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Unusual Alkyne–Alkylidene Coupling Reactions at a Rhodium–Rhodium Bond. Crystal and Molecular Structure of the Bridging Butadiene Complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)H{=}C(CF_3)CMe{=}CH_2\}$

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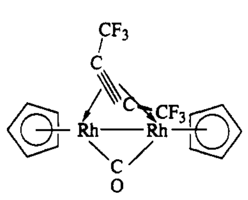
Two products isolated from the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) and N_2CMe_2 have been characterized spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}CF_3C_2CF_3{\cdot}CO{\cdot}N_2CMe_2\}$ (4) and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3{\cdot}CMe_2)$ (5). The structure of 4 is analogous to that previously established for the related N_2CMePh derivative. It is proposed that the structure of 5 incorporates a $\mu\text{-}\eta^1$-alkylidene with CF_3 and $C(CF_3){=}CMe_2$ substituents and a bridging carbonyl. When 5 is left in solution, there is a 1,4-hydrogen shift that converts the bridging alkylidene to a bridging diene ligand. The resultant complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)H{=}C(CF_3)CMe{=}CH_2\}$ (6) has been characterized by determination of the X-ray crystal structure. Crystal data: $C_{18}H_{16}F_6ORh_2$; $M = 568.1$, $P\bar{1}$, $a = 12.313(2)$ Å, $b = 9.365(2)$ Å, $c = 8.758(2)$ Å, $\alpha = 112.16(1)°$, $\beta = 91.97(1)°$, $\gamma = 105.40(1)°$; $V = 891.4(3)$ Å^3, $D_{calcd} = 2.12$ g cm^{-3} ($Z = 2$), $D_{measd} = 2.11(1)$ g cm^{-3}, $\mu = 18.9$ cm^{-1} for Mo Kα radiation ($\lambda = 0.7107$ Å), final $R = 0.040$, $R_w = 0.044$, from 4252 observed reflections (5201 measured). The reaction of 1 with diazocyclopentadiene, $N_2C_5H_4$, follows a different course. There is elimination of nitrogen and a 1,2-hydrogen shift within the C_5H_4 unit to form a cyclic "ene–yne". A product of formula $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CF_3C_2CF_3{\cdot}CO)(C{\equiv}CCH_2CH{=}CH)$ is obtained, but it has not been possible to determine if the C_5 ring is attached directly to the Rh—Rh bond (7a) or has condensed with $CF_3C_2CF_3{\cdot}CO$ to form a bridging pentadienone (7b). Nitrogen elimination is also the primary step in the reaction of the diazomalonates $N_2C(CO_2R)_2$, R = Me or *t*-Bu, with 1. The bridging alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)\{\mu\text{-}C(CO_2R)_2\}$ are formed, and these complexes undergo a rearrangement when chromatographed or irradiated with sunlight to form the bridging divinyl ether complexes $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C(CF_3){=}C(CF_3)OC(OR){=}C\text{-}(CO_2R)\}$ (8; R = Me, *t*-Bu). With the *t*-Bu system, a second rearrangement occurs as a consequence of hydrolysis of the ester functions. This gives a product formulated as $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}\eta^2{:}\eta^1\text{-}CH(CF_3)C(CF_3)OC(O)C(CO_2H)\}$ (9).

Introduction

In previous papers,[1–4] we have reported two fundamentally different types of behavior when diazo compounds are added to the metal–metal bond in $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1). In one set of reactions, the diazo nitrogens are readily lost, and complexes with bridging alkylidene groups μ-CRR′ are formed. In other reactions done under identical conditions, complexes are formed in which the entire diazo group N_2CRR' is retained; we have demonstrated that these complexes are extremely stable with respect to loss of nitrogen. It is tempting to attribute these marked differences in behavior to the stereoelectronic influences of the substituents, but the patterns of behavior are not obvious. In this paper, we describe further pathways that can be followed in reactions between 1 and diazoalkanes. The reactions with 2-diazopropane, diazocyclopentadiene, and the diazomalonates $N_2C(CO_2R)_2$ all lead to facile loss of nitrogen, but there are fascinating differences in the nature of the subsequent alkylidene–alkyne coupling reactions. We have provided a preliminary account[5] of the reactions with diazopropane and diazocyclopentadiene. In this paper, we present a detailed account of all reactions, and an attempt to rationalize the substituent effects for these and the previously studied reactions.



(1)

Results and Discussion

In earlier papers,[1–3] we described the formation of bridging alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CHR)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (2; R′ = H) from reactions of diazoalkanes N_2CHR (R = H, $SiMe_3$, CF_3, $CH{=}CH_2$) with $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1). With most of these complexes (but not 2; R = CF_3; R′ = H), there is a

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[1] Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pain, G. N. *Organometallics* **1985,** *4,* 355.

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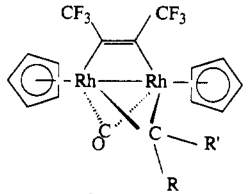
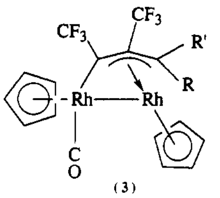
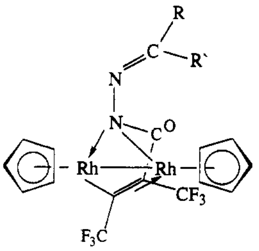


(2)

facile migration of the alkylidene to an alkyne carbon when the complexes are left in solution. This yields σ,π-allyl complexes of the type $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(CF_3)C(CF_3)CHR\}$ (**3**; R = R' = H). Some further reactions between diazoalkanes N_2CRR' (e.g. RR' = Ph_2, MePh) and **1** were described in a recent paper.[4] Generally, these gave products in which N_2CRR', CO, and $CF_3C_2CF_3$ had condensed to form a bridging group of the type shown in **4**. Retention of the diazoalkane nitrogens was a notable feature of these reactions.

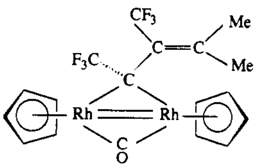


(3)

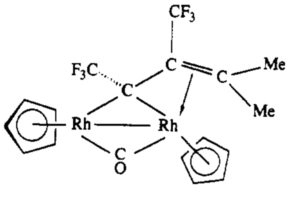


(4)

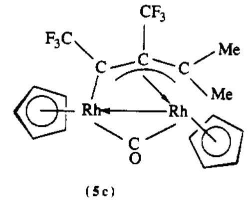
Reaction with N_2CMe_2. A complex analogous to **4** is obtained when **1** is treated with N_2CMe_2. This complex (**4**; R = R' = Me) has been characterized by comparison of its spectroscopic properties (see Experimental Section) with those for the structurally characterized[4] complex (**4**; R = Me, R' = Ph). There is however a second product formed by nitrogen loss from the diazoalkane, and it is formulated as $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3{\cdot}CMe_2)$ (**5**) from consideration of the spectroscopic results. A bridging carbonyl band is observed at 1860 cm^{-1} in the infrared spectrum, and the NMR spectra reveal two cyclopentadienyl resonances, two methyl resonances, and inequivalent trifluoromethyl groups. The NMR spectra indicate an unsymmetrical structure, unlike that established previously for the related complexes (**2**; R = H, CF_3, or $SiMe_3$; R' = H). Moreover, the bridging carbonyl observed in the infrared spectrum of **5** is inconsistent with a structure analogous to that established previously for the σ,π-allyl complexes **3**. It is evident that the CMe_2 complex **5** has a structure different from those of complexes previously isolated in these investigations.



(5a)



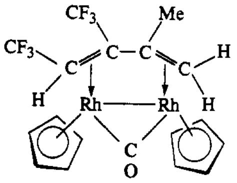
(5b)



(5c)

It does seem likely that CMe_2 has condensed with the alkyne in the new product **5**, and we have considered three possible structures for the complex. These are shown in **5a**–**5c**. Each of the bonding modes has been recognized in other complexes, most of which have been structurally characterized. The binuclear iron complex $(\eta\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CHCH{=}C(Me)H\}$[6] incorporates a "σ-alkylidene–(free) vinyl" ligand like that shown in **5a**. The σ,π-"alkylidene–vinyl" coordination shown in **5b** also applies for the complexes $(\eta\text{-}C_5H_5)_2M_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(R)C(R)CHMe\}$ (M = Fe, R = CO_2Me;[6] M = Ru, R = Ph[7]). In these two representations, the alkylidene carbon is equidistant from the two metal atoms. The σ,π-allylic bonding depicted in **5c** has been observed in $Fe_2(CO)_6\{C(Ph)C(Ph)CHPh\}$[8] and $(\eta^4\text{-}COD)_2Ir_2\{C(Ph)C(Ph)CH_2\}$.[9] The equivalence of the C–C distances within the allylic unit is a characteristic of these structures.

The distinctions between the three proposed structures **5a**–**5c** are fine and are not readily achieved by spectroscopic means. Therefore, an X-ray crystallographic study of the complex was undertaken. Surprisingly, the structure determined is not consistent with any of the proposed structures. It is evident that complex **5** has undergone an intramolecular rearrangement in solution during the attempt to grow crystals suitable for X-ray crystallography. A 1,4-proton shift has occurred to form the new complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(CF_3)HC(CF_3)C(Me)CH_2\}$ (**6**). A view of the molecular structure which includes the atom labeling scheme is presented in Figure 1.



(6)

A metal—metal single bond is indicated by the Rh—Rh distance of 2.6846(4) Å. There is slight asymmetry in the attachment of the bridging carbonyl to this Rh—Rh bond, with a 0.073-Å difference in the two Rh—C(O) bond distances. The major feature of the structure is the bridging unit, $CH(CF_3){=}C(CF_3)C(Me){=}CH_2$. The bond parameters indicate that this is reasonably described as a bridging diene; the C(1)—C(2), C(2)—C(3), and C(3)—C(4) distances are 1.439(6), 1.500(6), and 1.427(6) Å, respectively, and the bond angles indicate sp^2 hybridization for the carbons. The coordinated alkene distances are similar to those found in other alkene–dirhodium com-

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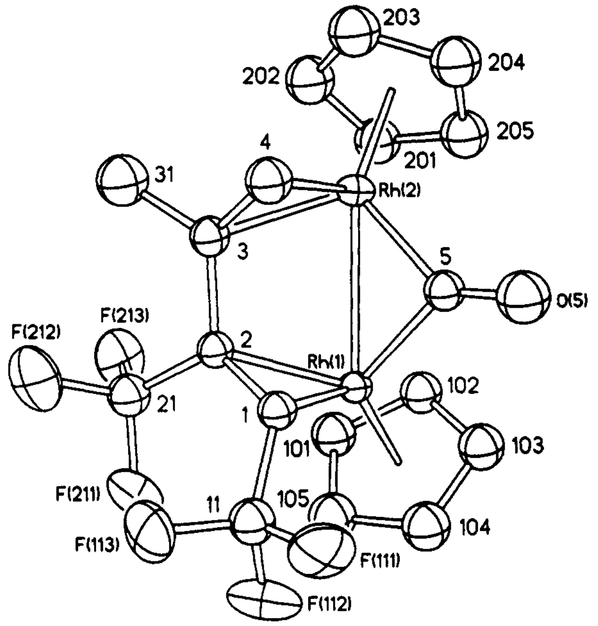

Figure 1. Molecular structure and atom labeling scheme for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)H{=}C(CF_3)CMe{=}CH_2\}$ (6). The hydrogen atom on C(1) and the two hydrogens on C(4) were not detected.

plexes including $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)C(O)C(Me)\text{-}C(Me)\}$[10] and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH{=}CHCN)\{\mu\text{-}C(CF_3)C\text{-}(CF_3)H\}$.[11] The bridging diene adopts the well-known[12,13] *s-cis*-η^2:η^2-conformation, and each alkene unit interacts with just one of the rhodium atoms. The two cyclopentadienyl rings are mutually *cis* with respect to the Rh—Rh bond, and there are no unusual features in their attachments to the rhodium atoms.

The plane defined by Rh(2), C(3), and C(4) (plane 1) is approximately perpendicular to the plane which includes Rh(1), Rh(2), C(2), and C(3) (plane 2), the dihedral angle being 97.4°. Plane 3 [Rh(1), C(1), C(2)] subtends an angle of 68.6° with plane 2. The methyl group, corresponding to C(31), is displaced by 1.963(11) Å from plane 1; this is reflected in the C(31)–C(3)–C(4) angle of 116.9(5)°.

It is interesting that *s-cis*-η^2:η^2-diene complexes of this type cannot be formed by direct reaction of dienes with 1. Instead, alkenyl complexes of the form $(\eta\text{-}C_5H_5)_2Rh_2\text{-}(\mu\text{-diene-H})\{\mu\text{-}C(CF_3)C(CF_3)H\}$ are produced.[14]

Having established the solid structure of this complex, it was important to show that the spectroscopic properties of the recrystallized sample 6 were different from those of the original sample 5. Not surprisingly, the mass spectra of the two samples are virtually identical. However, in the infrared spectra, the carbonyl absorption is shifted by 50 cm^{-1} to lower frequency upon conversion of 5 to 6. There are also major differences in the NMR spectra. The ^1H NMR spectrum of 6 reveals inequivalent cyclopentadienyl resonances at δ 5.66 and 5.61. A well resolved quartet resonance at δ 2.24 is assigned to the unique methyl group. The splitting of 2.4 Hz arises from coupling with a CF_3 group; coupling of similar magnitude is observed in the related complex $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C_4(CF_3)_2Me(CO_2Me)\}$.[15] There is a substantial difference in the chemical shifts (δ 0.79 and 2.68) of the two chemically inequivalent vinylic protons H_a and H_b on C(6). It is known that in the ^1H NMR spectra of diene–metal complexes, the signals of *anti* protons on the terminal carbon atom appear at higher field than those of *syn* protons.[16,17] On the basis of these results, the low field resonance at δ 2.68 can be assigned to the *syn* proton H_a, and the higher field resonance to the *anti* proton H_b. Each of these proton resonances appears as a well resolved triplet due to accidental degeneracy of the coupling constants $J(H_a\text{–}H_b)$ and $J(Rh\text{–}H_a/H_b)$. There is a further peak of relative intensity 1H at δ 0.95 in the ^1H NMR spectrum, and this is assigned to the remaining vinylic proton H_c. It is a quartet of multiplets, with the quartet splitting of 11 Hz arising from coupling to CF_3, and the additional unresolved splitting due to coupling to a rhodium atom.

There are two resonances of equal intensity at δ −47.6 and −51.6 in the ^{19}F NMR spectrum. The low field resonance has the appearance of a 1:4:6:4:1 quintet, but we believe that it is best viewed as two overlapping 1:3:3:1 quartets with $J(F\text{–}F) = J(F\text{–}H) = 11$ Hz. We assign this resonance to the CF_3 group attached to C(1). The higher field resonance is an unresolved multiplet and is assigned to the CF_3 group on C(2). These assignments are consistent with those for related complexes incorporating the $C(CF_3)C(CF_3)H$ unit within a ligand.[18-22] Resonances for all CH_x carbon atoms and one of the CF_3 carbons were clearly discerned in the ^{13}C NMR spectrum, and the chemical shifts and splittings arising from C–F and C–Rh couplings (see Experimental Section) are again consistent with retention of the solid state structure.[10,23] Assignment of the unique CH, CH_2, and CH_3 resonances was confirmed by use of the DEPT sequence.

In organometallic chemistry, there are many other examples of internal hydrogen migrations involving methyl groups.[24] For example, the formation of $[MoFe\{\mu\text{-}C(R)C\text{-}(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)]$ from $[MoFe(\mu\text{-}CR)(CO)_6(\mu\text{-}C_5H_5)]$ and $MeC{\equiv}CMe$ results from an initial coupling reaction followed by a 1,3-hydrogen shift.[25] Examples of 1,4-hydrogen shifts are rare, but one has been reported recently.[26] The 1,1-dimethylallene complex $NiMo(CO)_2\text{-}\{\mu\text{-}\eta^2{:}\eta^2\text{-}CMe_2{=}C{=}CH_2\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ isomerizes on silica gel to form $NiMo(\mu\text{-}CO)(CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)C\text{-}(Me)CH_2\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$. A deuterium labeling study indicated that a 1,4-proton migration, rather than a 1,2-methyl migration, had indeed occurred. We propose that the conversion of 5 to 6 also involves a 1,4-proton

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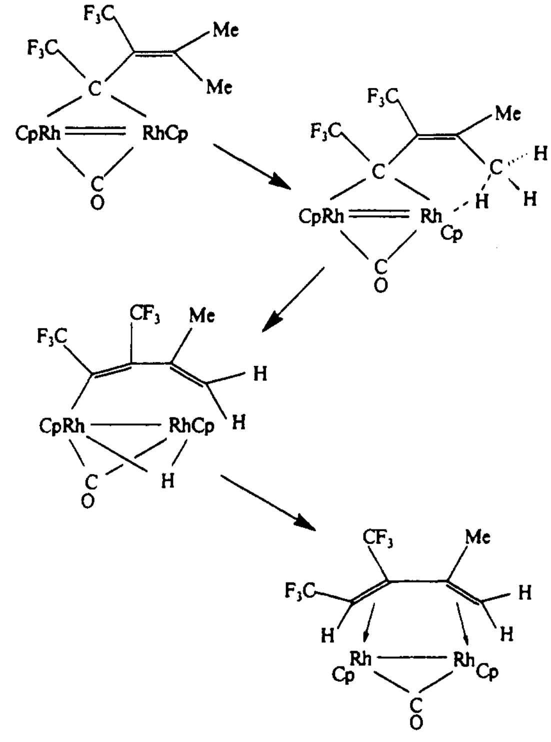
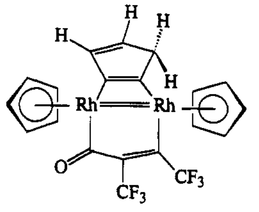
Scheme I. Proposed Pathway for the Formation of Complex 6, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(CF_3)H{=}C(CF_3)CMe{=}CH_2\}$, from Complex 5, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}(CF_3)C_2(CF_3){\cdot}CMe_2)$

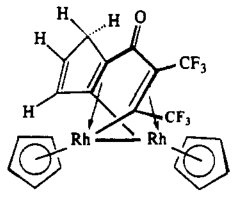


shift. A possible pathway for the conversion, which implicates an agostic C—H—Rh interaction and a bridging hydrido intermediate, is shown in Scheme I.

Reaction with $N_2C_5H_4$. Within 30 min of mixing solutions of 1 and $N_2C_5H_4$ at room temperature, a red-brown powder had deposited from a brown solution. Purification of the powder gave a complex of formula $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3{\cdot}CO\}(C_5H_4)$ (7) in greater than 60% yield. The mass spectrum shows a prominent parent ion, as well as a peak corresponding to loss of one CO from the molecular ion. In the infrared spectrum, an absorption at 1680 cm^{-1} indicates that the carbonyl is ketonic. Molecular asymmetry is indicated by the NMR spectra (see Experimental Section), which reveal two cyclopentadienyl and two trifluoromethyl resonances. These data, supported by microanalysis results, indicate that nitrogen has been lost from the diazo compound to yield complex 7.



(7a)



(7b)

We probed the mode of attachment of the C_5H_4 unit in 7 by analysis of the ^1H and ^{13}C NMR spectra. In the ^1H spectrum, there are four signals each of relative intensity 1H that can be assigned to the C_5H_4 protons. Two of these fall in the olefin region (δ 7.09 and 6.17) and the other two in the aliphatic region (δ 3.12 and 2.49) of the spectrum. This is inconsistent with the $\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4$[27–29] and $\mu\text{-}\eta^1\text{-}C_5H_4$[27] modes of attachment that have been reported previously for cyclopentadienyl type C_5H_4 ligands in binuclear complexes. Instead, it indicates that a 1,2-hydrogen shift has occurred to yield formally a $\overline{C{\equiv}CCH_2\text{-}CH{=}CH}$ unit. The coupling network involving the four protons in this unit was disclosed from a ^1H—^1H COSY spectrum, and our detailed assignments of the ^1H NMR data are given in the Experimental Section. In the ^{13}C NMR spectrum, only three of the five C_5H_4 carbons were detected, and this is again consistent with a hydrogen shift that leaves two of the carbons without attached hydrogens. Assignment of the CH and CH_2 resonances was confirmed by use of the DEPT sequence.

In principle, the cyclic "ene–yne" could be attached as an alkyne directly to the Rh–Rh bond as in **7a**, or it could condense with the $CF_3C_2CF_3$ and CO ligands to produce a bridging pentadienone ligand as in **7b**. There are some osmium complexes that provide reasonable models for the alkyne–metal bonding in **7a**. Thus, the cluster complexes $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}C_5H_4)$[30] and $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-indyne})$[31] have been characterized, and the C_5 ring in each is attached as an "ene–yne". Moreover, the binuclear complex $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-SPh})$ and the cluster complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-SPh})(\mu\text{-}H)$, each of which contains a cyclobutyne ligand, have been characterized by single-crystal X-ray diffraction analysis.[32] Thus there is no impediment to the formation of a complex of the type **7a**.

In previous investigations, we have characterized the dimetallacycloheptadienone complexes $Cp_2Rh_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)C(O)CRCR')\}$[33] that are formally analogous to **7b**; these complexes are formed by addition of alkynes RC≡CR′ to 1. Clearly, it is also possible for this type of complex to be formed from 1 and the "ene–yne" fragment, or even from an intramolecular condensation reaction involving **7a**. Regretably, we were not able to eliminate either of the possible structures **7a** or **7b** from the available spectroscopic results. Despite considerable effort, we were not able to obtain crystals of suitable quality for X-ray analysis.

Reactions of 1 with $N_2C(CO_2Me)_2$ and $N_2C(CO_2\text{-}t\text{-}Bu)_2$. Our earlier investigations of the reactions of 1 with diazoalkanes included two systems with esters as substituents. The reaction with the diazoacetate, $N_2CH(CO_2Et)$, produced the complex 2 (R = H; R′ = CO_2Et)[2] which converted relatively slowly to 3. Monitoring of the conversion by NMR spectroscopy revealed two isomers of each complex, and there was an interesting twist of the alkylidene about the newly formed C–C bond after transfer to the alkyne carbon. When the diazomalonate $N_2C(CO_2$-

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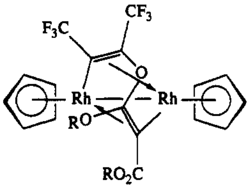
$Et)_2$ was used, complex **2** ($R = R' = CO_2Et$)[1] was again formed initially, but this time the condensation reaction followed a markedly different course to give the divinyl ether complex (**8**, R = Et). The repeated observation that the reactions between **1** and NCRR′ are extremely sensitive to the nature of the substituents led us to examine the reactions of **1** with $N_2C(CO_2Me)_2$ and $N_2C(CO_2\text{-}t\text{-}Bu)_2$. These reactions are affected by the size of the alkyl group within the ester function.

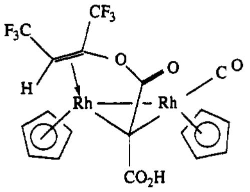


(**8**)

Rapid reactions were observed upon addition of an excess of the diazomalonates to solutions of **1**. The major products obtained in high yields were red crystalline solids, and spectroscopic results (see Experimental Section) for the two complexes indicated bridging alkylidene structures **2**, $R = R' = CO_2Me$ or $CO_2\text{-}t\text{-}Bu$. Key features of the spectra for the methyl complex match those for the analogous complex **2** with $R = R' = CO_2Et$. When R and R′ are $CO_2\text{-}t\text{-}Bu$, there are indications of slight asymmetry in the molecule which we believe is induced by the bulk of the alkyl groups.

Repeated TLC of **2** ($R = R' = CO_2Me$) resulted in formation of small amounts of an orange-red compound. The same compound was obtained in greater than 40% yield by sunlight irradiation for 1 week. Spectroscopic and analytical data (see Experimental Section) are consistent with formation of the divinyl ether complex **8** (R = Me). There is a good match of the spectroscopic features of this and the related complex with R = Et which has been structurally characterized.[1]

Sunlight irradiation of **2** ($R = R' = CO_2\text{-}t\text{-}Bu$) yielded two products in approximately equal amounts (30–40% yields). Both were very air sensitive compounds, and neither could be obtained analytically pure. However, each was characterized from analysis of the spectroscopic data. One of the products is clearly the divinyl ether complex (**8**; R = *t*-Bu). The second is formulated as a carboxylic acid derivative $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{CH(CF_3){=}C(CF_3)OC(O)C(CO_2H)\}$ (**9**).



(**9**)

The mass spectrum of **9** shows a molecular ion peak and fragment peaks corresponding to the loss of CO and [H + COOH]. Absorptions for the terminal carbonyl (at 2020 cm^{-1}) and the carboxylate group (at 1720 and 1660 cm^{-1}) are clearly seen in the infrared spectrum. The ^1H NMR spectrum includes peaks for two cyclopentadienyl groups, the proton of a $C(CF_3){=}C(CF_3)H$ moiety, and a broad low field resonance at δ 10.8 which we assign to the acidic proton of a carboxylate group.

We propose that the formation of **9** occurs by a two step process. The first involves a metal catalyzed hydrolysis of both ester functions in **2** with $R = R' = CO_2\text{-}t\text{-}Bu$ to produce **2** with $R = R' = CO_2H$. A trace of adventitous water in the system would be sufficient to achieve this conversion. We note that the metal ion catalyzed hydrolysis of esters is well-known.[34] In the second step, concomitant proton transfer from one carboxylate group to an alkyne carbon and C–O bond formation involving the deprotonated oxygen and the other alkyne carbon would produce the bridging ligand in **9**. We have encountered several examples of proton transfers of the type proposed,[35–37] and the condensation reaction is similar to those described above for the diesters.

Conclusions

Two fundamentally different pathways can be followed when **1** is treated with diazoalkanes at room temperature. Sometimes nitrogen is eliminated; at other times it is retained. After the initial reaction, a variety of different rearrangement pathways can be followed. In this paper alone, seven different types of final products are described. Can a rationale be developed for this remarkable diversity of reactions?

In Scheme II, we show two pathways that may be followed. We propose that initial attack is always through the terminal nitrogen of the diazoalkane to yield (a). There are many reports of $\mu\text{-}\eta^1$-coordination of diazoalkanes to dinuclear complexes, with $(t\text{-}BuO)_6W_2\{\mu\text{-}N_2C(C_6H_4Me)_2\}$[38] and $Rh_2\{\mu\text{-}N_2CH(CO_2Et)\}(CO)_2(dppm)_2$[39] being typical examples. Conversion of (a) to the bridging diazoalkane intermediate (b) could be followed by rearrangement to a cyclic intermediate (c) which is then able to eliminate nitrogen to produce the bridging alkylidene product (d). A similar mechanism has been proposed for the conversion of $(\eta\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^1\text{-}N_2CAr_2)$ to $(\eta\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}CAr_2)$.[40] For the dirhodium system, it is apparent that this pathway can be followed provided the steric bulk of one of the diazoalkane substituents is small. Thus the reactions with N_2CHR all proceed with facile elimination of nitrogen.

The reaction chemistry of disubstituted diazoalkanes N_2CCR' with **1** is considerably more complex. With these systems, we propose that formation of (b) is again the initial step. However, the subsequent steps are influenced by both steric and electronic factors. If R and R′ are small and electron donating (e.g. R = R′ = Me), the conversion of (b) to (d) through (c) can still occur. It should be noted however that the reaction of **1** with N_2CMe_2 gives two products, one of which retains nitrogen. Clearly, there is some steric inhibition to this pathway with disubstituted diazoalkanes. An alternative pathway can then be followed, and this involves the conversion of (b) to (f) possibly through an intermediate such as (e). This pathway is strongly favored, for example, in the reaction of **1** with

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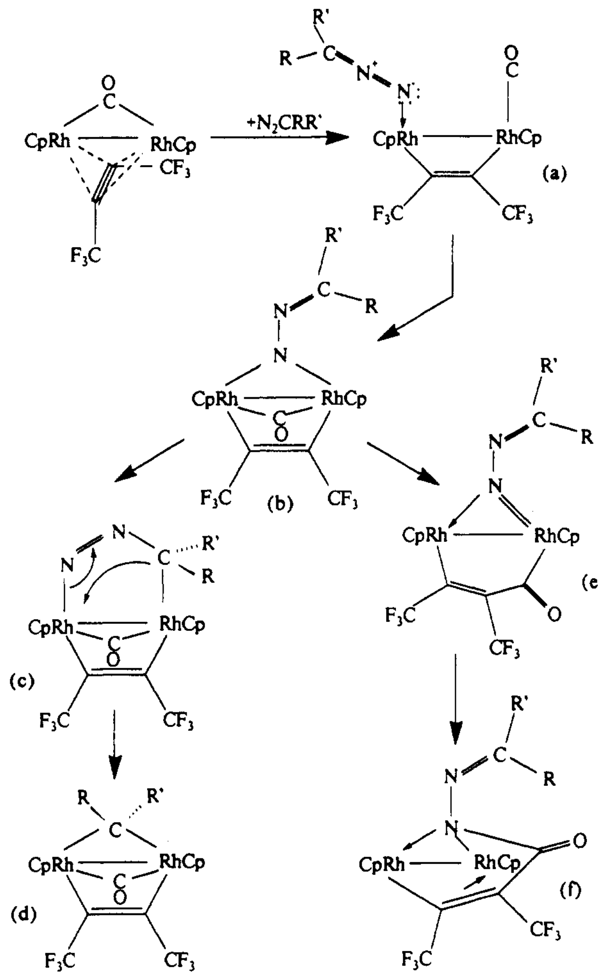
Scheme II. Possible Rearrangements of the Intermediate Formed in the Reactions of 1 with Diazoalkanes



N_2CPh_2. The reaction with $N_2C(t\text{-}Bu)_2$ seems to be a special case, with the diazoalkane acting as a 1,3-dipole and adding across the polar $\mu\text{-}C^+{=}O^-$ bond.[3] The very large substituents in this case probably inhibit access to the Rh—Rh bond.

The chemistry of these systems can be modified by electronic factors. In the reactions with $N_2C(CO_2R)_2$ and $N_2C_5H_4$, we propose that delocalization of π-electron density from the substituents onto the diazoalkane carbon renders this atom more nucleophilic and hence better able to form an alkylidene–rhodium bond with elimination of nitrogen. The subsequent rearrangement reactions that occur in these and other systems are presumably in response to steric strain or the favorable proximity of reactive atoms within the intermediates formed.

The study of the addition of diazoalkanes to 1 has certainly exposed a rich diversity of reaction pathways and bonding modes. It emphasizes how crucial the substituent effects can be in organometallic chemistry.

Experimental Section

The general experimental procedures and instrumentation used are described in a previous paper.[4] The diazoalkanes N_2CMe_2,[41] $N_2\overline{\text{CCHCHCHC}}\text{H}$,[42] $N_2C(CO_2Me)_2$,[43] and $N_2C(CO_2\text{-}t\text{-}Bu)_2$[43] were prepared by published procedures and were used without isolation. The dirhodium complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ was prepared by the literature procedure.[44]

Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) with N_2CR_2. N_2CMe_2. Under reduced pressure (50 mmHg) with a bleed of dry nitrogen, excess 2-diazopropane and diethyl ether were codistilled into a solution of 1 (0.145 g) in diethyl ether (10 mL) cooled to −78 °C. Nitrogen was admitted until a pressure of 1 atm was achieved, and the reaction mixture was allowed to warm to room temperature. Within 5 min, the color of the solution had changed from green to deep red. Removal of some solvent and TLC with a 2:3 mixture of dichloromethane/hexanes as eluent separated two major bands from minor products which were not extracted. The first brown band (R_f = 0.7) was extracted with dichloromethane. Subsequent evaporation of solvent yielded fine red-brown crystals of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3{\cdot}CMe_2)$ (5) (0.031 g, 20%), mp 153 °C. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1860 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (d, 5H, J(Rh–H) = 0.7 Hz, C_5H_5), 5.32 (d, 5H, J(Rh–H) = 0.8 Hz, C_5H_5), 1.49 (s, 3H, CH_3), 1.19 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ −53.6 (m, 3F, CF_3), −57.7 (m, 3F, CF_3); MS *m/z* (relative intensity) 568 (5, M^+), 538 (20, $[M - 2Me]^+$), 372 (12, $[(C_5H_5)Rh(CF_3C_2CF_3)CMe_2]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

Slow recrystallizations of **5** from toluene/hexane gave well formed, red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3{\cdot}CMe_2)$ (6). Anal. Calcd for $C_{18}H_{16}F_6ORh_2$: C, 38.0; H, 2.8; F, 20.1. Found: C, 37.9; H, 2.8; F, 19.9. However, the mp (168 °C) and spectroscopic properties of the recrystallized complex (6) were significantly different from those of the initial product (5). Spectroscopic data for (6): IR (CH_2Cl_2) ν(CO) 1810 (vs) cm^{-1}; ^1H NMR (acetone-d_6) δ 5.66 (s, 5H, C_5H_5), 5.61 (d, 5H, J = 0.8 Hz, C_5H_5), 2.68 (t, 1H, J(H–H) = J(Rh–H) = 2.4 Hz, CH_2), 2.24 (q, 3H, J = 2.4 Hz, CH_3), 0.95 (qm, 1H, J(H–F) = 11.0 Hz, $CH(CF_3)$), 0.79 (t, 1H, J(H–H) = J(Rh–H) = 2.4 Hz, CH_2); ^{19}F NMR (acetone-d_6) δ −47.6 (m, 3F, J(H–F) = J(F–F) = 11 Hz and J(Rh–F) = 2.4 Hz, $C(H)CF_3$), −51.6 (m, 3F, CF_3); ^{13}C NMR ($CDCl_3$) δ 128.0 (q, J(F–C) = 274 Hz, CF_3), 91.0 (d, J(Rh–C) = 4 Hz, C_5H_5), 90.0 (d, J(Rh–C) = 4 Hz, C_5H_5), 38.0 (qd, J(F–C) = 39 Hz and J(Rh–C) = 20 Hz, $CH(CF_3)$), 32.0 (d, J(Rh–C) = 15 Hz, CH_2), 28.0 (d, (br) $J \approx 5$ Hz, CH_3); MS *m/z* (relative intensity) 568 (5, M^+), 538 (20, $[M - 2Me]^+$), 372 (8, $[(C_5H_5)Rh(CF_3C_2CF_3)CMe_2]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

The second band (R_f = 0.1) afforded red-brown crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}CF_3C_2CF_3{\cdot}CO{\cdot}N_2CMe_2\}$ (4) (0.049 g, 30%). The compound was characterized spectroscopically: IR (CH_2Cl_2) ν(CO) 1670 (m), other bands at 1620 (s), 1590 (m), 1520 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.65 (d, 5H, J(Rh–H) = 0.9 Hz, C_5H_5), 5.25 (s, 5H, C_5H_5), 1.96 (s, 3H, CH_3), 1.74 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ −47.8 (m, 3F, CF_3), −57.4 (q, 3F, J(F–F) = 13 Hz, CF_3); MS *m/z* (relative intensity) 596 (11, M^+), 581 (1, $[M - CH_3]^+$), 568 (1, $[M - N_2/CO]^+$), 526 (10, $[M - N_2CMe_2]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

$N_2C_5H_4$. A slight excess of diazocyclopentadiene was injected into a cooled solution (0 °C) of 1 (0.290 g) in hexane (10 mL). During the time it took the solution to warm to room temperature, the color changed from green to brown. The solution was stirred for a further 30 min. A red-brown powder which had deposited was isolated by filtration, dissolved in dichloromethane, and purified by two cycles of preparative radial chromatography with a 2:1 mixture of dichloromethane/hexanes as eluent. This separated several minor products from one major orange-red band. Solvent was evaporated from the latter to give orange-red microcrystals of $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}C_5H_4)$ (7) (0.167 g, 62%), mp 210 °C dec. Anal. Calcd for $C_{20}H_{14}F_6ORh_2$: C, 40.7; H, 2.4; F, 19.3. Found: C, 40.4; H, 2.3; F, 19.3. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1690 (sh), 1680 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.09 (dt, 1H, J(H–H) = 5.2 and 2.0 Hz, C_5H_4), 6.17 (dt, 1H, J(H–H) = 5.2 and 2.0 Hz, C_5H_4), 5.58 (s, 5H, C_5H_5),

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Table I. Final Positional and Thermal Parameters for (η-C_5H_5)$_2$$Rh_2$($\mu$-CO){$\mu$-$\eta^2$:$\eta^2$-C($CF_3$)H=C($CF_3$)CMe=$CH_2$} (6) with Esd Values in Parentheses

atom	x	y	z	U(iso) (Å^2)[a]
Rh(1)	0.21232(3)	0.38311(4)	0.00788(4)	0.0219(1)
Rh(2)	0.23845(3)	0.09822(4)	−0.18810(4)	0.0254(1)
F(111)	−0.0081(3)	0.3440(4)	0.3124(5)	0.055(2)
F(112)	0.1333(3)	0.5521(4)	0.3768(5)	0.059(2)
F(113)	0.1391(4)	0.3762(6)	0.4733(4)	0.066(2)
F(211)	0.3444(3)	0.5432(4)	0.3939(4)	0.052(1)
F(212)	0.3835(3)	0.3413(5)	0.4150(4)	0.056(1)
F(213)	0.4598(2)	0.4376(4)	0.2441(4)	0.051(1)
C(1)	0.1484(4)	0.2952(5)	0.1846(5)	0.025(1)
C(11)	0.1070(4)	0.3939(6)	0.3356(6)	0.034(1)
C(2)	0.2623(3)	0.2843(5)	0.1696(5)	0.024(1)
C(21)	0.3604(4)	0.4017(6)	0.3041(6)	0.034(1)
C(3)	0.2788(4)	0.1244(5)	0.0675(6)	0.028(1)
C(31)	0.3912(5)	0.0936(7)	0.0982(8)	0.049(1)
C(4)	0.1833(4)	−0.0141(6)	−0.0214(7)	0.036(1)
C(5)	0.1037(4)	0.1729(5)	−0.1601(6)	0.029(1)
C(101)	0.3520(5)	0.6039(7)	0.0146(7)	0.042(1)
C(102)	0.2847(4)	0.5233(6)	−0.1446(7)	0.037(1)
C(103)	0.1704(5)	0.5280(7)	−0.1284(7)	0.042(1)
C(104)	0.1682(5)	0.6105(7)	0.0428(8)	0.046(1)
C(105)	0.2795(5)	0.6558(7)	0.1329(8)	0.046(1)
C(201)	0.3663(5)	0.1491(7)	−0.3627(7)	0.044(1)
C(202)	0.3938(5)	0.0369(7)	−0.3133(8)	0.048(1)
C(203)	0.2908(5)	−0.1022(7)	−0.3651(8)	0.050(1)
C(204)	0.2045(5)	−0.0573(7)	−0.4548(8)	0.048(1)
C(205)	0.2508(5)	0.0842(7)	−0.4454(7)	0.045(1)
O(5)	0.0067(3)	0.1294(5)	−0.2170(5)	0.048(1)

Anisotropic Thermal Parameters[b]

atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Rh(1)	0.0264(2)	0.0205(2)	0.0201(2)	0.0096(1)	0.0044(1)	0.0079(1)
Rh(2)	0.0288(2)	0.0196(2)	0.0257(2)	0.0087(1)	0.0050(1)	0.0057(1)
F(111)	0.035(2)	0.066(2)	0.060(2)	0.021(2)	0.021(2)	0.017(2)
F(112)	0.076(2)	0.036(2)	0.055(2)	0.019(2)	0.031(2)	0.005(2)
F(113)	0.082(3)	0.109(3)	0.028(2)	0.055(2)	0.019(2)	0.031(2)
F(211)	0.052(2)	0.043(2)	0.035(2)	0.005(1)	−0.007(1)	−0.003(1)
F(212)	0.050(2)	0.078(2)	0.040(2)	0.009(2)	−0.013(1)	0.031(2)
F(213)	0.024(1)	0.065(2)	0.055(2)	0.001(1)	0.003(1)	0.024(2)

[a] Equivalent isotropic temperature factors for Rh and F are defined as one-third of the orthogonalized U tensor (Å^2). [b] Of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$

5.09 (s, 5H, C_5H_5), 3.12 (dt, 1H, J(H–H) = 22.8 and 2.0 Hz, C_5H_4), 2.49 (dm, 1H, J = 22.8 Hz, C_5H_4); ^{19}F NMR ($CDCl_3$) δ −52.3 (qd, 3F, J(F–F) = 12 and J(Rh–F) = 2.0 Hz, CF_3), −55.4 (q, 3F, J(F–F) = 12 Hz, CF_3); ^{13}C NMR ($CDCl_3$) δ 198.0 (br s, CO), 143.9 (s, C^2 H), 135.6 (s, C^3 H), 88.7 (d, J(Rh–C) = 5 Hz, C_5H_5), 88.3 (d, J(Rh–C) = 5 Hz, C_5H_5), 41.5 (s, CH_2); MS m/z (relative intensity) 590 (95, M^+), 562 (8, $[M - CO]^+$), 542 (25, $[M - CO - HF]^+$), 496 (23, $[M - C_2CF_3H]^+$), 400 (53, $[M - CF_3C_2CF_3 - C_3H_2]^+$), 383 (23, na), 375 (33, $[M - CF_3C_2CF_3 - C_5H_3]^+$), 355 (20, na), 233 (100, $[C_{10}H_{10}Rh]^+$).

$N_2C(CO_2Me)_2$. An excess of dimethyl diazomalonate in diethyl ether was added to a cold (0 °C) solution of 1 (0.120 g) in diethyl ether (15 mL). Within 15 s, the color of the solution had changed from green to orange-brown. Solvent was removed, the residue was dissolved in dichloromethane, and two products were separated by TLC with a 8:1 mixture of dichloromethane/hexanes as eluent. The minor product (R_f = 0.7) was identified spectroscopically[45] as (η-C_5H_5)$_2$$Rh_2${$\mu$-C($CF_3$)C($CF_3$)C(O)N($SO_2C_6H_4$-Me)}; this was formed from p-$MeC_6H_4SO_2N_3$, an impurity from the preparation of the diazoalkane. The major product (R_f = 0.4) was isolated as red crystals which were recrystallized from dichloromethane/hexane and dried in a vacuum. This gave (η-C_5H_5)$_2$$Rh_2$($\mu$-CO){$\mu$-C($CO_2Me$)$_2$}($\mu$-$CF_3C_2CF_3$) (2; R = R′ = CO_2Me) (0.120 g, 80%), mp 132 °C. Anal. Calcd for $C_{20}H_{16}F_6O_5Rh_2$: C, 36.6; H, 2.5; F, 17.4. Found: C, 36.7; H, 2.4; F, 17.3. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1880 (vs), 1710 (m), 1670 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.55 (s, 10H, 2 × C_5H_5), 3.69 (s, 3H, CH_3), 3.62 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ −54.5 (s, CF_3); MS m/z (relative intensity) 656 (<10, M^+), 628 (40, $[M - CO]^+$), 569 (100, $[M - CO - CO_2Me]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

When a solution of 2 with R = R′ = CO_2Me in dichloromethane was rechromatographed by TLC with an 8:1 mixture of dichloromethane/hexanes as eluent, there was evidence of a new red band. Repeated TLC progressively increased the amount of the new band (R_f = 0.4) at the expense of the old (R_f = 0.7). The conversion was ca. 50% after three applications to a TLC plate. Removal of solvent from the accumulated red bands gave orange-red crystals of (η-C_5H_5)$_2$$Rh_2${$\mu$-C($CF_3$)C($CF_3$)C($CO_2Me$)$_2$} (3; R = R′ = CO_2Me), mp 160 °C. Anal. Calcd for $C_{19}H_{16}F_6O_4Rh_2$: C, 36.3; H, 2.6; F, 18.2. Found: C, 36.5; H, 2.4; F, 18.3. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1690 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.41 (s, 5H, C_5H_5), 5.38 (s, 5H, C_5H_5), 3.76 (s, 3H, CH_3), 3.52 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ −48.6 (qm, 3F, J(F–F) = 12 Hz, CF_3), −61.7 (qm, 3F, J(F–F) = 12 Hz, CF_3); MS m/z (relative intensity) 628 (38, M^+), 609 (<10, $[M - F]^+$), 581 (<10, $[M - F - CO]^+$), 569 (95, $[M - CO_2Me]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

The conversion of 2 with R = R′ = CO_2Me to 3 with R = R′ = CO_2Me could also be achieved by exposure of solutions of the former complex to Pyrex filtered sunlight for 1 week (>40% conversion).

N_2C{CO_2(t-Bu)}$_2$. The hexane solution of the crude di-*tert*-butyl diazomalonate contained a small amount of p-MeC_6H_4-SO_2N_3. When the solution of ligand was added to a cooled solution

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(0 °C) of **1** in hexane, the azide reacted preferentially, resulting in the immediate formation of crimson crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)C(O)N(SO_2C_6H_4Me)\}$. These were removed immediately by filtration of the cold solution. The filtrate now contained **1** (remaining mass available for reaction, 0.190 g) and an excess of pure $N_2C(CO_2\text{-}t\text{-}Bu)_2$. This solution was allowed to warm to room temperature; within a short time, red crystals precipitated. These were isolated by filtration and washed with hexane to give $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(CO_2\text{-}t\text{-}Bu)_2\}(\mu\text{-}CF_3C_2CF_3)$ (**2**; R = R′ = CO_2-*t*-Bu) (0.241 g, 90%), mp 139 °C dec. Anal. Calcd for $C_{26}H_{28}F_6O_5Rh_2$: C, 42.2; H, 3.8; F, 15.4. Found: C, 42.0; H, 3.7; F, 15.3. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1880 (vs), 1690 (sh), 1680 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.56 and 5.52 (2 × overlapping br s, 2 × 5H, 2 × C_5H_5), 1.53 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ −53.6 (m, 3F, CF_3), −54.2 (m, 3F, CF_3); MS *m/z* (relative intensity) 712 (<10, $[M - CO]^+$), 656 (3, $[M - CO - C_4H_8]^+$), 600 (4, $[M - CO - (2 \times C_4H_8]^+$), 582 (18, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)(C_2O_3)]^+$).

A solution of **2** with R = R′ = CO_2-*t*-Bu (0.097 g) in a mixture of toluene and hexane (15 mL) was exposed to Pyrex filtered sunlight for 2 weeks. Solvent was then removed from the orange-red solution, and products were separated by TLC with dichloromethane as eluent. Two major bands developed. Evaporation of solvent from the first band (R_f = 0.8) gave red crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)C(CO_2\text{-}t\text{-}Bu)_2\}$ (**3**; R = R′ = CO_2-*t*-Bu) (0.032 g, 33%), mp 100 °C dec. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 1680 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (s, 5H, C_5H_5), 5.23 (d, 5H, *J*(Rh–H) = 0.7 Hz, C_5H_5), 1.51 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ −47.7 (qd, 3F, *J*(F–F) = 12 Hz and *J*(Rh–F) = 2 Hz, CF_3), −61.9 (qm, 3F, *J*(F–F) = 12 Hz, CF_3); MS *m/z* (relative intensity) 712 (<1, M^+), 656 (3, $[M - C_4H_8]^+$), 600 (2, $[M - (C_4H_8)_2]^+$), 582 (18, $[M - (C_4H_8)_2 - O]^+$), 526 (12, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)(CO)]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). Although this compound was spectroscopically pure, satisfactory microanalyses could not be obtained.

The orange solid isolated from the other band (R_f = 0.1) yielded orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}CH(CF_3)C(CF_3)OC(O)C(CO_2H)\}$ (**9**) (0.032 g, 39%), mp 162 °C. Spectroscopic data: IR (CH_2Cl_2) ν(CO) 2020 (vs), 1720 (s), 1660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.8 (m br, 1H, COOH), 5.79 (s, 5H, C_5H_5), 5.39 (s, 5H, C_5H_5), 3.88 (q, 1H, *J*(H–F) = 9 Hz, $CH(CF_3)$); ^{19}F NMR ($CDCl_3$) δ −53.5 (pseudoquintet, 3F, *J*(F–F) = *J*(F–H) = 9 Hz, CF_3), −65.9 (q, 3F, *J*(F–F) = 9 Hz, CF_3); MS *m/z* (relative intensity) 628 (1, M^+), 600 (2, $[M - CO]^+$), 582 (8, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)(C_2O_3)]^+$), 554 (4, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)(C_2O_2)]^+$), 526 (6, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)(CO)]^+$), 514 (38, $[(C_5H_5)_2Rh_2(CF_3C_2CF_3)O]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). Although this compound was spectroscopically pure, satisfactory microanalyses could not be obtained.

Crystallography for Complex 6. Crystal data: formula = $C_{18}H_{16}F_6ORh_2$; M = 568.1; space group $P\bar{1}$ (No. 2); cell parameters a = 12.313(2) Å, b = 9.365(2) Å, c = 8.758(2) Å, α = 112.16(1)°, β = 91.97(1)°, γ = 105.40(1)°, V = 891.4(3) Å^3; Z = 2; D_{calcd} = 2.12, D_{measd} = 2.11(1) g cm^{-3} (by flotation in chloroform and 1,1,2,2-tetrabromoethane); $F(000)$ = 552; μ = 18.9 cm^{-1} for Mo Kα radiation (λ = 0.7107 Å), T = 20(1) °C.

Structure Determination. Well formed single crystals of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3\cdot CMe_2)$ were grown from toluene/hexane. A representative dark red tabular crystal of dimensions 0.36 × 0.22 × 0.16 mm was used for data collection. Intensity measurements were made at 295 K on a Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation with 6° < $2\theta \le$ 60°, operating in an ω scan mode with a symmetric scan range of ±(0.75 + 0.3 tan θ)° in ω from the calculated Bragg scattering angle at a scan rate of 0.04° s^{-1}. A total of 5201 unique data were collected, (±*h*,±*k*,±*l*), 4252 of which were considered to be observed [$I \ge 3\sigma(I)$]. Three standard reflections monitored every 4 h showed no significant variation in intensity over the data collection period. Intensity data were processed as described previously.[11] A numerical absorption correction was applied, the maximum and minimum transmission factors being 0.775 and 0.602, respectively. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion.[12] All calculations were performed on a VAX 11/780 computer. The program for least-squares refinement was that of Sheldrick.[13]

Table II. Interatomic Bond Distances and Selected Angles for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(CF_3)H{=}C(CF_3)CMe{=}CH_2\}$ (6), with Esd's in Parentheses

(a) Bond Distances (Å)

Rh(1)–Rh(2)	2.6846(4)	C(11)–F(113)	1.339(8)
Rh(1)–C(5)	2.027(4)	C(11)–F(111)	1.350(6)
Rh(1)–C(1)	2.096(5)	C(2)–C(3)	1.500(6)
Rh(1)–C(2)	2.115(5)	C(2)–C(21)	1.508(5)
Rh(1)–C(104)	2.249(7)	C(21)–F(211)	1.334(6)
Rh(1)–C(103)	2.255(7)	C(21)–F(212)	1.351(8)
Rh(1)–C(102)	2.255(6)	C(21)–F(213)	1.359(6)
Rh(1)–C(105)	2.261(6)	C(3)–C(4)	1.427(6)
Rh(1)–C(101)	2.291(6)	C(3)–C(31)	1.521(9)
Rh(2)–C(5)	1.954(5)	C(5)–O(5)	1.179(6)
Rh(2)–C(4)	2.132(6)	C(101)–C(102)	1.412(7)
Rh(2)–C(3)	2.182(5)	C(101)–C(105)	1.421(9)
Rh(2)–C(203)	2.204(6)	C(102)–C(103)	1.430(8)
Rh(2)–C(205)	2.220(7)	C(103)–C(104)	1.409(8)
Rh(2)–C(204)	2.232(6)	C(104)–C(105)	1.430(9)
Rh(2)–C(201)	2.316(7)	C(201)–C(202)	1.388(11)
Rh(2)–C(202)	2.333(7)	C(201)–C(205)	1.434(8)
C(1)–C(2)	1.439(6)	C(202)–C(203)	1.465(8)
C(1)–C(11)	1.496(7)	C(203)–C(204)	1.430(11)
C(11)–F(112)	1.327(6)	C(204)–C(205)	1.419(9)

(b) Bond Angles (deg)

C(5)–Rh(1)–C(1)	84.4(2)	C(2)–C(1)–C(11)	127.5(4)
C(5)–Rh(1)–C(2)	96.1(2)	C(1)–C(2)–C(3)	119.2(3)
C(1)–Rh(1)–C(2)	40.0(2)	C(1)–C(2)–C(21)	120.4(4)
C(5)–Rh(2)–C(4)	87.1(2)	C(3)–C(2)–C(21)	115.3(4)
C(5)–Rh(2)–C(3)	97.8(2)	C(4)–C(3)–C(2)	120.7(4)
C(4)–Rh(2)–C(3)	38.6(2)	C(4)–C(3)–C(31)	116.9(5)
Rh(2)–C(5)–Rh(1)	84.8(2)	C(2)–C(3)–C(31)	119.8(3)

The structure was solved by conventional Patterson and Fourier methods. Full matrix least-squares refinement employing anisotropic thermal parameters for Rh and F and isotropic thermal parameters for all other atoms reduced R to 0.040 and R' to 0.044, respectively, at convergence, where

$$R' = \sum w^{1/2}(||F_o| - |F_c||)/\sum w^{1/2}|F_o|$$

and $w = [\sigma^2(F_0)]^{-1}$. The goodness of fit value $(\sum w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$ was 2.16. The highest peak in the difference Fourier map was 1.20 e Å^{-3}. Final atomic parameters are given in Table I, selected bond lengths and bond angles are in Table II, and Figure 1 shows the atomic labeling scheme used.

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Supplementary Material Available: Tables of bond angles and equations for planes (4 pages). Ordering information is given on any current masthead page.

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