Mechanism of Formation of $[(PMe_3)_3Rh(-C\equiv C-R)_2(H)]$ via C−H Oxidative Addition: Isomerization, Alkyne Exchange, and Hydride Replacement

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The mechanism of formation of *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$ from $[(PMe_3)_4Rh(Me)]$ and terminal alkyne has been studied. The initial step of the reaction is the elimination of methane and the formation of the trigonal bipyramidal complex $[(PMe_3)_4Rh(-C\equiv C-R)]$, a reaction that is complete in time of mixing at −78 °C. This intermediate undergoes an oxidative addition reaction with a second equivalent of alkyne to give *fac*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$ as the kinetic product. This *fac* isomer is not stable above −20 °C and isomerizes to the thermodynamic product *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$. *fac*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$ will exchange alkynyl groups with free alkyne, a reaction that has a lower energetic barrier than the isomerization to *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$. Density functional theory studies on all stages of the formation of *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$ have been carried out and give ground state energies in line with those experimentally observed. Once formed, *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2H]$ is configurationally stable and not prone to scrambling, although it will react with chloroform, whereupon the hydride is replaced by chloride. The initial product of this reaction is *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2Cl]$, and this compound has been studied by single-crystal X-ray diffraction. In solution *mer,trans*-$[(PMe_3)_3Rh(-C\equiv C-R)_2Cl]$ isomerizes slowly to *mer,cis*-$[(PMe_3)_3Rh(-C\equiv C-R)_2Cl]$.

Introduction

The chemistry of transition metal alkynyls has been the subject of much interest in recent years.[1,2] These compounds have been investigated for a number of technological applications, in particular as molecular wires,[3−6] polymeric systems,[7,8] catalysts for polymerization,[9,10] liquid crystals,[11−14] organometallic catananes,[15] dendrimers,[16,17] molecular scaffolds,[18] luminescent materials,[19−22] and as materials for nonlinear optics (NLO).[23−28] Some systems have received more attention than others, and in particular, those containing platinum or palladium,[11,12,20,21,27,29−33] rhodium,[13,34−36]

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(1) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.
(2) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79.
(3) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *180*, 431.
(4) Ziessel, R.; Hissler, M.; El-Ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1999**, *180*, 1251.
(5) Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121.
(6) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810.
(7) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.
(8) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123.
(9) Zhan, X. W.; Yang, M. J.; Sun, H. M. *J. Mol. Catal.* **2001**, *196*, 63.
(10) Zhan, X. W.; Yang, M. J. *J. Mol. Catal.* **2001**, *169*, 57.
(11) Kaharu, T.; Matsubara, H.; Takahashi, S. *J. Mater. Chem.* **1991**, *1*, 145.
(12) Kaharu, T.; Matsubara, H.; Takahashi, S. *J. Mater. Chem.* **1992**, *2*, 43.
(13) Rourke, J. P.; Bruce, D. W.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **1995**, 317.
(14) Kaharu, T.; Ishii, R.; Adachi, T.; Yoshida, T.; Takahashi, S. *J. Mater. Chem.* **1995**, *5*, 687.
(15) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3376.
(16) Onitsuka, K.; Iuchi, A.; Fujimoto, M.; Takahashi, S. *Chem. Commun.* **2001**, 741.
(17) Onitsuka, K.; Fujimoto, M.; Oshiri, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 689.
(18) Siemsen, P.; Gubler, U.; Bosshard, C.; Gunter, P.; Diederich, F. *Chem. Eur. J.* **2001**, *7*, 1333.
(19) Yam, V. W.-W. *Chem. Commun.* **2001**, 789.
(20) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447.
(21) Wong, W. Y.; Choi, K. H.; Cheah, K. W. *J. Chem. Soc., Dalton Trans.* **2000**, 113.
(22) Osakada, K.; Yamamoto, T. *Coord. Chem. Rev.* **1999**, *198*, 379.
(23) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.
(24) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.
(25) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.
(26) Meyers, L. K.; Ho, D. M.; Thompson, M. E.; Langhoff, C. *Polyhedron* **1995**, *14*, 57.
(27) Nguyen, P.; Lesley, G.; Marder, T. B.; Ledoux, I.; Zyss, J. *Chem. Mater.* **1997**, *9*, 406.
(28) Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. In *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symp. Ser. 455; 1991; p 605.
(29) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165.

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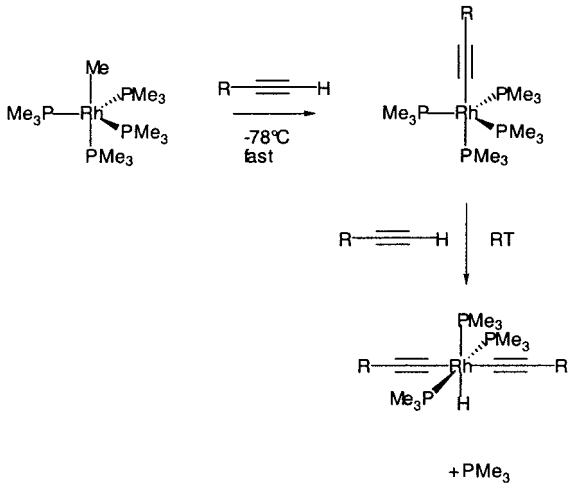
ruthenium,[37−41]rhenium,[6,19,42,43] and osmium[44] have received the bulk of the attention.

Whereas we were previously able to prepare the unsymmetrically substituted donor−acceptor *trans*-[$(PR_3)_2Pt(-C\equiv C-D)(-C\equiv C-A)$] complexes necessary for useful second-order NLO effects[27,28] (others have recently investigated the mechanism of alkynyl exchange in these systems[45]), we were unsuccessful in synthesizing related unsymmetrical octahedral Rh(III) bis(alkynyls) in the absence of their symmetrical counterparts.[46] We thus decided to investigate the mechanistic details of the reaction pathway in order to determine whether it would be possible to make the desired unsymmetrical rhodium compounds cleanly. We present the results of these investigations here.

Results and Discussion

The system we elected to study, *mer,trans*-[$(PMe_3)_3Rh(-C\equiv C-R)_2H$], is ideally set up for liquid crystalline behavior[13] and one-dimensional polymer formation,[7,8,47,48] and if two different alkynyls could be introduced, it would be appropriate for second-order NLO studies. Our previously reported route for the synthesis of these compounds simply involves the addition, at room temperature, of 2 equiv of a terminal alkyne to the rhodium precursor [$(PMe_3)_4RhMe$] (Scheme 1) and results in essentially quantitative yields.[49] The reaction can also be carried out sequentially, as the trigonal bipyramidal [$(PMe_3)_4Rh(-C\equiv C-R)$] intermediate can be isolated.[50] However, when two different alkynes were added sequentially, a statistical mixture of bis(alkynyl) complexes resulted.[46]

Scheme 1

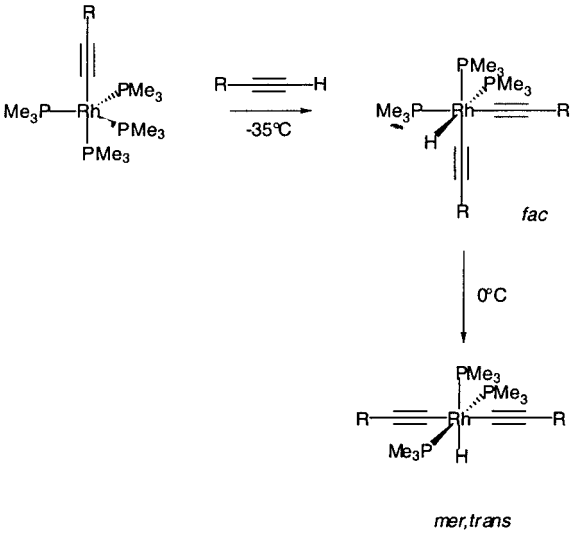


To elucidate the reaction pathway, we cooled a solution of [$(PMe_3)_4RhMe$] to −78 °C and added 1 equiv of a terminal alkyne. With both ethynyltrimethylsilane (trimethylsilylacetylene, TMSA) and *p*-methoxyphenylethyne, an instantaneous reaction occurred, liberating methane (confirmed by GC−MS) and forming [$(PMe_3)_4Rh(-C\equiv C-R)$]. While [$(PMe_3)_4Rh(-C\equiv C-R)$] compounds are fluxional on the NMR time scale at temperatures above −70 °C, they can be unambiguously assigned a trigonal bipyramidal structure with the alkynyl ligand in the axial position on the basis of low-temperature NMR spectroscopy, where two signals are observed in the ^{31}P spectrum with relative intensities 3:1 and appropriate Rh−P and P−P coupling constants. Related species have been isolated in previous work, and their solid state structures confirmed by single-crystal X-ray diffraction.[47,50]

When a second equivalent of the same alkyne was added at low temperature (−40 °C), a new species was observed in the ^1H and ^{31}P NMR spectra. The new species had two distinct phosphine ligand environments, in a 2:1 ratio, and contained a hydride. Thus for R = $-C_6H_4$-4-OMe the hydride signal at −9.42 ppm is split into a doublet with a large (196 Hz) coupling and then further split into two apparent quartets with a smaller (18 Hz) coupling. Assigning the large coupling to a *trans* phosphorus and the smaller couplings to two *cis* phosphoruses and the rhodium ($^2J_{H-P} = {}^1J_{H-Rh}$) allows us to assign the geometry of this new species as *fac*-[$(PMe_3)_3Rh(-C\equiv C-R)_2H$], as we know on the basis of ^{31}P chemical shifts that it is not the previously fully characterized *mer,trans*-[$(PMe_3)_3Rh(-C\equiv C-R)_2H$], for which the hydride resonates at −9.17 ppm. When the temperature of the reaction was maintained below −20 °C, this *fac* species was the only one that was observed to form, albeit slowly (i.e., after one week at −35 °C, less than 25% of the starting [$(PMe_3)_4Rh(-C\equiv C-R)$] was converted to this *fac* compound). When the temperature of the reaction mixture was increased to ca. 0 °C, significant quantities of *mer,trans*-[$(PMe_3)_3Rh(-C\equiv C-R)_2H$] were also observed, and eventually this became the only species present. This indicates that the *fac* isomer is the kinetic product of the reaction, with the *mer,trans* isomer being the thermodynamic product

(30) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227.
(31) Kaharu, T.; Tanaka, T.; Sawada, M.; Takahashi, S. *J. Mater. Chem.* **1994**, *4*, 859.
(32) D'Amato, R.; Furlani, A.; Colapietro, M.; Portalone, G.; Casalboni, M.; Falconieri, M.; Russo, M. V. *J. Organomet. Chem.* **2001**, *627*, 13.
(33) Diederich, F.; Faust, R.; Gramlich, V.; Seiler, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2045.
(34) Werner, H.; Nurnberg, O.; Wolf, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 693.
(35) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.
(36) Gil-Rubio, J.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 1365.
(37) Menendez, C.; Morales, D.; Perez, J.; Riera, V.; Miguel, D. *Organometallics* **2001**, *20*, 2775.
(38) Matsumi, N.; Chujo, Y.; Lavastre, O.; Dixneuf, P. *Organometallics* **2001**, *20*, 2425.
(39) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 3719.
(40) Bruce, M. I.; Low, P. J.; Costaus, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949.
(41) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293.
(42) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115.
(43) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Fallon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 11071.
(44) Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J.; Page, N. A.; White, A. J. P.; Williams, D. J.; Colbert, M. C. B.; Hodge, A. J.; Khan, M. S.; Parker, D. G. *J. Organomet. Chem.* **1999**, *578*, 198.
(45) Osakada, K.; Hamada, M.; Yamamoto, T. *Organometallics* **2000**, *19*, 458.
(46) Fyfe, H. B.; Mlekuz, M.; Stringer, G.; Taylor, N. J.; Marder, T. B. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; NATO ASI Series E; 1992; Vol. 206, p 331.
(47) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.
(48) Davies, S. J.; Johnson, B. F.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187.
(49) Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1545.
(50) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540.

Scheme 2

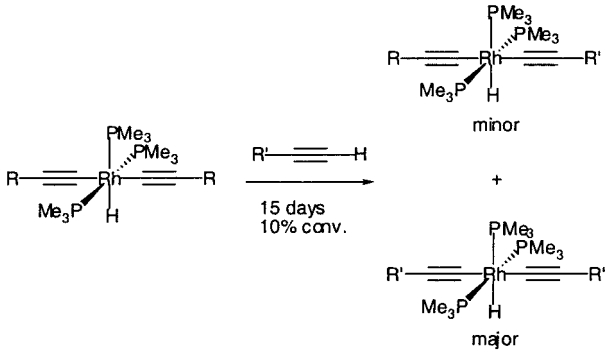


(Scheme 2). When the second equivalent of alkyne was added at room temperature, all of the [(PMe$_3$)$_4$Rh(−C≡C−R)] was converted smoothly to *mer,trans*-[(PMe$_3$)$_3$-Rh(−C≡C−R)$_2$H] with no other compounds visible in the ^{1}H and ^{31}P NMR spectra. That the *fac* isomer should be unstable with respect to the *mer,trans* is not surprising: simple arguments based on steric congestion clearly indicate a preference for the *mer,trans* isomer. DFT modeling studies (vide infra) allow us to quantify the relative energies of the isomers: the *mer,trans* isomer of [(PMe$_3$)$_3$Rh(−C≡C-Me)$_2$H] is some 21 kJ mol^{-1} more stable than the *fac*, which is in turn 9 kJ mol^{-1} more stable than the only other possibility, the *mer,cis* isomer.

When a second equivalent of a different alkyne was added to [(PMe$_3$)$_4$Rh(−C≡C−R)] at room temperature, all three possible *mer,trans*-hydrido-bis(alkynyl) compounds were formed in statistical proportions. In another experiment, 2 equiv of *p*-methoxyphenylethyne was added to [(PMe$_3$)$_4$RhMe] at −78 °C and the sample was allowed to warm to −35 °C, whereupon only [(PMe$_3$)$_4$Rh(−C≡C−C$_6$H$_4$−OMe)] and *fac*-[(PMe$_3$)$_3$Rh-(−C≡C−C$_6$H$_4$−OMe)$_2$H] were observed. When 16 equiv of TMSA was added to this mixture a new set of signals corresponding to the mixed *fac* compound was observed. On cooling to −78 °C to remove the appearance of fluxionality, signals corresponding to both [(PMe$_3$)$_4$Rh-(−C≡C−R)] (R = TMS, R = *p*-methoxyphenyl) compounds were observed. When this sample was allowed to warm to room temperature and react completely, the rhodium-containing species were dominated by *mer,-trans*-[(PMe$_3$)$_3$Rh(−C≡C-TMS)$_2$H], which accounted for some 80% of the sample. Thus, most of the −C≡C−C$_6$H$_4$−OMe groups that had been bound to rhodium had been replaced by −C≡C−TMS moieties.

To investigate further the phenomenon of alkyne exchange, a number of additional experiments were carried out. Thus, when 1 equiv of TMSA was added at room temperature to a solution of *mer,trans*-[(PMe$_3$)$_3$-Rh(−C≡C−R)$_2$H] (R = *p*-methoxyphenyl), both in the presence of 1 equiv of added PMe$_3$ and with no added phosphine present, no scrambling of the alkynyls in the rhodium species was visible in the NMR spectra until at least a week later. No significant difference in the

Scheme 3



rates of scrambling between the two samples was apparent, and after 15 days ca. 10% of the rhodium species contain the TMS group. Interestingly, the major new species contained two TMS groups, not one (Scheme 3). When 3 equiv of PEt$_3$ was added at room temperature to a solution of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$H] (R = *p*-methoxyphenyl), scrambling of the phosphines also occurred. The rate of phosphine scrambling was comparable with that of acetylene scrambling, with little evidence of scrambling after a week and noticeable quantities after 15 days. While the species were not isolated, it is obvious from the NMR spectra that PEt$_3$ incorporates into both phosphine sites, with multiple incorporation also being observed.

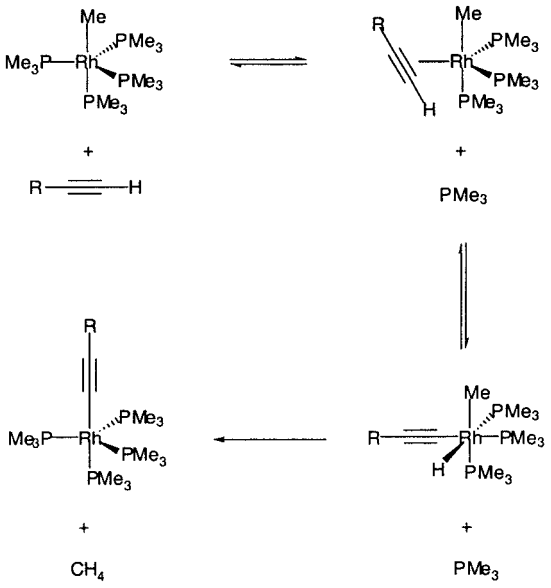
Equimolar quantities of the two symmetric *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$H] (R = trimethylsilyl and R = *p*-methoxyphenyl) compounds were mixed in toluene. At room temperature, no exchange was observed, even after one week. However, on heating the solution to 100 °C for 7 h, complete scrambling was observed, with the mixed alkynyl complex accounting for roughly 50% of the sample.

A preference for the nature of the alkynyl group has also been observed. For example, when a mixture of 2 equiv of each of *p*-methoxyphenylethyne and *p*-cyanophenylethyne was added to [(PMe$_3$)$_4$RhMe] at room temperature, a statistical mixture did not result: more than 90% of the product was *mer,trans*-[(PMe$_3$)$_3$Rh-(−C≡C−C$_6$H$_4$−CN)$_2$H].

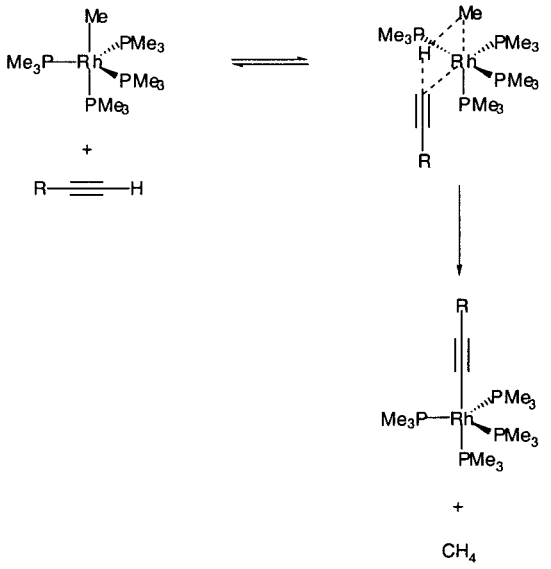
Mechanistic Implications. Considering the fact that the hydride ligand in the *mer,trans*-[(PMe$_3$)$_3$Rh-(−C≡C−R)(−C≡C−R′)H] lies mutually *cis* to both alkynyl ligands, a simple mechanism that would explain alkynyl scrambling would be one in which reductive elimination of either H−C≡CR or H−C≡CR′ was facile. This would provide both alkynes as well as both Rh(I) alkynyls species in solution. However, it is apparent from the experiments performed on isolated pure samples that *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$H] complexes are not very labile at room temperature and that any scrambling of alkynyl ligands that takes place during the attempted synthesis of the mixed compounds must involve intermediates rather than the final product. Conversely, it is also apparent that *fac*-[(PMe$_3$)$_3$Rh-(−C≡C−R)$_2$H] complexes are labile, even at −35 °C.

Before we address this issue however, we first consider the formation of [(PMe$_3$)$_4$Rh(−C≡C−R)] and its observed lability (alkyne exchange observed even at −35 °C). The reaction of [(PMe$_3$)$_4$RhMe] with alkynes is remarkably fast: complete in time of mixing at −78 °C.

Scheme 4

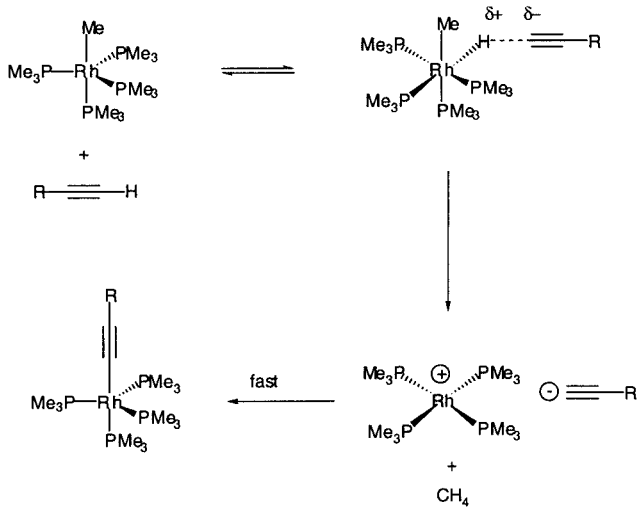


Scheme 5

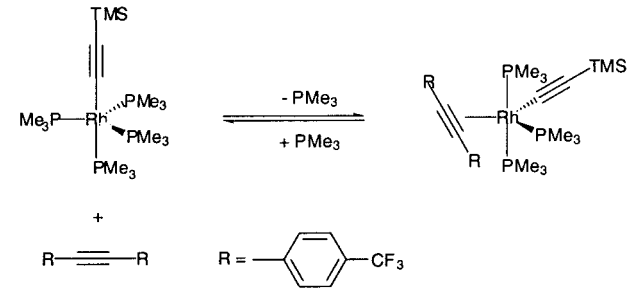


Given the fluxionality of the five-coordinate, 18-electron $[(PMe_3)_4RhMe]$ on the NMR time scale at temperatures down to −60 °C and the fact that phosphine scrambling is known to take place via both intramolecular (pseudorotation) and dissociative mechanisms, the possibility of π-coordination of an alkyne followed by an oxidative addition and then a reductive elimination of methane arises as a reaction route (Scheme 4). Alternatively a concerted σ-bond metathesis reaction such as that depicted in Scheme 5 would lead directly to $[(PMe_3)_4Rh(-C\equiv C-R)]$ and methane without phosphine dissociation. The dependence of the rate of this process on added phosphine has not been examined. A related process involving formal protonation of the electron-rich $[(PMe_3)_4RhMe]$, either at Rh or directly at the Rh−C bond by the relatively acidic sp ≡C−H moiety, reductive elimination of methane, and collapse of the ion pair, Scheme 6, cannot be ruled out. Once formed, $[(PMe_3)_4Rh(-C\equiv C-R)]$ is observed to exchange alkynyl groups with free alkyne, though this exchange is not nearly as fast as the replacement of Me, where, presumably, the

Scheme 6



Scheme 7

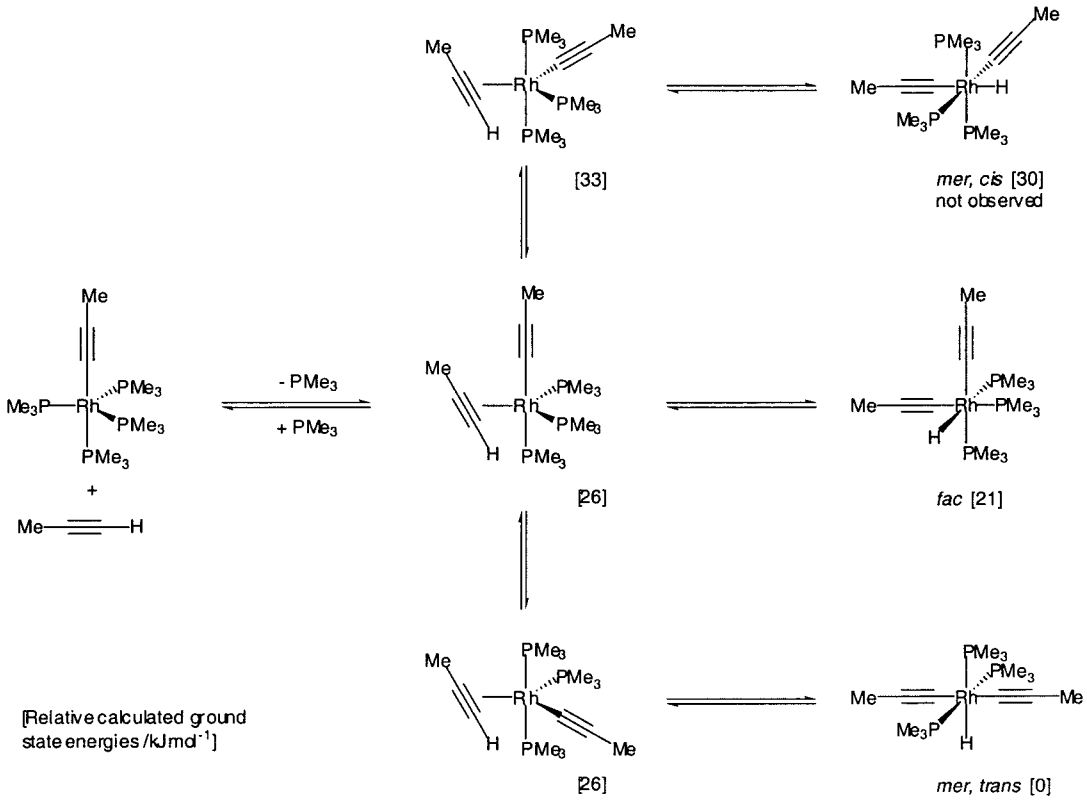


elimination of methane is a factor. Both of the proposed mechanisms outlined in Schemes 4 and 5 allow for alkyne scrambling.

That a compound such as $[(PMe_3)_4Rh(-C\equiv C-R)]$ can dissociate a phosphine ligand and π-coordinate another alkyne is not in doubt. Thus, when 1 equiv of 4-CF_3−C_6H_4−C≡C−4-C_6H_4−CF_3 was added to $[(PMe_3)_4Rh(-C\equiv C-R)]$ at room temperature, a new set of resonances appeared in both the ^{19}F and ^{31}P NMR consistent with the formation of $[(PMe_3)_3Rh(-C\equiv C-TMS)(\eta^2\text{-}CF_3-C_6H_4-C\equiv C-C_6H_4-CF_3)]$, though this new species represented less than 10% of the sample. Repeatedly removing the solvent in vacuo and redissolving the sample (so as to remove the volatile PMe_3 byproduct) led to the isolation of pure $[(PMe_3)_3Rh(-C\equiv C-TMS)(\eta^2\text{-}CF_3-C_6H_4-C\equiv C-C_6H_4-CF_3)]$ (Scheme 7). While we have been unable to obtain single crystals of this particular complex suitable for X-ray diffraction, ^1H, ^{19}F, and ^{31}P NMR, IR, and elemental analysis data support our proposed formulation. The IR stretching frequency of 1750 cm^{-1} in addition to that of 2009 cm^{-1} indicates an η^2-bound alkyne as well as the σ-bonded alkynyl ligand. We[51] and others[52] have synthesized related species with η^2-bound alkenes. In these examples, the π-bound C=C moiety lies in the equatorial plane of the distorted, but formally trigonal bipyramidal, structure, as would be expected for a π-acceptor bound to a d^8-ML_4 center.[53] The ^{19}F NMR evidence suggests that in the present case both the σ-bound alkynyl group and

(51) Chow, P.; Taylor, N. J.; Marder, T. B. Unpublished results.
(52) Fine, S. M.; Andersen, R. A.; Muetterties, E. L. Unpublished results.
(53) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

Scheme 8



the η^2-bound alkyne are equatorial, as resonances for two different CF_3 groups were observed in a 1:1 ratio. This arrangement is the same as that found for [(PMe$_3$)$_3$Rh(−C$_6$H$_4$-4-CH$_3$)(η^2-CF$_2$═CF$_2$)] by Andersen et al.[52]

A compound such as [(PMe$_3$)$_3$Rh(−C≡C−TMS)(η^2-H−C≡C−TMS)] can clearly be considered a viable intermediate in the synthesis of our rhodium(III) species, as it is one oxidative addition step away from it. The geometry of this intermediate becomes very important; thus, the *fac* isomer must arise from the intermediate with the η^2-alkyne in an equatorial and the alkynyl in an axial site. The three possible geometries of the intermediate and their resultant products, together with their ground state energies (R = Me), as calculated by DFT, are illustrated in Scheme 8. The relative energies of the points in Scheme 8 are based on solvated species, using parameters for THF (the solvent used experimentally). A preliminary comparison of the DFT calculated structure of the *mer,trans*-Rh(III) hydride and the experimentally determined geometry was favorable (Table 1): the calculated bond lengths are slightly longer than the observed ones, except for the Rh−H contact, which is apparently too short by 0.3 Å; however, this is more likely a reflection of a large experimental uncertainty in the Rh−H distance. Overall, the chosen combination of basis set and functional appears adequate, and we are confident that the calculated ground state energies are reliable.

The DFT calculations show that the ground state energies of the potential Rh(I) intermediates leading to the *fac* and the *mer,trans* complexes are the same, within experimental error, with the energy of the other intermediate being some 7 kJ mol^{-1} higher. The geometries that we arrive at for the intermediates are all distorted away from a pure trigonal bipyramidal structure and could even be considered as being closer to a distorted square-based pyramid. Figure 1 shows a perspective view of the calculated structure of the intermediate leading to the *mer,trans* product. The rate of interconversion of such five-coordinate species is known to be rapid,[54] and isomerization could easily take

Table 1. Comparison between Observed and Calculated Bond Distances (Å) and Angles (deg) in the Structure of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$(H)]

bond length	obs	calc	bond angle	obs	calc
Rh−P(1)	2.297(1)	2.35	P(1)−Rh−P(2)	161.43(3)	156.4
Rh−P(2)	2.298(1)	2.34	P(1)−Rh−P(3)	98.26(4)	105.0
Rh−P(3)	2.348(1)	2.43	P(1)−Rh−C(1)	85.8(1)	90.1
Rh−C(1)	2.019(4)	2.06	P(1)−Rh−C(9)	92.0(1)	90.4
Rh−C(9)	2.031(4)	2.06	P(2)−Rh−P(3)	99.61(4)	98.5
Rh−H(1)	1.90	1.60	P(2)−Rh−C(1)	88.3(1)	86.5
C(1)−C(2)	1.204(6)	1.23	P(2)−Rh−C(9)	92.7(1)	93.2
C(9)−C(10)	1.213(6)	1.23	P(3)−Rh−C(1)	93.0(1)	93.5
			P(3)−Rh−C(9)	87.9(1)	86.0
			C(1)−Rh−C(9)	178.6(2)	179.4
			Rh−C(1)−C(2)	173.9(2)	178.1
			Rh−C(9)−C(10)	178.4(2)	177.5

Observed data refer to R = Ph,[49] calculated data refer to R = Me.

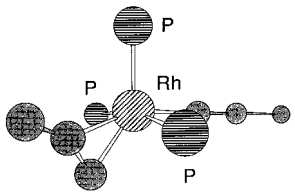


Figure 1. Model of the intermediate that would lead to the *mer,trans* compound. The methyl groups on the phosphines and all hydrogens are omitted for clarity.

place at the temperature of our reaction, potentially leading to any of the three possible Rh(III) species.

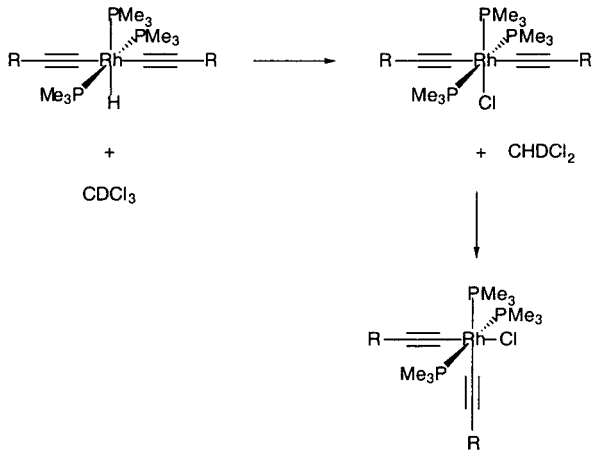
The calculated energy for *mer,cis*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2H$] is higher than that of the lowest intermediates, suggesting that such a product would be thermodynamically unstable with respect to the intermediates, in keeping with the absence of any experimental evidence for its formation. In contrast, the calculated energy for the *fac* and *mer,trans* isomers are, respectively, some 5 and 26 kJ mol^{-1} lower in energy than the intermediates. That we observed *fac*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2H$] as the kinetic product of the reaction implies that there must exist a lower energy transition state leading to *fac* than there is leading to *mer,trans*.

Isomerization of the *fac* isomer to the *mer,trans* could conceivably take place via a direct rotation of 120° of a trigonal $(PMe_3)_2(-C{\equiv}C-R)$ face of the octahedron or by C−H reductive elimination back to the Rh(I) π-complex followed by axial to equatorial isomerization of the alkynyl ligand and oxidative addition of C−H. This second scenario seems more likely, given the known high barriers to rotation at 18-electron octahedral compounds and the relatively low temperature (−20 °C) at which our isomerization occurs. A reductive elimination of the *fac* isomer back to the alkyne/alkynyl intermediate also provides a potential route for alkyne scrambling, as the intermediate would be in equilibrium with [$(PMe_3)_4Rh(-C{\equiv}C-R)$]. The relatively slow rate of scrambling exhibited by the *mer,trans* in comparison with the *fac* isomer could be ascribed simply to its greater thermodynamic stability with respect to the alkyne/alkynyl intermediate, but even more important is the high-energy transition state which must connect the *mer,trans* Rh(III) and the (η^2-alkyne)Rh(I) species.

While we have no definitive evidence that the *mer,trans* (or, indeed, the *fac*) isomer does undergo a reductive elimination back to the alkyne/alkynyl intermediate, we do have some evidence that lends support to this suggestion. When a free alkyne was added to a sample of pure *mer,trans*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2H$] containing a different alkynyl, very slow exchange was observed, with the major product having had both alkynyls exchanged (Scheme 3). This suggests that once the *mer,trans* product is in a position to exchange one alkyne, it can then exchange the second one more easily, and given the relative concentrations of the free alkynes, this leads to double exchange in the early stages of the reaction (before equilibrium concentrations are achieved). The fact that phosphine exchange takes place at a rate at least qualitatively similar to that of alkynyl exchange, yet added phosphine does not inhibit alkynyl exchange, suggests that phosphine dissociation from *mer,trans*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2H$] is not a key step in the alkynyl exchange process. The data, when taken together, suggest that alkynyl scrambling in the *mer,trans* complexes takes place through the [$(PMe_3)_3Rh(-C{\equiv}C-R)$] species formed by C−H reductive elimination. This 16-electron Rh(I) complex can undergo associative phosphine exchange as well as associative reaction with terminal alkyne.

Cobalt Analogues. Earlier reports on the cobalt analogues of our rhodium species have also attempted to deal with the question of which isomers formed and in which order. Thus, one report noted the precipitation of a compound with formulation [$(PMe_3)_3Co(-C{\equiv}C-C_6H_5)_2H$], but was unable to determine whether the compound was the *fac* or the *mer,trans* isomer (though they were able, on the basis of ^{31}P coupling to the hydride resonance in the ^1H NMR, to eliminate the possibility of *mer,cis*).[55] A later paper was able to confirm the structure of this compound as *mer,trans*-[$(PMe_3)_3Co(-C{\equiv}C-C_6H_5)_2H$].[56] This paper also reported some mechanistic investigations into the formation of the *mer,trans* compound, with an observed $\nu(C{\equiv}C)$ absorption at 1717 cm^{-1} in the IR suggesting that phenylethyne π-coordinates to the metal in an initial step. However, the suggestion that there were two subsequent intermediates (*mer,cis* and then *fac*) in the synthesis of the *mer,trans* isomer of [$(PMe_3)_3Co(-C{\equiv}C-C_6H_5)_2H$] was based solely on the observation of IR bands in the solid state, evidence that cannot be considered definitive. It is possible that the *mer,cis* isomer may be accessible energetically for cobalt, but our experimental and theoretical results indicate that it is very high in energy for rhodium and is thus not observed.

Scheme 9



Formation of Chlorides. One further reaction of the *mer,trans*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2H$] species was observed: dissolution in chloroform exchanged H for Cl cleanly forming *mer,trans*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2Cl$], with complete conversion in 16 h at room temperature (Scheme 9). The chloride-containing product has been fully characterized: NMR, IR, and elemental analysis are consistent with this formulation, which has been confirmed by single-crystal X-ray diffraction. When the reaction was followed by ^1H NMR in deuterated chloroform it was clear that 1 equiv of $CHDCl_2$ was formed as a byproduct. Such a reaction has many precedents.[57] Once formed, *mer,trans*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2Cl$] isomerizes slowly to *mer,cis*-[$(PMe_3)_3Rh(-C{\equiv}C-R)_2Cl$], with complete isomerization taking about 5 weeks at room temperature (Scheme 9). While a suitable single crystal for X-ray analysis of the *mer,cis* isomer has not yet been obtained, the NMR spectra are definitive, in that the absence of a relatively large $^1J(Rh^{III}-P)$

(54) Shaply, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305.

(55) Habadie, N.; Dartiguenave, M.; Dartiguenave, Y.; Britten, J. F.; Beauchamp, A. L. *Organometallics* **1989**, *8*, 2564.

(56) Klein, H.-F.; Beck, H.; Hammerschmitt, B.; Koch, U.; Koppert, D.; Cordier, G.; Paulus, H. *Z. Naturforsch.* **1991**, *46b*, 147.

(57) Green, M. L. H.; Jones, D. J. *Adv. Inorg. Radiochem.* **1965**, *7*, 115.

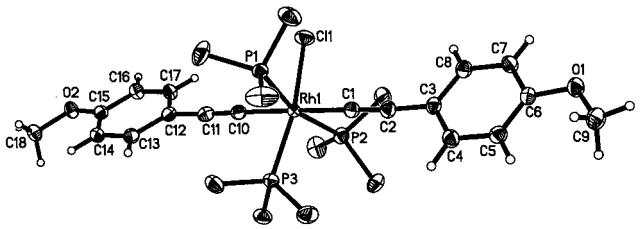


Figure 2. Molecular structure of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−C$_6$H$_4$−4-OMe)$_2$Cl] with ellipsoids shown at 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) in the Crystal Structure of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−C$_6$H$_4$−4-OMe)$_2$(Cl)]

Rh(1)−C(1)	2.035(1)	Rh(1)−P(1)	2.3475(4)
Rh(1)−C(10)	2.037(1)	Rh(1)−P(2)	2.3436(4)
Rh(1)−Cl(1)	2.4493(4)	Rh(1)−P(3)	2.2506(4)
C(1)−C(2)	1.214(2)	C(10)−C(11)	1.207(2)
C(1)−Rh(1)−C(10)	178.63(6)	C(1)−Rh(1)−Cl(1)	95.17(4)
C(1)−Rh(1)−P(1)	84.32(4)	C(1)−Rh(1)−P(2)	83.69(4)
C(1)−Rh(1)−P(3)	96.63(4)	C(10)−Rh(1)−Cl(1)	86.05(4)
C(10)−Rh(1)−P(1)	95.19(4)	C(10)−Rh(1)−P(2)	97.01(4)
C(10)−Rh(1)−P(3)	82.16(4)	P(1)−Rh(1)−P(2)	164.429(14)
P(1)−Rh(1)−P(3)	96.790(13)	P(2)−Rh(1)−P(3)	94.425(14)
Cl(1)−Rh(1)−P(1)	84.772(13)	Cl(1)−Rh(1)−P(2)	86.457(14)
Cl(1)−Rh(1)−P(3)	168.200(14)	Rh(1)−C(1)−C(2)	178.40(13)
C(1)−C(2)−C(3)	175.03(15)	Rh(1)−C(10)−C(11)	177.58(12)
C(10)−C(11)−C(12)	176.41(15)	C(6)−O(1)−C(9)	116.47(12)
C(15)−O(2)−C(18)	117.64(11)		

coupling constant in the ^{31}P NMR spectrum (cf. 118 Hz in the *mer,trans* isomer) allows us to rule out any structure with a P *trans* to a Cl, thus leaving the *mer,cis* isomer as the only possibility. IR data confirms the presence of two different C≡C stretching modes, consistent with a *cis* disposition of the two alkynyls, and elemental analysis confirms the overall composition.

Crystals of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$Cl] obtained by slow evaporation of $CDCl_3$ confirm the octahedral geometry and the *mer,trans*-arrangement of the ligands (Figure 2) suggested by the ^{31}P NMR data. Thus, the hydride ligand in the precursor compound is replaced by chloride with retention of the stereochemistry about the Rh center. The molecular structure is similar to that of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−Ph)$_2$H] reported previously,[50] and the symmetry about the Rh center is very close to C_{2v}. The two Rh−C distances (Table 2) of 2.035(1) and 2.037(1) Å are identical within experimental error and are similar to those of 2.019(4) and 2.031(4) Å in the hydride precursor. The Rh(1)−P(1) and Rh(2)−P(2) distances of 2.3475(4) and 2.3436(4) Å for the mutually *trans* PMe$_3$ ligands are slightly longer than the related distances of 2.297(1) and 2.298(1) Å in the hydride analogue, perhaps because the Cl ligand occupies more space than an H ligand, whereas the distance for the Rh−P bond *trans* to the chloride (Rh(1)−P(3)) of 2.2506(4) Å is much shorter than that *trans* to the hydride (2.348(1) Å) in the hydride analogue, consistent with the relative *trans* influence of Cl vs H. The angles about Rh are close to those expected for octahedral coordination, with the largest deviation being the P(1)−Rh(1)−P(2) angle of 164.429(14)° for the mutually *trans* PMe$_3$ ligands. This is a result of P(1) and P(2) being displaced slightly toward C(1), whereas the unique P(3) leans slightly toward C(2), relieving steric interactions between pairs of mutually *cis* PMe$_3$ groups. The alkynyl groups form a nearly linear chain

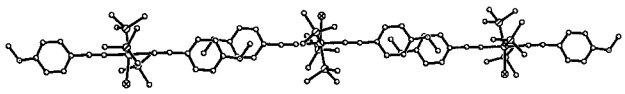


Figure 3. Crystal structure of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−C$_6$H$_4$−4-OMe)$_2$Cl] showing the molecules in infinite ladder-like chains along the 101 direction.

with angles about C(2), C(1), Rh(1), C(10), and C(11) being 175.03(15)°, 178.40(13)°, 178.63(6)°, 177.58(12)°, and 176.41(15)°, respectively.

The planes of the two phenyl rings are rotated with respect to each other by 19.3°. In crystals of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$Cl], the terminal MeO−C$_6$H$_4$− groups of adjacent molecules (related by the inversion centers) are overlapping, with mean interplanar spacings of 3.370 and 3.400 Å between the planes of parallel Ph-rings. These interactions combine molecules in infinite ladder-like chains along the 101 direction (Figure 3).

Conclusions

We have clearly shown that it is not possible to prepare cleanly the desired unsymmetric *mer,trans* hydrido-bis(alkynyl)rhodium compounds in the absence of their symmetric counterparts via the direct C−H activation approach. Likewise, the synthesis of well-defined alternating or block polymers employing different dialkynyl linkers would be unfeasible via this route.

While the *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−R)$_2$H] complexes, once formed, are configurationally stable and not prone to scrambling at ambient temperature, they are synthesized via a route that involves nonconfigurationally stable species which are prone to scrambling. In addition, the barrier to scrambling of the intermediates is lower than the activation energy required to make the final compounds. The facile and high-yield synthesis of two isomers of [(PMe$_3$)$_3$Rh(−C≡C−R)$_2$Cl] may allow the preparation of novel tris(alkynyl) complexes via the use of M′−C≡C−R′ reagents, and such studies are in progress.

Experimental Section

General Considerations. All reagents were used as supplied, unless noted otherwise; solvents were distilled under nitrogen from appropriate drying agents. NMR spectra were obtained on either Bruker AC 300, Varian Mercury 200, or Mercury 300 spectrometers and are referenced to external TMS (^{1}H), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). IR spectra were recorded on solid samples on a Perkin-Elmer Paragon 1600 FTIR spectrophotometer. Elemental analyses were performed by MWH Laboratories, Warwick Analytical Services, and in the Department of Chemistry, University of Durham. Reactions were carried out, and NMR samples were prepared in Innovative Technology Inc. gloveboxes under an atmosphere of dry nitrogen. The [(PMe$_3$)$_4$RhMe] was prepared via a modification of a literature route[58] (MeLi was used instead of MeMgI).

Synthesis of *mer,trans*-[(PMe$_3$)$_3$Rh(−C≡C−C$_6$H$_4$−4-OMe)$_2$H]. A solution of *p*-methoxyphenylethyne (12.5 mg, 0.095 mmol) in THF (5 cm^3) was added to a solution of [(PMe$_3$)$_4$RhMe] (20 mg, 0.047 mmol) in THF (3 cm^3), and the mixture was stirred for 16 h under a N_2 atmosphere. The solvent was removed in vacuo and the product crystallized from THF/hexane (yield: 24 mg, 86%). NMR (C_6D_6): ^{31}P{^{1}H} (80.96 MHz), δ −5.92 (2P, dd, $^1J_{Rh-P}$ = 93 Hz, $^2J_{P-P}$ = 27 Hz, P *trans*

to P), −23.43 (1P, dt, $^1J_{Rh-P}$ = 76 Hz, $^2J_{P-P}$ = 27 Hz, P *trans* to H); ^{1}H (200.1 MHz), δ 7.42 (4H, (AB)′, aromatic), 6.76 (4H, (AB)′, aromatic), 3.27 (6H, s, OMe), 1.42 (18H, vt, J = 4 Hz, PMe_3 *trans* to PMe_3), 1.20 (9H, d, J = 8 Hz, PMe_3 *trans* to H), −9.17 (1H, dq, $^1J_{Rh-H} = {}^2J_{Pcis-H}$ = 17 Hz, $^2J_{Ptrans-H}$ = 195 Hz, Rh−H). Anal. Found ($C_{27}H_{42}O_2P_3Rh$ requires): C 54.43 (54.55), H 7.23 (7.12). IR (solid state): ν(C≡C) = 2088 cm^{-1}, ν(Rh−H) = 1943 cm^{-1}.

Synthesis of *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−$SiMe_3$)$_2$H]. Ethynyltrimethylsilane (9 mg, 0.09 mmol) was added to a solution of [$(PMe_3)_4$RhMe] (20 mg, 0.047 mmol) in THF (8 cm^3), and the mixture was stirred for 16 h under a N_2 atmosphere. The solvent was removed in vacuo and the product crystallized from THF/hexane (yield: 24 mg, 95%). NMR (C_6D_6): ^{31}P{^{1}H} (80.96 MHz), δ −7.75 (2 P, dd, $^1J_{Rh-P}$ = 94 Hz, $^2J_{P-P}$ = 27 Hz, P *trans* to P), −25.37 (1 P, dt, $^1J_{Rh-P}$ = 77 Hz, $^2J_{P-P}$ = 27 Hz, P *trans* to H); ^{1}H (200.1 MHz), δ 1.40 (18 H, vt, J = 4 Hz, PMe_3 *trans* to PMe_3), 1.18 (9 H, d, J = 8 Hz, PMe_3 *trans* to H), 0.31 (18 H, s, TMS), −9.29 (1H, dq, $^1J_{Rh-H} = {}^2J_{Pcis-H}$ = 17 Hz, $^2J_{Ptrans-H}$ = 192 Hz, Rh−H). Anal. Found ($C_{19}H_{46}Si_2P_3Rh$ requires): C 43.14 (43.34), H 8.88 (8.81). IR (solid state): ν(C≡C) = 2022 cm^{-1}, ν(Rh−H) = 1944 cm^{-1}.

Synthesis of *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-CN)$_2$H]. A solution of *p*-cyanophenylethyne (12 mg, 0.095 mmol) in THF (5 cm^3) was added to a solution of [$(PMe_3)_4$-RhMe] (20 mg, 0.047 mmol) in THF (3 cm^3), and the mixture was stirred for 16 h under a N_2 atmosphere. The solvent was removed in vacuo and the product recrystallized from THF/hexane (yield: 23 mg, 82%). NMR (C_6D_6): ^{31}P{^{1}H} (80.96 MHz), δ −6.69 (2 P, dd, $^1J_{Rh-P}$ = 92 Hz, $^2J_{P-P}$ = 26 Hz, P *trans* to P), −24.27 (1 P, dt, $^1J_{Rh-P}$ = 76 Hz, $^2J_{P-P}$ = 26 Hz, P *trans* to H); ^{1}H (200.1 MHz), δ 7.06 (8H, s, aromatic), 1.29 (18 H, vt, J = 3 Hz, PMe_3 *trans* to PMe_3), 1.04 (9 H, d, J = 7 Hz, PMe_3 *trans* to H), −9.24 (1 H, dq, $^1J_{Rh-H} = {}^2J_{Pcis-H}$ = 16 Hz, $^2J_{Ptrans-H}$ = 192 Hz, Rh−H). Anal. Found ($C_{27}H_{36}N_2P_3Rh$ requires): C 55.19 (55.49), H 6.19 (6.21), N 4.81 (4.79). IR (solid state): ν(C≡N) = 2219 cm^{-1}, ν(C≡C) = 2080 cm^{-1}, ν(Rh−H) = 1944 cm^{-1}.

Synthesis of *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$Cl]. *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$H] (20 mg, 0.034 mmol) was dissolved in $CHCl_3$ and left to stand for 16 h. The solvent was removed in vacuo, and the product was recrystallized from THF (yield: 19 mg, 92%). NMR ($CDCl_3$): ^{31}P{^{1}H} (80.96 MHz), δ 11.18 (1 P, dt, $^1J_{Rh-P}$ = 118 Hz, $^2J_{P-P}$ = 30 Hz, P *trans* to Cl), −6.74 (2 P, dd, $^1J_{Rh-P}$ = 85 Hz, $^2J_{P-P}$ = 30 Hz, P *trans* to P); ^{1}H (200.1 MHz), δ 7.18 (4 H, (AB)′), 6.73 (4 H, (AB)′), 3.77 (6 H, s, OMe), 1.77 (18 H, vt, J = 4 Hz, PMe_3 *trans* to PMe_3), 1.72 (9 H, d, J = 9 Hz, PMe_3 *trans* to Cl). Anal. Found ($C_{27}H_{41}O_2P_3ClRh$ requires): C 51.70 (51.57), H 6.32 (6.57), Cl 5.61 (5.57). IR (solid state): ν(C≡C) = 2108 cm^{-1}.

X-ray Structural Analysis. A fawn crystal (0.72 × 0.44 × 0.34 mm^3), obtained by slow evaporation of a $CDCl_3$ solution, was used for the X-ray structure determination. Data were collected at 120.0(2) K on a Bruker SMART CCD 1K diffractometer equipped with an Oxford Cryostream low-temperature attachment using graphite-monochromated Mo Kα radiation. Crystal data, data collection, and refinement parameters are given in Table 3. The structure was solved by direct methods and refined by full-matrix least squares against F^2. All non-hydrogen atoms were refined anisotropically; H atoms were located on the difference Fourier maps and refined isotropically. Final $wR_2(F^2)$ = 0.0588 for all data (471 refined parameters) and R_1 = 0.0236 for 7768 reflections with $I \geq 2\sigma(I)$.

Synthesis of *mer,cis*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$-Cl]. *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$Cl (15 mg, 0.024 mmol) was dissolved in $CHCl_3$ and left to stand for 30 days. The solvent was removed in vacuo, and the product was recrystallized from THF (yield: 12 mg, 92%). NMR ($CDCl_3$): ^{31}P{^{1}H} (80.96 MHz), δ −8.30 (2 P, dd, $^1J_{Rh-P}$ = 85 Hz, $^2J_{P-P}$ = 30 Hz, P *trans* to P), −17.74 (1 P, dt, $^1J_{Rh-P}$ = 83 Hz, $^2J_{P-P}$ = 30 Hz, P *trans* to C≡C); ^{1}H (200.1 MHz), δ 7.28 (2 H, (AB)′), 7.12 (2 H, (AB)′), 6.73 (4 H, (AB)′), 3.77 (6 H, s, OMe), 1.72 (18 H, vt, J = 4 Hz, PMe_3 *trans* to PMe_3), 1.54 (9 H, d, J = 9 Hz, PMe_3 *trans* to C≡C). Anal. Found ($C_{27}H_{41}O_2P_3ClRh$ requires): C 51.47 (51.57), H 6.37 (6.57). IR (solid state): ν(C≡C) = 2120, 2114 cm^{-1}.

Table 3. Crystal Data, Data Collection, and Refinement for *mer,trans*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$(Cl)]

emp formula	$C_{27}H_{41}ClO_2P_3Rh$
fw	628.87
temp	120.0(2) K
λ(Mo K$_\alpha$), Å	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	18.5752(6)
b, Å	11.7546(4)
c, Å	13.8703(5)
β, deg	95.71(1)
V, Å^3	3013.5(2)
Z	4
D_{calc}, g cm^{-3}	1.386
μ, mm^{-1}	0.836
F(000)	1304
cryst size, mm	0.72 × 0.44 × 0.34
2θ range, deg	2.20−60.72
index ranges	$-24 \leq h \leq 25$, $-16 \leq k \leq 15$, $-19 \leq l \leq 19$
no. of data collected	34 012
no. of unique data	8280 [R(int) = 0.0484]
no. of params refined	471
max and min transmn	0.7642 and 0.5843
R1[a] [$I \geq 2\sigma(I)$]	0.0236
wR2[b] (all data)	0.0588
GoF[c] on F^2	1.088
largest diff peak and hole, e Å^{-3}	0.695 and −0.458

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Spectroscopic Data for [$(PMe_3)_4$Rh(−C≡C−C_6H_4−4-OMe)]. Compound only observed in solution, not isolated. NMR ([$^2H_8$]THF): ^{31}P{^{1}H} (80.96 MHz, 180 K), δ 0.55 (1 P, dq, $^1J_{Rh-P}$ = 107 Hz, $^2J_{P-P}$ = 44 Hz, axial P *trans* to C≡C), −24.94 (3 P, dd, $^1J_{Rh-P}$ = 144 Hz, $^2J_{P-P}$ = 44 Hz, equatorial P); ^{1}H (200.1 MHz, 280 K), δ 7.5 (2 H, (AB)′, aromatic), 6.9 (2 H, (AB)′, aromatic), 3.9 (3 H, s, OMe), 1.2−1.8 (36 H, br m, PMe_3).

Spectroscopic Data for [$(PMe_3)_4$Rh(−C≡C−$SiMe_3$)]. Compound only observed in solution, not isolated. NMR ([$^2H_8$]-THF): ^{31}P{^{1}H} (80.96 MHz, 180 K), δ −0.60 (1 P, dq, $^1J_{Rh-P}$ = 107 Hz, $^2J_{P-P}$ = 45 Hz, axial P *trans* to C≡C), −25.00 (3 P, dd, $^1J_{Rh-P}$ = 145 Hz, $^2J_{P-P}$ = 45 Hz, equatorial P).

Spectroscopic Data for *fac*-[$(PMe_3)_3$Rh(−C≡C−C_6H_4−4-OMe)$_2$H]. Compound only observed in solution, not isolated. NMR ([$^2H_8$]THF): ^{31}P{^{1}H} (80.96 MHz, 180 K), δ −13.25 (2 P, dd, $^1J_{Rh-P}$ = 86 Hz, $^2J_{P-P}$ = 24 Hz, P *trans* to C≡C), −26.97 (1 P, dt, $^1J_{Rh-P}$ = 71 Hz, $^2J_{P-P}$ = 24 Hz, P *trans* to H); ^{1}H (200.1 MHz, 242 K), δ 7.0 (4 H, (AB)′, aromatic), 7.4 (4 H, (AB)′, aromatic), 3.7 (6 H, s, OMe), 0.8−1.4 (27 H, br m, PMe_3), −9.42 (1 H, dq, $^1J_{Rh-H} = {}^2J_{Pcis-H}$ = 18 Hz, $^2J_{Ptrans-H}$ = 196 Hz, Rh−H).

Spectroscopic Data for *fac*-[$(PMe_3)_3$Rh(−C≡C−$SiMe_3$)$_2$H]. Compound only observed in solution, not isolated. NMR ([$^2H_8$]THF): ^{31}P{^{1}H} (80.96 MHz, 242 K), δ −15.33 (2P, dd, $^1J_{Rh-P}$ = 85 Hz, $^2J_{P-P}$ = 25 Hz, P *trans* to CC), −29.01 (1P, dt, $^1J_{Rh-P}$ = 72 Hz, $^2J_{P-P}$ = 25 Hz, P *trans* to H); ^{1}H (200.1 MHz, 242 K), δ 0.8−1.4 (27 H, br m, PMe_3), 0.27 (9 H, s TMS), −9.30 (1 H, dq, $^1J_{Rh-H} = {}^2J_{Pcis-H}$ = 18 Hz, $^2J_{Ptrans-H}$ = 192 Hz, Rh−H).

Synthesis of [$(PMe_3)_3$Rh(−C≡C−TMS)(η^2-4-CF_3−C_6H_4−C≡C−C_6H_4−4-CF_3)]. Ethynyltrimethylsilane (5 mg, 0.047

mmol) was added to a solution of [(PMe$_3$)$_4$RhMe] (20 mg, 0.047 mmol) in THF (5 cm^3), and the mixture was stirred for 10 min under a N_2 atmosphere. Bis(4-trifluoromethylphenyl)ethyne (14.9 mg, 0.047 mmol) was added, and the mixture was stirred for 5 min. The solvent was removed in vacuo, and the mixture redissolved in THF and then stirred for 5 min. This step was repeated four further times (to remove the PMe$_3$) before collecting the product as a dark orange powder (yield: 29 mg, 92%). NMR (C_6D_6): $^{31}P\{^1H\}$ (80.96 MHz), δ −1.29 (2P, dd, $^1J_{Rh-P}$ = 95 Hz, $^2J_{P-P}$ = 33 Hz), −23.7 (1P, dt, $^1J_{Rh-P}$ = 115 Hz, $^2J_{P-P}$ = 33 Hz); $^{19}F\{^1H\}$ (188.1 MHz), δ −62.30 (3F, s), −62.37 (3F, s); ^1H (200.1 MHz), δ 8.06 (2H, (AB)′), 7.46 (2H, (AB)′), 7.43 (4H, s), 1.17 (9H, d, J = 7 Hz, equatorial PMe$_3$), 0.94 (18H, vt, J = 3 Hz, axial PMe$_3$), 0.43 (9H, s, TMS). Anal. Found ($C_{30}H_{44}P_3F_6RhSi$ requires): C 48.84 (48.52), H 6.11 (5.97). IR (solid state): ν(C≡C) = 2009 cm^{-1}, $\nu(\eta^2$-C≡C) = 1750 cm^{-1}.

Theoretical Studies. DFT geometry optimizations were based on the numerical Amsterdam Density Functional (ADF) program system version 2.3.0.[59,60] The basis sets comprised set IV for Rh and set III for all other atoms. Basis set IV is an uncontracted triple-ζ Slater-type-orbital (STO) expansion plus an additional 5p orbital, while basis set III is a double-ζ STO plus polarization expansion. All ADF calculations were based on the uniform electron gas local density approximation[61] (LDA) and analytical energy gradients.[62] The LDA correlation energy was computed according to Vosko, Wilk, and Nusair's[63] parametrization of electron gas data. Gradient-corrected (GC) functionals for the LDA exchange and correlation terms employed the formulations of Becke[64] and Perdew,[65,66] respectively (BP). The BP functional was used for both geometry optimization and binding energy calculations with default SCF and geometry optimization convergence criteria. The lower core shells on the atoms (1s on C, 1s to 2p on P, 1s to 3d on Rh) were treated by the frozen core approximation.[67] The total molecular electron density was fitted in each SCF cycle by auxiliary s, p, d, f, and g STO functions. Coordinates of the optimized structures are available as Supporting Information. The later version of ADF (1999.02)[68] contains an option for computing solvation energies using the COSMO formulation. Unfortunately, bugs in the COSMO routines precluded the use of ADF1999. Instead, we used the polarized continuum model implemented in Jaguar 3.5.[69] The BP functional and lacvp* basis sets were used at the geometry previously computed using ADF. The parameters for THF were as follows: density = 0.8892 kg L^{-1}, molecular weight = 72.12 g mol^{-1}, and a dielectric constant of 7.58, which give a calculated probe radius of 2.524 Å. Default SCF and geometry optimization convergence criteria were used together with a fine grid for the DFT SCF part of the calculation.

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Supporting Information Available: Tables of X-ray crystallographic data, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for *mer*,*trans*-[(PMe$_3$)$_3$Rh(−C≡C−C$_6$H$_4$−4-OMe)$_2$Cl] (cif format) and coordinates of the DFT optimized structures of the alkyne/alkynyl intermediates and the Rh(III) products in Scheme 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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(58) Thorn, D. L. *Organometallics* **1985**, *4*, 192.
(59) *ADF 2.3.0*; Theoretical Chemistry, Free University of Amsterdam, 1997.
(60) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.
(61) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1.
(62) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.
(63) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(64) Becke, A. J. *Chem. Phys.* **1986**, *84*, 4524.
(65) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.
(66) Perdew, J. P. *Phys. Rev.* **1987**, *B34*, 7406.
(67) Baerends, E. J.; Ellis, D. E.; Ros, P. *Theor. Chim. Acta* **1972**, *27*, 339.
(68) *ADF 1999.02*; Theoretical Chemistry, Free University of Amsterdam, 2000.
(69) *Jaguar 3.5*; Schrodinger Inc.: Portland, OR, 1998.