Mechanism of the Insertion Reactions of Alkynes with **Phosphanickelacycles**

Manuel Martinez,* Guillermo Muller,* David Panyella, and Mercè Rocamora

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Xavier Solans and Mercè Font-Bardía

Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Marti i Franqués s/n, E-08028 Barcelona, Spain

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The mechanism of the insertion reaction of substituted alkynes (PhCCPh (X), PhCCCOOEt (Y), MeOOCCCCOOMe (Z)) into the Ni-C bond of trans-[${Ni(2-C_6H_4CH_2PPh_2)(\mu-Cl)}_2$] and trans-[NiCl(C-P)P'] (C-P = 2-C₆H₄CH₂PPh₂, P' = PBz₃ (1a), PMe₂Ph (1b); C-P = 2-C₆H₄- CH_2PEt_2 , $P' = PBz_3$ (1'a)) complexes has been investigated by means of ³¹P NMR and UVvis spectroscopy; in all cases insertion of only one molecule of alkyne has been found. The regioselectivity of the reaction is very well defined; only the regioisomer arising from a 1,2cis addition on the Ni-C bond is obtained. The kinetics of the reactions have been studied via UV-vis spectroscopy. Results agree with the formation of a highly ordered transition state still containing the monodentate phosphine P' in its coordination sphere, the effect of the metalated phosphine being less important (for example $\Delta H^{*} = 43, 60, 40 \text{ kJ mol}^{-1}$ and $\Delta S^{\dagger} = -118, -67, -125 \text{ J } \text{K}^{-1} \text{ mol}^{-1}$ for the **1a** + Y, **1b** + Y, and **1'a** + Y systems, respectively). A mechanism proceeding via the formation of a pentacoordinate intermediate aggregate, not detectable by NMR or visible spectroscopy, under the conditions of the study, is proposed. Only for the weaker π -acceptor alkyne PhCCPh is the observed rate constant found to be dependent on the alkyne concentration, indicating that for the other two alkynes studied the formation of the above-mentioned aggregate is complete under the kinetic conditions used (>10-fold excess of alkyne).

Introduction

The insertion of carbon-carbon multiple bonds into metal-carbon or metal-hydrogen bonds has been assumed to be a key step in many reactions in homogeneous catalysis.¹

Reactions of acetylenes with trans-[PtClH(PEt₃)₂], in polar solvents such as methanol, proceed via a previous substitution of the chloride ligand followed by a migratory insertion of acetylene into the Pt-H bond, leading to the *cis* product. A reaction mechanism involving a four-center transition state seems to be operating for that reaction system. Nevertheless, when the same reaction is carried out in a nonpolar solvent, benzene, a mixture of cis- and trans-alkenyl compounds is produced. In this case a radical chain mechanism is interpreted to be responsible for the behavior observed.²

Electron-transfer processes are also involved in the formation of alkenyl compounds, as found in acetylene insertion reactions with platinum dihydrides.³ The insertion of alkynes into $Pt-C^4$ and $Pd-C^{4,5}$ bonds has also been observed, usually leading to products that

contain two molecules of alkyne; in particular, the reaction with cyclopalladated organometallic compounds has been studied thoroughly.⁶ The insertion reaction of alkynes into [Ni(acac)(CH₃)(PPh₃)] has also been studied,⁷ and the results observed have been interpreted as a 1,2-cis addition of the methyl-nickel bond to the alkyne plus a concurrent isomerization to produce cisand *trans*-alkenyl derivatives. The same pattern has also been observed in other studies of reactions of PhCCPh or PhCCH with compounds containing Nialkyl or Ni-acyl bonds.8,9

Theoretical analysis of the reactions of ethylene and alkynes with trans- $[PtClH(PH_3)_2]^{10}$ or $[NiCl(CH_3)(C_2H_4)$ - (PH_3) ¹¹ led to the common conclusion that the insertion reaction is likely to proceed via a tetracoordinate intermediate, having the unsaturated molecule in a position cis to the M-H or M-C bond. Nevertheless, insertion of tetrafluoroethylene in a Pt-O bond via a pentacoordinate intermediate has also been proposed.¹²

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Scheme 1



The insertion into the Ni-C bond has some characteristic features: (i) only one alkyne molecule is usually inserted; (ii) in spite of some differences, 7, 13, 14 the reaction is interpreted as a concerted 1,2-addition with a dissociation of neutral ligand prior to the insertion reaction; (iii) the regioselectivity is such that unsymmetrical alkynes produce the regioisomer that has the bulkier substituent attached to the nickel-bound carbon, but when PMe₃ is used as the stabilizing monodentate ligand, the reaction is less regioselective.^{13,15}

In spite of the wide documentation available for the insertion reactions of alkynes, careful kinetic studies dealing with the proposed mechanisms are scarce. Only a few studies on insertions of alkynes into different Pd-C and Pt-C bonds are available.^{16,17} Kinetic studies with organonickel compounds are severely limited by the instability of the organometallic compounds in the presence of a large excess of other ligands.

In this paper we present the study of the kinetics and mechanisms of a series of insertion reactions of metallacyclic organonickel compounds in nonpolar solvents as depicted in Scheme 1. The metallacyclic compounds 1a, 1b, 3aX, 3aY, and 3bX have already been reported,^{18a} and compounds 1'a, 3aZ, 3bY, 3bZ, 3'aX, and 3'aY have been prepared and fully characterized in this work. The stability of these metallacycles in the presence of a moderate excess of alkynes allows this type of work. Another fact that led us to consider this study is that the proposed mechanism for the isomerization of the alkenyl compounds⁷ is disfavored in this case. It would include rotation about the vinyl $C_{\alpha}-C_{\beta}$ bond and, thus, the twist of the whole chelate ring on type 3 compounds.

Results

Compounds. The phosphanickelacycles 1a and 1b have been prepared as reported by reaction of $[Ni(cod)_2]$ with $(2-ClC_6H_4CH_2)PPh_2$ in the presence of the different free phosphine ligands.^{18a} Compound 1'a has been prepared by the same procedure using $(2-ClC_6H_4CH_2)$ - PEt_2 as chelating phosphine. When the synthesis of compounds 1 is carried out in the absence of free phosphine, the dinuclear complex trans-[{Ni(2-C₆H₄CH₂- $PPh_2(\mu-Cl)_2$ (4) is obtained.^{18a} Addition of phosphine to solutions of compound 4 led to the cleavage of the chlorine bridge, giving type 1a or 1b compounds (see Scheme 1). Reactions of compounds 1 and 1' with a slight excess of the corresponding PhCCPh (X) and PhCCCOOEt (Y) alkynes produce the corresponding compounds of types 3 and 3' (see Scheme 1). The same reaction with MeOOCCCCOOMe (Z) produces dark red (with 1a) or purple-violet solutions (with 1b and 1'a). ³¹P NMR of these solutions shows that the inserted **3aZ**, 3bZ, and 3'aZ complexes and some other material are present in the solution. From these mixtures only a low yield of compounds **3aZ** and **3bZ** could be isolated and fully characterized. In order to increase yields, reaction of 1a with MeOOCCCCOOMe (Z) was carried out in the presence of free PBz₃; under these conditions a better yield of a yellow compound, characterized as **3aZ** by elemental analyses and ³¹P and ¹H NMR, is achieved. The same procedure is not useful to obtain compound 3bZ since the formation of the previously described purple pentacoordinated species [NiCl(2-C₆H₄CH₂PPh₂)- $(PMe_2Ph)_2$ ^{18a} is dominant. For compound **3a'Z** the secondary material becomes the predominant species after the insertion reaction, and isolation of a pure sample has not been possible with any of the abovementioned procedures.

The nature of the other species present in the 1 + Z \rightarrow 3 reaction medium could be associated with the formation of a pentacoordinated or a zwitterionic species

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Table 1. ¹H NMR Data^a for the Nonaromatic Protons of the Compounds Studied in Toluene Solution

compd	R_2PCH_2Ph bridge	R' and R'' alkyne substituents	P' monodentate phosphine
$1a^b$ $1b^b$	$3.58 (d, J_{PH} = 9.0)$ 3.6		$PCH_2Ph, 3.17 (d, J_{PH} = 8.2)$ $PCH_3, 1.46$
$3\mathbf{a}\mathbf{X}^b$	$\begin{array}{l} 3.88 \; ({\rm t}, J_{\rm PH} = J_{\rm HH} \simeq 10), \\ 2.91 \; ({\rm t}, J_{\rm PH} = J_{\rm HH'} \simeq 10) \end{array}$		$\begin{array}{l} {\rm PCH_2Ph,\ 3.51\ (dd,\ J_{\rm PH}=7.6,}\\ J_{\rm HH'}=14.2),\ 3.26\ (dd,\\ J_{\rm PH}=7.3,\ J_{\rm HH'}=14.2) \end{array}$
$3 \mathbf{a} \mathbf{Y}^b$	$\begin{array}{l} 4.07 \; (\mathrm{dd}, J_{\mathrm{HH}'} = 12, J_{\mathrm{PH}} = 8), \\ 2.86 \; (\mathrm{t}, J_{\mathrm{PH}'} = J_{\mathrm{HH}'} \simeq 12) \end{array}$	$\begin{array}{l} {\rm CO}_2{\rm CH}_2{\rm CH}_3, \ 3.84 \ ({\rm q}, J_{\rm HH}=7); \\ {\rm CO}_2{\rm CH}_2{\rm CH}_3, \ 0.66 \ ({\rm t}, J_{\rm HH}=7) \end{array}$	$\begin{array}{l} {\rm PCH_2Ph,\ 3.34\ (dt,\ J_{\rm PH+P'H}\simeq 14,}\\ J_{\rm HH'}\simeq 8),\ 3.21\ (dt,\ J_{\rm PH+P'H}\simeq \\ 14,\ J_{\rm HH'}\simeq 8) \end{array}$
3aZ	3.7 (t, $J_{PH} = J_{HH'} \approx 10$), 2.7 (t, $J_{PH'} = J_{HH'} \approx 10$)	NiC-CO ₂ CH ₃ , 3.27; NiC=CCO ₂ CH ₃ , 3.33	PCH ₂ Ph, 3.7 (t, $J_{PH} = J_{HH'} \approx 10$), 2.7 (t, $J_{PH} = J_{HH'} \approx 10$)
$\mathbf{3bX}^b$	3.71 (t, $J_{PH} = J_{HH'} \approx 8$), 2.91 (t, $J_{PH'} = J_{HH'} \approx 8$)		PCH_3 , 1.61 (d, $J_{PH} = 8.8$), 1.43 (d, $J_{PH} = 8.32$)
3bY	3.67 (dd, $J_{PH} \approx 8$, $J_{HH'} \approx 12$), 2.91 (t, $J_{PH'} = J_{HH'} \approx 12$)	$CO_2CH_2CH_3$, 3.82 (q, $J_{HH} = 7.2$); $CO_2CH_2CH_3$, 0.78 (t, $J_{HH} = 7.2$)	$\begin{array}{l} {\rm PC}H_3, 1.57 \; ({\rm d}, J_{\rm PH}=8), 1.62 \\ ({\rm d}, J_{\rm PH}=9) \end{array}$
3bZ	4.3 (d, $J_{\rm HH'} \simeq 13.2$), 2.64 (t, $J_{\rm PH'} = J_{\rm HH'} \simeq 13.5$)	NiC-CO ₂ CH ₃ , 3.30; NiC=CCO ₂ CH ₃ , 3.36	PCH_3 , 1.71 (d, $J_{PH} = 10.6$), 1.51 (d, $J_{PH} = 10$)
3'aX	2.5 (t, $J_{PH} = J_{HH'} \simeq 10.7$), 2.85 (t, $J_{PH'} = J_{HH'} \simeq 10.7$) (PCH ₂ CH ₃ , 1.3 (m); PCH ₂ CH ₃ , 0.95 (m))		PCH ₂ Ph, 3.0 (m), 3.55 (m)
3'aY	$\begin{array}{l} 2.65 \; ({\rm t}, J_{\rm HH'} = J_{\rm PH} \simeq 11), \\ 3.19 \; ({\rm dd}, J_{\rm HH'} \simeq 9.5, J_{\rm PH} \simeq \\ 12.5) \; ({\rm PCH}_2{\rm CH}_3, 1.55 \; ({\rm m}), 2.22 \\ ({\rm m}); \; {\rm PCH}_2{\rm CH}_3, 1.2({\rm m})) \end{array}$	$\begin{array}{l} {\rm CO_2CH_2CH_3, 4.05, 4.15 (dq, J_{\rm HH}=7, \\ J_{\rm HH'}=11); {\rm CO_2CH_2CH_3, 0.91} \\ ({\rm t}, J_{\rm HH}=7) \end{array}$	$\begin{array}{l} {\rm PC}{H_2}{\rm Ph,\ 3.30\ (dd,\ J_{\rm PH}\simeq 13.8,}\\ J_{\rm HH}\simeq 7),\ 3.60\ (dd,\ J_{\rm PH}\simeq 14.3,\ J_{\rm HH}\simeq 7) \end{array}$

^{*a*} δ in ppm relative to TMS (*J* in Hz), in C₆D₆ or toluene-*d*₈. ^{*b*} Reference 23.



Figure 1. Ortep view of the structure of complex 3aX, trans-[NiCl{PhC=CPh(2-C₆H₄CH₂PPh₂)}PBz₃], showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

and its subsequent decomposition.^{7,9} When the stoichiometric reaction of 1'a with MeOOCCCCOOMe (Z) is carried out in THF solution, two groups of signals, one corresponding to the **3'aZ** inserted compound and two doublets at 14.7 and 21.5 ppm ($J_{PP'} = 10.3$ Hz) are observed by ³¹P NMR immediately after mixing. This signal pattern collapses in a few minutes, producing a single signal at 18 ppm which is that observed under any other conditions. The same reaction and signal patterns are observed for the reactions of **1a** and **1b** with Z, but in these cases the formation of the inserted complexes is favored. The insertion reactions of alkynes PhCCPh (X) and PhCCCOOEt (Y) have been studied also with compound 4, only compound **5X** has been fully characterized in the solid state and the reaction of the inserted compounds with P' (Scheme 1) allowed us to confirm its nature. Reactions run with a [Ni]/[alkyne] ratio of 1/2 at 273 K were complete in few minutes, and no intermediates were detected, as observed by ³¹P NMR monitoring. Although compounds 1 are stable in solution under a dinitrogen atmosphere, compound 4 is much less stable and, even under these conditions, decompose rather quickly with the appearance of a yellow precipitate. The stabilities of all the 1 and 4 compounds studied are enhanced by the formation of the corresponding insertion products.

³¹P and ¹H (Table 1) NMR spectra of compounds of types 1 and 3 have been recorded. The ³¹P NMR spectra clearly indicate their *trans* geometry;^{18a} however, dinuclear complexes 4 and 5 may be a mixture of the sym and anti isomers, since the phosphorus NMR signal is broad and complex. Small quantities of *cis*-1a were found in solutions of its *trans* isomer complex. The relative amount of *cis/trans* isomerization was found to be dependent on the size of the different ligands, compound 1b not showing any percentage of *cis* isomer.^{18a} This behavior was related to the production of a more labile species *via* the equilibrium process

$$[\text{NiCl}(2\text{-}\text{C}_{6}\text{H}_{4}\text{C}\text{H}_{2}\text{PPh}_{2})\text{P}'] + \text{S} \rightleftharpoons$$
$$[\text{NiCl}(2\text{-}\text{C}_{6}\text{H}_{4}\text{C}\text{H}_{2}\text{PPh}_{2})\text{S}] + \text{P}' (1)$$

S = solvent

This process is strongly displaced to the left-hand side, since no signals of free phosphine can be detected by ³¹P NMR. An equimolar mixture of **1'a** and **1b** compounds in toluene solution at room temperature equilibrates on standing, producing an almost equimolar amount of the four organometallics **1'a**, **1b**, **1a**, and **1'b** $(\delta_{\rm P} - 8.1 \text{ ppm}, \delta_{\rm P'} - 57.3 \text{ ppm}, J_{\rm PP'} = 340 \text{ Hz at } 220 \text{ K})$, as can be monitored by ³¹P NMR at 220 K. This fact agrees with the presence of catalytic amounts of free

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Table 2.	Selected Bond Distances and Angles			
	(Esd's in Parentheses) for			
trans.[NiCl{PhC=CPh(2.C.H.CH.PPh_)}PBz_]				

Bond Lengths (Å)					
Cl-Ni	2.244(1)	C(2)-C(3)	1.548(4)		
P(1)-Ni	2.256(1)	C(3) - C(8)	1.427(4)		
P(2)-Ni	2.212(1)	C(8)-C(9)	1.500(4)		
C(1)-Ni	1.929(3)	C(9) - P(2)	1.857(3)		
C(1) - C(2)	1.362(4)				
Bond Angles (deg)					
P(1)-Ni-Cl	88.6(1)	Ni-P(2)-C(9)	112.1(1)		
P(2)-Ni-Cl	93.8(1)	C(8) - C(9) - P(2)	109.9(2)		
P(1) - Ni - P(2)	169.3(1)	C(9) - C(8) - C(3)	118.6(3)		
C(1)-Ni-Cl	177.5(1)	C(8) - C(3) - C(2)	121.6(2)		
C(1) - Ni - P(1)	92.2(1)	C(1) - C(2) - C(3)	119.9(2)		
C(1) - Ni - P(2)	85.8(1)	Ni-C(1)-C(2)	119.3(2)		

phosphine in solution. Nevertheless, when large amounts of free PBz_3 were added to toluene solutions of *trans*-[NiCl(2-C₆H₄CH₂PPh₂)PBz₃] (1**a**), no line broadening was observed. ¹H NMR signals, collected in Table 1, indicate that the two methylene protons of the ring give different signals according to the rigidity of the ring and the lack of a symmetry plane in the complex. ¹H NMR spectra (500 MHz) recorded for the **3a**Y compound showed that all the methylene protons are diasterotopic.

Molecular Structure of trans-[NiCl{PhC=CPh-(2-C₆H₄CH₂PPh₂)}PBz₃] (3aX). The molecular and crystal structure of compound **3aX** was determined by X-ray diffraction. The crystal structure consists of discrete molecules (Figure 1) separated by van der Waals distances. Selected bond lengths and angles and atomic coordinates are listed in Tables 2 and 3, respectively. The bond distances are in the range expected; the complex exhibits a distorted-square-planar geometry. The observed displacements (Å) from the leastsquares plane of the coordination sphere (plane A) are as follows: Ni, -0.0640; P1, 0.1372; Cl, -0.0962; P2, 0.1412; Cl, -0.1183. Despite the fact that a greater steric hindrance for the Ni-C(Ph)=C(Ph)- than for the Ni-C(Ph)=C(COOEt)- fragments of the rings can be assumed, these displacements are lower than those observed for the previously described 3aY complex (-0.0402, -0.2908, 0.2843 - 0.2897, 0.3365 Å).^{18a} Nevertheless, the steric hindrance is present. On one hand, the alkenyl plane defined by C1C2C3C10C16 (plane B) in **3aX** shows a displacement from the least-squares plane of -0.1043, -0.0280, 0.0641, 0.0817, and -0.0135 Å, respectively, and the nickel atom directly bonded to C1 is displaced -0.4435 Å (compared with 0.3761 Å for the **3aY** compound). On the other hand, the bite angle for $3aX (85.8(1)^{\circ})$ is very strained when compared with that for the **3aY** complex $(90.1(2)^{\circ})$.

The benzyl group of the phosphine included in the seven-membered ring C2-C9 also forms a well-defined plane (C); the angles formed between normals to the planes AB, AC, and BC are respectively 94.89, 68.32, and 62.51° , showing a nearly perpendicular arrangement of the alkenyl group with respect to the square-planar coordination sphere.

Mechanistic Studies. The reaction of *trans*-[NiCl-(C-P)P'] (1) and [NiCl(C-P)]₂ (4) compounds with several alkynes, (PhCCPh (X), PhCCCOOEt (Y), and MeOOC-CCCOOMe (Z)) was studied kinetically in toluene solutions by means of UV-vis spectroscopy. The *in situ* monitoring of these processes *via* ³¹P NMR (see above) proved that the reactions followed were effectively the

Table 3. Final Atomic Coordinates (×10⁴; ×10⁵ for Ni, Cl, P(1), and P(2)) for *trans*-[NiCl{PhC=CPh(2-C₆H₄CH₂PPh₂)}PBz₃]

	- t	,	<u> </u>	2× J =
	x/a	y/b	z/c	$B_{ m eq}({ m \AA}^2)^a$
Ni	17667(3)	17162(1)	24306(2)	2.87(2)
P (1)	462(6)	13395(3)	17496(4)	3.10(3)
P(2)	32028(6)	21864(3)	31771(4)	3.29(3)
Cl	21464(6)	20341(3)	11813(4)	3.83(3)
C(1)	1502(2)	1424(1)	3503(2)	3.07(11)
C(2)	756(2)	1665(1)	4003(2)	3.09(11)
C(3)	344(3)	2213(1)	3799(2)	3.26(11)
C(4)	-923(3)	2334(1)	3593(2)	4.30(14)
C(5)	-1293(4)	2840(2)	3403(2)	5.66(19)
C(6)	-437(5)	3227(1)	3448(2)	6.06(21)
C(7)	816(4)	3121(1)	3687(2)	5.14(17)
C(8)	1227(3)	2615(1)	3860(2)	3.82(13)
C(9)	2591(3)	2496(1)	4086(2)	4.30(14)
C(10)	2156(2)	930(1)	3755(2)	3.37(12)
C(11)	2200(3)	508(1)	3209(2)	3.99(13)
C(12)	2622(3)	$\frac{30(1)}{10(1)}$	3478(2)	5.02(16)
C(13)	3410(3) 9490(9)	10(1)	4293(3)	0.00(10)
C(14)	0420(0) 0914(9)	420(2) 991(1)	4000(2)	0.04(10)
C(16)	2014(3)	1449(1)	4071(2)	4.30(14)
C(10)	-47(3)	921(1)	4771(2)	3.27(11) 3.89(13)
C(18)	-520(3)	730(1)	5535(2)	4.79(15)
C(19)	-680(3)	1056(2)	6196(2)	5.12(10)
C(20)	-353(3)	1573(2)	6156(2)	5.12(10) 5.17(17)
C(21)	126(3)	1765(1)	5456(2)	4.15(13)
C(22)	4576(3)	1823(1)	3610(2)	4.48(14)
C(23)	4876(3)	1381(2)	3190(3)	5.84(19)
C(24)	5907(4)	1089(2)	3501(4)	8.96(30)
C(25)	6639(5)	1238(3)	4243(6)	11.41(43)
C(26)	6362(5)	1662(3)	4639(4)	10.26(39)
C(27)	5327(4)	1965(2)	4354(3)	7.01(21)
C(28)	3814(3)	2743(1)	2642(2)	3.60(12)
C(29)	2982(3)	3096(1)	2215(2)	4.66(15)
C(30)	3394(4)	3519(2)	1806(2)	5.67(18)
C(31)	4661(5)	3591(2)	1789(3)	7.24(24)
C(32)	5487(4)	3240(2)	2191(3)	8.16(26)
C(33)	5079(3)	2823(2)	2622(2)	5.75(18)
C(34)	-1012(3)	975(1)	2380(2)	3.99(13)
C(35)	-1563(3)	461(1)	2066(2)	3.77(12)
C(30)	-1675(3)	0(1) 479(1)	2409(2)	0.30(10)
C(31)	-1070(4) -9610(4)	-473(1) -497(1)	2194(3) 1599(9)	0.02(22)
C(30)	-2019(4) -3048(3)	-457(1)	1136(3)	5.27(21)
C(33)	-9593(3)	-44(1)	130(2)	5.47(17)
C(40)	2020(3)	950(1)	805(2)	3 9/(13)
C(42)	1286(3)	542(1)	941(2)	4.08(13)
C(42)	2541(3)	695(2)	1005(2)	5.23(17)
C(44)	3489(4)	335(2)	1159(3)	6.54(22)
C(45)	3234(5)	-178(2)	1241(3)	7.04(24)
C(46)	2011(5)	-337(2)	1159(3)	6.69(23)
C(47)	1029(4)	21(1)	1006(2)	5.34(17)
C(48)	-930(3)	1890(1)	1307(2)	4.15(13)
C(49)	-2255(3)	1786(1)	925(2)	3.66(11)
C(50)	-2542(3)	1604(1)	107(2)	4.72(15)
C(51)	-3766(4)	1497(2)	-234(2)	5.72(18)
C(52)	-4719(3)	1579(2)	237(3)	5.72(18)
C(53)	-4465(3)	1765(2)	1039(3)	6.38(20)
C(54)	-3241(3)	1866(2)	1378(2)	5.46(17)

^{*a*} $B_{\rm eq} = {}^{8}\!/_{3}\pi^{2}\Sigma U_{ij}A_{i}^{*}A_{j}^{*}A_{i}^{\cdot}A_{j}.$

alkyne insertion into the Ni-C bond present in compounds 1 and 4 to produce compounds 3 and 5 (see Scheme 1).

Table 4 shows the spectral electronic data for the reactions studied. In all cases a good retention of isosbestic points was observed (Figure 2), indicating that only the insertion reaction was being monitored. For systems where a subsequent reaction was detected, only the first fast spectral changes were monitored as the insertion reaction.

The observed rate constants obtained for all these systems, collected in Table S1 (Supporting Information),



Figure 2. UV-vis consecutive spectra showing the advance of the insertion reaction of compound **1b** with the alkyne PhCCPh (X) (T = 15 °C, [**1b**] = 1 × 10⁻³ M, [X] = 0.0250 M, t = 0-600 s, toluene solution).

Table 4. UV-Vis Spectral Data for the Compounds Studied (T = 15 °C; Toluene Solution)

compd	λ/nm	$\epsilon/\mathrm{M}^{-1}\mathrm{cm}^{-1}$	extra alkyne added (ca. 0.4 M)	λ/nmª
trans-[NiCl ₂ (PBz ₃) ₂]	488, 374	680, 17 500		·
1a	448	1700	Z	570^{b}
1b	442	850	\mathbf{Z}	570^{b}
1'a	428	1000	Z	575^{b}
4	450			
3aX	456	1600	Х	dec
			Y	450
			Z	475
3aY	448	1600	Х	dec
			Y	446
			Z	472
3aZ	431	650		
3'aX	447	1300		
3'aY	436	1400		
3bX	462	1300		
3bY	456	2400		
3bZ	438	700		
5X	486^{a}			

 a No ϵ values are given due to subsequent decomposition reactions and/or concentration uncertainties. b Final purple solution, isosbestics points observed in all cases.

were found to have a linear correlation with the alkyne concentration only for the reaction of compounds of type 1 with the PhCCPh (X) alkyne to produce **3aX**, **3bX**, and **3'aX** inserted products. For all other systems the observed rate constants were found to be independent of the alkyne concentration used for the runs. Figure 3 represents an example of such behavior. Some runs were carried out in THF solution, and the observed rate constants were found to be independent of the solvent used.

The results obtained agree with any of the reaction mechanisms depicted in Schemes 2 and 3, which produces the rate law^{19}

$$k_{\rm obs} = \frac{kK[alkyne]}{1 + K[alkyne]}$$
(2)

where

$$K = \frac{[\mathbf{2}]}{[\mathbf{1}][\mathrm{alkyne}]} \tag{3}$$



Figure 3. Alkyne concentration and temperature dependence on the observed rate constants for the insertion reaction of compound 1'a with alkynes PhCCPh (X) (above) and PhCCCOOEt (Y) (below) alkynes. Open points correspond to toluene solution and solid points to THF solution.

For PhCCCOOEt (Y) and MeOOCCCCOOMe (Z) alkynes the K[alkyne] term becomes much larger than 1, and rate law 2 becomes $k_{obs} = k$, while for alkyne PhCCPh (X) the K[alkyne] term becomes very small and rate law 2 becomes $k_{obs} = kK$ [alkyne].

Table 5 collects all the first- and second-order rate constants derived from these systems, as well as the thermal activation parameters derived from its temperature dependence and standard Eyring plots.

In view of these data a clear distinction must be made between the insertion reactions leading to 3aX, 3bX, and 3'aX and the rest. These three reactions produce second-order rate constants that cannot be separated in equilibrium and kinetic constants; consequently, any comparison of these values with those for the reaction systems with the PhCCCOOEt (Y) and MeOOCCC-COOMe (Z) alkynes is meaningless.

In order to clarify the role of the two monodentate phosphine ligands of compounds 1 in the nature of the insertion reaction, compound 4 was reacted with alkynes PhCCPh (X) and PhCCCOOEt (Y) to produce compounds 5 shown in Scheme 1. Given the lesser stability of compound 4 when compared with 1a or 1'a, only runs at 15 °C at varying alkyne concentration were carried out, thermal activation parameters not being determined. The results obtained showed, again, different [alkyne]-dependence behavior, and the rate constants obtained are much larger than those corresponding to the mononuclear equivalent 1a and 1b species, as shown in Table 5.

(19) (a) Wilkins, R. G. Kinetics and Mechanisms of Reactions of Transition Metal Complexes; VCH: Weinheim, Germany, 1991. (b) Crespo, M.; Martinez, M.; Sales, J. Organometallics **1992**, *11*, 1288.



Table 5. Insertion Reaction Rate Constants and
Thermal Activation Parameters for the SystemsStudied ([Starting Nickel Compound] = 1×10^{-3} M,
Toluene Solution)

				$\Delta H^{*/}$	$\Delta S^*/$
compd	alkyne	<i>T</i> /°C	k	kJ mol ⁻¹	J K mol ⁻¹
1a	Х	15	$0.31 \text{ M}^{-1} \text{ s}^{-1}$	57 ± 5	-57 ± 17
		25	$0.61 \ \mathrm{M^{-1} \ s^{-1}}$		
		35	$1.5 \text{ M}^{-1} \text{ s}^{-1}$		
	Y	15	$0.084 \ s^{-1}$	43 ± 4	-118 ± 14
		25	0.17 s^{-1}		
		35	$0.29 \ s^{-1}$		
	Z	15	0.28 s^{-1}	41 ± 5	-114 ± 18
		25	$0.57 \ { m s}^{-1}$		
		35	$0.92 \ { m s}^{-1}$		
1′a	Х	15	$0.037 \ { m M^{-1} \ s^{-1}}$	81 ± 12	5 ± 1
		25	$0.11 \text{ M}^{-1} \text{ s}^{-1}$		
		35	$0.29 \ { m M}^{-1} \ { m s}^{-1}$		
	Y	15	$0.10 \ s^{-1}$	40 ± 3	-125 ± 10
		25	$0.20 \ s^{-1}$		
	_	35	0.32 s^{-1}		
	Z	15	0.14 s^{-1}	41 ± 1	-118 ± 3
		25	0.28 s^{-1}		
		35	0.51 s^{-1}		
1b	Х	15	$0.35 \text{ M}^{-1} \text{ s}^{-1}$	84 ± 6	35 ± 12
		25	$1.2 \text{ M}^{-1} \text{ s}^{-1}$		
		35	$3.4 \text{ M}^{-1} \text{ s}^{-1}$		
	Y	15	0.031 s^{-1}	60 ± 1	-67 ± 3
		25	0.074 s^{-1}		
	-	35	0.17 s^{-1}		
	Z	15	0.049 s^{-1}	53 ± 3	-85 ± 8
		25	0.12 s^{-1}		
	v	35	0.22 5		
4	X	15	4.18 MI * S *		
1	Y V	15	1.20 s^{-1}		
18	А	15	$0.23 \text{ M}^{-1} \text{ s}^{-1} b$		
			$0.22 \text{ M}^{-1} \text{ s}^{-1}$		
10	7	15	$0.00 W + s^{+0}$		
18	2	19	0.43 5		
a [PBz ₃]/[1a] = 0.01, b [PBz ₃]/[1a] = 0.1, c [PBz ₃]/[1a] = 1.					

Some runs were also carried out in order to check possible concentration effects of the nickel starting organometallic, type 1 compounds, on the insertion rate constants. The results obtained for most of the systems indicate that a very important increase in the reaction rate constant is observed on decreasing the nickel starting material concentration. Decomposition reactions, occurring much more readily at lower concentrations, could be responsible for the dilution effects observed. For concentrations higher than 5×10^{-4} M no dilution effects were observed; consequently [1] was set to 1×10^{-3} M.

Experiments at varying added phosphine concentrations were carried out also for the reaction of 1a with alkynes PhCCPh (X) and MeOOCCCCOOMe (Z) in order to check possible mass-retardation effects.⁷ Even though the degree of advance of the reaction decreases on increasing the phosphine concentration, producing less reliable observed rate constants, the results clearly show (Table 5) that the rate constants for the insertion reaction do not vary significantly at reasonable concentration values of added PBz₃.

Discussion

Reactions of type 1 and 4 compounds in toluene solution with alkynes such as diphenylacetylene (X) ethyl phenylpropiolate (Y), and dimethyl acetylenedicarboxylate (Z) take place readily at room temperature. For example, 1 h is enough to complete the reaction when a [Ni]/[X] ratio of 1/2 is used. The insertion of only one molecule of alkyne into the Ni-C bond was observed for these compounds, further reaction with a second alkyne molecule being blocked by the bulky substituents of the alkenyl derivative. For the less sterically hindered alkyne MeOOCCCCOOMe, other definite changes that could be attributed to the formation of compounds where an attack at the double C=Cbond by the neighboring P' phosphine has occurred⁹ or to the formation of a pentacoordinated species were observed in both the ³¹P NMR and UV-vis spectra (Table 5). In this respect, changes in the UV-vis spectra of solutions of the inserted compounds with an excess of different alkynes (Table 4) seem to agree with the pentacoordinate assumption.

Only one of the two possible cyclic alkenyl isomers was obtained in each reaction (see Scheme 1). The stereochemistry of the addition was established unambiguously from the molecular structure determination for two of the alkenyl products, **3aX** and **3aY**.^{18a} Both structures showed that the alkyne substituents remain in a *cis* distribution in the alkenyl addition products. For the ethyl phenylpropiolate inserted compound **3aY**, the largest substituent lies on the carbon directly bonded to the nickel center, indicating that possible interactions of the $-CO_2R$ groups with the nickel center should not be very important.

The stereochemistry of the reaction can be considered as a *cis* 1,2-addition of the nickel-carbon bond to the alkyne, which is in good agreement with proposals found in the literature.⁷ Although results from other groups suggest that a *trans*-insertion alkenyl compound is the kinetic product of the reaction,¹³ the fact that no isomerization processes are readily accessible in our case indicates that the *cis* addition must be the kinetic product of the reaction.

As a previous step to the insertion reaction, the existence of reaction equilibrium 1 suggests that the presence of large amounts of alkyne could favor the displacement of the phosphine in the starting type 1 nickel compounds. Although a ³¹P signal of free phosphine is observed when a large excess of alkyne is present in the reaction medium, NMR measurements cannot rule out the decomposition of the organometallic



compound as the source of it. In this respect, compounds 5X and 5Y (the latter not characterized in the solid state) are stable in the presence of a large excess of the corresponding alkynes, indicating that such poor ligands cannot even displace the bridging chloride in the dinuclear compounds. Allowing for these facts, the alternate reaction mechanism depicted in Scheme 3 does not fit to the experimental observations.

Although the presence of free phosphine in the insertion reactions *via* intermediates of type 2_p (Scheme 2) and 2_t (Scheme 3) should not produce any difference in the first-order rate constants for alkynes PhC-CCOOEt (Y) and MeOOCCCCOOMe (Z) ($k_{obs} = k$ in both cases, given the large value of K), a [P]_{added} mass-retardation effect should be observed in the second-order rate constants^{7,10} obtained for the systems with alkyne PhCCPh (X), where the rate law derived is²⁰

$$k_{\rm obs} = k K \frac{[\rm alkyne]}{[\rm P']} \tag{4}$$

The $[P]_{added}$ independence of the second-order rate constants of the reaction of compound **1a** with alkyne PhCCPh (X) (Table 5) indicates that a rate law such as that indicated in eq **4** does not apply. Consequently, an intermediate species of type **2**_p (Scheme 2) seems to fit much better to the experimental kinetic data. Formation of a tetracoordinate intermediate *via* displacement of the chloride ligands in type **1** compounds by alkynes is also unexpected. Kinetic runs carried out in THF solution showed that the observed rate constants were independent of the solvent used, as expected for the absence of ionic species during the insertion process.

The presence of an aggregate, similar to that depicted as 2_p in Scheme 3, having two monodentate PBz₃ ligands and the chelating phosphine phosphorus interacting with the nickel center, could account for the lesser degree of advance in the insertion reaction when free PBz₃ is present in the solution. As already pointed out in the literature for Pt(II) systems,²¹ it is very difficult to distinguish between a pentacoordinated compound and a tight outer-sphere complex; therefore, the nature of the possible intermediate aggregate is by no means clear. Furthermore, ³¹P NMR at these concentrations, or UV-vis spectroscopy when other highly absorbing species exist in the reaction medium, makes it very difficult to assert its nature. Even so, the steric congestion around the Ni center has to be very important and the decomposition of type **1a** compounds in the presence of excess free PBz₃ to produce a nonreacting mixture of *trans*-[NiCl₂(PBz₃)₂] and phosphonium salts seems to be another plausible explanation of the lesser extent of the insertion reaction observed under these conditions.

Examination of data in Table 5 clearly indicates that the insertion process goes through a highly ordered transition state, as seen by the very negative values of ΔS^{*} for the systems where these values have been derived from the first-order rate constants (alkynes PhCCCOOEt (Y) and MeOOCCCCOOMe (Z)). The more negative ΔS^{\dagger} values found for the systems having PBz_3 as the monodentate phosphine ligand have to be interpreted in view of the more important space rearrangement necessary for these systems for the insertion reaction to take place. For the **1a** and **1'a** systems ΔH^{\dagger} values are smaller than those for the 1b systems, indicating that the higher ν electronic parameter of the PBz₃ phosphine in these systems makes the insertion reaction more favorable.²² An important fact that should also be considered is that ΔS^{\dagger} and ΔH^{\dagger} values derived from first-order rate constants, while independent of the metalated phosphine, vary significantly with the monodentate P' phosphine ligand. Given the fact that the alkyne has to be close to the P' ligand for the insertion reaction to take place, the above-mentioned difference seems to indicate that a reaction intermediate aggregate of type 2_p (Scheme 2), where the chelating phosphine has very little influence on the transition state, is a very plausible explanation of the observed facts.

Furthermore, if this is true, a simultaneous interaction of the much bulkier PhCCPh (X) alkyne with type 1 compounds is very unfavorable with respect to that of the smaller PhCCCOOEt (Y) and MeOOCCCCOOMe (Z) alkynes. The results for the systems studied agree with this assumption; the differences in the magnitude of K in rate law 2 are important enough as to make Kunobservable for the two systems with less bulky and more electronically activated alkynes by its π -acceptor character.⁷ A possible interaction of the $-CO_2R$ groups of alkynes PhCCCOOEt (Y) and MeOOCCCCOOMe (Z) with the nickel center could also be related to the large magnitude of K. Nevertheless, the determined crystal structure of compound **3aY**^{18a} does not show this interaction in the inserted species, and steric effects seem to dominate.

The insertion reactions studied with the dinuclear compounds type 4 agree, again, with the existence of this aggregate intermediate species. If the reaction takes place *via* a species where the chlorine bridge has been cleaved to introduce an alkyne in the coordination

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 J. Am. Chem. Soc. 1970, 92, 2953.

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sphere (to produce a species similar to 2_t), no important differences should be detected in the first-order rate constants when compared with those for the insertion of 1a or 1'a. Data in Table 5 show the contrary, indicating that in this case the intermediate species of the insertion reaction of compound 4 with alkyne PhCCCOOEt (Y) should be rather different from a compound of type 2_t . A dinuclear species having a pentacoordinate structure fits perfectly the experimental data. Furthermore, the final reaction mixture, as monitored by ³¹P NMR, showed only the presence of the dinuclear inserted species, even in the presence of large amounts of free alkyne, somehow indicating that the dinuclear structure is maintained during the insertion process. Nevertheless, the fact that no activation parameters have been determined for these reactions (due to the inherent starting material instability) does not allow us to rule out that some other reaction mechanism, such as that observed for dimeric palladacycles,^{6c} could be operating for the processes.

Experimental Section

Compounds. All manipulations of the organonickel compounds were carried out using Schlenk techniques under a dinitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and toluene were distilled over sodium-benzophenone under a dinitrogen atmosphere before use. Phosphines were obtained commercially or prepared according to established procedures.²³ [Ni(cod)₂] was prepared, with small modifications, by the method reported.²⁴

¹H NMR spectra were recorded on Varian XL 200 or Bruker WP80SY instruments. ³¹P NMR spectra at variable temperatures were obtained on a Bruker WP80SY instrument (32.38 MHz). The reference used was 85% H₃PO₄ for ³¹P spectra; all chemical shifts are reported as downfield from standards. NMR solvents used were toluene and THF, with a 5 mm coaxial insert tube containing [²H₆]acetone-P(OMe)₃. Infrared spectra were recorded on a Nicolet 520 FT-IR instrument. Elemental analyses were carried out at the Servei d'Anàlisis Elementals de la Universitat de Barcelona on an Eager 1108 microanalyzer.

trans-[NiCl(2-C₆H₄CH₂PEt₂)PBz₃] (1'a). PBz₃ (4.80 × 10^{-3} mol) and (2-ClC₆H₄CH₂)PEt₂ (4.80 × 10^{-3} mol) were added to a suspension of [Ni(cod)₂] (4.80 × 10^{-3} mol) in toluene (40 cm³) at -78 °C. The reaction mixture was warmed to room temperature and maintained for 30 min under these conditions. After the solvent was partially removed under vacuum, the yellow complex was precipitated on adding absolute ethanol (yield 1.94 g, 70%; dec temp 155 °C). Anal. Found: C, 66.1; H, 6.30. Calcd for C₃₂H₃₇ClNiP₂: C, 66.57; H, 6.45. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃-PO₄, J in Hz): 55.9, 10.8, ²J = 335.

trans-[NiCl{MeOOCC=CCOOMe(2-C₆H₄CH₂PPh₂)}-PBz₃] (3aZ). MeOOCC=CCOOMe (0.1 g, 0.7 × 10⁻³ mol) dissolved in 20 cm³ of THF was added at room temperature under nitrogen to a solution of 1a (0.35 g, 0.5 × 10⁻³ mol) and PBz₃ (0.15 g, 0.5 × 10⁻³ mol) in THF (20 cm³). After 45 min of stirring the brownish solution became red. The solvent was removed under vacuum, and after addition of methanol a yellow solid was collected. Recrystallization from methanol afforded the insertion product (yield 0.1 g, 25%). Anal. Found: C, 68.5; H, 5.4. Calcd for C₄₆H₄₃ClNiO₄P₂: C, 67.71; H, 5.32. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄, J in Hz): 34.0, 4.6, ²J = 318. *trans*-[NiCl{PhC=CCOOEt(2-C₆H₄CH₂PPh₂)}PMe₂-Ph] (3bY). PhC=CCOOEt (0.2 g, 1.12×10^{-3} mol) was added at -78 °C under nitrogen to a solution of 1b (0.58 g, 1.12×10^{-3} mol) in toluene (20 cm³). After 20 min of stirring at -78 °C the solution was warmed to room temperature. The solvent was removed under vacuum, and after addition of absolute ethanol a red solid was obtained (yield 0.5 g, 75%). Anal. Found: C, 67.2; H, 5.6; Cl, 5.0. Calcd for C₃₈H₃₇ClNiO₂P₂: C, 66.94; H, 5.47; Cl, 5.20. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄, J in Hz): 29.5, -10.5, ²J = 294.

trans-[NiCl{MeOOCC=CCOOMe(2-C₆H₄CH₂PPh₂)}-PMe₂Ph] (3bZ). MeOOCC=CCOOMe (0.13 g, 0.9 × 10⁻³ mol) was added at 0 °C under nitrogen to a solution of 1b (0.47 g, 0.9×10^{-3} mol) in THF (20 cm³). The solution became violet, and after 30 min of stirring the solvent was removed under vacuum. After addition of hexane a dark red solid was collected (yield 0.1 g, 17%). Anal. Found: C, 59.3; H, 5.3. Calcd for C₃₃H₃₃ClNiO₄P₂: C, 61.00; H, 5.12. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄, J in Hz): 33.48, -6.49, ²J = 338.

trans-[NiCl{PhC=CPh(2-C₆H₄CH₂PEt₂)}PBz₃] (3'aX). PhC=CPh (0.2 g, 1.2×10^{-3} mol) was added at room temperature under nitrogen to a solution of 1'a (0.58 g, 1×10^{-3} mol) in toluene (20 cm³). After 60 min of stirring the solvent was removed under vacuum. The solid was extracted with 2×10 cm³ of hexane. The hexane was removed under vacuum and the residue dissolved in 10 cm³ of methanol. After the solution was cooled to -20 °C for several days, a yellow solid was collected (yield 0.27 g, 35%). Anal. Found: C, 72.5; H, 6.2. Calcd for C₄₆H₄₇ClNiP₂: C, 73.08; H, 6.26. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄, J in Hz): 32.8, 5.7, ²J = 310.

trans-[NiCl{PhC=CPCOOEt(2-C₆H₄CH₂PEt₂)}PBz₃] (3'aY). PhC=CCOOEt (0.2 g, 1.2×10^{-3} mol) was added at 0 °C under nitrogen to a solution of 1'a (0.58 g, 1×10^{-3} mol) in toluene (20 cm³). The solution was warmed to room temperature, and after 2 h of stirring the solution was filtered over Celite and the solvent removed under vacuum. The solid was extracted with 2×10 cm³ of ether. The addition of hexane produced an orange solid that was collected and dried (yield 0.34 g, 45%). Anal. Found: C, 68.6; H, 6.5. Calcd for C₄₃H₄₇-ClNiO₂P₂: C, 68.68; H, 6.30. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄, J in Hz): 32.0, 4.85, ²J = 301.

trans-[NiCl{CPh=CPh(2-C₆H₄CH₂PPh₂)]₂ (5X). PhC-CPh (2 × 10⁻³ mol) was added at room temperature and under a dinitrogen atmosphere to 25 cm³ of a toluene solution of trans-[NiCl(2-C₆H₄CH₂PPh₂)]₂ (1 × 10⁻³ mol). After several minutes of stirring the orange solution became red. After the solvent was partially removed under vacuum, hexane was added and the red solid obtained was filtered (yield 0.60 g, 55%; dec temp 130 °C). Anal. Found: C, 72.0; H, 5.14. Calcd for C₅₂H₄₂Cl₂Ni₂P₂: C, 72.45; H, 4.80. ³¹P{¹H} NMR (in toluene solution, δ in ppm referenced to H₃PO₄): 30.7.

Kinetics. All UV-vis spectra were recorded on a HP8452A instrument. Solutions for the kinetic measurements were made up in degassed toluene, and careful gastight syringe and dinitrogen handling techniques were necessary in order to avoid extensive decomposition of the nickel compounds at those concentrations.

Runs with $t_{1/2} > 170$ s were recorded on a HP8452A instrument equipped with a thermostated multicell transport, and runs with $7 < t_{1/2} < 170$ s were recorded on a HP8452A instrument equipped with a High-Tech SFA-11 rapid kinetics accessory; for $t_{1/2} < 7$ s runs were recorded on a Durrum D-110 stopped-flow instrument. All kinetic runs were initially followed at the full 700–325 nm range in toluene solutions. The observed rate constants, $k_{\rm obs}$, were derived at the wavelength where the difference in absorbance between the initial and final species was large enough. Pseudo-first-order conditions were used for all runs with a nickel starting compound (1) concentration of 1×10^{-3} M. Absorbance *versus* time traces

⁽²³⁾ Kosolapoff, G. M.; Maier, L. Organic Phosphorus Compounds; Wiley: New York, 1972; Vol. 1.

⁽²⁴⁾ Guerrieri, F.; Salerno, G. J. Organomet. Chem. 1976, 114, 339.

Table 6. Crystallographic Data Collection for the trans-[NiCl{PhC=CPh(2-C₆H₄CH₂PPh₂)}PBz₃] Compound

compound				
formula	C ₅₄ H ₄₇ P ₂ ClNi			
mol wt	852.08			
cryst dimens (mm)	0.1 imes 0.1 imes 0.2			
cryst syst	monoclinic			
space group	$P2_1/c$			
a (Å)	10.755(2)			
b (Å)	26.657(4)			
c (Å)	15.897(3)			
β (deg)	97.39(2)			
Z	4			
F(000)	1784.0			
$V(m \AA^3)$	4520(2)			
$T(\mathbf{K})$	298			
$\rho (\mathrm{g} \mathrm{cm}^{-3})$	1.252			
μ (cm ⁻¹)	5.95 (Mo Ka)			
radiation (Å)	0.710 69 (Mo Ka)			
no. of data collected	13424			
collecn range (deg)	$2 \le \theta \le 30$			
scan method	$\omega/2\theta$			
no. of independent data obsd	6980			
R (obsd reflection)	0.042			
R'	0.045			

were fitted to exponential form by the Marquardt algorithm. All the k_{obs} errors were in the range of 5-15% of the actual value obtained, indicating a very good fit up to 3-4 half-lives. The k_{obs} versus [alkyne] plots were fitted by unweighted least squares. Thermal activation parameters were derived from standard Eyring plots by the same method.

Crystallographic Studies. Crystals of complex **3aX** were grown from a dichloromethane—ethanol mixture by cooling to -20 °C. A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unitcell parameters were determined from automatic centering of 25 reflections ($12 \le \theta \le 22^\circ$) and refined by the least-squares method.

Intensities were collected with graphite-monochromatized Mo K α radiation, by the $\omega/2\theta$ -scan technique. A total of 13 424 reflections were measured $(\pm h, k, l)$ in the range $2 \le \theta \le 30^\circ$, 6980 of which were assumed as observed by applying the condition $I \ge 2.5\sigma(I)$. $R_{\rm int}$ (on F) was 0.012. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentzpolarization, 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 the SHELX76 computer program.²⁵ The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = [\sigma^2(F_o) + 0.0008 \cdot (F_o)^2]^{-1}$; *f*, *f*', and *f*'' were taken from ref 26.

The positions of all H atoms were computed from a difference synthesis and refined with an overall isotropic thermal parameter. The final R factor was 0.042 (R' = 0.045) for all observed reflections. The number of refined parameters was 664, the maximum shift/esd was 0.06, and maximum and minimum peaks in the final difference synthesis were 0.3 and -0.3 Å⁻³, respectively. Crystal parameters, data collection details, and results of the refinements are summarized in Table 6.

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Supporting Information Available: Tables of observed reaction rate constants for 1a, 1b, 1'a, and 4 and of bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for 3aX (10 pages). Ordering information is given on any current masthead page.

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^{(25) (}a) Sheldrick, G. M. Acta Crystallogr., Sect. A 1990, 46, 467.
(b) SHELX, a Computer Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976.

⁽²⁶⁾ International Tables of X-ray Crystallography; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, pp 99, 100, 149.