Organometallics **2004,** *23,* 4478−4485

Alkene Carbon−Hydrogen Bond Activation at a Heterobimetallic Center: [RuCo(CO)$_3$(μ-CO)(η-C$_5$Me$_5$){μ-η^2:η^2-C(CF$_3$)C(CF$_3$)}]

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Received March 2, 2004

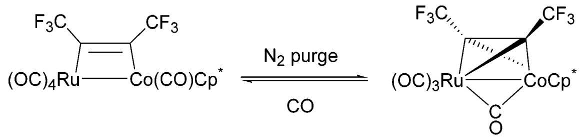
Reaction of [RuCo(CO)$_3$(μ-CO)(η-C$_5$Me$_5$){μ-η^2:η^2-C(CF$_3$)C(CF$_3$)}] (**3**) with alkenes gave the bis(vinyl) complexes [RuCo(CO)$_3$(η-C$_5$Me$_5$){μ-η^1:η^2-C(CF$_3$)CH(CF$_3$)}(μ-η^1:η^2-CHCRH)] (**4a**, R = H; **4b**, R = Me; **4c**, R = CO$_2$Me), through loss of carbon monoxide and via regiospecific alkene carbon−hydrogen bond activation. Low-temperature ^{13}C{^{1}H}, ^{1}H, and ^{2}D NMR spectroscopic studies of the reaction of **3** with ethene suggest the reaction proceeds via several coordinated ethene intermediates and a dimetallacyclic intermediate. Reaction of **3** with 1,1-dimethylallene resulted in carbon−carbon bond formation between the allene and alkyne, giving [RuCo(CO)$_3$(η-C$_5$Me$_5$){μ-η^2:η^4-C(CF$_3$)C(CF$_3$)C(CMe$_2$)(CH$_2$)}] (**5**). The structures of [RuCo(CO)$_3$(η-C$_5$Me$_5$){μ-η^1:η^2-C(CF$_3$)CH(CF$_3$)}(μ-η^1:η^2-CHCH$_2$)] (**4a**), [RuCo(CO)$_3$(η-C$_5$Me$_5$)-{μ-η^1:η^2-C(CF$_3$)CH(CF$_3$)}{μ-η^1:η^2-CHCH(CH$_3$)}] (**4b**), and [RuCo(CO)$_3$(η-C$_5$Me$_5$){μ-η^2:η^4-C(CF$_3$)C(CF$_3$)C(CMe$_2$)(CH$_2$)}] (**5**) have been determined by X-ray crystallographic studies.

Introduction

Over the past 30 years, the study of bimetallic complexes has been driven not only by their role as models for heterogeneous catalysts,[1] but also by their potential to act as homogeneous catalysts.[2] An added impetus for much of this research was the possibility of cooperative reactivity: that is, two metal centers enhancing the activation of an organic substrate compared to that exhibited by the individual partners.[3] Recently, as advances in experimental techniques have allowed the synthesis of synthetically more demanding heterobimetallic species, a new catalog of potential mixed-metal catalysts has emerged.[4] These heterobimetallic species may combine the catalytic features of each metal to provide new and unique reactivity that is inaccessible by the homobimetallic systems.[2a,4b,5]

Previously in this laboratory, we have studied the chemistry of [M(CO)$_4$(η^2-alkyne)] (M = Fe, Ru, Os) compounds.[6] Interestingly, the ruthenium hexafluorobutyne derivative [Ru(CO)$_4${η^2-C$_2$(CF$_3$)$_2$}] (**1**) reacts with [Co(CO)$_2$(η-C$_5$Me$_5$)] to give both the ruthenium−cobalt dimetallacyclobutene [RuCo(CO)$_5$(η-C$_5$Me$_5$){μ-η^1:η^1-C(CF$_3$)C(CF$_3$)}] (**2**) and the tetrahedrane [RuCo(CO)$_3$-(μ-CO)(η-C$_5$Me$_5$){μ-η^2:η^2-C(CF$_3$)C(CF$_3$)}] (**3**).[7] Complex **3** forms exclusively by purging the reaction solution with nitrogen, whereas **2** is obtained by purging with carbon monoxide. This reversible carbon monoxide loss/addition demonstrates the ability of the alkyne to switch smoothly between two-electron parallel and four-electron perpendicular bonding modes (Scheme 1). This behavior implies the presence of incipient unsaturation in **3** and potential for reactivity toward Lewis bases. With this in mind, we set out to study and report herein the reactivity of this heterobimetallic complex toward alkenes and 1,1-dimethylallene.

Scheme 1



2 **3**

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10.1021/om040026p CCC: $27.50
Publication on Web 08/17/2004

Experimental Section

All reactions were carried out using standard Schlenk techniques under a dry and oxygen-free nitrogen atmosphere. Hydrocarbon solvents were dried over CaH_2 and distilled under nitrogen using normal procedures prior to use. $[RuCo(CO)_3(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)C(CF_3)\}]$ (**3**) was prepared as described in the literature.[7] Ethene (Linde Union Carbide), carbon-13 labeled ethene (Icon Services Inc), propene (Matheson Gas Products), methyl acrylate, deuterated ethene (both Aldrich), and 1,1-dimethylallene (Fluka) were used as supplied. IR solution spectra (KBr cell) were recorded on a Bomem MB-100 FTIR spectrometer. NMR samples were prepared under a nitrogen atmosphere. NMR spectra were recorded on either a Bruker AM 400 MHz or a Varian Inova 400 MHz spectrometer. The chemical shifts are reported in ppm relative to external TMS (δ 0.00; ^{1}H and ^{13}C), and coupling constants are given in Hz. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Alberta. Electron impact (EI) mass spectra were recorded on a AEI/Kratos MS 50 spectrometer. Electrospray (ES) mass spectra were recorded on a Micromass ZabSpec Hybrid Sector-TOF spectrometer.

Reaction of 3 with Ethene. A cooled (−70 °C) hexane (25 cm^3) solution of **3** (40 mg; 0.071 mmol) was purged with ethene while it was warmed to room temperature over 2 h. The solution was then stirred for a further 1.5 h. The solvent was removed in vacuo. Precipitation from dichloromethane at −78 °C gave $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)CH(CF_3)\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2)]$ (**4a**; 24 mg) as a dark brown solid in 60% yield. Crystals suitable for X-ray crystallography were grown from a saturated pentane solution cooled to −30 °C. IR (*n*-hexane, cm^{-1}): 2072 (s), 2013 (m), 1998 (m). ^{1}H NMR (CD_2Cl_2, room temperature): δ 9.16 (dd, $^3J_{HH} = 8.5$, $^3J_{HH} = 13$, 1H, μ-C*H*), 2.90 (dd, $^3J_{HH} = 8.5$, $^2J_{HH} = 3.5$, 1H, CH_2), 1.83 (s, 15H, $C_5(CH_3)_5$), 1.40 (dd, $^3J_{HH} = 13$, $^2J_{HH} = 3.5$, 1H, CH_2), 0.71 (q, $^3J_{HF} = 11.3$, 1H, C*H*CF_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature): δ 196.9, 195.8, 193.0 (Ru-*C*O), 182.1 (s, μ-*C*H), 141.3 (m, μ-*C*(CF_3)) (at −80 °C, signal too weak at room temperature), 131.8 (q, $^1J_{CF} = 276$, *C*F_3), 127.9 (q, $^1J_{CF} = 275$, *C*F_3), 98.9 (s, *C*$_5$Me$_5$), 59.2 (q, $^2J_{CF} = 36$, *C*H(CF_3)), 57.9 (s, *C*H_2), 10.6 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2, room temperature): −46.60 (q, $^5J_{FF} = 14$, CF_3), −51.36 (qd, $^3J_{FH} = 11.5$, $^5J_{FF} = 14$, CHCF_3). Anal. Calcd for $C_{19}H_{19}CoF_6O_3Ru$: C, 40.08; H, 3.36. Found: C, 40.37; H, 3.42. MS (EI, 16 eV): *m/z* 570.

Reaction of 3 with Propene. A stirred hexane (30 cm^3) solution of **3** (64.3 mg; 0.113 mmol) was purged with propene at room temperature for 4 h. The solvent was removed in vacuo to give a dark red-purple residue. The residue was dissolved in pentane, and the solution was filtered and concentrated prior to recrystallization at −78 °C, to give $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)CH(CF_3)\}\{\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH(CH_3)\}]$ (**4b**; 37.2 mg) as red-brown microcrystals in 56% yield. IR (pentane, cm^{-1}): 2068 (s), 2009 (m), 1996 (m). ^{1}H NMR (CD_2Cl_2, room temperature): δ 8.56 (dd, $^3J_{HH} = 12$, $^4J_{HH} = 0.4$, 1H, μ-C*H*), 2.10 (dq, $^3J_{HH} = 5.6$, $^3J_{HH} = 12$, 1H, C*H*Me), 1.85 (s, 15H, $C_5(CH_3)_5$), 1.76 (dd, $^3J_{HH} = 5.6$, $^4J_{HH} = 0.4$, 3H, CH_3), 0.86 (q, $^3J_{HF} = 11.2$, 1H, C*H*CF_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature): δ 196.9, 196.7, 193.1 (Ru−*C*O), 177.2 (s, μ-*C*H), 143.06 (q, $^2J_{CF} = 41.9$, μ-*C*(CF_3)), 131.8 (q, $^1J_{CF} = 274$, *C*F_3), 128.1 (q, $^1J_{CF} = 275$, *C*F_3), 98.5 (s, *C*$_5$Me$_5$), 76.1 (s, *C*HMe), 58.21 (qq, $^2J_{CF} = 36$, $^3J_{CF} = 3$, *C*H(CF_3)), 25.22 (s, *C*H_3), 10.61 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2, room temperature): −46.59 (q, $^5J_{FF} = 14$, CF_3), −51.52 (dq, $^3J_{FH} = 12$, $^5J_{FF} = 14$, CHCF_3). Anal. Calcd for $C_{20}H_{21}CoF_6O_3Ru$: C, 41.18; H, 3.63. Found: C, 41.03; H, 3.53. MS (EI): *m/z* 583.9 (M^+), 554.9 ($M^+ - CO$), 499.9 ($M^+ - 3CO$).

Reaction of 3 with Methyl Acrylate. To a cooled (−78 °C) hexane (100 cm^3) solution of **3** (55 mg; 0.097 mmol) was added methyl acrylate (10 μL; 0.107 mmol), and the solution was allowed to warm to room temperature overnight. An IR spectrum of the reaction solution showed that the reaction had not gone to completion; therefore, additional methyl acrylate was added (10 μL; 0.107 mmol) and the solution stirred overnight. The solvent was removed in vacuo to give a dark red-purple residue. The residue was dissolved in pentane, and the solution was filtered and concentrated prior to recrystallization at −78 °C to give $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)CH(CF_3)\}\{\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH(CO_2CH_3)\}]$ (**4c**; 39 mg) as dark red-black crystals in 64% yield. IR (pentane, cm^{-1}): 2081 (s), 2026 (m), 2009 (m/w), 1722 (w). ^{1}H NMR (CD_2Cl_2, room temperature): δ 9.82 (d, $^3J_{HH} = 11$, 1H, μ-C*H*), 3.63 (s, 3H, CO_2CH_3), 1.90 (d, $^3J_{HH} = 11$, integral merged with Cp*, C*H*(CO_2Me)), 1.85 (s, 16H, $C_5(CH_3)_5$), 1.01 (q, $^3J_{HF} = 11$, 1H, C*H*CF_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature): δ 195.8, 193.5, 190.9 (Ru−*C*O), 187.0 (s, μ-*C*H), 146.3 (q, $^2J_{CF} = 37$, μ-*C*(CF_3)), 131.2 (q, $^1J_{CF} = 275$, *C*F_3), 127.2 (q, $^1J_{CF} = 275$), 99.6 (s, *C*$_5$Me$_5$), 62.8 (s, *C*HCO_2Me), 61.1 (q, $^2J_{CF} = 35$, $^3J_{CF} = 3$, *C*H(CF_3)), 51.9 (s, *C*H_3), 10.7 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2, room temperature): −46.72 (q, $^5J_{FF} = 14$, CF_3), −51.64 (dq, $^3J_{FH} = 11$, $^5J_{FF} = 14$, CHCF_3). Anal. Calcd for $C_{21}H_{21}CoF_6O_5Ru$: C, 40.20; H, 3.35. Found: C, 40.62; H, 3.34. MS (ES): *m/z* 629.0 ($M^+ + H$).

Reaction of 3 with 1,1-Dimethylallene. To a hexane (120 cm^3) solution of **3** (125 mg; 0.22 mmol) at room temperature was added 1,1-dimethylallene (26 μL; 0.26 mmol), and the solution was stirred for 4 h. An additional amount of 1,1-dimethylallene was added (6 μL; 0.06 mmol), and the solution was stirred for 2 h more to complete the reaction. The solvent was removed in vacuo to give a dark red-black residue. The residue was dissolved in pentane, and the solution was filtered and concentrated prior to recrystallization at −78 °C, to give $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^4\text{-}C(CF_3)C(CF_3)C(CMe_2)(CH_2)\}]$ (**5**; 43.5 mg) as dark red-black crystals in 32% yield. IR (pentane, cm^{-1}): 2054 (s), 1990 (w/sh), 1980 (s). ^{1}H NMR (CD_2Cl_2, room temperature): δ 3.74 (s, 1H, CH_2), 2.53 (s, 1H, CH_2), 1.77 (s, 15H, $C_5(CH_3)_5$), 1.27 (s, 3H, CH_3), 1.21 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature): δ 196.8 (q, $^4J_{CF} = 4.5$, Ru−*C*O), 199.5 (q, $^4J_{CF} = 2.8$, Ru−*C*O), 194.3 (q, $^4J_{CF} = 1{-}2$, Ru−*C*O), 135.4 (m, $^2J_{CF} = 40$, μ-*C*(CF_3)), 129.5 (q, $^1J_{CF} = 273$, *C*F_3), 126.7 (q, $^1J_{CF} = 276$), 113.8 (s, $C_{quaternary}$), 98.3 (s, *C*$_5$Me$_5$), 76.3 (m, *C*(CF_3)), 45.9 (s, *C*H_2), 37.2 (s/br, *C*Me$_2$), 33.9, 28.66 (s, 2*C*H_3), 11.1 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2, room temperature): −50.63 (q, $^5J_{FF} = 11$, CF_3), −53.58 (q, $^5J_{FF} = 11$, CF_3). Anal. Calcd for $C_{22}H_{23}CoF_6O_3Ru$: C, 43.36; H, 3.8. Found: C, 43.35; H, 3.62. MS (EI): *m/z* 609.9 (M^+), 581.7 ($M^+ - CO$), 553.8 ($M^+ - 2CO$), 525.9 ($M^+ - 3CO$).

General Procedure for Low-Temperature NMR Reactions. A CD_2Cl_2 solution of **3** was prepared in an NMR tube with a PTFE valve. The solution was freeze−thaw-degassed three times; on the third time the tube was warmed to −80 °C and filled with ^{13}C enriched ethene or deuterated ethene to approximately 1 atm. The tube was then sealed and frozen in liquid nitrogen prior to introduction into the precooled NMR spectrometer.

X-ray Structure Analyses. Single crystals, suitable for X-ray diffraction studies, of **4a** (dark red crystals), **4b** (red-brown crystals), and **5** (dark red-black crystals) were obtained by cooling saturated pentane solution to −80 °C. Summaries of crystal data and X-ray collection information are collected in Table 1.

Results and Compound Characterization

Reaction of 3 with Alkenes. Reaction of **3** with ethene, propene, or methyl acrylate gave only one isolable product in all cases. It was clear from the spectroscopic signatures that loss of one carbon monoxide ligand was accompanied by the activation of an alkene carbon−hydrogen bond to form the bis(vinyl) species $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)CH(CF_3)\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCRH)]$ (**4**, R = H, Me, CO_2Me). Two possible isomers of **4**, **a−c and a′−c′**, are shown in Scheme 2.

Table 1. Crystallographic Experimental Details for Compounds 4a,b and 5

	4a	**4b**	**5**
	Crystal Data		
formula	$C_{19}H_{19}CoF_6O_3Ru$	$C_{20}H_{21}CoF_6O_3Ru$	$C_{22}H_{23}CoF_6O_3$
formula wt	569.34	583.37	609.40
cryst dimens (mm)	0.33 × 0.23 × 0.12	0.27 × 0.09 × 0.03	0.18 × 0.14 × 0.11
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (alternate setting of $P2_1/c$ (No. 14))	$P\bar{1}$ (No. 2)	$P2_1/n$ (alternate setting of $P2_1/c$ (No. 14))
unit cell params			
a (Å)	9.2295(6)[a]	8.0546(16)[b]	9.4030(19)[c]
b (Å)	25.9055(16)	8.6323(17)	16.401(3)
c (Å)	9.5611(6)	15.932(3)	14.826(3)
α (deg)		102.008(4)	
β (deg)	118.1311(12)	90.108(4)	94.991(4)
γ (deg)		104.059(4)	
V (Å^3)	2016.0(2)	1049.4(4)	2277.8(8)
Z	4	2	4
ρ_{calcd} (g cm^{-3})	1.876	1.846	1.777
μ (mm^{-1})	1.644	1.582	1.462
	Data Collection and Refinement Conditions		
diffractometer	Bruker PLATFORM/SMART 1000 CCD[d]		
radiation (λ (Å))	graphite-monochromated Mo Kα (0.710 73)		
temp (°C)	−80	−80	−80
scan type	ω scans (0.2°, 20 s exposures)	ω scans (0.2°, 25 s exposures)	ω scans (0.2°, 25 s exposures)
data collecn 2θ limit (deg)	52.78	52.80	52.76
total no. of data collected	9972 ($-11 \leq h \leq 10$, $-32 \leq k \leq 32$, $-7 \leq l \leq 11$)	6148 ($-10 \leq h \leq 10$, $-10 \leq k \leq 9$, $-17 \leq l \leq 19$)	12068 ($-11 \leq h \leq 10$, $-20 \leq k \leq 20$, $-18 \leq l \leq 15$)
no. of indep rflns	4113	4051 ($R_{int} = 0.0836$)	4655 ($R_{int} = 0.1868$)
no. of obsd rflns (NO)	3659 ($F_o^2 \geq 2\sigma(F_o^2)$)	2282 ($F_o^2 \geq 2\sigma(F_o^2)$)	2239 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure soln method	direct methods/fragment search (DIRDIF-96[e])	Patterson search/structure expansion (DIRDIF-96[e])	Patterson search/structure expansion (DIRDIF-96[e])
refinement method	full-matrix least squares on F^2 (SHELXL-93[f])		
abs cor method	multiscan (SADABS)	Gaussian integration (face-indexed)	multiscan (SADABS)
range of transmissn factors	0.8271−0.6129	0.9595−0.7056	0.8557−0.7788
no. of data/restraints/params	4113 ($F_o^2 \geq -3\sigma(F_o^2)$)/0/276	4051 ($F_o^2 \geq -3\sigma(F_o^2)$)/0/280	4655 ($F_o^2 \geq -3\sigma(F_o^2)$)/0/325
goodness of fit (S)[g]	1.050 ($F_o^2 \geq -3\sigma(F_o^2)$)	0.965 ($F_o^2 \geq -3\sigma(F_o^2)$)	0.967 ($F_o^2 \geq -3\sigma(F_o^2)$)
final R indices[h]			
R_1 ($F_o^2 \geq 2\sigma(F_o^2)$)	0.0270	0.0824	0.0860
wR_2 ($F_o^2 \geq -3\sigma(F_o^2)$)	0.0690	0.1925	0.1873
largest diff peak and hole (e Å^{-3})	0.653 and −0.453	1.734 and −1.255	1.533[i] and −1.350[j]

[a] Obtained from least-squares refinement of 4394 centered reflections. [b] Obtained from least-squares refinement of 2090 centered reflections. [c] Obtained from least-squares refinement of 2466 centered reflections. [d] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker. [e] Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. The DIRDIF-96 program system; Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1996. [f] Sheldrick, G. M. SHELXL-93: Program for crystal structure determination; University of Göttingen, Göttingen, Germany, 1993. [g] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$ and a_0 and a_1 are adjusted during refinement; for **4a**, $a_0 = 0.0394$, $a_1 = 0.625$; for **4b**, $a_0 = 0.0886$, $a_1 = 0$; for **5**, $a_0 = 0.0712$, $a_1 = 0$). [h] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [i] Located 1.07 Å from Ru. [j] Located 0.94 Å from Ru.

Complexes **4** were fully characterized by IR and NMR (^1H, ^{19}F and $^{13}C\{^1H\}$) spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **4** (R = H) shows three mutually coupled signals due to the vinyl protons at δ 9.16 (H_a), 2.90 (H_b), and 1.40 (H_c). The low-field H_a resonance, typical of a bridging vinyl CH moiety,[8] has a coupling constant of 8.5 Hz to H_b and 13 Hz to H_c, indicating cis and trans dispositions, respectively, of these pairs of H atoms. The proton H_d is seen at δ 0.71 as a quartet due to fluorine coupling, corroborating activation and migration of the ethene hydrogen to hexafluorobutyne and production of a second vinyl moiety. In the cases of propene and methyl acrylate, it was clear that these reactions were regiospecific, giving vinyl units with the metal and R groups trans to each other. This was evident from the ^1H NMR spectra, with trans H_a/H_c coupling constants for **4** (R = Me, CO_2Me) of 12.0 and 11.2 Hz, respectively. Dickson has observed similar chemistry with the $[Rh_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)C(CF_3)\}]$ (**I**) system (Scheme 3),[9] although only a limited degree of regioselectivity was observed and this was with bulkier alkenes, such as styrene and 3,3-dimethylpropene. We note also that the thermal reaction of **I** with alkenes was slow at room temperature, but it was greatly accelerated by sunlight. No such light activation was required in our system, although purging the reaction solutions with gas (either the reactant gas or nitrogen), to remove liberated carbon monoxide, did increase the rate.

The $^{13}C\{^1H\}$ NMR spectra of complexes **4** show low-field shifts around δ 180 for the bridging carbons (C_a) of the vinyl units formed from the incoming alkene. The

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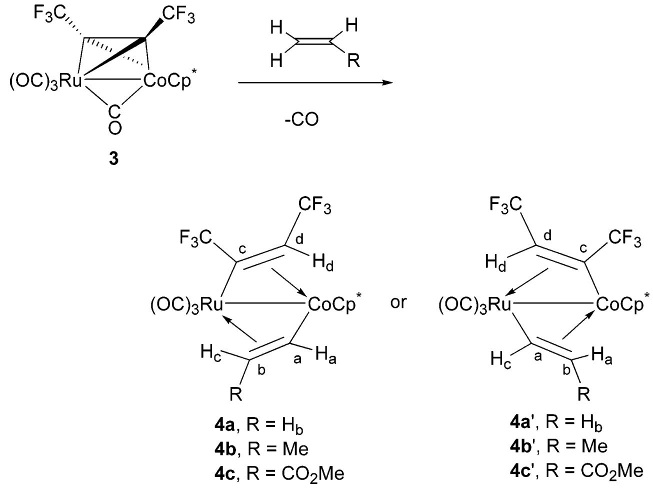
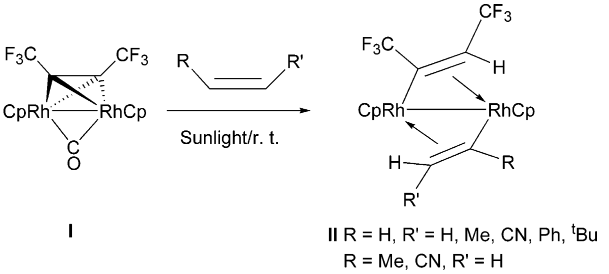
(8) (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (b) Gracey, B. P.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G.; Stobart, R. S. *J. Chem. Soc., Dalton Trans.* **1985**, 1935. (c) Anwar, M. K.; Hogarth, G.; Senturk, O. S.; Clegg, W.; Doherty, S.; Elsegood, M. R. J. *J. Chem. Soc., Dalton Trans.* **2001**, 341. (d) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1986**, *314*, 333.

(9) Dickson, R. S. *Polyhedron* **1991**, *10*, 1995.

Scheme 2



Scheme 3



bridging carbons of the hexafluorobutyne-derived vinyls (C_c) are observed at higher field, in the δ 143−146 range. Both sets of values are within the range expected for bridging vinyl carbons.[8] The higher field position of C_c probably indicates that it is experiencing more π back-bonding from the cobalt center and therefore more shielding. The increase in π back-bonding is a consequence of the electron-withdrawing CF_3 and the π-type bonding between the vinyl unit and the electron-rich $Co(C_5Me_5)$ center. Therefore, the favored structures are more likely to be **4a**−**c** rather than **4a′**−**c′**.

The β-vinyl carbons (C_b and C_d) for **4** (R = H, CO_2Me) appear around δ 60, whereas C_b of **4** (R = Me) resonates at δ 76.10. This anomaly is probably related to the methyl substituent. In free alkenes, methyl substituents are known to cause ca. 10 ppm downfield shifts of the carbons to which they are attached.[8a,10]

Vinyl group fluxionality by σ,π isomerization is a well-known process in homobimetallic systems.[11] A similar bilateral isomerization in this system would interchange **4a**−**c** and **4a′**−**c′**. However, no such process was detected here. Variable-temperature ^1H NMR studies show only one isomer of each complex present at low temperatures for **4** (R = H, CO_2Me). Attempts to induce such an isomerization at elevated temperatures resulted in decomposition (at 80 °C for **4** (R = H) and at 40 °C for **4** (R = CO_2Me)).

Although the spectroscopic data pointed to **4a**−**c** as the correct orientation of the vinyl units, a corroboration of this assignment was sought and, consequently, X-ray crystallographic studies were performed on **4** (R = H, R = Me).

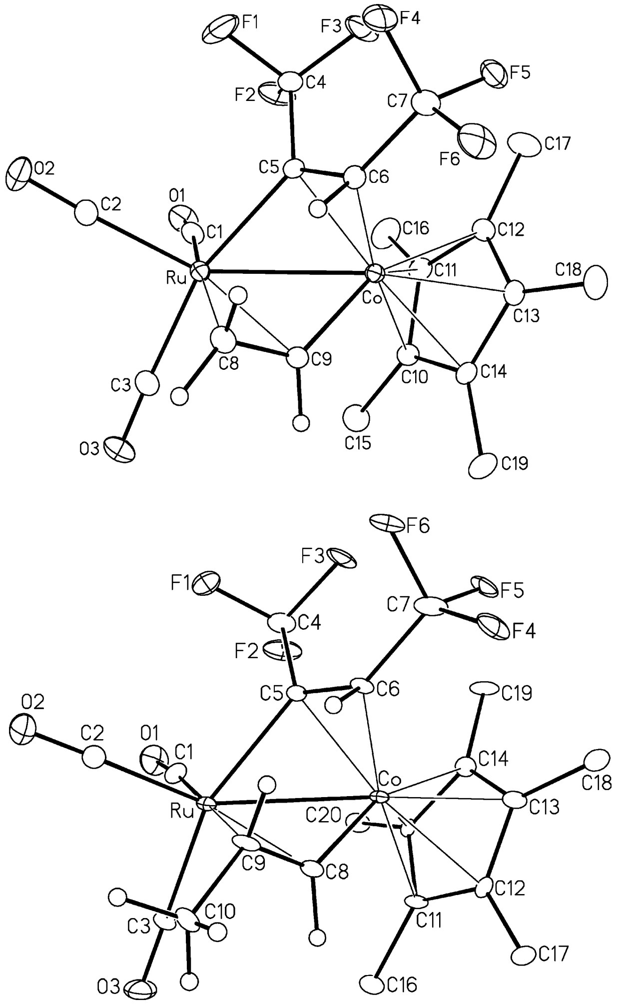


Figure 1. Perspective view of (a, top) $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1:\eta^2\text{-}C(CF_3)CH(CF_3)\}(\mu\text{-}\eta^1:\eta^2\text{-}CHCH_2)]$ (**4a**) and (b, bottom) $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1:\eta^2\text{-}C(CF_3)CH(CF_3)\}\{\mu\text{-}\eta^1:\eta^2\text{-}CHCH(Me)\}]$ (**4b**), showing the atom-labeling scheme. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms of the $\mu\text{-}F_3CCCHCF_3$ and $\mu\text{-}CHCH_2$ groups are shown with arbitrarily small thermal parameters; hydrogens of the pentamethylcyclopentadienyl group are not shown.

The structures of **4a**,**b** are shown in Figure 1, and pertinent bond lengths and angles are given in Tables 2 and 3. It is apparent from the structure of **4a** that the vinyl unit is σ-bound to cobalt and π-bound to ruthenium. Consequently, the hexafluorobutyne-derived vinyl is bound in the reverse fashion. The Ru−C5 and Co−C9 bond distances are 2.120(2) Å and 1.908(2) Å, respectively, indicative of metal−carbon σ bonds.[12] Bond distances of 2.259(3) Å (Ru−C8) and 2.193(2) Å (Ru−C9) for ruthenium and 1.979(2) Å (Co−C5) and 2.058(2) Å (Co−C6) for cobalt imply metal−carbon π interactions.[12]

It is interesting to compare these metal−carbon σ- and π-bond distances to average values calculated in Orpen's survey of organometallic crystal structures.[12]

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(10) Levy, G. C.; Nelson, G. L. In *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience: New York, 1972; Chapter 2, p 59.

(11) (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Farrugia, L. J.; Chi, Y.; Tu, W.-C. *Organometallics* **1993**, *12*, 1616.

(12) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Table 2. Bond Lengths and Angles for $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)CH(CF_3)\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2)]$ (4a)

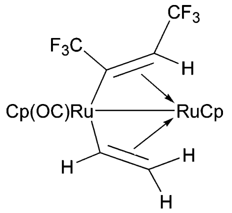
(a) Selected Interatomic Distances (Å)

Ru–Co	2.6000(4)	Co–C5	1.979(2)
Ru–C1	1.913(3)	Co–C6	2.058(2)
Ru–C2	1.930(3)	Co–C9	1.908(2)
Ru–C3	1.940(3)	Co–C10	2.072(2)
Ru–C5	2.120(2)	C5–C6	1.422(3)
Ru–C8	2.259(3)	C8–C9	1.393(4)
Ru–C9	2.193(2)		

(b) Selected Interatomic Angles (deg)

Ru–Co–C9	55.70(7)	Co–C9–C8	129.13(18)
Ru–C5–C4	119.21(17)	C4–C5–C6	119.7(2)
Ru–C5–C6	120.46(17)	C5–C6–C7	129.1(2)
Co–Ru–C5	48.28(6)		

The Co–C9 σ distance is short, as are the Co–C5 and Co–C6 π bond distances,[13] although due to the small sample size of comparable cobalt–vinyl interactions, not too much should be read into these figures. However, the larger sample size for Ru–vinyl interactions provides for a better comparison. The Ru–C5 σ bond distance appears to be long, whereas the Ru–C8 and Ru–C9 π bond distances are toward the shorter end of the range. These findings are in keeping with those made by Knox in his diruthenium bis(vinyl) species $[Ru_2(CO)(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3){=}CH(CF_3)\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)]$,[14] in which the ethenyl metal–carbon σ bond is shorter than the hexafluorobutenyl metal–carbon σ bond and the hexafluorobutenyl metal–carbon π distances are shorter than their ethenyl counterparts. These observations may be explained by the presence of the electron-withdrawing trifluoromethyl groups. These cause increased π-back-bonding and hence a shortening of the metal–carbon π interactions. In our system, similar factors are probably shortening the cobalt–carbon π interactions. In agreement with this, the C5–C6 bond length, 1.422(3) Å, is longer than the corresponding C8–C9 distance of 1.393(4) Å.



The orientation of the vinyl groups is assumed to be favored electronically. The configuration maximizes π donation from the electron-rich ethenyl to the relatively electron-poor $Ru(CO)_3$ center and allows the electron-poorer vinyl (derived from hexafluorobutyne) to benefit from increased back-donation from the relatively electron-rich $Co(C_5Me_5)$ center.

The two vinyl units are oriented so that the π-bound carbons of both vinyl groups are on the same face of the molecule. The torsion angle along the ruthenium–cobalt bond between the two σ-bound carbons C5 and C9 is 122.76(12)°. A similar torsion angle between the two π-bound carbons C6 and C8 is 65.97(10)°, indicating the two vinyl units are bent in toward each other with their π-bound carbons twisted toward each other.

Table 3. Bond Lengths and Angles for $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)\text{-}CH(CF_3)\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHMe)]$ (4b)

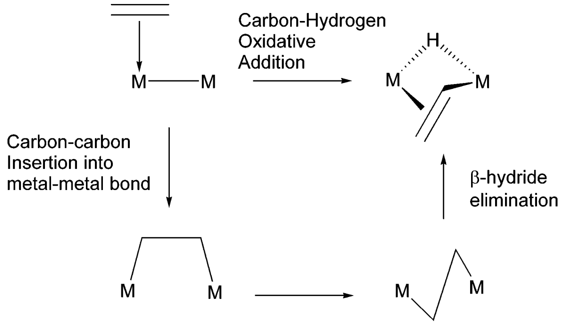
(a) Selected Interatomic Distances (Å)

Ru–Co	2.5916(17)	Co–C5	1.993(10)
Ru–C1	1.880(14)	Co–C6	2.035(9)
Ru–C2	1.900(13)	Co–C8	1.932(11)
Ru–C3	1.929(11)	Co–C11	2.059(9)
Ru–C5	2.131(10)	C5–C6	1.395(14)
Ru–C8	2.187(10)	C8–C9	1.346(14)
Ru–C9	2.282(10)		

(b) Selected Interatomic Angles (deg)

Ru–Co–C8	55.5(3)	Co–C8–C9	130.6(8)
Ru–C5–C4	117.0(7)	C4–C5–C6	122.7(10)
Ru–C5–C6	119.9(8)	C5–C6–C7	127.9(10)
Ru–C9–C10	121.5(7)	C8–C9–C10	121.2(10)
Co–Ru–C5	48.7(3)		

Scheme 4. Bimetallic Activations of an Alkene Carbon–Hydrogen Bond



The σ-ruthenium-bound C5 is approximately sp^2 hybridized, the sum of the bond angles around it (excluding those to cobalt) being 359.37°. The Ru–C5–C6–C7 torsion angle is 172.9(2)°, a 7.1° distortion from the planarity expected for an alkene; the deviation is probably due to the twisting of the vinyl moiety in order to π-bond to the cobalt.

The structure of **4b** is very similar to that of **4a**, with the same arrangement of the vinyl units. The methyl group of the vinyl unit is trans to the cobalt, presumably for steric reasons. This is in keeping with observations made in a number of other laboratories, in which large substituents are generally found trans to the metal–vinyl σ bond.[8a,b,9,15]

The vinyl unit in **4b** allows for a comparison of the planarity of the two vinyl units. The Ru–C5–C6–C7 and Co–C8–C9–C10 torsion angles are very similar at 175.4(9) and 175.0(8)°, respectively, indicating that both vinyl units deviate only slightly from planarity.

Formation of Compounds 4

The activation of an alkene carbon–hydrogen bond by complex **1** is the first example of this type of reactivity by a preformed heterobimetallic species.[16] Fryzuk proposed two mechanisms for the homobimetallic activation of an alkene carbon–hydrogen bond.[17] Both involve initial coordination of the olefin and then either carbon–hydrogen bond activation to give a vinyl hydride or olefin insertion into the metal–metal bond followed by a β-hydride elimination (Scheme 4.)

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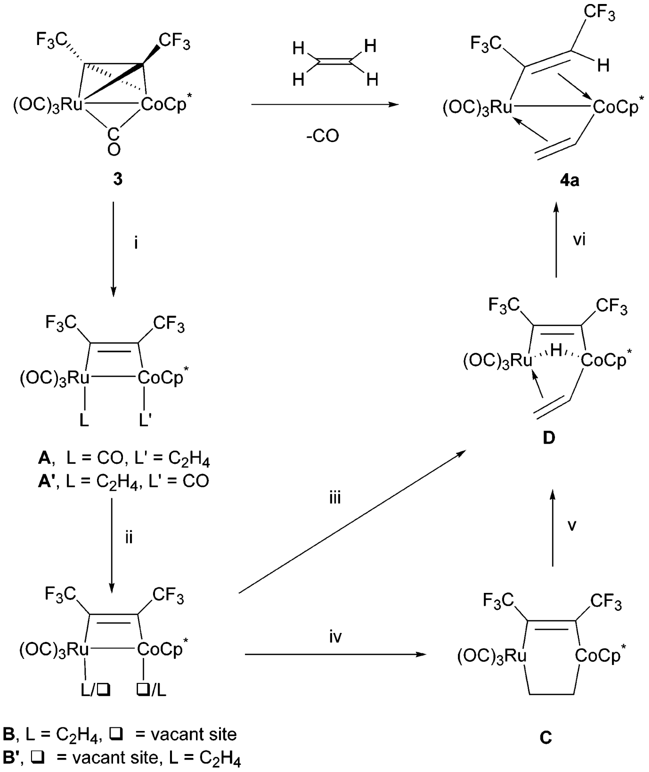
(13) (a) Tyler, S. J.; Burlitch, J. M. *J. Organomet. Chem.* **1986**, *361*, 231. (b) Bennett, M. A.; Donaldson, P. B. *Inorg. Chem.* **1978**, *17*, 5. (c) Aime, S.; Osella, D.; Milone, L.; Manotti-Lafredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1983**, *71*, 141.

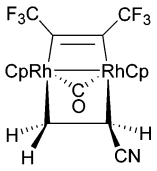
(14) Brady, L. A.; Dyke, A. F.; Garner, S. E.; Guerchais, V.; Knox, S. A. R.; Maher, J. P.; Nicholls, S. M.; Orpen, A. G. *J. Chem. Soc., Chem, Commun.* **1992**, 310.

Scheme 5. Potential Alkene Carbon−Hydrogen Bond Activation Pathway[a]



[a] Legend: (i) initial alkene coordination; (ii) loss of CO; (iii) oxidative addition; (iv) insertion into metal−metal bond; (v) β-hydride elimination; (vi) hydride migration.

In support of the olefin insertion into the metal−metal bond, Dickson presented some evidence for a dimetallacyclobutane intermediate (**III**), in the formation of the bis(vinyl) complexes [$Rh_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}(\mu\text{-}\eta^1{:}\eta^2\text{-}CRCR'H)$] (**II**: R = H, R′ = CN; R = CN, R′ = H) derived from [$Rh_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)C(CF_3)\}$] (**I**) and acrylonitrile.[9]



III

Similar processes could be occurring here, with initial alkene coordination followed by either of the carbon−hydrogen activation routes and then hydrogen migration to hexafluorobutyne giving the bis(vinyl) complexes **4a**−**c**. The two plausible routes are shown in Scheme 5. The ability of the hexafluorobutyne in **3** to switch easily between four-electron and two-electron bonding modes undoubtedly plays a significant role in any potential mechanism.

To gain a better understanding of the intimate mechanism or at least identify spectroscopically some of the intermediates, the reaction was monitored by multinuclear NMR spectroscopy. Unfortunately, our attempts have been a mixed success. Placing a cooled (−80 °C) CD_2Cl_2 solution of **3** under a $^{13}C_2H_4$ atmosphere immediately gave two new ^{13}C resonances at δ 43.26 (br/s) and 70.41 (br/s) (Figure 2). These are thought to correspond to the terminally π-bound ethene species [$RuCo(CO)_4(\eta^2\text{-}C_2H_4)(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^1{:}\eta^1\text{-}C(CF_3)C(CF_3)\}$] (**A** and **A′**), as a result of the alkyne switching from a four-electron perpendicular to a two-electron parallel bonding mode (Scheme 5). It is likely that both **A** and **A′** are in equilibrium with **3** in much the same way as **2** is. Over the course of 2 h, these two peaks gradually increase in intensity.

Briefly raising the temperature to ambient and then recooling to −80 °C gave rise to several other ^{13}C resonances, including those associated with product **4a** (Figure 2). The other peaks are seen at δ 56.4 (br/s), 44.70 (d, $^1J_{CC} = 28.6$ Hz), and 6.80 (d, $^1J_{CC} = 28.6$ Hz), the last two clearly sharing a coupling constant. We propose that these three peaks relate to two intermediates in the formation of **4a**. The broad singlet nature of the δ 56.4 peak suggests a rapidly rotating π-bound ethene much like that in the proposed complexes **A** and **A′**, perhaps in a species such as **B** or **B′**, formed through loss of carbon monoxide from **A** and **A′**. The formation of a vacant site at one of the metal atoms would then allow the alkene to insert into the metal−metal bond, giving a dimetallacycle, perhaps such as **C**. The pair of mutually coupled doublets at δ 44.70 and 6.80 are consistent with sp^3-hybridized carbons of a dimetallacycle. In the few literature examples of comparable ring systems, similar high-field shifts are seen.[18]

Formation of **4a** would then occur via a β-hydride elimination to give **D** followed by a hydride to alkyne migration (Scheme 5, steps v and vi, respectively).

Attempts to corroborate the intermediacy of the heterobimetallic hydride **D** by low-temperature $^1H/^2D$ NMR spectroscopy proved inconclusive. Low-temperature ^1H NMR spectroscopic monitoring of the reaction of **3** with ethene showed a number of very weak hydride resonances, along with a weak low-field multiplet (a potential vinylic CH_a). However, no correlation could be seen (by integral and correlation spectroscopy) between any of the hydride signals and the vinylic proton and, therefore, no concrete evidence for **D**. A low-temperature ^2D NMR spectroscopic study on the reaction of **3** with deuterated ethene showed a very broad resonance (between δ 2 and 4) thought to contain resonances due to **A**, **A′**, **B**, and **C** but no deuteride or low-field vinyl deuterium resonances (other than the product). On the basis of these results we can neither confirm nor deny the intermediacy of **D** in the mechanism.

Reaction of 3 with 1,1-Dimethylallene. Reaction of **3** with 1,1-dimethylallene proceeded by a very different path and gave [$RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^4\text{-}C(CF_3)C(CF_3)C(CMe_2)(CH_2)\}$] (**5**) as the major product and an unidentified minor product (Scheme 6). Complex **5** is the result of carbon−carbon bond formation between

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(15) (a) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 694. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 3479.

(16) The formation of heterobimetallic vinyl species through reaction of discrete monometallic complexes with [$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$] has been reported by Stang: Cao, D. H.; Stang, P. J.; Arif, A. M. *Organometallics* **1995**, *14*, 2733.

(17) Piers, W. E.; Fryzuk, M. D. *Polyhedron* **1988**, *7*, 1001.

(18) (a) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092. (b) Burke, M. R.; Seils, F.; Takats, J. *Organometallics* **1994**, *13*, 1445. (c) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1991**, *10*, 376. (d) Bender, B. R.; Ramage, D. L.; Norton, J. R.; Wiser, D. C.; Rappe, A. K. *J. Am. Chem. Soc.* **1997**, *119*, 5628.

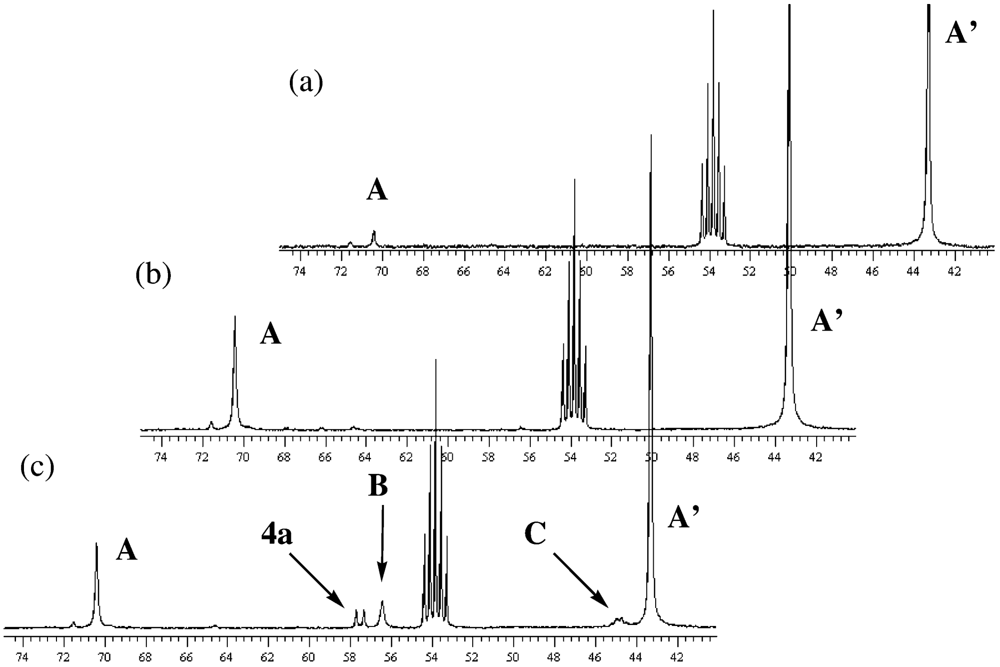
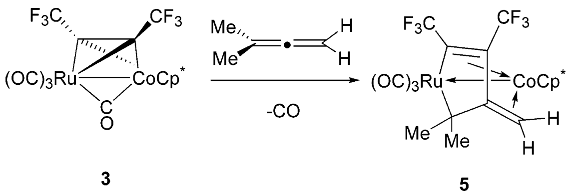


Figure 2. $^{13}C\{^1H\}$ NMR monitoring of the reaction between **3** and $^{13}C_2H_4$ in CD_2Cl_2: (a) after 1 h at −80 °C; (b) after 2 h at −80 °C; (c) after 6 h, with brief period of warming, recorded at −80 °C.

Scheme 6



the central allene carbon and one of the hexafluorobutyne carbons. Linkage between alkynes and allenes at metal centers has been observed a number of times.[19] Of particular relevance to our observations are the systems of Knox and Adams, in which the alkyne/allene linkage occurs between the central allene carbon and one of the alkyne carbons.[19a,b] Additionally, in this laboratory, we have observed alkyne/allene carbon bond formation between a coordinated alkyne carbon and the central allene carbon, in a monometallic iron complex, $[Fe(CO)_2(PR_2R')\{\eta^2\text{-}C_2(CF_3)_2\}]$.[20]

Complex **5** was characterized by IR and NMR (^1H, ^{19}F, $^{13}C\{^1H\}$) spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography. Indirect NMR techniques such as gHMBC and gHMQC were used to assign unambiguously the resonances of the carbons of the organic fragment. The carbon that was formally the quaternary allene carbon resonates at δ 113.8, while the other former allene carbons are found at δ 37.19 (CMe$_2$) and 45.88 (CH_2). The vinylic C_α and C_β resonate at δ 135.4 and 76.3, respectively, reflecting their bridging carbene-like and coordinated olefin character.

As before, assigning absolute regiochemistry proved impossible using spectroscopic methods alone, and an X-ray crystallographic study was performed. The structure of **5** is shown in Figure 3, and pertinent bond lengths and angles are given in Table 4. Carbon−carbon bond formation between the allene and the hexafluorobutyne results in an organic fragment with $\eta^2{:}\eta^2$ connectivity to the cobalt and $\eta^1{:}\eta^1$ connectivity to the ruthenium. The incoming allene is orientated with its methyl groups away from the pentamethylcyclopentadienyl−cobalt center, probably as a consequence of unfavorable interactions between the two.

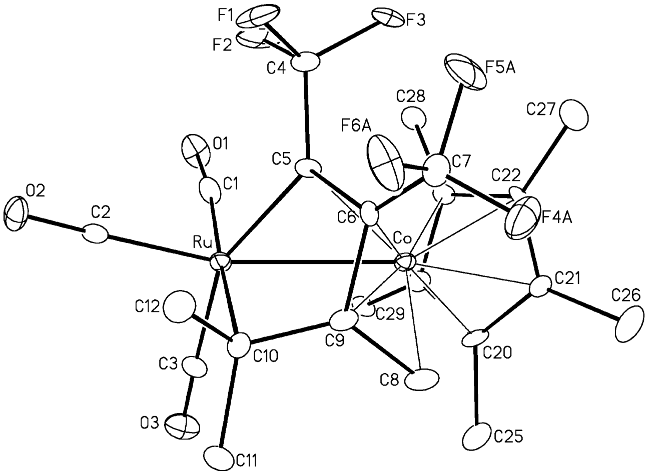


Figure 3. Perspective view of $[RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^4\text{-}C(CF_3)C(CF_3)C(CMe_2)(CH_2)\}]$ (**5**), showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Only one part of the rotationally disordered CF_3 (C7) group is shown for clarity. Hydrogen atoms are not shown.

Carbons C5−C6−C9−C8 of the organic fragment have a butadienyl type interaction with the cobalt. The cobalt−carbon bond distances are 2.081(11) Å (C5), 1.989(10) Å (C6), 2.097(11) Å (C9), and 2.148(11) Å (C8). Of note is the relatively short vinylic Co−C6 π bond distance compared to the other cobalt−carbon distances,

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(19) (a) Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Winter, M. J. *New J. Chem.* **1988**, *12*, 581. (b) Adams, R. D.; Wang, S. *Organometallics* **1986**, *15*, 1274. (c) Aumann, R.; Melchers, H.-D.; Weidenhaupt, H.-J. *Chem. Ber.* **1990**, *123*, 351. (d) Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81.

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although a similar situation was observed by Knox with the dimolybdenum complex [$Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2{:}\eta^2C\text{-}(CO_2Me)C(CO_2Me)\}\{\mu\text{-}\eta^2{:}\eta^4\text{-}C(CO_2Me)C(CO_2Me)C(CH_2)(CH_2)\}$].[19a] The sums of the bond angles around carbons C5, C6, and C9 (excluding the carbon−cobalt angles) are 358.9, 358.8, and 358.9°, respectively, indicating that they are all approximately sp^2 hybridized. The carbon−carbon bond distances of the organic fragment are 1.447(14) Å (C5−C6), 1.477(14) Å (C6−C9), and 1.385(15) Å (C9−C8). The long C5−C6 distance suggests the C5−C6 cobalt interaction has more metallacyclopropane character. This is probably due to the electron-withdrawing trifluoromethyl groups on C5 and C6 encouraging more π^* back-donation from the pentamethylcyclopentadienyl−cobalt center, thus lowering the C5−C6 bond order. In contrast, the long Co−C8 distance and short C8−C9 bond suggest a weaker cobalt−alkene π interaction. The four-electron-donating nature of this bonding to cobalt requires that there be a dative cobalt to ruthenium bond to satisfy the 18-electron rule.

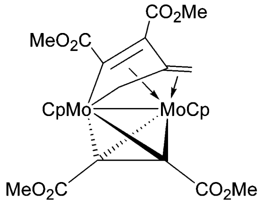
Table 4. Bond Lengths and Angles for [$RuCo(CO)_3(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^4\text{-}C(CF_3)C(CF_3)C(CMe_2)(CH_2)\}$] (5)

(a) Selected Interatomic Distances (Å)

Ru−Co	2.6717(17)	Co−C8	2.148(11)
Ru−C1	1.942(13)	Co−C9	2.097(11)
Ru−C2	1.892(11)	C5−C6	1.447(14)
Ru−C3	1.908(13)	C6−C9	1.477(14)
Ru−C5	2.063(10)	C8−C9	1.385(15)
Ru−C10	2.205(10)	C9−C10	1.453(14)
Co−C5	2.081(11)	C10−C11	1.559(15)
Co−C6	1.989(10)		

(b) Selected Interatomic Angles (°)

Ru−C10−C9	91.7(6)	C6−C9−C8	114.1(10)
Ru−C10−C11	114.9(7)	C9−C10−C11	113.6(9)
Ru−C10−C12	114.6(7)	C8−C9−C10	127.8(11)
C5−Ru−C10	80.7(4)	C9−C10−C12	112.3(9)
Co−C6−C5	72.6(6	Ru−C5−C4	127.6(8)
Co−C9−C10	120.8(7)	Ru−C5−C6	111.9(7)
C4−C5−C6	119.4(9)	C5−C6−C9	106.2(8)
C5−C6−C7	131.7(11)	C6−C9−C10	107.0(10)
C7−C6−C9	120.9(10)		



Conclusion

We have shown that the heterobimetallic complex **3** readily activates alkene carbon−hydrogen bonds and promotes carbon−carbon bond formation with 1,1-dimethylallene. Alkene carbon−hydrogen bond activation by **3** is regiospecific, whereas with comparable homobimetallic systems only limited regioselectivity is seen.

Although the intimate details of the mechanism of alkene carbon−hydrogen bond activation by **3** could not be deduced unequivocally, evidence for several π-bound alkenes and a putative dimetallacyclohexene species was presented. Our observations point toward the second mechanism proposed by Fryzuk (Scheme 4), involving insertion of the alkene into the metal−metal bond. The carbon−hydrogen bond activation step probably proceeds via a β-hydride elimination/hydride migration pathway, although we could not conclusively identify these intermediates. We hope to explore further these carbon−hydrogen bond activation reactions with the rhodium−ruthenium analogue of **3**, the NMR-active rhodium providing more insight into this intriguing mechanism.

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding. We thank Dr. Nathan Jones for preprint of his manuscript and for useful discussions. We also thank the NMR laboratory staff of the University of Alberta.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters for compounds **4a**,**b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040026P