05%).

Reaction of [NiCl(*o*-$\mathrm{C_6H_4CH_2PPh_2}$)L] *with* PhC≡CPh; [NiCl{(CPh=CPh)$\mathrm{C_6H_4CH_2PPh_2}$}L] [L = $\mathrm{PMe_2Ph}$ **7a** *or* $\mathrm{P(CH_2Ph)_3}$ **7c**]. The compound PhC≡CPh (0.39 g, 2.18 mmol) was added at room temperature under nitrogen to a solution of [NiCl(*o*-$\mathrm{C_6H_4}$)$\mathrm{CH_2PPh_2}$)L] (2 mmol) in toluene

(20 cm^3). After 20 min of stirring the brownish solution became red. The solvent was removed under vacuum, and after addition of absolute ethanol an orange solid was collected (**7a**, 1.17 g, 80%; **7c**, 1.2 g, 80%). The formation of **7b** was followed by ^{31}P NMR spectroscopy (Found: C, 69.55; H, 5.90. Calc. for $C_{41}H_{37}ClNiP_2$ **7a**: C, 71.80; H, 5.45. Found: C, 75.80; H, 5.80. Calc. for $C_{54}H_{47}ClNiP_2$ **7c**: C, 76.10; H, 5.55%).

$[NiCl\{2\text{-}(CPh{=}CCO_2Et)C_6H_4CH_2PPh_2\}\{P(CH_2Ph)_3\}]$ **7c′**. To a solution of compound **1c** (0.5 g, 0.742 mmol) in toluene (20 cm^3) was added $PhC{\equiv}CCO_2Et$ (0.142 g, 0.82 mmol). After 30 min of stirring the solvent was removed, and after addition of hexane an orange precipitate was collected in quantitative yield (Found: C, 70.55; H, 5.70. Calc. for $C_{51}H_{47}ClNiO_2P_2$: C, 72.30; H, 5.55%).

$[NiCl(o\text{-}C_6H_4CH_2PPh_2)(PMe_2Ph)_2]$ **8a**. Dimethylphenylphosphine (1.33 g, 9.6 mmol) and (*o*-chlorobenzyl)diphenylphosphine (1.48 g, 4.8 mmol) were added to a suspension of $[Ni(cod)_2]$ (1.32 g, 4.8 mmol) in thf (30 cm^3) at −78 °C. The initial yellow mixture became very dark when the mixture was allowed to warm to room temperature. After 30 min the solvent was partially removed under vacuum and pentane was added. The dark purple solid obtained was filtered off (2.17 g, 70%) (Found: C, 65.05; H, 6.05. Calc. for $C_{35}H_{38}ClNiP_3$: C, 65.10; H, 5.95%).

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