Applied Organometallic Chemistry (1990) 4 493–501

0268-2605/90/050493-09$05.00

C–H and N–H bond activation in reactions of vinyl acetate, allyl cyanide, allylamine and other amines with $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$

Ron S Dickson and Susan M Jenkins
Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

Received 30 November 1989 *Accepted 12 January 1990*

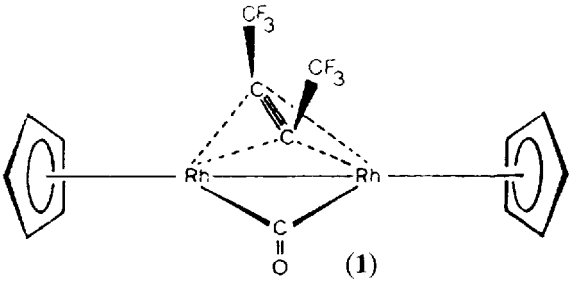
There is activation of olefinic C–H bonds when $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ is treated with vinyl acetate or allyl cyanide. These reactions are initiated by exposure to sunlight. In the vinyl acetate reaction, each of the three vinylic C–H bonds can be broken, but there is strong preference for cleavage at the substituted carbon. The products formed in these reactions are bisalkenyl complexes of the type $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)H\}(\mu\text{-}CR{=}CR'R'')$, and all isomers have been thoroughly characterized by NMR analysis. Similar reactions with allylamine and other amines (NH_2R, $NHMe_2$) occur in the dark and proceed by N–H bond cleavage. Near-quantitative amounts of the products, $(\eta\text{-}C_5H_5)_2Rh_2\{C(CF_3)C(CF_3)H\}(C(O)NRR')$ are isolated. Spectroscopic data indicate a bridging carboxamide ligand attached to the Rh–Rh bond from oxygen and nitrogen donor sites. It is proposed that coordination of O or N to rhodium has a strong influence on all of the reactions studied.

Keywords: C–H activation, N–H activation, $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, alkenyl, carboxamide

INTRODUCTION

Bond activation is at the heart of metal-mediated organic synthesis. It is important to improve our understanding of the circumstances that lead to bond breaking and making when organic substrates and metal complexes interact. One way of doing this is through use of appropriate model compounds. We believe that $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (**1**) is a very useful model for investigating the additions of diverse reactive organic species with a bimetallic metal cluster.

In previous papers,[1,2] we described some reactions of **1** with a range of alkenes, polyenes and arenes. The reactions were promoted by sunlight and involved facile C–H bond activation. Some typical results are summarized in Eqns [1] and [2]. In other papers[3] and in unpublished work, we have established that various donor atoms add coordinatively to **1**. The addition of tertiary phosphines[4] to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PR_3)(CF_3C_2CF_3)$ is representative of this type of reaction. We were therefore interested to determine what course the reactions would follow when **1** was treated with alkenes and aromatic compounds containing potentially coordinating hetero-atoms. We report the results of our study with some vinylic, allylic and related compounds in this paper. A subsequent paper will cover reactions with some heterocyclic aromatic compounds.



(1)

$$\mathbf{1} + MeCH{=}CH_2 \xrightarrow{\downarrow\ \text{sunlight}} (\eta\text{-}C_5H_5)_2Rh_2(CH{=}CHMe)\text{-}\{C(CF_3){=}C(CF_3)H\}(\text{major}) + (\eta\text{-}C_5H_5)_2Rh_2(CMe{=}CH_2)\text{-}\{C(CF_3){=}C(CF_3)H\}\ (\text{minor}) + (\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3) \quad [1]$$

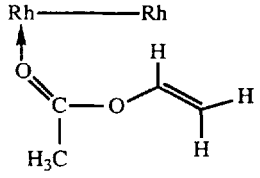
$$\mathbf{1} + C_6H_6 \xrightarrow{\downarrow\ \text{sunlight}} [(\eta\text{-}C_5H_5)_2Rh_2\text{-}\{C(CF_3){=}C(CF_3)H\}]_2(C_6H_4) + (\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3) \quad [2]$$

RESULTS AND DISCUSSION

Vinyl acetate

To determine whether oxygen-containing substituents would influence the regioselectivity of C–H bond activation, the reaction of **1** with vinyl acetate was studied. Little reaction occurred in the dark, but in the presence of sunlight all three olefinic C–H bonds were activated. The three isomeric products were readily distinguished from NMR data. The major product was **2b** ($R^2 = OCOCH_3$), the absence of a low-field μ-CH signal in the ^1H NMR spectrum being diagnostic[1] of this isomer. The minor isomers, **2a** ($R^3 = OCOCH_3$) and **2c** ($R^4 = OCOCH_3$), were identified from the μ-CH resonances near δ9 ppm and the characteristic magnitudes of the vicinal *trans* and *cis* H–H coupling constants (see Table 2).

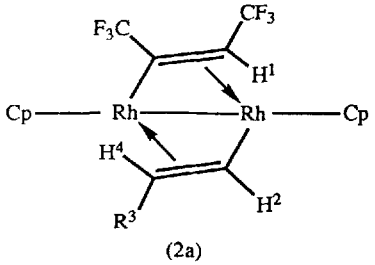
A number of interesting features emerge from further consideration of the NMR data for the three isomers. First, we note the combination of increased *geminal* H–H coupling (**2b**) and reduced *vicinal trans* and *cis* couplng (**2a**, **2c**) compared with other vinylic complexes previously studied.[1] This reflects a significant reduction of C=C bond order within the μ-alkenyl ligand caused by the electron-withdrawing acetate substituent. Second, the appearance and position of the H^1 resonance in the spectrum of **2c** is striking. For **2a** and **2b**, the characteristic quartet of triplets pattern is observed near δ1.5 ppm. However, $\delta(H^1)$ is located at δ4.45 ppm for **2c**, and appears as a quartet of doublets. The dramatic downfield shift of about 3 ppm can probably be attributed to hydrogen bonding between H^1 and a carboxylate oxygen in the R^4 substituent; there is further comment on this point in the discussion below. Loss of the triplet component of the resonance indicates that H^1 couples more strongly to one rhodium than to the other and indicates it is not situated above the mid-point of the Rh–Rh bond; this displacement may also be linked to the hydrogen-bonding requirements. Finally, significant variation in the H^3 (for **2b**, **2c**) and H^4 (for **2a**, **2b**) chemical shifts is apparent; this can be attributed to the location of the strongly deshielding acetate group relative to the appropriate proton within the μ-alkenyl group.



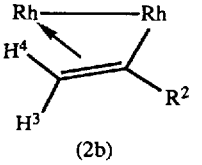
(3)

The overall distribution of **2a**:**2b**:**2c** was 1:8:1. The dominance of **2b** is significant, indicating a strong preference for C–H bond cleavage at the substituted alkenyl carbon. In contrast, the previously studied reaction with $H_2C{=}CHR$ (R = Me, t-Bu or Ph) and MeCH=CHEt showed the opposite regioselectivity with preference for C–H bond cleavage at the least crowded carbon. The strong preference for formation of **2b** may be a consequence of the vinyl acetate coordinating initially through oxygen (see **3**). Alternatively, if the alkene function is the principal donor site, then additional bonding from the oxygen could control the orientation of the coordinated alkene. In either case, H^1 will be held preferentially close to a rhodium atom.

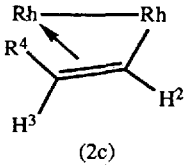
The most outstanding feature of this reaction was the formation of **2c**; this stereoisomer, with the substituent in the 4-position, has not been detected in any of our previous studies[1,2] with alkyl- or aryl-substituted alkenes. Consideration of molecular models of **2c** ($R = OCOCH_3$) establishes that a carboxylate oxyen is likely to be located close to H^1 and any resultant hydrogen bonding would presumably stabilize this configuration. A related H · · · F interaction is indicated



(2a)



(2b)



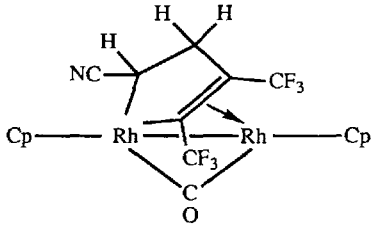
(2c)

* In **2b** and subsequent structures, the cyclopentadienyl and $C(CF_3){=}C(CF_3)H$ groups are omitted for clarity.

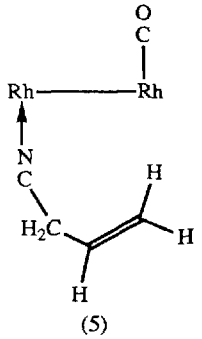
for the complex $(\eta\text{-}C_5H_5)_2Rh_2(CH{=}CF_2)\{C(CF_3){=}C(CF_3)H\}$; the crystal structure of this complex has been reported,[1] and with the alkenyl hydrogens placed in idealized positions the $H^1 \cdots F$ distance is determined to be 192 ppm. This is a reasonable hydrogen-bonding distance. Similar stabilization is, of course, not possible when R is a hydrocarbon group, and steric factors then inhibit the formation of **2c**.

Allyl cyanide

We reported previously[1] that the reaction between **1** and excess acrylonitrile occurred immediately in the absence of sunlight to give the product $(\mu\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(H_2CCHCN)$ (**4**). In contrast, the reaction of **1** with allyl cyanide was slow in the absence of sunlight. After several weeks in the dark, small amounts of **2a** ($R^3 = CH_2CN$) and **2b** ($R^2 = CH_2CN$) were isolated, but there was no sign of a carbonyl-containing intermediate analogous to **4**. This reaction was greatly accelerated by sunlight irradiation, and after 30 min good yields of **2a** (18%), **2b** (24%) and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (46%) were obtained. As before, the individual isomers were readily identified from NMR data (Table 2). The observed yields indicate a slight preference for C–H bond cleavage at the substituted alkenyl carbon. A similar **2b**:**2a** isomer ratio of 2:1 was found previously[1] in the sunlight-assisted reaction of **1** with $H_2C{=}CHCN$. Clearly, the stereoselectivity with cyano-substituted alkenes is much lower than with vinyl acetate. Moreover, there is no evidence for formation of isomer **2c** when R is CN or CH_2CN.



(4)

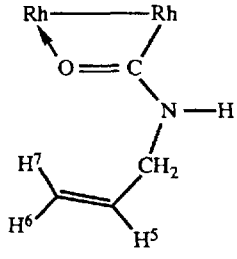


(5)

Consideration of molecular models for these systems establishes two points: first, formation of **2c** would be severely inhibited on steric grounds and stabilization of this isomer by $N \cdots H^1$ hydrogen bonding cannot be achieved. Second, the geometry of the alkenes prevents formation of an intermediate in which there is simultaneous coordination from nitrogen and alkene functions. Independent coordination from either function is, of course, possible. Although there is no direct evidence for **5**, its formation does seem likely on the basis of other observations. Thus, as stated previously, **4** is formed from **1** and acrylonitrile in the absence of light; we also have spectroscopic data[5] indicating that the *N*-donor ligand acetonitrile binds reversibly to **1** in solution. Moreover, *N*-coordination is thought[6] to apply in the formation of $Re_2(CO)_8(H_2C{=}CHCN)$. If allyl cyanide does bind to **1** through nitrogen in the first instance, it is not clear how this would affect the regioselectivity of the subsequent C–H bond cleavage reactions. In an attempt to improve our understanding of these systems, we decided to investigate an allylic system with a different nitrogen-containing substituent.

Allylamine

The reaction of **1** with allylamine is remarkable in several respects. It occurred rapidly in the absence of sunlight, no $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ was obtained, and the only major product was formed by activation of an N–H rather than a C–H bond. Spectroscopic results (Tables 1 and 2) are consistent with the structure **6**. Peaks for the molecular ion and loss of the carbonyl were evident in the mass spectrum. There were no strong absorptions in the normal carbonyl region of the infrared spectrum, but a strong band at 1478 cm^{-1} is tentatively assigned to



(6)

the μ-$\eta^1\eta^1$-carbonyl within a bridging carboxamido group. The ^1H and ^{19}F NMR spectra indicate the presence of the μ-$C(CF_3)$=$C(CF_3)H$ unit, and showed peaks for three olefinic protons, two methylene protons, and a single amine proton. The allylic signals can be analysed as an $AA'BX_2$ spin system with the olefinic protons (AA'B) all resonating at low field. If the alkene bond was coordinated to rhodium, a significant shielding of H^7 and a reduced H^5–H^7 coupling would be expected. A single proton resonance at δ5.82 ppm is attributed to an N–H proton; this assignment is confirmed by D_2O exchange experiments. This proton is considerably deshielded relative to the N–H protons in free allylamine (δNH at 1.21 ppm), and this is presumably a consequence of the adjacent carbonyl group.

Primary and secondary amines

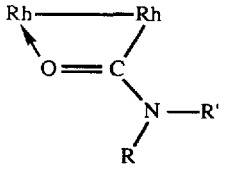
To confirm this mode of reaction, **1** was treated under similar conditions with the simple amines NH_2R(R = Me, t-Bu, CH_2Ph), $NHMe_2$ and NEt_3. The tertiary amine did not react at all, but the primary and secondary amines all reacted in similar manner to allylamine. The yields of the products, **7**, were almost quantitative.

Each of the compounds **7** showed a parent peak in the mass spectrum. A strong infrared absorption at 1510–1480 cm^{-1} was assigned to a C–O stretching frequency within the μ-$\eta^1\eta^1$-C(O)NNR′ group. Support for this assignment comes from independent reports that ν(CO) occurs at 1515–1505 cm^{-1} in the related complexes $Fe_2(CO)_6(AsMe_2)(OCNMe_2)$,[7] $HRu_3(CO)_{10}(OCNMe_2)$,[8] and $HOs_3(CO)_{10}(OCNCH_2Ph)$.[9,10] For the iron and ruthenium complexes, the μ-$\eta^1\eta^1$ attachment of the carboxamide ligands has been confirmed by X-ray crystal structure determinations. In the ^1H NMR spectra of the bis-μ-alkenyl complexes (**2**), including **2a** and **2b** with R = $OCOCH_3$ or CH_2CN, the resonance for H^1 is observed as a quartet of triplets indicating that the proton couples with the *geminal* CF_3 group and equally with both rhodium atoms. In contrast, this proton resonance is a quartet of doublets in all the carboxamido complexes **7** (and in **6**). It is not clear why H^1 should couple with just one rhodium atom in these complexes. The presence of two methyl signals in the spectrum of the $NHMe_2$ derivative, and the ABX spin pattern observed for the $C\underline{H_2}N\underline{H}$ protons in the spectrum of the benzylamine derivative, indicate that there is restricted rotation about the C–N bond of the carboxamide unit. This introduces the possibility of isomer formation (see **7a** and **7b**), but only one product is formed. We do not have data that enable us to identify the preferred isomer.

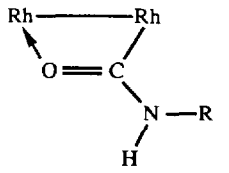
In the formation of mononuclear carboxamido complexes by the reactions of amines with metal carbonyls, a direct nucleophilic addition of the amine to the carbonyl carbon is proposed in most cases.[11–15] A similar pathway can be envisioned in the formation of the dirhodium complexes (**7**). Initial coordinative addition of an intact amine would generate a complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(NHR_2)(CF_3C_2CF_3)$ containing a terminal carbonyl which could be attacked subsequently by more amine. A possible reaction pathway is outlined in Scheme 1.

Aniline

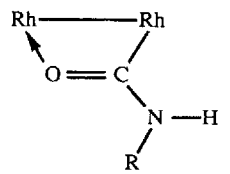
In contrast to the above systems, the addition of aniline to a solution of **1** did not result in a spontaneous reaction. Even after several hours of sunlight irradiation, the reaction remained incomplete. NMR spectral data on the crude reaction mixture indicated the presence of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ plus one other major product (**8**). Although **8** was not sufficiently stable to allow isolation, characterization was accomplished by analysis of the NMR results. The ^{19}F spectrum exhibits resonances that are characteristic of a μ-$C(CF_3)$=$C(CF_3)H$ unit. The =$C(CF_3)H$ proton is observed in the ^1H spectrum as a quartet of doublets at δ1.97 ppm. Further consideration of the ^1H NMR data indicates that C–H rather than N–H bond cleavage has



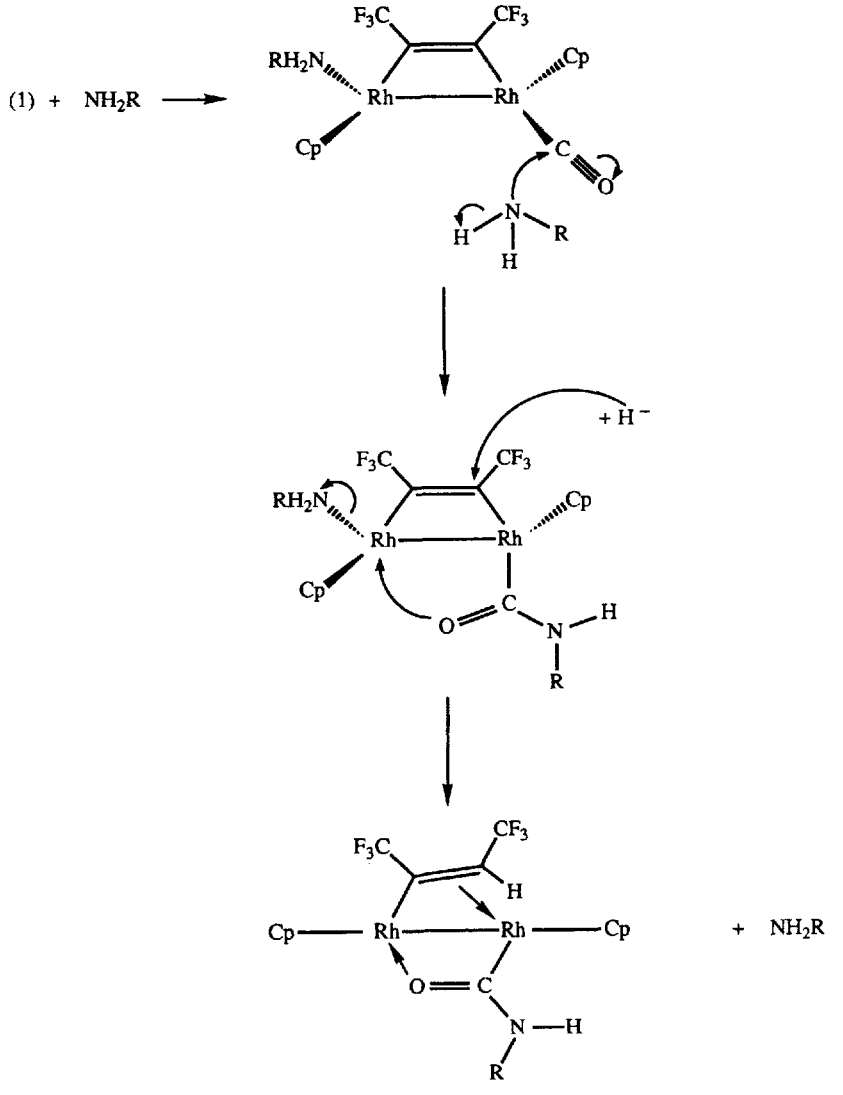
(7)



(7a)

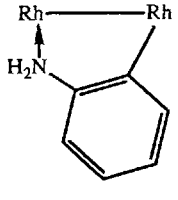


(7b)



Scheme 1 Possible pathway for the reactions between **1** and amines

occurred. Thus, a broad two-proton amine resonance is observed at δ 3.65 ppm; this is shifted about 0.4 ppm downfield from the NH_2 resonance for free aniline implying that the amine-nitrogen is coordinated. Unfortunately, the ring proton resonances of free aniline masked those of the complex and prevented a definitive assignment of these resonances. However, by deduction, it is proposed that arene C–H bond cleavage has occurred. Thus it is proposed that the product **8** is formed by orthometallation of the aniline.



(8)

CONCLUSIONS

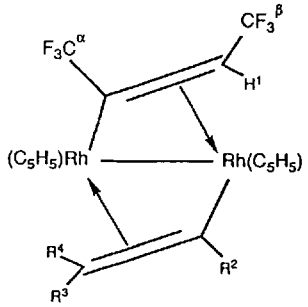
The presence of donor atoms within substituents on alkenes can have a substantial influence on the stereoselectivity of reactions with metal complexes. This is particularly evident in the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and vinyl

Table 1 Yields and analytical data for products obtained from $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and substituted alkenes or amines

Reactant[a]	Product[b] Isomer yield, %	M.p. (°C)	Analysis (%)[c] C	H	F	N	MS (P^+)
Vinyl acetate[s]	**2a** (4)	162–164	37.1 (37.0)	2.8 (2.8)	19.3 (19.5)		584
	2b (32)	166–167	36.8	2.6	19.4		584
	2c (4)	157–158	37.1	2.8	19.7		584
Allyl cyanide[s]	**2a** (18)	180	38.3 (38.3)	2.8 (2.7)	20.2 (20.2)	2.9 (2.5)	565
	2b (24)	148	38.6	2.7	20.2	2.5	565
Allylamine	**6** (97)	139	37.3 (37.1)	3.0 (2.9)	19.7 (19.6)	2.3 (2.4)	583
NH_2Me	**7** (95)	136	34.8 (34.5)	2.9 (2.7)	20.4 (20.5)	2.5 (2.5)	557
$NH_2(t\text{-}Bu)$	**7** (97)	137	38.3 (38.1)	3.8 (3.5)	19.2 (19.0)	2.1 (2.3)	599
$NH_2(CH_2Ph)$	**7** (96)	136	42.0 (41.7)	2.9 (3.0)	18.1 (18.0)	2.4 (2.1)	631[d]
$NHMe_2$	**7** (93)	138	36.1 (35.8)	3.0 (3.0)	19.8 (20.0)	2.4 (2.5)	571

[a]Superscript s indicates sunlight irridation for 30 min required. All other reactions were in the dark. [b] In the sunlight-assisted reactions, a small amount of the purple compound $(C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ was formed also. [c] Calculated values in parentheses. [d] $M^+ - 2$.

Table 2 NMR chemical shift (δ) and coupling constant (J) data for $CDCl_3$ solutions of products of the type



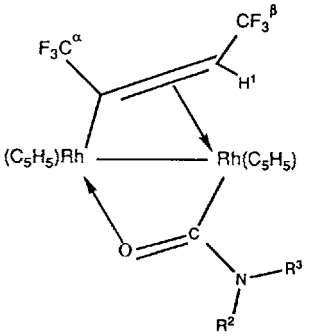
Product	^1H (300 MHz) δ;[a] multiplicity, rel. area, assignment	J (Hz)	^{19}F (282.4 MHz) δ;[a] multiplicity	F^α–F^β H^1–F^β Rh–F
2a, $R^3 = OCOCH_3$	8.89; ddd, 1H, H^2	H^2H^4, 8.4	49.5; q	13.1
	5.50; s, 5H, C_5H_5	RhH^1, 2.0	54.0; m	9.4
	5.33; dd, 1H, H^4	RhH^2, 3.0 and 1.5		2.6
	5.30; s, 5H, C_5H_5	RhH^4, 3.0		
	2.01; s, 3H, CH_3	$F^\beta H^1$, 9.4		
	1.50; qt, 1H, H^1			
2b, $R^2 = OCOCH_3$	5.48: s, 5H, C_5H_5	H^3H^4, 4.6	49.1; q	13.3
	5.41; s, 5H, C_5H_5	RhH^1, 1.9	53.7; m	9.4
	3.39; ddd, 1H, H^3	RhH^3, 2.6 and 1.1		2.8
	2.10; s, 3H, CH_3	RhH^4, 2.6		
	1.80; dd, 1H, H^4	$F^\beta H^1$, 9.4		
	1.57; qt, 1H, H^1			
2c, $R^4 = OCOCH_3$	8.62; ddd, 1H, H^2	H^2H^3, 5.9	49.7; q	13.2
	7.24; ddd, 1H, H^3	RhH^1, 2.6 and 1.5	53.8; m	10.3
	5.55; s, 5H, C_5H_5	RhH^2, 3.6 and 2.3		2.8
	5.45; s, 5H, C_5H_5	RhH^3, 3.5 and 2.2		
	4.45; qdd, 1H, H^1	$F^\beta H^1$, 10.3		
	1.96; s, 3H, CH_3			

Table 2 (*continued*)

Product	^{1}H (300 MHz)		^{19}F (282.4 MHz)	
	δ;[a] multiplicity, rel. area, assignment	J (Hz)	δ;[a] multiplicity	F^{α}–F^{β} H^1–F^{β} Rh–F
2a, $R^3 = CH_2CN$	9.77; ddd, 1H, H^2	H^2H^4, 10.9	48.8; q	13.4
	6.07; s, 5H, C_5H_5	$H^{3a}H^{3b}$, 18.3	54.0; m	9.3
	5.97; s, 5H, C_5H_5	$H^{3a}H^4$, 4.1		3.0
	3.55; ddd, 1H, CH_2CN	H^{3b}, H^4, 5.8		
	3.43; ddd, 1H, CH_2CN	RhH^1, 2.0		
	3.09; m, 1H, H^4	RhH^2, 3,0		
	1.93; qt, 1H, H^1	RhH^{3a}, 2.0		
		RhH^{3b}, 1.6		
		$F^{\beta}H^1$, 9.3		
2b, $R^2 = CH_2CN$	5.53; s, 5H, C_5H_5	$H^{2a}H^{2b}$, 18.1	49.6; q	13.3
	5.44; s, 5H, C_5H_5	RhH^1, 2.0	53.5; m	9.6
	3.96; d, 1H, CH_2CN	$F^{\beta}H^1$, 9.6		1.8
	3.88; d, 1H, CH_2CN			
	3.60; m, 1H, H^3			
	1.70; m, 1H, H^4			
	1.52; qt, 1H, H^1			

[a] ^{1}H, $\delta(Me_4Si) = 0.00$; ^{19}F, $\delta(CCl_3F) = 0.00$. CF_3 resonances are of equal intensity; the higher field multiplets are analysed as A_3B_3MX spin systems and are assigned to CF_3^{β}.

Table 3 NMR chemical shift (δ) and coupling constant (J) data for $CDCl_3$ solutions of products of the type



Product	^{1}H (300 MHz)		^{19}F (282.4 MHz)	
	δ; multiplicity, rel. area, assignment	J (Hz)	δ; multiplicity	F^{α}–F^{β} H^1–F^{β} Rh–F
$R^2 = H$	5.82; brt, 1H, NH^2	CH_2H^5, 5.2	50.3; q	12.6
$R^3 =$	5.73; ddt, 1H, H^5	CH_2H^6, 1.5	52.9; m	10.3
	5.50; d, 5H, C_5H_5	CH_2H^7, 1.5		2.3
$CH_2^{3,4}$ H^5	5.23; s, 5H, C_5H_5	H^5H^6, 10.3		
C	5.13; dq, 1H, H^7	H^5H^7, 17.1		
‖	5.12; dq, 1H, H^6	H^6H^7, 1.5		
C	3.79; m, 2H, $CH_2^{3,4}$	CH_2NH, 5		
H^7 H^6	1.86; qd, 1H, H^1	RhC_5H_5, 0.6		
		RhH^1, 2.1		
		$F^{\beta}H^1$, 10.3		

Table 3 (*continued*)

Product	^{1}H (300 MHz) δ; multiplicity, rel. area, assignment	J (Hz)	^{19}F (282.4 MHz) δ; multiplicity	F^α–F^β H^1–F^β Rh–F
R^2=H R^3=Me	5.74; brs, 1H, NH 5.48; d, 5H, C_5H_5 5.24; d, 5H, C_5H_5 2.73; d, 3H, CH_3 1.86; qd, 1H, H^1	RhC_5H_5, 0.6 H^2CH_3, 4.9 RhH^1, 2.0 $F^\beta H^1$, 10.3	50.2; q 52.8; m	12.5 10.3 2.4
R^2=H R^3=t-Bu	5.68; brs, 1H, NH 5.45; s, 5H, C_5H_5 5.23; s, 5H, C_5H_5 1.81; qd, 1H, H^1 1.21; s, 9H, Bu^t	RhH^1, 2.1 $F^\beta H^1$, 10.1	50.3; q 52.9; m	12.5 10.4 2.0
R^2=H R^3=CH_2Ph	7.31; m, 3H, Ph 7.18; m, 2H, Ph 6.12; brt, 1H, NH 5.49; d, 5H, C_5H_5 5.17; d, 5H, C_5H_5 4.39; dd, 1H, CH_2 4.32; dd, 1H, CH_2 1.92; qd, 1H, H^1	RhC_5H_5, 0.6 RhH^1, 2.0 $F^\beta H^1$, 10.3 $NHCH_2$ gives AMX spin system: HCH′, 15.0 HNCH, 5.8 HNCH′, 6.1	50.4; q 52.9; m	12.7 10.3 3.3
R^2=CH_3 R^3=CH_3	5.53; s, 5H, C_5H_5 5.23; s, 5H, C_5H_5 3.22; s, 3H, CH_3 2.81; s, 3H, CH_3 1.82; qd, 1H, H^1	RhH^1, 2.0 $F^\beta H^1$, 10.3	50.2; q 53.2; m	12.3 10.3 1.0

acetate, where formation of the least sterically favoured isomer of the bisalkenyl complex $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)H\}(\mu\text{-}C(OCOCH_3)CH_2)$ is preferred. In the reactions with allylamine and with primary and secondary amines, N–H bond cleavage takes precedence over C–H bond activation.

EXPERIMENTAL

The general procedures and instrumentation used are described in previous papers.[1,16] The allylic compounds and amines were commercial samples, and were used as received (gases) or distilled (liquids) prior to use.

An excess of the appropriate reactant was condensed into an evacuated Carius tube or Schlenk flask containing $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (generally 0.050–0.100 g) and hexane or CH_2Cl_2 (10 cm^3). Reactions that required sunlight initiation are indicated in Table 1; in other reactions, the Carius tube was kept upright within a length of metal tubing. When the colour of the solution had changed from green to orange or red, solvent and any unchanged volatile reactants were removed under reduced pressure. Soluble products were then extracted with the minimum quantity of dichloromethane and were separated by TLC on 20 cm × 20 cm plates with a 1:1 silica gel G-HF_{254} mixture as adsorbent. In general, the eluent mixtures were petroleum spirit/dichloromethane/ether. Yields and analytical data for products are included in Table 1. NMR data used to characterize the complexes are listed in Tables 2 and 3.

Acknowledgments We thank the Australian Research Council and the Monash Research Fund for financial support (RSD), the Australian Government for a postgraduate scholarship (SMJ), and Johnson Matthey for the loan of rhodium trichloride.

REFERENCES

1. Dickson, R S, Fallon, G D, Jenkins, S M, Skelton, B W and White, A H *J. Organomet. Chem.*, 1986, 314: 333
2. Dickson, R S, Jenkins, S M, Skelton, B W and White, A H *Polyhedron*, 1988, 7: 859

3. Bixler, J W, Bond, A M, Dickson, R S, Fallon, G D, Nesbit, R J and Pateras, H *Organometallics*, 1987, 6: 2508, and references therein
4. Dickson, R S, Oppenheim, A P and Pain, G N *J. Organomet. Chem.*, 1982, 224: 377
5. Bixler, J W, Bond, A M and Dickson, R S *Organometallics*, 1986, 5: 1435
6. Nubel, P O and Brown, T L *J. Am. Chem. Soc.*, 1984, 106: 644, 3474.
7. Keller, E, Trenkle, A and Vahrenkamp, H *Chem. Ber.*, 1977, 110: 441
8. Szostak, R, Strouse, C E and Kaesz, H D *J. Organomet. Chem.*, 1980, 191: 243
9. Azam, K A, Yin, C C and Deeming, A J *J. Chem. Soc., Dalton Trans.*, 1978: 1201
10. Lin, J-C, Mayr, A, Knobler, C B and Kaesz, H D *J. Organomet. Chem.*, 1984, 272: 207
11. Angelici, R J *Acc. chem. Res.*, 1972, 5: 335, and references therein
12. Angelici, R J and Blacik, L J *Inorg. Chem.*, 1972, 11: 1754
13. Green C R and Angelici, R J *Inorg. Chem.*, 1972, 11: 2095
14. Jetz, W and Angelici, R J *J. Am. Chem. Soc.*, 1972, 94: 3799
15. Dell'Amico, D B, Calderazzo, F and Pelizzi, G *Inorg. Chem.*, 1979, 18: 1165
16. Dickson, R S, Fallon, G D, McLure, F I and Nesbit, R J *Organometallics*, 1987, 6: 215