$(SCH_2CH_2S)MoCp]^+$ was present.

(b) With O_2 or H_2O_2. Complex **3** (~15 mg, 0.020 mmol) was dissolved in CD_3CN, and an aqueous solution of H_2O_2 (~0.8 equiv) or gaseous O_2 (~1 equiv) was added. The NMR tubes were frozen at −196 °C, evacuated, and then sealed. Each of the reactions proceeded cleanly over a period of 2–4 days at 25 °C to form $[CpMo(S_2CH)(SCH_2CH_2S)MoCp]BF_4$, which was identified by NMR spectroscopy.

Reaction of $(CpMo)_2(S_2CH_2)(SCH_2CH_2S)$ with *tert*-Butylethene and Acid. $(CpMo)_2(S_2CH_2)(SCH_2CH_2S)$ (28 mg, 0.06 mmol) was dissolved in CD_3CN in an NMR tube, and triflic acid (1 equiv) and *tert*-butylethene (1.6 equiv) were added. The solution was degassed and sealed under vacuum. After 5 days, a small amount of $[(CpMo)_2(S_2CH)(SCH_2CH_2S)]^+$ (~20%) was observed by NMR spectroscopy but no *tert*-butylethane was detected.

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Reactions of $(C_5Me_5)Rh(PMe_3)(R)H$ with Electrophiles. Insertion of Unsaturated Molecules into Activated Carbon–Hydrogen Bonds

William D. Jones,*,† Valerie L. Chandler, and Frank J. Feher

Department of Chemistry, University of Rochester, Rochester, New York 14627

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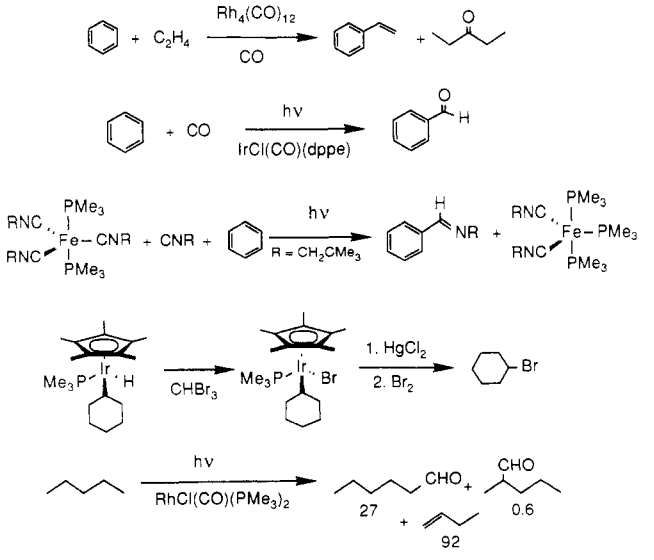
The complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ (aryl = C_6H_5, 2,6-$C_6H_3Me_2$) are found to react with several electrophiles. Treatment with CS_2 gives two products, the major species resulting from the elimination of benzene and formation of $(C_5Me_5)Rh(PMe_3)(CS_2)$. The minor product is formed by insertion into the Rh–H bond to give $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}S)$. Reaction of the aryl hydride complex with PhNCS gives only the insertion product $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}NPh)$. These two sulfur-bound derivatives react with either aniline or H_2S, respectively, to give $(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$, which cleaves during isolation to give $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$ and PhNHCH=S. Reaction of the aryl hydride complex with dimethyl acetylenedicarboxylate results in insertion of acetylene into the Rh–H bond, producing a mixture of the cis and trans vinyl complexes. HI cleaves the rhodium–aryl bond, and iodine induces both elimination of substituted styrene and iodination of the metal–xylyl bond in the cis complex. Treatment of the trans isomer with HI also cleaves the Rh–aryl bond, and iodine gives a mixture of products. The methyl complex $(C_5Me_5)Rh(PMe_3)(CH_3)H$ reacts with dimethyl acetylenedicarboxylate to give a mixture of cis and trans vinyl methyl complexes. Addition of iodine results in the formation of methyl iodide and $(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)]I$. *cis*-$(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3Me_2)[C(COOMe){=}CH(COOMe)]$ crystallizes in the triclinic space group $P\bar{1}$ with a = 8.928 (5) Å, b = 19.111 (4) Å, c = 8.590 (2) Å, α = 94.21 (2)°, β = 111.86 (4)°, γ = 94.08 (3)°, V = 1348.9 (1.8) Å^3, and Z = 2. *trans*-$(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)](2,6\text{-}C_6H_3Me_2)$ crystallizes in the monoclinic space group $P2_1/n$ with a = 15.090 (2) Å, b = 11.361 (2) Å, c = 16.886 (4) Å, β = 109.54 (2)°, V = 2728.4 (1.8) Å^3, and Z = 4.

Introduction

Many complexes have been discovered recently that form stable oxidative-addition adducts with carbon–hydrogen bonds of arenes and alkanes.[1] The next goal for the application of these reactions is the transformation of the M–C bond of the aryl and alkyl ligands to functionalized species prior to their elimination from the metal. Ultimately, the metal might be cycled back into the species that was found to activate the C–H bond, resulting in catalytic hydrocarbon functionalization.

The insertion of an adjacent unsaturated ligand into a metal–carbon bond has ample precedent in the organometallic literature and offers a pathway for transforming an activated hydrocarbon into a new organic group. Many molecules that activate C–H bonds have no such ligand in their coordination spheres, however. Furthermore, their coordinative saturation and lack of ligand lability prevents potentially reactive molecules in solution from coordinating to the metal. Consequently, only strong electrophiles have been found to be generally reactive with the oxidative-addition adducts of hydrocarbons with low-valent metals.[2]

Scheme I



Several notable exceptions have appeared in the literature recently,[3-5] including the insertion of CO, CNR, and olefins

† Alfred P. Sloan Fellow, 1984–1986; Camille and Henry Dreyfus Teacher-Scholar, 1985–1989.

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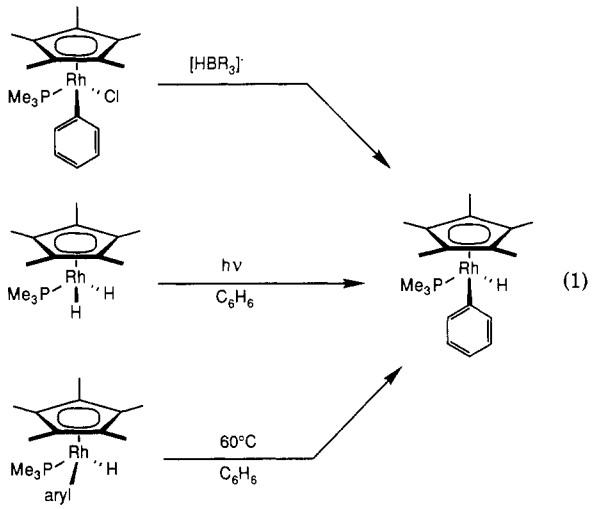
into activated C–H bonds. Some of these thermodynamically uphill reactions must be photochemically driven. Some examples are shown in Scheme I.

Earlier studies have shown that the intermediate $[(C_5Me_5)Rh(PMe_3)]$ reacts with both alkane and arene C–H bonds to give oxidative-addition adducts.[6] In this paper, reactions of electrophiles with complexes of the type $(C_5Me_5)Rh(PMe_3)(R)H$, where R = methyl, phenyl, and 2,6-xylyl, are discussed. While insertion into the metal–hydrogen bond results in the formation of a stable functionalized metal complex containing the alkane or arene, elimination of organic products is found to proceed only under oxidizing conditions.

Results

Aryl hydride complexes of the formula $(C_5Me_5)Rh(PMe_3)(aryl)H$ can be prepared in several ways (eq 1).



(1)

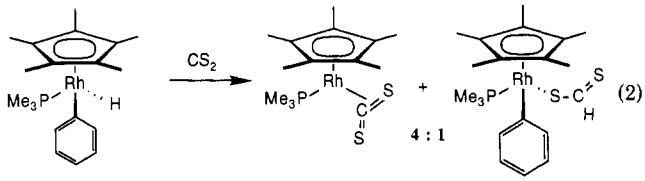
They can be directly synthesized by the reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with aryl Grignard reagent to generate $(C_5Me_5)Rh(PMe_3)(aryl)Cl$, which then is reduced to the desired product with a borohydride reagent, $[HBR_3]^-$. They can also be prepared by irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ in arene solvent to give initially the reactive intermediate $[(C_5Me_5)Rh(PMe_3)]$, which then coordinates to the arene and undergoes oxidative addition to a C–H bond. Finally, they can be prepared in an arene-exchange reaction by thermolysis of one aryl hydride complex in the presence of a different arene.[7]

The phosphine ligand is not very labile in these aryl hydride complexes. Treatment of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1a**) with $P(CD_3)_3$ in C_6D_6 results in only slow exchange of the coordinated phosphine. No exchange with coordinated PMe_3 is seen after 15 min, and only 22% exchange is observed after 12 h at 25 °C.

The reactions of **1a** with a variety of electrophiles were examined. In these experiments, benzene solutions of **1a** were treated with 1–2 equiv of the electrophile and the reactions monitored by ^1H NMR spectroscopy. Combinations of **1a** with $CNCH_2CMe_3$, CH_3NCO, CH_2=CHCOOMe, and CO_2 resulted in no reaction at 25 °C. Reactions of **1a** with CS_2, PhNCS, and dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of new organometallic products. On occasion, the less complicated 3,5-xylyl aryl substituent was used on rhodium (**1b**) in order to simplify interpretation of the ^1H NMR spectra.

Reaction of 1a with CS_2. Upon reaction of **1a** with CS_2 in benzene at room temperature, a red solution forms that is observed to contain a pair of distinct C_5Me_5 and PMe_3 ligands by ^1H NMR spectroscopy in a 4:1 ratio. Chromatography on silica gel with 40:60 THF/hexane allows separation of the products. The major product elutes first and is isolated as a red microcrystalline powder. The second product to elute is isolated as a yellow waxy solid.

The IR spectrum of the major product shows strong bands at 1159, 1146, 636, 617 cm^{-1}, consistent with the product formulation as an η^2-CS_2 adduct, $(C_5Me_5)Rh(PMe_3)(CS_2)$ (**2**; eq 2).[8] The mass spectrum displays the



(2)

expected parent ion at m/e 390. NMR data are consistent with this structure, although the ^{13}C resonance for the η^2-CS_2 ligand was not observed, perhaps due to coupling (to Rh and P) and the typical decreased intensity associated with quaternary carbons. The high-field chemical shift of the ^{31}P NMR resonance (δ –6.54) is also consistent with a rhodium(I) complex (cf. $(C_5Me_5)Rh(PMe_3)(C_2H_4)$, δ –2.84), although the coupling constant J_{Rh-P} is smaller than that typically seen in a series of similar Rh(I) derivatives.[8] ^1H and ^{31}P NMR data are given in Tables I and II. Other η^2-CS_2 complexes are well-known in the literature.[9,10]

The second minor product shows strong bands in the IR region at 1015, 990, 951, and 732 cm^{-1}. The mass spectrum gives a parent ion at m/e 468, and the ^1H NMR spectrum shows a resonance at δ 11.897 in addition to

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Table I. ^{1}H NMR Spectroscopic Data (ppm, J in Hz) for Complexes in C_6D_6 Solvent

complex	resonances		
	C_5Me_5	PMe_3	other
$(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1a**)	1.790 (d, J = 1.4)	0.900 (dd, J = 9.8, 0.8)	−13.50 (dd, J = 49.5, 32.8, 1 H, Rh-*H*) 7.64 (d, J = 7.1 Hz, 2 H, *o*-Ph) 7.10 (m, 3 H, *m*-Ph + *p*-Ph)
$(C_5Me_5)Rh(PMe_3)(CS_2)$ (**2**)	1.607 (d, J = 2.4)	0.891 (d, J = 10.2)	
$(C_5Me_5)Rh(PMe_3)(Ph)(SCHS)$ (**3**)	1.258 (d, J = 2.7)	0.814 (d, J = 10.2)	11.897 (s, 1 h, SC*H*S) 7.366 (d, J = 8.3, 2 H, *o*-Ph) 7.088 (t, J = 7.0, 2 H, *m*-Ph) 7.038 (d, J = 6.5, 1 H, *p*-Ph)
$(C_5Me_5)Rh(PMe_3)(Ph)SCH{=}NPh)$ major isomer (**4a**)	1.468 (d, J = 2.7)	1.125 (d, J = 10.2)	8.916 (dd, J = 3.0, 1.6, 1 H, SC*H*=NPh) 7.550 (d, J = 7.5, 2 H, *o*-Ph) 7.218 (t, J = 7.8, 2 H, *m*-Ph) 7.09, 7.00 (m, 6 H, aryl)
minor isomer (**4b**)	1.313 (d, J = 2.6)	0.916 (d, J = 10.0)	8.797 (br s, 1 H, SC*H*=NPh) 7.648 (d, J = 7.4, 2 H, *o*-Ph) 7.346 (t, J = 7.9, 2 H, *m*-Ph) 7.26 (m, 2 H, aryl)
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$ (**5**)	1.434 (d, J = 2.7)	1.036 (d, J = 10.0)	9.8 (br s, 2 H, Rh-Ph) 7.56 (br s, 2 H, Rh-Ph) 7.11 (m, 1 H, Rh-Ph) 7.04 (m, 1 H, N-Ph) 6.842 (t, J = 7.5, 2 H, N-Ph) 6.455 (d, J = 7.8, 2 H, N-Ph) 9.537 (dd, J = 5.0, 2.5, 1 H, H-CS_2N) −2.474 (d, J = 3.6, 1 H, H-S) 0.3 (br s, 1 H, H-N)
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$ (**6**, other diastereomer of **5**)	1.410 (d, J = 3.0)	1.220 (d, J = 10.4)	−2.474 (d, J = 3.6, 1 H, H-S) 9.69 (s, 1 H, H-CS_2N) 8.11 (d, J = 8.0, 1 H, Rh-Ph) 7.68 (d, J = 8.0, 1 H, Rh-Ph) 6.77 (m, 5 H, N-Ph)[c]
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)_2]$ (**7**)	1.383 (d, J = 2.9)	1.114 (d, J = 10.3)	−2.027 (d, J = 4.4, 1 H, S-H) −2.120 (d, J = 3.6, 1 H, S-H) 11.888 (t, J = 3.7, 1 H, H-CS_3)[c]
$(C_5Me_5)Rh(PMe_3)(Ph)(SH)$[b] (**8**)	1.598 (d, J = 2.6)	1.324 (d, J = 10.2)	−2.994 (d, J = 3.6, 1 H, S-H) 6.764 (d, J = 7.1, 1 H, *p*-Ph) 6.824 (t, J = 7.2, 2 H, *m*-Ph) 7.290 (d, J = 8.8, 2 H, *o*-Ph)
$(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)](3,5\text{-}C_6H_3Me_2)$[a] cis isomer (**9c**)	1.510 (d, J = 2.6)	1.388 (d, J = 9.7)	2.190 (s, 3 H, C_6H_3Me) 3.567 (s, 3 H, OMe) 3.818 (s, 3 H, OMe) 5.566 (t, J = 2.6, 1 H, vinylic) 6.514 (br s, 1 H, $C_6H_3Me_2$) 6.875 (br s, 2 H, $C_6H_3Me_2$)
trans isomer (**9t**)	1.69 (br s)	1.212 (d, J = 10.1)	2.140 (s, 3 H, C_6H_3Me) 3.157 (br s, 3 H, OMe) 3.681 (br s, 3 H, OMe) 6.815 (dd, J = 6.8, 3.6, 1 H, vinylic) 6.435 (br s, 1 H, $C_6H_3Me_2$) 6.825 (br s, 2 H, $C_6H_3Me_2$)
$(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)](Me)$[a]	1.625 (d, J = 2.6)	1.280 (d, J = 10.2)	−0.044 (dd, J = 6.3, 2.2, 3 H, Rh-CH_3) 3.618 (s, 3 H, OMe) 3.654 (s, 3 H, OMe) 6.406 (dd, J = 3.3, 3.0, 1 H, vinylic)

[a] $CDCl_3$ solvent. [b] THF-d_8 solvent. [c] Other phenyl resonances obscured.

C_5Me_5, PMe_3, and phenyl resonances. The ^{13}C NMR spectrum shows a resonance at δ 239.99, consistent with an S-bound thioaldehyde functionality (eq 2).[10,11] The product is formulated as the insertion adduct $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}S)$ (**3**) on the basis of the spectral and analytical data.

Reaction of 1a with PhNCS. The reaction of **1a** with PhNCS is similar to the reaction with CS_2 in that it also results in an insertion reaction. Two metal-containing products (**4a** and **4b**) are observed in a 3.2:1 ratio. Both complexes display resonances for C_5Me_5, PMe_3, and C_6H_5 ligands. In addition, the major isomer **4a** displays a resonance at δ 8.916 (dd, J = 3.0, 1.6 Hz, 1 H), while the minor isomer **4b** displays a broad singlet at δ 8.797.

All attempts to separate these isomers failed. Upon chromatography on silica gel with 50:50 THF/hexane, a broad yellow band was observed with R_f values between 0.44 and 0.88. The band was divided into leading and tailing fractions, which were evaporated and examined by ^1H NMR spectroscopy in C_6D_6. The spectra of the two fractions were identical with that of the initial mixture, suggesting that either the separation had failed or that the two isomers were in fact interconverting E/Z isomers. The material was analyzed as $C_{26}H_{35}NSPRh$, consistent with

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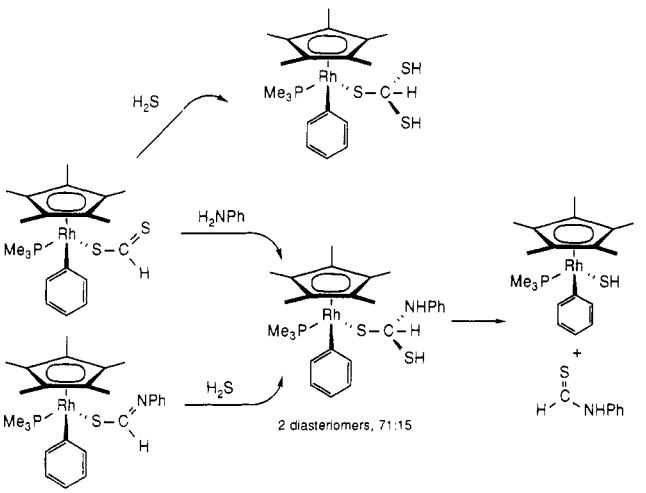
Table II. ^{13}C NMR and $^{31}P\{^1H\}$ NMR Spectroscopic Data (ppm, J in Hz) for Complexes in C_6D_6 Solvent

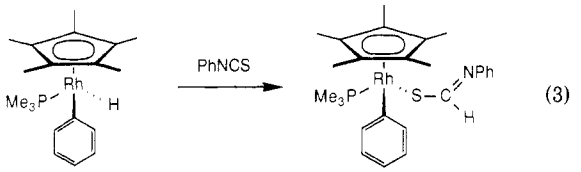
complex	resonances	
	^{13}C NMR	^{31}P NMR[c]
$(C_5Me_5)Rh(PMe_3)(CS_2)$ (**2**)	9.46 (q, J = 126.4, C_5Me_5)	−6.54 (d, J = 185)
	14.94 (qd, J = 128.4, 30.2, PMe_3)	
	99.69 (s, C_5Me_5)	
$(C_5Me_5)Rh(PMe_3)(Ph)(SCHS)$[a] (**3**)	9.55 (q, J = 127.6, C_5Me_5)	0.22 (d, J = 153.3)
	15.77 (qd, J = 96.1, 32.5, PMe_3)	
	101.03 (s, C_5Me_5)	
	123.35 (d, J = 157.6, phenyl)	
	128.34 (d, J = 155.4, phenyl)	
	139.85 (d, J = 153.9, phenyl)	
	239.99 (d, J = 173.7, SCHS)	
$(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}NPh)$		
major isomer (**4a**)	9.88 (q, J = 127, C_5Me_5)	1.30 (d, J = 154)
	16.58 (qd, J = 129, 32, PMe_3)	
	100.07 (s, C_5Me_5)	
	120.71 (dd, J = 157, 6, phenyl)	
	122.84 (d, J = 161, phenyl)	
	127–128 (m, obscured by solvent)	
	129.27 (dd, J = 160, 8, phenyl)	
	139.92 (d, J = 155, phenyl)	
	154–155 (m)	
	171.42 (d, J = 166, SCH=NPh)	
minor isomer (**4b**)	9.44 (q, J = 127, C_5Me_5)	3.28 (d, J = 147)
	15.36 (qd, J = 129, 32, PMe_3)	
	99.67 (s, C_5Me_5)	
	122.15 (d, J = 156, phenyl)	
	123.41 (dt, J = 161, 7, phenyl)	
	127–128 (m, obscured by solvent)	
	128.86 (s, phenyl)	
	139.35 (d, J = 155, phenyl)	
	154–155 (m)	
	170.66 (d, J = 188, SCH=NPh)	
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$ (**5**)	9.27 (q, J = 127, C_5Me_5)	6.12 (d, J = 195)
	15.38 (qd, J = 128, 33, PMe_3)	
	98.54 (s, C_5Me_5)	
	109.29 (d, J = 158, Ph)	
	122.51 (dd, J = 153, 9, Rh–Ph, ortho)	
	125.52 (d, J = 167, Ph)	
	130.00 (d, J = 99, Ph)	
	139.78 (d, J = 156, Ph)	
	139.17 (s, N–Ph, ipso)	
	150.00 (dd, J = 16, 14, Rh–Ph, ipso)	
	187.53 (d, J = 177, CHS_2N)	
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$	2.00 (q, J = 118, C_5Me_5)	2.21 (d, J = 155)
(**6**, other diastereomer of **5**)	99.98 (s, C_5Me_5)	
$(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)_2]$ (**7**)		7.62 (d, J = 195)
$(C_5Me_5)Rh(PMe_3)(Ph)(SH)$ (**8**)		4.36 (d, J = 155)
$(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)]$-$(3,5\text{-}C_6H_3Me_2)$[b] cis isomer (**9c**)	9.13 (q, J = 127.0, $C_6H_3Me_2$)	
	15.81 (qd, J = 129.8, 30.8, PMe_3)	
	21.23 (q, J = 125.8, C_5Me_5)	
	50.61 (q, J = 146.0, 2 MeO)	
	100.50 (br s, C_5Me_5)	
	123.75 (ddd, J = 152.5, 21.4, 13.2, vinyl CH)	
	126.95 (d, J = 167, o- or p-$C_6H_3Me_2$)	
	135.57 (s, m-$C_6H_3Me_2$)	
	138.57 (d, J = 156.6, p- or o-$C_6H_3Me_2$)	
	158.69 (dd, J = 32.7, 16.8, ipso-$C_6H_3Me_2$)	
	163.57 (s, CO_2Me)	
	176.23 (s, CO_2Me)	
	179.72 (dd, J = 38.8, 23.3, vinyl C–Rh)	
trans isomer (**9t**)	9.84 (q, J = 127.2, $C_6H_3Me_2$)	
	16.38 (qd, J = 129.3, 33.7, PMe_3)	
	21.36 (q, J = 124.1, C_5Me_5)	
	50.67 (q, J = 146.0, MeO)	
	50.76 (q, J = 146.0, MeO)	
	100.82 (br s, C_5Me_5)	
	122.80 (br dd, J = 149.3, 10.5, vinyl CH)	
	131.81 (d, J = 154.9, o- or p-$C_6H_3Me_2$)	
	133.82 (s, m-$C_6H_3Me_2$)	
	138.60 (d, J = 156.3, p- or o-$C_6H_3Me_2$)	
	152.97 (t, J = 30.3, ipso $C_6H_3Me_2$)	
	168.38 (s, CO_2Me)	
	178.34 (s, CO_2Me)	
	181.1 (dd, J = 40.0, 10, vinyl C–Rh)	

[a] THF-d_8 solvent. [b] $CDCl_3$ solvent. [c] ^1H decoupled.

Scheme II



the formulation $(C_5Me_5)Rh(PMe_3)(Ph)(\eta^1\text{-}SCH{=}NPh)$ (eq 3), and is similar to the insertion product seen in the CS_2



(3)

reaction. Furthermore, the mass spectrum of the mixture of isomers showed a single parent ion at m/e 527, along with fragments at m/e 451 ($M^+ - PMe_3$), 390 ($M^+ - SCH{=}NPh - H$), and 314 ($M^+ - SCH{=}NPh - Ph$). The IR spectrum (KBr) shows strong bands at 1532, 955, 754, 735, and 698 cm^{-1}. The ^{13}C NMR spectrum of the mixture confirms the presence of the -S—CH=N- moiety in the adducts with the observation of doublet resonances at δ 171.42 (**4a**) and 170.66 (**4b**). Consequently, it is reasonable to assign **4a** and **4b** to the E/Z isomers for the insertion product, although assignment of a specific geometry (E or Z) to each isomer was not possible. The observed isomerism cannot be due to the geometry of the ligands at the metal, as has been seen in other η^2-thioformamido complexes.[12] Furthermore, as this appears to be the first example of an η^1-thioformamido complex (those in the literature are η^2), the occurrence of E/Z isomerism has not been previously possible. No evidence for the formation of an η^2-PhNCS complex,[13] analogous to the η^2-CS_2 complex, was found.

Interconversions of 2, 3, and 4. As complexes **3** and **4** are related by substitution of the =S group for =NPh at the carbon center, it seemed likely that their interconversion might be effected by treating **3** with aniline or **4** with H_2S. The involvement of the common dithio-aminal intermediate shown in Scheme II was anticipated.

Treatment of a mixture of isomers of **4** with ~1 equiv of H_2S at ambient temperature in benzene solution led to a slow reaction. The reaction was complete after 4 days, producing four new products in a ratio of 71:15:9:5 as judged by the appearance of four sets of C_5Me_5 and PMe_3 resonances. $^{31}P\{^1H\}$ NMR spectroscopy of the solution confirmed the presence of four phosphine-containing products in the above ratio. Attempts to separate and purify the products was not possible, as described below, although spectroscopic studies allow the reasonable formulation of the major products of the reaction.

The dominant product formed in 71% yield (NMR) was identified as the dithio-aminal **5** on the basis of ^1H, ^{13}C, and ^{31}P NMR data (Tables I and II). The dithio-aminal C-H resonance appears at δ 9.537 in the ^1H NMR spectrum and is coupled to both the S-H hydrogen and the rhodium metal center. The ^{13}C NMR spectrum shows a doublet for this carbon resonance at δ 187.53. The H-S resonance appears distinctively at δ -2.474 and is split by coupling to the dithio-aminal hydrogen. Two broad temperature-dependent resonances with areas of 2 H each were seen for the Rh-phenyl protons near δ 9.8 and 7.6 as a consequence of hindered Rh-Ph rotation. When the sample is warmed to 56 °C, the high-field resonance sharpens to a doublet, consistent with an assignment to the two meta phenyl hydrogens. The low-field resonance broadens and shifts toward higher field, as is typically seen prior to coalescence with other $(C_5Me_5)Rh(PMe_3)(Ph)X$ complexes displaying hindered Rh-Ph rotation.[14]

The product formed in 15% yield (**6**) could not be definitively assigned, as it is a relatively minor product and most of the resonances other than those of the C_5Me_5 and PMe_3 ligands were obscured by the resonances for **5**. In that both the rhodium metal center and the dithio-aminal center in **5** are chiral, it is quite likely that this product is the companion diastereomer for **5**. Distinct resonances can be seen for the dithio-aminal hydrogen (δ 9.682, s) and phenyl-Rh ortho hydrogens (δ 8.109, d, J = 7.8 Hz, 1 H; δ 7.682, d, J = 7.6 Hz, 1 H). There should be no reason for this product not to form in the condensation of **4** and H_2S under conditions where **5** forms readily.

The product formed in 9% yield was easily identified as **3** by comparison with the resonances of the product of the reaction of **1** with CS_2. Aniline was also seen (δ 6.392, d, J = 8.1 Hz, 2 H; δ 6.698, t, J = 8 Hz, 1 H; other resonance obscured by C_6D_6 solvent) as a coproduct with this complex in about 19% yield.

The small amount of the product produced in 5% yield (**7**) made it difficult to assign a structure to this compound. The ^1H NMR spectrum provides evidence for the formulation of this product as the H_2S adduct of **3**, $(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)_2]$. With use of the C_5Me_5 and PMe_3 resonances as references, three peaks with areas of 1 H each are seen at δ -2.027 (d, J = 4.4 Hz), -2.120 (d, J = 3.6 Hz), and 11.851 (dd, J = 3.7, 2.2 Hz). The two S-H moieties are rendered inequivalent due to the chirality of the metal center. While these hydrogens do not couple to each other, they do couple to the trithiane hydrogen with slightly different coupling constants.

Scheme II summarizes the proposed interconversions responsible for the above products. Attempts to purify and separate the major components of this complex mixture were unsuccessful. Upon evaporation of the solvent and recrystallization from toluene/hexane at -20 °C, orange crystals were isolated and characterized. The ^1H NMR spectrum showed the product to contain only resonances in the aromatic region: δ 6.19, d, J = 7 Hz, 2 H; δ 6.76, m, 3 H; δ 8.86, br s, 1 H; δ 9.43, d, J = 15 Hz, 1 H. The mass spectrum shows an ion at m/e 137, allowing identification of the product as the thioformamide PhNHCH=S. Concentration of the mother liquor fol-

(12) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2722-2727 and references therein. Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, R. E. *Organometallics* **1983**, *2*, 315-322.

(13) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834-1838.

(14) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376-2388.

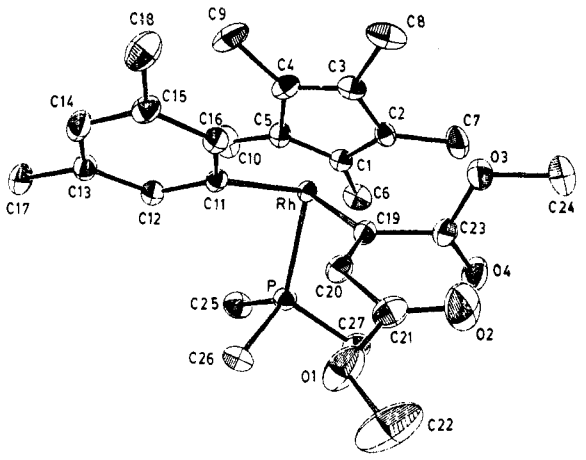
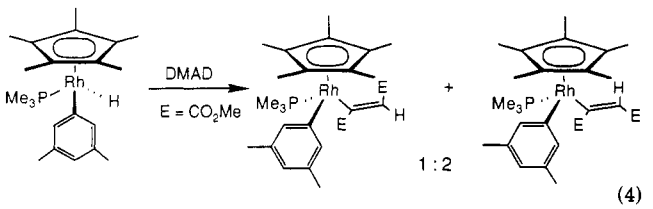


Figure 1. ORTEP diagram of *cis*-$(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl). Ellipsoids are shown at the 50% probability level.

lowed by precipitation with hexane produced a red solid that was identified as $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$ (**8**). The characteristic S–H resonance was observed at δ −2.458, and a parent ion was seen in the mass spectrum at m/e 424. This product was identical with a sample prepared independently by the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)Br$ with NaSH.

The same set of compounds is also entered by the reaction of **3** with aniline in benzene, also indicated in Scheme II. The solution was heated to 41 °C in order to effect reaction in a reasonable time (14 days). ^1H NMR spectroscopy showed resonances for **8** and the thioformamide PhNHCH=S. Chromatography on silica gel with a 30:70 mixture of THF/hexane allowed isolation of **8** but not the thioformamide.

Reactions of 1 with Acetylenes. Reactions of the aryl hydride complexes with electron-deficient acetylenes R—C≡C—R (R = CF_3, COOMe) also result in Rh–H insertion products. $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ (**1b**) displays a simple ^1H NMR spectrum and is useful for monitoring the progress of the reactions spectroscopically. Dimethyl acetylenedicarboxylate (DMAD) and **1b** react spontaneously in benzene solution to give a ~2:1 mixture of two products as determined by the presence of two distinct sets of C_5Me_5, 3,5-xylyl, and PMe_3 resonances in the ^1H NMR spectrum of the crude reaction mixture. New methoxy resonances appear at δ 3.818, 3.681, 3.567, and 3.157, each corresponding to a single methyl group. Two additional vinylic resonances at δ 5.566 (t, J = 2.6 Hz) and 6.815 (dd, J = 6.8, 3.6 Hz) with areas corresponding to one hydrogen each were also observed. The reaction of DMAD with **1a** gives similar results, although the aromatic region of the spectrum is more complicated and a 1.1:1 ratio of products was observed. Isolated yields of ~80% were obtained in both of these reactions and the products formulated as indicated below (eq 4).



(4)

As the NMR data did not allow absolute determination of the chemical structure of these two complexes, the materials were subjected to X-ray structural analysis following separation. Chromatography on silica gel with CH_2Cl_2/hexane eluent provided two orange fractions with R_f = 0.4 and R_f = 0.5.

Crystals from the faster moving major fraction were examined on a CAD4 automated diffractometer and found to crystallize in space group $P\bar{1}$. Routine data collection and Patterson map solution of the structure revealed a cis-vinyl moiety in the molecule $(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl) (**9c**) with an intact Rh–xylyl unit as shown in Figure 1. Distances and angles are given in Table III, and coordinates are given in Table IV.

Table III. Selected Distances (Å) and Angles (deg) in *cis*- and *trans*-$(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl)[a]

distance			angle		
bond	cis	trans	bonds	cis	trans
Rh–P	2.266 (1)	2.262 (1)	P–Rh–C11	93.37 (8)	82.82 (7)
Rh–C11	2.051 (3)	2.080 (2)	P–Rh–C19	85.76 (8)	96.25 (8)
Rh–C19	2.065 (3)	2.056 (3)	C11–Rh–C19	91.6 (1)	91.23 (9)
O1–C21	1.354 (5)	1.360 (3)	Rh–C19–C20	127.1 (2)	129.9 (2)
O1–C22	1.439 (5)	1.440 (4)	Rh–C19–C23	116.3 (2)	116.8 (2)
O2–C21	1.189 (4)	1.196 (3)	C20–C19–C23	116.3 (3)	113.1 (2)
O3–C23	1.351 (4)	1.333 (3)	C19–C20–C21	124.8 (3)	127.4 (2)
O3–C24	1.458 (4)	1.461 (4)	C19–C20–H	122.2 (3)	115.2 (3)
O4–C23	1.192 (4)	1.195 (3)	C21–C20–H	112.4 (3)	117.4 (3)
C19–C20	1.342 (5)	1.338 (4)	C21–O1–C22	116.0 (4)	114.5 (2)
C19–C23	1.491 (4)	1.493 (4)	C23–O3–C24	114.6 (3)	116.3 (3)
C20–C21	1.465 (4)	1.474 (4)	O1–C21–O2	121.8 (3)	122.2 (3)
C20–H	1.001 (3)	0.966 (2)	O1–C21–C20	109.4 (3)	109.9 (2)
			O2–C21–C20	128.8 (4)	127.7 (3)
			O3–C23–O4	123.2 (3)	121.0 (3)
			O3–C23–C19	111.6 (3)	112.9 (3)
			O4–C23–C19	125.1 (3)	126.1 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Positional Parameters for *cis*-$(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl)[a]

atom	x	y	z	B, Å^2
Rh	0.14797 (3)	0.25703 (1)	0.04543 (3)	2.158 (5)
P	0.2498 (1)	0.19401 (5)	0.2680 (1)	2.88 (2)
O1	0.5271 (3)	0.0832 (2)	−0.1024 (4)	5.93 (8)
O2	0.2742 (5)	0.0567 (2)	−0.2890 (4)	7.5 (1)
O3	−0.0032 (3)	0.1411 (1)	−0.3647 (3)	3.82 (6)
O4	−0.0088 (4)	0.0780 (2)	−0.1572 (3)	5.34 (8)
C1	−0.0897 (4)	0.2792 (2)	0.0757 (4)	2.97 (8)
C2	−0.1260 (4)	0.2588 (2)	−0.0953 (4)	2.88 (8)
C3	−0.0392 (4)	0.3084 (2)	−0.1552 (4)	3.20 (8)
C4	0.0456 (4)	0.3608 (2)	−0.0216 (5)	3.36 (8)
C5	0.0210 (4)	0.3424 (2)	0.1260 (4)	3.11 (8)
C6	−0.1713 (4)	0.2465 (2)	0.1805 (4)	4.22 (9)
C7	−0.2558 (5)	0.2014 (3)	−0.2008 (5)	4.9 (1)
C8	−0.0596 (6)	0.3094 (3)	−0.3371 (5)	5.4 (1)
C9	0.1376 (5)	0.4285 (2)	−0.0312 (6)	5.7 (1)
C10	0.0736 (5)	0.3883 (2)	0.2884 (5)	5.0 (1)
C11	0.3688 (4)	0.3116 (2)	0.0902 (4)	2.51 (7)
C12	0.4590 (4)	0.3515 (2)	0.2434 (4)	2.77 (7)
C13	0.5831 (4)	0.4035 (2)	0.2608 (4)	3.22 (8)
C14	0.6209 (4)	0.4151 (2)	0.1229 (5)	3.44 (9)
C15	0.5374 (4)	0.3756 (2)	−0.0323 (4)	3.21 (8)
C16	0.4134 (4)	0.3238 (2)	−0.0467 (4)	2.72 (7)
C17	0.6704 (5)	0.4484 (2)	0.4280 (5)	4.5 (1)
C18	0.5766 (5)	0.3896 (2)	−0.1848 (5)	4.6 (1)
C19	0.1957 (4)	0.1750 (2)	−0.0936 (4)	2.63 (7)
C20	0.3419 (4)	0.1580 (2)	−0.0843 (4)	3.09 (8)
C21	0.3693 (5)	0.0950 (2)	−0.1739 (5)	3.99 (9)
C22	0.5736 (6)	0.0230 (3)	−0.1775 (8)	9.0 (1)
C23	0.0531 (5)	0.1251 (2)	−0.2038 (4)	3.33 (8)
C24	−0.1285 (5)	0.0892 (3)	−0.4842 (5)	5.1 (1)
C25	0.2560 (5)	0.2343 (2)	0.4681 (5)	4.5 (1)
C26	0.4573 (5)	0.1720 (2)	0.3289 (5)	4.2 (1)
C27	0.1379 (6)	0.1090 (2)	0.2479 (5)	4.6 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

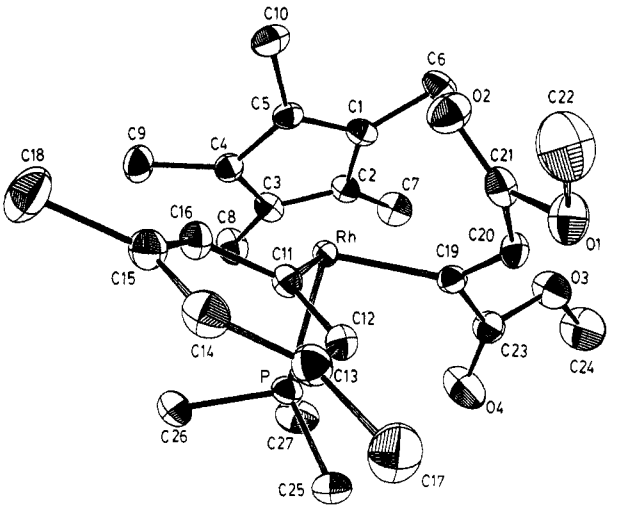


Figure 2. ORTEP diagram of *trans*-$(C_5H_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl). Ellipsoids are shown at the 50% probability level.

Similarly, the slower moving minor fraction was recrystallized and found to crystallize in space group $P2_1/n$. Routine data collection and Patterson map solution of this sample showed a trans-vinyl moiety and an intact xylyl group as indicated in Figure 2 for $(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl) (**9t**). Distances and angles are given in Table III, and coordinates are given in Table V.

The trans insertion product **9t** was found to display fluxional behavior on the basis of studies of its ^1H NMR spectrum. The variable-temperature ^1H NMR spectrum of the complex in $CDCl_3$ shows changes only in the δ 3.0–4.0 and vinyl regions of the spectrum, indicative of a process involving the vinylic ester methoxy groups. At low temperature (244 K), two minor (~5%) methoxy resonances are seen at δ 3.640 and 3.401 in addition to the two major methoxy resonances at δ 3.670 and 3.128. When the sample is heated from 244 to 284 K, the minor resonances coalesce into the base line and the major methoxy resonances begin to broaden. The last two peaks continue to broaden up to 329 K and shift toward one another, ultimately becoming sharper at 374 K with chemical shifts of δ 3.613 and 3.290.

At the coalescence limit of the minor isomer at 284 K the vinylic resonance broadens and disappears into the base line. Continuous irradiation of either the minor resonance at δ 3.401 or the major resonance at δ 3.670 results in the complete collapse of *all* of the methoxy resonances. An attempt to perform spin transfer by inversion of the low-field resonance of the major isomer with a selective 180° pulse showed no decrease in magnetization of the high-field methoxy resonance.

The fluxional process does not involve phosphine loss or exchange. Treatment of a benzene-d_6 solution of **9t** with PMe_3 does not change the ^1H NMR spectrum of the complex or of free PMe_3. Treatment of **9t** with $P(CD_3)_3$ shows no evidence for the exchange of coordinated phosphine after 15 min at 25 °C.

The acetylene $CF_3—C\equiv C—CF_3$ also reacts with **1a** to give a mixture of two products with distinct C_5Me_5, phenyl, vinyl, and PMe_3 resonances in the ^1H NMR spectrum. While these two compounds were not fully characterized, their identity as the cis- and trans-vinyl complexes arising from acetylene insertion into the Rh–H bond seems likely in comparison to the results of the reaction with DMAD.

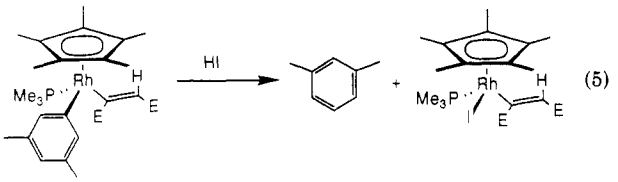
The reactions of the DMAD insertion products with HI and iodine were also examined. The cis isomer **9c** reacts

Table V. Positional Parameters for *trans*-$(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)](3,5-xylyl)[a]

atom	x	y	z	B, Å²
Rh	0.00643 (1)	0.26488 (2)	0.23311 (1)	2.224 (5)
P	−0.13635 (6)	0.23100 (7)	0.24488 (6)	3.24 (2)
O1	0.1905 (2)	0.5032 (2)	0.4587 (1)	4.22 (6)
O2	0.1962 (2)	0.4598 (2)	0.3312 (1)	4.19 (5)
O3	0.1518 (2)	0.0771 (2)	0.4383 (2)	5.25 (6)
O4	−0.0028 (2)	0.0855 (3)	0.3941 (2)	7.58 (8)
C1	0.1350 (2)	0.2075 (3)	0.2021 (2)	3.05 (7)
C2	0.0706 (2)	0.1103 (3)	0.1863 (2)	3.16 (7)
C3	−0.0112 (2)	0.1438 (3)	0.1198 (2)	3.31 (7)
C4	−0.0006 (2)	0.2615 (3)	0.0955 (2)	3.13 (7)
C5	0.0914 (2)	0.2998 (3)	0.1459 (2)	2.87 (6)
C6	0.2344 (2)	0.2040 (3)	0.2604 (2)	3.88 (8)
C7	0.0930 (3)	−0.0115 (3)	0.2245 (3)	4.73 (9)
C8	−0.0901 (3)	0.0621 (3)	0.0709 (3)	5.1 (1)
C9	−0.0661 (3)	0.3208 (4)	0.0192 (2)	4.43 (9)
C10	0.1377 (2)	0.4120 (3)	0.1349 (2)	4.05 (8)
C11	−0.0244 (2)	0.4385 (3)	0.2532 (2)	2.48 (6)
C12	−0.0218 (2)	0.4865 (3)	0.3299 (2)	2.85 (7)
C13	−0.0368 (2)	0.6058 (3)	0.3406 (2)	3.07 (7)
C14	−0.0573 (2)	0.6797 (3)	0.2725 (2)	3.35 (7)
C15	−0.0651 (2)	0.6367 (3)	0.1941 (2)	3.13 (7)
C16	−0.0493 (2)	0.5177 (3)	0.1853 (2)	2.99 (7)
C17	−0.0305 (3)	0.6509 (3)	0.4268 (2)	4.91 (9)
C18	−0.0907 (3)	0.7158 (3)	0.1187 (2)	5.02 (9)
C19	0.0824 (2)	0.2436 (3)	0.3584 (2)	2.87 (7)
C20	0.1477 (2)	0.3132 (3)	0.4105 (2)	3.22 (7)
C21	0.1781 (2)	0.4302 (3)	0.3920 (2)	3.24 (7)
C22	0.2193 (3)	0.6208 (4)	0.4469 (3)	5.8 (1)
C23	0.0703 (2)	0.1297 (3)	0.3977 (2)	3.87 (8)
C24	0.1461 (4)	−0.0347 (4)	0.4792 (3)	7.8 (1)
C25	−0.1649 (3)	0.2785 (4)	0.3367 (2)	4.71 (9)
C26	−0.2291 (2)	0.3054 (4)	0.1618 (2)	4.78 (9)
C27	−0.1783 (3)	0.0809 (4)	0.2341 (3)	5.9 (1)

[a] See footnote *a* in Table IV.

with excess aqueous HI to give *m*-xylene and *cis*-$(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)]I in good yield (eq 5). Chromatography on silica gel allows isolation



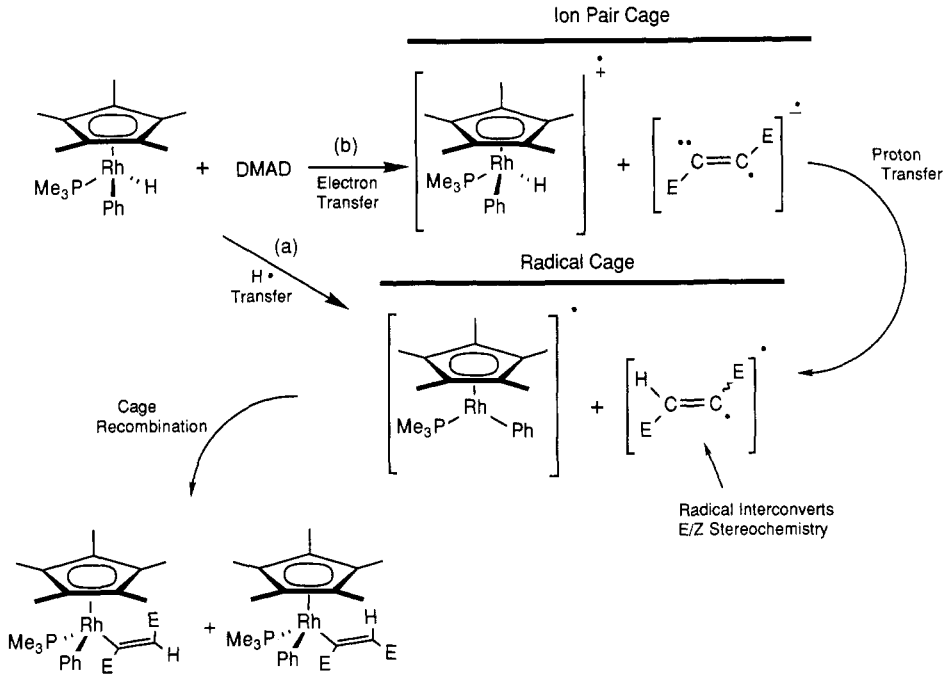
(5)

of the organometallic product, whose ^1H NMR spectrum ($CDCl_3$) displays resonances at δ 1.632 (d, J = 10.6 Hz, 9 H), 1.834 (d, J = 2.9 Hz, 15 H), 3.643 (s, 3 H), 3.706 (s, 3 H), and 6.06 (br s, 1 H). A similar reaction of the trans isomer **9t** with aqueous HI gives *m*-xylene and the trans-vinyl iodide complex. The ^1H NMR spectrum of the latter is similar to that of the cis analogue, with resonances at δ 1.658 (d, J = 10.4 Hz), 1.827 (d, J = 3.1 Hz, 15 H), 3.625 (s, 3 H), 3.667 (s, 3 H), and 6.491 (dd, J = 2.9, 1.9 Hz, 1 H).

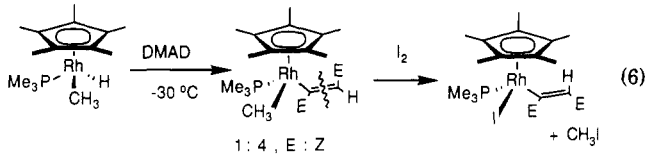
The reaction of the cis-vinyl complex **9c** with iodine in chloroform resulted in the formation of the substituted styrene $C_6H_3Me_2C(COOMe)=CH(COOMe)$ in 50% yield. The two metal products $(C_5Me_5)Rh(PMe_3)I_2$ and $(C_5Me_5)Rh(PMe_3)$[C(COOMe)=CH(COOMe)]I could be identified each in ~50% yield. A similar reaction of the trans isomer **9t** with iodine in chloroform solution resulted in gross decomposition.

Reaction of $(C_5Me_5)Rh(PMe_3)(CH_3)H$ with DMAD. The reaction of the methyl hydride complex $(C_5Me_5)Rh(PMe_3)(CH_3)H$ with DMAD was examined at low temperature (methane is lost above −20 °C) in order to assess the feasibility of functionalizing alkanes by this pathway.

Scheme III



At −50 °C, the methyl hydride complex reacts with DMAD to give a 4:1 ratio of two new complexes containing C_5Me_5, PMe_3, and DMAD moieties on the basis of the ^1H NMR spectrum. These compounds are assigned to the cis- and trans-vinyl methyl derivatives $(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](CH_3)$ (eq 6). Chromatography on silica gel allowed isolation of the minor trans isomer, while the cis isomer appeared to be destroyed on the support.



(6)

Reaction of the vinyl methyl derivative with iodine in benzene-d_6 gave a quantitative reaction to produce methyl iodide and the vinyl iodide complex *tran*-$(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)]I$. A similar reaction in $CDCl_3$ gave *tran*-$(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)]Cl$.

Discussion

The aryl hydride complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ have been found to be in equilibrium with η^2-arene complexes at room temperature, although the equilibrium lies heavily in favor of the oxidative-addition adduct. This lability of the Rh-C and Rh-H bonds does not translate into arene lability, since dissociation of unhindered arenes such as benzene, toluene, and *m*-xylene does not occur at a reasonable rate until the complexes are heated to 60 °C. More crowded complexes such as those formed from *p*-xylene and *p*-diisopropylbenzene eliminate their arene ligands at lower temperatures. With *p*-di-*tert*-butylbenzene, steric crowding is so unfavorable in the aryl hydride complex that the equilibrium is tipped in favor of the η^2-arene complex.[7]

As a result of the combined effects of coordinative saturation and stability of the aryl hydride species, a major reaction pathway with CS_2 involves substitution of the incoming electrophile for C_6H_6. The reaction of **1a** with CS_2 occurs at 25 °C, at which temperature the complex does not dissociate benzene but does reversibly form the η^2 adduct $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6H_6)$ about once per second. The electrophile apparently displaces the arene in a bimolecular reaction, similar to the earlier observations by Cramer in the associative reaction of CS_2 with $CpRh(C_2H_4)_2$.[15] The η^2-arene adduct is formally Rh(I), whose electron-rich character permits a more facile associative reaction with electrophiles than with nucleophiles. Werner's preparation of this complex was carried out at 25 °C, suggesting that the reaction of CS_2 with $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ is also associative.

The electron-deficient acetylenes DMAD and hexafluoro-2-butyne, and the heteroallene PhNCS, do not displace arene from **1b** but instead undergo "direct" insertion into the Rh–H bond. The reaction is termed direct in that the ligands in **1b** are not labile and consequently a coordination–insertion mechanism would require the intermediacy of a high-energy, sterically unreasonable, 20-electron complex or η^3-C_5Me_5 intermediate, or other coordinatively unsaturated complex. Insertion of a metal-bound acetylene via a 16-electron intermediate would be expected to give only the cis-insertion product **9c**, contrary to the observed lack of specificity. The insertion reactions of activated acetylenes into M–H bonds in other metal complexes often gives both cis- and trans-vinyl insertion products, although some complexes are reported to give only cis or trans insertion products.[16] Of these examples, the reactions of acetylenes with $CpRu(PPh_3)_2H$ and $CpRu(PPh_3)(CO)H$ are perhaps the most relevant to the present studies. With DMAD, these ruthenium hydrides give only trans-vinyl isomers.[17]

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We can postulate two similar mechanisms to account for the observed products. The first involves transfer of a hydrogen atom from the rhodium to the acetylene to produce a 17-electron metal intermediate and a vinyl radical. The vinyl radical would be configurationally unstable and would rapidly isomerize between the cis and trans forms. Collapse of the radical pair would give rise to the observed mixture of **9c** and **9t** as indicated in Scheme IIIa. The second mechanism is similar to the first except that the hydrogen atom transfer involves two steps. First, the acetylene oxidizes the metal and a proton is transferred in an independent step. This produces the same radical pair as described in Scheme IIIa leading to the same set of products (Scheme IIIb). Evidence for such an electron-transfer/radical mechanism has been put forth by Clark in studying the reactions of $Pt(PR_3)_2H_2$ with acetylenes.[18]

The transfer of a hydrogen atom to an unsaturated C–C bond is similar to the mechanism proposed for the reaction of styrene with the metal hydrides $HCo(CO)_4$ and $HMn(CO)_5$ studied by Halpern,[19] Sweany,[20] and Orchin.[21] In many of these other reactions, CIDNP was observed as a proof of the intermediacy of radical species. No CIDNP effects were observed in the reaction of **1b** with DMAD, nor were any color changes indicative of the formation of charge-transfer complexes observed. Consequently, we favor the electron-transfer pathway (Scheme IIIb).

While the cleavage of the metal–carbon bond could be effected with iodine or acid, these reactions are far from ideal for functionalizing aromatic C–H bonds. The failure of these functionalizations can be attributed to the preferential insertion of the acetylene into the rhodium–hydride bond rather than into the rhodium–aryl or rhodium–alkyl bond. In contrast to the observed elimination behavior of palladium aryl vinyl complexes,[22] reductive elimination does not occur in the vinyl aryl derivatives **9c** and **9t**, whereas the desired hydrido styryl complex would undoubtedly have eliminated a substituted styrene. Indeed, the reaction of DMAD with $(C_5Me_5)Rh(PMe_3)H_2$ results not only in insertion into the M–H bond but also in reductive elimination of the vinyl hydride complex.[23] These reductive-elimination trends fall in line with the general reluctance of organometallic complexes to eliminate C–C bonds. While the methyl hydride complex undergoes insertion reactions with DMAD similar to those of the aryl hydride complex, the oxidative-cleavage results do not lead to functionalized alkane products incorporating this ligand but rather to methyl iodide. A similar cleavage of the rhodium–alkyl bond in $(C_5Me_5)Rh(PMe_3)(R)H$ with bromine to give alkyl bromide was reported by Bergman.[2]

The variable-temperature NMR spectroscopy of the trans insertion complex **9t** shows that a dynamic process is occurring that interconverts the neighborhoods of the ester MeO groups. While the exact nature of these interconversions was not elucidated, the ^1H NMR data are consistent with the presence of both a major and a minor conformer that interconvert upon warming. The observation that saturation of one of the minor methoxy resonances results in collapse of *all three* of the remaining methoxy resonances suggests that the two ends of the incipient disubstituted acetylenic group are interconverting.

The broadening of the vinylic hydrogen resonance also suggests that its environment is changed in the exchange process. One can speculate that the two isomers observed correspond to two rotational conformations of the vinylic moiety (on the basis of the coalescence observations), similar to those observed in $(C_5Me_5)Rh(PMe_3)(aryl)X$ complexes and other vinyl complexes produced by acetylene insertion into the M–H bond. However, the vinylic hydrogen and the metal must also undergo an exchange reaction involving simultaneous 1,2-shifts that exchange the ends of the vinyl group attached to the metal, on the basis of the spin transfer results (eq 7). This postulate

(7)

should be viewed with some skepticism in the absence of more substantive dynamic NMR and labeling studies. A mechanism involving phosphine dissociation and formation of an η^2-vinyl intermediate prior to the 1,2-shift, similar to the rearrangement proposed by Green in Mo–η^2-vinyl complexes,[24] can be ruled out since the phosphine was shown not to be labile.

Conclusions

In summary, the coordinatively saturated species $(C_5Me_5)Rh(PMe_3)(R)H$ react with electrophilic substrates to give products in which either displacement of RH and coordination of the electrophile is seen (CS_2) or in which insertion of the electrophile into the Rh–H bond is seen (CS_2, PhNCS, RC≡CR). These insertion adducts are formed unselectively and cannot be cleaved efficiently with acid or halogens to give functionalized products.

Experimental Section

All solvents were distilled from dark purple solutions of sodium benzophenone ketyl under a nitrogen atmosphere. All compounds were handled in a Vacuum Atmospheres Dri-Lab equipped with a −20 °C freezer. All experiments were performed in sealed NMR tubes or ampules prepared and degassed on a high-vacuum line. $(C_5Me_5)Rh(PMe_3)(Ph)H$, $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$, and $(C_5Me_5)Rh(PMe_3)(Me)H$ were prepared as previously described.[7] CS_2, PhNCS, and DMAD were purchased from Aldrich Chemical Co. and used as received after freeze–pump–thaw degassing.

NMR spectra were recorded on a Bruker WH-400 spectrometer. X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer and solved by using the TEXRAY software package adapted to a PDP11/23 computer. Mass spectra were recorded on a Nermag R10-10c GC/MS instrument. IR spectra were recorded on a Mattson Sirius 100 FTIR spectrometer.

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with CS_2. A C_6D_6 solution of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (0.19 mmol, 75 mg) in a septum-capped NMR tube was reacted with 1.1 equiv of CS_2 (0.21 mmol, 13 μL). (The CS_2 was freeze–pump–thaw-degassed prior to use.) After 1 h at 25 °C the reaction quantitatively produces $(C_5Me_5)Rh(PMe_3)(CS_2)$ (84%) and $(C_5Me_5)Rh(PMe_3)(SCHS)(Ph)$ (16%). The products were separated by column chromatography under nitrogen with using a 40:60 THF/hexane mixture as eluent. The first product eluted was $(C_5Me_5)Rh(PMe_3)(CS_2)$, which was recrystallized from benzene to yield a red microcrystalline powder. Anal. Calcd (found) for $C_{14}H_{24}S_2PRh$: C, 43.08 (44.35); H, 6.20 (6.44); S, 16.43 (14.80). IR (KBr): 1159, 1146 cm^{-1} (out-of-ring C=S); 636, 617 cm^{-1} (in-ring C—S). Mass spectrum (calcd (obsd)):

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m/e 390.0103 (390.0262). The second product to elute was recrystallized from benzene to yield a yellow waxy solid identified as $(C_5Me_5)Rh(PMe_3)(SCHS)(Ph)$. Anal. Calcd (found) for $C_{15}H_{30}S_2PRh$: C, 51.28 (50.98); H, 6.45 (6.66); S, 13.69 (12.14). IR (KBr): 1015, 990, 951, 732 cm^{-1}. Mass spectrum (calcd (obsd)): *m/e* 468 (468).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with PhNCS. A sample of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (235 mg, 0.6 mmol) was dissolved in 0.4 mL of C_6D_6 and 100 μL of PhNCS (0.854 mmol) added. A ^1H NMR spectrum recorded after 15 min showed ~67% reaction to give two new $(C_5Me_5)Rh(PMe_3)$-containing products. After 5 days, the solution was spotted onto a silica gel TLC plate and chromatographed with 50:50 THF/hexane as eluent. A wide yellow band traveled up the plate ($0.4 < R_f < 0.8$). The band was divided into two parts and each part extracted with THF (3 × 10 mL) and evaporated (25 °C, 10^{-4} mm). Examination of these leading and trailing fractions by ^1H NMR spectroscopy showed identical spectra. The combined isolated yield was 150 mg (47%), although the ^1H NMR yield was quantitative. The low isolated yield was attributed to the affinity of the yellow compound for the silica gel, as the THF washings did not remove all of the product. IR (KBr): 1532 (s), 754 (s) cm^{-1}, and absorptions seen in $(C_5Me_5)Rh(PMe_3)(Ph)Br$. Mass spectrum (60 eV): *m/e* 527 (M^+), 451 ($M^+ - PMe_3$), 390 ($M^+ - SCH{=}NPh - H$), 314 ($M^+ - SCH{=}NPh - Ph$). Anal. Calcd (found) for $RhSPNC_{26}H_{35}$: C, 59.20 (59.32); H, 6.68 (6.83); N, 2.65 (2.67).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}NPh)$ with H_2S. A 50-mg (0.95-mmol) amount of $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}NPh)$ was dissolved in C_6D_6 (0.73 mL) in an NMR tube. ^1H and ^{31}P NMR spectra showed only resonances for the two isomers of the complex (see text). The solution was then put under a pressure of 700 mm of H_2S gas and the tube sealed. The reaction at 25 °C was monitored by ^1H NMR spectroscopy, showing 14% completion after 6 h. After 88 h, all starting material had disappeared and the ^{31}P NMR and ^1H NMR spectra showed four products, as discussed in the text. In an attempt to isolate the major product, the tube was broken open and the solution evaporated to dryness, leaving a red-orange solid. The solid was taken up in 2 mL of toluene, filtered through a cotton plug, and treated with 3 mL of hexane. Orange crystals grew after standing at −20 °C overnight and were collected by decanting the supernatant liquid. The crystals were washed with cold hexane (1 mL) and dried under vacuum; yield 10 mg. Examination of the solid by ^1H NMR spectroscopy showed mainly resonances for $PhNHCH{=}S$ with a small amount (<5%) of contamination by $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$. ^1H NMR (C_6D_6): δ 6.19 (d, J = 7 Hz, 2 H), 6.76 (m, 3 H), 8.86 (br s, 1 H), 9.43 (d, J = 15 Hz, 1 H). Mass spectrum (70 eV): *m/e* 137 (M^+), 136, 110, 104, 93, 77. The mother liquor was concentrated to 0.5 mL and 2 mL of hexane added, producing a red solid that was collected by filtration. Examination of the solid by ^1H NMR spectroscopy showed mainly resonances for $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$ with a small amount (~25%) of contamination by $PhNHCH{=}S$. Mass spectrum (70 eV): *m/e* 424 (M^+), 391 ($M^+ - SH$), 347 ($M^+ - Ph$), 314 ($M^+ - PhSH$), 237 ($M^+ - PMe_3 - PhSH - H$). ^1H NMR (C_6D_6): δ 1.598 (d, J = 2.6 Hz, 15 H), 1.324 (d, J = 10.2 Hz, 9 H), −2.994 (d, J = 3.6 Hz, 1 H), 6.764 (d, J = 7.1 Hz, 1 H), 6.824 (t, J = 7.2 Hz, 2 H), 7.290 (d, J = 8.8 Hz, 2 H).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}S)$ with Aniline. A solution of $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}S)$ (4 mg, 0.0085 mmol) in 0.5 mL of C_6D_6 was placed in an NMR tube attached to a ground-glass joint. An aliquot (1.3 equiv) of aniline (0.011 mmol, 1 μL) was added to the solution with a syringe and the tube sealed under vacuum following freeze–pump–thaw degassing. The tube was heated to 41 °C in an oil bath and the reaction followed by NMR spectroscopy. Complete reaction required 15 days. A new metal-containing product was isolated by cracking open the tube and removing aniline under vacuum (10^{-4} mm, 25 °C). The crude product was purified by thin-layer (2000-μm) chromatography on silica gel with a 70:30 hexane/THF solvent mixture as eluent (R_f = 0.9), yielding a yellow-brown waxy solid identified as $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$. The remaining non-metal-containing product could not be isolated by thin-layer chromatography.

Preparation of $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$. $(C_5Me_5)Rh(PMe_3)(Ph)Br$ (10.1 mg, 0.0214 mmol) was dissolved in 0.5 mL of C_6D_6 and placed in an NMR tube attached to a ground-glass joint. A 3.6-equiv amount of NaHS (6 mg, 0.077 mmol) was added to the solution and the sample freeze–pump–thaw-degassed. After the tube was sealed under vacuum, the sample was heated to 34 °C. A slow reaction occurred ($\tau_{1/2}$ = 50 days) to give $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$.

Reaction of $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ with DMAD. A 290-mg (0.69-mmol) amount of $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ was dissolved in THF (10 mL), the solution cooled to −40 °C, and 110 μL (0.8 mmol) of DMAD added with a syringe. The solution was warmed to 25 °C and the solvent removed (25 °C, 10^{-4} mm). The product was filtered through a thin pad of silica gel with use of 1% THF/CH_2Cl_2 and the solvent evaporated, producing 301 mg (77% yield) of isolated product (**9c + 9t**). The material was then chromatographed on silica gel with use of 1% THF/CH_2Cl_2. The leading fraction (R_f = 0.5) yielded 160 mg of the cis isomer **9c**. The slower fraction (R_f = 0.4) yielded 90 mg of the trans isomer **9t**. ^1H and ^{31}P NMR data are given in Tables I and II. Spectral and analytical data for **9c**: IR (KBr) 2976 (m), 2950 (m), 2913 (s*), 1710 (s), 1552 (s*), 1198 (s), 1145 (s), 955 (s*) (asterisks indicate bands also seen in $(C_5Me_5Rh(PMe_3)(Ph)Br)$; mass spectrum (70 eV) *m/e* 562 (M^+, 1%), 559 ($M^+ - 3H$, 10%), 485 (M^+ - xylyl, 20%), 313 (M^+ - xylyl - $C_2H(COOMe)_2$, 46%). Anal. Calcd (found) for $RhPO_4C_{27}H_{40}$: C, 57.65 (55.91); H, 7.17 (6.97).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with DMAD. A THF solution (20 mL) of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (456 mg, 1.16 mmol) was treated with 230 μL of DMAD (1.87 mmol) at −40 °C. The solution was allowed to warm to 25 °C, and the volatiles were removed under vacuum. The product was then chromatographed on silica gel with use of 0–4% THF/CH_2Cl_2. While two distinct bands were not observed, the leading cut yielded 192 mg (32%) of the cis insertion product and the tailing cut yielded 149 mg (24%) of the trans insertion product. A middle cut (112 mg, 18%) contained a mixture of the two isomers; combined isolated yield 73%. The trans isomer was recrystallized by slow evaporation of a 2:1 CH_2Cl_2/hexane solution. The cis isomer was recrystallized from hot hexane with a small amount of $CHCl_3$ added to give a bright yellow microcrystalline product. Both crystalline products were characterized by single-crystal X-ray diffraction. IR (KBr): 3065 (m*), 2961 (s), 2919 (s*), 1705 (s), 1198 (s), 1146 (s), 952 (s*), 734 (s*). Mass spectrum (70 eV): *m/e* 534 (M^+, 3%), 531 ($M^+ - 3H$, 97%), 455 ($M^+ - Ph - 2H$, 100%), 313 ($M^+ - Ph - C_2H(COOMe)_2$). Anal. Calcd (found) for $RhPO_4C_{25}H_{36}$: C, 56.18 (56.33); H, 6.79 (6.67). ^{31}P NMR (C_6D_6): δ 2.10 (d, J = 155 Hz, major isomer, cis) 3.29 (d, J = 155 Hz, minor isomer, trans). ^1H NMR (C_6D_6): cis isomer, δ 1.35 (d, J = 3 Hz, 15 H, C_5Me_5), 1.07 (d, J = 9 Hz, 9 H, PMe_3), 3.47 (s, 3 H, MeO), 3.57, (s, 3 H, MeO), 5.96 (t, J = 1.5 Hz, 1 H, vinyl H), 7.10 (m, 1 H, Ph), 7.25 (d, J = 7 Hz, 1 H, Ph), 7.45 (d, J = 7 Hz, 2 H, Ph), 8.29 (d, J = 7 Hz, 1 H, Ph); trans isomer δ 1.35 (d, J = 3 Hz, 15 H, C_5Me_5), 1.01 (d, J = 9 Hz, 9 H, PMe_3), 3.39 (s, 3 H, MeO), 3.85 (s, 3 H, MeO), 7.03 (m, 1 H, vinyl H), 7.10 (m, 3 H, Ph), 7.55 (d, J = 7 Hz, 2 H, Ph).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with $CF_3C{\equiv}CCF_3$. A solution of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (17 mg, 0.043 mmol) in C_6D_6 (0.4 mL) was prepared in an NMR tube and $CF_3C{\equiv}CCF_3$ bubbled through the solution with a needle. A ^1H NMR spectrum was recorded, showing two new organometallic products.

Reaction of $(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)](3,5\text{-xylyl})$ with HI. A solution of the cis complex **9c** (8.3 mg, 0.015 mmol) in 1 mL of $CDCl_3$ was reacted with 1 drop of aqueous HI (57%), and the solution was stirred for 4 h at 25 °C. The reaction progress was monitored by TLC (silica gel, 2% THF/CH_2Cl_2) until the starting material vanished. A ^1H NMR spectrum showed resonances attributable to free *m*-xylene at δ 2.316 (s, 6 H), 6.974 (d, J = 7.4 Hz, 2 H), 6.998 (s, 1 H), and 7.144 (t, J = 7.4 Hz, 1 H). A single product was isolated by preparative TLC (R_f = 0.2) and identified as *cis*-$(C_5Me_5)Rh(PMe_3[C(COOMe){=}CH(COOMe)]I$. ^1H NMR ($CDCl_3$): δ 1.837 (d, J = 2.9 Hz, 15 H), 1.637 (d, J = 10.6 Hz, 9 H), 3.706 (s, 3 H), 3.643 (s, 3 H), 6.05 (br s, 1 H). Mass spectrum (70 eV): *m/e* 584 (M^+), 508 ($M^+ - PMe_3$), 457 ($M^+ - I$), 441 ($M^+ - C_2H(COOMe)_2$), 381 ($M^+ - PMe_3 - I$).

A solution of the trans complex **9t** (1.2 mg, 0.002 mmol) was dissolved in $CDCl_3$ (0.4 mL) and 2 μL of aqueous HI (57%) added. The solution was stirred for 1 h, during which time the starting material disappeared as determined by monitoring with TLC. A

Table VI. Summary of Crystallographic Data for *cis*- and *trans*-(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](3,5-xylyl)

	trans isomer	cis isomer
	Crystal Parameters	
formula	$RhPO_4C_{27}H_{40}$	$RhPO_4C_{27}H_{40}$
fw	562.50	562.50
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
Z	4	2
a, Å	15.090 (2)	8.928 (5)
b, Å	11.361 (2)	19.111 (4)
c, Å	16.886 (4)	8.590 (2)
α, deg	90	94.21 (2)
β, deg	109.54 (2)	111.86 (4)
γ, deg	90	94.08 (3)
V, Å^3	2728.4 (1.8)	1348.9 (1.8)
d_{calc}, g/cm^3	1.37	1.38
cryst dimens, mm	0.20 × 0.27 × 0.31	0.22 × 0.48 × 0.10
temp, °C	25	25
	Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD4, κ geometry	
radiation (monochromator)	Mo, 0.71073 Å (graphite)	
scan type	$2\theta/\omega$	
scan rate, deg/min	2–16.5	
total bkgd time	(scan time)/2	
takeoff angle, deg	2.6	
scan range, deg	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ
2θ range, deg	4–47	4–46
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$
no. of data collected	4241	4030
no. of unique data $>3\sigma$	3479	3309
no. of params varied	298	298
abs coeff, cm^{-1}	7.00	7.08
systematic absences	$0k0$, k odd; $h0l$, $h + l$ odd	none
abs cor	none	empirical
range of transmission factors		88.3–100.0
equiv data	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$, $0\bar{k}l = 0k\bar{l}$
agreement between equiv data (F_o)	0.007	
R_1	0.0280	0.0301
R_2	0.0406	0.0407
goodness of fit	1.62	1.54

^{1}H NMR spectrum of the solution showed free *m*-xylene and resonances for *trans*-(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)]I: δ 1.828 (d, J = 3.2 Hz, 15 H), 1.658 (d, J = 10.4 Hz, 9 H), 3.624 (s, 3 H), 3.667 (s, 3 H), 6.481 (dd, J = 2.9, 1.9 Hz).

Reaction of (C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](3,5-xylyl) with I_2. The cis complex **9c** (7.6 mg, 0.014 mmol) was dissolved in $CDCl_3$ (0.5 mL) and a small amount of I_2 added (3.8 mg, 0.015 mmol). The products (C_5Me_5)Rh(PMe_3)I_2, *cis*-(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)]I, and *cis*-($C_6H_3Me_2$)(COOMe)C=CH(COOMe) were identified by comparison of ^{1}H NMR and mass spectral data with those of authentic samples. A similar reaction with the trans complex **9t** led to gross decomposition of the sample upon addition of I_2.

Reaction of (C_5Me_5)Rh(PMe_3)(CH_3)H with DMAD. A solution of (C_5Me_5)Rh(PMe_3)(CH_3)Cl in 1 mL of THF was treated with 16.8 mg (0.066 mmol) of $AgPF_6$. After it was stirred for 5 min, the solution was filtered through a cotton plug to remove AgCl precipitate. The solution was cooled to −78 °C and 70 μL of 1 M Li$^+$[HB(*s*-Bu)$_3$]$^-$ (0.070 mmol) added, followed by 1 mL of THF containing 20 mg of DMAD. The solution was warmed to 25 °C over 30 min, and the volatiles were removed (25 °C, 10^{-4} mm). A ^{1}H NMR spectrum showed two products in a 5:1 ratio. The major species observed was unreacted [(C_5Me_5)Rh(PMe_3)(CH_3)(THF)]$^+$[PF_6]$^-$. ^{1}H NMR (C_6D_6): δ 1.66 (d, J = 2 Hz, 15 H), 0.94 (d, J = 9 Hz, 9 H), 0.02 (dd, J = 2, 1 Hz, 3 H), 3.56 (br s, 4 H), 1.41 (br s, 4 H). While this product did (expectedly) not survive chromatography on silica gel (3% THF/CH_2Cl_2 eluent), the minor product did. It was identified as the insertion adduct *trans*-(C_5Me_5)Rh(PMe_3)(CH_3)[C(COOMe)=CH(COOMe)] on the basis of comparison with model compounds. ^{1}H NMR (C_6D_6): δ 1.618 (d, J = 2.6 Hz, 15 H), 1.117 (d, J = 10.0 Hz, 9 H), 0.275 (dd, J = 4.6, 2.3 Hz, 3 H), 3.448 (s, 3 H), 3.516 (s, 3 H), 6.914 (dd, J = 3.6, 2.2 Hz, 1 H). Mass spectrum (20 eV, M^+ not observed): m/e 441 (M^+ − OMe), 329 (M^+ − C_2H(COOMe)$_2$), 314 (M^+ − CH_3 − C_2H(COOMe)$_2$).

Reaction of (C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](CH_3) with I_2. Treatment of the minor product from the above experiment with I_2 in $CDCl_3$ confirmed its formulation as the methyl vinyl complex. Reactant resonances in $CDCl_3$ are given in Table I. The product solution showed a singlet resonance for free MeI at δ 2.165, as well as resonances for the product (C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)]I. ^{1}H NMR ($CDCl_3$): δ 1.827 (d, J = 3.2 Hz, 15 H), 1.658 (d, J = 10.7 Hz, 9 H), 3.624 (s, 3 H), 3.666 (s, 3 H), 6.491 (m, 1 H). Mass spectrum (20 eV): m/e 584 (M^+), 508 (M^+ − PMe_3), 457 (M^+ − I), 381 (M^+ − PMe_3 − I), 143 (C_2H(COOMe)$_2^+$).

Reaction of *trans*-(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](3,5-xylyl) with $P(CD_3)_3$. A $CDCl_3$ solution of the trans insertion adduct **9t** (3.6 mg/0.4 mL) was treated with 3 μL of $P(CD_3)_3$. A ^{1}H NMR spectrum showed no exchange of the free deuterated phosphine with the coordinated PMe_3 after 15 min at 25 °C.

Reaction of (C_5Me_5)Rh(PMe_3)(Ph)H with Methyl Acrylate, CO_2, and Methyl Isocyanate. A 10-mg (0.025-mmol) amount of (C_5Me_5)Rh(PMe_3)(Ph)H and 7 μL of methyl acrylate were dissolved in 0.5 mL of C_6D_6 in an NMR tube. No reaction was observed after 2 days at 25 °C. A similar reaction was run with methyl isocyanate as the added substrate. Again no reaction was observed. A third sample of the rhodium complex in benzene was placed under 1 atm of CO_2. No reaction occurred at 25 °C.

X-ray Structural Determination of *cis*- and *trans*-(C_5Me_5)Rh(PMe_3)[C(COOMe)=CH(COOMe)](3,5-xylyl). A similar procedure was used for both complexes. Well-formed orange crystals of each compound were prepared by slow evaporation of a CH_2Cl_2/hexane solution. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction with the program TRACER revealed a primitive monoclinic crystal system for the trans isomer, and a triclinic crystal system for the cis-isomer. Data were collected on each crystal in accord with the parameters in Table VI. Data for the cis isomer were corrected for decay (4.6%) and absorption. The space group for the trans isomer was uniquely assigned as $P2_1/n$ on the basis of the systematic absences ($0k0$, k odd; $h0l$, $h + l$ odd), and the correctness of this choice was confirmed by successful solution of the Patterson map. The cis isomer was solved correctly in the centric space group $P\bar{1}$. The Molecular Structure Corp. and Enraf-Nonius SDP programs were used for solution and refinement of the structure.[25] In each structure, least-squares refinement of the rhodium followed by a difference Fourier map revealed a peak for the phosphorus atom. Introduction of these two peaks revealed all non-hydrogen atoms in subsequent difference Fourier maps. Some hydrogen atoms were located on a difference Fourier map, and others were placed in idealized locations. Final anisotropic refinement was carried out on all non-hydrogen atoms.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms (19 pages); listings of calculated and observed structure factors (69 pages). Ordering information is given on any current masthead page.

(25) $R_1 = [\sum\|F_o| - |F_c\|]/[\sum|F_o|]$ and $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/[\sum wF_o^2]$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.