stabilize the trivalent thorium oxidation state, rendering eq 7 more endothermic. Equally important may be differences in metal–hydrocarbyl ligand orbital overlap (bonding), although these are not immediately obvious in observables such as He I, II photoelectron spectra.[24] Likewise, differential π-accepting tendencies of the Cp_3Th[25] and Cp'_2Th[10e] centers may significantly affect the bonding of alkoxide ligands,[26] hence the measured exothermicity of eq 3. In any case, it is clear that the nature of the ancillary hydrocarbon ligands does affect D(M–R) values for organoactinides.

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Registry No. $CP_3ThOCH_2CF_3$, 92473-15-9; CP_3ThCH_3, 92473-15-9; $CP_3ThC(CH_3)_2H$, 58920-14-2; $CP_3ThCH_2Si(CH_3)_3$, 89746-39-4; $CP_3ThCH_2C_6H_5$, 89746-40-7; $CP_3ThCH_2CH_2CH_2CH_3$, 54067-92-4; F_3CCH_2OH, 75-89-8.

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[26] Both d and f orbitals of appropriate symmetry are available for π bonding in Cp_3ThOR and $Cp'_2Th(OR)_2$ compounds.

Addition of Small Molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. 2.[1] Intramolecular Reactions between μ-Alkylidene Groups and the μ-Alkyne in Some Complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$. Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3){=}C(CF_3)OC(OEt){=}C(CO_2Et)]$

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Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) with diazoalkanes $N_2CR^1R^2$ in diethyl ether at 0 °C gives the μ-alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$ ($R^1 = R^2 = H$, **2a**; $R^1 = R^2 = CO_2Et$, **2b**). Migration of the alkylidene group to the coordinated alkyne occurs when each of the complexes is kept in solution at room temperature. With **2a**, there is formation of a new C–C bond to give a σ,π-allyl complex, $(\eta\text{-}C_5H_5)_2Rh_2(CO)[\mu\text{-}C(CF_3)C(CF_3)CH_2]$ (**3**). In contrast, **2b** gives $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3){=}C(CF_3)OC(OEt){=}C(CO_2Et)]$ (**4**) in which a new C—O bond has been formed. Determination of the crystal and molecular structure of **4** establishes that the bridging group is a divinyl ether which spans the Rh–Rh bond in "flyover" fashion. Crystal data: $C_{21}H_{20}F_6O_4Rh_2$, $M_r = 656.2$, monclinic, $P2_1/n$, $a = 17.666\ (8)$ Å, $b = 13.679\ (6)$ Å, $c = 9.526\ (4)$ Å, $\beta = 103.62\ (8)°$, $U = 2237.3$ Å^3, $D_{calcd} = 1.95$ ($Z = 4$), $D_{measd} = 1.90\ (3)$ g cm^{-3}, λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 14.0 cm^{-1}, final $R = 0.052$, $R_w = 0.051$, from 2945 observed reflections (6518 measured).

Introduction

The first (μ-methylene)dimetal complex was reported[2] as recently as 1975, but already there is a substantial review[3] on the topic. This high level of interest and activity has been stimulated by the possible involvement of these and related compounds in important catalytic reactions such as alkene metathesis, Fischer–Tropsch chemistry, and alkyne polymerization.[3,4]

Recently, we described[1] the synthesis of a coordinatively unsaturated dirhodium complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) and the coordinative addition of some π-acid ligands to yield the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(\mu\text{-}CF_3C_2CF_3)$. These reactions include the additions of CO and CNR, and it therefore seemed likely that related complexes should be formed with $=CR_2$. In fact, the reactions of 1 with various diazoalkanes, $N_2CR^1R^2$, lead to elimination of N_2 and formation of μ-alkylidene complexes of formula $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$. Some of these complexes undergo interesting intramolecular reactions in which the alkylidene migrates to the coordinated alkyne. In this paper, we describe two such reactions; these results have been briefly communicated.[5]

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. ^1H and ^{19}F NMR spectra were recorded at 90 and 84.66 MHz, respectively, on a Brüker WH-90 spectrometer; the ^1H spectra are reported as δ values, and the ^{19}F chemical shifts are upfield from CCl_3F internal reference. A V.G. Micromass 7070-F spectrometer was used to measure the mass

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spectra. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

All reactions were carried out in standard Schlenk equipment under dry N_2. Ether was freshly distilled from $LiAlH_4$ before use. Preparative scale thin-layer chromatography was carried out on 20 by 20 cm plates with a 1:1 silica gel G-HF_{254} mixture as adsorbent.

Starting Materials. $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) was prepared by the published[1] procedure. Diazomethane was generated from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide and KOH in ether;[6] $N_2C(CO_2Et)_2$ was prepared by a published method.[7]

Reaction of 1 with N_2CH_2. A slight excess of diazomethane in diethyl ether was added to a solution of 1 (0.120 g) in diethyl ether at 0 °C. Within a few minutes, orange crystals had deposited and the supernatant was red. The orange crystals were separated by filtration and washed with pentane to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CH_2)(CF_3C_2CF_3)$ (0.105 g, 85%) (**2a**), mp 124 °C dec. Anal. Calcd for $C_{16}H_{12}F_6ORh_2$: C, 35.6; H, 2.2; F, 21.1. Found: C, 35.6; H, 2.5; F, 21.3. Spectroscopic data: IR (KBr) ν(CO) at 1883 (vs), 1871 (vs) cm^{-1}; ^1H NMR (acetone-d_6) δ 10.55 (dt, 1 H, J = 5.0 and 2.5 Hz, methylene H), 7.84 (dt, 1 H, J = 5.0 and 0.9 Hz, methylene H), 5.65 (s, 10 H, C_5H_5); ^{19}F NMR (acetone-d_6) δ 53.2 (s); MS, *m/e* 540 $[M]^+$, 512 $[M - CO]^+$.

Excess N_2CH_2 and ether were removed from the red filtrate under reduced pressure. Subsequent TLC with hexane as eluent separated a major red band from minor bands which were discarded. Removal of solvent from the red solution gave red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)[C(CF_3)C(CF_3)CH_2]$ (**3**) (0.018 g, 14%), mp 132 °C. Anal. Calcd for $C_{16}H_{12}F_6ORh_2$: C, 35.6; H, 2.2; F, 21.1. Found: C, 36.5; H, 2.5; F, 21.1. Spectroscopic data: IR (KBr) ν(CO) at 2005 (vs), 1995 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.39 (d, 5 H, J = 0.6 Hz, C_5H_5), 5.29 (d, 5 H, $J < 0.5$ Hz, C_5H_5), 3.41 (m, 1 H, CH), 2.46 (m, 1 H, CH); ^{19}F NMR ($CDCl_3$), multiplets ($J \approx 13$ Hz) at δ 46.5 and 57.4; MS, *m/e* 540 $[M]^+$, 512 $[M - CO]^+$.

Reaction of 1 with $N_2C(CO_2Et)_2$. A slight excess of $N_2C(CO_2Et)_2$ was added to 1 (0.110 g) in diethyl ether. The color changed from green to orange as the solution was stirred for a few minutes as 0 °C. TLC separated several minor products from one major band. The latter yielded orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)[C(CO_2Et)_2](CF_3C_2CF_3)$ (**2b**) (0.141 g, 98%), mp 92–94 °C. Anal. Calcd for $C_{22}H_{20}F_6O_5Rh_2$: C, 38.6; H, 3.0; F, 16.7. Found: C, 39.2; H, 3.1; F, 16.9. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1885 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.55 (s, 10 H, C_5H_5), 4.1 (2 × overlapping q, 4 H, J = 7 Hz, ester CH_2), 1.32 and 1.26 (overlapping t, 6 H, J = 7 Hz, ester CH_3); ^{19}F NMR ($CDCl_3$) δ 54.5 (s); MS, *m/e* 684 $[M]^+$, 656 $[M - CO]^+$.

Repeated TLC caused an increase in the amount of one of the minor products at the expense of **2b**. After several TLC runs, sufficient of this compound was obtained for complete characterization. It was isolated as red crystals, $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(CO_2Et)_2]$ (**4**), mp 125–6 °C. Anal. Calcd for $C_{21}H_{20}F_6O_4Rh_2$: C, 38.4; H, 3.1; F, 17.4. Found: C, 38.4; H, 3.1; F, 17.0. Spectroscopic data: IR (CH_2Cl_2) no ν(CO) observed between 2100 and 1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.40 (d, 5 H, $J < 1$ Hz, C_5H_5), 5.33 (d, 5 H, $J < 1$ Hz, C_5H_5), 4.20 (q, 2 H, J = 7 Hz, ester CH_2), 3.91 (q, 1 H, J = 7 Hz, ester CH_2), 3.85 (q, 1 H, J = 7 Hz, ester CH_2), 1.34 and 1.23 (overlapping t, 6 H, J = 7 Hz, 2 × ester CH_3); ^{19}F NMR ($CDCl_3$) δ 48.5 (q, 3 F, J = 12 Hz, CF_3) and 61.8 (q, 3 F, J = 12 Hz, CF_3); MS, *m/e* 656 $[M]^+$.

Crystallography. Well-formed single crystals of 4 were grown from hexane/dichloromethane. A suitable crystal was mounted on a Philips PW1100 computer-controlled diffractometer; the cell parameters were determined from 24 reflections and were calculated by the standard Philips program. Data are summarized in Table I. Three standard reflections were monitored every 3 h and showed no significant variation of intensity over the data collection period.

Table I. Summary of Crystal Structure Data for Complex 4

(a) Crystal Data

formula	$C_{21}H_{20}F_6O_4Rh_2$		
mol wt	656.2		
cryst system	monoclinic		
	space group	$P2_1/n$	
a, Å	17.666 (8)	Z	4
b, Å	13.679 (6)	D_{calcd}, g cm^{-3}	1.95
c, Å	9.526 (4)	D_{measd}, g cm^{-3}	1.90 (3)
β, deg	103.62 (8)	$F(000)$	1288
U, $Å^3$	2237.3	μ(Mo Kα), cm^{-1}	14.0

(b) Data Collection

radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
2θ limits, deg	6–60
ω scan angle, deg	$\pm(1.4 + 0.3 \tan \theta)$
scan rate, deg s^{-1}	0.06
total data	6518
data $I > 3\sigma(I)$	2945
final R and R_w	0.052 and 0.051
weight w	$[\sigma^2(F)]^{-1}$

Table II. Atomic Positional Parameters (×10^4)

atom	x/a	y/b	z/c
Rh(1)	0.1770 (1)	0.1583 (1)	0.1444 (1)
Rh(2)	0.3102 (1)	0.0945 (1)	0.1076 (1)
C(1)	0.2118 (5)	0.1230 (7)	−0.0452 (10)
C(2)	0.1897 (5)	0.2243 (7)	−0.0472 (10)
C(3)	0.3059 (6)	0.2724 (7)	0.0924 (10)
C(4)	0.2835 (5)	0.2203 (6)	0.2076 (9)
C(5)	0.3274 (5)	0.2401 (6)	0.3609 (10)
C(6)	0.1733 (8)	0.0513 (10)	−0.1534 (14)
F(61)	0.1992 (6)	0.0349 (6)	−0.1340 (11)
F(62)	0.1766 (8)	0.0741 (8)	−0.2795 (9)
F(63)	0.0990 (5)	0.0381 (8)	−0.1642 (11)
C(7)	0.1234 (8)	0.2749 (10)	−0.1490 (14)
F(71)	0.0566 (4)	0.2254 (6)	−0.1720 (8)
F(72)	0.1377 (5)	0.2910 (7)	−0.2772 (8)
F(73)	0.1081 (5)	0.3611 (6)	−0.0957 (10)
C(8)	0.3948 (8)	0.3433 (12)	−0.0279 (16)
C(9)	0.4636 (9)	0.3711 (19)	−0.0090 (18)
C(10)	0.3477 (8)	0.1927 (10)	0.6053 (12)
C(11)	0.3889 (11)	0.1104 (13)	0.6584 (16)
O(1)	0.2517 (4)	0.2933 (5)	−0.0276 (7)
O(2)	0.3720 (4)	0.3230 (5)	0.1096 (7)
O(3)	0.3136 (5)	0.1770 (6)	0.4539 (8)
O(4)	0.3717 (7)	0.3044 (8)	0.3975 (8)
C(12)	0.0742 (6)	0.2075 (9)	0.2174 (13)
C(13)	0.0520 (6)	0.1247 (8)	0.1237 (12)
C(14)	0.0962 (6)	0.0428 (8)	0.1920 (12)
C(15)	0.1448 (6)	0.0775 (8)	0.3238 (12)
C(16)	0.1308 (6)	0.1777 (8)	0.3395 (12)
C(17)	0.3744 (7)	−0.0212 (9)	0.0252 (14)
C(18)	0.3320 (7)	−0.0626 (9)	0.1215 (13)
C(19)	0.3638 (7)	−0.0231 (10)	0.2608 (14)
C(20)	0.4203 (7)	0.0444 (9)	0.2524 (14)
C(21)	0.4300 (7)	0.0479 (9)	0.1080 (13)

Interesting data were processed as described earlier.[8] A numerical absorption correction was applied. The atomic scattering factors for neutral atoms[9] were corrected for anomalous dispersion.[9] All calculations were performed on a Monash University DEC/VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick.[10]

The structure was solved by conventional heavy-atom methods. Full-matrix least-squares refinement of all positional atom coordinates and anisotropic thermal parameters for all atoms except those in the cyclopentadienyl rings, which were refined with isotropic thermal parameters, reduced R to 0.052 and R_w to 0.051; $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. Hydrogen atoms were not included in the calculations.

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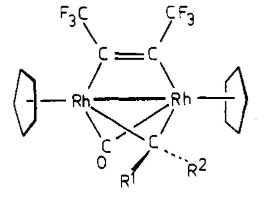
[10] Sheldrick, G. M. SHELX, "Program for Crystal Structure Determination"; Cambridge, England, 1974.

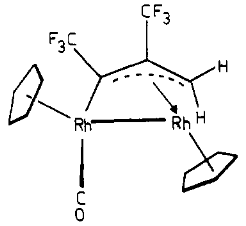
Final positional parameters are presented in Table II; thermal parameters are deposited as Table II-S (supplementary material).

Results and Discussion

The μ-Alkylidene Complexes. The complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$ ($R^1 = R^2 = H$, **2a**; $R^1 = R^2 = CO_2Et$, **2b**) are formed within a few minutes when the appropriate diazoalkane, $N_2CR^1R^2$, is added to a solution of **1** at 0 °C. The yield of **2b** is near quantitative—**2a** converts readily to **3**, and this caused a slight reduction in the yield of **2a**.



2a, $R^1 = R^2 = H$
b, $R^1 = R^2 = CO_2Et$



3

Spectroscopic data for these complexes can be interpreted in terms of a bridging alkylidene structure, **2**. In the infrared spectra, ν(CO) is observed in the bridging carbonyl region near 1880 cm^{-1}. The ^1H NMR spectrum of each complex shows a singlet resonance near δ 5.6 which is assigned to two equivalent cyclopentadienyl rings. In the spectrum of **2a**, two additional resonances are observed at δ 10.55 (dt, $^2J_{HH} = 5$ and $^2J_{RhH} = 2.5$ Hz) and 7.84 (dt, $^2J_{HH} = 5$ and $^2J_{RhH} = 1$ Hz) and these are attributed to the diastereotopic protons of the μ-methylene group. These resonances lie within the range (6.0–10.7 ppm) observed for other metal–metal bonded μ-alkylidene complexes.[3] The ethyl protons of the ester appear as well-defined quartets plus triplets for **2b**.

The Alkylidene Migration Reaction 2a → 3. A second product was isolated from the reaction of **1** with N_2CH_2. TLC of the filtrate from the reaction mixture yielded a red solid in 14% yield. The spectroscopic properties of this complex are consistent with structure **3**. Thus, a terminal carbonyl stretching frequency is observed near 2000 cm^{-1} in the infrared, and the ^1H NMR spectrum reveals inequivalent cyclopentadienyl resonances at δ 5.39 and 5.29 plus two multiplets attributed to the terminal CH_2 protons of an allyl group at δ 3.41 and 2.46. In the ^{19}F NMR spectrum, two quartets are observed at δ 46.5 and 57.4 for the inequivalent CF_3 groups. Evidence that this complex is formed via **2a** is obtained by monitoring changes in the IR and NMR spectra of solutions of **2a**.

The Alkylidene Migration Reaction 2b → 4. Complex **2b** also undergoes an alkylidene to alkyne migration in solution, but spectroscopic results indicate formation of a different type of product. In particular, no terminal or bridging carbonyl stretching frequency is observed in the infrared spectrum. Asymmetry within the molecular structure is indicated by the observation of two C_5H_5 resonances in the ^1H NMR spectrum and of two CF_3 resonances in the ^{19}F spectrum. One of the CF_3 resonances is at higher field (δ 61.8) than those observed for complexes **2** and **3**.

Crystal and Molecular Structure of Complex 4. The spectroscopic data do not distinguish between several alternative structures in which a heterooxygen atom has been incorporated into a metalladiene or dimetalladiene ring system. Consequently, the structure of the complex was determined from X-ray diffraction data.

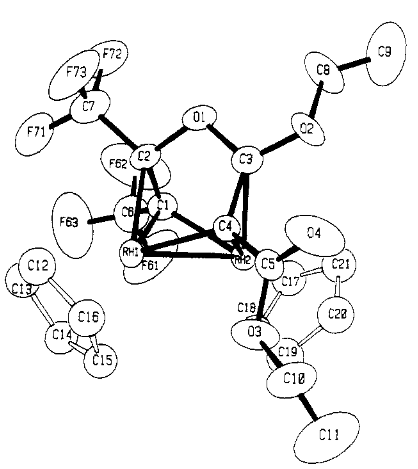


Figure 1. Molecular structure of complex 4 $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3){=}C(CF_3)OC(OEt){=}C(CO_2Et)]$.

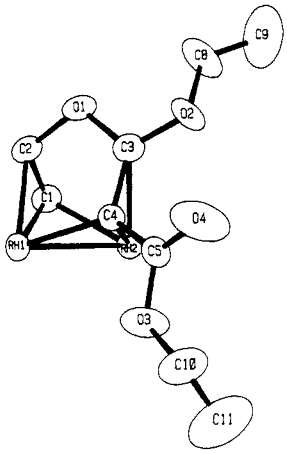


Figure 2. View of the bridging region of complex 4 with substituents removed for clarity.

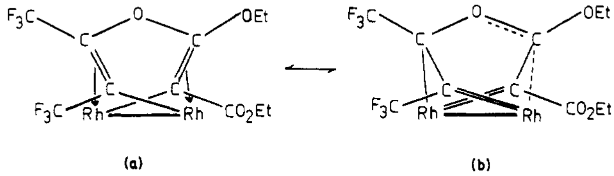


Figure 3. Representations of the bonding in complex 4.

The molecular structure is shown in Figure 1, which also indicates the labeling of the atoms. Intramolecular distances and angles are collected in Tables III and IV. Figure 2 presents an uncluttered view of the bridging region of the molecule; the trifluoromethyl substituents on C(1) and C(2) and the two cyclopentadienyl rings have been omitted.

The existence of a Rh–Rh bond is indicated by the distance of 2.609 Å. Figure 2 reveals that the Rh–Rh bond is bridged by a divinyl ether which adopts a "flyover" conformation. Formally, it is attached to the dimetal center by two σ-bonds, Rh(1)–C(4) and Rh(2)–C(1), plus two π-bonds, Rh(1)–C(1):C(2) and Rh(2)–C(3):C(4) (see Figure 3a). The Rh(1)–C(1) and Rh(1)–C(2) distances are equal (both 2.10 (1) Å), but Rh(2)–C(3) (2.438 (9) Å) is considerably longer than Rh(2)–C(4) (2.074 (8) Å). This asymmetry may be related to the apparent delocalization of π-electron density over the atoms C(4)–C(3)–O(1). The C(3)–O(1) distance (1.34 (1) Å) is considerably shorter than the C(3)–O(2) single-bond distance of 1.42 (1) Å but similar to the double-bond distance of 1.37 (1) Å between C(5) and O(4). A further indication of this asymmetry is provided by the bond angles around the carbon atoms C(1)–C(4). The sum of the angles around each of C(1), C(3),

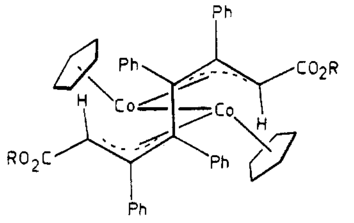
Table III. Interatomic Distances (Å) and Esd's[a]

Rh(1)-Rh(2)	2.609 (1)	C(3)-O(2)	1.33 (1) [1.42 (1)]	C(7)-F(71)	1.33 (1) [1.48 (2)]
Rh(1)-C(1)	2.097 (10)	C(3)-C(4)	1.44 (1)	C(7)-F(72)	1.32 (1) [1.50 (2)]
Rh(1)-C(2)	2.095 (9)	C(8)-O(2)	1.49 (1) [1.63 (2)]	C(7)-F(73)	1.34 (1) [1.51 (2)]
Rh(1)-C(4)	2.022 (8)	C(8)-C(9)	1.25 (2) [1.54 (2)]	C(12)-C(13)	1.44 (1)
Rh(2)-C(1)	2.024 (9)	C(4)-C(5)	1.51 (1) [1.56 (1)]	C(12)-C(16)	1.40 (1)
Rh(2)-C(3)	2.438 (9)	C(5)-O(3)	1.30 (1) [1.43 (1)]	C(13)-C(14)	1.43 (1)
Rh(2)-C(4)	2.074 (8)	C(5)-O(4)	1.18 (1) [1.37 (1)]	C(14)-C(15)	1.43 (1)
C(1)-C(2)	1.44 (1)	C(10)-O(3)	1.44 (1) [1.61 (1)]	C(15)-C(16)	1.41 (1)
C(1)-C(6)	1.47 (1)	C(10)-C(11)	1.37 (2) [1.55 (2)]	C(17)-C(18)	1.43 (2)
C(2)-C(7)	1.50 (1)	C(6)-F(61)	1.26 (1) [1.50 (2)]	C(17)-C(21)	1.45 (2)
C(2)-O(1)	1.43 (1)	C(6)-F(62)	1.26 (1) [1.52 (2)]	C(18)-C(19)	1.42 (2)
C(3)-O(1)	1.34 (1)	C(6)-F(63)	1.31 (1) [1.51 (2)]	C(19)-C(20)	1.37 (2)
				C(20)-C(21)	1.43 (2)

[a] Bond lengths corrected for thermal vibration in square brackets.

Table IV. Interatomic Angles (deg) with Esd's

C(1)-Rh(1)-Rh(2)	49.5 (3)	C(1)-Rh(1)-C(4)	84.9 (3)	C(2)-Rh(1)-C(4)	78.2 (3)
C(1)-Rh(1)-C(2)	40.1 (3)	C(2)-Rh(1)-Rh(2)	75.0 (2)	C(4)-Rh(1)-Rh(2)	51.3 (2)
C(1)-Rh(2)-Rh(1)	50.0 (3)	C(1)-Rh(2)-C(4)	85.5 (3)	C(3)-Rh(2)-C(4)	36.1 (3)
C(1)-Rh(2)-C(3)	75.9 (3)	C(3)-Rh(2)-Rh(1)	70.0 (2)	C(4)-Rh(2)-Rh(1)	49.5 (2)
Rh(1)-C(1)-Rh(2)	78.5 (3)	Rh(1)-C(1)-C(6)	125.2 (8)	Rh(2)-C(1)-C(6)	123.6 (8)
Rh(1)-C(1)-C(2)	69.9 (5)	Rh(2)-C(1)-C(2)	112.3 (6)	C(2)-C(1)-C(6)	123.7 (9)
Rh(1)-C(2)-C(1)	70.0 (5)	Rh(1)-C(2)-C(7)	122.3 (8)	C(1)-C(2)-C(7)	128.4 (9)
Rh(1)-C(2)-O(1)	114.1 (6)	C(1)-C(2)-O(1)	116.0 (8)	O(1)-C(2)-C(7)	103.7 (8)
Rh(2)-C(3)-C(4)	58.0 (4)	O(1)-C(3)-O(2)	115.1 (8)	C(4)-C(3)-O(2)	123.6 (8)
O(1)-C(3)-C(4)	119.1 (8)				
Rh(1)-C(4)-Rh(2)	79.1 (3)	Rh(1)-C(4)-C(5)	126.4 (6)	Rh(2)-C(4)-C(5)	118.2 (6)
Rh(1)-C(4)-C(3)	112.6 (6)	Rh(2)-C(4)-C(3)	85.9 (5)	C(3)-C(4)-C(5)	118.5 (7)
C(4)-C(5)-O(3)	113.9 (7)	C(4)-C(5)-O(4)	125.2 (9)	O(3)-C(5)-O(4)	120.9 (1)
C(3)-O(1)-C(2)	110.1 (7)	C(5)-O(3)-C(10)	118.8 (9)	O(3)-C(10)-C(11)	107.9 (12)
C(3)-O(2)-C(8)	113.6 (8)	O(2)-C(8)-C(9)	112.8 (14)		



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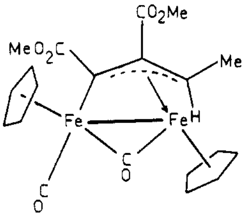

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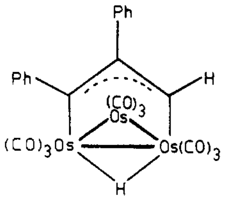

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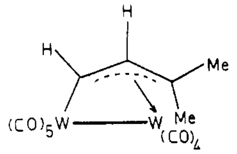

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and C(4) is close to 360°, but the bond angles around C(2) add to only 348°. To account for this asymmetry in the attachment of the divinyl ether to the Rh–Rh bond, an alternative representation of the bonding within the bridging group is given in Figure 3b.

Parameters within the CF_3 groups and the C_5H_5 rings are similar to those found in related molecules, including $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$[11] and $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3)C(CF_3)C(O)C(Me)C(Me)]$.[12]

Comparisons with Related Systems. The recent literature contains a number of examples of reactions between alkylidenes and alkynes where one of these reactants is initially coordinated to a M–M center. In most of these systems, a μ-alkylidene complex is treated with an alkyne;[13–18] a few involve the addition of diazoalkane to an (alkyne)metal complex.[19–21] In all cases, there is

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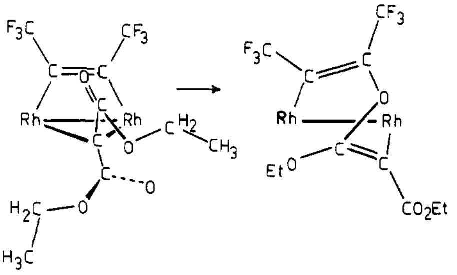
formation of a new C–C bond resulting from interaction between the alkylidene carbon and an alkyne carbon. Some representative examples of the complexes obtained are shown in 5–8. Isolation of the μ-alkylidene–μ-alkyne intermediate was described only in the Os system, and here further conversion to the migration product 7 requires heating in xylene at 135 °C.

The reaction sequence

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)[\mu\text{-}(\eta^2\text{-}CF_3C_2CF_3)] + N_2CR^1R^2 \xrightarrow{-N_2} (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)[\mu\text{-}(\eta^1\text{-}CF_3C_2CF_3)] \xrightarrow{\text{soln}} (\eta\text{-}C_5H_5)_2Rh_2(CO)[\eta^1,\eta^3\text{-}C(CF_3)C(CF_3)CR^1R^2]$$

is unique among these systems in that a stable μ-alkylidene–μ-alkyne complex can be isolated *and* converted to the η^1,η^3-allyl complex under mild conditions.

The different form of the conversion reaction when $R^1 = R^2 = CO_2Et$ is also unique among these systems. The preference for formation of a new C–O bond rather than a new C–C bond is presumably due to a combination of stereochemical and electronic effects. Consideration of molecular models establishes that the most sterically favored arrangement of the μ-alkylidene ligand orients the ketonic oxygen toward the alkyne (see 9). Retention of two Rh–C bonds in the final product can be attributed to the stabilizing influence of the electron-withdrawing substituents CF_3 and CO_2Et.



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Conclusion

The complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is an excellent model system for investigating the coordination and subsequent reactions of carbenes. The two systems described in this paper represent two different types of behavior. In one, the carbene C is involved in the formation of a new C–C bond via an intramolecular migration reaction. With the other, formation of a new C–O bond involves the carbonyl O of an ester substituent. A number of other systems are currently being investigated to determine the factors affecting the course of these reactions.

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Registry No. 1, 71844-53-6; **2a**, 84330-33-6; **2b**, 84349-75-7; 3, 92641-70-8; 4, 84330-38-1; N_2CH_2, 334-88-3; $N_2C(CO_2Et)_2$, 5256-74-6.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Regioselective Pentadienylation of Carbonyl Compounds by Oligosilylated Pentadienylmetals

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Pentadienylation of simple aliphatic ketones or aldehydes by [1,5-bis(trimethylsilyl)pentadienyl]lithium was found to proceed regioselectivity at the C_3 atom of the pentadienyl moiety while the reaction with [1,3,5-tris(trimethylsilyl)pentadienyl]lithium preferred addition at the terminal carbon atom, resulting in conjugated trienes through Peterson elimination. A conjugated hexaene was obtained by treating [1,10-bis(trimethylsilyl)-2,4,6,8-octatetraene-1,10-diyl]dilithium with 2,4-dimethyl-3-pentanone via double Peterson elimination. Pentadienylation of α,β-unsaturated ketones or aldehydes with [1,5-bis(trimethylsilyl)pentadienyl]- or [1,3,5-tris(trimethylsilyl)pentadienyl]lithium occurred selectively in a 1,4 fashion at the C_3 atom of pentadienyl moiety. Although the reaction of [1-(trimethylsilyl)pentadienyl]lithium with carbonyl compounds gave a mixture of regioisomers, the selective addition at the C_3 atom of pentadienyl group was realized by transmetalation to [5-(trimethylsilyl)-2,4-pentadienyl]magnesium, -boron, and -copper.

Introduction

Direct allylation or pentadienylation[1] of electrophiles with allylic anions[2] or pentadienyl anions[3] is one of the important fundamental procedures in organic synthesis for elongation of carbon chains. However, the process often suffers a disadvantage that the reaction results in a complex mixture of regioisomers by uncontrolled attack at α-, γ-, or ϵ-positions of the carbanions because the electron

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