Reaction of Alkynes with a Methylnickel Complex: Observation of a Cis Insertion Mechanism Capable of Giving Kinetically Controlled Trans Products

Sir:

The commonly accepted mechanism for the 1,2 addition of transition metal hydrides and alkyls to alkynes and alkenes involves concerted cis addition. Recently, however, products that result from trans addition have been observed in a number of cases.[1] In one of these an intricate mechanism, involving a highly organized trans addition transition state, was postulated and discussed at some length.[2] Two recent papers also report the observation of insertion of metal alkyls with trans mechanisms.[3]

We report here the facile reaction of both internal and terminal acetylenes with methyl(acetylacetonato)(triphenylphosphine)nickel (**1**) (Scheme I). In all cases this reaction gives different kinetic and thermodynamic ratios of *E* and *Z* vinylnickel products.[3c,d] The product of trans addition is kinetically predominant for some acetylenes. Nevertheless, we have obtained evidence that the mechanism of this reaction involves initial cis addition, giving an intermediate which forms *E* and *Z* products by kinetically controlled pathways.

$Ni(acac)(PPh_3)CH_3$ (**1**) was prepared as a yellow-brown crystalline solid by the method of Cotton et al.[4] for the corresponding ethyl complex, and was purified by recrystallization from toluene–hexane mixtures: mp 150–152 °C dec; ^1H NMR (C_6D_6) δ 7.82–7.10 (complex, 15 H, PPh_3), 5.32 (s, 1 H, acac-H), 1.98, 1.48 (s, 3 H each, acac-CH_3's), 0.15 ppm (s, 3 H, Ni-CH_3).[5] Anal. Calcd for $C_{24}H_{25}O_2NiP$: C, 66.25; H, 5.79; Ni, 13.49. Found: C, 65.92; H, 5.85, Ni, 13.65. **1** reacts rapidly with a number of acetylenes at room temperature[6] to give in nearly quantitative yield a single vinylnickel complex as product, as determined by NMR. These include diphenylacetylene, phenyl-1-propyne, phenylacetylene, and *tert*-butylacetylene. Internal alkyl acetylenes such as 2-butyne and 3-hexyne also react with **1**; in these cases, however, mixtures of products result. The vinylnickel complexes **2** may be treated with either $LiAlH_4$ or acid to give mixtures of *E* and *Z* olefins in high yield. In this manner it was possible to determine that terminal acetylenes give exclusively addition of the methyl to the terminal carbon, while phenylacetylene and phenyl-1-propyne give the product with the phenyl group next to the nickel atom. Other reagents (e.g., CO/CH_3OH; I_2, CH_3Li, $Al(CH_3)_3$) also convert the vinylnickel complexes into organic products (Scheme I).

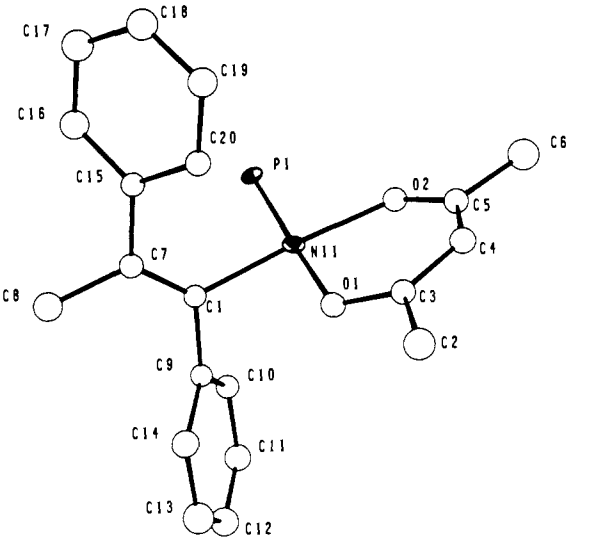


Figure 1. ORTEP drawing of (*Z*)-(acac)(PPh_3)Ni[(Ph)C=C(Ph)(CH_3)] (**3**). Some selected distances and angles: distances, Ni(1)–P(1) = 2.178, Ni(1)–O(1) = 1.910, Ni(1)–O(2) = 1.923, Ni(1)–C(1) = 1.897, C(1)–C(7) = 1.327, C(1)–C(9) = 1.468, C(7)–C(8) = 1.527, C(7)–C(15) = 1.482 Å; angles, Ni(1)–C(1)–C(7) = 123.95, Ni(1)–C(1)–C(9) = 125.93, C(1)–C(7)–C(8) = 123.56°.

Scheme I

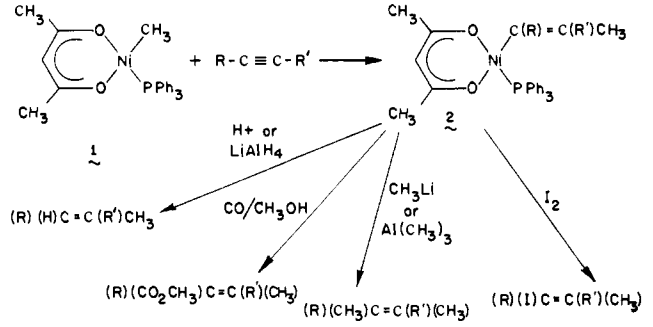
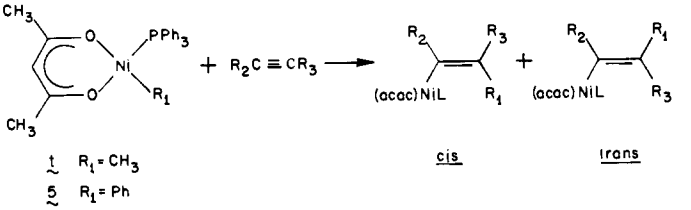


Table I. Stereochemistry of Addition of Nickel Complexes to Alkynes



1 $R_1 = CH_3$
5 $R_1 = Ph$

reaction	R_1	R_2	R_3	kinetic product, % cis	kinetic product, % trans	thermodynamic product, % cis	thermodynamic product, % 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[a]	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] See ref 11. [b] In these reactions the rate of isomerization of the kinetic product is competitive with the rate of addition, making the numbers approximate.

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complex with an excess of acid gave a mixture of (*E*)- and (*Z*)-1,2-diphenylpropenes. Although yields of these olefins were quantitatively based on **1**, mixtures of the two stereoisomers were always formed, preventing the use of protonation for the determination of the stereochemistry of **3**. Other methods for converting the vinyl complex into organic compounds also gave mixtures of isomers. However, some of these reactions gave predominantly *E* products (those having phenyl groups trans), suggesting that **3** is a (*Z*)-vinyl complex (i.e., the trans addition product). Furthermore, heating a solution of **3** in benzene-d_6 to 56 °C for 1.25 h, or allowing it to stand at room temperature for several days, converted it partially into a new vinyl complex (**4**). The similarity of **3** and **4** has so far prevented separation of the two complexes, but, on the basis of its NMR, **4** appears to be the *E* isomer (phenyl groups cis) of **3**. **4**: ^{1}H NMR (C_6D_6) δ 5.32 (s, 1 H, acac-H), 3.42 (d, J = 1.5 Hz, C=C(CH_3)), 1.92, 1.35 (s, 3 H each, acac-CH_3's), in addition to phenyl protons. The *Z*/*E* ratio remained unchanged after reaching a value of 3.0:1, indicating that equilibrium had been reached. The fact that such an equilibrium can be established, at a rate considerably slower than that of the initial addition, indicates that **3** is the kinetic production of the reaction.

The unusual nature of this result prompted us to confirm the structural assignment of **3** by X-ray diffraction. **3** was conclusively determined to be the *Z* isomer by X-ray crystallography on a single crystal obtained from a toluene–hexane solution.[8] An ORTEP drawing of **3** (excluding the phosphine phenyls) is shown in Figure 1.

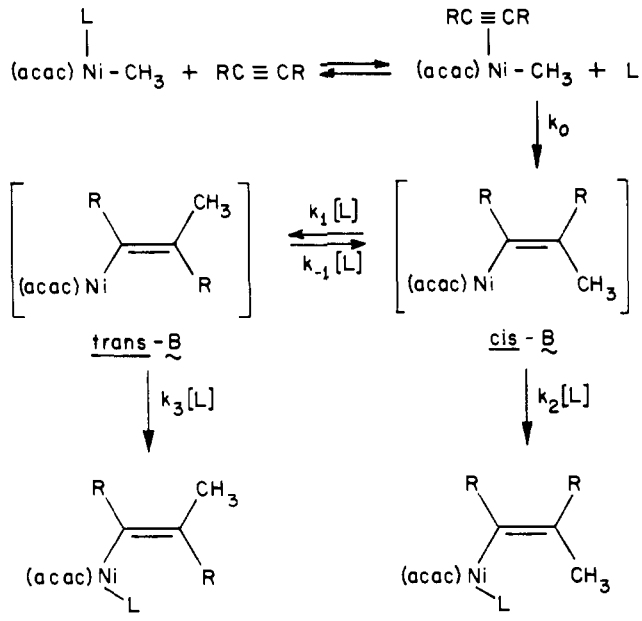
In addition, Ni(acac)(PPh_3)C_6H_5 (**5**)[9] was found to react with PhC≡CCH_3 to give exclusively **3** as kinetic product.[10] It is clear that the reaction of **1** with PhC≡CPh and **5** with PhC≡CCH_3 must therefore involve a common intermediate for which **3** is the sole kinetic product.

The strong downfield shift of the NMR absorption for the vinyl methyl cis to the nickel has allowed us to assign the stereochemistry of addition for a number of acetylenes. These results, summarized in Table I, demonstrate several important points: (a) depending upon the alkyne, either the *E* or *Z* isomer can be the favored product; (b) the subsequent, and slower, isomerization of the initially obtained products to an equilibrium ratio of isomers establishes they are the result of kinetically controlled pathways; (c) the observation of more cis than trans addition in reactions 3 and 4 (Table I) suggests that the insertion step proceeds in a cis manner; (d) the inversion of the product distribution in reactions 3 and 4 rules out the possibility that an isotope effect is the cause of the observed predominance of cis addition.

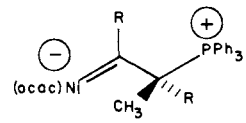
The effect of added phosphine on the course of these reactions is of some interest. By elemental and spectral analysis, **1** is clearly a monophosphine complex in the solid state and in solution. Observation of an unsplit singlet for the nickel methyl resonance in the ^{1}H NMR indicates that phosphine is exchanging rapidly on the NMR time scale.[12] Addition of excess PPh_3 to a benzene solution of **1** leads to broadening of the initially nonequivalent acac methyl signals, but *no* change is observed in either the unique acac hydrogen signal or the nickel methyl resonance. We conclude, therefore, that solutions of **1** and excess phosphine do not contain any appreciable concentration of the bis phosphine complex isolated by Yamamoto and co-workers.[13] Nevertheless the presence of excess phosphine strongly inhibits the reaction of **1** with alkynes. Thus it appears the initial step in the reaction involves reversible substitution at nickel of phosphine by alkyne. However, large changes in the concentration of PPh_3 produce only a very small effect on the kinetic *E*/*Z* ratio of vinylnickel products formed in the insertion reaction.[14]

We cannot rigorously rule out the operation of parallel concerted cis and trans addition pathways, where slight

Scheme II



changes in the structure of the alkyne involved can strongly affect the relative rates of cis and trans addition. However, the predominance of the trans addition pathway operating exclusively with **1** and PhC≡CPh, combined with the necessity of postulating a completely reversed preference in the reaction of **5** with PhC≡CCH_3 to give the *same* product (as well as the lack of any consistent trend in the effect of changes in alkyne structure upon the stereochemistry of other additions; cf. Table I), makes this possibility seem unlikely. The appearance of an identical product from two different pathways is better accommodated by the intervention of a common intermediate or set of intermediates. A mechanism of this type that accounts reasonably for our results (Scheme II) involves cis addition to give an unsaturated vinylnickel species *cis*-B. *cis*-B may then either add ligand to give the observable (coordinatively saturated) cis addition product, or isomerize to *trans*-B. The observation of more cis than trans addition product in reactions 3 and 4 indicates that *cis*-B is formed first, and that k_1 and k_2 are comparable. *The lack of dependence of the product ratio upon* [PPh_3] *suggests strongly that the rapid cis-B/trans-B isomerization is catalyzed by phosphine.* This can occur if PPh_3 has two modes of addition to the intermediate B. Addition at the nickel atom gives product, whereas reversible addition to the β-vinyl carbon leads to complex **8**, and results in



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isomerization of the double bond. Whatever the mechanism of cis/trans isomerization, however, our results require the following cautionary note concerning stereochemical studies in organometallic addition reactions: The observation of a given stereochemical mode of addition, *even when the observed complex is found to be the kinetic product of the reaction,* does not necessarily mean that the crucial insertion step proceeds with that same stereochemistry.

Acknowledgments. We are grateful to Dr. Richard Marsh for extensive assistance in the X-ray diffraction study. We also thank the National Institutes of Health (Grant GM 12459) for financial support.

Supplementary Material Available: ORTEP drawing of (*Z*)-Ni(acac)(PPh_3)[C(Ph)=C(Ph)(CH_3)] (**3**), excluding the phosphine

phenyls (Figure 1), stereoview of Figure 1 (Figure 2), ORTEP drawing of full asymmetric unit (Figure 3), schematic of atom numbering scheme (Figure 4), interatomic distance and angles (Table 1), structure factor list (Table 2), fractional coordinates (Table 3) (54 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) H. C. Clark and K. E. Hine, *J. Organomet. Chem.*, **105**, C32 (1976); N. C. Rice and J. D. Oliver, *ibid.*, **145**, 121 (1978). (b) B. L. Booth and A. D. Lloyd, *ibid.*, **35**, 195 (1972). (c) D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. A*, 1765 (1968). (d) See also 3a and references therein.

(2) (a) A. Nakamura and S. Otsuka, *J. Mol. Catal.*, **1**, 285 (1975/6); (b) S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, 245 (1976).

(3) (a) M. Michman and S. Weksler-Nussbaum, *J. Chem. Soc., Perkin Trans. 2*, 872 (1978). (b) J. J. Eisch, R. J. Manfre, and D. A. Konar, *J. Organomet. Chem.*, **159**, C13 (1978). (c) We are sympathetic to (if not a little amused by) a referee's comment concerning the current IUPAC ("*E*/*Z*") rules[3d] for naming alkenes ("define for reader not up on lingo"), but we have felt obligated to utilize this system because it has become accepted for naming organic compounds. In order to minimize confusion, we have used *E*/*Z* nomenclature when referring to the stereochemistry of *compounds*, and cis/trans nomenclature for referring to the stereochemistry of addition *processes* (i.e., cis addition can in principle give either an *E* or *Z* product, depending upon the substituents involved). (d) IUPAC Commission on Nomenclature of Organic Chemistry, *Pure Appl. Chem.*, **45**, 11 (1976).

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

(5) **1** is air stable as a solid, but rapidly decomposes in solution. It is soluble in aromatic and ether solvents and insoluble in hydrocarbons. All of the reactions of **1** were carried out using standard inert atmosphere techniques in thoroughly dried solvents.

(6) These reactions are first order in **1** and alkyne. Using a mixture of 1 and **1**-d_3 it was possible to determine that k_H/k_D is ~1.2.

(7) The assignment of this doublet of doublets as the *o*-phenyl protons on the β-phenyl remains tentative. This unusual downfield absorption has also been observed in similar complexes containing PCy_3 instead of PPh_3.

(8) Space group $P\bar{1}$; a = 17.892, b = 12.339, c = 16.732 Å; α = 106.27, β = 73.17, γ = 110.77°; Z = 4. The two nickel and two phosphorus atoms were refined anisotropically; the other 80 non-H atoms were refined isotropically; R = 0.082, goodness of fit = 1.54 for all 5258 observed reflections ($2\theta \leq 38°$), R = 0.053 for 3198 reflections ($F_o > 3\sigma(F_o)$). Intensity data were collected on a Syntex $P2_1$ diffractometer with monochromatic Mo Kα radiation using θ–2θ scanning.

(9) **5** was prepared by the method of Yamamoto et al.[15] from $Ni(acac)_2$, PPh_3, and $AlPh_3{\cdot}Et_2O$ (1:1.05:0.33) and purified by extensively washing the crude product with ether: ^1H NMR (C_6H_6) δ 7.55, 7.0 (complex, PPh_3), 6.8 (complex, Ni–Ph), 5.30 (s, 1 H, acac–H), 1.72, 1.40 (s, 3 H each, acac-CH_3).

(10) This reaction proceeds at a rate comparable to the rates of reaction for **1** with PhC≡CPh and PhC≡CCH_3 ($t_{1/2}$ < 10 min at 23 °C).

(11) **1**-d_3 was prepared in the same manner as **1**, using $Al(CD_3)_2OCH_3$. 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.

(12) J_{PH} = 5 Hz in the analogous complex Ni(acac)$(PCy_3)CH_3$, where the phosphine is not as labile (cf. ref 16).

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

(14) The cis/trans addition ratio of 1.57 (±0.1), obtained in the reaction of **1**-d_3 (0.1 M) with PhC≡CCH_3 (0.1 M) in benzene-d_6 at room temperature, became 1.67 (±0.1) for 0.1 M added PPh_3 and 1.85 (±0.1) for 1.0 M added Ph_3 (both at 60 °C).

(15) K. Maruyama, T. Ito, and A. Yamamoto, *J. Organomet. Chem.*, **155**, 359 (1978).

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Electroreduction of Retinal. Formation of Pinacol in the Presence of Malonate Esters

Sir:

Reductive electrodimerization of α,β-unsaturated carbonyl compounds most frequently results in a mixture of dimeric products.[1-10] In contrast, we have accomplished the high-yield electrosynthesis of retinal pinacol (III) from the one-electron reduction of retinal (I) in acetonitrile. This electrosynthesis is successful only in the presence of carbon acids such as diethyl malonate (II); electrodimerization of retinal in solutions containing water, phenol, or acetic acid leads to a mixture of less-conjugated dimeric products. Thus, the use of malonate esters as proton donors demonstrates a new method for directing the pathway of electrodimerization. Procedures for coupling unsaturated carbonyl compounds are of particular significance—in the case of retinal, pinacolization provides a useful synthetic route to the C_{40} carotenoids.

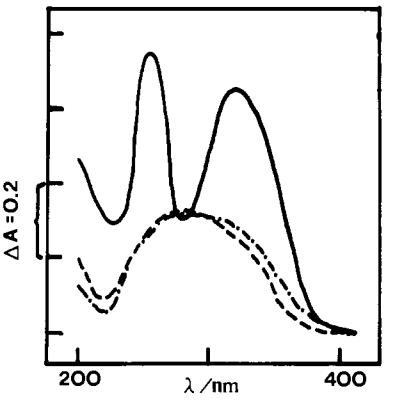

Figure 1. Spectra of dimeric products resulting from electrolysis of 2.05 mM retinal at the first reduction wave in the presence of different proton donors in an OTTLC. All solutions were 0.5 M TBAP in acetonitrile. Proton donor concentrations follow: (– · –) 1000-fold excess water; (– – –) 2-fold excess acetic acid; (—) 5-fold excess diethyl malonate.

High yield of the "head-to-head" coupling products can be obtained by chemical reduction of retinal with a zinc amalgam to form pinacol[11] or by reduction with a $LiAlH_4$–$TiCl_3$ reagent to form β-carotene.[12] However, previous electrochemical attempts to synthesize pinacols from retinal[9] and related compounds[7,8] have been markedly unsuccessful. Electroreduction of retinal in acetonitrile with tetra-*n*-butylammonium acetate yields 11% pinacol.[9] Electrochemical reduction of 3-methylcrotonaldehyde in pH 5.00 acetate buffer results in a pinacol yield of 10%.[7] Similar quantities of pinacol are obtained in the reduction of geranial and farnesal in aqueous, micelle, or ethanolic solutions.[8] Electroreductive pinacol formation has been achieved only when the β position is totally blocked (e.g., acetophenone[13]) or, in some cases, if there is steric hindrance at the β position (e.g., 71% yield of pinacol by electrodimerization of β-ionone[9]). Our unique electrochemical route for pinacolization of retinal demonstrates that judicious selection of proton donor results in high yield of the desired product in a rapid, one-step synthesis.

Using cyclic voltammetry with a hanging mercury drop electrode, as well as spectroelectrochemistry, we have examined the electrochemical behavior of retinal in acetonitrile with tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte.[14] Spectroelectrochemistry was performed with an optically transparent thin-layer cell (OTTLC) containing a gold minigrid working electrode.[14] Retinal (λ_{max} 375 nm) is reduced to the radical anion (λ_{max} 515 nm ($E_{p/2}$ −1.33 V)) in a quasi-reversible, one-electron process. With equal amounts of diethyl malonate and retinal, the latter undergoes an irreversible, one-electron reduction and the absorption spectrum after electrolysis shows peaks at 325 and 260 nm (Figure 1). The absorbance at 325 nm corresponds to that for retinal pinacol in 89% yield.[11] The peak at 260 nm is ascribed to the diethyl malonate anion (IV); a mixture of diethyl malonate and tetraethylammonium hydroxide in acetonitrile–TBAP has the same absorption maximum. Consumption of 1 mol of protons/mol of retinal reduced is confirmed by the appearance of a one-electron wave for oxidation of diethyl malonate anion that is equal in height to the reduction wave for retinal. The

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