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Addition of Small Molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. 6.[1] Formation of the μ-Alkylidene Complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CHR)(\mu\text{-}CF_3C_2CF_3)$ (R = CO_2Et, $SiMe_3$, CF_3, or $CH{=}CH_2$) and Coupling Reactions of the Alkyne and Carbene Ligands within These Complexes. X-ray Crystal Structure of $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C(CF_3)C(CF_3)CH(CO_2Et)\}$

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The μ-alkylidene complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}CH(CO_2Et)\}(\mu\text{-}CF_3C_2CF_3)$ (**2a**) is formed when $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (**1**) is treated with $N_2CH(CO_2Et)$ at 0°C. In solution at room temperature, **2a** converts slowly (several days) to an η^1,η^3-allyl complex, $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH(CO_2Et)\}$ (**3a**). This transformation has been monitored by NMR spectroscopy, and the data indicate that the alkylidene migration reaction is accompanied by the isomerization of both **2a** and **3a**. Determination of the crystal and molecular structure of the final product establishes that the groups CF_3 and CO_2Et are mutually cis within the allyl ligand of **3a**. Crystal data: $C_{19}H_{16}F_6O_3Rh_2$, M_r 612.1, monoclinic $P2_1/n$, a = 13.832 (11) Å, b = 11.918 (9) Å, c = 12.041 (10) Å, β = 93.42 (8)°, Z = 4, final R = 0.051 for 2499 observed reflections. Analogous alkylidene addition and migration reactions occur when **1** is treated with $N_2CH(SiMe_3)$ or $N_2CH(CH{=}CH_2)$ at 0 °C; in these cases, the conversion of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CHR)(\mu\text{-}CF_3C_2CF_3)$ (R = $SiMe_3$, **2b**; R = $CH{=}CH_2$, **2c**) to $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CHR\}$ (**3b,c**) is rapid (hours) in solution at room temperature; indeed, pure samples of **2b** and **2c** could not be isolated. The carbene source $N_2CH(CF_3)$ reacts instantly with **1** at 0 °C, but there is no migration of $CH(CF_3)$ within the μ-alkylidene product $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}CH(CF_3)\}(\mu\text{-}CF_3C_2CF_3)$ (**2d**), even in refluxing solvents. However, the migration reaction can be achieved indirectly as follows. Exposure to sunlight of a solution of **2d** results in decarbonylation to give $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}CH(CF_3)\}(\mu\text{-}CF_3C_2CF_3)$ (**4**); subsequent treatment of **4** with CO under irradiation with sunlight yields $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH(CF_3)\}$ (**3d**).

Introduction

In a previous paper,[2] we presented some reasons for the considerable current interest in μ-alkylidene–dimetal complexes and then described the formation of two μ-alkylidene–dirhodium complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$. In solution at room temperature, these complexes undergo intramolecular migration of the alkylidene group to an alkyne–carbon. When $R^1 = R^2$ = H, there is formation of a new C–C bond to give the η^1,η^3-allyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH_2\}$. In contrast, when $R^1 = R^2 = CO_2Et$, there is formation of the complex $(\eta\text{-}C_5H_5)_2\overline{Rh_2\{C(CF_3)C(CF_3)OC(OEt)C}(CO_2Et)\}$ in which the bridging group incorporates a new C–O bond. It was therefore of interest to investigate the corresponding system with R^1 = H and $R^2 = CO_2Et$. To determine the effect of other substituents on the course of reactions between carbenes and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$, the study has been extended to other systems with R^1 = H and $R^2 = SiMe_3$, CF_3, or $CH{=}CH_2$. We describe some interesting differences in the solution behavior of the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$ obtained from this set of carbenes.

Experimental Section

The general experimental procedures have been described previously.[1,2] The solvent "X4" refers to petroleum fraction of bp 30–60 °C. The diazoalkanes N_2CHR (R = CO_2Et,[3] $SiMe_3$,[4] CF_3,[5] and $CH{=}CH_2$[6]) were prepared by published procedures. These reagents were not isolated as pure products but were used in situ. The amounts used in subsequent reactions were calculated on the basis of published yields, with sufficient solution being added to provide a slight excess of the diazo compound; generally, the mole ratio of reagents was estimated to be ca. 1.1:1.0.

A. Reaction of 1 with $N_2CH(CO_2Et)$. A slight excess of $N_2CH(CO_2Et)$ in pentane was added to a solution of **1** (0.140 g) in hexane (10 mL) at 0 °C. [This reaction can be done in diethyl ether, but it is then more difficult to crystallize the product]. Orange crystals were deposited immediately, and these were isolated by filtration, washed with hexane, and dried in vacuo. This gave $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}CH(CO_2Et)\}(\mu\text{-}CF_3C_2CF_3)$ (**2a**) (0.160 g, 100%), mp 115 °C. Anal. Calcd for $C_{19}H_{16}F_6O_3Rh_2$: C, 37.3; H, 2.6; F, 18.6. Found: C, 37.6; H, 2.7; F, 18.2. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1880 vs and 1670 m, ν(C=C) at 1600 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50 (poorly resolved t, 1 H, $J \approx 1.5$ Hz, alkylidene H), 5.50 (s, 10 H, 2 × C_5H_5), 4.16 (q, 2 H, J = 7 Hz, ester CH_2), 1.37 (t, 3 H, J = 7 Hz, ester CH_3); ^{19}F NMR ($CDCl_3$) δ 54.5 (s); MS, m/z (relative intensity) 612 (<2, M^+), 584 (58, M^+ – CO), 511 (50, M^+ – CO – CO_2Et), 233 (100, $C_{10}H_{10}Rh^+$).

A solution of **2a** in boiling hexane was gently refluxed for 10 min. On cooling, red crystals were deposited. These were isolated by filtration, dissolved in dichloromethane, and chromatographed by TLC with a 10:5:2 mixture of $CH_2Cl_2/X4/Et_2O$ as eluent. This separated several minor products from one major band ($R_f \sim 0.9$). Evaporation of solvent from the major band yielded red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH(CO_2Et)\}$ (**3a**), mp 132–133 °C. Anal. Calcd for $C_{19}H_{16}F_6O_3Rh_2$: C, 37.3; H, 2.6; F, 18.6. Found: C, 37.6; H, 2.8; F, 18.2. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 2000 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.41 (d, 5 H, J = 1 Hz, C_5H_5), 5.36 (s, 5 H, C_5H_5), 4.13 (q, 2 H, J = 7 Hz, ester CH_2), 3.14 (poorly resolved d, 1 H, $J \approx 2$ Hz, allylic H), 1.29 (t,

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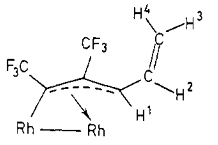
3 H, *J* = 7 Hz, ester CH_3); ^{19}F NMR ($CDCl_3$) quartets (*J* = 13 Hz) of equal intensity at δ 52.1 and 49.7; MS, *m/z* (relative intensity) 612 (<1, M^+), 584 (66, M^+ - CO), 511 (55, M^+ - CO - CO_2Et), 233 (100, $C_{10}H_{10}Rh^+$).

B. Reaction of 1 with $N_2CH(SiMe_3)$. A stirred solution containing 1 (0.075 g), a slight excess of $N_2CH(SiMe_3)$, and hexane or ether (10 mL) was kept at 0 °C; the color changed from green to orange-brown over 30 min. When the mixture was warmed to room temperature, there was a rapid color change to red-orange. The solution was concentrated by removal of solvent. TLC with a 3:1 mixture of X4/CH_2Cl_2 as eluent separated numerous trace bands from one major orange-red product (R_f ~0.6). Extraction of the major band with CH_2Cl_2 and removal of solvent gave orange-red crystals of (η-C_5H_5)$_2Rh_2$(CO){μ-C(CF_3)C(CF_3)CH($SiMe_3$)} (**3b**) (0.082 g, 94%), mp 111 °C. Anal. Calcd for $C_{19}H_{20}F_6ORh_2Si$: C, 37.3; H, 3.3; F, 18.6. Found: C, 37.6; H, 3.2; F, 18.7. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1992 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.39 (d, 5 H, *J* = 0.6 Hz, C_5H_5), 5.28 (s, 5 H, C_5H_5), 2.67 (br s, 1 H, allylic H), 0.17 (d, 9 H, *J* = 0.9 Hz, $SiMe_3$); ^{19}F NMR ($CDCl_3$) δ 48.3 (qd, 3 F, *J* = 15 and *J′* = 4 Hz, CF_3), 50.9 (q, 3 F, *J* = 15 Hz, CF_3); MS, *m/z* (relative intensity) 612 (2, M^+), 584 (8, M^+ - CO) 524 (36, na), 233 (100, $C_{10}H_{10}Rh^+$).

Infrared monitoring revealed the presence of some (η-C_5H_5)$_2Rh_2$(μ-CO){μ-CH($SiMe_3$)}(μ-$CF_3C_2CF_3$) (**2b**) in the early stages of this reaction. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1880 cm^{-1}.

C. Reaction of 1 with $N_2CH(CH{=}CH_2)$. Formation of 3c. When a slight excess of $N_2CH(CH{=}CH_2)$ in pentane was added to a solution of 1 (0.100 g) in hexane (10 mL), there was an immediate color change from green to orange-red. TLC of the reaction mixture with a 9:1 mixture of X4/Et_2O as eluent separated minor products from a major orange band (R_f ~0.6). Evaporation of solvent from the latter gave orange-red crystals of (η-C_5H_5)$_2Rh_2$(CO){μ-C(CF_3)C(CF_3)CH(CH=CH_2)} (**3c**) (0.082 g, 76%) mp 110–111 °C. Anal. Calcd for $C_{18}H_{14}F_6ORh_2$: C, 38.2; H, 2.5; F, 20.1. Found: C, 38.1; H, 2.3; F, 20.2. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1984 s, ν(C=C) at 1617 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.11 (m, $ABCDX_3$ spin system, 1 H, $J_{H^2H^1}$ = 11 Hz, $J_{H^2H^3}$ = 10 Hz, $J_{H^2H^4}$ = 17 Hz, J_{H^2F} = 3 Hz, H^2), 5.36 (s, 5 H, C_5H_5), 5.30 (d, 5 H, *J* = 0.7 Hz, C_5H_5), 5.12 (dd, 1 H, $J_{H^4H^2}$ = 17 Hz, $J_{H^4H^3}$ = 1 Hz, H^4), 4.93 (dd, 1 H, $J_{H^3H^2}$ = 10 Hz, $J_{H^3H^4}$ = 1 Hz, H^3), 4.23 (d, 1 H, $J_{H^1H^2}$ = 11 Hz, H^1); ^{19}F NMR ($CDCl_3$) quartets (*J* = 13 Hz) of equal intensity at δ 49.6 and 49.9; MS, *m/z* (relative intensity) 566 (18, M^+), 538 (41, M^+ - CO), 233 (100, $C_{10}H_{10}Rh^+$).



D. Reaction of 1 with $N_2CH(CF_3)$. Formation of 2d. Treatment of 1 (0.080 g) with a slight excess of N_2(CH(CF_3) in ether (10 mL) at 0 °C resulted in a slow (ca. 30 min) color change from green to orange. Removal of solvent and chromatography on a column of Florisil with a 3:1 mixture of X4/CH_2Cl_2 as eluent separated two minor products from a major orange band. (The chromatographic separation can be achieved by TLC, but some decomposition is evident and it is necessary to extract the major product as soon as possible.) Evaporation of solvent from the major band gave orange crystals of (η-C_5H_5)$_2Rh_2$(μ-CO){μ-CH(CF_3)}(μ-$CF_3C_2CF_3$) (**2d**) (0.085 g, 92%), mp 93–95 °C dec. To avoid decomposition, this compound needs to be stored under nitrogen. Anal. Calcd for $C_{17}H_{11}F_9ORh_2$: C, 33.6; H, 1.8; F, 28.1. Found: C, 33.2; H, 1.8; F, 27.7. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1880 vs, ν(C=C) at 1600 s, 1585 sh cm^{-1}; ^1H NMR (acetone-d_6) δ 7.12 (qt, 1 H, *J* = 13 and *J′* = 3 Hz, C*H*CF_3), 5.77 (s, 10 H, 2 × C_5H_5); ^{19}F NMR (acetone-d_6) δ 50.1 (d, 3 F, *J* = 13 Hz, CHC*F*$_3$), 53.4 (s, 6 F, $CF_3C_2CF_3$); MS, *m/z* (relative intensity), 608 (5, M^+), 580 (18, M^+ - CO), 579 (18, M^+ - CO - H), 560 (10, M^+ - CO - HF), 233 (100, $C_{10}H_{10}Rh^+$).

The spectroscopic properties of one of the minor products matched those of complex 4 which is described below. The other minor product was not obtained in sufficient amount for complete characterization. Spectroscopic data: IR (CH_2Cl_2) no ν(CO); ^1H NMR ($CDCl_3$) δ 5.55 (s, 5 H, C_5H_5), 5.44 (s, 5 H, C_5H_5), 1.66 (q, 2 H, *J* = 10 Hz, C*H*CF_3); ^{19}F NMR ($CDCl_3$) δ 55.5 (pseudoquintet, 3 F, CF_3), 52.2 (s, 3 F, CF_3), 53.4 (pseudoquintet, 3 F, CF_3), 58.9 (q, 3 F, *J* = 12 Hz, CF_3); MS, *m/z* (relative intensity) 690 (60, (C_5H_5)$_2Rh_2$($CHCF_3$)(N_2CHCF_3)($CF_3C_2CF_3$)$^+$), 592 (10), 233 (100, $C_{10}H_{10}Rh^+$).

Table I. Cell Data, Data Collection, and Refinement Parameters for (η-C_5H_5)$_2$$Rh_2$(CO){C($CF_3$)C($CF_3$)CH($CO_2Et$)} (3a)

formula	$C_{19}H_{16}F_6O_3Rh_2$
mol wt	612.1
cryst system	monoclinic
space group	$P2_1/n$
cell consts	
a, Å	13.832 (11)
b, Å	11.918 (9)
c, Å	12.041 (10)
β, deg	93.42 (8)
V, Å^3	1981.4
systematic absences	*h0l*, *h* + *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1
Z	4
d_{calcd}, g cm^{-3}	2.05
d_{measd}, g cm^{-3}	1.98 (4)
radiatn (λ, Å)	graphite monochromated Mo K_α (0.7107)
temp, K	293
μ, cm^{-1}	15.7
scan mode	ω
2θ limits, deg	6–52
scan width, deg	±(1.30 + 0.3 tan θ)
scan rate	variable
total data	3885
data *I* > 3σ(*I*)	2499
no. of parameters refined	156
final *R*, R_w	0.051, 0.049
weight *w*	$\sigma^{-2}(F)$

Conversion of 2d to 4. A solution of **2d** (0.155 g) in hexane (20 mL) was exposed to Pyrex-filtered sunlight for ca. 8 h. During this time, the color of the solution changed from orange to red. Removal of solvent gave a red solid (upon exposure to air, this solid rapidly went black). TLC of the solid with X4/CH_2Cl_2 (3:1) as eluent separated two major products from a large amount of black material that remained on the base line.

Evaporation of solvent from the first orange band (R_f ~0.7) gave orange crystals of (η-C_5H_5)$_2Rh_2${μ-CH(CF_3)}(μ-$CF_3C_2CF_3$) (**4**) (0.081 g, 52%), mp 150–152 °C dec. Anal. Calcd for $C_{16}H_{11}F_9Rh_2$: C, 33.1; H, 1.9; F, 29.5. Found: C, 32.9; H, 1.7; F, 29.9. Spectroscopic data: IR (CH_2Cl_2) no ν(CO) absorption, ν(C=C) at 1618 m cm^{-1}; ^1H NMR (acetone-d_6) δ 7.34 (qt, 1 H, *J* = 13 and *J′* = 3 Hz, C*H*CF_3), 5.55 (s, 10 H, 2 × C_5H_5); ^{19}F NMR (acetone-d_6) δ 50.4 (dt, 3 F, *J* = 13 and *J′* = 2.5 Hz, CHC*F*$_3$), 50.8 (q, 3 F, *J* = 2 Hz, CF_3), 53.8 (q, 3 F, *J* = 2 Hz, CF_3); MS, *m/z* (relative intensity), 580 (17, M^+), 560 (4, M^+ - HF), 233 (100, $C_{10}H_{10}Rh^+$).

Removal of solvent from the second orange band (R_f ~0.6) gave orange crystals of (η-C_5H_5)$_2Rh_2$(CO){μ-C(CF_3)C(CF_3)CH(CF_3)} (**3d**) (0.025 g, 16%), mp 125–126 °C. Anal. Calcd for $C_{17}H_{11}F_9ORh_2$: C, 33.6; H, 1.8; F, 28.1. Found: C, 34.0; H, 1.9; F, 28.2. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 2006 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.49 (s, 5 H, C_5H_5), 5.36 (s, 5 H, C_5H_5), 3.20 (qd, 1 H, *J* = 9 and *J′* = 2 Hz, C*H*CF_3); ^{19}F NMR ($CDCl_3$) δ 51.0 (overlapping m, 6 F, 2 × CF_3), 54.6 (m, 3 F, CF_3); MS, *m/z* (relative intensity) 608 (2, M^+), 580 (12, M^+ - CO), 233 (100, $C_{10}H_{10}Rh^+$).

Conversion of 4 to 3d. CO was bubbled through a solution of 4 in CH_2Cl_2 at 20 °C for 4 h. No color change was observed, and IR monitoring showed no uptake of CO. In a separate experiment, a Carius tube containing a solution of 4 in CH_2Cl_2 was purged with CO (1 atm) and left in the sunlight for 4 days. TLC of the solution with X4/CH_2Cl_2 (7:3) as eluent separated some unchanged **4** from **3d**.

E. Crystallography. Single crystals of **3a** were grown from hexane/dichloromethane solution. A well-formed crystal on a silica capillary was mounted on a Philips PW 1100 four-circle diffractometer. Refined lattice constants were determined from least-squares analysis of setting angles for 25 centered, high angle reflections. The unit cell data and data collection parameters are summarized in Table I. Over the data collection period, three

Table II. Final Positional Parameters for (η-C_5H_5)$_2$$Rh_2$(CO){C($CF_3$)C($CF_3$)CH($CO_2$Et)} (3a) (Esd Values in Parentheses)

atom	*x*	*y*	*z*
Rh(1)	0.21979 (5)	0.07043 (6)	-0.00280 (6)
Rh(2)	0.14330 (5)	0.25728 (6)	0.08896 (6)
F(1)	0.4002 (4)	0.3108 (5)	0.1785 (5)
F(2)	0.3216 (4)	0.1830 (5)	0.2572 (5)
F(3)	0.4307 (4)	0.1366 (5)	0.1488 (5)
F(4)	0.4568 (4)	0.0927 (5)	-0.0817 (5)
F(5)	0.4763 (5)	0.2585 (6)	-0.0165 (6)
F(6)	0.4252 (4)	0.2377 (5)	-0.1843 (5)
O(1)	0.3087 (5)	0.0679 (6)	-0.2635 (6)
O(2)	0.1778 (5)	0.1709 (5)	-0.3154 (6)
O(3)	0.1208 (6)	0.1144 (8)	0.2891 (8)
C(1)	0.3583 (7)	0.2118 (8)	0.1606 (8)
C(2)	0.2842 (6)	0.2129 (7)	0.0645 (7)
C(3)	0.3132 (6)	0.1995 (7)	-0.0486 (7)
C(4)	0.4199 (7)	0.1941 (9)	-0.0812 (9)
C(5)	0.2352 (6)	0.1896 (7)	-0.1316 (7)
C(6)	0.2475 (7)	0.1357 (8)	-0.2413 (8)
C(7)	0.1765 (8)	0.1192 (9)	-0.4256 (9)
C(8)	0.1259 (9)	0.0106 (10)	-0.4228 (11)
C(9)	0.1321 (8)	0.1681 (9)	0.2105 (9)
C(10)	0.0545 (7)	0.4016 (8)	0.1401 (8)
C(11)	-0.0050 (7)	0.3341 (9)	0.0672 (8)
C(12)	0.0328 (7)	0.3368 (8)	-0.0378 (8)
C(13)	0.1177 (7)	0.4029 (8)	-0.0286 (8)
C(14)	0.1302 (7)	0.4454 (8)	0.0808 (8)
C(15)	0.2860 (14)	-0.0965 (16)	0.0302 (25)
C(16)	0.2176 (17)	-0.0790 (12)	0.1108 (14)
C(17)	0.1247 (14)	-0.0688 (14)	0.0494 (22)
C(18)	0.1386 (18)	-0.0801 (16)	-0.0651 (21)
C(19)	0.2402 (18)	-0.0954 (13)	-0.0786 (17)
C(20)	0.2824 (26)	-0.0983 (25)	-0.0308 (39)
C(21)	0.2724 (32)	-0.0856 (28)	0.0821 (37)
C(22)	0.1640 (32)	-0.0697 (26)	0.0950 (30)
C(23)	0.1218 (24)	-0.0752 (27)	-0.0102 (43)
C(24)	0.1862 (32)	-0.0903 (22)	-0.0890 (25)

standard reflections were monitored every 2 h and showed no significant variation of intensity.

The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares methods.[7-9] No absorption correction was applied, the crystal shape being indeterminate. Anisotropic temperature factors were used for rhodium atoms, and anomalous dispersion corrections for all atoms were applied. Weights were based upon intensity statistics.[8] Hydrogen atoms were placed in geometrically calculated positions and had a common isotropic temperature factor that was refined. For the final refinement, the scattering factors were from ref 10. The largest shift at the end of the refinement was 0.04σ.

Final positional parameters are contained in Table II. Interatomic distances and bond angles are given in Table III. Listings of structure factor amplitudes, thermal parameters for all non-hydrogen atoms, and hydrogen atom positional coordinates are available as supplementary material.

Results and Discussion

Formation of Complexes 2. When $N_2CH(CO_2Et)$ is added to a solution of 1 at 0 °C, the μ-alkylidene complex (η-C_5H_5)$_2$$Rh_2$($\mu$-CO){$\mu$-CH($CO_2$Et)}($\mu$-$CF_3C_2CF_3$) is precipitated immediately and quantitatively. IR and NMR data are consistent with those of structure **2a**. Distinctive spectroscopic features are a bridging carbonyl stretching frequency at 1880 cm^{-1} in the IR and a low-field triplet at δ 7.50 in the ^1H NMR. This NMR signal is close to one of the μ-methylene resonances detected[2] for the complex (η-C_5H_5)$_2$$Rh_2$($\mu$-CO)($\mu$-$CH_2$)($\mu$-$CF_3C_2CF_3$) and is indicative of a μ-alkylidene proton.

Table III. Selected Interatomic Distances and Bond Angles for (η-C_5H_5)$_2$$Rh_2$(CO){C($CF_3$)C($CF_3$)CH($CO_2$Et)}

(a) Interatomic Distances (Å)

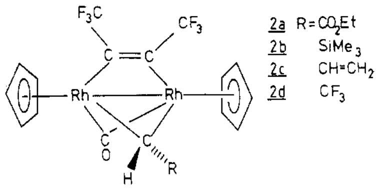
Rh(1)-Rh(2)	2.727 (1)	O(2)-C(7)	1.46 (1)
Rh(1)-C(2)	2.060 (8)	C(7)-C(8)	1.47 (2)
Rh(1)-C(3)	2.104 (9)	C(9)-O(3)	1.16 (2)
Rh(1)-C(5)	2.123 (9)	C(10)-C(11)	1.42 (1)
Rh(2)-C(2)	2.057 (9)	C(10)-C(14)	1.40 (1)
Rh(2)-C(9)	1.823 (11)	C(11)-C(12)	1.40 (1)
C(1)-C(2)	1.50 (1)	C(12)-C(13)	1.41 (1)
C(1)-F(1)	1.33 (1)	C(13)-C(14)	1.41 (1)
C(1)-F(2)	1.34 (1)	C(15)-C(16)	1.41 (3)
C(1)-F(3)	1.36 (1)	C(15)-C(19)	1.42 (3)
C(2)-C(3)	1.45 (1)	C(16)-C(17)	1.45 (3)
C(3)-C(14)	1.55 (1)	C(17)-C(18)	1.41 (4)
C(4)-F(4)	1.31 (1)	C(18)-C(19)	1.44 (4)
C(4)-F(5)	1.32 (1)	C(20)-C(21)	1.38 (7)
C(4)-F(6)	1.35 (1)	C(20)-C(24)	1.47 (6)
C(3)-C(5)	1.43 (1)	C(21)-C(22)	1.53 (6)
C(5)-C(6)	1.49 (1)	C(22)-C(23)	1.36 (6)
C(6)-O(1)	1.21 (1)	C(23)-C(24)	1.35 (6)
C(6)-O(2)	1.34 (1)		

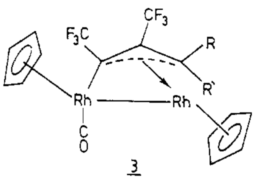
(b) Bond Angles (deg)

Rh(2)-C(2)-C(3)	118.7 (6)	C(2)-C(3)-C(5)	115.1 (8)
Rh(2)-C(2)-C(1)	120.1 (6)	C(5)-C(3)-C(4)	120.6 (8)
C(1)-C(2)-C(3)	120.5 (8)	C(3)-C(5)-C(6)	122.2 (8)
C(2)-C(3)-C(4)	124.2 (8)	C(3)-C(5)-Rh(1)	69.5 (5)

In a similar manner, 1 and $N_2CH(CF_3)$ give (η-C_5H_5)$_2$$Rh_2$($\mu$-CO){$\mu$-CH($CF_3$)}($\mu$-$CF_3C_2CF_3$) (**2d**) in 92% yield. In the ^1H NMR spectrum of this complex, the alkylidene proton signal is observed at δ 7.12 as a quartet of triplets due to coupling with the geminal CF_3 group ($^3J_{HF}$ = 13 Hz) as well as the two equivalent rhodium atoms ($^2J_{HRh}$ = 3 Hz).

Spectroscopic data indicate that the reactions of 1 with $N_2CH(SiMe_3)$ and $N_2CH(CH{=}CH_2)$ give **2b** and **2c**, but these complexes transform rapidly in solution to the new species **3b** and **3c**; complexes **3** have a terminal carbonyl absorption in the IR near 1995 cm^{-1}. IR monitoring of each system shows that approximately equal amounts of the complexes **2** and **3** are present in solution only 10 min (R = $CH{=}CH_2$) or 40 min (R = $SiMe_3$) after 1 and the appropriate N_2CHR were mixed. The proportion of **3** continues to grow with time. Attempts to isolate pure **2b** and **2c** by precipitating the product directly from a reaction performed in hexane were not successful; the products always contained some **3b** or **3c**, and all attempts at purification resulted in an increase in the proportion of **3b** and **3c**.





3

The Transformation 2 → 3. As indicated above, the complexes **2b** (R = $SiMe_3$) and **2c** (R = $CH{=}CH_2$) transform rapidly in solution to **3b** and **3c**. There is a

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(8) Sheldrick, G. M. SHELX-76, A Program for Crystal Structure Determination; University of Cambridge: Cambridge, 1976.

(9) One C_5H_5 ring was found to be disordered and was allowed for in the refinement. The final occupancy factors were 0.65 and 0.35.

(10) Cromer, D. T.; Waber, J. T.; Cromer, D. T.; Ibers, J. A. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

Table IV. NMR Results for Isomers of 2a and 3a

compd	chemical shift (multiplicity) for various groups, δ				
	C_5H_5	C*H*R	CH_2	CH_3	CF_3
2a	5.50 (s)	7.50 (t)	4.16 (q)	1.37 (t)	54.5 (s)
2a′	5.50 (s), 5.24 (s)	10.49 (br s)	~4.2 (q)	~1.4 (t)	54.0 (q), 48.5 (q)
3a′	5.59 (d), 5.50 (s)	2.56 (t)	4.15 (q), 4.05 (q)	1.21 (t)	52.1 (q), 49.7 (q)
3a	5.41 (d), 5.36 (s)	3.14 (d)	4.13 (q)	1.29 (t)	52.1 (q), 46.7 (q)

Table V. Changes, with Time in the Relative Amounts (%, ±10%) of the Isomers of 2 and 3 in Solution ($CDCl_3$)

time	2a	2a′	3a′	3a
	(a) 25 °C			
0 h	100			
6 h	90	10	tr	
12 h	70	20	10	
24 h/1 day	40	30	30	
2 days	20	50	30	
4 days	tr	50	45	<5
8 days		50	50	<5
20 days		55	45	<5
	(b) 61 °C[a]			
2 min	tr	15	70	15
10 min		15	60	25
20 min		10	55	35
30 min		10	50	40

[a] Solution refluxed for time indicated and then rapidly cooled before NMR spectrum recorded.

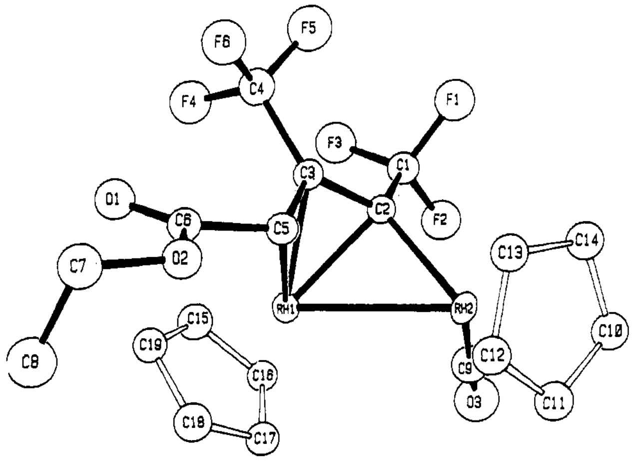

Figure 1. Molecular structure of complex 3a, $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C(CF_3)C(CF_3)CH(CO_2Et)\}$.

related conversion of **2a** to **3a** (R = CO_2Et) in solution at room temperature, but it occurs much more slowly. The transformation is indicated by gradual changes in the IR and NMR spectra that also provide evidence of concomitant isomerization reactions. The NMR spectra for freshly prepared solutions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}CH(CO_2Et)\}(\mu\text{-}CF_3C_2CF_3)$ (**2a**) show only the peaks listed in Table IV. Upon aging of the solution, new peaks are observed in the spectrum. Of particular significance is the emergence of a low-field signal at δ 10.49. Since resonances were observed[2] at δ 10.55 and 7.84 for the individual methylene protons in $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)$, it seems reasonable to attribute this new signal to a second isomer **2a′** in which the groups H and CO_2Et have been interchanged. Presumably, rotation of the alkylidene group occurs via a transition state in which $-CH(CO_2Et)$ temporarily occupies a terminal position. Other ^1H and ^{19}F NMR signals associated with **2a′** are shown in Table IV and are discussed later.

Changes in relative intensities (^1H and ^{19}F spectra) with time establish that the relative amount of **2a′** continues to increase over a period of at least 48 h at room temperature; after 4 days, there is no evidence for **2a** in the solution (see Table V, section a). There are other changes in the spectra with time. The emergence of new peaks near δ 3 is attributed to the formation of an η^1,η^3-allyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH(CO_2Et)\}$. This is obtained from **2a** or **2a′** by migration of the alkylidene group to an unsaturated carbon of the bridging $CF_3C_2CF_3$ ligand and concomitant rearrangement of the bridging carbonyl to a terminal position. The NMR data (Table IV) establish that two isomers of this complex are present in solution. One isomer, **3a′**, is formed much more quickly than the other, **3a**; readily detectable amounts of **3a′** are present in the solution after about 12 h at room temperature, and the amount continues to increase for several days. The isomer **3a** is evident after about 4 days at room temperature, but only trace amounts are present.

If the reaction solution is kept for 4 days and then worked up by TLC, the only major product isolated is **3a**. This is unexpected because **3a** is a minor species in the solution after this time. When pure **3a** is redissolved, the NMR spectra indicate it is the only isomer present in the solution; thus **3a** and **3a′** are not in rapid equilibrium. To determine whether the conversion to **3a** had been accelerated by the chromatographic support, a 4-day-old reaction solution was evaporated and the solid residue immediately redissolved. The NMR spectrum of this solution revealed the presence of substantial amounts of **2a′** and **3a′**. This indicates that the chromatographic silica is a catalyst for the isomerization of **3a′** to **3a**.

This conversion of **2a** to **3a**, which is slow at 25 °C, is greatly accelerated when the solution is refluxed. Relevant data are summarized in Table V (section b). Again, **3a** is the only major product isolated after several runs up a TLC plate. Although there is evidence, during the chromatography, of a second band containing **3a′**, it was never isolated free of **3a**.

The position of the NMR peaks at δ 2.56 and 3.14, respectively, for **3a′** and **3a** are similar to those for $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH_2\}$ (δ 2.46 and 3.41).[2] Presumably, these isomers have different orientations of H and CO_2Et on the terminal carbon of the allyl chain. The crystal structure of **3a** was determined to establish the precise orientation of these groups in this isomer.

Description of the Structure of $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CH(CO_2Et)\}$ (3a). The molecular structure of **3a** is formally derived from **2a** by intramolecular coupling of the carbene to an unsaturated carbon of the coordinated hexafluorobut-2-yne. The ORTEP[11] diagram (Figure 1) and the bond parameters (Table III) indicate that the resultant group is reasonably described as a bridging allyl system. Thus the C(2)–C(3) and C(3)–C(5) distances are equal (1.45 (1) and 1.43 (1) Å, respectively), and the angles around C(2), C(3), and C(5) are essentially trigonal. Bond distance data show that each of the carbon atoms C(2), C(3), and C(5) is attached to Rh(1) whereas only C(2) is bonded to Rh(2). Carbon atom C(2) is equidistant from Rh(1) and Rh(2) (2.06 (1) Å), and

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[11] Johnson, C. A. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-3974, 1970; Oak Ridge National Laboratory, Oak Ridge, TN.

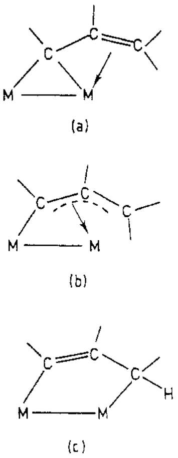


Figure 2. Alternative bonding modes for the $M_2(\mu\text{-CRCRCHR}')$ moiety.

this distance is somewhat shorter than the Rh(1)–C(3) (2.10 (1) Å) and Rh(1)–C(5) (2.12 (1) Å) distances. The orientation of the allyl plane relative to the metal–metal bond axis is given by the angle of 113.2 (3)° between the Rh(1)–Rh(2) and C(2)–C(5) vectors.

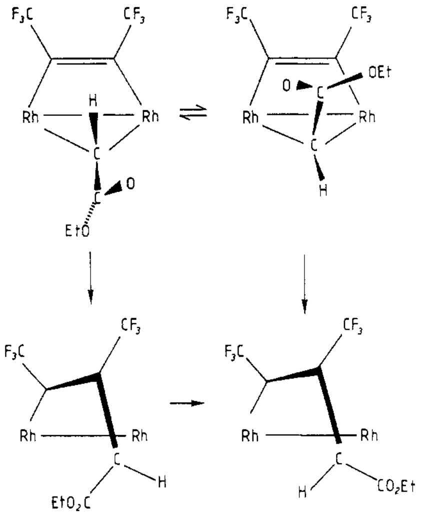
Three types of "μ-allyl–M_2" bonding have been proposed previously on the basis of bond parameters and NMR data. A "vinylcarbene" representation (see Figure 2a) is indicated for $(\eta\text{-}C_5H_5)_2M_2(CO)(\mu\text{-CO})\{\mu\text{-C(R)C(R)CHMe}\}$ (M = Fe and R = CO_2Me[12] or M = Ru and R = Ph[13]); the distinctive feature of the structures of these complexes is that the "carbene" carbon is equidistant from the two metal atoms. For $Fe_2(CO)_6\{C(R)C(R')CHPh\}$ (R = CO_2Et, R′ = Ph,[14] or R = R′ = Ph[15]) and $(\eta^4\text{-COD})_2Ir_2\{C(Ph)C(Ph)CH_2\}$,[16] a σ–π attachment of the allyl group (see Figure 2b) seems to be a more appropriate description of the bonding interaction; here, the M–C σ-bond is significantly shorter than the three M–C π-bonds. NMR results for some complexes are consistent with a contribution from another canonical form (Figure 2c). This applies when the allyl CH resonance is observed at high field (e.g. at δ −1.00 for $(\eta\text{-}C_5H_5)_2Fe_2(CO)(\mu\text{-CO})\{\text{-C(CO}_2\text{Me)C(CO}_2\text{Me)CHMe}\}$[12]).

The results for the dirhodium complex **3a** seem to be most consistent with the "vinylcarbene" description shown in Figure 2a. We note in particular that carbon atom C(2) is equidistant from the two rhodium atoms and that the chemical shift for the allylic hydrogen is at δ 3.14.

A point of major interest to us in the structure of **3a** is the orientation of the $CH(CO_2Et)$ unit at one end of the allyl chain. This is revealed clearly in Figure 1 which shows that the ester substituent is cis to the CF_3 substituent on the neighboring carbon. This orientation presumably minimizes steric interactions with other ligands attached to the rhodium atoms.

There are no unusual features associated with the geometry of the trifluoromethyl or ester groups. The cyclopentadienyl rings are essentially planar, and each is η^5-attached to a rhodium atom; one of these rings is disordered.[9]

Scheme I. Possible Pathways for Interconversions between the Isomers of 2a and 3a[a]



[a] The $\eta\text{-}C_5H_5$ and μ-CO groups are omitted for clarity.

Proposed Pathway for the Conversion of 2 to 3. Proposed assignments of the conformations of the various isomers of **2** and **3** (R = CO_2Et) are given in Scheme I. The initial formation of **2a** is presumably favored on steric grounds. With this orientation, the ester group occupies an uncrowded location, and it can sit in a plane of symmetry that bisects the Rh–Rh and coordinated alkyne bond axes; this symmetry is reflected in the $\delta(C_5H_5)$ and $\delta(CF_3)$ regions of the NMR spectra (Table IV). Inversion of the alkylidene group to give **2a′** seems likely to lead to twisting of the ester group to relieve steric strain. The mirror plane is then lost, and this is indicated by the inequivalence of the two cyclopentadienyl and the two trifluoromethyl group resonances in the NMR spectra. Attempts to substanstiate these stereochemical ideas by X-ray diffraction studies on **2a** were not successful because suitable crystals could not be grown.

Migration of the alkylidene group could occur within **2a** and/or **2a′**. Conversion of the isomer **2a** to **3a′** followed by isomerization to **3a** seems straightforward. With **2a′** two migration routes are theoretically possible. One would produce a new C–O bond (as occurs with $C(CO_2Et)_2$[2]) and lead to $(\eta\text{-}C_5H_5)_2\overline{Rh_2\{C(CF_3)C(CF_3)OC(OEt)CH}\}$; this does not occur. The other would give **3a** directly through formation of a new C–C bond. Based on the available data, it is not possible to determine the relative importance of the alternative routes [**2a** → **3a′** → **3a**] and [**2a** → **2a′** → **3a**]; all that can be said is that the former does occur and the latter may occur.

The conversions of **2b** to **3b** (R = $SiMe_3$) and of **2c** to **3c** (R = $CH{=}CH_2$) are so rapid that NMR monitoring is not possible with these systems. In each case, analytically pure samples of the appropriate **3** are obtained by TLC; full spectroscopic results for each complex are given in the Experimental Section. The NMR spectra of the purified samples and those of the crude species before TLC are identical; thus any isomerization reactions, if they occur, are complete before workup. The probable stereochemistry of **3b** is that with R = H and R′ = $SiMe_3$; the proposed trans arrangement of the CF_3 and $SiMe_3$ substituents is based on the observed coupling (J_{HF} = 4 Hz) between the allylic proton and the CF_3 on the neighboring C. In contrast, the geometry within **3c** incorporates a vinyl substituent cis to the CF_3 (i.e. R = $CH{=}CH_2$, R′ = H); NMR assignments for this complex are detailed in the Experimental Section.

Different Behavior of the CHCF₃ System. The complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-CO})\{\mu\text{-CH(CF}_3)\}(\mu\text{-CF}_3C_2CF_3)$ (**2d**)

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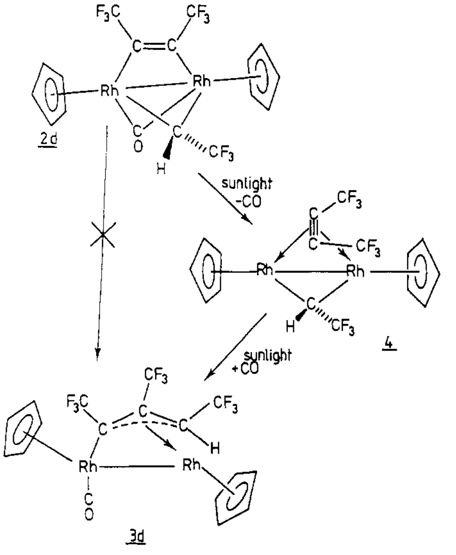
Scheme II. Pathway for the Conversion of 2a to 3a (R = CF_3) via the Intermediate 4



is unique among the various complexes of this type in that no coupling between the bridging alkylidene and alkyne ligands can be induced, even in refluxing solvents. This coupling reaction can, however, be promoted indirectly. When solutions of **2d** in hexane are exposed to Pyrex-filtered sunlight, the major product obtained is $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}CH(CF_3)\}(\mu\text{-}CF_3C_2CF_3)$; this is formed by decarbonylation of **2d**. The spectroscopic properties of this complex are consistent with a structure incorporating symmetrically bridging carbene and π-alkyne ligands (see 4 in Scheme II). In this structure, the two different groups (H and CF_3) attached to the alkylidene carbon render the two CF_3 groups on the alkyne ligand inequivalent. This is reflected in the ^{19}F NMR spectrum where a total of three CF_3 resonances are observed. The $CHCF_3$ resonance is found as a doublet of triplets ($^3J_{HF}$ = 13 Hz, J_{RhF} = 2.5 Hz) at δ 50.4, and the $CF_3C_2CF_3$ resonances are quartets at δ 50.8 and 53.8. The F–F coupling of 2 Hz in these quartets can be compared with the coupling constant of 12–14 Hz commonly found[17] in binuclear complexes where the alkyne is σ-attached along the Rh–Rh bond.

Since the structure suggested for 4 is analogous to that previously established[18] for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (**1**), it seemed likely that 4 would display the high chemical reactivity that has been found for 1. Surprisingly, 4 does not react with CO at room temperature in the absence of light. However, a slow reaction does proceed in the presence of sunlight. Workup of the reaction solution shows that 4 has been transformed to **3d**. Of the two possible arrangements of the substituents in the allyl group of **3d**, the one shown in Scheme II is indicated by the NMR spectra.

The inability of **2d** to convert directly to 4 may be due to a steric barrier that inhibits the coupling reaction and/or the twisting of the carbene. Presumably, this steric barrier is relieved when CO is removed from **2d** and the alkyne twists from its position along the Rh–Rh bond to one across this bond (see Scheme II). The subsequent coupling reaction is then jointly promoted by the addition of CO and irradiation with sunlight.

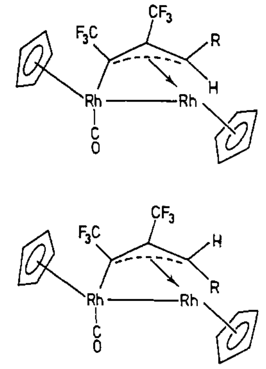


Figure 3. Alternative configurations in the allylic group of $M_2(\mu\text{-}CRCRCHR')$ systems.

Comparisons with Other Examples of Coupling Reactions between Alkylidenes and Alkynes on Polynuclear Centers and Some Concluding Remarks

There are a number of examples in the literature of coupling reactions between alkynes and carbenes on polynuclear metal centers. Some involve the addition of a carbene source to an alkyne complex; the additions of N_2CH_2 to $Os_3(CO)_9(\mu\text{-}PhC_2Ph)$[20] or $(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-}CO)(\mu\text{-}PhC_2Ph)$[13] provide examples of this sort of reaction. In other instances, alkynes are added to polynuclear μ-alkylidene complexes; examples include the addition of alkynes to $(\eta\text{-}C_5H_5)_2M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)$ (M = Fe, Ru),[12,21] $W_2(CO)_{10}(\mu\text{-}CMe_2)$,[22] $Fe_2(CO)_8(\mu\text{-}CH_2)$,[23] and $(\eta^4\text{-}COD)_2Ir_2(\mu\text{-}CH_2)$.[16]

Most of the above reactions lead (at least initially) to the formation of allyl complexes. In the Os_3 system,[20] only a CH fragment of the μ-CH_2 ligand migrates, the remaining H atom being left as a bridging hydride. In some systems, the initial coupling reaction is followed by further insertion of a second carbene[13] or alkyne.[21,22]

For C–C bond formation to occur in coupling reactions of this type, the spatial proximity of the carbon atoms that are forming the new bond is clearly important. Structure determinations have established that the appropriate carbons are reasonably close (ca. 2.8 Å) in the complexes $(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CH_2)\{\mu\text{-}C(Ph)C(Ph)CH_2\}$[13] and $Os_3(CO)_9(\mu\text{-}CH_2)(\mu\text{-}PhC_2Ph)$.[20] In coupling reactions that involve an alkyne and a monosubstituted alkylidene, CHR, the product geometry shown in Figure 3a is strongly preferred over that in Figure 3b. This stereospecificity is attributed[21] to steric factors, with the R group preferring the less crowded site away from the ancillary ligands.

With our dirhodium complexes **2a–d**, the alkylidene substituents clearly affect the rate of conversion to 3. The observed rate is R = $CH{=}CH_2$ > $SiMe_3$ >> CO_2Et >>> CF_3. They seem also to influence the ligand geometry within 3, with R = $CH{=}CH_2$, CO_2Et, and CF_3 adopting the geometry shown in Figure 3a, but the complex with R = $SiMe_3$ having the alternative and uncommon geometry indicated in Figure 3b.

It is clear that the bulk of the alkylidene substituents could affect the appropriate C···C distance in 2 and the

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ability of CHR to twist within **2** and **3**; both factors could influence the overall rate of the coupling reactions. Electronic factors may be important too, with electronegative substituents stabilizing the M_2–(μ-CHR) bonding. Perhaps a clearer picture of these stereoelectronic effects will emerge when we have completed further studies involving disubstituted alkylidenes.

Acknowledgment. We gratefully acknowledge support of this work by a grant (R.S.D.) from the Australian Research Grants Scheme. S.M.J. thanks the Commonwealth Government for a Postgraduate Research Award. Help with spectroscopic monitoring of reactions was provided by Ian Grayson, Felicity McLure, and Jo Weigold.

Registry No. **1**, 98395-25-6; **2a**, 107870-63-3; **2a′**, 107870-66-6; **2b**, 107799-58-6; **2d**, 107870-65-5; **3a**, 107799-56-4; **3a′**, 107870-64-4; **3b**, 107799-57-5; **3c**, 107799-59-7; **3d**, 107799-60-0; 4, 107819-48-7; $N_2CH(CO_2Et)$, 623-73-4; $N_2CH(SiMe_3)$, 18107-18-1; $N_2CH(CH{=}CH_2)$, 2032-04-4; $N_2CH(CF_3)$, 371-67-5; Rh, 7440-16-6.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and equations for planes (3 pages); a listing of the structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

1,2-Siloxetanes: Formation, Structure, and Rearrangements

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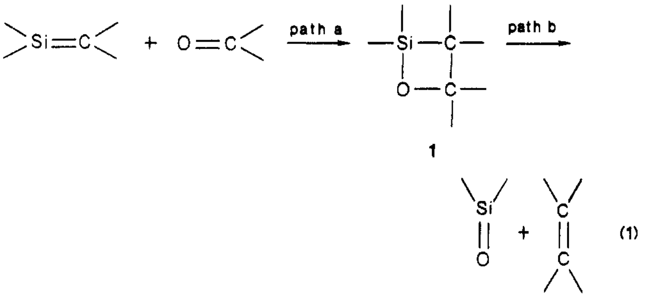
A variety of relatively stable silenes react with representative nonenolizable aldehydes and ketones to yield moderately stable 1,2-siloxetanes, some of which have been isolated as solids. A crystal structure of one siloxetane, 2,2-bis(trimethylsilyl)-4,4-diphenyl-3-adamantyl-3-(trimethylsiloxy)-2-siloxetane, has been obtained [crystal data: $C_{33}H_{52}O_2Si_4$, monoclinic, space group $C2/c$, a = 38.652 (13) Å, b = 10.470 (2) Å, c = 17.081 (8) Å, β = 101.99 (3)°, U = 6761 Å^3, D_{calcd} = 1.14 g cm^{-3} for Z = 8; R = 0.062 for 1605 observed ($I > 3\sigma(I)$) reflections] which shows all bonds of the slightly folded ring to be somewhat elongated, especially the C–C bond (1.67 Å). In some cases, in addition to the [2 + 2] siloxetane adducts, related [2 + 4] bicyclo [4.4.0] isomers were observed from the silene + ketone reactions, where the 4π component was derived either from the silene or from an aromatic ketone. Examples of interconversions between the [2 + 2] and [2 + 4] isomers were noted. Only one of the siloxetanes, **1g**, underwent the "normal" [2 + 2] retroreaction to silanone and alkene on thermolysis [crystal data of the siloxyalkene **16**: $C_{26}H_{28}OSi$, monoclinic, space group $P2_1/n$, a = 9.335 (2) Å, b = 10.868 (2) Å, c = 22.211 (6) Å, β = 98.02 (2)°, U = 2231 Å^3, D_{calcd} = 1.15 g cm^{-3} for Z = 4; R = 0.077 for 801 observed ($I > 3\sigma(I)$) reflections]. All the other siloxetanes underwent an intramolecular rearrangement involving siloxy and aryl group migrations. A two-step dipolar mechanism best explains the cycloaddition reactions while the interconversions between [2 + 2] and [2 + 4] products appear to involve 1,3-sigmatropic processes.

Introduction

Siloxetanes **1** have long been regarded as the product of reaction of a silene with a carbonyl compound[1] (eq 1, path a). However, until recently direct proof that siloxetanes were actually formed has been lacking because of their apparent instability, and evidence for their formation has rested primarily on the detection and/or isolation of the alkene and the silanone (oligomers) expected if the anticipated siloxetanes had broken down in a retro [2 + 2] sense (path b). Some direct evidence for siloxetanes has recently become available. Thus Märkl postulated the formation of several siloxetanes by thermolysis of a silene head-to-head dimer in the presence of a variety of nonenolizable carbonyl compounds.[2] In some cases siloxetanes were apparently isolated, but in other cases different types of product were obtained, believed to arise from complex rearrangements of the initially formed siloxetanes. Wiberg has described the formation of a remarkably stable siloxetane as well as a related [2 + 4] adduct from reaction of a relatively stable silene with benzophenone[3] and Ando recently described the formation of a siloxetene under rather special circumstances.[4]



Discussion

We have examined the reactions of the relatively stable silenes obtained by photolysis of a variety of polysilylacylsilanes with several nonenolizable aldehydes and ketones under two sets of conditions (Scheme I). Co-photolysis of the acylsilane **2** in the presence of the carbonyl compound at $\lambda \geqslant 360$ nm gave essentially identical results to those obtained when the carbonyl compound was added in the dark to a solution of the preformed silene **3**. Thus the additions occurring are "dark" reactions of the silene

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