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Reactions of activated alkynes with organonickel complexes. Crystal structure of *trans*-[NiBr(C(COOMe)=C(COOMe)(3,5-$Cl_2C_6H_3$))$(PPh_3)_2$]

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Abstract

Reaction of [$NiBrRL_2$] (R = 2,4,6-$Me_3C_6H_2$, 2,5-$Cl_2C_6H_3$, 3,5-$Cl_2C_6H_3$; L = PPh_3, dppe (1,2-diphenylphosphinoethane), $PEtPh_2$) with alkynes PhC≡CPh, MeOOCC≡CCOOMe, PhC≡CMe and PhC≡CCOOEt in toluene gave alkenyl compounds only when R was 3,5-$Cl_2C_6H_3$. The rate depends on the nature of both the ligand L and the alkyne, and is strongly inhibited by free phosphine, in keeping with an associative mechanism for the substitution of L by alkyne. Reactions with MeOOCC≡CCOOMe gives *cis*-addition products, as indicated by the structure of [NiBr(C(COOMe)=C(COOMe)(3,5-$Cl_2C_6H_3$))$(PPh_3)_2$], determined by X-ray diffraction. In the case of PhC≡CPh a mixture of *cis*- and *trans*-addition products is obtained. A separate isomer [NiBr(C(Ph)=C(Ph)(3,5-$Cl_2C_6H_3$))dppe] was shown to undergo isomerisation to an equilibrium mixture of both isomers. The reaction in the case of unsymmetrical alkynes PhC≡CR′ (R′ = COOEt, Me) gives one *cis*-addition product when R′ is COOEt and a mixture of *cis*- and *trans*-addition complexes when R′ is Me. The regioisomers obtained are those with the sterically largest substituent next to the nickel atom. The results suggest that the mechanism is a *cis*-addition process, with the possibility of isomerization depending on the lability of the phosphine ligands in the alkenyl complex. No intermediate in the insertion or isomerization processes was detected.

Introduction

The insertion of alkynes into a transition metal–carbon bond is still not a well-defined process. The insertion gives various addition products depending on

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the nature of both the metal and alkyne [1,2]. Recently several studies have been carried out with organometallic compounds of nickel; for example, Huggins and Bergman [2] observed that insertion into the σ(Ni–C) bond of [Ni(acac)(CH_3)(PPh_3)] gave *cis*- and *trans*-addition vinyl products. They proposed that the reaction involves a concerted *cis*-addition process followed by isomerization at the alkenyl ligand, by a reversible 1,3-dissociative shift of PPh_3, to give *trans*-addition products. Insertions of alkynes into [NiBrPh(PPh_3)$_2$] and [NiCl(COR)(PMe_3)$_2$] complexes have been studied by Bergman et al. [3] and by Carmona et al. [4]; in these cases only the *cis*-addition products were isolated. Strong interactions between the ketovinyl oxygen and Ni were observed in the vinylketone derivatives obtained by Carmona. Subsequently the compound [NiCl(C(Ph)=CH($COCH_2CMe_2Ph$))(PMe_3)$_2$] reversibly rearranges in solution to yield the nickelacyclopropane complex [NiC(Ph)(PMe_3)CH($COCH_2CMe_2Ph$))Cl(PMe_3)]. These metallated ylide structures are also formed when benzene solutions of similar complexes [PdI(CH=CH(COOR))(PPh_3)$_2$] [5] (with vinyl ligand of *E* or *Z* configuration) are heated, but the rearrangement is suppressed by free triphenylphosphine, and so a dissociative 1,2-phosphine shift from the metal atom on the vinyl α-carbon was proposed for the initial step of this isomerization process.

Several questions about the mechanism of the addition remain unclear, since the *cis*-addition stereochemistry of the ketovinyl products isolated by Carmona et al. may be favoured by pseudopentacoordination in the vinyl complex. Moreover the same metallated ylide was obtained from both the *E* and *Z* configurations of the vinyl ligand with the palladium complex. Presumably the isomerization process, either by a 1,3- or a 1,2-dissociative phosphine shift, requires some lability of the phosphine ligands and may be independent of the insertion process.

We describe here the reactions of several alkynes with [NiBr(3,5-$Cl_2C_6H_3$)L_2] and [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)(dppe)]ClO_4 complexes (γ-pic = 4-methylpyridine). We have used alkynes that lead to vinyl groups with different electron-withdrawing effects, and both neutral and ionic nickel substrates in order to have a wide range of relative lability of the phosphine ligands.

Results and discussion

(A) Syntheses of the organometallic compounds

Several organometallic complexes of the well-known stoichiometry [$NiBrRL_2$] were prepared. The R ligands (2,5-$Cl_2C_6H_3$, 3,5-$Cl_2C_6H_3$, mesityl) were selected to give a range of sizes and electronic character of these ligands. The stabilizing ligand was usually PPh_3 or dppe, but $PEtPh_2$ was also used in some cases because it has similar basicity to dppe.

The [NiBrR(PPh_3)$_2$] compounds were prepared by published methods involving either oxidative addition reactions to [Ni(PPh_3)$_n$] (R = 2,5-$Cl_2C_6H_3$ and 3,5-$Cl_2C_6H_3$) [6] or reaction of [NiX_2L_2] with Grignard reagents (R = mes) [7]. Compounds with dppe were obtained by substitution.

These compounds show at 37 °C a very simple ^{31}P spectrum that remains unchanged when free phosphine is added. Upon cooling of the toluene solutions with or without free phosphine to -70 °C, the signals undergo no broadening and no significant narrowing, and a slight change of chemical shift is observed.

The ionic compound [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)dppe]ClO_4 was obtained in two successive steps; [NiBr(3,5-$Cl_2C_6H_3$)(PPh_3)$_2$] was treated with γ-pic and $NaClO_4$ in acetone/benzene to give [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)$_3$]ClO_4, and addition of dppe to the latter gave the desired compound. The ^{31}P NMR spectra of this compound in acetone at 20 °C showed the signal (56.75 ppm) assigned to the phosphorus *trans* to γ-pic ligand to be clearly wider than the signal (47.75 ppm) from the phosphorus atom *trans* to the 3,5-$Cl_2C_6H_3$ ligand.

(B) Reactions of [NiBrRL$_2$] complexes with symmetrical alkynes

Some of the [NiBrRL_2] complexes react with internal symmetrical alkynes such as diphenylacetylene and dimethylacetylene dicarboxylate to give vinyl complexes (in 60–80% yields as recrystallized solids). The products identified contain only one molecule of inserted alkyne (see Scheme 1).

(i) The insertion reaction. The reaction between [NiBrRL_2] complexes and PhC≡CPh in toluene solutions at room temperature gave alkenyl compounds when R was the 3,5-$Cl_2C_6H_3$ ligand

$$[\text{NiBrRL}_2] + \text{PhC}{\equiv}\text{CPh} \rightarrow [\text{NiBr(C(Ph)=C(Ph)(3,5Cl}_2\text{C}_6\text{H}_3\text{))L}_2]$$

$$(\text{R} = 3{,}5\text{-Cl}_2\text{C}_6\text{H}_3,\ 2{,}5\text{-Cl}_2\text{C}_6\text{H}_3,\ 2{,}4{,}6\text{-Me}_3\text{C}_6\text{H}_2;\ \text{L} = \text{PPh}_3,\ \text{PEtPh}_2,\ 1/2\text{dppe})$$

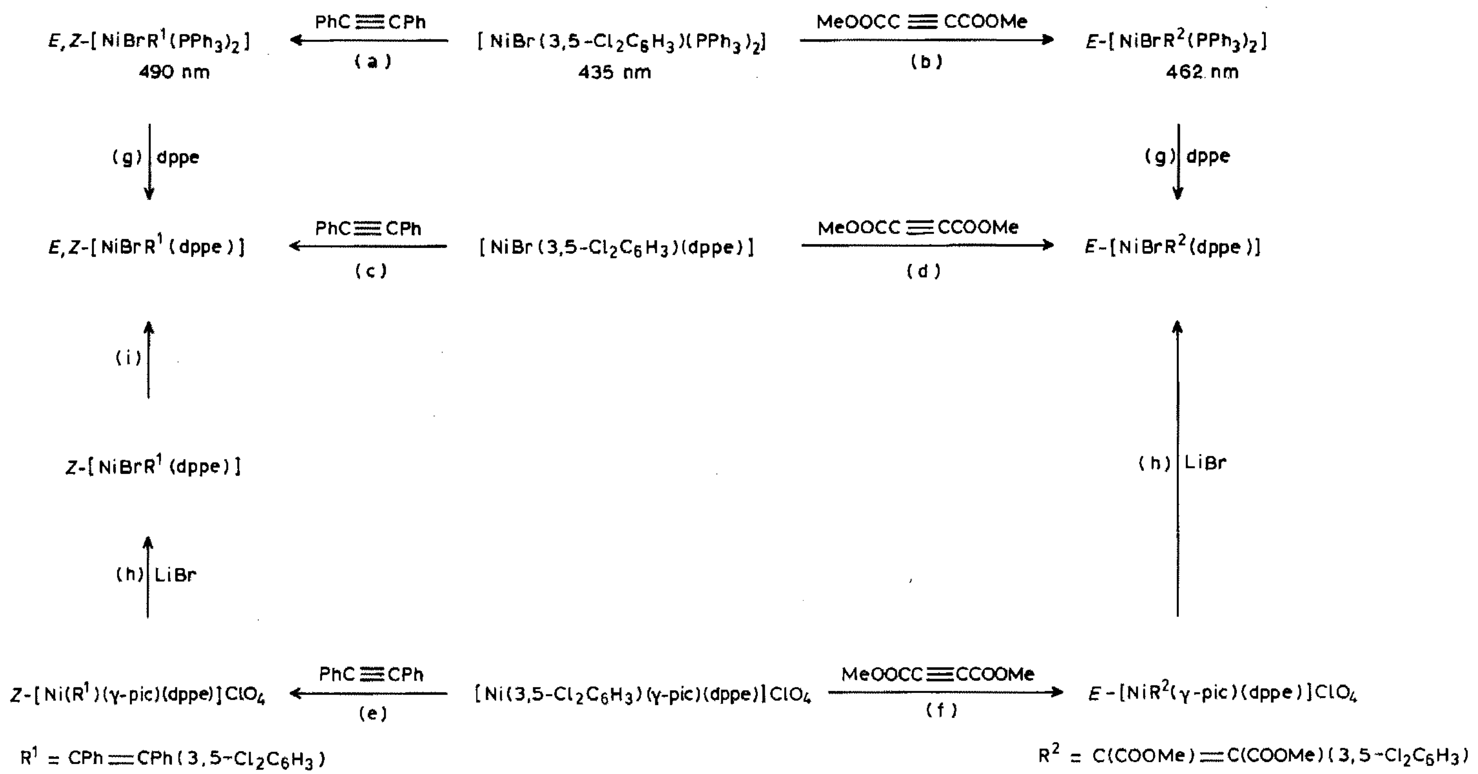
The solutions were reddish after a half hour reaction when R = 3,5-$Cl_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$ for L = PPh_3, but the starting organometallic was recovered unaltered when R contained *ortho*-substituents. The behaviour did not change when the reaction temperature was increased. After 3 days mesitylene and small amounts of bimesityl were detected in the solutions containing [NiBr(2,4,6-$Me_3C_6H_3$)(PPh_3)$_2$] and PhC≡CPh showing that some decomposition of the organometallic had occurred [8].

The rate of insertion depends on the nature of the stabilizing ligand L. When L = PPh_3 the reaction was complete in 6 h, but 4 days were necessary for completion of the reaction under the same conditions when L was 1/2 dppe or $PEtPh_2$. These reactions are accelerated by keeping the solutions at 80 °C.

Similar behaviour was observed when $MeO_2CC{\equiv}CCO_2Me$ was used. The reaction with [NiBr(3,5-$Cl_2C_6H_3$)L_2] (L = PPh_3, 1/2dppe) under the same conditions is faster, as shown in Scheme 1. The vinyl compounds are orange or red, air stable solids depending on the mode of precipitation.

When a great excess of the alkyne was used the insertion was followed by decomposition of the alkenyl compounds. Reactions between the alkenyl compounds and alkynes also led to decomposition. Thus, in contrast to the behaviour observed for palladium(II) complexes [9], only one molecule of alkyne can be inserted into the nickel–aryl bond.

The insertion process was strongly inhibited when free phosphine was added. The presence of free phosphine decreases the rates of both insertion and decomposition. Since no effect was observed in either the NMR or UV-visible spectra when the solutions of [NiBr(3,5-$Cl_2C_6H_3$)L_2] and phosphine were mixed, competition between PPh_3 and alkyne for the fifth coordination position may be ruled out as the cause of the inhibition. Thus some kind of substitution of phosphine by alkyne must be involved in the insertion. The dependence of the rates on the nature of both the phosphine and alkyne ligand suggests an associative substitution of phosphine by alkyne.

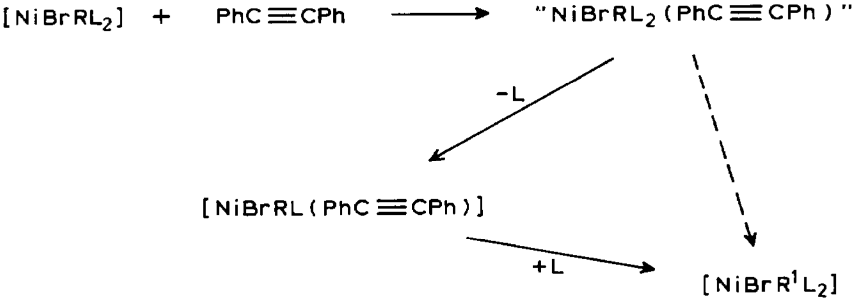


Scheme 1. The isomers *E*-R^2 and *Z*-R^1 are compounds formed by *cis*-addition of the σ(Ni–C) bond in the alkyne. (a,b,c,d) Toluene, Ni/≡:1/2, Room temperature (a): 6 h; (b): 2 h; (c): 4 d; (d): 16 h, 80 °C; (c): 36 h; (e,f) acetone, Ni/≡:1/4, 60 °C, (i): 24 h; (f): 16 h; (g) toluene, Ni/dppe = 1/1.1; room temperature, 1 h; (h) acetone, Ni/LiBr = 1/2, room temperature, 1/2 h; (i) acetone or toluene, room temperature, 12 d or acetone, 60 °C, 12 h.

Moreover, when great excess of PhC≡CPh was used in the reaction with $[NiBrR(PPh_3)_2]$ (R = 3,5-$Cl_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$) (Ni/PhC≡CPh: 1/15) the signal from free PPh_3 was observed by ^{31}P NMR spectroscopy in the first minutes of the reaction. The red species observed in these mixtures, which led only to the alkenyl compound when R was 3,5-$Cl_2C_6H_3$, must be formed from the substitution product "$NiBrR(PPh_3)$(PhC≡CPh)" or the precursor "$NiBrR(PPh_3)_2$(PhC≡CPh)".

When the reaction of $[NiBr(3,5\text{-}Cl_2C_6H_3)(PPh_3)_2]$ with PhC≡CPh takes place in the presence of large amounts of free PPh_3 (Ni/PPh_3/PhC≡CPh = 1/10/20. [Ni] = 10^{-3} *M*) the presence of a red species can be detected by visible spectroscopy (maximum at 495 nm). This process reaches a steady state after 3 h, and no decomposition is observed in 24 h.

When the same reaction is followed by ^{31}P NMR spectroscopy the formation of the two vinyl isomers of $[NiBrR^1(PPh_3)_2]$ can be detected and these are present throughout in the same isomeric ratio as that observed for the reaction without free phosphine. Another slowly increasing signal is observed at 24.12 ppm. After 3 h the system remains stable, and then the PPh_3 signal begins to widen (presumably because of a little decomposition) while the signal from the starting complex disappears. The signal at 24.12 ppm can be assigned to a pentacoordinate intermediate formed in the substitution of the phosphine of the starting complex.



The formation of products of insertion even when free phosphine is added to the reaction is consistent with the possibility of an insertion process directly through the pentacoordinate intermediate, as previously proposed for carbonylation reactions [10]. The presence of free PPh_3 and $MeO_2CC≡CCO_2Me$ in solution could not be established since a toluene solution of both species gave an orange solid when mixed. The ^{31}P NMR spectrum of this solid showed several signals that were not further investigated.

(ii) Stereochemistry of the addition. The reactions of $[NiBr(3,5\text{-}Cl_2C_6H_3)L_2]$ L = PPh_3 and 1/2 dppe with PhC≡CPh or $MeO_2CC≡CCO_2Me$ were monitored by ^{31}P NMR spectroscopy. No intermediates were observed under the conditions indicated in Scheme 1. When $[NiBr(3,5\text{-}Cl_2C_6H_3)(PPh_3)_2]$ reacts with PhC≡CPh, a signal at 16.13 ppm is initially observed, followed a few minutes later by another signal at 17.06 ppm, and the ratio between the areas of these two signals is approximately 2/1 throughout the reaction. The reaction of the compound having L = dppe gave similar results; two coupled signals centered at 54.10 and 35.84 ppm were observed and another set was evident at 52.56 and 38.11 ppm. The ratio between these two sets of signals was again about 2/1.

The proton and ^{31}P NMR spectra of the vinylic compounds obtained with $MeO_2CC≡CCO_2Me$ (see Table 1) show the presence of only one isomer. The ^{31}P

NMR spectra of all the vinyl complexes containing PPh_3 is as expected for *trans*-phosphines.

The vinyl compound obtained with $[NiBr(3,5\text{-}Cl_2C_6H_3)(PEtPh_2)_2]$ and PhC≡CPh also contains two isomers, as shown by the ^{31}P spectra. Thus whether one or two isomers is formed may depend either on the alkyne or on the corresponding vinyl complex or both, but is independent of the nature of the phosphine. Bubbling gaseous HCl through the solution of the vinylnickel complex afforded the organic product $CH(Ph)=C(Ph)(3,5\text{-}Cl_2C_6H_3)$ that may contain two isomers. Mass spectra showed the correct pattern at *m/z* 324, 326, and 328 for the molecular cation. However the ^{13}C NMR spectra showed the presence of only one isomer ($(CH)_2$: 129.49, 128.47, 128.83, 128.27, 127.55; (CH): 129.79, 127.98, 127.65, 127.44; (CCl): 135.15; (C): 143.52, 142.21, 139.85, 136.35 ppm). The proton NMR spectra (200 MHz) did not distinguish between the two isomers. However the stereochemistry determined after decomposition of a σ-alkenyl complex is sometimes ambiguous because of possible geometrical isomerization during decomposition [3]. We conclude that the two pairs of compounds obtained in the insertion with PhC≡CPh arise from *cis*- and *trans*-dispositions about the double bond.

It was not possible to separate the *Z* and *E* isomers of $[NiBrR^1L_2]$ from the mixtures obtained by reaction of the $[NiBr(3,5\text{-}Cl_2C_6H_3)L_2]$ with PhC≡CPh. We initially assumed that the different results in insertion of PhC≡CPh and MeOOCC≡CCOOMe came from the nature of the vinylnickel product and not from the alkyne itself. Thus the isomerization may be related to the lability of the phosphine in the vinylnickel organometallic, and this depends on the electronegativ-

Table 1

^1H and ^{31}P NMR data [a] for organonickel(II) complexes

	δ(P)	J(PP) (Hz)		δ(Me)
trans-$[NiBr(3,5\text{-}Cl_2C_6H_3)(PPh_3)_2]$	22.53			
trans-$[NiBrR^1PPh_3)_2]$ [e]	17.06			
	16.13			
trans-$[NiBrR^2(PPh_3)_2]$ [e]	18.92			3.23, 3.28 [b]
				3.34, 3.46 [c]
trans-$[NiBrR^3(PPh_3)_2]$ [e]	15.44			1.60(2)
	14.98			2.44(1)
trans-$[NiBrR^1(PEtPh_2)_2]$	13.70			0.98(J^3(P–H) 7.6 Hz [d])
	12.98			
$[NiBr(3,5\text{-}Cl_2C_6H_3)dppe]$	59.40	40.10	27	
$[NiBrR^1dppe]$	54.10	35.84 [c]	24.2	
	52.56	38.11 [c]	24.3	
$[NiBrR^2dppe]$	56.34	40.27	35.7	3.25, 3.65 [b]
$[NiBrR^3dppe]$	53.51	36.40	17.3	2.55 (1)
	53.43	37.07	21.6	1.78 (2.6)
$[NiBrR^4dppe]$ [e]	55.67	41.56	36.7	4(CH_2), 1(CH_3) J(HH) 7.1 Hz
$[Ni(3,5Cl_2C_6H_3)(\gamma\text{-pic})(dppe)]ClO_4$	56.75	47.75 [c]	24.7	
$[NiR^1(\gamma\text{-pic})dppe]ClO_4$	51.92	36.48 [c]	17.3	
$[NiR^2(\gamma\text{-pic})dppe]ClO_4$	51.80	36.53 [c]	17.4	3.31, 3.48, 2.56 (γ-pic) [c]

[a] Chemical shifts in ppm with respect to internal 85% H_3PO_4 (in toluene). [b] In C_6D_6. [c] In CD_3COCD_3. [d] Virtual coupling. [e] $R^1 = CPh{=}C(Ph)(3,5\text{-}Cl_2C_6H_3)$, $R^2 = C(COOMe){=}C(COOMe)(3,5\text{-}Cl_2C_6H_3)$, $R^3 = CPh{=}C(CH_3)(3,5\text{-}Cl_2C_6H_3)$, $R^4 = C(Ph){=}C(COOEt)(3,5\text{-}Cl_2C_6H_3)$.

ity of the vinyl ligand. Thus, the reaction of $[Ni(3,5\text{-}Cl_2C_6H_3)(\gamma\text{-pic})dppe]ClO_4$ with $PhC{\equiv}CPh$ in refluxing acetone solution for 24 h afforded only one isomer of the product $[Ni(C(Ph){=}C(Ph)(3,5\text{-}Cl_2C_6H_3)(\gamma\text{-pic})dppe]ClO_4$. The low lability of the ligand also affects the rate of insertion, as shown in Scheme 1.

When an acetone solution of $[NiR^1(\gamma\text{-pic})dppe]ClO_4$ was stirred with LiBr only one isomer of $[NiBrR^1dppe]$ was obtained ($\delta(^{31}P)$: 54.10 and 35.84 ppm). When solutions of this isomer were kept for several days at room temperature, the other isomer, with ^{31}P signals at 52.56 and 38.11 ppm, appeared. After 12 d the ratio of the two isomers reached its equilibrium value of 2/1. The isomerization of the neutral compound was not affected significantly by change of the solvent (toluene for acetone) or by the presence of free dppe [Ni/dppe = 1/1)].

One isomer of $[Ni(C(COOMe){=}C(COOMe)(3,5\text{-}Cl_2C_6H_3))(\gamma\text{-pic})dppe]ClO_4$ was also obtained in the insertion reaction with $MeOOCC{\equiv}CCOOMe$. Thus all the organometallics with the ligand R^2 contain the same *E*-isomer (the product of *cis*-addition), in accord with the substitution reactions shown in Scheme 1 and the structure of the vinyl compound containing PPh_3 (see below). By analogy we assume that the *Z*-isomer (the product of *cis*-addition) $[Ni(C(Ph){=}C(Ph)(3,5\text{-}Cl_2C_6H_3))(\gamma\text{-pic})dppe]ClO_4$ was obtained in the insertion involving the cationic organometallic.

(C) *Molecular structure of* $[NiBr(C(CO_2Me){=}C(CO_2Me)(3,5\text{-}Cl_2C_6H_3))(PPh_3)_2]$

The assignment of the stereochemistry of the vinyl ligand in the organometallic complexes was essential to test one model proposed for the addition process. We were able to obtain a single crystal of $[NiBr(C(CO_2Me){=}C(CO_2Me)(3,5\text{-}Cl_2C_6H_3))(PPh_3)_2]$ from acetone solution.

The molecular structure of this compound shows it to be the *E*-vinyl isomer, the product of *cis*-addition. The molecule is shown in Fig. I, and relevant interatomic distances and angles are given in Table 2.

Table 2

Selected inter atomic distances (Å) and angles (deg) for *E*-$[NiBr(C(COOMe){=}C(COOMe)(3,5\text{-}Cl_2C_6H_3))(PPh_3)_2]$

Ni–Br	2.350(1)	P(1)–Ni–Br	90.9(1)
P(1)–Ni	2.291(2)	C(1)–Ni–P(1)	93.0(2)
C(1)–Ni	1.895(7)	P(2)–Ni–Br	86.2(1)
P(2)–Ni	2.232(2)	P(2)–Ni–C(1)	91.0(2)
C(4)–C(1)	1.324(11)	C(1)–Ni–Br	167.2(2)
C(2)–C(1)	1.488(10)	P(2)–Ni–P(1)	173.9(1)
O(21)–C(2)	1.330(9)	C(4)–C(1)–Ni	132.8(6)
O(22)–C(2)	1.202(9)	C(2)–C(1)–Ni	105.1(5)
O(21)–C(3)	1.478(17)	C(4)–C(1)–C(2)	122.0(6)
C(5)–C(4)	1.520(11)	O(22)–C(2)–O(21)	122.9(7)
O(51)–C(5)	1.351(10)	O(22)–C(2)–C(1)	124.0(7)
O(52)–C(5)	1.155(11)	C(3)–O(21)–C(2)	114.5(7)
O(51)–C(6)	1.447(12)	C(1)–C(4)–C(41)	125.4(7)
C(4)–C(41)	1.479(10)	C(5)–C(4)–C(1)	117.7(7)
		O(52)–C(5)–O(51)	123.1(8)
		O(52)–C(5)–C(4)	127.2(8)

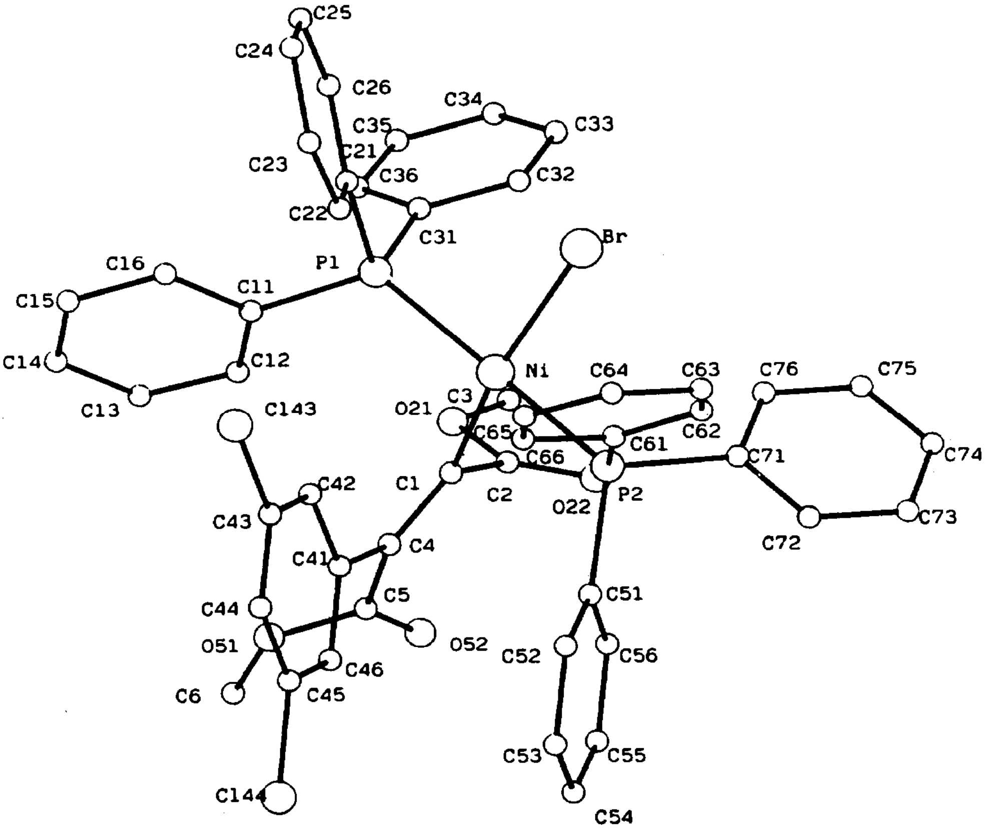


Fig. 1. Molecular structure of E[NiBr(C(COOMe)=C(COOMe)(3,5-Cl_2Ph))(PPh_3)$_2$] with the atom numbering.

The Ni atom has a distorted square-planar geometry, with P(1) and P(2), respectively, 0.143(3) and 0.157(3) above and Br and C(1), respectively, 0.161(2) and 0.189(8) Å below the mean plane defined by the five atoms. The steric hindrance between the vinyl ligand and the triphenylphosphine ligand (P1) (C(1)...C(12) 3.417 and C(4)...C(12) 3.493 Å) may be responsible for the lengthening of the Ni–P(1) bond (2.291(2) Å) and increase of the C(1)–Ni–P(1) bond angle (93.0(2)°). These effects are associated with a decrease in the P(2)–Ni–Br bond angle (86.2(1)°). The Ni, C(1), C(2), C(4), C(41) and C(5) atoms lie close to a plane arising from the double bond nature of the C(1)–C(4) bond. The dihedral angle between this plane and that defined by the Ni, P(1), P(2), C(1) and Br atoms is 84.3(2)°.

The carbon–carbon double bond distance, 1.324(11) Å, is similar to those in Z-[Ni(acac)(C(Ph)=C(Ph))(CH_3)(PPh_3)] [2] (1.327 Å) and [NiCl(C(Ph)=C(H)-($COCH_2SiMe_3$))(PMe_3)$_2$] [4] (1.34(1) Å).

In the vinyl ligand the C(2), O(22), O(21) and C(3) atoms lie in a plane, since there is some degree of double bond delocalization of the C(2)–O(21) bond (1.330(9) Å). The dihedral angle between this plane and those defined by the C(1)=C(4) bond is 77.2(7)°. The planes of the benzene ring and of the C(5)–O(51)–O(52) group around C(4) are twisted by 33.7(7)° and 36.2(7)° with respect to the C(1)=C(4) plane.

No interaction is possible between the oxygen atoms O(51) and O(52) with nickel because the CO_2Me group on the β-carbon is *trans* to nickel. The distance between O(22) and Ni is 3.195(4) Å, which is too long to permit interaction such as in the complex $[NiCl(C(Ph){=}C(H)(COCH_2SiMe_3))(PMe_3)_2]$ (Ni...O 2.537(7) Å).

(D) Reactions of $[NiBr(3,5\text{-}Cl_2C_6H_3)L_2]$ L = PPh_3 or dppe with unsymmetrical alkynes $PhC{\equiv}CMe$, $PhC{\equiv}CCOOEt$

The reactions of $[NiBr(3,5\text{-}Cl_2C_6H_3)L_2]$ (L = PPh_3 or 1/2 dppe) with $PhC{\equiv}CMe$ gave small yields of the alkenyl derivatives $[NiBrR^3L_2]$ (R^3 = $C(Ph){=}(3,5\text{-}Cl_2C_6H_3)Me$), but only the compound $[NiBrR^3dppe]$ was obtained as a pure solid. The solutions became reddish after the first minutes of reaction. The ^{31}P NMR spectra of the vinyl products showed signals from two complexes. The ^1H NMR spectra showed two CH_3 resonances (Table 1) in an integration ratio of ca. (2–3)/1 intensities. The isomer with the methyl signal at higher fields was the one in excess. Evidently only one regioisomer of the vinylnickel complex was obtained, as observed by Bergman et al. [3].

Decomposition of the vinyl complex by acid gives a mixture of two alkenes, and the ratio between the ^1H NMR signals is not the same as in the starting material. The methyl signals appear as doublets at 2.16 (J 1.5 Hz) and 2.23 (J 1.3 Hz), in accord with the formulation of $CH(Ph){=}CMe(3,5\text{-}Cl_2C_6H_3)$. The corresponding olefinic protons appear at 6.54 and 6.84 ppm, respectively. 1D and 2D NOE measurements did not permit unequivocal assignment. The mass spectrum shows the expected pattern of the molecular ions $C_{15}H_{11}Cl_2{}^+$ and $C_{15}H_{12}Cl_2{}^+$. Thus only the Z and E vinylnickel complexes with the larger group nearest the nickel atom was obtained in the insertion reactions. The signal with the larger downfield shift, attributable to the minor isomer can be assigned to the E isomer (the product of *trans*-addition), since in this position the methyl group lies directly over the nickel atom [11].

Reaction of $[NiBr(3,5\text{-}Cl_2C_6H_3)L_2]$ (L = PPh_3 or 1/2 dppe) with $PhC{\equiv}CCOOEt$ is more complex. In this case precipitation of the alkyne oligomer was observed even for reactions at room temperature in the dark. No new organometallic complex was isolated or observed by NMR spectroscopy when L was PPh_3, but when L was dppe a small amount of the vinyl complex was obtained. We assume that the polymerization is favoured by the presence of free Ni^{II} or Ni^0 arising from the decomposition of the organometallic.

The ^{31}P NMR spectra showed only the two doublets corresponding to one isomer. Addition of acid gave alkene $CH(Ph){=}C(3,5\text{-}Cl_2C_6H_3)(COOEt)$, characterized by the ^1H NMR signal of the C–H proton (CH 7.88, CH_3 1.3t(J 7 Hz), CH_2 4.28q, $3,5\text{-}Cl_2C_6H_3$: *para* 7.36t (J 2 Hz), *ortho* 7.12d, Ph unresolved). By analogy and, taking account of the chemical shifts, we suggest that the vinyl isomer formed has the phenyl group nearest the nickel atom, and has arisen from a *cis*-addition.

If the isomerization is controlled by the electron-withdrawing ability of the vinyl complex, the electronic effect comes, in this case, from the *trans*-substituent on the β-carbon.

(E) Conclusions

The results described allow us to identify the insertion process as a 1,2 *cis*-concerted addition. The process is very sensitive to the size of the organic ligand R, as was observed for palladium compounds [12]. Furthermore the difference in the behaviour of [NiBr(3,5-$Cl_2C_6H_3$)dppe] and [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)dppe]ClO_4 arising from the different charges on the central atom, indicates that the insertion and isomerization processes are consecutive.

The precise natures of the intermediate of the insertion and isomerization processes remains unclear. For some alkynes, formation of radical species similar to those described by Clark [13] in the reaction of alkynes with hydrides cannot be ruled out.

Experimental

All manipulations of the organonickel compounds were carried out by standard Schlenk techniques under nitrogen. The solvents were distilled under nitrogen prior to use. The ^1H NMR spectra were recorded on a Varian XL 200 instrument, and ^{31}P spectra (at 310 K) with a Bruker WP80SY instrument (32.38 MHz). The reference used were, respectively, internal tetramethylsilane and internal 85% aqueous H_3PO_4. All chemical shifts are shown with positive values downfield from the standards. The solvent was C_6D_6 for neutral complexes and CD_3COCD_3 for ionic compounds. Infrared spectra were recorded on a Perkin–Elmer 1330 instruments. UV-vis spectra were obtained with a Beckman UV 5230 spectrophotometer. GLC was performed with a Hewlett–Packard 5710A chromatograph (connected to a Hewlett–Packard 3390A integrator) fitted with a 2 m column packed with 15% SE 30 on Chromosorb Q. Mass spectra were obtained with a Hewlett–Packard 5988A Mass spectrometer coupled to a Hewlett–Packard 5890 chromatograph. Elemental analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.).

The alkynes were purchased from Fluka (PhC≡CPh, PhC≡CCOOEt and MeOOCC≡CCOOMe) or Aldrich (PhC≡CMe and PhC≡CPh), and their identities checked by GLC.

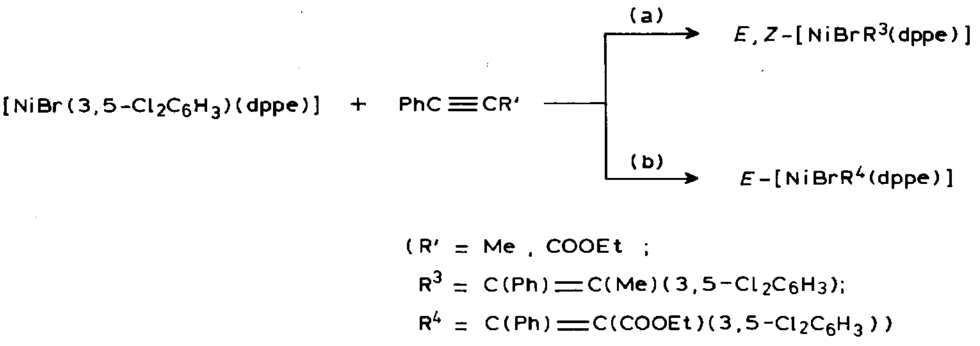
Preparation of the organometallics

The neutral compounds [NiBr(2,3-$Cl_2C_6H_3$)(PPh_3)$_2$] (6), [NiBr(3,5-$Cl_2C_6H_3$)(PPh_3)$_2$] (6), [NiBr(2,4,6-$Me_3C_6H_2$)(PPh_3)$_2$] (7), were obtained by published methods. If [NiClRL$_2$] was present it was removed by treatment with LiBr in acetone solution at room temperature.

The ionic compound [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)dppe]ClO_4 was obtained from a solution of [NiBr(3,5-$Cl_2C_6H_3$)(PPh_3)$_2$] (2 g, 2.5 mmol), γ-picoline (2 g, 20 mmol) and $NaClO_4 \cdot H_2O$ (0.75 g, 5 mmol) in 25 ml of acetone/toluene (1/1). After 20 min stirring, 1 g (2.5 mmol) of dppe was added. The product was precipitated by addition of ethanol and subsequent cooling to −78° C. The ionic compound was recrystallized from acetone/ethanol in an overall yield of 50%.

Reactions with alkynes

The reactions of neutral organometallics with alkynes were carried out in toluene under nitrogen. 0.1 *M* solutions of the neutral compound were prepared and an excess of the alkyne was added (Ni/alkyne = 1/2). The solution was stirred at room temperature for some hours or days and the reaction monitored by ^{31}P NMR spectroscopy. The colour changed from light orange to red as the reaction progress.



Scheme 2. (a,b) Toluene, room temperature, a: 48 h, Ni/ ≡ 1/2, b: 24 h Ni/ ≡ 1/4.

The reaction conditions used for the preparation of the vinyl complexes are summarized in Schemes 1 and 2. When the ligand was dppe, increase of the reaction temperature to 60–90 ° C markedly reduced the reaction time.

When the reactions of $[NiBr(3,5-Cl_2C_6H_3)L_2]$ ($L = PPh_3$ or 1/2 dppe) with the alkynes PhC≡CPh, MeOOCC≡CCOOMe, PhC≡CMe, were complete, as indicated by the ^{31}P NMR spectra, the solutions were concentrated at reduced pressure to one quarter of the initial volume, and hexane was added dropwise until an orange precipitate appeared. After cooling the suspension was filtered, and the collected solid dried under vacuum then recrystallized from toluene/hexane.

$[NiBrR^4dppe]$ ($R^4 = C(Ph)=C(COOEt)(3,5-Cl_2C_6H_3)$) was obtained by the same procedure. The toluene suspension was filtered and the solvent was removed at reduced pressure. The crude product was recrystallized from toluene/hexane. Reactions of $[Ni(3,5-Cl_2C_6H_3)(\gamma\text{-pic})dppe]ClO_4$ were performed in acetone solution. After 24 h the solvent was removed in vacuo and the residue was purified by repeated recrystallization from acetone/ethanol (1/4). The yields of the isolated vinylnickel complexes are shown in Table 3; and the yields indicated by the ^{31}P NMR spectra of the reaction solutions were always about 90–100% except for the reactions involving PhC≡CCOOEt.

Rate measurements

Rate measurements were carried out only to permit comparisons within pairs of reactions. In the presence of a very large excess of alkyne, the insertion is followed immediately by decomposition of the alkenyl compounds. In the presence of free phosphine, both insertion and decomposition processes are slowed.

Solutions used for UV-vis spectroscopy were 10^{-3} *M* in the organometallic and contained molar ratios of alkyne and free PPh_3 between 1/1 and 1/20.

Reactions to be monitored by ^{31}P NMR spectroscopy were usually carried out in an NMR tube. Typically, 50 mg of $[NiBr(3,5-Cl_2C_6H_3)(PPh_3)_2]$ and 160 mg of PhC≡CPh were placed in a 10 mm tube in the dry box and 1.5 ml of toluene was added. A 5 mm tube (with a coaxial adapter) containing C_6D_6 and H_3PO_4 capillary was introduced. The tube was capped and sealed with parafilm, and spectra were recorded at preselected times by means of a computer program. The relative areas of the ^{31}P signals were measured by use of the H_3PO_4 signal as reference.

Data obtained from visible and NMR analysis were in agreement.

Table 3

Analytical data and decomposition temperatures

	Yield (%)	Dec. temp (°C)	Analysis (Found (calcd.)(%))		
			C	H	N
$[NiBrR^1(PPh_3)_2]$ [a]	80	118–120	68.0	4.5	
			(68.12)	(4.39)	
$[NiBrR^1dppe]$	70	130–132	63.9	4.4	
			(64.15)	(4.33)	
$[NiBrR^1(PEtPh_2)_2]$	65	132–134	65.0	5.0	
			(64.68)	(4.86)	
$[NiR^1(\gamma\text{-pic})dppe]ClO_4$	40	160–162	64.2	4.7	1.4
			(64.13)	(4.55)	(1.44)
$[NiBrR^3dppe]$	40	154–156	60.5	4.5	
			(61.62)	(4.46)	
$[NiBrR^2(PPh_3)_2]$	70	153–155	64.1	4.4	
			(64.39)	(4.39)	
$[NiR^2(\gamma\text{-pic})dppe]ClO_4$	80	140–142	56.7	4.3	1.5
			(56.35)	(4.30)	(1.49)
$[NiBrR^2dppe]$	70	105–107	54.0	4.0	
			(55.30)	(4.03)	
$[NiBrR^4dppe]$	10	138–140	59.5	4.3	
			(60.25)	(4.35)	

[a] R^1 = $C(Ph)=C(Ph)(3,5\text{-}Cl_2C_6H_3)$; R^2 = $C(COOMe)=C(COOMe)(3,5\text{-}Cl_2C_6H_3)$; R^3 = $C(Ph)=C(Me)(3,5\text{-}Cl_2C_6H_3)$; R^4 = $C(Ph)=C(COOEt)(3,5\text{-}Cl_2C_6H_3)$.

Isomerization reactions

Preparation of Z-[NiBr(C(Ph)=C(Ph)(3,5-$Cl_2C_6H_3$))dppe]. A mixture of 0.4 g of $[NiR^1(\gamma\text{-pic})dppe]ClO_4$ (R^1 = $C(Ph)=C(Ph)(3,5\text{-}Cl_2C_6H_3)$) and 0.1 g of LiBr in 20 ml of acetone was stirred at room temperature for 1/2 h. The solvent was removed at low pressure and the residue washed with water then dried under vacuum.

A solution of Z-$[NiBrR^1dppe]$ in 2 ml of toluene was placed in an NMR tube which was capped and wrapped with parafilm. The tube was kept at room temperature and the reaction monitored by ^{31}P NMR spectroscopy for several days.

The same procedure was used for the acetone solutions at room temperature and at 60 °C, but the NMR tube was sealed. A stable equilibrium ratio between the isomers was reached in 10–12 days at room temperature or 12 h at 60 °C.

X-Ray diffraction study of $[NiBrR^2(PPh_3)_2]$

Crystal data. $C_{48}H_{39}O_4P_2Cl_2BrNi \cdot H_2O$, F_w 969.3, monoclinic, *a* 18.176(3), *b* 15.440(2), *c* 15.938(3) Å, β 91.56(2)°, V 4471(2) Å^3, $P2_1/a$, D_x 1.44 g cm^{-3}, $Z = 4$, $F(000) = 1984$, (Mo-K_α) 0.71069 Å, μ(Mo-K_α) 16.2 cm^{-1}. Room temperature.

Experimental: A prismatic crystal (0.1 × 0.1 × 0.12 mm) obtained from acetone/ethanol was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from the centring of 25 reflections ($4 \leq \theta \leq 12°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo-K_α radiation by the ω-scan technique, scan width 1° and scan speed 0.03° s^{-1}, 4390 independent reflections were measured in the range $2 \leq \theta \leq 25°$ and 4294 of which were taken as observed by application of the condition $I \geq 2.5\sigma(I)$. Three intensities were checked every 2 h, and no significant

Table 4

Final atomic coordinates for $C_{48}H_{39}O_4P_2Cl_2BrNi$ ($\times 10^{-4}$ for Br $\times 10^5$ for Ni and 10^3 for H) $B_{eq} = 8\pi\frac{1}{3}(u_{ij} \times a_i \times a_j \times a_i a_u)$

	a	b	c	B_{eq}
Br	81970(5)	10617(6)	10899(6)	3.87(4)
Ni	77917(5)	−852(6)	19298(6)	2.30(4)
P(1)	6659(1)	−62(1)	1263(1)	2.64(9)
C(11)	5843(4)	−514(5)	1734(5)	3.0(4)
C(12)	5788(4)	−1395(6)	1903(6)	3.8(4)
C(13)	5128(5)	−1743(6)	2203(7)	5.0(5)
C(14)	4531(5)	−1233(7)	2353(7)	5.3(5)
C(15)	4576(5)	−356(7)	2192(8)	5.7(6)
C(16)	5227(5)	17(6)	1873(7)	4.8(5)
C(21)	6677(4)	−585(4)	246(5)	3.1(4)
C(22)	6102(5)	−1102(6)	−78(6)	4.5(5)
C(23)	6164(6)	−1498(7)	−844(7)	5.3(5)
C(24)	6768(6)	−1420(7)	−1304(7)	5.7(6)
C(25)	7335(6)	−912(8)	−1022(6)	5.9(6)
C(26)	17291(5)	−519(7)	−248(6)	5.0(5)
C(31)	16372(4)	1053(5)	1036(5)	3.0(4)
C(32)	6507(4)	1677(6)	1652(6)	3.9(4)
C(33)	6240(5)	2532(6)	1543(7)	5.1(5)
C(34)	5875(5)	2746(6)	800(7)	4.9(5)
C(35)	5746(5)	2136(7)	172(7)	5.7(6)
C(36)	5996(4)	1276(6)	285(6)	3.9(4)
C(41)	7190(4)	−744(5)	3880(5)	2.4(3)
C(42)	7373(4)	−930(5)	4720(5)	3.4(3)
C(43)	7254(5)	−331(6)	5347(5)	3.9(4)
C(44)	6972(5)	479(7)	5137(7)	5.2(5)
C(45)	6791(5)	673(6)	4305(6)	4.4(5)
C(46)	6095(5)	72(5)	3688(5)	3.5(4)
Cl(43)	7495(2)	−555(2)	6388(2)	7.3(2)
Cl(44)	6450(2)	1683(2)	4067(2)	7.6(2)
C(1)	7606(4)	−1160(4)	2458(5)	2.1(3)
C(2)	7851(4)	−1829(5)	1854(5)	2.6(3)
C(3)	7514(7)	−2774(10)	7429(10)	6.5(7)
C(4)	7363(4)	−1366(5)	3208(5)	2.5(3)
C(5)	7234(5)	−2320(6)	3393(5)	3.2(4)
C(6)	6410(7)	−3286(7)	4048(8)	6.3(6)
O(21)	7293(3)	−2177(4)	1415(4)	3.9(3)
O(22)	8484(3)	−1970(4)	1705(4)	4.2(3)
O(51)	6636(3)	−2408(4)	3871(4)	4.1(3)
O(52)	7584(4)	−2899(4)	3177(5)	6.2(4)
O(2)	8870(1)	36(1)	2624(1)	2.46(8)
C(51)	9039(4)	−545(5)	3617(5)	2.6(4)
C(52)	9155(6)	−1443(6)	3574(7)	3.8(5)
C(53)	9299(6)	−1898(6)	4301(8)	5.1(6)
C(54)	9353(6)	−1519(8)	5062(8)	5.4(6)
C(55)	9231(6)	−630(9)	5117(6)	5.5(6)
C(56)	9090(5)	−151(6)	4388(5)	3.6(4)
C(61)	9689(4)	−274(5)	2024(5)	2.8(4)
C(62)	10364(5)	−270(7)	2433(6)	4.5(5)
C(63)	10989(5)	−475(9)	2010(7)	5.6(6)
C(64)	10922(8)	−688(10)	1177(9)	6.0(8)
C(65)	10248(6)	−744(8)	770(7)	5.0(6)
C(66)	9637(5)	−515(7)	1207(6)	3.7(5)
C(71)	9016(4)	1172(5)	2927(5)	2.8(3)

Table 4 (continued)

C(72)	9621(5)	1638(5)	2688(6)	4.0(4)
C(73)	9699(6)	2507(7)	2937(7)	5.1(5)
C(74)	9157(7)	2895(7)	3417(7)	5.7(6)
C(75)	8546(7)	2434(7)	3626(8)	5.8(7)
C(76)	8459(6)	1558(6)	3390(7)	4.6(5)
O	4869(9)	649(12)	5667(10)	2.6(8)
O	4688(8)	878(8)	5400(12)	2.2(6)

intensity change was observed. Lorentz polarization, but not absorption corrections, were made. Br and Ni atoms were located from a Patterson synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares by use of the SHELX76 computer program [14]. The function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma(F_o)^2 + 0.0043(F_o)^2)^{-1}$. f, f' and f'' were taken from International Tables of X-ray Crystallography [15]. After isotropic refinements two peaks were located from a difference synthesis, which were assigned as oxygen of hydrate water molecules in disordered positions with an occupancy factor of 0.5. Thirty hydrogen atoms (of 39) were located from a difference synthesis and refined with an overall isotropic temperature factor and the remaining atoms anisotropically. The final R value was 0.058 (R_w 0.065) for all observed reflections. Atom coordinates are shown in Table 4. Tables of thermal parameters, hydrogen atom coordinates, a full list of bond lengths and angles, and a list of observed and calculated structure factors are available from the authors.

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