4,4,6,6,8,8-hexamethyl-2,2-diphenyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**6**). MS: *m/z* 484 (M^+, 32.2%), 469 (M^+ - Me, 40.24%), 407 (M^+ - Ph, 14%), 251 ($Me_6Si_4O_3^+$, 100%) with appropriate isotope distribution. ^1H NMR ($CDCl_3$): δ 7.1 (s, broad, C_6H_5), 0.2 (s, broad, Si-Me). ^{13}C NMR ($CDCl_3$): δ 137.4, 134.1, 130.0, 127.8 ($-C_6H_5$), 1.0 ($-CH_3$). ^{29}Si NMR ($CDCl_3$): δ 3.3, -16.6, -17.1, -17.7. ^{77}Se NMR ($CDCl_3$): δ -234. An analytically pure sample was obtained by preparative GC. Anal. Calcd for $C_{18}H_{28}O_3SeSi_4$: C, 44.71; H, 5.84. Found: C, 45.07; H, 5.98.

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Insertion of Acetylenes into Carbon–Hydrogen Bonds Catalyzed by Rhodium–Trimethylphosphine Complexes

William T. Boese and Alan S. Goldman*

Department of Chemistry, Rutgers—The State University of New Jersey,
New Brunswick, New Jersey 08903

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The insertion of terminal acetylenes ($RC{\equiv}CH$) into benzene C—H bonds has been found to be photochemically ($\lambda > 350$ nm) catalyzed by $Rh(PMe_3)_2(CO)Cl$. Chemical yields (e.g. R = *t*-Bu, 58%; R = *p*-$MeOC_6H_4$–, 95%) and turnover numbers (>200/Rh) are fairly good, although the quantum efficiency is low (e.g. λ = 366 nm, R = *p*-$MeOC_6H_4$, $\varnothing = 3.6 \times 10^{-3}$). Crossover experiments reveal that both the H atom and Ph group added to the triple bond are derived from the same molecule of benzene. The orientation of addition is dependent upon the R group; for R = aryl, exclusively 1,1-substituted (branched) olefins are produced, while for R = *n*-propyl or *tert*-butyl a mixture of 1,1- and 1,2-substituted (linear) olefins is formed. The linear olefins are those resulting from exclusively syn addition across the $C{\equiv}C$ bond. These results are consistent with a mechanism that involves a concerted addition across a triple bond; in particular addition of the Rh—H bond of a hydridophenylrhodium species is suggested. Additional results consistent with such a pathway include a primary isotope effect ($k_{C_6H_6/C_6D_6} = 1.4$) and a reactivity order among alkynes (and olefins) that is inconsistent with a variety of nonconcerted pathways such as transfer of hydrogen atom or hydride. Labeling experiments reveal that the stereochemistry of the branched olefinic products is that resulting from anti addition across the triple bond; possible mechanistic implications are discussed. In a nonphotochemical reaction, $[(Rh(PMe_3)_2Cl]_2$ efficiently catalyzes the dimerization of terminal acetylenes by insertion into the acetylenic C—H bond. Similar reactivity patterns are found between this reaction and the $Rh(PMe_3)_2(CO)Cl$-catalyzed reaction with benzene. All products from the dimerization result from syn addition.

A large body of reactions of hydrocarbons with low-valent soluble transition-metal complexes has been developed in the past decade.[1] Progress toward the goal of *catalytic* functionalization has also been made in this field but has been considerably more limited.[2-6] Notably, several such examples have been revealed by complexes of the form $RhL_2(CO)Cl$ (L = PPh_3,[7] PMe_3[8-13]). These have been found to photochemically catalyze a variety of C—H bond functionalization reactions including arene[7,8] and alkane[8] carbonylation, aldehyde decarbonylation,[7,8] alkane[9,13] and arene[10] dehydrogenation and transfer dehydrogenation, and the insertion of isocyanides into benzene C—H bonds.[11] The insertion of olefins into C—H bonds with very low yields (<5%)[14] has also been reported.[12] Herein

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(1) For reviews of this area see: (a) Bergman, R. G. *Science (Washington D.C.)* **1984**, *223*, 902. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (e) *Activation and Functionalization of Alkanes*; Hill, C., Ed.; John Wilery and Sons: New York, 1989 (see also references therein).

(2) Notable alkane functionalizations catalyzed by low-valent soluble transition-metal systems include those reported by Felkin,[3] Crabtree,[4,5] and Jones.[6] Also see reference 1e.

(3) (a) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243–1244. (b) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 788–789. (c) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Lin, Y. *Tetrahedron Lett.* **1985**, *26*, 1999–2000. (d) Cameron, C.; Felkin, H.; Fillebeen-Khan, T.; Forrow, N. J.; Guittet, E. *J. Chem. Soc., Chem. Commun.* **1986**, 801–802.

(4) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816–817.

(5) (a) Burk, M. J.; Crabtree, R. H.; McGrath, D. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1829–1830. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032.

(6) (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (b) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (c) Reference 1e, pp 111–150.

(7) (a) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764–767. (b) Kunin, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 535–536. (c) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124–2129. (d) Gordon, E. M.; Eisenberg, R. *J. Mol. Catal.* **1988**, *45*, 57–71.

(8) (a) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758–759. (b) Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 249–252. (c) Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 1113–1116. (d) Sakakura, T.; Sasaki, K.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 155–158.

(9) (a) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. *Chem. Lett.* **1988**, 263–264. (b) Sakakura,T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1988**, 885–888.

(10) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. *Chem. Lett.* **1987**, 2211–2214.

(11) Tanaka, M.; Sakakura, T.; Tokunaga, Y.; Sodeyama, T. *Chem. Lett.* **1987**, 2373–2374.

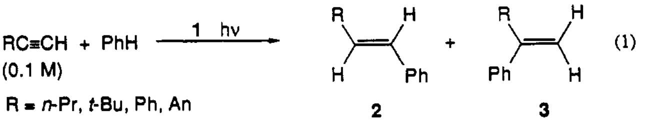
(12) (a) Sakakura, T.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1988**, 683–684. (b) Sasaki, K.; Sakakura, T.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 685–688.

(13) (a) Maguire, J. M.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088–7093. (b) Maguire, J. M.; Boese, W. T.; Goldman, M. E.; Goldman, A. S. *Coord. Chem. Rev.* **1990**, *97*, 179–192.

we report the insertion of acetylenes into the C—H bond of benzene[15,16] and some mechanistic aspects of this reaction. We also report an apparently related reaction that is thermally catalyzed by the complex $[Rh(PMe_3)_2Cl]_2$, the insertion of the C≡C bond into the acetylene C—H bond.

Results and Discussion

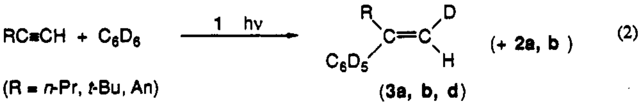
Insertion of Acetylenes into Phenyl-Hydrogen Bonds. Irradiation ($\lambda > 350$ nm) of a benzene solution (50 °C) of terminal alkynes and $Rh(PMe_3)_2(CO)Cl$ (**1**) results in the insertion of the alkyne into a benzene C—H bond;[17] this reaction may also be considered as the hydrophenylation of the alkyne (eq 1). Yields[17] and product distributions indicated are for the reactions of 0.1 M alkyne solutions. A solution with an initial AnC≡CH (An = p-$MeOC_6H_4$) concentration of 0.5 M afforded 225 turnovers (90% yield of **3d**; $[1]_0 = 2.0$ mM). The infrared spectrum revealed that 0.8 mM **1** was remaining after completion of the reaction.



2 **3** (1)

(An = p-$MeOC_6H_4$-)	R = n-Pr	**2a** (68%)	**3a** (14%)
	R = t-Bu	**2b** (48%)	**3b** (10%)
	R = Ph	**2c** (0%)	**3c** (90%)
	R = An	**2d** (0%)	**3d** (95%)

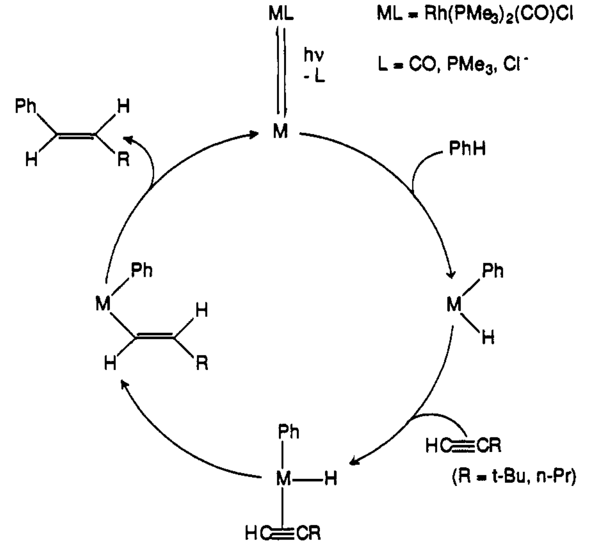
Less than 2% cis isomers of **2a** and **2b** were observed in the early stages of reaction 1 (<25% completion); i.e., addition to give 1,2-substituted olefins occurs with syn stereoselectivity (some isomerization occurred subsequently). The reaction of RC≡CH (R = n-Pr, t-Bu) with C_6D_6 afforded (E)-RDC=$CHPh_{d5}$ (**2a**,**b**-d_6).[18] The formation of **3a**,**b**,**d** also proceeds stereoselectively (>95%), but in an anti fashion,[18,19] as shown in eq 2. The reaction of AnC≡CD with C_6H_6 was found to give (E)-Ph(An)C=CHD (D trans to An).[19]



(**3a**, **b**, **d**) (2)

GC-MS analysis of the products of reactions of n-PrC≡CH or AnC≡CH with C_6H_6/C_6D_6 mixtures (taken to 10% completion), revealed that both the H(D) atom and the phenyl group that added to the triple bond are derived from the same molecule of benzene. Two major isotopomers of each product (**2a** and **3a**,**d**) were found, with mass spectra identical with those of products formed in separate experiments with pure C_6H_6 and C_6D_6, respectively. Thus, within the limits of our detection (ca. 2%),[20] *there is no formation of crossover product.*

Scheme I. Possible Mechanistic Pathway for Formation of Products 2 (Eq 1)



In competition experiments of RC≡CH (50 mM) versus PhC≡CH (50 mM), the arylacetylenes were found to be markedly more reactive than n-PrC≡CH and t-BuC≡CH; the observed reactivity order is An (2.7) > Ph (1) > n-Pr (0.06) > t-Bu (0.04). In independent runs ([RC≡CH] = 100 mM) the relative reactions rates are An (1.8) > Ph (1) > n-Pr (0.9) > t-Bu (0.5). Where R = An the quantum yield (366 nm), $\varnothing = 3.6 \times 10^{-3}$, was measured. Neither PhC≡CPh nor HC≡CC(O)OMe were found to undergo reaction 1. 1-Pentene showed no insertion products, while styrene underwent addition very slowly to give $PhCH_2CH_2Ph$[21] (5% yield).

In independent runs the rate of the reaction with RC≡CH (R = An, Hx; Hx = n-C_6H_{11}) was identical with the rate using RC≡CD. A competition experiment employing a 1:1 mixture of HxC≡CH and HxC≡CD also showed no deuterium isotope effect. For the reaction of AnC≡CH in a 1:1 mixture of C_6H_6 and C_6D_6, a kinetic isotope effect of 1.4 was found.

The rate of reaction 1 is found to vary linearly with irradiation intensity. Although irradiation ($\lambda > 350$ nm) of the reaction solution results in a slightly increased absorbance in the visible region (ca. 380–450 nm), when the resulting colored mixture was subsequently irradiated with wavelengths not absorbed by pure **1** ($\lambda > 420$ nm), no additional product was formed. Neither did the long-wavelength light have any effect on the reaction in experiments in which the sample was simultaneously irradiated with UV (366 nm) light.

The above observations and the reported photochemical reactivity with benzene[22] are consistent with a "one-photon" mechanism of the form shown in Scheme I. Note

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[14] We have calculated yields as moles of product per mole of limiting organic reagent.

[15] Preliminary accounts of this work have been given: (a) 23rd Middle Atlantic Regional Meeting of the American Chemical Society, Cherry Hill, NJ, 1989; INOR 86. (b) 199th National Meeting of the American Chemical Society, Boston, MA, 1990; INOR 430.

[16] During the course of this work, reaction 1 was reported independently: Tokunaga, Y.; Sakakura, T.; Tanaka, M. *J. Mol. Catal.* **1989**, *56*, 305–314.

[17] Products were identified by GC, GC-MS, and ^1H NMR spectroscopy in comparison with literature values and/or authentic samples. Yields are determined from ^1H NMR and/or GC data and are estimated to be accurate within 10% of the given value.

[18] Deuterated species were identified by GC-MS and by comparison of their ^1H NMR spectra and GC retention times with the corresponding perproteo species.

[19] The vinyl protons of **3d** were assigned on the basis of NOE experiments (see Experimental Section for details) as follows: δ 5.32, cis to Ph; δ 5.36, cis to An.

[20] No evidence of Ph-d_5(R)C=CH_2 (R = n-Pr, An) or Ph-d_5HC=CHPr was observed. Less than 8% Ph-h_5(R)C=CHD and Ph-h_5DC=CHPr/Ph-h_5HC=CDPr was observed, which is consistent with the occurrence of H/D exchange between RC≡CH and C_6D_6 (revealed by GC-MS analysis of the unreacted acetylene).

[21] Tanaka has found[12] that methyl acrylate can be inserted into the C-H bond of benzene also in ca. 5% yield[14] and with the same ("1,2") regiochemistry.

[22] (a) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1794–1796. (c) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5566–5567. (d) Spillet, C. T.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1932–1933.

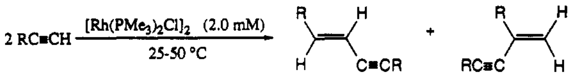
that the catalytic cycle itself is *non*photochemical, which is consistent with the very negative ΔH of reaction 1 (-40.3 kcal mol^{-1} for R = Ph[23]). In the mechanism of Scheme I, a coordinated alkyne is directly inserted into a metal–hydrogen bond (a "concerted" insertion). Alternative routes for such insertions can be envisaged. Pathways involving electron transfer followed by proton transfer have been frequently proposed.[24,25] However, such pathways would appear to be incongruous with the observed reactivity order, e.g., AnC≡CH > PhC≡CH ≫ HC≡CC(O)OMe. For similar reasons, pathways involving direct hydride transfer to free alkyne seem unlikely. A mechanism involving transfer of a hydrogen atom[26] (or a phenyl radical) cannot presently be excluded but does not appear consistent with the observed selectivity for alkynes (vs alkenes),[27,28] the high observed stereospecificity,[25] nor the complete absence of crossover products. Notably, the observed selectivity for arylacetylenes is consistent with the thermodynamics of addition (e.g. of H_2, Ph—H, or Me—H) to triple bonds; $\Delta H°$ for such reactions is anomalously negative for acetylenes (cf. alkenes) and particularly for arylacetylenes.[29] The observed selectivity may therefore imply a transition state in which the C—C bond has considerable double-bond character, as in linkages, for example, such as RhCH=C(Ph)R or RhCH=CHR.

Concerted insertions into metal–H bonds generally[25,30-32] (if not always[25]) result in syn addition. Thus the mechanism of Scheme I is consistent with the stereoselectivity observed in the formation of 1,2-substituted products, **2**. Furthermore, the observed regioselectivity is that which is expected to result from such a mechanism on the basis of steric considerations; insertion into the Rh–H bond should favor formation of the less crowded 1,2-rhodioalkylethene.[33]

The stereochemistry observed for the formation of products **3** (that resulting from anti addition) is rather enigmatic. In this context we note that higher kinetic isotope effects are found for the formation of **2** than for **3**. On the basis of experiments with C_6H_6/C_6D_6 mixtures, $k_{C_6H_6/C_6D_6}$ is found to be ca. 1.6 for the formation of **2** and 1.2 for the formation of **3**. Consistent with this result, in independent experiments (pure solvents), the ratio of products **2**:**3** from the reaction with C_6H_6 (R = *n*-Pr, 4.9:1; R = *t*-Bu, 5.6:1) is greater than that from C_6D_6 (R = *n*-Pr, 3.5:1; R = *t*-Bu, 3.8:1). One possible explanation is that alkyne insertion into the Rh–H bond (or a subsequent step) is rate-determining for the formation of **2**, whereas C–H bond formation in the production of **3** occurs after the rate-determining step. A speculative mechanism involves rate-determining anti insertion into the Rh–Ph bond[34] followed by vinyl–H reductive elimination. On steric grounds this would be expected to yield the observed 1,1-substituted products.

The nature of the species "M" in Scheme I is not yet elucidated. Precedent[13,22] suggests the product resulting from photoextrusion of CO, i.e. $Rh(PMe_3)_2Cl$. However, in view of the low quantum yield it is plausible that a different, minor photoprocess leads to the catalysis. We find that the reaction is suppressed by both CO atmosphere (25 Torr, 150-fold suppression) and the presence of excess trimethylphosphine (2.0 mM, 17-fold suppression).

Insertion of Acetylenes into Alkynyl–Hydrogen Bonds. In an effort to explore the possible catalytic activity of the $Rh(PMe_3)_2Cl$ moiety, RC≡CH (R = *n*-Pr, *t*-Bu, Ph, An) was added to a benzene solution of $[Rh(PMe_3)_2Cl]_2$. The insertion of the C≡C bond into a Ph—H bond was not observed; instead, efficient insertion into the *acetylene* C—H bond occurred in the absence of light (eq 3). (The ratio of products **4**:**5** remained constant during each reaction.)



4 **5** (3)

R = *n*-Pr	**4a** (37%)	**5a** (63%)
R = *t*-Bu	**4b** (100%)	**5b** (0%)
R = Ph	**4c** (0%)	**5c** (100%)
R = An	**4d** (0%)	**5d** (100%)

Acetylene dimerizations of this form have received attention as potentially valuable routes to conjugated enynes,[35-37] which are of biological and synthetic importance. In particular, $Rh(PPh_3)_3Cl$[35,36] and $Pd(OAc)_2$/tris(2,6-dimethoxyphenylphosphine)[37] have been reported to catalyze such dimerization (somewhat less rapidly than $[Rh(PMe_3)_2Cl]_2$).

Compounds **4** and **5** were also found to be side products from reaction 1 and in all cases account for the remainder of alkyne unaccounted for in eq 1. Note that the regios-

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(23) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Robert E. Kreiger Publishing: Malabar, FL, 1987.

(24) (a) Jones, W. D.; Chandler, V.; Feher, F. J. *Organometallics* **1990**, *9*, 164–174. (b) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961–6972.

(25) (a) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245–282 and references therein. (b) Otsuka, S.; Nakamura, A. *J. Mol. Catal.* **1975/1976** *1*, 285 and references therein.

(26) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575–584 and references therein.

(27) For example, the transfer of a *free* H atom to ethylene (to give $C_2H_5^\bullet$, $\Delta H° = -52.2$ kcal mol^{-1}) is significantly more favorable than to acetylene (to give $C_2H_3^\bullet$, $\Delta H° = -40.3$ kcal mol^{-1}), based on the following values of $\Delta H_f°$ (kcal mol^{-1}): H$^\bullet$, 52.1; C_2H_4, 28.1; $C_2H_5^\bullet$, 28.0; C_2H_2, 54.2; $C_2H_3^\bullet$, 66.[21,28]

(28) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1989.

(29) For example the addition of H_2 to PhC≡CH is $\Delta H° = -43.0$ kcal mol^{-1} as compared with 1-butyne ($\Delta H° = -39.5$ kcal mol^{-1}), styrene ($\Delta H° = -28.1$ kcal mol^{-1}), or 1-butene ($\Delta H° = -30.1$ kcal mol^{-1}) (all values for the gas phase).[21]

(30) In particular, hydridometal acetylene complexes and coordinatively unsaturated metal hydrides (which are most likely to add to acetylenes via concerted pathways) give syn insertion products. (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 102. For some additional examples see: (b) Eaborn, C.; Farrel, N.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1973**, 766–767. (c) Trocha-Grimshaw, M. J.; Henbest, H. B. *Chem. Commun.* **1968**, 757–758. (d) Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, 2, 1555, 1561. (e) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97–104.

(31) Theoretical calculations also support the formation of syn insertion products from the concerted reactions of metal hydrides with alkenes or alkynes: Thorn, D. L.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(32) In at least one case an apparently concerted anti insertion has been shown to proceed via syn addition and subsequent isomerization: Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410–4412. This is not likely to be occurring in the formation of products **3** in view of the fact that of the two (thermodynamically equivalent) isomers only the anti addition product is initially observed.

(33) This explanation for the observed regioselectivity is strongest if the insertion step is proposed to be irreversible, which is consistent with the fact that vinyl ligands do not easily undergo β-hydride elimination.

(34) For examples of insertions of acetylenes into transition-metal–carbon bonds, see refs 1–9 in: Stack, J. G.; Simpson, R. D.; Hollander, F. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 2716–2729.

(35) Carlton, L.; Read, G. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1631–1633.

(36) Yoshikawa, S.; Kiji, J.; Furukawa, J. *Makromol. Chem.* **1977**, *178*, 1077–1087.

(37) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486–3487.

electivity pattern of reaction 3 is quite similar to that of reaction 1 and in particular that aryl-substituted acetylenes yield only branched products. None (<2%) of the cis isomer of **4** was detected in any of the reactions, in accord with syn addition of the hydrogen atom and alkynyl group across the triple bond. To determine the stereochemistry of the formation of products **5**, a benzene solution of $[Rh(PMe_3)_2Cl]_2$ (2.0 mM), $AnC{\equiv}CD$ (0.1 M), and $HxC{\equiv}CH$ (0.5 M) was reacted. The resulting homodimers were separated from the heterodimers by fractional distillation. Three (of four possible) heterodimers were formed, $(Hx)(AnC{\equiv}C)C{=}CHD$ (5e), $(HxC{\equiv}C)(An)C{=}CHD$, and *trans*-$(AnC{\equiv}C)HC{=}CH(Hx)$ (in a ratio of 2.8:2.1:1.0). The vinyl protons of **5e** were assigned on the basis of NOE experiments (see Experimental Section); the D atom is found to be cis to the $AnC{\equiv}C-$ group. Thus the stereochemistry of the addition process is stereoselectively (ca. 95%) syn (in contrast to the stereochemistry of the formation of **3**, the 1,1-substituted product of eq 1).

A reactivity order very similar to that of reaction 1 was found for reaction 3 in independent experiments ($[RC{\equiv}CH]$ = 0.1 M): An (1.6), Ph (1.0), *t*-Bu (0.05), *n*-Pr (0.03). The similar reactivity order and regiochemistry suggests that reactions 1 and 3 proceed through related pathways. The syn addition found for both sets of products (**4** and **5**) is supportive of a concerted mechanism for reaction 3. The very different selectivity for C—H bonds (i.e. Ph—H vs alkynyl—H) is unsurprising because $Rh(PMe_3)_2Cl$ is not expected to form under the conditions of reaction 3 (i.e. in the absence of light and in the presence of high concentrations of excess alkyne). Thus the initial C—H activation product, possibly of the form $Rh(PMe_3)_2Cl(H)(C{\equiv}CR)$, likely forms via intermediates other than free $Rh(PMe_3)_2Cl$. Reactions analogous to those proposed for $Rh(PMe_3)_2Cl(H)(Ph)$ could then follow.

Conclusions

In summary, rhodium–trimethylphosphine species have been found to catalyze the insertion of alkyne triple bonds into phenyl-H and alkynyl-H bonds. Several observations are consistent with a thermal catalytic cycle involving a concerted addition to the triple bond. These include the results of crossover experiments, the determination of product stereochemistry (and high stereospecificity), isotope effects for the aryl C-H bond, and an unusual reactivity order among alkynes. The stereochemistry of the 1,1-substituted products of the benzene reactions, **3**, is the only apparently incongruous observation. Further study of the scope and mechanism of these insertion reactions is currently underway.

Experimental Section

Compound **1** was synthesized by the addition of trimethylphosphine and carbon monoxide to $[Rh(C_2H_4)_2Cl]_2$.[38] $[Rh(PMe_3)_2Cl]_2$ was synthesized by the method of Werner.[39] Both compounds were characterized by infrared, ^1H NMR, and ^{31}P NMR spectroscopy and elemental analysis.[40,41] Trimethylphosphine, deuteriobenzene, deuteriochloroform, benzene, 1-pentyne, 1-octyne, phenylacetylene, and 3,3-dimethyl-1-butyne were obtained from Aldrich. (*p*-Methoxyphenyl)acetylene was synthesized by a literature method.[42] (*p*-Methoxyphenyl)acetylene-d_1 ($AnC{\equiv}CD$) and 1-octyne-d_1 were synthesized by deprotonation of the proteo compounds with 1 equiv of *n*-butyllithium, followed by deuteration with D_2O. Carbon monoxide was used as received from Matheson (99.99% grade).

All reactions were conducted in benzene, which was purified by a standard procedure to remove alkene impurities,[43] and distilled from sodium–benzophenone ketyl under argon. Alkyne substrates were distilled under vacuum and stored at −30 °C. All chemicals were maintained in a nitrogen-filled glovebox.

Gas chromatographic analyses were performed with a Varian 3400 GC equipped with a 50-m methylsilicone gum phase capillary column and a flame ionization detector. All NMR spectra were obtained with a Varian XL-200 spectrometer. GC–MS analyses were performed with a Varian 3400 gas chromatograph interfaced with a Finnigan-Mat 8230 high-resolution magnetic sector mass spectrometer, using electron ionization (70 eV).

Reactions were monitored by gas chromatography, and products were characterized by GC retention times, ^1H NMR spectra, and mass spectral analysis. The resonances of the vinyl protons (ppm) of the olefinic products and the m/e values of their parent MS peaks are as follows.

(*E*)-Phenylpent-1-ene (2a):[44] 6.09 (dt, J_{H-H} = 15.7, 6.4 Hz), 6.38 (d, J_{H-H} = 15.7 Hz); M^+ = 146.

(*E*)-3,3-Dimethyl-1-phenylbut-1-ene (2b):[45] 6.27 (s), 6.28 (s); M^+ = 160.

2-Phenylpent-1-ene (3a):[46,47] 5.26 (d, J_{H-H} = 1.4 Hz), 5.05 (d, J_{H-H} = 1.4 Hz); M^+ = 146.

3,3-Dimethyl-2-phenylbut-1-ene (3b):[46] 4.77 (s), 5.18 (s); M^+ = 160.

1,1-Diphenylethylene (3c):[48] 5.35 (s); M^+ = 180.

1-(*p*-Methoxyphenyl)-1-phenylethylene (3d):[49] 5.36 (d, J_{H-H} = 1.6 Hz), 5.32 (d, J_{H-H} = 1.6 Hz); M^+ = 210.

(*E*)-4-Decen-6-yne (4a):[50,51] 6.13 (dt, J_{H-H} = 16.1, 6.8 Hz), 5.49 (dt, J_{H-H} = 16.1, 1.6 Hz); M^+ = 136.

(*E*)-2,2,7,7-Tetramethyl-3-octen-5-yne (4b):[50,51] 6.09 (d, J_{H-H} = 16.2 Hz), 5.41 (d, J_{H-H} = 16.2 Hz); M^+ = 164.

2-Propyl-1-hepten-3-yne (5a):[50,51] 5.42 (s), 5.10 (s); M^+ = 136.

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[47] The assignment of the vinyl protons was verified by the following NOE experiment. The allylic protons (δ 2.05 ppm) were irradiated, and a 3.1% enhancement was observed for the resonance at δ 5.05 ppm, while no enhancement for the resonance at δ 5.26 ppm resulted. When the aryl protons were irradiated (δ 7.00 ppm), a 2.8% enhancement was observed for the resonance at δ 5.26 ppm and none for that at δ 5.05 ppm. Thus the cis relationship of each vinyl proton to the respective group was confirmed.

[48] Sample was compared to commercially obtained material (Aldrich).

[49] Sample was compared to authentic material synthesized from the Wittig reaction of 4-methoxybenzophenone and methyltriphenylphosphonium iodide. The assignments of the vinyl protons were made on the basis of the following NOE experiment. $(C_6D_5)(An)C{=}CHD$ was prepared (eq 2) and allowed to isomerize to a ca. 1:1 mixture upon continued irradiation. Irradiation of the $MeOC_6H_4-$ (An) protons, which are assigned as meta to the MeO group (δ 7.27 ppm), results in 3% enhancement of the vinyl proton resonance at δ 5.36 ppm and no enhancement of the δ 5.32 ppm vinyl proton resonance, which is therefore inferred to be trans to the $MeOC_6H_4$ group. (Irradiation of the $MeOC_6H_4$ protons, which are assigned as ortho to the MeO group (δ 6.72 ppm), results in no enhancement of either vinyl resonance). The validity of this approach was confirmed by conducting analogous experiments with $An(H)C{=}CH_2$, for which the assignment of the vinyl proton resonances can be determined independently on the basis of H—H coupling constants.

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2,4-Diphenyl-1-buten-3-yne (5c):[50,51] 5.74 (d, $J_{H\text{-}H}$ = 1.4 Hz), 5.68 (d, $J_{H\text{-}H}$ = 1.4 Hz); M^+ = 204.

2,4-Di(*p*-methoxyphenyl)-1-buten-3-yne (5d):[50,51] 5.79 (d, $J_{H\text{-}H}$ = 1.4 Hz), 5.75 (d, $J_{H\text{-}H}$ = 1.4 Hz); M^+ = 264.

1-(*p*-Methoxyphenyl)-3-methylenenonyne (5e):[52] 5.05 (s), 5.23 (s).

Anti addition in the case of formation of compound 3 was determined on the basis of the ^1H NMR spectra of compounds derived from C_6D_6. Photochemical experiments and quantum yield determinations were done by using apparatus previously described;[13] all photochemical reactions were maintained at 50 °C in a Pyrex oil bath. Typically, an Oriel focused beam system with a 500-W high-pressure Hg arc lamp was used as a light source.

A Corning CS 0-52 filter was used to transmit wavelengths >350 nm, corresponding to the lowest energy absorption band in the spectrum of 1, which has been assigned previously.[53] For photokinetic experiments, benzene solutions (2.0 mL) of 1 (2.0 mM) and alkyne (100 mM, unless stated otherwise) were used. Crossover experiments were done in a 2:1 mixture of C_6D_6:C_6H_6 with aliquots removed from the solution as the reaction progressed. These aliquots were analyzed by GC–MS and compared to standard samples derived from pure C_6D_6 and C_6H_6. Crossover experiments were typically allowed to proceed to <10% completion, as H/D exchange with the alkyne substrate was observed after extended periods. Thermal reactions were carried out in a thermostatically controlled bath.

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[52] The assignments of the vinyl protons were made on the basis of NOE experiments similar to those described earlier, using the perproteo compound. When the allylic protons (δ 2.10 ppm) were irradiated, a 3.1% enhancement for the vinyl resonance at δ 5.05 ppm was observed; we therefore assign this as cis to the *n*-hexyl group. When the protons of the *p*-methoxyphenyl group (δ 7.01 ppm) were irradiated, a 2.8% enhancement was observed for the other vinyl resonance at δ 5.23 ppm; we therefore assign this as cis to the *p*-methoxyphenyl group.

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Use of Dimethyl Sulfide in Organocopper Chemistry: X-ray Crystal Structures of *cyclo*-Tetrakis(μ-2-methylphenyl)bis(dimethyl sulfide)tetracopper(I) and of the Polymeric Copper Bromide Adduct Bromo(dimethyl sulfide)copper(I)

Bernd Lenders,[†] David M. Grove,[†] Wilberth J. J. Smeets,[‡] Paul van der Sluis,[‡] Anthony L. Spek,[‡]
and Gerard van Koten*[,†]

Department of Metal-Mediated Synthesis, Debye Research Institute, and Laboratory of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

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The structure of the 1:1 copper(I) bromide–dimethyl sulfide adduct ([$CuBr(SMe_2)$]) consists of a layered polymeric network. The compound crystallizes in space group $P2_1/c$ ($Z = 4$), $a = 7.161$ (1) Å, $b = 6.636$ (1) Å, $c = 11.039$ (1) Å, $\beta = 93.92$ (1)°, and its X-ray structure was refined to $R = 0.021$ for 1225 reflections ($I > 2.5\sigma(I)$). The preparation of [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$] is described; the compound crystallizes in the tetragonal space group $P4_2$ ($Z = 2$), $a = b = 14.595$ (2) Å, $c = 7.513$ (1) Å, and its X-ray structure was refined to $R = 0.025$ for 2355 reflections. The crystal structure of [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$] comprises discrete tetranuclear clusters having a virtually planar "flattened butterfly" Cu_4 core. Adjacent copper atoms are three-center two-electron bridge-bonded by a C_{ipso} atom of one *o*-tolyl group (Cu⋯Cu 2.4126 (5) and 2.4626 (5) Å) with two nonadjacent copper atoms each being further bonded to the sulfur atom of a coordinating dimethyl sulfide; i.e., there are two two-coordinate and two three-coordinate Cu(I) sites. The cluster exists in two stereoisomeric forms; one form having all the *o*-tolyl methyl groups on the same side of the Cu_4 core and a second in which these methyl groups are alternately orientated above and below this core. Variable-temperature ^1H and ^{13}C NMR spectra provide evidence for fluxionality and interconversion of various tetranuclear species in solution.

Introduction

The copper bromide reagent [$CuBr(SMe_2)$] has gained a pivotal position as the starting compound for the preparation of cuprates,[1-3] and although it is insoluble in most solvents, it does dissolve in pure dimethyl sulfide (DMS) and in organic solvents to which DMS has been added. Studies of other copper salt–Lewis base adducts with a 1:1 stoichiometry have shown that they can crystallize either in the cubane cluster form (e.g., [$CuI(PEt_3)$][4] and [$CuI(AsEt_3)$][4]) or with a "step" skeleton (e.g., [$CuBr(PPh_3)$][5]).

[†] Department of Metal-Mediated Synthesis, Debye Research Institute.

[‡] Laboratory of Crystal and Structural Chemistry.

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