Mechanism, Regiochemistry, and Stereochemistry of the Insertion Reaction of Alkynes with Methyl(2,4-pentanedionato)(triphenylphosphine)nickel. A Cis Insertion That Leads to Trans Kinetic Products

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Abstract: This study reports the rapid reaction under mild conditions of internal and terminal alkynes with methyl(2,4-pentanedionato)(triphenylphosphine)nickel (**1**) in aromatic and ethereal solvents. In all cases vinylnickel products (**2**) are formed by insertion of the alkyne into the nickel-methyl bond. The regiochemistry is unusual; unsymmetrical alkynes give selectively the one regioisomer with the sterically largest substituent next to the nickel atom. So that the stereochemistry of the initial insertion could be investigated, an X-ray diffraction study of the reaction of **1** and diphenylacetylene was carried out. This showed that the vinylnickel complex formed by overall trans insertion was the product of the reaction. Furthermore, subsequent slow isomerization of this complex, to a mixture of it and the corresponding cis isomer, demonstrated that this trans addition product is the kinetic product of the reaction. In studies with other alkynes, the product of trans addition was not always exclusively (or even predominantly) formed, but the ratio of the stereoisomers formed kinetically was substantially different from the thermodynamic ratio. Isotope labeling, added phosphine, and other experiments have allowed us to conclude that the mechanism of this reaction does involve cis addition. However, a coordinatively unsaturated vinylnickel intermediate is initially formed, which can undergo rapid, phosphine-catalyzed cis-trans isomerization in competition with its conversion to the isolable phosphine-substituted products.

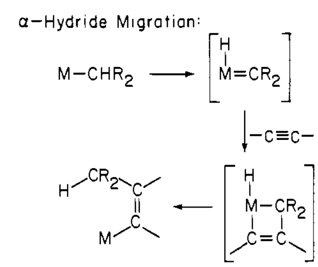
The insertion of an unsaturated organic molecule into a transition-metal–carbon or –hydrogen bond is one of the most general reactions in organotransition-metal chemistry. However, in contrast to the large number of well-studied cases of M–H additions to alkenes and alkynes and M–R (metal–alkyl)/CO insertions, direct studies of the 1,2-addition of transition-metal alkyl complexes to alkenes or alkynes have been relatively rare.[1,3,7,8] The few stoichiometric insertion reactions of transition-metal alkyl complexes that have been observed are usually specific to highly "activated" alkenes or alkynes such as tetrafluoroethylene, hexafluoro-2-butyne, or diphenylacetylene,[1-3] with some exceptions.[7,8]

Despite the common belief that the mechanism of these reactions involves concerted cis addition, a number of reactions of metal alkyl and hydride complexes with alkynes have been observed to give either stereorandom or exclusively trans products, sometimes under kinetic conditions.[1-6] Some complexes have even been observed to give exclusively cis insertion for one alkyne but trans insertion for others.[4,5]

Finding an explanation for these highly variable results has presented considerable difficulty, and this has led in turn to suggestions of alternative mechanisms for this process. One such suggestion would account for trans addition products with a concerted trans addition pathway.[5] Others have proposed that trans insertion occurs by backside attack upon coordinated alkyne.[3b] In their discussion of possible mechanisms for Ziegler–Natta polymerization of alkenes, Rooney, Green, and co-workers[9] proposed an alternative involving an initial α-hydride migration, forming a metal alkylidene hydride intermediate. This intermediate can then add alkene to the alkylidene ligand to form a metallocyclobutane complex. The reverse of the original α-hydride migration step specifically to the original carbon atom then leads to overall cis addition by a stepwise mechanism. Application of this type of mechanism to "insertion" of alkynes is illustrated in Scheme I. The significance of these proposals is not that present evidence is sufficient to establish their viability but rather that existing studies cannot rule out these possibilities.

In the present study[10] we have observed the facile reaction at room temperature of a variety of alkynes with methyl(2,4-pentanedionato)(triphenylphosphine)nickel (**1**) to give vinylnickel complexes (the product of 1,2-addition) in nearly quantitative yield.

Scheme I



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(3) (a) Michman, M.; Weksler-Nussbaum, S. *J. Chem. Soc., Perkin Trans. 2* **1978**, 872. (b) Eisch, J. J.; Manfre, R. J.; Konar, D. H. *J. Organomet. Chem.* **1978**, *159*, C13. (c) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624.
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The mechanism of this reaction has significant bearing on both the question of cis vs. trans addition and Green's α-hydride migration pathway. In particular this reaction was observed to give both cis and trans addition products under kinetically controlled conditions; for some alkynes the trans addition product was found to be predominant. Nevertheless we have obtained evidence that this reaction involves initial cis addition, giving an intermediate which forms (*E*)- and (*Z*)-vinylnickel products by kinetically controlled pathways.[10]

Results and Discussion

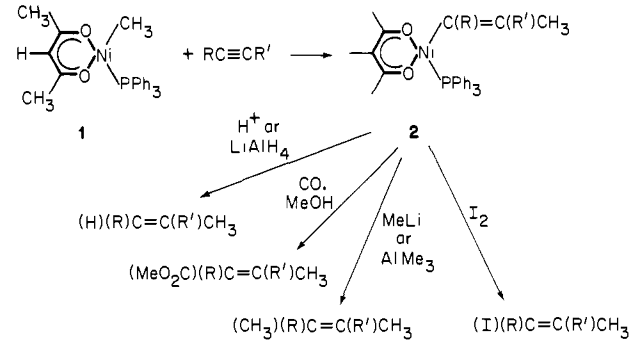
A. Synthesis and Properties of $Ni(acac)(PPh_3)CH_3$. In 1973 Yamamoto and co-workers reported the synthesis and characterization of $Ni(acac)(PPh_3)CH_2CH_3$ and $Ni(acac)(PPh_3)_2CH_3$ (acac = 2,4-pentanedionato).[11] The square-planar geometry of the ethyl complex was firmly established in a subsequent X-ray crystal structure analysis by Cotton and co-workers.[12] The ^1H, ^{13}C, and ^{31}P NMR spectra of these complexes were used to establish that the phosphine ligand is very labile at room temperature (vide infra) and that both acac exchange and β-hydride elimination processes are quite slow. These complexes have been observed to insert carbon monoxide at low temperature to give acyl derivatives which decompose by disproportionation upon warming.[13] In addition, the synthesis and characterization of Ni(acac)-$(PPh_3)C_6H_5$ and its reaction with olefins and alkyl halides has been reported.[8]

$Ni(acac)(PPh_3)CH_3$ (**1**) was prepared by the method of Cotton[12] for the corresponding ethyl complex from $Ni(acac)_2$, PPh_3, and $Al(CH_3)_2OCH_3$. The crude reaction product contains considerable excess PPh_3 which may be removed by repeated recrystallization from toluene–hexane or toluene–acetonitrile mixtures. Analytically pure **1** crystallizes as yellow-brown needles. ^1H NMR (C_6D_6): δ 0.07 (s, 3 H, Ni CH_3), 1.40, 1.90 (s, 3 H each, acac CH_3's), 5.28 (s, 1 H, acac H), 6.9–7.1, 7.6–8.0 (complex, 15 H, Ph). Complex **1** is stable as a solid, but solutions decompose rapidly upon exposure to air. It is soluble in aromatic and ethereal solvents and insoluble in hydrocarbons.

By elemental and spectral analysis **1** is clearly a monophosphine complex in the solid state and in solution. Observation of two distinct singlets in the ^1H NMR for the methyl absorptions of the acac ligand indicates a rigid square-planar geometry. The absence of splitting of the nickel methyl resonance at room temperature can be explained by the rapid exchange of phosphine on the NMR time scale. Using the temperature dependence of the ^{31}P NMR spectrum, Yamamoto was able to determine that the rate constant for phosphine exchange is 1.6×10^2 s^{-1} for Ni(acac)(PPh_3)-CH_2CH_3 and 2.8×10^3 s^{-1} for $Ni(acac)(PPh_3)_2CH_3$ in toluene. In a similar manner acac exchange was determined to be much slower; a rate constant of 1.1×10^1 s^{-1} was measured for Ni-(acac)$(PPh_3)CH_2CH_3$ at 40 °C in toluene.[11]

In contrast to the reported isolation by Yamamoto and co-workers of the bis(phosphine) complex $Ni(acac)(PPh_3)_2CH_3$,[11] we were unable to detect this species in solutions of **1** and added phosphine. Likewise we were unable to isolate a bis(phosphine) complex, even when **1** was recrystallized from solutions saturated in PPh_3. The room-temperature ^1H NMR spectra of **1** with and without added PPh_3 are completely superimposable, except for some broadening of the acac methyl resonances.[14a] Cooling a toluene-d_8 solution of **1** results in a downfield shift of the nickel methyl resonance; below −75 °C this resonance splits into a broad doublet, $J = 5$ Hz, at δ 0.30. In the presence of added PPh_3, the nickel methyl resonance shifts in a similar manner. However no coupling to phosphorous is observed at −75 °C.

Scheme II



The ^{31}P NMR spectra of **1** are much more informative. The spectrum of **1** in toluene-d_8 contains one singlet at 42.5 ppm downfield from external free PPh_3. Upon cooling of the solution to −90 °C, this signal remains sharp, shifting slightly to 43.8 ppm downfield, and no coalescence or broadening was observed at intermediate temperatures. Addition of PPh_3 to these solutions, however, results in drastic changes in these spectra. The ^{31}P NMR spectrum of solutions of **1** and 1 equiv of added PPh_3 exists as a very broad singlet centered at 24 ppm downfield at room temperature. Upon being cooled, the spectrum virtually disappears until temperatures below −60 °C are reached. At −90 °C two sharp singlets at 43 and −3.8 ppm are observed in roughly equal intensity.[14b] In the presence of only 0.5 equiv of added PPh_3 analogous behavior is observed. At room temperature a broad singlet at 28 ppm downfield is observed; upon cooling of the solution to −90 °C, two absorptions appear at 43 and −3.8 ppm in a ratio of 2:1. These spectra can be explained by the existence of a very rapid exchange between free and bound PPh_3 which becomes slower than the NMR time scale only below about −75 °C. Furthermore the integrated intensities of the absorptions for bound and free PPh_3 at −90 °C and the position of the averaged signal at room temperature indicate that added PPh_3 is largely dissociated both at room temperature and below.

These observations lead to the conclusion that solutions of **1** and added PPh_3 do not contain any observable concentration of the bis(phosphine) complex $Ni(acac)(PPh_3)_2CH_3$. The possibility that $Ni(acac)(PPh_3)_2CH_3$ is formed and paramagnetic is inconsistent with the observation that the UV–vis spectrum of **1** (benzene, 425 nm max) is unaffected by addition of excess PPh_3. This behavior is entirely analogous to the observations by both Yamamoto and Cotton on $Ni(acac)(PPh_3)CH_2CH_3$,[11,12] which does not form a bis(phosphine) complex. It is, however, inconsistent with the reported preparation of $Ni(acac)(PPh_3)_2CH_3$ and its properties.[11] We do not have a good explanation for this discrepancy.[15]

The analogues of **1**, $Ni(acac)(PPh_3)CD_3$ (**1**-d_3), Ni(acac)-$(PPh_3)C_6H_5$ (**5**),[8] and $Ni(acac)(P(c\text{-}Hx)_3)CH_3$ (**6**),[16] were prepared from the appropriate aluminum reagents. Both **5** and **6**

(8) Maruyama, K.; Ito, T.; Yamamoto, A. *J. Organomet. Chem.* **1978**, *155*, 359; *Ibid.* **1975**, *90*, C28.

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(10) This work has been reported in part in a preliminary communication: Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410. In order to minimize confusion, we have used *E*/*Z* nomenclature when referring to stereochemistry of compounds, and cis/trans nomenclature for referring to the stereochemistry of addition processes (i.e., cis addition can in principle give either and *E* or *Z* product, depending upon the substituents involved). cf. IUPAC Commission on Nomenclature of Organic Chemistry: *Pure Appl. Chem.*, **1976**, *45*, 11.

(11) Yamamoto, T.; Saruyama, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 589; *J. Am. Chem. Soc.* **1973**, *95*, 5073.

(12) Cotton, F. A.; Frenz, B. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 4820.

(13) Saruyama, T.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 546.

(14) (a) This broadening can be explained by an associative phosphine-catalyzed exchange of the acac CH_3's. See ref 11, 12, and 32. (b) The free PPh_3 resonance is not at 0 ppm at −90 °C because the ^{31}P chemical shift of PPh_3 is temperature dependent, see: Dickert, F. L.; Hellmann, S. W. *Anal. Chem.* **1980**, *52*, 996.

(15) The ^{31}P NMR observations of Yamamoto and co-workers (ref 11) might be accounted for if the compound they assign as $Ni(acac)(PPh_3)_2CH_3$ is really **1** with about 10% excess PPh_3. This will give a singlet at 47 ppm at −80 °C, and a broad averaged signal at about 40 ppm at room temperature as observed. However also observable should be a small singlet at 0 ppm at −80 °C, which they do not report.

(16) Jolly, P. W.; Jonas, K.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1971**, *33*, 109.

have been reported previously. These complexes all have similar properties, except that in the ^{1}H NMR spectrum of **6** in benzene-d_6 the nickel methyl resonance (δ -0.18) is a doublet due the coupling to phosphorous (J_{PH} = 5 Hz), indicating that the P(c-Hx)$_3$ ligand in **6** is not labile on the NMR time scale.

B. The Reaction of 1 with Alkynes. Stoichiometry and Kinetics. Complex **1** reacts rapidly at room temperature with equimolar amounts of a number of terminal and internal alkynes to give nearly quantitative NMR yields of vinylnickel complexes formed by the 1,2-addition of the metal carbon bond to the alkyne (Scheme II). These alkynes include diphenylacetylene, phenyl-1-propyne, phenylacetylene, dimethylacetylene dicarboxylate, 3,3-dimethyl-1-butyne, and 4,4-dimethyl-2-pentyne. Internal alkynes such as 2-butyne and 3-hexyne also react with **1**; in these cases, however, more than 1 equiv of alkyne is consumed and mixtures of products result.[17] Only 1-pentyne and acetylene itself failed to give tractable products.[18] These vinylnickel complexes were treated (without isolation, except in the case of the vinylnickel complex formed from diphenylacetylene; vide infra) with either $LiAlH_4$ or acid to give mixtures of *E* and *Z* alkenes in good yield (Scheme II). In this manner it was possible to confirm the gross structure of the organic ligand. Similarly Ni(acac)(P(c-Hx)$_3$)CH_3 (**6**) reacts with alkynes but much more sluggishly; for example, reaction of **6** with an equimolar amount of PhC≡CCH_3, both 0.1 M in benzene, has a half-life of about 10 h at 40 °C.

The reaction of **1** with alkynes follows bimolecular kinetics (as measured by ^{1}H NMR), first order in both **1** and alkyne. Comparable rates are observed in THF and benzene solvent. Qualitatively the relative rates of reaction follow the order: PhC≡CPh ≃ PhC≡CH ≃ $MeO_2CC≡CCO_2Me$ ≃ PhC≡CCH_3 ≫ $Me_3CC≡CH$ ≃ $Me_3CC≡CCH_3$ ≫ $CH_3C≡CCH_3$ ≃ $CH_3CH_2C≡CCH_2CH_3$. This order follows a trend of increasing reactivity with increasing ability of the alkyne substituents to support *p* back-bonding in a metal–alkyne π complex. In addition terminal alkynes appear to react somewhat faster than their methyl-substituted analogues, suggesting some steric control of alkyne reactivity as well.

Complex **1** does not react with alkenes at room temperature. With prolonged heating (56 °C) minimal conversions have been observed for a few highly activated alkenes (e.g., dimethyl maleate). Other alkenes either do not react or polymerize without consumption of the nickel complex. This is in contrast to the facile reaction of Ni(acac)(PPh$_3$)C_6H_5 (**5**) with alkenes reported by Yamamoto and co-workers.[8]

A significant secondary deuterium isotope effect is observed in a comparison of the reactivity of **1** and **1**-d_3. Diphenylacetylene was allowed to react with an excess of a mixture of **1** and **1**-d_3 at room temperature. Protonation of the resulting product gave a mixture of (*E*)- and (*Z*)-1,2-diphenylpropenes-d_0 and -d_3. After purification by preparative gas chromatography, analysis of these alkenes by 180-MHz ^{1}H NMR and mass spectroscopy determined that $k(\mathbf{1})/k(\mathbf{1}\text{-}d_3)$ = 1.24 (±0.05). This corresponds to an isotope effect of 1.07/deuterium.

The reaction of **1** with alkynes is strongly inhibited by added phosphine (Table V). In the presence of excess PPh$_3$, the second-order rate constant for the reaction of **1** with diphenylacetylene at 40 °C exhibits a linear dependence on 1/[PPh$_3$]. Two mechanisms which account for phosphine inhibition are illustrated in Scheme III. The crucial distinction is that in mechanism A phosphine inhibition can occur only if significant concentrations of Ni(acac)(PPh$_3$)$_2CH_3$ build up under the reaction conditions, whereas in mechanism B a preequilibrium involving loss of phosphine accounts for the observed inhibition. Because solutions of **1** and added PPh$_3$ contain no detectable concentrations of this bis(phosphine) complex (vide supra), we conclude that the initial step in this reaction is the reversible substitution at nickel of phosphine by alkyne (mechanism B).

(17) In the reaction of **1** with 2 equiv of 2-butyne, after protonation, GC analysis identified three longer retention time products in ca. 10% yield each. These products were not identified.

(18) In the reactions of **1** with acetylene and 1-pentyne, polymerization of the alkyne appeared to take place.

Scheme III

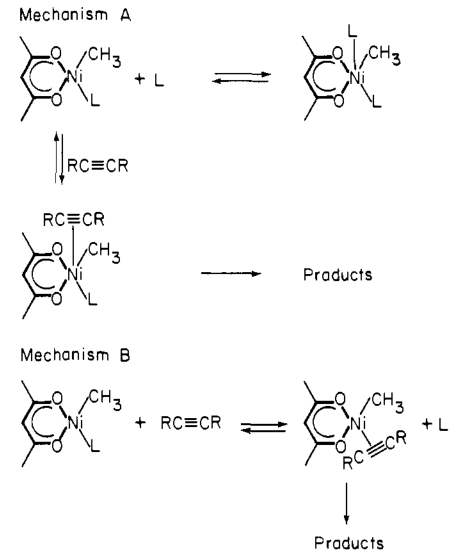


Table I. Products Formed on Reaction of Vinylnickel Complexes with Acid and $LiAlH_4$

$$\text{Ni(acac)(PPh}_3)\text{CH}_3 + \text{alkyne} \xrightarrow[\text{room temperature}]{\text{THF}} \xrightarrow{\text{reagent}} \text{alkenes}$$

alkyne	alkenes	reagent	% yield[c]
PhC≡CPh	(*E*)-, (*Z*)-Ph(H)C=C(CH_3)Ph	TsOH[a]	100
PhC≡CPh	(*E*)-, (*Z*)-Ph(H)C=C(CH_3)Ph	$LiAlH_4$	79
PhC≡CCH_3	Ph(H)C=C(CH_3)$_2$	$LiAlH_4$	78
PhC≡CH	(*E*)-, (*Z*)-Ph(H)C=C(H)CH_3	TsOH	68
t-BuC≡CH	(*E*)-, *Z*-(*t*-Bu)(H)C=C(H)CH_3	$LiAlH_4$	
$CH_3C≡CCH_3$	CH_3(H)C=C(CH_3)$_2$	TsOH	60[b]
EtC≡CEt	(*E*)-, (*Z*)-(Et)(H)C=C(CH_3)Et	$LiAlH_4$	47
t-BuC≡CCH_3	*t*-Bu(H)C=C(CH_3)$_2$	TsOH	

[a] TsOH = *p*-toluenesulfonic acid. [b] A twofold excess of 2-butyne was employed. GC of the organic products revealed three longer retention time products in ca. 10% yield each; these products were not identified. [c] All yields were calculated by GC.

In a competition experiment, a mixture of PhC≡CPh and PhC≡CCH_3 was allowed to react with a deficiency of **1** (L = PPh$_3$), yielding a mixture of vinylnickel complexes corresponding to a ratio k(PhC≡CPh)/k(PhC≡CCH_3) = 1.4 (±0.1). In a parallel experiment reaction of **6** (L = P(c-Hx)$_3$) with a mixture of PhC≡CPh and PhC≡CCH_3 gave a ratio k(PhC≡CPh)/k(PhC≡CCH_3) = 1.2 (±0.1). This result, that the reactivity ratio depends upon the nature of the phosphine, suggests that the substitution of phosphine by alkyne proceeds by an associative mechanism. A dissociative mechanism would have predicted a constant ratio independent of the phosphine present or the concentration of the dissociated nickel species. Consistent with this conclusion is the observed broadening of the acac CH_3 resonances in the ^{1}H NMR spectrum of **1** upon addition of excess phosphine, which can be explained by an associative phosphine-catalyzed acac exchange process.[14]

Taken together, these observations suggest that the square-planar π complex Ni(acac)(RC≡CR)CH_3 is most likely the intermediate which precedes the insertion step. The absence of phosphine in this intermediate will be significant in our later discussion of the mechanism of this reaction. This conclusion, that the alkyne must enter a square-planar coordination site prior to insertion, has precedent in the reaction of the square-planar complexes Pt(L)$_2$(X)(vinyl) with $CF_3C≡CCF_3$; insertion occurs only if X is an easily displaced ligand such as acetone but not at all for nonlabile ligands such as chloride.[19]

(19) Clark, H. C.; Milne, C. R. C.; Wong, C. S. *J. Organomet. Chem.* **1977**, *136*, 265.

Table II. Reactions of the Vinylnickel Complexes $Ni(acac)(PPh_3)(C(R_1)=C(R_2)CH_3)$

R_1	R_2	reagent	products	% yield[b]
Ph	Ph	TsOH[a]	(*E*)-, (*Z*)-Ph(H)C=C(CH_3)Ph	100
Ph	Ph	$LiAlH_4$	(*E*)-, (*Z*)-Ph(H)C=C(CH_3)Ph	79
Ph	Ph	$AlMe_3$	(*E*)-, (*Z*)-Ph(CH_3)C=C(CH_3)Ph	88
Ph	Ph	MeLi	(*E*)-, (*Z*)-Ph(CH_3)C=C(CH_3)Ph	52
Ph	Ph	I_2	(*E*)-, (*Z*)-Ph(I)C=C(CH_3)Ph	66
Ph	Ph	CO-MeOH	(*E*)-, (*Z*)-Ph(MeO_2C)C=C(CH_3)Ph	39
Ph	H	TsOH	(*E*)-, (*Z*)-Ph(H)C=C(H)CH_3	68
Ph	H	I_2	(*E*)-, (*Z*)-Ph(I)C=C(H)CH_3	30
Ph	H	CO-MeOH	(*E*)-, (*Z*)-Ph(MeO_2C)C=C(H)CH_3	29

[a] *p*-Toluenesulfonic acid. [b] Determined by GC or NMR.

Regioselectivity. The reaction of **1** with unsymmetrical alkynes was observed to be highly regioselective, always giving only one regioisomeric vinylnickel complex. The direction of this specificity was confirmed by treatment of the vinylnickel complexes with either $LiAlH_4$ or acid to give mixtures of *E* and *Z* alkenes in high yield. These results, presented in Table I, show that even alkynes with two different alkyl substituents (for example, 4,4-dimethyl-2-pentyne) give predominantly one regioisomer. Interestingly an alkyne with sterically dissimilar substituents *always gives the vinylnickel complex with the larger group nearest the nickel atom.*

That this selectivity arises from steric and not electronic influences was confirmed by a study of the reaction of a variety of substituted diphenylacetylenes ArC≡CPh (Ar = *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, and 2,4,6-$C_6H_2(CH_3)_3$) with **1**. The para-substituted acetylenes with both electron-withdrawing and electron-donating substituents gave mixtures of regioisomers. The ^1H NMR spectra of the resulting vinylnickel products clearly show two sets of trans vinyl CH_3 and two sets of downfield shifted *o*-phenyl proton resonances in nearly equal intensities; in no case was a significant excess of one regioisomer observed. On the other hand reaction of **1** with 2,4,6-C_6H_2-$(CH_3)_3C$≡CPh appeared to give one predominant isomer by NMR. The direction of this selectivity was established by protonation of the vinylnickel product to give a mixture of *E* and *Z* alkenes, ozonolysis of this mixture in methanol, and reduction of the ozonide with dimethyl sulfide. This gave acetophenone and mesitylaldehyde as the predominant products; a minor amount of acetaldehyde was identified. GC analysis of these products suggests that at least 88% of the addition product arises from migration of the methyl ligand to the least hindered alkyne carbon.

These observations are consistent with a transition state for insertion that is sensitive only to steric crowding. Somewhat unexpectedly, it is the metal end of the Ni–CH_3 bond rather than the CH_3 group which behaves as the sterically *less* active substituent in the insertion transition state. Although sterically controlled selectivity of this kind exists in the hydrozirconation reaction, the reversed preference is observed; in that case the hydride preferentially migrates to the more hindered carbon in unsymmetrical alkynes.[20]

Reactions of the Vinylnickel Complexes. In addition to acid or $LiAlH_4$, a variety of reagents convert the vinylnickel complexes into organic products (Scheme II, Table II). Nucleophilic reagents such as CH_3Li, $LiAlH_4$, and $Al(CH_3)_3$, as well as electrophilic reagents such as H^+ and I_2 give reasonable yields of their respective organic products. The organometallic products formed in these reactions have not been well-characterized, but importantly all gave mixtures of *E* and *Z* alkene products in variable ratios. In no case was a single stereoisomer observed in good yield. The lack of stereoselectivity in the reactions of the vinylnickel complexes required that an alternate method for determining the stereochemistry of these complexes be found.

(20) (a) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. A referee has pointed out that regioselectivity similar to the type exhibited by this nickel system has been observed earlier in the palladium series. (b) cf. Heck, R. F. *Ibid.* **1971**, *93*, 6896.

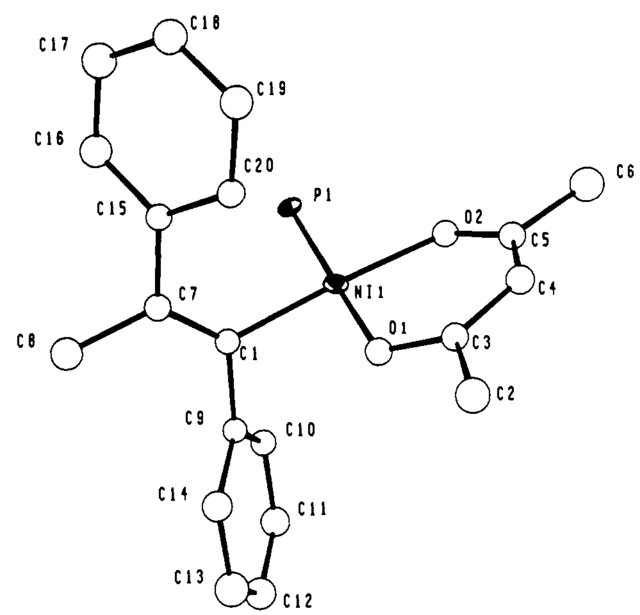


Figure 1. ORTEP drawing of (*Z*)-(acac)(PPh_3)[C(PH)=C(Ph)CH_3]Ni (**3**), excluding the phosphine phenyls.

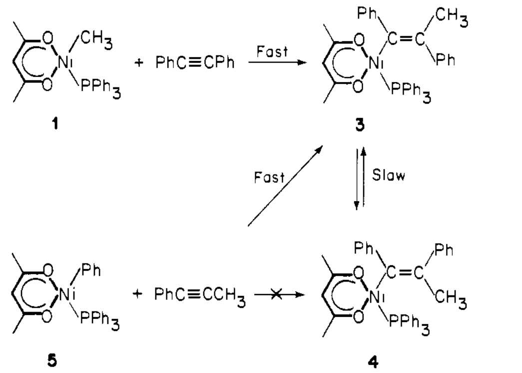
C. Stereochemistry of Addition. Reaction of 1 with Diphenylacetylene. We have examined the reaction of **1** with diphenylacetylene especially closely. A solution of 205 mg (1.15 mmol) of PhC≡CPh in 1 mL of toluene was added to 500 mg (1.15 mmol) of **1** in 20 mL of toluene at room temperature to give Ni(acac)(PPh_3)[C(Ph)=C(Ph)CH_3] (**3**) in quantitative yield. Precipitation with hexane allowed isolation of **3** as an orange solid in 89% overall yield. The conversion of **1** into **3** can be conveniently monitored by NMR; no intermediates could be observed. In benzene this reaction, 0.1 M in both reagents, is complete in less than 30 min at room temperature.

The vinylnickel complex **3** is an orange-red solid with solubility properties similar to those of **1**. Treatment of a solution of **3** in THF with excess *p*-toluenesulfonic acid gave (*E*)- and (*Z*)-1,2-diphenylpropenes in quantitative yield. The ^1H NMR spectrum of **3** has acac absorptions at δ 1.18 and 1.78 (s, 3 H each) and 5.09 (s, 1 H), and a vinyl methyl resonance at δ 2.03 (d, J_{PH} = 1.5 Hz, 3 H). The vinyl methyl signal is split by coupling to phosphorous (J_{PH} = 1.5 Hz), indicating that in this complex phosphine exchange is slow on the NMR time scale. This slower phosphine exchange is general for all the vinylnickel complexes. In addition there is an unusual aromatic proton resonance, a doublet of doublets at δ 8.70 integrating as two protons (A_2MM' quartet, J_{AM} = 1, $J_{AM'}$ = 7 Hz). This low-field absorption, assigned to a pair of *o*-phenyl protons on the β-phenyl group of the vinyl ligand, will be discussed further below.

Complex **3** is the initial product of the reaction. However after standing in solution at room temperature for several days, or heating to 56 °C, **3** is converted partially into a new vinyl complex **4**. Complex **4** has a new set of acac absorptions at δ 5.20, 1.87, and 1.41 and a new vinyl methyl doublet shifted strongly downfield at δ 3.37 (J_{PH} = 1 Hz). Additionally the absorption at δ 8.70 in **3** is absent in **4**. The similarity of **3** and **4** has prevented separation of these two compounds; however, on the basis of the NMR and the fact that protonation of mixtures of **3** and **4** also give only 1,2-diphenylpropenes, we conclude that **3** and **4** are cis/trans isomers about the double bond. This conclusion is supported by the observation that on continued heating the above solution of **3** and **4** reaches an equilibrium ratio for **3**/**4** of about 3.0 in 1 h at 56 °C. Clearly **3** is the kinetic product of the reaction of **1** and PhC≡CPh, and heating converts it to an equilibrium mixture of two isomers.

Crystal and Molecular Structure of 3. Assignment of the stereochemistry of the vinyl ligand in **3** was essential to this investigation. This prompted us to undertake the structure determination of **3** by X-ray diffraction. Complex **3** was conclusively shown to be the *Z* isomer, the product of trans addition, by X-ray

Scheme IV



crystallography on a single crystal obtained from a toluene–hexane solution. Details of the structure determination are given in the Experimental Section. An ORTEP drawing of 3, excluding the phosphine phenyls, is shown in Figure 1 and significant interatomic distances and angles are given in Table VI. Complex 3 is a square-planar vinylnickel complex with the carbon–carbon double bond almost perpendicular to the plane of the complex. Both the carbon–carbon double bond distance of 1.327 Å and the Ni1–C1–C7 angle of 123.7° support the characterization of the organic ligand as a vinyl group.

With the assumption that the structure of 3 in solution is similar to that in the solid state, the X-ray study allows us to rationalize the unusual NMR chemical shift of the aromatic resonance at δ 8.70. This resonance is assigned to the two *o*-phenyl protons on the β-phenyl group cis to the nickel. With the vinyl ligand at right angles to the plane of the nickel complex these ortho protons are placed directly over the nickel atom, although the distance in the crystal is nonbonding (greater than 2.0 Å). A similar effect is observed in the strong downfield shift of the cis vinyl methyl in 4 relative to the trans vinyl methyl in 3. Relative shifts of this kind are observed in the products of the reaction of 6 with PhC≡CPh and PhC≡CCH$_3$. In (*Z*)-Ni(acac)(P(c-Hx)$_3$)[C(Ph)=C(Ph)CH$_3$] absorptions at δ 9.28 (A_2MM' quartet, J_{AM} = 1 Hz, $J_{AM'}$ = 7 Hz) and 8.0 (A_2MM' quartet, J_{AM} = 1 Hz, $J_{AM'}$ = 7 Hz) are observed, whereas in Ni(acac)(P(c-Hx)$_3$)[C(Ph)=C(CH$_3$)$_2$] the only low-field absorption is at δ 7.95 (A_2MM' quartet, J_{AM} = 1 Hz, $J_{AM'}$ = 7 Hz). Since there is no triphenylphosphine in these complexes to confuse the assignment, it is clear that the *o*-phenyl protons of both the α- and β-vinyl phenyl groups are strongly shifted downfield, with the cis β-phenyl protons shifted further. Overlap of the triphenylphosphine absorptions probably obscures the protons for the α-phenyl group in complexes 3 and 4. The observed coupling pattern in these absorptions is also consistent with their assignment as *o*-phenyl protons.

Reaction of Ni(acac)(PPh$_3$)Ph (5) with PhC≡CCH$_3$. The unusual result that 3, the kinetic product of the reaction of 1 and PhC≡CPh, was the product of overall trans addition led us to investigate the reaction of Ni(acac)(PPh$_3$)Ph (5) with PhC≡CCH$_3$. If this reaction also proceeded with trans stereoselectivity then 4, the isomer opposite to 3, should be the kinetic product. Contrary to this prediction, 3 was the only kinetic product of the reaction of 5 with PhC≡CCH$_3$. This reaction proceeded at a rate comparable to that for PhC≡CPh with 1, and again heating the product solution led to an equilibrium mixture of 3 and 4. Clearly 3 is the sole kinetic product of both reactions, and heating leads to an equilibrium mixture of the cis and trans vinyl products (Scheme IV).

Reaction of 1 with PhC≡CCH$_3$. Complex 1 reacts with PhC≡CCH$_3$ to give Ni(acac)(PPh$_3$)[C(Ph)=C(CH$_3$)$_2$] (7) as the only product. The ^{1}H NMR spectrum of 7 shows two vinyl methyl signals. One at δ 2.95 (d, J_{PH} = 1 Hz) can be assigned as cis and the other at 1.75 (d, J_{PH} = 1 Hz) as trans to the nickel atom by analogy to 3 and 4. Treatment of 7 with LiAlH$_4$ gave 1-phenyl-2-methylpropene in 78% yield. In this reaction, using a deuterium-labeled methyl group, it is possible to distinguish *cis* and *trans* reaction pathways directly.

Scheme V

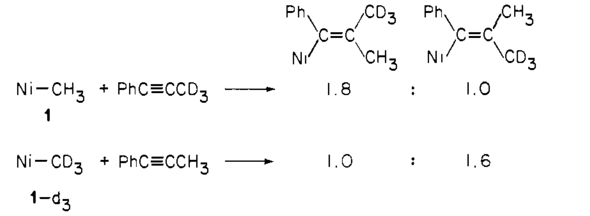
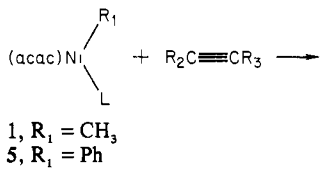
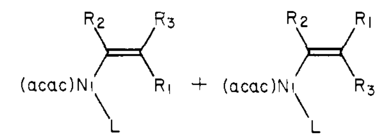


Table III. Stereochemistry of Addition of Nickel Complexes to Alkynes



1, R$_1$ = CH$_3$
5, R$_1$ = Ph



cis *trans*

				% product^a			
				kinetic		thermodynamic	
rxn	R$_1$	R$_2$	R$_3$	cis	trans	cis	trans
1	CH$_3$	Ph	Ph	0	100	25	75
2	Ph	Ph	CH$_3$	100	0	75	25
3	CH$_3$	Ph	CD$_3$	65	35	50	50
4	CD$_3$	Ph	CH$_3$	61	39	50	50
5^b	CH$_3$	*t*-Bu	H	30	70	100	0
6^b	CH$_3$	Ph	H	65	35	100	0

^{a} Relative percent. ^{b} For these alkynes determining the kinetic ratio of products is approximate because isomerization of the products is competitive with the initial insertion reaction.

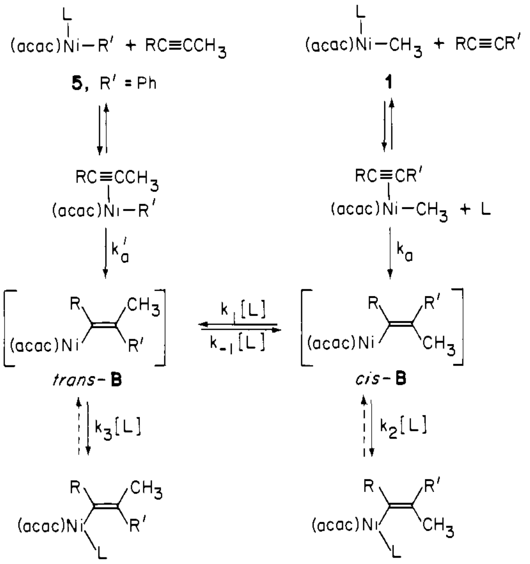
Reaction of 1-d_3 with PhC≡CCH$_3$ gave a ratio of *cis*-7-CD$_3$/*trans*-7-CD$_3$ = 1.6 (±0.1) as kinetic products. Likewise the reaction of 1 with PhC≡CCD$_3$ gave a ratio of *cis*-CH$_3$/*trans*-CH$_3$ = 1.8 (±0.1) (Scheme V). Both product mixtures approach an equilibrium ratio of about 1.0 after several hours. The inversion of the product ratio in these two reactions excludes a deuterium isotope effect as the cause of the observed predominance of cis addition.[21]

Reaction of 1 with Other Alkynes. Using the strong downfield shift of the cis-vinyl methyl in the ^{1}H NMR spectrum to assign stereochemistry, it was possible to determine both the kinetic and thermodynamic ratios of cis and trans addition products for a number of alkynes. These results, summarized in Table III, contribute to several important conclusions: (a) in all cases, different kinetic and thermodynamic ratios of (*E*)- and (*Z*)-vinylnickel products are observed; (b) the subsequent and slower isomerization of the initially obtained products to an equilibrium mixture of isomers establishes that they are the result of kinetically controlled pathways; (c) depending upon the alkyne involved, either the *E* or *Z* isomer can be the favored kinetic product; (d) the predominant thermodynamic product has the larger substituent on the β-carbon cis to nickel.

D. Mechanism of Addition. One way to account for the stereochemical and kinetic observations presented here would be to postulate a mechanism involving parallel concerted cis and trans addition pathways, where slight changes in the structure of the alkyne involved can strongly affect the relative rates of cis and trans addition. This mechanism would require that PhC≡CPh

(21) We assume the small difference between the two product ratios is due to a secondary deuterium isotope effect of magnitude 1.8/1.6 = 1.15.

Scheme VI



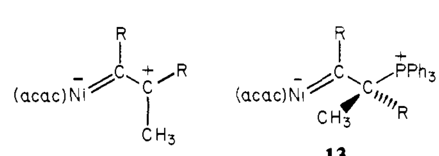
and PhC≡CCH$_3$, as well as $(CH_3)_3$CC≡CH and PhC≡CH, have opposite stereochemical preferences. Moreover this mechanism would require some pathway for cis–trans isomerization of the products that is independent of the mechanism of addition. We find these requirements rather arbitrary and prefer the alternative hypothesis that only one addition pathway exists. This requires that there exist an intermediate capable of isomerization about the carbon–carbon double bond.

A mechanism of this type that reasonably accounts for our results is presented in Scheme VI. The initial step is the reversible substitution at nickel of phosphine by alkyne to form the intermediate Ni(acac)(RC≡CR)CH$_3$. Then, in what is probably the slow step in the reaction, the alkyne inserts into the nickel methyl bond in a cis manner to give a coordinatively unsaturated intermediate *cis*-B. *Cis*-B is the crucial intermediate that can either add phosphine to give the coordinatively saturated cis addition product or isomerize to give *trans*-B (see section E for a discussion of the effect of [PPh$_3$] on the rate of this isomerization). *trans*-B can then add phosphine to give the trans addition product.

The results summarized in Table III require that k_1 be competitive with (if not faster than) k_2. The predominant kinetic product under these circumstances will depend upon the relative rates of k_1, k_{-1}, k_2, and k_3 and not on either the cis/trans product equilibrium or the stereochemistry of the insertion step. Only in the case where both R_1 and R_3 are CH_3 or CD_3 (reactions 3 and 4, Table III) can the stereochemistry of the insertion step be observed in the products. In this case, k_1 and k_{-1}, and k_2 and k_3 are expected to be nearly equal, and the predominance of one isomer among the products can only arise from a competition between k_1 and k_2. Therefore the observation of more cis than trans product in reactions 3 and 4 requires that *cis*-B is formed first. That is, the insertion step proceeds cis.

These stereochemical observations do not provide detailed information about the mechanism of the insertion process itself. The observed predominance of the cis addition product in reactions 3 and 4 argues against a direct trans addition pathway. An alternative hypothesis involving α-hydride migration (Scheme I) might also give a cis specific result, but this mechanism would predict a primary kinetic deuterium isotope effect. The observed kinetic ratio $k(\mathbf{1})/k(\mathbf{1}\text{-}d_3) = 1.24$ is too small to be primary and clearly represents a secondary effect. On the basis of these arguments we conclude that the most likely mechanism involves a concerted cis insertion process.

E. Mechanism of Isomerization. The most direct mechanism for the *cis*-B ⇄ *trans*-B isomerization involves a simple unimolecular rotation about the π bond (perhaps assisted by contributions from resonance forms of type **12**). This mechanism, or any other involving a unimolecular pathway for isomerization of B, would predict a strong phosphine concentration dependence on the ratio



12 **13**

of cis and trans products in reactions 3 and 4, where the rate of isomerization is competitive with the rate of addition of phosphine to give product. This dependence was *not* observed: over concentrations ranging from 0 to 1.0 M, added PPh$_3$ (0.1 M in **1**) the cis/trans product ratio from the reaction of **1**-d_3 with PhC≡CCH$_3$ changed very little. Likewise, highly charge-separated transition states can be discounted because virtually no effect upon the cis/trans product ratio was observed in changing solvent from benzene to THF or adding 0.2 M NaBPh$_4$ in THF.

In order to account for these observations, we suggest that both the isomerization and the product-forming steps involve phosphine. Phosphine can catalyze isomerization of the carbon–carbon double bond if free PPh$_3$ has *two* modes of addition to the intermediate B. Addition at the nickel center gives product, whereas reversible addition to the β-vinyl carbon leads to complex **13**, resulting in isomerization of the double bond. Addition of phosphine to the vinyl ligand might be enhanced in B by delocalization of electron density toward nickel, through resonance forms of the type **12**, making the β-carbon somewhat electrophilic. Equilibration of the kinetic products would then involve loss of phosphine to regenerate intermediate B (dotted arrows in Scheme VI), followed by competitive readdition of phosphine either at nickel or at carbon. This mechanism is supported by the observation that phosphine is much less labile in the vinylnickel complexes than in **1**, accounting for the slow approach to equilibrium. As expected in this mechanism the rate of approach to equilibrium is retarded by addition of excess phosphine.

Summary and Conclusion

The reaction of the methylnickel complex **1** with alkynes occurs rapidly under mild conditions to give vinylnickel complexes, the product of 1,2-addition to the alkyne, in high yield. A wide variety of both internal and terminal alkynes can be employed. This reaction is bimolecular, first order in both **1** and alkyne, and gives highly regioselective products. Only the regioisomer resulting from migration of the methyl ligand to the least hindered alkyne carbon is observed. Thus this system constitutes a general example of the 1,2-addition of a transition-metal alkyl to alkynes.

The formation of both cis and trans addition products in kinetically controlled pathways demonstrates that 1,2-addition reactions can give products which have stereochemistry that differs significantly from the stereochemistry of the addition process itself. To account for this we have suggested the initially concerted cis insertion of the alkyne into the nickel–methyl bond gives a coordinatively unsaturated vinylnickel intermediate capable of isomerization of the carbon–carbon double bond at a rate competitive with product formation. Kinetic competition between the rates of isomerization and of formation of cis and trans products then leads to product stereochemistry that may be independent of the stereochemistry of addition. The observed stereochemistry is also independent of the relative thermodynamic stabilities of the cis and trans addition products and is not affected by changes in phosphine concentration. Mechanisms of this type help explain how different alkynes can give opposite stereochemistry in reactions with the same metal alkyl, even under kinetic conditions, without postulating different addition pathways in each case.[5,6]

In this study the observation of products stereochemically distinct from the pathway for addition was dependent upon phosphine catalysis for the isomerization of an intermediate. Nevertheless, independent of the mechanism of isomerization, the following conclusion concerning stereochemical studies in organometallic addition reactions still pertains: the observation of a given stereochemical mode of addition, even when the observed complex is found to be the kinetic product of the reactions, does not necessarily mean that the crucial insertion step proceeds with that same stereochemistry.

Experimental Section

General Proceedings. All manipulations involving organonickel or aluminum compounds were done under either nitrogen or argon with use of standard Schlenk techniques or in a Vacuum/Atmospheres Corporation model HE-553 inert-atmosphere glovebox with a model MO-40 recirculating purification system and continuously circulating nitrogen. All organonickel compounds were stored in the glovebox. All solvents were thoroughly dried and degassed prior to use. Tetrahydrofuran (THF) and diethyl ether were vacuum distilled directly from sodium benzophenone ketyl solution. Benzene, toluene, and hexanes were added to a solution of sodium benzophenone ketyl performed in tetraglyme and then vacuum distilled. Additionally, hexane was also extensively washed with sulfuric acid, potassium permanganate (10% H_2SO_4 solution), and water to remove olefins, prior to ketyl formation.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian EM-390 or a 180-MHz FT-NMR instrument equipped with a Brucker superconducting magnet and a Nicolet Instrument Corp. NIC-1180 data system, and electronics assembled by Mr. Rudi Nunlist (University of California, Berkeley). ^{31}P spectra were obtained at 72.9016-MHz on the latter instrument. All ^1H NMR spectra are reported in δ downfield from tetramethylsilane, and ^{31}P spectra are reported in ppm downfield from external PPh_3 (−5.9 ppm vs. trimethyl phosphite in benzene). The following abbreviations are used for the observed peak multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = complex multiplet. Most chemical shifts were determined with the use of the residual proton absorption of benzene-d_6 at δ 7.15, THF-d_8 at δ 3.58, or added Cp_2Fe at δ 3.96. Infrared spectra were recorded on a Perkin-Elmer 237 Grating Spectrophotometer. UV-vis spectra were recorded with use of a Cary 118 Spectrophotometer. Gas chromatography (GC) was performed on Hewlett-Packard 5750 or Varian 90-P chromatograph, with helium as the carrier gas. Two columns were employed: (A) 10 ft × $^1/_8$ in. 20% SE-30 on 100/120 chromasorb P; (B) 2 ft × $^1/_4$ in. 5% SE-30 on 60-80 chromasorb W. All peak areas were determined by electronic integration with use of a Spectra-Physics Autolab System I integrator.

$Ni(acac)_2$ was prepared by drying commercially available $Ni(acac)_2(H_2O)$ (100 °C, 24 h at full vacuum). Triphenylphosphine (Alfa) and diphenylacetylene (Aldrich) were recrystallized from hexanes. Liquid alkynes were purified by distillation or preparative gas chromatography when necessary.

Preparation of Ni(acac)(PPh$_3$)CH$_3$ (1). Compound **1** was prepared by analogy to the method of Cotton et al.[12] for the synthesis of $Ni(acac)(PPh_3)CH_2CH_3$. A solution of 0.68 g (7.8 mmol) of $Al(CH_3)_2OCH_3$[22] in 7 mL of hexanes was added dropwise over a 20-min period to an ice/salt bath cooled (−15 °C), stirred suspension of 4.0 g (15.6 mmol) of $Ni(acac)_2$ and 4.5 g (17 mmol) of PPh_3 in 50 mL of diethyl ether under nitrogen. The solution was allowed to warm to about 0 °C for about 2 h. Then the solution was cooled to −15 °C again, and the yellow precipitate was collected by filtration. The crude product was washed three times with cold ether, and residual solvent was removed at reduced pressure and taken into the drybox. This gave 5.75 g of crude product containing considerable excess PPh_3 as evidenced by NMR integration. This crude product was purified by repeated recrystallization from toluene–hexane (1/10) or toluene–acetonitrile ($^1/_4$) to give 3.5 g (51% yield) of pure **1**. The UV-vis spectrum of **1** in benzene (2 × 10^{-4} M, 425-nm max) is not affected by addition of excess PPh_3 (2 × 10^{-4} to 2 × 10^{-2} M). Compound **1** does not sublime: mp(sealed tube) 150–152 °C dec.; ^1H NMR(benzene-d_6) δ 0.07 (s, 3 H), 1.40, 1.90 (s, 3 H each), 5.28 (s, 1 H), 6.9–7.1, 7.6–8.0 (complex, 15 H); IR(CH_2Cl_2) 3300 (br), 1580 (s), 1520 (s), 1440 (w), 1400 (s), 1190 (w), 1100 (m), 1020 (m), 860 (w), 830 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{25}O_2NiP$: C, 66.24; H, 5.79; Ni, 13.49. Found: C, 65.92; H, 5.85; Ni, 13.65.

Preparation of Ni(acac)(PPh$_3$)CD$_3$ (1-d_3). Compound **1**-d_3 was prepared as described above from 2.0 g (7.8 mmol) of $Ni(acac)_2$, 2.05 g (7.8 mmol) of PPh_3, and $Al(CD_3)_2OCH_3$ prepared in situ from $Al(CD_3)_3(Et_2O)$[25] (0.65 g, 3.9 mmol) and CH_3OH (157 μL, 3.9 mmol) in 20 mL of hexane–ether (1:3). Three recrystallizations from toluene–hexane yielded 0.75 g (22% theoretical) of pure **1**-d_3. Anal. Calcd for $C_{24}D_3H_{22}O_2NiP$: C, 65.79; H + D, 6.44. Found: C, 66.20, H + D, 6.66.

Preparation of Ni(acac)(P(c-Hx)$_3$)CH$_3$ (6).[16] Compound **6** was prepared in an analogous manner from $Ni(acac)_2$ (7.8 mmol), $P(c\text{-}Hx)_3$ (7.8 mmol), and $Al(CH_3)_2OCH_3$ (3.9 mmol) to yield 1.32 g of crude product. The crude product was purified by repeated recrystallization from ether; yield 0.73 g (21% theoretical), dark brown cubic crystals. ^1H NMR(benzene-d_6) δ −0.18 (d, J = 5 Hz, 3 H), 1.68, 1.85 (s), 1.0–1.4, 1.4–2.2 (m), 5.28 (s, 1 H) (lit.[16] ^1H NMR δ −0.32 (d, J = 5 Hz), 0.75–1.75 (m), 1.69, 1.84 (s), 5.28 (s)).

Preparation of Ni(acac)(PPh$_3$)Ph (5). Attempts to prepare **5** by the method of Maruyama et al.[8] gave very poor yields of product and large amounts of $Ni(PPh_3)_n$ (n = 3, 4) as primary product. Results were highly variable, sometimes giving no **5** at all. The following modified procedure enabled the isolation of **5** sufficient for these experiments.

A solution of $Al(Ph)_3(Et_2O)$[26] (0.35 g, 1.3 mmol) in 25 mL of toluene–ether (1:4) was added very slowly to a slurry of 2.0 g (7.8 mmol) of $Ni(acac)_2$ and 2.15 g (8.2 mmol) of PPh_3 in 35 mL of diethyl ether with cooling to −78 °C. Upon warming of the solution to −20 °C, a yellow color developed and 50 mL of cold hexane was added. The solution was cooled to −78 °C and filtered. Only a small amount of a yellow-green solid was collected. The filtrate was allowed to warm to room temperature, turning yellow-brown (no precipitate). The solvent was removed to yield a red residue. Extensive washing of this crude product with ether at room temperature gave 0.55 g (14% theoretical) of essentially pure **5** as a yellow powder. Compound **5** could be recrystallized from toluene–ether. ^1H NMR(benzene-d_6) δ 1.40, 1.72 (s, 3 H each), 5.30 (s, 1 H), 6.8–7.1, 7.4–7.6 (m) (lit.[8] ^1H NMR δ 1.50 (s, 3 H), 1.72 (s, 3 H), 5.30 (s, 1 H), 6.8–7.1, 7.4–7.8 (m)).

Reaction of 1 with Alkynes. General Reaction. The reaction of **1** with alkynes was carried out in either THF or benzene under air-free conditions by one of two methods. **Method A.** In the glovebox a solution of **1** was prepared (typically around 0.1 M in **1**), and an equimolar amount of the alkyne was added. The resulting solution was transferred to an NMR tube and capped, and the cap was wrapped with parafilm. The reaction was then monitored by NMR over a period of hours or days depending upon the alkyne. **Method B.** A solution of **1** prepared in the glovebox was transferred to an NMR tube and capped with a rubber septum. Outside the drybox the alkyne was then added through the septum via syringe, and the reaction was monitored by NMR. All reactions involving heating of the reaction solution were carried out in sealed NMR tubes. Typically the solutions changed from a light yellow-brown to red as the reaction progressed. The ^1H NMR spectra of the resulting vinylnickel complexes are summarized in Table IV. With the exception of **3**, these complexes were not isolated. The structures of these complexes were deduced from their NMR spectra and through identification of the organic products resulting from cleavage of the nickel–carbon bond with acid or $LiAlH_4$ (Table I). These alkenes (Table I) were identified by a number of methods depending upon physical properties and availability of authentic samples. (E),(Z)-Ph(H)C=C(CH$_3$)Ph and Ph(H)C=C(CH$_3$)$_2$ were identified by GC coinjection with authentic samples and by the ^1H NMR spectra of samples purified by preparative GC. (E)- and (Z)-Ph(H)C=C(H)CH$_3$, CH$_3$(H)C=C(CH$_3$)$_2$, and (E)- and (Z)-Et(H)C=C(CH$_3$)Et were identified by GC coinjection with authentic samples. (E)- and (Z)-(t-Bu)(H)C=C(H)CH$_3$ and t-Bu(H)C=C(CH$_3$)$_2$ were identified by NMR spectra of samples isolated by vacuum transfer of the volatiles from a tetraglyme solution following treatment of the corresponding vinylnickel complexes with $LiAlH_4$ or p-TsOH. t-Bu(H)C=C(CH$_3$)$_2$: ^1H NMR(CDCl$_3$)[35] δ 1.06 (s), 1.63 (dd, J = 1.5, 4 Hz), 5.0 (m). (E)-(t-Bu)(H)C=C(H)(CH$_3$): ^1H NMR(CDCl$_3$)[36] δ 1.0 (s), 1.60 (d, J = 5 Hz), 5.32 (complex m).

Reaction of 1 with PhC≡CPh. A solution of 205 mg (1.15 mmol) of PhC≡CPh in 1 mL of toluene was added to 500 mg (1.15 mmol) of **1** in 20 mL of toluene in the glovebox. After the solution stirred at room temperature overnight, the solvent was reduced by evaporation to 8–10 mL and diluted with 200 mL of hexanes. An orange precipitate (280 mg) was collected. A second crop was realized by reducing the filtrate to yield a total of 450 mg (89% theoretical) of a mixture of **3** and **4**. Anal. Calcd. for $C_{38}H_{35}O_2NiP$: C, 74.41; H, 5.75. Found: C, 74.65; H, 5.92. In a similar experiment, addition of excess PhC≡CPh had no effect upon the reaction other than to accelerate it; no evidence of multiple insertion could be detected by NMR.

In a separate experiment, a solution of **3** prepared in THF from 75 mg (0.17 mmol) of **1** and 31 mg (0.17 mmol) of PhC≡CPh was treated with 0.4 mL (0.4 mmol) of 1 M p-toluenesulfonic acid in THF. Analysis

(22) Mole, T. *Aust. J. Chem.* **1963**, *16*, 794.

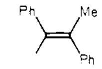
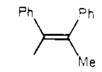
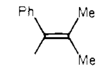
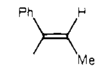
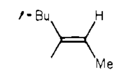
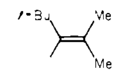
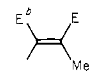
(23) An authentic sample of (E)- and (Z)-1,2-diphenylpropenes was prepared from benzylphosphonium chloride, BuLi, and acetophenone by the method of Wittig and Haag, *Chem. Ber.* **1955**, *88*, 654: mp 113–37 °C; ^1H NMR(CDCl$_3$) δ 2.25 (d, J = 2 Hz, 3 H), 6.8 (d, J = 2 Hz, 1 H), 7.2–7.5 (m, 10 H).

(24) An authentic sample of (E)- and (Z)-2,3-diphenyl-2-butenes was obtained from E. Evitt. See Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 3239: ^1H NMR(CDCl$_3$) δ 1.87 (s, 3 H), 2.10 (s, 3 H, Z isomer), 7.0–7.5 (m). Lit. (CCl$_4$) 1.88 (E isomer), 2.16 (Z isomer): Umbert, M. A.; White, E. H. *J. Org. Chem.* **1976**, *41*, 479.

(25) [Al(CD$_3$)$_3$(Et$_2$O)] was prepared by the method of Krause and Wendt for the corresponding protio compound; bp 50–65 °C at 15 mm. Lit. bp 68 °C at 15 mm: Krause, E.; Wendt, B. *Chem. Ber.* **1923**, *B56*, 466.

(26) [AlPh$_3$(Et$_2$O)] was prepared by the method of Eisch and Kaska; mp 127–129 °C. Lit. 129–129.5 °C: Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2976.

Table IV. ^{1}H NMR Data for Vinylnickel Complexes of General Structure $Ni(acac)(PPh_3)[C(R_1)=C(R_2)CH_3]$

complex	vinyl ligand	chemical shifts[a] =C(CH₃)	R_1	R_2	acac
3		2.03 (d, J = 1)	6.9–7.6 (m)	6.9–7.6 (m)	1.78, 1.18 (s, 3 H), 5.09 (s, 1 H)
4		3.37 (d, J = 1)	6.9–7.6 (m)	6.9–7.6 (m)	1.87, 1.41 (s, 3 H), 5.20 (s, 1 H)
7		2.95 (d, J = 1)	6.9–7.1, 7.6–7.9 (m)	1.75 (d, J = 1)	1.88, 1.30 (s, 3 H), 5.22 (s, 1 H)
8		2.80 (dd, J = 1, 7)	6.9–7.2, 7.6–7.9 (m)	5.05 (q, J = 1)	1.83, 1.38 (s, 3 H), 5.22 (s, 1 H)
9		2.75 (dd, J = 1, 6)	1.50 (s)	4.65 (q, J = 6)	1.80, 1.30 (s, 3 H), 5.25 (s, 1 H)
10		3.12 (d, J = 1.5)	1.58 (s)	1.85 (d, J = 1)	1.87, 1.38 (s, 3 H), 5.28 (s, 1 H)
11		2.72 (s)	3.32 (s)	3.56 (s)	1.78, 1.22 (s, 3 H), 5.15 (s, 1 H)

[a] δ in benzene-d_6 (multiplicity, J in Hz). [b] E = CO_2CH_3.

Table V. Rate Constants for the Reaction of 1 with PhC≡CPh and Added PPh_3 at 40 ± 1 °C

[1],[b] M	[PPh₃], M	10^3k_{obsd},[a] L M^{-1} s^{-1}
0.0945	0.05	6.2 ± 0.08
0.945	0.71	3.63 ± 0.08
0.855	0.107	2.98 ± 0.15
0.085	0.197	1.70 ± 0.07
0.080	0.43	0.733 ± 0.02
0.070	1.05	0.30 ± 0.02

[a] Rate constant from plot of $1/[1] - 1/[1]_0$ vs. time. [b] [1] = [PhC≡CPh].

of the resulting solution by gas chromatography identified (E)- and (Z)-1,2-diphenylpropenes in 104% calculated yield and a ratio of Z/E = $^5/_4$, with use of naphthalene as an internal standard and molar response factors determined with use of an authentic sample. However this Z/E ratio was variable from experiment to experiment. The 1,2-diphenylpropenes were identified by coinjection of an authentic mixture[23] and by mass spectral analysis on a sample purified by preparative gas chromatography (column B; 110–130 °C, flow rate 60 mL/min).

Reaction of 1 with PhC≡CPh and Added PPh₃. A solution of 235 mg (0.54 mmol) of **1**, 78 mg (0.298 mmol) of PPh_3, and 50 mg (0.269 mmol) of Cp_2Fe (internal standard) in 6 mL of benzene-d_6 was prepared in the glovebox. Then 96 mg (0.54 mmol) of PhC≡CPh was dissolved in the solution, and 1-mL aliquots were added to weighed amounts of PPh_3. The resulting solutions were then transferred to NMR tubes, frozen, and sealed off under a vacuum. Six NMR tubes were prepared in this manner containing the concentrations listed in Table V. These NMR tubes were heated in a temperature-controlled water bath at 40 (±1) °C, and the concentration of **1** was determined by cooling the NMR tube in ice water and integrating the nickel–methyl resonance vs. Cp_2Fe. The second-order rate constants determined in this way are presented in Table V.

Reaction of 1 with ArC≡CPh. Solutions of **1** (0.05 mmol) and equimolar amounts of ArC≡CPh (Ar = p-$CH_3OC_6H_4$, p-ClC_6H_4, p-MeC_6H_4, p-$NO_2C_6H_4$) in 0.5–0.7 mL of benzene-d_6 were prepared in the glovebox, transferred to NMR tubes, and capped. The reactions all proceed at room temperature to give the ^{1}H NMR spectra summarized here. These spectra are consistent with the presence of both possible regioisomers of the p-substituted analogues of compound **3**. A, the product of **1** and p-$MeOC_6H_4C$≡CPh: ^{1}H NMR δ 1.23 (s, 3 H), 1.85 (s, 3 H), 2.10 (2 d, J = 1.5 Hz, 3 H), 3.42, 3.50 (s, 3 H, ratio 1.45), 5.17 (s, 1 H), 7.0–7.8 (m), 8.65 (d, J = 9 Hz), 8.75 (dd, J = 1, 7 Hz). B, the product of **1** and p-ClC_6H_4C≡CPh: ^{1}H NMR δ 1.27 (d, J < 1 Hz, 3 H), 1.85 (d, J = 1.5 Hz, 3 H), 2.03 (2 d, J = 1.5 Hz, 3 H), 5.12 (s, 1 H), 6.9–7.6 (m), 8.48 (d, J = 9 Hz), 8.67 (d, J = 6 Hz). C, the product of **1** and p-MeC_6H_4C≡CPh: ^{1}H NMR δ 1.20 (s, 3 H), 1.78 (s, 3 H), 2.05 (d, J = 1 Hz, 3 H), 2.12 (s), 2.25 (s), 5.05 (s, 1 H), 6.7–7.8 (m), 8.60 (d, J = 6 Hz), 8.78 (dd, J = 1,6 Hz). D, the product of **1** and p-$NO_2C_6H_4C$≡CPh: ^{1}H NMR δ 1.22 (s), 1.35 (s), 1.80 (s), 1.86 (s), 1.90 (2 d), 3.34 (d, J < 1 Hz), 5.10 (s), 5.12 (s), 5.20 (s), 6.8–7.8 (m), 8.0 (m), 8.62 (m).

Reaction of **1** with 2,4,6-$C_6H_2(CH_3)_3C$≡CPh proceeds much more slowly than that with other diarylacetylenes. The reaction of 20 mg (0.046 mmol) of **1** and 10 mg (0.045 mmol) of 2,4,6-$C_6H_2(CH_3)_3C$≡CPh in 0.6 mL of benzene-d_6 had consumed only 50% of the starting material after 20 h at room temperature. The resulting NMR sectrum is consistent with both E and Z isomers of one predominant regioisomer. Product resonances were observed at δ 1.35 (s), 1.68 (s), 2.02 (s), 2.09 (s), 2.26 (s), 2.30 (s), 2.38 (s), 3.32 (s), 5.18 (s), 5.25 (s), 6.6–7.8 (m), 8.25 (br m).

The direction of addition was established by protonation of the vinylnickel complex and ozonolysis of the resulting alkenes. In a separate experiment, a solution of 50 mg (0.115 mmol) of **1** and 26 mg (0.115 mmol) of 2,4,6-$C_6H_2(CH_3)_3C$≡CPh in 2 mL of benzene was allowed to stir at room temperature for 3 days. The solvent was removed, and the resulting residue was dissolved in 2 mL of THF. This solution was then treated with 100 mg (0.58 mmol) of p-toluenesulfonic acid in 1 mL of THF. After being stirred overnight, the solution had discolored and a precipitate formed. The solution was extracted with H_2O–ether, the combined ether extracts were dried with $MgSO_4$, and the ether was removed to yield a mixture of alkenes as a white solid. This solid was dissolved in 2 mL of MeOH, the solution was cooled to −78 °C, and ozone was passed through the solution until the pale blue color of excess ozone was observed (~5 min). The excess ozone was purged with a stream or air; then 10 μL (0.136 mmol) of Me_2S was added still at −78 °C. The solution was allowed to warm to room temperature and then analyzed by GC (column A: 150 °C, 30 mL/min). The two major products of the reaction, $PhC(O)CH_3$ and 2,4,6-$C_6H_2(CH_3)_3CHO$, were identified by coinjection of authentic samples obtained commercially. A small amount of PhCHO was observed. The ratio $PhC(O)CH_3$/PhCHO = 7.61 was calculated from the observed integrations. This method of analysis was checked by the ozonolysis of an authentic sample of 1,2-diphenyl-1-propene under identical conditions. Equal amounts of PhCHO and $PhC(O)CH_3$ were observed by GC.

Reaction of 1 with PhC≡CCD₃ and 1-d_3 with PhC≡CCH₃. A solution of 40 mg (0.09 mmol) of **1** and 11 mg (0.09 mmol) of PhC≡CCD_3 in 1.0 mL of benzene-d_6 was prepared in the glovebox, transferred to an NMR tube, and capped. Monitoring by NMR showed the reaction was 70% complete in less than 30 min, and 100% complete in 1.25 h at room temperature. A ratio of the cis/trans isomers could be calculated by comparing the integrations for the acac H at δ 5.22 and the cis vinyl CH_3 at δ 2.95 and correcting for the theoretical number of protons. Integration of the trans vinyl CH_3 at δ 1.75 was very unreliable due to the proximity of the acac CH_3 absorption at δ 1.88. In this way the initial ratio was calculated to be cis-CH_3/$trans$-CH_3 = 1.70 (±0.1). Alternatively, in a separate experiment in protiobenzene integration of the deuterium NMR (180-MHz FT NMR), resonances for the vinyl CD_3 at δ 2.95 and 1.75 directly gave a ratio of $trans$-CD_3/cis-CD_3 = 1.87; the later experiment was considered more accurate.

Table VI. Selected Interatomic Distances (Å) and Angles (Deg) for (Z)-(acac)(PPh_3)[(Ph)C=C(Ph)CH_3]Ni

Ni1–P1	2.1783	O2–Ni1–P1	87.01
Ni1–C1	1.8970	O2–Ni1–O1	92.90
Ni1–O1	1.9101	O2–Ni1–C1	176.22
C1–C7	1.3271	C1–Ni1–P1	93.16
C1–C9	1.4685	C7–C1–Ni1	109.71
C7–C8	1.5268	C7–C1–C9	127.93
C7–C15	1.4825	C1–C7–C8	123.57
		C15–C7–C8	113.85

A similar reaction involving 68 mg (0.15 mmol) of **1**-d_3 and 18 mg (0.15 mmol) of PhC≡CCH_3 in 1 mL of benzene gave a ratio of *cis*-CD_3/*trans*-CD_3 = 1.56 by deuterium NMR.

These product ratios were found to be almost totally insensitive to added PPh_3 or solvent. In the reaction of **1**-d_3 with PhC≡CCH_3 in benzene-d_6 the cis/trans product ratio was 1.55 (±0.1) with no added PPh_3, 1.67 (±0.1) with 0.1 M added PPh_3, and 1.85 (±0.1) with 1.0 M added PPh_3 (all at 60 °C). In the reaction of **1** with PhC≡CCD_3 the cis/trans product ratio was 1.6 (±0.1) in THF-d_8 and 1.7 (±0.1) in 0.2 M $NaBPh_4$ in THF-d_8.

Kinetic Deuterium Isotope Effect. A solution of 9 mg (0.05 mmol) of PhC≡CPh was added to a solution of 102 mg (0.23 mmol) of **1** and 114 mg (0.26 mmol) of **1**-d_3 in 4.5 mL of THF. After 2 h a solution of 430 mg (2.2 mmol) of *p*-toluenesulfonic acid in 2 mL of THF was added. The solvent was removed, and the residue was extracted with H_2O–ether in air. The combined ether fractions were dried with $MgSO_4$ and then the ether was removed to yield a white solid. About 1–2 mg of (*E*)- and (*Z*)-1,2-diphenylpropenes were isolated from this mixture by preparative gas chromatography (column B; 130 °C, 80 mL/min). Mass spectral analysis gave a d_0/d_3 ratio of 1.05 and 1.085 for the (*Z*)- and (*E*)-1,2-diphenylpropenes, respectively. Similarly the 180-MHz NMR spectrum of (*Z*)-1,2-diphenylpropene gave a d_0/d_3 ratio of 1.16. Averaging and correcting for the starting concentrations gives a value for $k(\mathbf{1})/k(\mathbf{1}\text{-}d_3)$ = 1.24 (±.0.5).

X-ray Crystal Structure of 3. A crystal of **3** measuring 0.36 × 0.24 × 0.28 mm obtained from a toluene–hexane solution was shown to be exclusively **3**, not **4**, by examination of the NMR spectrum of the remaining crystals in the same batch. Compound **3** crystallizes in space group $P\bar{1}$ with cell parameters a = 17.892 Å, b = 12.339 Å, c = 16.732 Å, α = 106.27, β = 73.17, γ = 110.77°, and Z = 4. The calculated density is 1.26 g/cc, and a density of 1.19 g/cc was measured by flotation of a crystal from the same batch. Intensity data on 5258 reflections $2\theta \le 38°$ were collected on a Syntex $P2_1$ diffractometer with monochromatic Mo Kα radiation with use of θ–2θ scanning. It was determined that no significant crystal decomposition occurred by monitoring ten standard reflections. The locations of the two nickel and two phosphorus atoms were obtained by examination of a Patterson map. Fourier-transform electron density maps then identified the positions of the other 80 nonhydrogen atoms. The nickel and phosphorus atom thermal parameters were refined anisotropically and the other 80 nonhydrogen atoms only isotropically. A difference Fourier map identified no sites of electron density greater than 1.0 $e^2/Å^2$ except within 2.0 Å of the nickel atoms. Finally H atom positions were calculated with the assumption of a carbon–hydrogen bond length of 0.95 Å and a B value 1 greater than for the attached carbon atom. Final refinement after a total of four least-squares routines gave R = 0.082 and a "goodness of fit" = 1.54 for all 5258 reflections ($2\theta \le 38°$), and R = 0.053 for the 3198 reflections [$F_0 > 3\sigma(F_0)$]. An ORTEP drawing of **3**, excluding the phosphine phenyls, is shown in Figure 1. Some relevant interatomic distances and angles are presented in Table VI. Additional crystallographic data are provided in the supplement to the earlier communication.[10]

Competition Experiment between PhC≡CPh and PhC≡CCH_3. A solution of 20 mg (0.181 mmol) of PhC≡CCH_3, 30 mg (0.168 mmol) of PhC≡CPh, and 21 mg (0.046 mmol) of **6** in 1 mL of benzene-d_6 was prepared in the glovebox, transferred to an NMR tube, and sealed off under vacuum. After the solution was heated to 44 °C for 2.5 h, a ratio of Ni(acac)(P(c-Hx)$_3$)[C(Ph)=C(Ph)CH_3] to Ni(acac)(P(c-Hx)$_3$)[C-(Ph)=C(CH_3)$_2$] of 1.1 (±0.1) was determined by integration of the NMR spectrum of the resulting solution, at this point 40% of **6** had been consumed. Correcting for the initial concentrations gives a ratio for k(PhC≡CPh)/k(PhC≡CCH_3) = 1.2 (±0.1).

In a similar manner a mixture of 30 mg (0.168 mmol) of PhC≡CPh, 21 mg (0.181 mmol) of PhC≡CCH_3, 21 mg (0.048 mmol) of **1**, and 13 mg (0.049 mmol) of PPh_3 (to slow the reaction at room temperature) in 1.0 mL of benzene-d_6 gave a value for the ratio of k(PhC≡CPh)/k-(PhC≡CCH_3) = 1.40 (±0.05) after heating to 45 °C for 100 min. Another experiment involving no added PPh_3 and conducted at room temperature resulted in an identical ratio within experimental error.

Reactions of the Vinylnickel Complexes. General Reactions. The vinylnickel complexes Ni(acac)(PPh_3)[C(Ph)=C(Ph)CH_3] (**3**) and Ni(acac)(PPh_3)[C(Ph)=C(H)CH_3] (**8**) were prepared in situ, usually in THF solvent, from equimolar amounts of **1** and either PhC≡CPh or PhC≡CH. After about 1 h at room temperature, these solutions were treated with the appropriate reagent under air-free conditions. The resulting organic products were analyzed by gas chromatography and/or NMR and identified by comparison with authentic samples in most cases. These results are summarized in Table II. Below are descriptions of the reactions of **3** with some of these reagents; the reactions of **8** were carried out in a similar manner.

$LiAlH_4$. A solution of 12 mg (0.32 mmol) of $LiAlH_4$ in 10 mL of THF was added to a solution of 0.2 mmol of **3**, prepared as above, in 3 mL of THF with 15 mg of biphenyl as internal standard. At various time intervals, 1-mL aliquots were removed, quenched with 1 mL of saturated Na_2SO_4, and analyzed by gas chromatography (column A, 195 °C, 60 mL/min). After 15 min a maximum yield of 85% of (*E*)- and (*Z*)-1,2-diphenylpropenes[23] was realized. However the (*E*)/(*Z*) ratio changed over the course of the reaction from an initial value of 1.1 to 1.8.

$Al(CH_3)_3$. A 1-mL solution of $Al(CH_3)_3$ (25% in hexane) was added dropwise to a solution of 0.1 mmol of **3** in 2 mL of benzene. After 5 min, 4 h, and 24 h, 1-mL aliquots were quenched with 2 mL of saturated Na_2SO_4. After 4 h a maximum yield of 88% (*E*)- and (*Z*)-2,3-diphenyl-2-butenes[24] were identified by gas chromatography.

CH_3Li. To a solution of 0.047 mmol of **3** in 1 mL of ether was added dropwise 0.5 mL of 1.45 M CH_3Li at room temperature. Extraction with H_2O–ether allowed isolation of a 52% yield of (*E*)-2,3-diphenyl-2-butene,[24] identified by its mass spectrum and NMR.

I_2. A solution of 150 mg (0.59 mmol) of I_2 and 50 μL of pyridine in 12 mL of CH_2Cl_2 was added to a solution of 0.57 mmol of **3** in 5 mL of THF. After overnight stirring of solution, addition of 230 μL of CH_3I (to precipitate PPh_3) and filtration through a plug of silica gel yielded 168 mg of a mixture of (*E*)-1,2-diphenylpropene and (*E*)- and (*Z*)-1-iodo-1,2-diphenylpropenes in yields of 24% and 66%, respectively. (*E*)- and (*Z*)-1-iodo-1,2-diphenylpropenes were identified by NMR and MS of samples purified by preparative GC. ^{1}H NMR($CDCl_3$): δ 1.98 (s), 2.42 (s), 7.0 (m), 7.3 (m). Mass spectrum: m/e 320 (4.4), 193 (9.3), 178 (2.0), 114 (5.5).

CO–MeOH. A solution of 520 mg (0.5 mL) of 25% methanolic $Bu_4N^+OH^-$ in 33 mL of benzene was added to a solution of 0.051 mmol of **3** in 2 mL of benzene under carbon monoxide purge. After 30 min, CO flow was discontinued, and then after 1 h the solution was extracted with 10% HCl–ether. The combined ether layers were dried with $MgSO_4$ and then evaporated to yield a mixture of (*E*)- and (*Z*)-methyl-2,3-diphenyl-2-butenoates in 39% yield, identified by NMR and mass spectrum of a sample purified by preparative GC. ^{1}H NMR($CDCl_3$): δ 2.01 (s), 2.32 (s), 3.40 (s), 3.72 (s), 6.9–7.6 (m). Mass spectrum m/e 252 (4.6), 220 (1.8), 193 (1.9), 178 (1.5).

Reaction of 6 with Alkynes. The reaction of Ni(acac)(PCy_3)CH_3 (**6**) with PhC≡CPh and PhC≡CCH_3 was carried out in a manner identical with that for **1**. These reactions, however, were much slower, and heating to temperatures of 40–60 °C were required for reasonable rates. The products of these reactions were not isolated; however, their NMR spectra are given here. The reaction of **6** with PhC≡CPh gave Ni-(acac)(P(c-Hx)$_3$)[C(Ph)=C(Ph)CH_3]: ^{1}H NMR(C_6D_6) δ 0.8–2.1 (m), 2.28 (s), 3.62 (s), 5.30 (s), 7.0–7.5 (m), 8.0 (dd, J = 1,7 Hz), 9.28 (dd, J = 1, 7 Hz). The reaction of **6** with PhC≡CCH_3 gave Ni(acac)(P(c-Hx)$_3$)[C(Ph)=C(CH_3)$_2$]: ^{1}H NMR(C_6D_6) δ 0.8–2.0 (m), 2.03 (d, J < 1 Hz), 3.39 (d, J < 1 Hz), 5.33 (s), 7.95 (dd, J = 1, 7.5 Hz).

Preparation of PhC≡CCD_3.[27] A 22-mL solution of BuLi (0.053 mol, 2.4 M) in hexane was added dropwise over a 20-min period to a solution of 5.5 mL (0.05 mol) of freshly distilled PhC≡CH in 40 mL of anhydrous ether with cooling to −20 °C under nitrogen. The solution was allowed to warm to room temperature, and 25 mL of dry THF was added, followed by 3.2 mL (0.05 mol) of CD_3I (Aldrich 99+%D) over a 10-min period. The reaction was exothermic, warming the solution considerably. The addition funnel was washed down with an additional 10 mL of THF. After 17 h the solution was poured over 100 mL of ice water and then extracted with ether. The combined ether extracts were dried with $MgSO_4$ and distilled at reduced pressure to yield 2.40 g (40% theoretical) of PhC≡CCD_3: bp 73–75 °C (17 mmHg); ^{1}H NMR-($CDCl_3$) 7.25 (m). By mass spectroscopy the product was determined to be >98 at.% D. Anal. Calcd for $C_9H_5D_3$: C, 90.70; H + D, 9.30. Found: C, 90.23; H + D, 9.52.

Synthesis of ArC≡CPh. The substituted diphenylacetylenes ArC≡CPh were prepared from PhC≡CCu and the appropriate *p*-iodobenzene

(27) Adapted from method in: Bradsma, L. "Preparative Acetylenic Chemistry"; Elsevier: New York, 1971; p 54–55. Addition of THF after formation of the anion was found to be essential.

by the method of Gastro and Stephens.[28] The p-substituted iodobenzenes were all obtained from Pfaltz and Bauer and used without further purification. Iodomesitylene was prepared from mesitylene, ICl, and $ZnCl_2$ by the literature method; mp 31 °C (lit 32 °C).[33] In all cases the resulting acetylene was recrystallized from methanol or hexanes until no change in melting point was observed. p-$ClC_6H_4C{\equiv}CPh$: mp 80.5–81.5 °C (lit.[29] 81.5–82 °C); IR(CCl_4) 2225 (w), 1605 (sh), 1595 (s), 1495 (s), 1445 (s), 1400 (s), 1090 (s), 1015 (s), 825 (s), 685 (s) cm^{-1}. p-$CH_3C_6H_4C{\equiv}CPh$: mp 70–71 °C (lit.[30] mp 72–74 °C); IR(CCl_4) 2215 (w), 1600 (s), 1515 (s), 1487 (s), 1445 (s), 685 (s) cm^{-1}; ^1H NMR(C_6D_6) δ 1.99 (s, 3 H), 6.97 (m, 5 H), 7.50 (m, 4 H). p-$MeOC_6H_4C{\equiv}CPh$: mp 57–61 °C (lit.[30,31] mp 58–60 °C); IR(CCl_4) 2210 (w), 1500 (s), 1435 (m), 1242 (s), 1168 (m), 1030 (s), 825 (s) cm^{-1}; ^1H NMR(C_6D_6) δ 3.17 (s, 3 H), 6.5–7.4 (m, 9 H). p-$NO_2C_6H_4C{\equiv}CPh$: mp 117–118 °C (lit.[30] mp 119–120 °C); IR(CCl_4) 2225 (m), 1600 (s), 1528 (s), 1350 (s), 855 (s), 689 (s) cm^{-1}. 2,4,6-$C_6H_2(CH_3)_3C{\equiv}CPh$: mp 36.5–37 °C (lit.[34] 36–37 °C); IR(CCl_4) 3100–2910 (mult, s), 2210 (m), 1612 (s), 1598 (s), 1495 (s), 850 (s), 685 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 2.10 (s, 3 H), 2.48 (s, 6 H), 6.71 (s, 2 H), 7.0 (m, 3 H), 7.48 (m, 2 H).

Acknowledgment. We are grateful to Dr. Richard Marsh (California Institute of Technology) for extensive assistance with the X-ray diffraction study. We also acknowledge the assistance of Mr. Rudi Nunlist in the NMR experiments and stimulating correspondence on the mechanism of insertion reactions with Professors H. C. Clark and M. L. H. Green. Financial support for this work was provided by the National Institutes of Health (Grant No. GM-12459).

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A Novel Molybdenum Thiolato Compound, Tetrakis(*tert*-butylthiolato)molybdenum(IV). Preparation and Crystal and Molecular Structure

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Abstract: The new dark red, diamagnetic Mo(t-BuS)$_4$ was prepared by treating anhydrous $MoCl_4$ with t-BuSLi in 1,2-dimethoxyethane (>45% yield). The molecular structure has been determined by a single-crystal X-ray analysis. The compound crystallizes in tetragonal space group $P4_22_12$ with a = 10.975 (1) Å, c = 10.249 (1) Å, and with two molecules in a unit cell. The structure, solved by the heavy-atom method, was refined to R = 0.065 for 578 reflections. The geometry of sulfur atoms around Mo(IV) has an approximately D_{2d} configuration with two distinct SMoS angles (average 116.9 and 95.6°) and a single MoS distance (2.235 (3) Å).

So far homoleptic tetracoordinate molybdenum(IV) compounds MoL_4 remain a rarity. Thermally stable $Mo(NR_2)_4$ (R = Me, Et) and relatively unstable $Mo(OR)_4$ (R = t-Bu, t-$BuCH_2$) derived therefrom are well-known[2,3] and constitute rare examples of monomeric, diamagnetic tetracoordinate d^2 ions. Conspicuously, tetrakis(thiolato)molybdenum(IV) compounds have not been reported yet. Closely related may be $Mo(SCH_2CH_2SCH_2CH_2S)_2$ which is, however, a hexacoordinate trigonal prismatic Mo(IV) compound.[4] We have been interested in obtaining $Mo(SR)_4$ since it would serve as a potential starting material for molybdenum sulfur compounds having no oxo ligands. In the molybdenum–sulfur chemistry, chelating disulfur ligands such as dithioacid (dithiocarbamate and xanthate) or dithiolate are commonly used.[5] Complexes thus obtained assume higher coordination numbers than four[5] and in general are rather inert. So that a new thiolato molybdenum family having no oxo ligands could be developed, more labile sulfur complexes are apparently needed as starting material. This paper describes the first successful preparation of a tetrakis(thiolate) compound, Mo(t-BuS)$_4$, and its molecular structure as determined by a single-crystal X–ray analysis. This compound indeed was found to be substitution active providing accesses to a variety of molybdenum thiolate compounds.

Experimental Section

Physical Measurements. All manipulations of air-sensitive molybdenum complexes were carried out under a nitrogen atmosphere. IR and UV–visible spectra were recorded on a Hitachi Model 295 and Hitachi EPS-3T spectrometer, respectively. ^1H NMR were recorded with a Jeol JNM-4H-100 or Jeol JNM-PMX-60. Cyclic voltammetric measurements were made with a Hokuto Denko Potentiostat Model HA-201 at 25 °C with use of DMF solutions containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Materials. Anhydrous $MoCl_4$ was prepared from $MoCl_5$ (Climax Molybdenum Co.) according to a literature method.[6] *tert*-Butyl mercaptan (Nakarai Chemical Co., Ltd.) was distilled before use. *tert*-Butyl

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