Reactions of the Benzonickelacyclopentene Complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ with Alkynes. Synthesis of 1,2-Dihydronaphthalenes

Juan Cámpora,[1a] Amadeo Llebaría,[1b] Josep M. Moretó,[1b] Manuel L. Poveda,*[,1a] and Ernesto Carmona*[,1a]

Departamento de Química Inorgánica-Instituto de Ciencias de Materiales, Facultad de Química, Universidad de Sevilla-CSIC, 41071 Sevilla, Spain, and Departamento de Química Orgánica Biológica, CID (CSIC), 08034 Barcelona, Spain

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A variety of alkynes have been shown to react with the nickelacyclopentene complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ in a highly selective manner. The reactions likely proceed with insertion of the alkyne into the Ni–aryl bond of the metallacycle, followed by reductive elimination to give good yields of the corresponding 1,2-dihydronaphthalenes, in addition to nickel side products. Ester and alcohol functionalities are tolerated, but acetylenes that have a halogen substituent provide new organometallic compounds containing an elaborate organic ligand, potentially useful for further synthetic enterprises. The unsymmetrically substituted alkynes RC≡CR′ yield, in general, a mixture of the 1,2-dihydronaphthalene regioisomers, with the regioselectivity of the reaction being strongly influenced by the nature of the alkyne substituents. Among these, the CO_2Me group exhibits the highest selectivity, RC≡CCO_2Me alkynes giving rise exclusively to one regioisomer. Both the electronic and the steric effects of the R and R′ groups must be taken into account to explain the reactivity and regioselectivity observed.

Introduction

The insertion of an alkyne into a M–C bond is a fundamental reaction that has been assumed to be a key step in some important homogeneous catalytic transformations.[2] If the M–C bond belongs to a cyclometalated unit, the reaction leads frequently to the selective functionalization of the chelating hydrocarbon fragment and it is therefore of potential importance in organic syntheses.

For an organometallic species to be useful as a stoichiometric reagent, at least some, if not most, of the following prerequisites must be fulfilled: (i) they should be readily available and have long-term stability, the latter condition applying to the corresponding precursor in the case of *in situ* reagents; (ii) the reagent should be compatible with common organic functionalities and workup of the reaction mixture, including release of the metal-ancillary ligands moiety, should be simple, and (iii) reagents based on cheap transition metals are preferable and their chemical performance should correspond to new, competitive methodologies or else provide higher yields, and (or) selectivity, than other known reagents.

The nickelabenzocyclopentene complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$, **1**, readily available on a multigram scale, fulfills some of the above criteria, and it has been further shown[3] to cleanly react with PhC≡CPh with formation of the substituted dihydronaphthalene $CH_2CMe_2C_6H_4C(Ph)$=CPh. The chemistry of 1,2-dihydronaphthalenes has attracted some interest in recent years.[4] Since there is a dearth of preparative routes available,[4a] we have investigated the reactivity of the nickelacycle **1** toward a variety of acetylenes. The ensuing insertion, for which a high regioselectivity could be anticipated on the basis of the pioneering work of Bergman and Huggins,[5] has been found to be chemoselective; only insertion into the Ni–C(aryl) bond is observed. In this contribution we report the outcome of this work which has afforded, among other results, the synthesis of a variety of substituted 1,2-dihydronaphthalenes. Recently, we and other workers have reported the formation of different organic products in reactions involving nickel complexes and alkynes.[6]

Results

We have previously shown[3] that the cyclometalated complex **1** is an orange crystalline solid which exhibits

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(1) (a) Universidad de Sevilla-CSIC. (b) CSIC-Barcelona.

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(5) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

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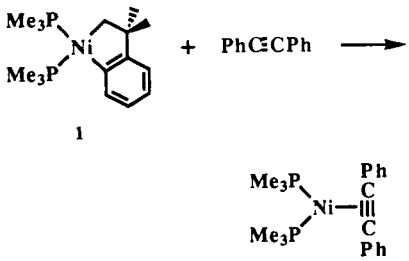
high solubility in common organic solvents and a fairly high thermal stability, no decomposition being observed when its solutions are heated at temperatures of 70–80 °C. This and the remarkable insertion chemistry it displays[3,7] make it an ideal candidate for alkyne insertions leading to the synthesis of functionalized 1,2-dihydronaphthalene derivatives.

In the aforementioned contribution,[3] it was found that treatment of 1 with 2 molar equiv of PhC≡CPh yielded a Ni(0) complex and a substituted 1,2-dihydronaphthalene, as depicted in eq 1. No intermediate products were detected, and the use of equimolar amounts of the starting complex 1 and PhC≡CPh left half of 1 unreacted.

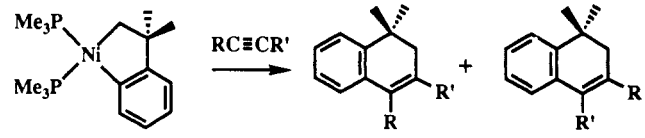


(1)

The development of a general procedure based on eq 1 for the synthesis of dihydronaphthalenes requires overcoming two important disadvantages: (i) only half of the usually expensive alkyne is synthetically useful; (ii) the resulting Ni(0)–alkyne complexes are frequently thermally unstable,[8] their decomposition making difficult the isolation of the pure dihydronaphthalenes. Both inconveniences can be avoided by trapping the leaving $Ni(PMe_3)_2$ fragment with a tertiary phosphine ligand. In the present work three tertiary phosphines, PPh_3, PBu^n_3, and PMe_3, have been employed in systematic studies to this end, the last having proved itself as the best option[9] despite well-known difficulties associated with its manipulation.[10] The advantage in the use of PMe_3 stems largely from its volatility and from the facility with which the nickel side product, $Ni(PMe_3)_4$, can be removed from the reaction mixture (see below) or recycled, if considered necessary.[11]

The optimized procedure involves addition of the neat alkyne (or a solution, in the case of solid reagents) to a cold solution of 1 in Et_2O in the presence of 2 equiv of PMe_3. The reaction can be followed by monitoring the formation of $Ni(PMe_3)_4$ by $^{31}P\{^1H\}$ NMR spectroscopy, or simply by a color change from the original orange to pale yellow. Under these conditions, most of the alkynes investigated (Table I) react fast at room temperature or below, but in some cases heating at 40 °C is required to achieve a reasonable reaction rate. When the reaction is judged complete, the Ni-containing products can be eliminated from the organic phase by washing with aqueous acid in the presence of $CuCl_2$, as an oxidizing reagent, and the crude dihydronaphthalene purified by flash chromatography or by crystallization.[12]

Table I. Synthesis of 1,2-Dihydronaphthalenes from 1 and Alkynes



1 a b

	R	R′	a:b	reacn conditions[a]	isolated yield (%)
1[b]	H	H		−15 °C	60
2	Ph	Ph		50 °C/25 min	71
3	p-C_6H_4Me	p-C_6H_4Me		40 °C/3 h	50
4	CH_2OH	CH_2OH		25 °C	55
5	CO_2Me	CO_2Me		<0 °C[c]	56
6[d]	H	Ph	1.8:1	25 °C	60
7	H	Bu^t	2.2:1	40 °C/10 h	51
8	H	CH_2CH_2OH	1:2.9	25 °C/40 min	91
9	H	CH(OH)Et	1.6:1	0 °C	73
10	H	CO_2Me	only a	−80 °C	56
11	Me	Ph	only a	40 °C/1 h	70
12	Me	CH_2OH	3:1	25 °C	63
13	Me	CO_2Me	only a	25 °C	81
14	CH_2OH	Ph	only a	25 °C/6 h	55

[a] These conditions refer to the insertion reactions when effected in the presence of 2 equiv of PMe_3. The same applies to the regioisomer ratio, **a**:**b**, although this ratio seems to be unaffected by the presence of PMe_3 since the same **a**:**b** values were observed for some individual runs carried out in the absence of phosphine. Only reaction times longer than a few minutes are quoted. All reactions investigated are quantitative by NMR. [b] Quillet, J. P.; Du Perrier, A.; Dreux, J. *Bull. Chim. Soc. Fr.* **1982**, II-161. [c] A darkening of the solution at low temperatures impedes the clear visualization of the yellow end point (see Results). At 0 °C the reaction was shown to be complete by NMR spectroscopy. [d] Jones, G. W.; Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 3906.

Table I collects the reaction conditions and the total yields of isolated products for the majority of the alkynes used in this work (some special reactions are discussed under a different heading). In most cases the reactions are quantitative, as deduced by NMR studies of the reaction mixtures, and hence the deviations of the yields of isolated products are due to nonoptimized purification and separation procedures.

All the 1,2-dihydronaphthalenes synthesized in this work have been fully characterized by IR, ^1H, and ^{13}C NMR, and mass spectroscopy. Although ^{13}C chemical shift arguments have been used as a complementary test for the proposed structure, product regiochemistry has been established mainly on the basis of ^1H NMR data, making use of the chemical shift of the olefin hydrogen atom in reactions involving terminal alkynes (at lower fields in isomer **a** than in **b**) and also of the values of the ^1H–^1H couplings between this H nucleus and the methylene ring protons.[13a] For regioisomer **b** this coupling is of about 4–5 Hz and only of 1–2 Hz for **a**. In dihydronaphthalenes derived from MeC≡CR′ alkynes, a homoallylic coupling, $^5J_{HH}$ = 1–2 Hz, between the methyl and methylene protons is observed in regioisomer **a**. To further substantiate the above characterization the stereochemistry of key com-

(7) (a) Cámpora, J.; Carmona, E.; Gutiérrez-Puebla, E.; Poveda, M. L.; Ruíz, C. *Organometallics* **1988**, *7*, 2577. (b) Cámpora, J.; Carmona, E.; Palma, P.; Poveda, M. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 180.

(8) Pörschke, K. R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch.* **1985**, *40B*, 199.

(9) In our first reported[3] experiments using PhC≡CPh, PPh_3 was successfully employed as the trapping agent. For other alkynes, however, the corresponding workup procedures are not straightforward and the use of PMe_3 as the trapping reagent is recommended.

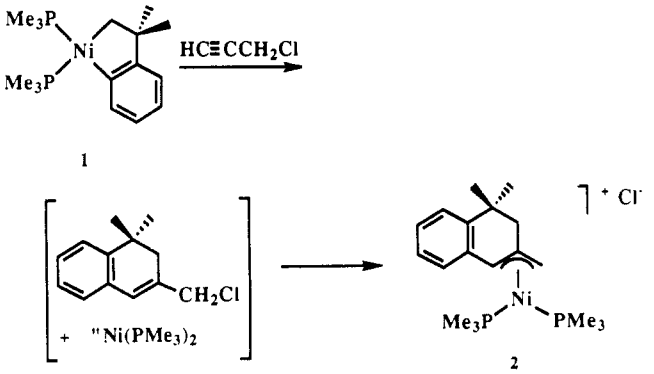
(10) (a) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149. (b) Luetkens, M. L., Jr.; Sattelberger, A. P. *Inorg. Synth.* **1990**, *28*, 305.

(11) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2515.

(12) Although nonapplicable to the compounds described herein, acid-sensitive final organic products could be separated by using CS_2 as a precipitating reagent. See: Mason, M. G.; Swepston, P. N.; Ibers, J. A. *Inorg. Chem.* **1983**, *22*, 411.

(13) (a) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tabellen zur strukturaufklärung organischer verbindungen mit spektroskopischen metoden*; Springer Verlag: New York, 1976. (b) Brieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: London, 1975; Chapter 11.

Scheme I



pound **11** was unambiguously proved by a combination of NOEDIFF and $^1H-^1H$ and $^1H-^{13}C$ 2D NMR spectroscopies at 500 MHz (Scheme II).

Some Special Cases. With halogenated alkynes, further reaction involving the halogen atom may occur. For instance, treatment of **1** with 1 equiv of propargyl chloride, $HC{\equiv}CCH_2Cl$, yields the cationic allylic complex **2** (Scheme I). It seems likely that in this case the dihydronaphthalene resulting from the insertion plus reductive elimination process, oxidatively adds to the Ni-$(PMe_3)_2$ fragment with formation of the corresponding π-allyl complex. The proposed regioselectivity is based on the absence of coupling between the C–H allylic proton and the ring methylene protons, which should be observable in the other regioisomer. In accordance with the proposed ionic formulation, **2** is only soluble in polar solvents like acetonitrile, and it is a fluxional molecule, in agreement with the behavior generally observed for this type of complex.[13b]

The reaction of **1** with an alkyne containing a halogen atom as a primary substituent, e.g. 1-bromo-2-phenylacetylene, $PhC{\equiv}CBr$, affords high yields of a neutral vinyl complex of nickel **3**, Scheme II, probably again as a consequence of the oxidative addition of the resulting bromo-substituted dihydronaphthalene to the $Ni(PMe_3)_2$ fragment. Spectroscopic data for **3** are fully consistent with the proposed formulation but do not allow us to unambiguously distinguish between the two possible regioisomers. The structural assignment for **3** has nevertheless been firmly established by characterization by NMR methods of the methylphenyl-substituted dihydronaphthalene shown in Scheme II, which forms almost quantitatively by treatment of **3** with MeLi. This dihydronaphthalene species can also be obtained by addition of $PhC{\equiv}CMe$ to solutions of **1**.

Complex **4**, related to **3**, is produced in the reaction of **1** and $CH_3CH_2CH(OH)C{\equiv}CBr$ (Scheme III). Full characterization of **4** is prevented by its low thermal stability, but *in situ* carbonylation of this species affords the butenolide[14] **5** that has been structurally characterized by spectroscopy. Salient spectroscopic features of **5** are the observation of a $^{13}C\{^1H\}$ NMR resonance at δ 173 due to the ester functionality and the appearance of a low field methyne signal at δ 81, with a characteristically large $^1J_{CH}$ coupling of 152 Hz, due to the CH carbon directly bonded to oxygen. As in previous cases, the proposed stereochemistry (around the C=C bond of the lactone ring) relies upon the observation of homoallylic coupling between the diastereotopic CH_2 ring protons and the H atom of the chiral carbon center ($^5J_{HH}$ = 1.5 Hz av). It seems likely that lactone formation proceeds by intramolecular attack of the pendant hydroxylic function at the acylic carbon, a process frequently invoked in the transition metal mediated (catalytic or stoichiometric) carbonylation of organic substrates.[15]

The facility with which **1** reacts with unactivated acetylenes can be used to trap rather unstable or elusive alkynes such as benzyne. This fleeting species has been generated in matrices at low temperatures and in the gas phase at low pressures, and it has also been stabilized by complex formation with various transition metals.[16] Its selective coupling with other unsaturated molecules, such as olefins, alkynes, and others, has been achieved in reactions involving a stable benzyne–Ni complex.[16,17] In the present work, benzyne has been used as a reactive alkyne. Its generation (for example, by reaction of *o*-$C_6H_4Br_2$ with $LiBu^n$), in the presence of **1**, induces a smooth insertion reaction which gives moderate yields of the dihydrophenanthrene **6**, as shown in Scheme IV. A somewhat similar reaction involving the insertion of free benzyne into a nickel–acetylide bond has been reported in the literature.[18]

Discussion

For some of the alkynes investigated complete regioselectivity is not observed, but the results collected in Table I allow some general trends to be recognized. For example, the formation of isomer **a** with terminal acetylenes is only achieved with complete regioselectivity for the strong electron-accepting CO_2Me substituent (entry 10), while for the other alkynes of this type (entries 6–9) a mixture of regioisomers **a** and **b** is produced, with bulkier substituents slightly favoring isomer **a**. Nonsymmetrical alkynes containing a small substituent other than hydrogen (like Me or CH_2OH) and a phenyl group (entries 11 and 14) also give regioisomer **a** exclusively, and this holds as well for $HC{\equiv}CCH_2Cl$ (*vide supra*). In the case of the bromo-substituted acetylenes, $RC{\equiv}CBr$, the final regiochemistry seems to be sensitive to the nature of the R group. Thus, for R = Ph, only a regioisomer of type **a** is formed while for R = CH(OH)Et a product derived from regiochemistry **b** is observed. However, this latter result should be treated with caution since the reaction seems to be complex and yields of isolated **5** are never superior to 50%.

An interesting feature of this transformation is that both ester and alcohol functionalities are compatible with the reaction conditions (see Table I). In the first instance, this is probably due to the reluctance of Ni(0) substrates to effect ester C–O bond cleavage,[19] while the second probably reflects the inertness of **1** and $Ni(PMe_3)_4$ toward water and other hydroxylic solvents. Finally, as far as the reactivity is concerned, it can be concluded that, in general,

(14) Barluenga, J.; Fernández, J. R.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1986**, 183. (b) Desshong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575 and references therein.

(15) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*; Plenum Press: New York, 1984; Chapter 6.

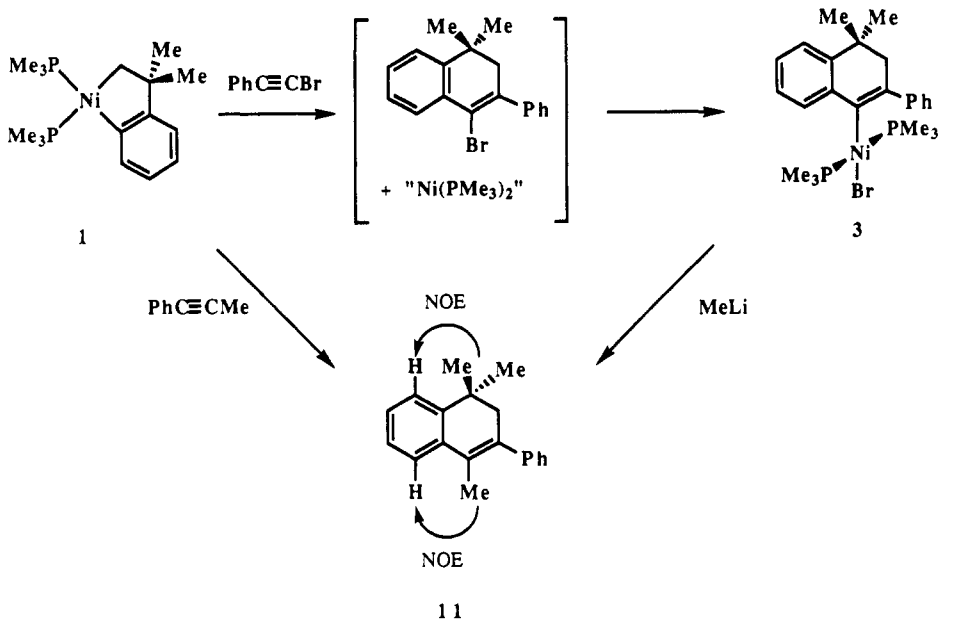
(16) (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(17) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

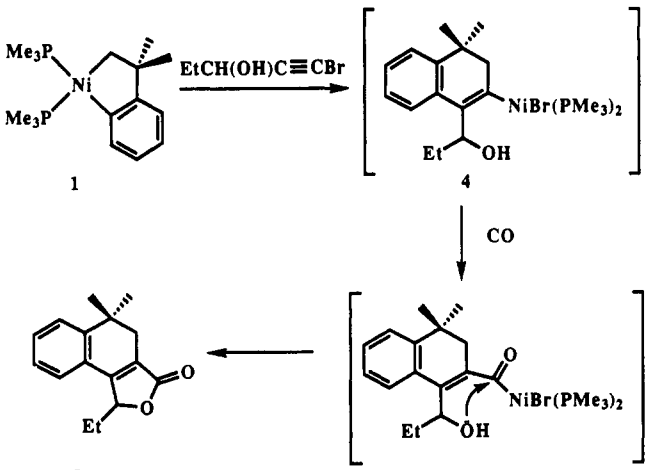
(18) Miller, R. G.; Kuhlman, D. P. *J. Organomet. Chem.* **1971**, *26*, 401.

(19) C–O bonds of acid anhydrides are cleaved. See: Yamamoto, T.; Sano, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1987**, *109*, 1092.

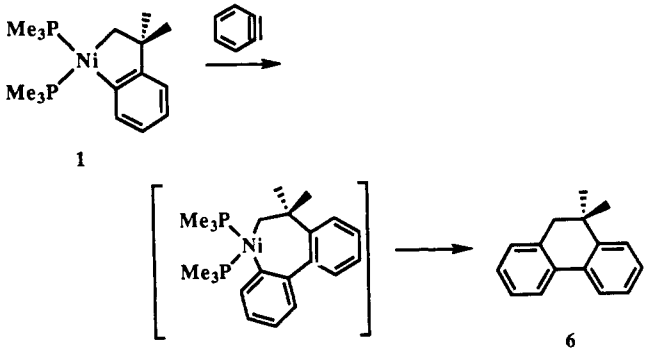
Scheme II



Scheme III



Scheme IV



bulky substituents retard the insertion reaction, while activating groups such as CO_2Me, CH_2Cl, or Br have a positive effect on reaction rates.

Previous work by Bergman and Huggins,[5] Klein,[6b] and Samsel and Norton[20] has shown that the insertion of alkynes into M–C bonds takes place *via* a preequilibrium involving substitution of a coordinated phosphine ligand (e.g. PPh_3 in Bergman's system, $Ni(CH_3)(acac)(PPh_3)$[5]) by the incoming alkyne. This was in agreement with earlier theoretical studies by Thorn and Hoffmann.[21] For the $Ni(CH_3)(acac)(PPh_3)$ complex,[5] the nature of the insertion product was determined by steric effects, with the acetylene carbon that bears the bulkier substituent becoming bonded to the metal center.

We have shown that the PMe_3 ligands in 1 are labile and exchange readily with added PMe_3. The process, believed to be associative,[3,22] is faster for the PMe_3 ligand trans to the Ni–C(alkyl) bond, as expected for the higher trans effect of the alkyl groups with respect to the aryls. As in Bergman's and Norton's systems, there is a strong inhibiting effect by added phosphine on the insertion reaction[23] and according to their results this could be ascribed to a preequilibrium of the type depicted in Scheme V. In our case, however, two different intermediate species, **A** and **B**, might be generated depending upon the chemoselectivity of the substitution reaction.

Regioisomer formation could then arise from the competitive generation of both kinds of intermediates which, coupled with the different reactivity of the two types of Ni—C bonds, would be responsible for the regioisomer ratio. This is nonetheless unlikely for the following reasons. Firstly, a number of insertion reactions of unsaturated substrates into the Ni—C bonds of 1 has been investigated[3,7] with the result that a certain reagent (e.g. CO, CO_2, CH_2O, CS_2, ...) inserts exclusively into either the Ni—alkyl or the Ni—aryl bond, but never into both. Secondly, and more importantly, as mentioned above, the PMe_3 ligand trans to the Ni—alkyl bond is more labile than the other and the substitution chemistry of this metallacycle occurs preferentially at this coordination

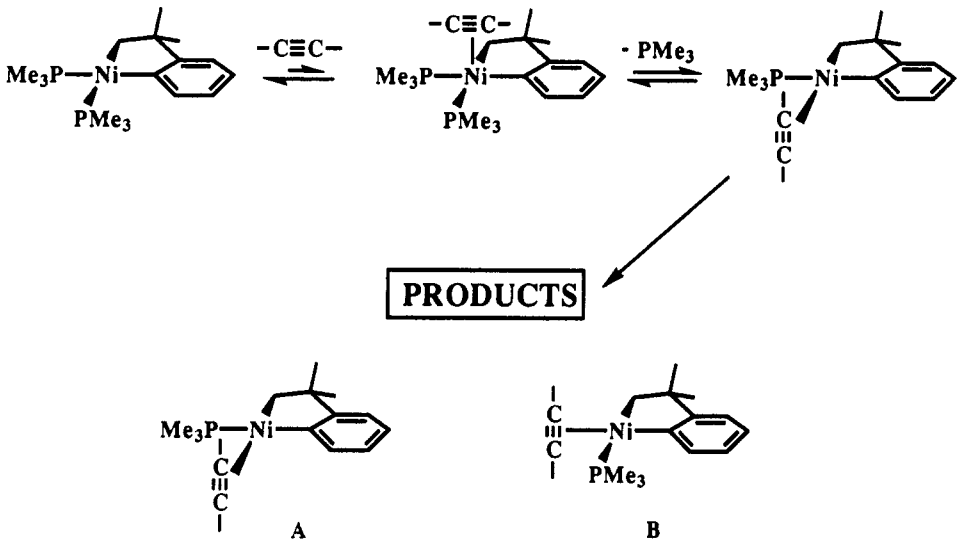
(20) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

(21) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(22) Complex 1 is a highly fluxional molecule even at −80 °C. Spectroscopic studies for this species[3] were in accord with the existence of extremely facile exchange processes with traces of free PMe_3. We have obtained further evidence for the associative nature of this reaction. Thus when the NMR spectra of 1 are recorded in the presence of an efficient PMe_3 trapping reagent such as $CpPd(\eta^3\text{-}C_3H_5)$, the exchange phenomena become slow on the NMR time scale even at ambient temperature. Unpublished observations from this laboratory.

(23) For instance, while 1 and PhC≡CPh react at −20 °C,[3] in the presence of 2 equiv of PMe_3, a reaction temperature of 50 °C is required to achieve a practical reaction rate (see Table I). No evidence for the existence of significant amounts of a tris(phosphine) species has been found.

Scheme V



A B

site.[3,24] On these grounds, it seems reasonable to propose that only intermediate **A** is formed in kinetically useful amounts in the preequilibrium step and hence that the insertion of the alkynes occurs exclusively into the Ni—C(aryl) bond of **1**.[27] Product partitioning would then be determined by the bulkiness of the alkyne substituent and also by electronic effects, that is, by the tendency of $RC^{\delta+}\equiv^{\delta-}CR'$ and $Ni^{\delta+}—C^{\delta-}$ dipoles to mutually cancel each other with strongly polarized alkynes,[28] giving rise to higher regioselectivity. A clear indication of the importance of electronic effects in our system (at variance with Bergman's studies in which the insertion reaction was controlled exclusively by steric effects) is provided by the fact that $MeO_2CC\equiv CCO_2Me$ is much more reactive than PhC≡CPh toward **1**, while in Bergman's investigations both displayed similar reactivity.[5]

In closing, it is worth mentioning that the marked thermal instability of the seven-member ring metallacycles resulting from the insertion reactions described herein, as compared to **1**, could be a consequence of the size of the nickelacycle.[19,29] However, it might simply reflect the unusually high stability of **1**, largely due to the high energy of the benzocyclobutene that would result from the reductive elimination of the organic fragment in this complex.[3,30]

Concluding Remarks

The nickelacyclopentene complex **1** has been successfully employed as a stoichiometric reagent for the facile synthesis of a series of 1,2-dihydronaphthalene derivatives *via* alkyne insertion into the Ni–C(aryl) bond. Inherently favorable circumstances make this method competitive with alternative procedures, particularly in those cases where the nature of the alkyne allows complete regioselectivity to give only one of the possible regioisomers.

The insertion of alkynes into the Ni–C(aryl) bond of **1** is followed by fast reductive elimination. If the alkyl bears a halogen substituent, the resulting halogen-containing dihydronaphthalene could oxidatively add to the generated $Ni(PMe_3)_2$ fragment, with formation of organometallic complexes of nickel containing an elaborate organic ligand. Rather than being a drawback, this opens new synthetic possibilities for the above reaction. The present synthetic methodology relies on the facility with which both the insertion reaction and the ensuing reductive elimination proceed. Both properties, characteristic of nickelacycles of this type, could prove of more importance when preparative routes to related metallacycles are developed. This is an important synthetic target for our group, which is currently being actively pursued.

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Remagen (Germany), and the Microanalytical Service of the University of Sevilla. The spectroscopic instruments used were Perkin-Elmer Model 577 and 684 for IR spectra, Varian XL-200 for NMR, and Kratos MS-80 for mass spectroscopy. Key compound **11** was further characterized by NOEDIFF and $^1H—^1H$ and $^1H—^{13}C$ 2D NMR spectroscopies using a Bruker AMX-500. The ^{13}C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to $SiMe_4$. The $^{13}C\{^1H\}$ NMR assignments were made in most cases with the help of gated decoupling and APT techniques. $^{31}P\{^1H\}$ NMR shifts are referenced to external 85% H_3PO_4. All preparations and other operations involving organometallics were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. Compounds **1**,[3] PMe_3,[10] PhC≡CBr,[31] and EtCH(OH)C≡CBr[31] were prepared according to literature methods.

Synthesis of 1,2-Dihydronaphthalenes. General Procedure. In a typical experiment, 10 mL of a stock solution of

(24) Complex **1** reacts with donor molecules like pyridine[25] or $CNBu^t$ [26] with formation of the corresponding substituted products, $(Me_3P)LNi(CH_2CMe_2\text{-}o\text{-}C_6H_4)$, in which the incoming ligand L is trans with respect to the Ni–CH_2 bond.

(25) Carmona, E.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *Polyhedron* **1989**, *8*, 1069.

(26) Cámpora, J.; Carmona, E. Unpublished results.

(27) Since Ni–alkyl bonds are also very prone to undergo insertion reactions, the chemoselectivity of **1** against alkynes may reflect the kinetic inaccessibility of intermediate **B** or alternatively a pronounced thermodynamic preference for **A** in the two possible preequilibrium steps. Therefore the reaction products may not necessarily reflect the intrinsic reactivity of the Ni–alkyl and Ni–aryl bonds of **1**.

(28) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985.

(29) Hoberg, H.; Hernández, E. *J. Chem. Soc., Chem. Commun.* **1986**, 544.

(30) cis-alkyl–aryl complexes of Ni(II) are somewhat unstable species, particularly in the presence of phosphines. See: Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466.

(31) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Oxford, U.K., 1988.

complex 1, 0.1 M in Et_2O (1 mmol), was mixed with 2 equiv of PMe_3 (2 mL of 1 M solution in Et_2O). The resulting mixture was cooled to −80 °C, and 1 equiv of the alkyne was added *via* syringe (in the case of solid acetylenes a toluene or Et_2O solution was employed and for HC≡CH the gas, taken directly from the commercial cylinder, was bubbled for a few minutes through the cold solution). The cooling bath was removed and the temperature allowed to rise to room temperature (or to the value indicated in Table I). In most cases the completion of the reaction could be inferred from a color change from orange to pale yellow but it was further checked by $^{31}P\{^1H\}$ NMR spectroscopy, at room temperature. The volatiles were removed under reduced pressure, the residue was extracted with 20 mL of Et_2O, and a deaerated solution of 0.17 g (1 mmol) of $CuCl_2 \cdot H_2O$ in 20 mL of aqueous 2 M HCl was added with stirring. After 15–30 min the now almost colorless organic phase was decanted and the aqueous layer extracted twice with 15 mL of Et_2O. The combined ether solutions were dried over Na_2CO_3 and Na_2SO_4 and filtered. The solvent was evaporated *in vacuo* and the resulting residue analyzed by NMR spectroscopy. This crude material was finally purified by crystallization in the case of solid compounds or by flash cromatography (Me_3COMe–petroleum ether eluent) for liquids or oily materials.

Analytical and Spectroscopic Data for 1,2-Dihydronaphthalenes. **$CH_2CMe_2C_6H_4CH{=}CH$**: ^1H NMR (C_6D_6) δ 1.14 (s, 6 H, CMe_2), 2.00 (dd, 2 H, $^3J_{HH_A} = 4.3$, $^4J_{HH_B} = 2.1$ Hz, CH_2), 5.73 (dt, 1 H, $^3J_{H_AH_B} = 9.6$ Hz, CH_2CH_A), 6.37 (dt, 1 H, $CH_A{=}CH_B$), 6.9–7.2 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 28.2 (CMe_2), 33.2 (CMe_2), 38.7 (CH_2), 123.7, 126.2, 126.7, 127.6, 127.9 (1:1:2:1:1 ratio, CH olefin and aromatics), 132.9, 143.9 (quaternary aromatics); MS *m/e* 158.

$CH_2CMe_2C_6H_4C(C_6H_4\text{-}p\text{-}Me){=}C(C_6H_4\text{-}p\text{-}Me)$: ^1H NMR (C_6D_6) δ 1.33 (s, 6 H, CMe_2), 1.99, 2.07 (s, 3 H and 3 H, 2 C_6H_4Me), 2.58 (s, 2 H, CH_2), 6.8–7.6 (m, 12 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 20.9, 21.0 (2 C_6H_4Me), 27.8 (CMe_2), 33.9 (CMe_2), 46.0 (CH_2), 123.2, 126.0, 128.3, 128.6, 128.9, 132.2 (CH aromatics), 134.9, 135.2, 135.3, 135.7, 136.5, 137.3, 140.8, 144.2 (quaternary olefin and aromatics); MS *m/e* 338.

$CH_2CMe_2C_6H_4C(CH_2OH){=}C(CH_2OH)$: IR (Nujol mull) 3300 (br) cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.17 (s, 6 H, CMe_2), 2.23 (s, 2 H, CMe_2CH_2), 3.10 (br, 2 H, 2 OH), 4.25, 4.55 (s, 2 H and 2 H, 2 CH_2OH), 7.1–7.6 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 27.9 (CMe_2), 33.2 (CMe_2), 42.1 (CH_2), 57.6, 62.5 (2 CH_2OH), 123.6, 124.5, 126.3, 127.5 (CH aromatics), 131.7, 133.8, 137.4, 144.4 (quaternary olefin and aromatics); MS *m/e* 218.

$CH_2CMe_2C_6H_4C(COOMe){=}C(COOMe)$: IR (Nujol mull) 1710 (s), 1730 (s) cm^{-1} (COO); ^1H NMR (C_6D_6) δ 1.03 (s, 6 H, CMe_2), 2.37 (s, 2 H, CH_2), 3.38, 3.68 (s, 3 H and 3 H, 2 COOMe), 6.9–7.5 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 27.6 (CMe_2), 33.4 (CMe_2), 37.4 (CH_2), 51.5, 51.8 (2 $COOMe$), 124.1, 126.6, 126.8, 130.5 (CH aromatics), 125.5, 129.3, 140.4, 145.4 (quaternary olefin and aromatics), 166.2, 168.3 (2 COO); MS *m/e* 274.

$CH_2CMe_2C_6H_4C(H){=}C(Ph)$: ^1H NMR (C_6D_6) δ 1.19 (s, 6 H, CMe_2), 2.42 (d, 2 H, $^4J_{HH} = 1.3$ Hz, CH_2), 6.77 (t, 1 H, $CH{=}C(Ph)$), 7.1–7.4 (m, 9 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 28.2 (CMe_2), 34.2 (CMe_2), 41.6 (CH_2), 123.6, 124.1, 125.3, 126.4, 127.3, 127.5, 127.7, 128.5 (CH olefin and aromatics), 133.8, 137.1, 141.5, 143.7 (quaternary olefin and aromatics); MS *m/e* 234.

$CH_2CMe_2C_6H_4C(Ph){=}C(H)$: ^1H NMR (C_6D_6) δ 1.22 (s, 6 H, CMe_2), 2.07 (d, 2 H, $^3J_{HH} = 4.8$ Hz, CH_2), 5.79 (t, 1 H, $C(Ph){=}CH$), 7.1–7.4 (m, 9 H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.1 (CMe_2), 33.6 (CMe_2), 38.8 (CH_2), 123.7, 125.7, 126.0, 126.3, 126.9, 127.5, 128.1, 128.7 (CH olefin and aromatics), 129.2, 130.5, 130.7, 141.0 (quaternary olefin and aromatics); MS *m/e* 234.

$CH_2CMe_2C_6H_4C(H){=}C(Bu^t)$: ^1H NMR (C_6D_6) δ 1.04 (s, 9 H, CMe_3), 1.17 (s, 6 H, CMe_2), 2.03 (d, 2 H, $^4J_{HH} = 1.3$ Hz, CH_2), 6.30 (t, 1 H, $C(Bu^t){=}CH$), 7.0–7.4 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.9 (CMe_2), 28.2 (CMe_3), 34.1 (CMe_2), 35.1 (CMe_3), 39.4 (CH_2), 118.5, 123.3, 126.1, 126.5, 126.7 (CH olefin and aromatics), 143.1, 148.0, 157.7 (quaternary olefin and aromatics); MS *m/e* 214.

$CH_2CMe_2C_6H_4C(Bu^t){=}C(H)$: ^1H NMR (C_6D_6) δ 1.16 (s, 6 H, CMe_2), 1.32 (s, 9 H, CMe_3), 1.99 (d, 2 H, $^3J_{HH} = 4.9$ Hz, CH_2), 5.84 (t, 1 H, $CH{=}C(Bu^t)$), 7.0–7.4 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.8 (CMe_3), 31.4 (CMe_2), 33.5 (CMe_2), 34.9 (CMe_3), 122.4, 124.0, 125.2, 125.4, 128.1 (CH olefin and aromatics); MS *m/e* 214.

$CH_2CMe_2C_6H_4C(H){=}C(CH_2CH_2OH)$: IR (neat film) 3350 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 1.24 (s, 6 H, CMe_2), 1.63 (br, 1 H, OH), 2.18 (d, 2 H, $^4J_{HH} = 1.3$ Hz, CMe_2CH_2), 2.42 (t, 2 H, $^3J_{HH} = 6.4$ Hz, CH_2CH_2OH), 3.78 (t, 2 H, CH_2OH), 6.31 (t, 1 H, $CH{=}C(R)$), 7.0–7.4 (aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.1 (CMe_2), 33.8 (CMe_2), 35.8 (CH_2CH_2OH), 40.4 (CMe_2CH_2), 60.0 (CH_2OH), 123.3, 123.9, 126.9, 127.3 (CH olefin and aromatics), 131.9, 133.0, 142.8 (quaternary olefin and aromatics).

$CH_2CMe_2C_6H_4C(CH_2CH_2OH){=}C(H)$: IR (neat film) 3350 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 1.24 (s, 6 H, CMe_2), 1.63 (br, 1 H, OH) 2.21 (dt, 2 H, $^3J_{HH} = 4.2$, $^5J_{HH} = 1.6$ Hz, CMe_2CH_2), 2.73 (tq, 2 H, $^3J_{HH} = 6.4$, $^4J_{HH} = {}^5J_{HH} = 1.6$ Hz, CH_2CH_2OH), 3.80 (t, 2 H, CH_2OH), 5.82 (tt, 1H, $C(R){=}CH$), 7.0–7.4 (aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.2 (CMe_2), 33.2 (CMe_2), 38.3 (CH_2CH_2OH), 42.6 (CMe_2CH_2), 61.1 (CH_2OH), 122.8, 123.8, 125.4, 125.8, 126.0 (CH olefin and aromatics), 132.7, 136.0, 144.8 (quaternary olefin and aromatics).

$CH_2CMe_2C_6H_4C(H){=}C(CH(OH)Et)$: IR (neat film) 3370 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 0.91 (t, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2CH_3), 1.17 (s, 6 H, CMe_2), 1.53 (q, 2 H, CH_2CH_3), 1.98 (br s, 1 H, OH), 2.06 (d, 2 H, $^4J_{HH} = 1.3$ Hz, CMe_2CH_2), 3.91 (t, 1 H, $^3J_{HH} = 6.4$ Hz, CH(Et)), 6.34 (br t, 1 H, $CH{=}CR$), 7.0–7.6 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 9.9 (CH_2CH_3), 27.6 (CH_2CH_3), 28.2 (CMe_2), 33.7 (CMe_2), 38.4 (CMe_2CH_2), 76.3 (CH(OH)), 122.3, 123.6, 126.2, 126.9, 127.4 (CH olefin and aromatics), 153.2, 141.4, 143.8 (quaternary olefin and aromatics).

$CH_2CMe_2C_6H_4C(CH(OH)Et){=}C(H)$: IR (neat film) 3370 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 0.95 (t, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2CH_3), 1.56 (s, 6 H, CMe_2), 1.67 (q, 2 H, CH_2CH_3), 2.03 (d, 2 H, $^3J_{HH} = 4.8$ Hz, CMe_2CH_2), 2.09 (br s, 1 H, OH), 4.50 (t, 1 H, $^3J_{HH} = 6.2$ Hz, $CH(Et)$), 5.96 (t, 1 H, $C(R){=}CH$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 10.3 (CH_2CH_3), 28.2 (CMe_2), 29.1 (CH_2CH_3), 33.4 (CMe_2), 38.2 (CMe_2CH_2), 73.0 (CH(OH)), 122.7, 123.7, 124.0, 125.9, 127.4 (CH olefin and aromatics), 132.3, 138.7, 145.2 (quaternary olefin and aromatics).

$CH_2CMe_2C_6H_4C(H){=}C(COOMe)$: IR (neat film) 1710 (s) cm^{-1} (COO); ^1H NMR (C_6D_6) δ 1.07 (s, 6 H, CMe_2), 2.52 (d, 2 H, $^4J_{HH} = 1.5$ Hz, CH_2), 3.48 (s, 3 H, COOMe), 6.9–7.2 (m, 4 H, aromatics), 7.59 (t, 1H, $CH{=}C(R)$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 28.1 (CMe_2), 33.8 (CMe_2), 37.6 (CH_2), 51.1 ($COOMe$), 123.9, 126.4, 129.1, 130.1, 136.0 (CH olefin and aromatics), 130.0, 136.0, 145.6 (quaternary olefin and aromatics), 167.2 (COO); MS *m/e* 216. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.8; H, 7.5. Found: C, 77.9; H, 7.7.

$CH_2CMe_2C_6H_4C(Me){=}C(Ph)$: ^1H NMR (C_6D_6) δ 1.21 (s, 6 H, CMe_2), 1.95 (t, 3 H, $^5J_{HH} = 1.5$ Hz, Me), 2.33 (q, 2 H, CH_2), 7.1–7.4 (m, 9 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) 15.6 (Me), 27.8 (CMe_2), 33.5 (CMe_2), 45.9 (CH_2), 123.3, 124.1 126.0, 126.4, 127.1, 128.1, 128.4 (CH aromatics), 134.7, 135.7, 143.6, 143.9 (quaternary olefin and aromatics); MS *m/e* 248.

$CH_2CMe_2C_6H_4C(Me){=}C(CH_2OH)$: IR (neat film) 3350 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 1.20 (s, 6 H, CMe_2), 1.92 (t, 3 H, $^5J_{HH} = 1.6$ Hz, Me), 2.23 (q, 2 H, CMe_2CH_2), 2.62 (br, 1 H, OH), 4.15 (s, 2 H, CH_2OH), 7.1–7.5 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 13.6 (Me), 28.2 (CMe_2), 33.2 (CMe_2), 41.2 (CMe_2CH_2), 62.5 (CH_2OH), 123.4, 124.0, 126.0, 127.2 (CH aromatics), 133.0, 134.1, 134.7,

144.4 (quaternary olefin and aromatics); MS *m/e* 202. Anal. Calcd for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 82.8; H, 9.2.

$CH_2CMe_2C_6H_4C(CH_2OH)=C(Me)$: IR (neat film) 3350 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 1.20 (s, 6 H, CMe_2), 1.74 (s, 3 H, Me), 1.89 (s, 2 H, CMe_2CH_2), 2.62 (br, 1 H, OH), 4.49 (s, 2 H, CH_2OH), 7.1–7.5 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 20.0 (Me), 27.9 (CMe_2), 45.9 (CMe_2CH_2), 58.2 (CH_2OH), 126.3, 126.6, 126.7, 127.3 (CH aromatics), 129.2, 133.0, 134.0, 143.4 (quaternary olefin and aromatics); MS *m/e* 202.

$CH_2CMe_2C_6H_4C(Me)=C(COOMe)$: IR (neat film) 1710 (s) cm^{-1} (COO); ^1H NMR (C_6D_6) δ 1.12 (s, 6 H, CMe_2), 2.45 (t, 3 H, $^5J_{HH}$ = 1.7 Hz, Me), 2.48 (q, 2 H, CH_2), 3.46 (s, 3 H, COOMe), 7.0–7.4 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 16.1 (Me), 27.6 (CMe_2), 33.0 (CMe_2), 39.7 (CH_2), 50.7 (COO*Me*), 123.5, 125.6, 126.1, 129.0 (CH aromatics), 124.8, 134.8, 140.5, 145.6 (quaternary olefin and aromatics), 168.6 (COO); MS *m/e* 230.

$CH_2CMe_2C_6H_4C(CH_2OH)=C(Ph)$: IR (Nujol mull) 3380 (br) cm^{-1} (OH); ^1H NMR (C_6D_6) δ 1.21 (s, 6 H, CMe_2), 2.35 (s, 2 H, CMe_2CH_2), 3.34 br t, 1 H, OH), 4.50 (d, 2 H, $^3J_{HH}$ = 4.3 Hz, CH_2OH), 7.0–8.0 (m, 9 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 27.9 (CMe_2), 33.6 (CMe_2), 45.9 ($CMeCH_2$), 59.5 (CH_2OH), 123.5, 125.6, 126.4, 126.9, 127.4, 128.3, 128.5 (CH aromatics), 131.4, 134.2, 138.3, 142.6, 144.3 (quaternary olefin and aromatics).

Reaction of 1 with $HC\equiv CCH_2Cl$. To a cold (−40 °C) stirred solution of 1 (0.43 g, 1 mmol) in Et_2O (30 mL) was added using a microsyringe 75 μL of the title alkyne. The cooling bath was removed from the dark reaction mixture, and after warming to room temperature, the volatiles were evaporated under reduced pressure. The residue was extracted with Et_2O (60 mL) and filtered. Concentration and cooling to −30 °C furnished complex **2** as a crystalline material in 75% yield. Analytical and spectroscopic data: ^1H NMR (CD_3CN) δ 1.27 (br s, 18 H, 2 PMe_3), 1.50 (br s, 6 H, CMe_2), 2.43, 3.05 (br s, 1 H and 1 H, CH_2), 4.58 (s, 1 H, CH), 7.1–7.5 (m, 4 H, aromatics); ^1H NMR (CD_3CN, −35 °C) δ 1.0–1.8 (br s, 2 PMe_3 and CMe_2), 2.07, 2.63 (br d, 1 H and 1 H, $^2J_{HH}$ = 15.6 Hz, CH_2), 4.44 (s, 1 H, CH), 7.1–7.5 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 16.3 (br s, PMe_3) 30.0 (br s, CMe_2), 35.1 (s, CMe_2), 44.6 (s, CMe_2CH_2), 56.1 (br s, Ni—CH_2), 77.7 (s, Ni—CH), 120.7 (s, Ni—C_q), 125.8, 127.4, 127.9, 130.0 (CH aromatics), 136.2, 144.0 (quaternary aromatics); $^{31}P\{^1H\}$ (CD_3CN) δ −9.0 (br s). Anal. Calcd for $C_{19}H_{33}P_2ClNi$: C, 54.6; H, 7.9. Found: C, 54.2; H, 7.9.

Reaction of 1 with PhC≡CBr. Freshly prepared PhC≡CBr (129 μL, 1 mmol) was added to a cold (−60 °C), stirred solution of 1 (0.34 g, 1 mmol) in THF (30 mL). After a few minutes of stirring the formation of a yellow precipitate was noted. The temperature was slowly raised to 20 °C and the reaction mixture cooled again to −60 °C. Complex **3** was filtered, washed twice with petroleum ether and dried in vacuo. Yield: 95%. The analytical sample was recrystallized from acetone–CH_2Cl_2. Analytical and spectroscopic data: ^1H NMR (CD_2Cl_2) δ 1.26 (pseudotriplet, 18 H, $J_{HP_{app}}$ = 3.7 Hz, 2 PMe_3), 1.37 (s, 6 H, CMe_2), 3.04 (t, 2 H, $^5J_{HP}$ = 2.5 Hz, CH_2), 6.7–7.7 (m, 9 H, aromatics); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 14.3 (pseudotriplet, $J_{CP_{app}}$ = 14 Hz, 2 PMe_3), 29.8 (s, CMe_2), 41.0 (s, CMe_2), 54.3 (s, CH_2), 121.8, 122.3, 125.0, 125.3, 125.4, 127.7, 127.8 (1:1:1:1:1:2:2 ratio, CH aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −11.3 (s). Anal. Calcd for $C_{24}H_{35}P_2BrNi$: C, 55.0; H, 6.7. Found: C, 55.2; H, 7.4.

For further structural characterization, complex **3** was reacted with MeLi at −60 °C in THF. The resulting yellow solution was heated for 2–3 h at 60 °C and the very dark reaction mixture treated with $CuCl_2$–HCl as described above. $CH_2CMe_2C_6H_4C(Me)=C(Ph)$ was isolated in almost quantitative yield.

Synthesis of the Butenolide 5. To a solution of complex **1** (0.34 g, 1 mmol) in 40 mL of Et_2O was added, at −40 °C, 128 μL (1 mmol) of EtCH(OH)C≡CBr. The cooling bath was removed, and when the resulting mixture reached room temperature, it was treated with carbon monoxide for 4–5 min. After filtration and evaporation to dryness the residue obtained was extracted with Et_2O (40 mL) and stirred with 20 mL of deaerated aqueous 2 M HCl. The organic phase was decanted and the aqueous layer washed with 3 × 10 mL of Et_2O. The combined Et_2O solutions were taken to dryness, and the residue was purified by flash chromatography using Me_3COMe–petroleum ether (1:5) as eluent. A 40% yield of colorless crystals, mp 85–86 °C, was obtained. IR (Nujol mull): 1740 (s) cm^{-1} (COO). ^1H NMR ($CDCl_3$): δ 0.93 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3), 1.12, 1.44 (s, 3 H and 3 H, diastereotopic CMe_2), 1.77 (1:4:7:8:7:4:1 multiplet, 1 H, $^2J_{HH}$ = 14.3, $^3J_{HH}$ = 7.3 Hz, $CH_AH_BCH_3$), 2.20 (ddq, 1 H, $^3J_{HH}$ = 3.2 Hz, $CH_AH_BCH_3$), 2.44 (strongly coupled AB quartet further split by homoallylic coupling to the CH proton, 2 H, $^2J_{H_AH_B}$ = 17.4, $^5J_{H_AH}$ = 2, $^5J_{H_BH}$ = 0.9 Hz, CMe_2CH_2), 5.38 (m, 1 H, CH), 7.1–7.5 (m, 4 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.4 (CH_2CH_3), 26.3 (CH_2CH_3), 28.0, 29.8 (diastereotopics CMe_2), 33.2 (CMe_2CH_2), 35.0 (CMe_2), 81.0 (CH, $^1J_{CH}$ = 152 Hz), 124.4, 125.2, 126.5, 131.3 (CH aromatics), 143.8, 146.6, 157.5 (quaternary olefin and aromatics), 173.2 (COO). MS: *m/e* 242.

Reaction of 1 with Benzyne. To a cold (−100 °C), stirred solution of 1 (0.34 g, 1 mmol) in Et_2O (40 mL) were successively added *o*-$C_6H_4Br_2$ (1.27 μL, 1 mmol) and $LiBu^n$ (0.63 mL of a 1.6 M solution in hexane). After a few minutes of stirring at −80 °C the temperature was slowly raised to 0 °C and the resulting yellow solution allowed to decompose at room temperature (15 min). The black mixture was taken to dryness and the residue extracted with Et_2O. After filtration, the solution was treated as above with a $CuCl_2$–HCl–H_2O mixture. Workup of the organic layer furnished a colorless solid that was purified by flash chromatography and recrystallized from MeOH. Yield: 35%. ^1H NMR ($CDCl_3$): δ 1.31 (s, 6 H, CMe_2), 2.83 (s, 2 H, CH_2), 7.3–7.9 (m, 8 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.9 (CMe_2), 34.1 (CMe_2), 44.0 (CH_2), 123.5, 124.1, 124.2, 126.5, 126.8, 127.4, 127.9, 128.6 (CH aromatics), 133,2 134.3, 136.0, 145.8 (quaternary aromatics). MS: *m/e* 208.

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