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Journal of Organometallic Chemistry 663 (2002) 145–150
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Proton induced coupling reactions in dinuclear σ-alkynyl-μ-methylene-rhodium complexes

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Received 30 May 2002; accepted 23 September 2002

Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

Addition of two equivalents of HBF_4 to suspensions of the di-alkynyl-di-μ-methylene-dirhodium complexes $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(C_2R)_2]$ (**2**, R = Ph; **3**, R = *p*-C_6H_4Me) (prepared from the chloro-complex $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**), and RC_2MgCl), gave the unexpected products *syn*- and *anti*-$[(C_5Me_5)_2Rh_2(\mu\text{-}\eta^5,\eta^{5'}\text{-}\{XC_6H_4CH(CH_2)CC(CH_2)CHC_6H_4X\}][BF_4]_2$ (**4**, X = H; and **5**, X = *p*-Me). The solid-state structure of *syn*-**5**, determined by single crystal X-ray diffraction, was shown to contain a hydrocarbon skeleton of two linked η^5-allylbenzenes. Complexes **4** and **5** underwent a dynamic process in solution; this was examined by VT-NMR spectroscopy for **5** and was shown to involve η^5-/η^3-/η^5-migration of the allylbenzene fragment, with a free energy of activation of 62 kJ mol^{-1}. The complexes **2** and **3** reacted with HCl to give **1** and RC_2H.

Keywords: Rhodium complexes; μ-Methylene ligand; Carbon–carbon bond formation

1. Introduction

Bridging methylene groups in dinuclear complexes undergo facile coupling with hydrocarbyl ligands bound to the metal through both sp^2 and *sp* carbons [1–5]. Knox et al. have investigated the coupling of one μ-CH_2 group on a diruthenium complex with acetylenes, which afforded a σ,π-allyl complex due to the formation of one C–C bond [6]. We previously reported [7] that reaction of $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(Cl)_2]$ (**1**) with RC≡CMgBr gave the di-σ-alkynyl-di-μ-methylene-dirhodium complexes, $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(C_2R)_2]$ (R = *t*-Bu; Ph). We now report that the reactions of $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(C_2R)_2]$ (**2**, R = Ph; and **3**, R = *p*-C_6H_4Me) with acids can lead to interesting and unexpected coupling reactions.

2. Results

Complexes **2** and **3** were synthesised as described previously [7] and were characterised spectroscopically [^{13}C-NMR: α-ethynyl carbons, dd at δ 101.7 (**2**) and 105.5 (**3**); ^1J(C–Rh) = 68 and 67 Hz; ^2J(C–Rh) = 2.8 and 2.3 Hz, respectively; β-ethynyl carbons, triplets at δ 86.0 (**2**) and 99.2 (**3**) (^2J(C–Rh) = ^3J(C–Rh) = 6.6 and 6.1 Hz, respectively]. These data are typical for rhodium σ-alkynyl complexes [8]. The structural proposals were reinforced by the presence of ν(C≡C) absorptions in the IR spectra at 1963 (**2**) and 2098 (**3**) cm^{-1} [9].

Reaction of the arylethynyl complexes **2** or **3** with HCl in diethyl ether solution gave complex **1** and the free acetylene (RC_2H) which was identified by GC-MS. However when $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(C_2R)_2]$ (**2**, R = Ph; or **3**, R = *p*-C_6H_4Me) was treated with two equivalents of HBF_4 in Et_2O at ambient temperature, brown solids precipitated from the solution. ^{1}H-NMR spectroscopy showed these solids to be composed of a number of compounds; from which it was possible to isolate single products, $[(C_5Me_5)_2Rh_2(\mu\text{-}\eta^5,\eta^{5'}\text{-}\{XC_6H_4CH(CH_2)CC(CH_2)CHC_6H_4X\}][BF_4]_2$ (**4**, X = H; **5**, X =

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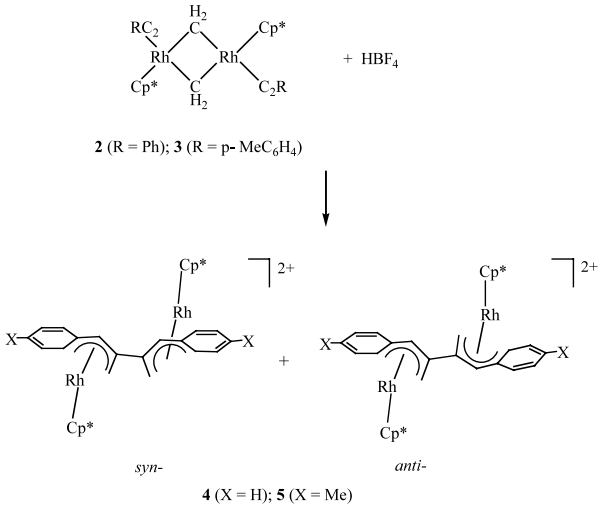
0022-328X/02/$ - see front matter
PII: S0022-328X(02)01964-2



Scheme 1. ($Cp^* = \eta^5$-C_5Me_5).

p-Me) as a 3:1 mixture of *syn*- and *anti*-isomers (Scheme 1).

Complexes **4** and **5** were fully characterised by spectroscopic and analytical methods and a single crystal X-ray diffraction study of [*syn*-**5**][BF_4]$_2$; the X-ray study shows a dinuclear pentamethylcyclopentadienyl rhodium complex in which the rhodium centres are bridged by a ligand composed of two C–C linked allylbenzenes (Fig. 1 and Table 1). The organic ligand is η^5-bonded approximately equivalently to five carbons (C(6), C(11), C(12), C(13), and C(20)) with Rh–C bond lengths in the range 2.165(6)–2.470(6) Å; three of the carbons are somewhat closer to the rhodium (C(12), 2.172(6); C(13), 2.194(6) and C(20), 2.165(7)) than the other two, which are part of the benzene ring (C(6), 2.278(6) and C(11), 2.470(6)). Furthermore the length of the C(6)–C(12) bond, linking the phenyl to the allyl, (1.463(9)) is similar to the others, 1.411(9)–1.433(9) Å. For the six-membered ring the C(7)–C(8) and C(9)–C(10) are shorter, 1.370(10) and 1.340(11) Å, than the other C–C bonds 1.411(9)–1.426(11) Å. The Rh–C distances to the C_5Me_5 ring carbons range from 2.132(6) to 2.228(7) Å, and the perpendicular distance from the rhodium atom to the C_5Me_5 ring plane is 1.808 Å and to the η^5-allylbenzene ligand is 1.703 Å; the angle between the planes defined by the C_5Me_5 and the allylbenzene ligand is 8.7°. The two halves of the cation are linked through C(13)–C(13A), which, at 1.513(10) Å, is the value for a single bond between two sp^2 carbons [10]. The symmetry of the *syn*-cation is C_2 and that of the *anti*-cation is C_i; the designations *syn*- and *anti*- refer to the orientations about the C(13)–C(13A) link, not to the relative positions of the Cp* ligands.

Table 1
Selected bond distances (Å) and angles (°) for [syn-**5**][BF_4]$_2$

Bond distances			
Rh(1)–C(20)	2.165(7)	Rh(1A)–C(20A)	2.173(7)
Rh(1)–C(13)	2.194(6)	Rh(1A)–C(13A)	2.174(6)
Rh(1)–C(12)	2.172(6)	Rh(1A)–C(12A)	2.171(6)
Rh(1)–C(6)	2.278(6)	Rh(1A)–C(6A)	2.269(6)
Rh(1)–C(11)	2.470(6)	Rh(1A)–C(11A)	2.448(6)
C(6)–C(7)	1.424(9)	C(7)–C(8)	1.370(10)
C(8)–C(9)	1.426(11)	C(9)–C(10)	1.340(11)
C(10)–C(11)	1.420(10)	C(6)–C(11)	1.411(9)
C(6)–C(12)	1.463(9)	C(6A)–C(11A)	1.425(9)
C(12)–C(13)	1.419(9)	C(6A)–C(12A)	1.436(9)
C(13)–C(20)	1.433(9)	C(12A)–C(13A)	1.417(9)
C(13A)–C(20A)	1.434(9)	C(13)–C(13A)	1.513(10)
Bond angles			
C(11)–C(6)–Rh(1)	80.3(4)	C(7)–C(6)–Rh(1)	120.4(5)
C(12)–C(13)–C(20)	119.6(6)	C(11)–C(6)–C(12)	125.5(6)
C(20)–C(13)–C(13A)	119.5(6)	C(7)–C(6)–C(12)	115.8(6)

The ^{1}H- and ^{13}C-NMR spectra recorded at room temperature showed the complexes to be fluxional in solution. The nature of this process was examined by a 400 MHz ^{1}H-NMR EXSY spectrum of [η^5-C_5Me_5)$_2$-

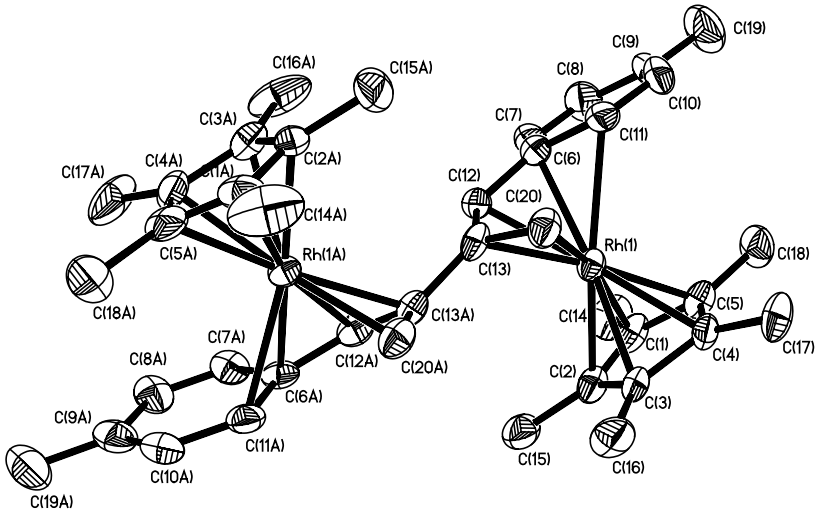


Fig. 1. ORTEP drawing of the cation of [*syn*-5][BF_4]$_2$.

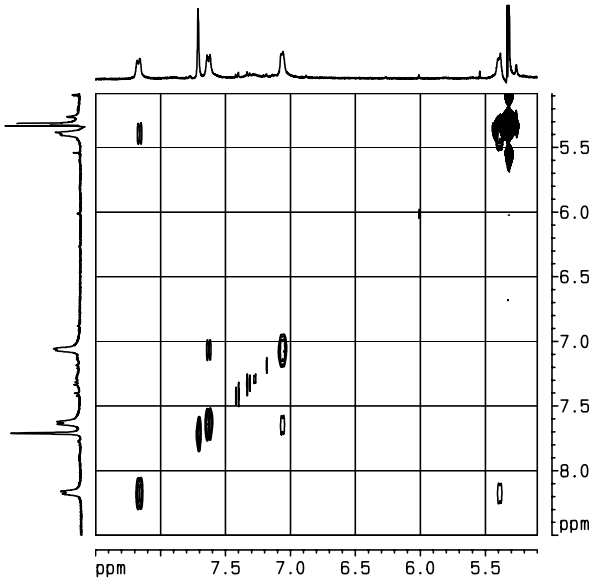


Fig. 2. The 400 MHz ^{1}H-NMR EXSY spectrum of $[\eta^5\text{-}C_5Me_5)_2\text{-}Rh_2\{p\text{-}MeC_6H_4CHC(CH_2)\}_2][BF_4]_2$ (**5**) in CD_2Cl_2 at −1.2 °C, acquired using the Bruker programme, noesytp. The spectrum was acquired using a 8192×85 points data set and transformed into $16\,384 \times 512$ data points. The mixing delay is 0.03 s and the relaxation delay is 3 s.

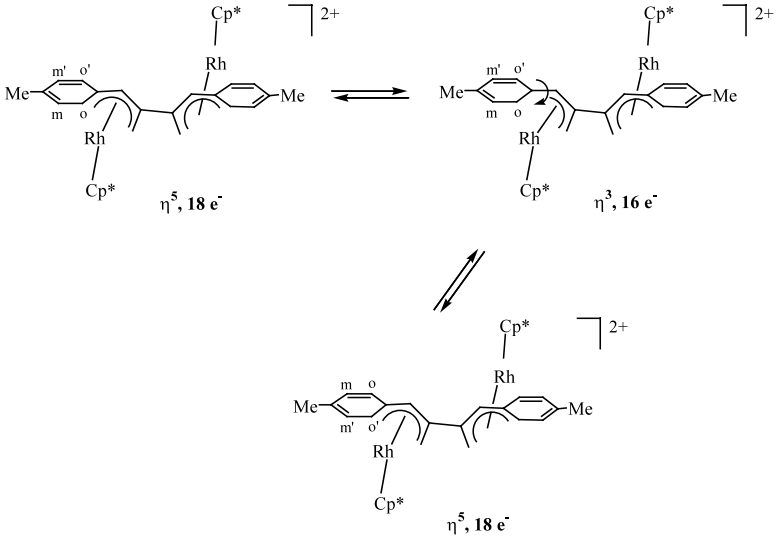
$Rh_2\{MeC_6H_4CH(CH_2)CC(CH_2)CHC_6H_4Me\}][BF_4]_2$ in CD_2Cl_2 at −1.2 °C (Fig. 2). This spectrum, acquired using the Bruker program *noesytp*, shows that while the two *ortho* (*o*- and *o′*-) and the two *meta* (*m*- and *m′*-) protons on each phenyl are distinct at low temperature, the signals undergo pair-wise exchange at higher temperature; this points to the fluxional process involving a rotation of the phenyl about the C(6)–C(12)-axis, for which we estimate $\Delta G^{\ddagger} = 62 \pm 1$ kJ mol^{-1}. This appears to be the first example of such a movement, and the activation energy for the dynamic process thus gives a measure of the barrier for an η^5 to η^3 shift. This process involves going from an 18- to a 16-electron count at rhodium and is illustrated in Scheme 2. Related processes have been seen in $Cl(PR_3)Rh(\eta^4\text{-}Ph_2C{=}C{=}O)$, $(PR_3{=}PMe(^tBu)_2)$ [11] where variable-temperature NMR studies show that the metal moves from the ketene C,O bond to the C,C bond and also coordinates weakly to two carbons of the ketene phenyl substituent. Similar processes have been characterised in palladium arene complexes [12].

3. Discussion

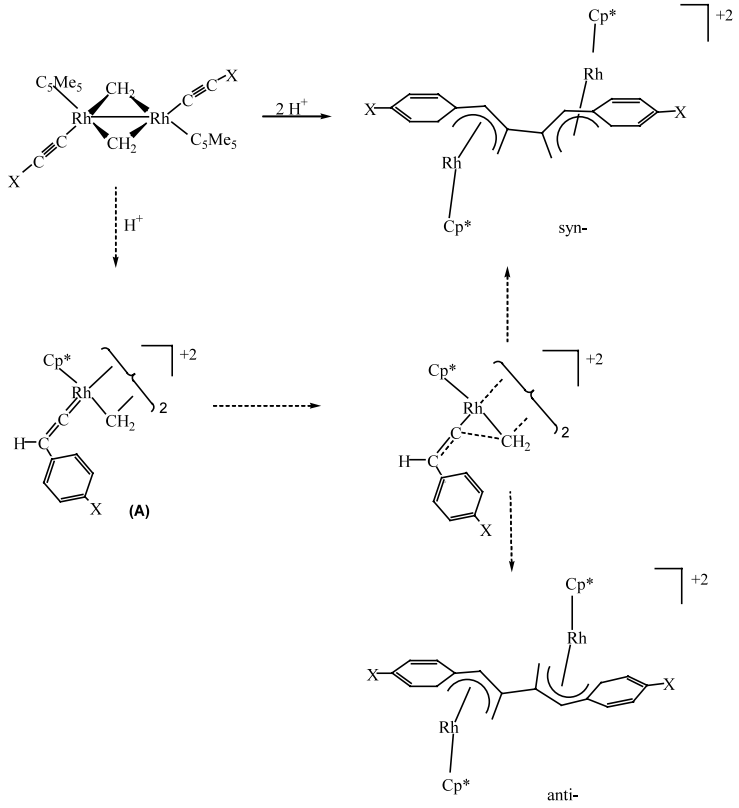
One surprising result from this work is that whereas HCl cleaves off the acetylene from **2** or **3**, presumably by attack of the proton either at the metal or at the α alkynyl carbon, HBF_4, which has a non-coordinating anion, gives a more complex reaction leading to the formation of a dimer with a new C–C bond.

A number of groups have reported that the protonation of σ-alkynyl complexes leads to vinylidenes [13]. Although no vinylidene intermediates were detected in the protonation of **2** and **3**, even when the reaction was followed by NMR spectroscopy at low temperature in CD_2Cl_2 solution, we suggest that in the reaction of **3** to give **5** (or **2** to give **4**), the first step involves protonation at the β-alkynyl carbon (giving (**A**)) followed by carbon–carbon bond formation between the α-alkynyl carbons and the μ-CH_2 in the dirhodium complex (Scheme 3). The reaction sequence is concluded by reductive elimination to give the carbon–carbon bond (C(13)–C(13A) linking the two halves together, and a low valent Rh species.

It may also be noted that the formal oxidation state of each Rh in **5** or **6** is +III, and therefore during the reaction of **2** or **3** with acid there has been a net



Scheme 2. (Cp* = η^5-C_5Me_5).

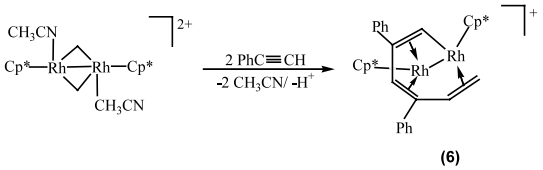


Scheme 3. **4** (X = H); **5** (X = Me); Cp* = η^5-C_5Me_5.

reduction of each Rh from IV to III, coincident with the formation of the C(13)–C(13A) single bond.

Another complex in which two acetylenes and two μ-methylenes couple is derived from $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}[PF_6^-]_2$ and monosubstituted alkynes (R′C≡CH). The C_6 skeleton of the coupled product was first formulated as $[(C_5Me_5Rh)_2(\mu\text{-}CH_2CHCR'CHCR'CH)]^+$ (R′ = aryl) on the basis of the NMR spectra [7]. In a later study Kaneko et al. [14] reported the crystallisation and the X-ray structure of the coupling product from a cleaner reaction system, using the BF_4^- or OTf^- (Tf = trifluoromethanesulfonyl) salts, and showed that the C_6 skeleton was better represented as $[(C_5Me_5Rh)_2(\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(Ph)CHC(Ph)CHCH_2)]^+$ (**6**), shown in Scheme 4.

Thus in the formation of **5** and of **6** two arylacetylenes and two methylenes couple. However, whereas in the formation of **5** it appears that one acetylene and one methylene couple first before joining the two C_3 units together, the formation of **6** is more easily explained if the two acetylenes couple with each other either before or after the methylenes couple together, and the reaction ends by the joining of the C_4 and the C_2 fragments.



Scheme 4.

4. Experimental

All reactions were carried out under nitrogen using carefully dried and purified solvents. Ethynylmagnesium chloride, 4-ethynyltoluene, HBF_4 and HCl (1 M solution in Et_2O) were obtained from Aldrich. $(MeC_6H_4C_2)MgCl$ was made by reaction of isopropylmagnesium chloride in Et_2O and 4-ethynyltoluene in tetrahydrofuran. *trans*-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**) and $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(C_2R)_2]$ (R = *t*-Bu, **3**; C_6H_5, **2**) complexes, were prepared by the literature procedures [17,7]. NMR spectra were recorded on Bruker AM-250 and WH-400 spectrometers; microanalytical data were obtained by the University of Sheffield Microanalytical Service. FAB mass spectra were recorded on a Micromass Prospec using nitrobenzyl alcohol as the matrix. Infrared spectra were measured on Nicolet Magna-IR 560 E.S.P. spectrometer. Free alkynes were identified using a Hewlett Packard 5890-5971A GC-MS instrument.

4.1. Preparation of trans-[(C_5Me_5)$_2$Rh$_2$(μ-CH_2)$_2$(C_2R)$_2$] (R = H, **2**; Me-C_6H_4, **3**)

A solution of 4-tolylethynylmagnesium chloride (6.25 ml, 2 mmol) was added to complex **1** (200 mg, 0.35 mmol) in toluene (20 ml). On workup this gave complex **3** as an orange solid (0.21 g, 82%). Anal. Calc. for $C_{40}H_{48}Rh_2$: C, 65.4; H, 6.6. Found: C, 65.9; H, 6.7%. IR (CH_2Cl_2, ν(C≡C)): 2098 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.14 (s, 2H, μ-CH_2), 7.10 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 2.27 (s, 3H), 1.82 (s, 15H); ^{13}C-NMR ($CDCl_3$): δ 164.4 (t, J_{Rh-C} = 24 Hz, μ-ÇH$_2$), 133.8, 130.9, 128.5, 126.2 (s, Ç$_6$H$_4$Me), 105.5 (dd, J_{Rh-C} = 67, 2.3 Hz, Rh–Ç≡), 103.1 (s, Ç$_5$Me$_5$), 99.2 (t, J_{Rh-C} = 6.1 Hz, ≡Ç–C$_6$H$_4$Me), 21.2 (s, Me), 10 (s, C$_5$Me$_5$). Complex **2** was prepared similarly [7].

4.2. Preparation of syn- and anti-[(C_5Me_5)$_2$Rh$_2$μ-η^5,$\eta^{5'}$-{$XC_6H_4CH(CH_2)CC(CH_2)CHC_6H_4X$}][BF4]$_2$ (X = H, **4**; Me, **5**)

$HBF_4 \cdot OMe_2$ (0.017 ml, 0.14 mmol) was added to a solution of **2** (50 mg, 0.07 mmol) in diethyl ether (30 ml) at 20 °C. In a few minutes a brown solid precipitated and after stirring the reaction for 2 h the solution was filtered. The resulting solid was repeatedly washed with acetone (1 ml) to give a red solid which was identified as a 3:1 mixture of *syn*- and *anti*-[(C_5Me_5)$_2$Rh$_2$(η^5-$C_6H_5CHCCH_2$)$_2$][BF$_4$]$_2$ (**4**), (0.025 g, 40%). Anal. Calc. for $C_{38}H_{46}B_2F_8Rh_2$: C, 51.2; H, 5.2. Found: C, 51.7; H, 5.3%. MS-FAB$^+$ m/z: 795 [M−(BF$_4$)]$^+$, 708 [M−(BF$_4$)$_2$]$^+$. IR (CH_2Cl_2, ν(BF$_4$)): 1056 cm^{-1}. ^{1}H-NMR (400 MHz, 298 K, CD_2Cl_2): δ 8.30 (br, 1H), 7.8 (br, 2H), 7.8 (s, 1H), 7.36 (br, 1H), 5.42 (br, 1H), 4.00 (d, J_{H-H} = 3.22 Hz, 1H), 2.36 (d, J_{H-H} = 3.22 Hz, 1H), 1.54 (s, 15H); ^{1}H-NMR (400 MHz, 233 K, CD_2Cl_2): *syn*-**4**, δ 8.15 (m, 1H), 7.75 (d, J_{H-H} = 6.4 Hz, 1H), 7.74 (d, J_{H-H} = 6.4 Hz, 1H), 7.66 (s, 1H), 7.27 (m, 1H), 5.32 (1H, partially obscured by deuterated solvent), 3.90 (d, J_{H-H} = 3.2 Hz, 1H), 2.21 (d, J_{H-H} = 3.2 Hz, 1H), 1.47 (s, 15H); *anti*-**4**, δ 7.95 (m, 1H), 5.45 (d, 1H), 4.67 (d, 1H), 2.20 (d, partially obscured, 1H), 1.47 (s, 15H); ^{13}C-NMR (400 MHz, 298 K, CD_2Cl_2): δ 132.1 (br, –Ç$_6$H$_4$), 131.1 (s, Ç–Me), 109.1 (d, J_{Rh-C} = 4.8 Hz, Cipso), 107.7 (d, J_{Rh-C} = 5.6 Hz, Cipso), 101.7 (d, J_{Rh-C} = 7.2, Ç$_5$Me$_5$), 94.6 (br, Çar), 90.3 (d, J_{Rh-C} = 4.8 Hz, ÇH), 58.4 (d, J_{Rh-C} = 13 Hz, CH_2), 8.9 (C$_5$Me$_5$).

An analogous reaction was carried out using a solution of **3** (50 mg, 0.068 mmol) and $HBF_4 \cdot OMe_2$ (0.016 ml, 0.136 mmol) and stirring for 12 h. This gave the complex **5** as a red solid (0.025 g, 40%). Anal. Calc. for $C_{40}H_{50}B_2F_8Rh_2$: C, 52.4; H, 5.5. Found: C, 52.8; H, 5.5%. MS−FAB$^+$ m/z: 823 [M−(BF$_4$)]$^+$, 736 [M−(BF$_4$)$_2$]$^+$. IR (CH_2Cl_2, ν(BF$_4$)): 1056 cm^{-1}. ^{1}H-NMR (400 MHz, 298 K, CD_2Cl_2): **5**, δ 8.19 (br, 1H), 7.73 (s, 1H), 7.63 (br, 1H), 7.07 (br, 1H), 5.42 (br, 1H), 3.90 (d, J_{H-H} = 3.2 Hz, 1H), 2.43 (s, 3H), 2.28 (d, J_{H-H} = 3.2 Hz, 1H), 1.52 (s, 15H). ^{1}H-NMR (400 MHz, 233 K, CD_2Cl_2): *syn*-**5**, δ 8.04 (d, J_{H-H} = 8.8 Hz, 1H), 7.60 (s, 1H), 7.60 (d, J_{H-H} = 8.2 Hz, 1H), 7.02 (d, J_{H-H} = 7.3 Hz, 1H), 5.30 (d, J_{H-H} = 0.0 Hz, 1H), 3.80 (d, J_{H-H} = 3.2 Hz, 1H), 2.39 (s, 3H), 2.12 (d, J_{H-H} = 3.2 Hz, 1H), 1.45 (s, 15H). *anti*-**5**, δ 7.83 (d, J_{H-H} = 8.2 Hz, 1H), 7.57 (d, partially obscured, 1H), 7.20 (s, 1H), 7.00 (d, partially obscured, 1H), 5.44 (d, J_{H-H} = 6.4 Hz, 1H), 4.57 (d, J_{H-H} = 5.3 Hz, 1H), 2.38 (s, 3H), 2.11 (d, partially obscured, 1H), 1.47 (s, 15H). ^{13}C-NMR (400 MHz, 298 K, CD_2Cl_2): **5**, δ 142.9 (s, Çipso), 134.7, 132.6, 129.4, 96.6 (br, –Ç$_6$H$_4$Me), 106.9 (d, J_{Rh-C} = 5.3 Hz), 106.3 (d, J_{Rh-C} = 4.6 Hz), 101.6 (d, J_{Rh-C} = 6.8 Hz), 90.1 (d, J_{Rh-C} = 5.3 Hz, CH), 57.8 (d, J_{Rh-C} = 13 Hz, CH_2), 22.1 (s, Me), 8.9 (s, C$_5$Me$_5$). ^{13}C-NMR (400 MHz, 223 K, CD_2Cl_2): *syn*-**5**, δ 141.9 (s, *C*-Me), 134.1 (s, CHar), 131.1, (s, CHar), 128.8, (s, CHar), 105.8 (d, J_{Rh-C} = 4.6 Hz, Cipso), 105.6 (d, J_{Rh-C} = 3.8 Hz, Cipso), 100.7 (d, J_{Rh-C} = 6.8 Hz, Ç$_5$Me$_5$), 93.7 (s, CHar), 89.3 (d, J_{Rh-C} = 3.8 Hz CH), 57.1 (d, J_{Rh-C} = 13 Hz, CH_2), 21.8 (s, Me), 8.5 (s, C$_5$Me$_5$).

4.3. X-ray structure determination

Crystal data for $C_{41}H_{22}B_2Cl_2F_8Rh_2$, *syn*-**5** are summarised in Table 2 and selected bond lengths and angle data are given in Table 1. *syn*-**5** crystallises from diffusion of pentane into dichloromethane solution as red blocks. Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. Of the reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections 6453 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 6.06P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL [15] as implemented on the Viglen Pentium computer.

4.4. Reaction of [(C_5Me_5)$_2$Rh$_2$(μ-CH_2)$_2$($C_2C_6H_4Me$)$_2$] (**3**) with HCl

A solution of HCl (1 M in Et_2O; 0.14 ml, 0.14 mmol) was added to a stirred solution of **3** (50 mg, 0.068 mmol)

Table 2
Crystallographic data for [syn-**5**][BF_4]$_2$

Empirical formula	$C_{41}H_{22}B_2Cl_2F_8Rh_2$
Formula weight	964.93
Temperature (K)	150(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.2719(12)
b (Å)	15.461(2)
c (Å)	32.998(5)
α (°)	90
β (°)	95.862(3)
γ (°)	90
V (Å^3)	4198.0(10)
Z	4
D_{calc} (Mg m^{-3})	1.527
Absorption coefficient (mm^{-1})	0.976
$F(000)$	1896
Crystal size (mm)	0.41 × 0.41 × 0.08
Theta range for data collection (°)	1.24–28.33
Index ranges	$-9 \le h \le 10$, $-13 \le k \le 20$, $-43 \le l \le 43$
Reflections collected	25336
Independent reflections	10 105 [$R_{int} = 0.1658$]
Completeness to theta = 28.33°	96.6%
Absorption correction	Semi-empirical
Max/min transmission	0.9260, 0.6903
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10 105/32/537
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0711$, $wR_2 = 0.1639$
R indices (all data)	$R_1 = 0.1188$, $wR_2 = 0.1816$
Largest difference peak and hole (e Å^{-3})	1.031 and −1.079

in diethyl ether (20 ml). The colour changed from orange to red and after 1 h the solvent from the suspension was removed and the residue washed with n-pentane (2 × 5 ml) to give **1** (0.035 g, 90%). GC-MS analysis of the ether solution showed the presence of p-$MeC_6H_4C_2H$.

Acknowledgements

This research has been supported by a Marie Curie Fellowship of the European Community programme under contract number HPMF-CT-2000-00982.

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