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Addition of Small Molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. 5.[1] The Formation of Several Different Bridging Diene and Dienone Ligands by the Co-oligomerization of $HC_2\text{-}t\text{-}Bu$ with the Coordinated $CF_3C_2CF_3$

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Six products are obtained when $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ is treated with *tert*-butylacetylene at room temperature; another two are formed during workup of the reaction mixture. Two of the products are isomers of the bridging pentadienone complex $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$. In the major isomer **1** (10% yield), the configuration of the bridging ligand is $-C(CF_3){=}C(CF_3)C(O)C(H){=}C(t\text{-}Bu)-$; the reverse arrangement of H and *t*-Bu is indicated for the minor isomer **2** (5% yield). A metalladiene complex $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}Bu\}$ (**3**) is the major product (29% yield) of the reaction. Only one isomer is obtained, and it has the C(*t*-Bu) and C(H) carbons α and β, respectively, to the ring metal. This product is isolated only when the product mixture is chromatographed on "nonactivated" supports. With oven-dried supports, **3** is converted to a new complex of formula $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuO_2\}$ (**4**). The structure of **4** has been determined from X-ray diffraction data; the bridging ligand is an unsaturated keto–ether of the type $O{=}C(t\text{-}Bu)C(H){=}C(CF_3)OC(CF_3)-$ which is attached to the Rh–Rh bond through the ketonic oxygen, the alkene bond, and the terminal $(CF_3)C$: carbon. Another major product is formulated as $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (**5**) (17% yield). This complex contains a terminal carbonyl and a bridging cyclopentadienone ligand. Crystal structure determination establishes that the bridging ligand is bound to one rhodium by a σ-bond from a $C(CF_3)$ ring carbon and to the other rhodium by an η^3-allyl attachment from $C(CF_3)$=–$C(H)$=–$C(t\text{-}Bu)$. Decarbonylation of this complex with Me_3NO results in opening of the cylopentadienone ring to give complex **1**. The final major product (19% yield) is $(\eta\text{-}C_5H_5)_2Rh_2(C_2H\text{-}t\text{-}Bu)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (**6**). The molecular geometry of **6** has been determined by X-ray analysis. It has two bridging groups. One is a cyclopentadienone ligand which is η^2,η^2-attached to the Rh–Rh bond; the other is a $\mu\text{-}\eta^2$-vinylidene group $C{=}CH\text{-}t\text{-}Bu$. This complex isomerizes during chromatography. The dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (12% yield) is also a product of the reaction. Crystal data: complex **4**, $C_{20}H_{20}F_6O_2Rh_2$, triclinic, $P\bar{1}$, $a = 16.455$ (8) Å, $b = 13.836$ (7) Å, $c = 10.876$ (5) Å, $\alpha = 115.09$ (10)°, $\beta = 98.64$ (10)°, $\gamma = 97.91$ (10)°, $Z = 4$, final $R = 0.052$, $R_w = 0.051$ from 6915 observed reflections (12 595 measured); complex **5**, $C_{22}H_{20}F_6O_2Rh_2$, monoclinic, $P2_1/n$, $a = 14.590$ (7) Å, $b = 16.694$ (8) Å, $c = 9.407$ (5) Å, $\beta = 104.90$ (10)°, $Z = 4$, final $R = 0.054$, $R_w = 0.052$ from 3472 reflections (6450 measured); complex **6**, $C_{27}H_{30}F_6ORh_2$, orthorhombic, $P2_12_12_1$, $a = 16.283$ (8) Å, $b = 14.946$ (7) Å, $c = 10.571$ (5) Å, $Z = 4$, final $R = 0.060$, $R_w = 0.054$ from 1739 reflections (4179 measured).

Introduction

In reactions between metal carbonyl compounds and alkynes, it is common[2-4] to observe the formation of cyclic systems such as cyclobutadienes, metallacyclopentadienes, *p*-benzoquinones, and arenes. In some products, the ring system is present as a ligand; in others, it is a free organic compound. For some time, we have been interested in possible influences of the alkyne substituents on these cyclic condensation reactions.

In recent work,[5,6] we have shown that the course of the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and alk-

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(1) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1986**, *314*, 333.

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(5) Corrigan, P. A.; Dickson, R. S.; Johnson, S. H.; Pain, G. N.; Yeoh, M. *Aust. J. Chem.* **1982**, *35*, 2203.

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ynes $RC{\equiv}CR'$ is strongly dependent on both steric and electronic effects associated with the substituents R and R'. Two main product types can be obtained, and the reactions are often very selective. Formation of the dimetallocycloheptadienone complexes $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2RR'CO\}$ is strongly favored with dialkylacetylenes including $BuC{\equiv}CBu$ and $MeC{\equiv}C\text{-}t\text{-}Bu$. However, the binuclear metallocyclopentadiene complexes $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2RR'\}$ are obtained preferentially, together with the dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$, when polar or aryl acetylenes such as $MeC{\equiv}CCO_2Me$ or $MeC{\equiv}CPh$ are used. The reaction with $t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu$ also gives the latter two products. As part of an extension of this study to include reactions with terminal acetylenes, we have worked with $HC{\equiv}C\text{-}t\text{-}Bu$. This acetylene gives a surprising range of products, some with metal–ligand bonding modes not encountered before.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. ^1H and ^{19}F NMR spectra were obtained on Brüker WH-90 or AM-300 spectrometers; the ^1H chemical shifts 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 spectra. The Australian Microanalytical Service, Melbourne, performed the microanalyses. 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. $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ was prepared by the published procedure.[7] *tert*-Butylacetylene was purchased from Farchan Laboratories Inc., Florida, and was used as received. Hexane was dried over molecular sieves.

Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ with $HC{\equiv}C\text{-}t\text{-}Bu$. $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.153 g) and *tert*-butylacetylene (0.25 g, mole ratio ca. 1:10) in hexane (20 mL) were kept under nitrogen at 20 °C. Within 2 h, the color of the solution had changed from green to red, but TLC monitoring of the reaction mixture showed that a large amount of starting material remained. After several days, a fine red precipitate had separated from an orange-red solution which contained no starting material. Two phases were isolated by filtration and were chromatographed separately on plates that had not been ovendried.

TLC of the filtrate with a mixture of X4 and dichloromethane (2:1) as eluent separated six bands from a red base band. The first yellow band gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.018 g, 12%), identified spectroscopically.

Evaporation of solvent from a major orange band gave orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}Bu\}$ (**3**) (0.049 g, 29%), mp 159–161 °C. Anal. Calcd for $C_{20}H_{20}F_6Rh_2$: C, 41.4; H, 3.5; F, 19.6. Found: C, 41.9; H, 3.4; F, 19.3. Spectroscopic data: IR (CH_2Cl_2) 1386 s, 1354m, 1312 s, 1236 s, 1168 s (sh), 1140 vs, 1110 s, 988 s, 821 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.90 (d, 1 H, J = 2 Hz, H), 5.52 (d, 5 H, J < 1 Hz, C_5H_5), 5.30 (s, 5 H, C_5H_5), 1.15 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ 50.1 (q, 3 F, J = 12 Hz, CF_3) and 51.6 (q, 3 F, J = 12 Hz, CF_3); MS, *m/z* 580 $[M]^+$, 565 $[M - Me]^+$, 524 $[M - C_4H_8]^+$.

Another yellow band was developed as the next major species on the plate. It gave yellow crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2\text{-}t\text{-}Bu)_2$ (**6**) (0.038 g, 19%), mp 223–225 °C. Anal. Calcd for $C_{27}H_{30}F_6ORh_2$: C, 47.0; H, 4.4; F, 16.5. Found: C, 47.2; H, 4.4; F, 16.4. Spectroscopic data: IR (CH_2Cl_2) 1710 vs, 1604 s, 1318 s, 1230 s, 1170 vs, 1150 s, 1120 vs, 1080 s, 1000 s, 910 s, 850 m, 830 m, 815 s, 800 m cm^{-1}; ^1H NMR (C_6D_6) δ 6.37 (t, 1 H, J = 3 Hz, H), 5.23 (d, 1 H, J = 2 Hz, H), 4.93 (s, 5 H, C_5H_5), 4.84 (s, 5 H, C_5H_5), 1.30 (s, 9 H, *t*-Bu), 0.97 (s, 9 H, *t*-Bu); ^{19}F NMR (C_6D_6) δ 55.8 (q, 3 F, J = 9 Hz, CF_3) and 58.2 (q, 3 F, J = 9 Hz, CF_3); MS, *m/z* 690 $[M]^+$, 608 $[M - HC_2\text{-}t\text{-}Bu]^+$.

Rechromatography (TLC) of this compound converts it to an isomeric form, mp 230–232 °C. Anal. Calcd for $C_{27}H_{30}F_6ORh_2$: C, 47.0; H, 4.4; F, 16.5. Found: C, 47.3; H, 4.4; F, 16.2. Spectroscopic data: IR (CH_2Cl_2) 1710 s, 1610 m, 1310 m, 1280 m (br), 1230 s, 1180 s, 1145 m, 1120 vs, 1070 m, 910 m, 890 m, 915 s cm^{-1}; ^1H NMR (C_6D_6) δ 6.26 (t, 1 H, J = 3 Hz, H), 5.42 (d, 1 H, J = 2 Hz, H), 5.05 (s, 5 H, C_5H_5), 4.73 (s, 5 H, C_5H_5), 1.32 (s, 9 H, *t*-Bu), 0.97 (s, 9 H, *t*-Bu); ^{19}F NMR (C_6D_6) δ 55.1 (q, 3 F, J = 9 Hz, CF_3) and 58.2 (q, 3 F, J = 9 Hz, CF_3); MS, *m/z* 690 $[M]^+$, 608 $[M - HC_2\text{-}t\text{-}Bu]^+$.

The remaining three bands obtained during chromatography of the filtrate were also developed when a solution of the red solid from the reaction mixture was chromatographed by TLC. The combined yields are given below.

An orange band gave orange-red crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (**2**) (0.009 g, 5%), mp >250 °C. Anal. Calcd for $C_{21}H_{20}F_6ORh_2$: C, 41.5; H, 3.3; F, 18.7. Found: C, 41.3; H, 3.3; F, 19.1. Spectroscopic data: IR (CH_2Cl_2) 1674 s, 1390 m, 1204 s, 1145 s, 1124 s, 1106 s, 810 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.97 (dd, 1 H, J = 2.5 and J = 0.9 Hz, H), 5.45 (s, 5 H, C_5H_5), 5.47 (s, 5 H, C_5H_5), 1.08 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ 51.2 (q, 3 F, J = 12 Hz, CF_3) and 55.6 (q, 3 F, J = 12 Hz, CF_3); MS, *m/z* 608 $[M]^+$, 580 $[M - CO]^+$.

A red band gave red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)(HC_2\text{-}t\text{-}Bu)$ (**5**) (0.029 g, 17%); mp 132 °C dec. Anal. Calcd for $C_{22}H_{20}F_6O_2Rh_2$: C, 41.5; H, 3.1; F, 17.9. Found: C, 41.1; H, 3.1; F, 18.8. Spectroscopic data: IR (CH_2Cl_2) 2000 vs, 1670 s, 1655 s, 1360 m, 1305 s, 1218 s, 1175 s, 1138 vs, 1120 vs, 1064 s, 1000 m, 882 m, 848 m, 812 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.73 (d, 1 H, J = 2 Hz, H), 5.62 (d, 5 H, J < 1 Hz, C_5H_5), 5.48 (s, 5 H, C_5H_5), 1.20 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ 58.0 (q, 3 F, J = 9 Hz, CF_3) and 60.6 (q, 3 F, J = 9 Hz, CF_3); MS, *m/z* 608 $[M - CO]^+$, 580 $[M - 2CO]^+$, 440 $[M - C_5H_5RhCO]^+$, 425 $[M - C_5H_5RhCO - Me]^+$, 398 $[M - C_5H_5RhCO - CMe_2]^+$.

The final yellow band gave yellow-orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (**1**) (0.017 g, 10%), mp >250 °C. Anal. Calcd for $C_{21}H_{26}F_6ORh_2$: C, 41.5; H, 3.3; F, 18.7. Found: C, 41.6; H, 3.6; F, 18.8. Spectroscopic data: IR (CH_2Cl_2) 1678 vs, 1388 s, 1205 vs, 1124 vs (br), 909 m, 815 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.59 (s, 5 H, C_5H_5), 5.46 (s, 5 H, C_5H_5), 4.51 (poorly resolved triplet, 1 H, H), 1.22 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ 52.0 (q, 3 F, J = 12 Hz, CF_3) and 55.6 (q, 3 F, J = 12 Hz, CF_3); MS, *m/z* 608 $[M]^+$, 580 $[M - CO]^+$.

Extraction of the base band and rechromatography by TLC with a mixture of ether and dichloromethane (1:1) as eluent gave an orange-red compound (0.020 g). Spectroscopic data indicated that two compounds were present. Although further TLC seemed to separate two bands, the spectrscopic results for each band were more complex than those for the initial orange-red compound. No further attempts were made to characterize these species.

All the above complexes were separated by TLC on deactivated plates. When the TLC was done on activated plates, the complex $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}Bu\}$ was not obtained. In its place was a new complex that was isolated as red crystals of formula $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuO_2\}$ (**4**) (0.046 g, 26%), mp 138–139 °C. Anal. Calcd for $C_{20}H_{20}F_6O_2Rh_2$: C, 39.2; H, 3.3; F, 18.6. Found: C, 39.2; H, 3.5; F, 18.3. Spectroscopic data: IR (CH_2Cl_2) 1608 s, 1572 m, 1555 (sh), 1405 s, 1290 vs, 1260 m, 1173 vs, 1150 vs, 1125 vs, 1100 vs, 1042 s, 1008 s, 930 vs, 848 m, 800 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.40 (d, 5 H, J = 0.6 Hz, C_5H_5), 5.12 (d, 5 H, J = 0.6 Hz, C_5H_5), 3.16 (d, 1 H, J = 1.5 Hz, H), 1.08 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) δ 67.6 (s, 3 F, CF_3) and 71.1 (s, 3 F, CF_3); MS, *m/z* 612 $[M]^+$, 593 $[M - F]^+$, 543 $[M - CF_3$, or $M - C\text{-}t\text{-}Bu]^+$, 527 $[M - CF_3O$ or $M - C\text{-}t\text{-}Bu - O]^+$, 515 $[M - CF_3 - CO$ or $M - C\text{-}t\text{-}Bu - CO]^+$, 498 $[M - HC_2\text{-}t\text{-}Bu - O_2]^+$.

Decarbonylation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)(HC_2\text{-}t\text{-}Bu)$ (5). Complex **5** (0.025 g) and Me_3NO (0.020 g) in acetone were stirred at room temperature for 48 h. Monitoring by TLC showed that no reaction had occurred. The solvent was replaced with dichloromethane, and this solution was gently refluxed for 5 h. Filtration, followed by TLC of the filtrate with CH_2Cl_2 as eluent, gave a single orange compound. This was identified spectroscopically (MS, IR, and NMR) and from its R_f value as $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2HBuCO\}$ (**2**) (0.020 g, 84%).

Crystallography

Well-formed single crystals of complexes **4**–**6** were grown from dichloromethane/hexane. Suitable crystals were mounted on a

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[7] Dickson, R. S.; Oppenheim, A. P.; Pain, G. N. *J. Organomet. Chem.* **1982**, *224*, 377.

[8] Fallon, G. D.; Gatehouse, B. M. *J. Solid State Chem.* **1980**, *34*, 193.

Table I. Summary of Crystal Structure Data for the Complexes $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuO_2\}$ (4), $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (5), and $(\eta\text{-}C_5H_5)_2Rh_2(C_2H\text{-}t\text{-}Bu)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (6)

	(a) Crystal Data		
formula	$C_{20}H_{20}F_6O_2Rh_2$	$C_{22}H_{20}F_6O_2Rh_2$	$C_{27}H_{30}F_6ORh_2$
mol wt	612.2	636.2	690.4
cryst system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a, Å	16.455 (8)	14.590 (7)	16.283 (8)
b, Å	13.836 (7)	16.694 (8)	14.946 (7)
c, Å	10.876 (5)	9.407 (5)	10.571 (5)
α, deg	115.09 (10)		
β, deg	98.64 (10)	104.90 (10)	
γ, deg	97.91 (10)		
U, Å^3	2160.3	2216.3	2572.6
Z	4	4	4
D(calcd), g cm^{-3}	1.88	1.91	1.78
D(measd), g cm^{-3}	1.88 (1)	1.90 (1)	1.79 (2)
$F(000)$	1200	1248	1376
μ(Mo Kα), cm^{-1}	15.4	15.0	12.9
	(b) Data Collection		
cryst dimens, mm	0.32 × 0.21 × 0.07	0.20 × 0.24 × 0.25	0.16 × 0.08 × 0.12
2θ limits, deg	6–60	6–60	6–60
ω scan angle, deg	$\pm(1.40 + 0.3 \tan \theta)$	$\pm(1.30 + 0.2 \tan \theta)$	$\pm(1.30 + 0.2 \tan \theta)$
scan rate, deg s^{-1}	0.06	0.05	0.06
total data	12595	6450	4179
data $I > 3\sigma(I)$	6915	3472	1739
final R and R_w	0.052 and 0.051	0.054 and 0.052	0.060 and 0.054
weight w	$\sigma^{-2}(F)$	$\sigma^{-2}(F)$	$\sigma^{-2}(F)$

Philips PW1100 computer-controlled diffractometer; cell parameters were determined from 24 accurately centered reflections and were calculated by the standard Philips program. Intensity measurements were made with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at a temperature of 295 K. Other data are summarized in Table I. Three standard reflections were monitored every 6 h and showed no significant variation of intensity over the data collection period.

Intensity data were processed as described earlier.[8] For each structure determination, a numerical absorption correction was applied. The maximum and minimum transmission factors were as follows: 0.908 and 0.690 for 4, 0.750 and 0.513 for 5, 0.886 and 0.773 for 6. The atomic scattering factors for neutral atoms were taken from ref 9 and were corrected for anomalous dispersion by using values taken from ref 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] Hydrogen atoms were not included in the calculations.

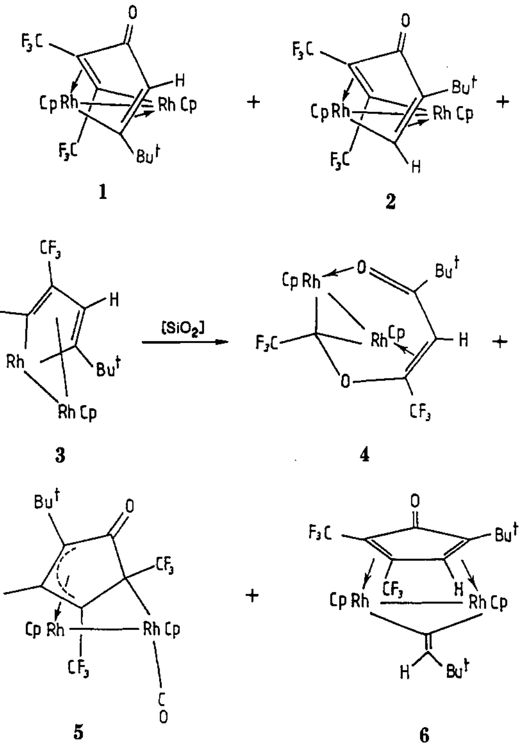
The structure of 4 was solved by direct methods. The best E map gave sites for four Rh atoms, indicating two molecules in the asymmetric unit. Subsequent difference Fourier syntheses revealed the rest of the molecules. The *tert*-butyl group and one of the cyclopentadienyl rings of one molecule (molecule 2) were disordered; they were included in the refinement with occupancy factors of 0.61/0.39 for C_5H_5 and 0.48/0.52 for *t*-Bu. The locations of all non-hydrogen atoms were refined by using full-matrix least-squares methods with anisotropic thermal parameters for the Rh and F atoms.

For 5 and 6, a combination of Patterson and Fourier techniques provided the locations of all non-hydrogen atoms, and these were refined by using full-matrix least-squares methods. One cyclopentadienyl ring in 5 was disordered, and an occupancy factor of 0.59/0.41 was used in the refinement. Anisotropic thermal parameters for all atoms except carbon atoms of the cyclopentadienyl rings were used in the refinement of 5. For 6, the refinement used anisotropic thermal parameters for all Rh and F atoms. The atomic coordinates in 6 were inverted to check the absolute configuration; this gave R = 0.061 and R' = 0.055.

Final positional parameters for 4, 5, and 6 are given in Tables II, III, and IV, respectively. Thermal parameters are deposited in Tables SUP-I, SUP-II, and SUP-III (supplementary material).

Scheme I. Products of the Reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and $t\text{-}BuC{\equiv}CH$

$Cp_2Rh_2(CO)(CF_3C_2CF_3) + Bu^tC{\equiv}CH \rightarrow$



Results

The reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and HC≡C-*t*-Bu occurs relatively slowly in hexane at room temperature. The color of the solution changes from green to red over 1–2 h, but the reaction is not complete for several days. Numerous products can be separated from the reaction mixture by chromatography; six are obtained in sufficient amount for characterization, and these are shown in Scheme I. Complex 4 is not formed directly in

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[9] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[10] Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination; Cambridge, England, 1976.

Table II. Final Positional Parameters for Complex 4, $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuO_2\}$ (Esd Values in Parentheses)

atom	*x*	*y*	*z*
	(a) Molecule 1		
Rh(11)	0.26224 (4)	0.20948 (5)	0.21312 (7)
Rh(12)	0.35396 (4)	0.07780 (5)	0.25621 (6)
F(11)	0.4618 (3)	0.3436 (5)	0.3491 (6)
F(12)	0.4842 (3)	0.3220 (5)	0.5323 (6)
F(13)	0.4028 (4)	0.4261 (4)	0.5147 (7)
F(14)	0.3687 (4)	−0.0143 (6)	0.5064 (8)
F(15)	0.3308 (5)	0.1163 (7)	0.6590 (7)
F(16)	0.4481 (4)	0.1445 (6)	0.6027 (7)
C(11)	0.4237 (6)	0.3302 (8)	0.4428 (10)
C(12)	0.3481 (4)	0.2364 (6)	0.3759 (8)
C(13)	0.3223 (5)	0.1119 (6)	0.4402 (8)
C(14)	0.3675 (7)	0.0911 (9)	0.5516 (12)
C(15)	0.2516 (5)	0.0314 (6)	0.3322 (8)
C(16)	0.1725 (4)	0.0620 (6)	0.3033 (7)
C(17)	0.0898 (5)	−0.0096 (7)	0.2967 (9)
C(18)	0.0153 (6)	0.0451 (8)	0.2876 (10)
C(19)	0.1000 (7)	−0.0306 (10)	0.4266 (13)
C(110)	0.0751 (7)	−0.1190 (10)	0.1584 (12)
C(111)	0.2955 (7)	0.3500 (9)	0.1745 (11)
C(112)	0.3163 (6)	0.2554 (9)	0.0730 (11)
C(113)	0.2412 (7)	0.1737 (9)	−0.0156 (11)
C(114)	0.1730 (7)	0.2135 (9)	0.0365 (12)
C(115)	0.2043 (7)	0.3215 (10)	0.1545 (12)
C(116)	0.4792 (6)	0.0319 (9)	0.2441 (11)
C(117)	0.4613 (6)	0.0834 (8)	0.1574 (10)
C(118)	0.3888 (6)	0.0134 (9)	0.0458 (11)
C(119)	0.3627 (6)	−0.0770 (9)	0.0728 (11)
C(120)	0.4150 (7)	−0.0656 (9)	0.1930 (12)
O(11)	0.3205 (3)	0.2240 (4)	0.4903 (6)
O(12)	0.1673 (3)	0.1426 (4)	0.2821 (6)
	(b) Molecule 2		
Rh(21)	0.67866 (3)	0.40369 (5)	0.10255 (6)
Rh(22)	0.83891 (4)	0.51368 (5)	0.22369 (6)
F(21)	0.7550 (4)	0.2668 (4)	−0.2055 (5)
F(22)	0.7669 (4)	0.4396 (5)	−0.1308 (5)
F(23)	0.8773 (3)	0.3779 (5)	−0.1072 (5)
F(24)	0.9728 (3)	0.2641 (5)	0.1945 (7)
F(25)	1.0004 (3)	0.3770 (5)	0.1140 (6)
F(26)	1.0144 (3)	0.4340 (5)	0.3348 (6)
C(21)	0.7959 (5)	0.3668 (7)	−0.0980 (9)
C(22)	0.7823 (4)	0.3773 (6)	0.0409 (7)
C(23)	0.8751 (4)	0.3744 (6)	0.1976 (7)
C(24)	0.9663 (5)	0.3641 (7)	0.2099 (9)
C(25)	0.8392 (4)	0.4066 (6)	0.3172 (8)
C(26)	0.7610 (4)	0.3395 (6)	0.3086 (7)
C(27)	0.7564 (6)	0.2911 (8)	0.4116 (10)
C(28a)	0.6727 (11)	0.2151 (17)	0.3774 (20)
C(29a)	0.8309 (13)	0.3180 (19)	0.5152 (24)
C(210a)	0.6697 (18)	0.2879 (26)	0.4500 (32)
C(28b)	0.7680 (17)	0.4068 (24)	0.5579 (29)
C(29b)	0.8287 (17)	0.2252 (24)	0.3953 (29)
C(210b)	0.7317 (22)	0.1592 (30)	0.3158 (37)
C(211)	0.5966 (5)	0.5263 (7)	0.1459 (9)
C(212)	0.5504 (5)	0.4313 (7)	0.1387 (9)
C(213)	0.5436 (5)	0.3424 (8)	0.0016 (9)
C(214)	0.5858 (6)	0.3852 (8)	−0.0761 (9)
C(215)	0.6233 (5)	0.4990 (8)	0.0166 (9)
C(216a)	0.8428 (13)	0.6885 (13)	0.3791 (22)
C(217a)	0.8149 (12)	0.6780 (16)	0.2451 (28)
C(218a)	0.8767 (15)	0.6524 (14)	0.1736 (17)
C(219a)	0.9499 (9)	0.6480 (12)	0.2620 (21)
C(220a)	0.9275 (11)	0.6682 (11)	0.3914 (16)
C(216b)	0.8158 (14)	0.6855 (16)	0.3151 (31)
C(217b)	0.8311 (17)	0.6597 (18)	0.1849 (27)
C(218b)	0.9142 (16)	0.6419 (17)	0.1842 (24)
C(219b)	0.9492 (16)	0.6579 (21)	0.3287 (38)
C(220b)	0.8821 (23)	0.6830 (22)	0.4116 (28)
O(21)	0.8236 (3)	0.2971 (4)	0.0653 (5)
O(22)	0.6953 (3)	0.3151 (4)	0.2179 (5)

Table III. Final Positional Parameters for Complex 5, $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ (Esd Values in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.68468 (4)	0.40848 (3)	0.28478 (6)
Rh(2)	0.67237 (4)	0.28285 (4)	0.45524 (7)
C(1)	0.7085 (6)	0.5147 (7)	0.5684 (13)
C(2)	0.7509 (5)	0.4490 (5)	0.4988 (8)
C(3)	0.7775 (5)	0.3670 (5)	0.5617 (7)
C(4)	0.8066 (6)	0.3583 (8)	0.7264 (10)
C(5)	0.8551 (5)	0.3429 (5)	0.4876 (8)
C(6)	0.8473 (4)	0.3980 (4)	0.3613 (7)
C(7)	0.8055 (5)	0.4695 (5)	0.3982 (8)
C(8)	0.9159 (5)	0.3918 (5)	0.2625 (9)
C(9)	0.8937 (8)	0.4559 (7)	0.1437 (12)
C(10)	1.0192 (6)	0.4038 (8)	0.3609 (12)
C(11)	0.9070 (8)	0.3108 (6)	0.1888 (12)
C(12)	0.5788 (6)	0.3328 (6)	0.5227 (12)
F(1)	0.7633 (4)	0.5391 (4)	0.6949 (8)
F(2)	0.6929 (5)	0.5802 (4)	0.4826 (9)
F(3)	0.6253 (4)	0.4967 (4)	0.5953 (8)
F(4)	0.8826 (4)	0.4039 (4)	0.7900 (6)
F(5)	0.7378 (4)	0.3807 (5)	0.7895 (6)
F(6)	0.8312 (4)	0.2828 (5)	0.7718 (6)
O(1)	0.9145 (4)	0.2911 (4)	0.5297 (6)
O(2)	0.5176 (5)	0.3568 (5)	0.5639 (11)
C(13)	0.5515 (7)	0.3701 (6)	0.1321 (11)
C(14)	0.6177 (7)	0.3854 (6)	0.0480 (12)
C(15)	0.6419 (8)	0.4634 (7)	0.0640 (13)
C(16)	0.5969 (8)	0.5005 (6)	0.1500 (12)
C(17)	0.5371 (7)	0.4444 (6)	0.2022 (12)
C(18)	0.7627 (17)	0.1844 (12)	0.3834 (29)
C(19)	0.7397 (15)	0.1632 (12)	0.5230 (28)
C(20)	0.6460 (20)	0.1542 (15)	0.5040 (32)
C(21)	0.5980 (14)	0.1746 (12)	0.3414 (32)
C(22)	0.6739 (20)	0.1906 (11)	0.2703 (24)
C(18′)	0.7533 (19)	0.1670 (16)	0.4742 (40)
C(19′)	0.6766 (33)	0.1598 (23)	0.5439 (45)
C(20′)	0.5932 (19)	0.1676 (16)	0.4179 (41)
C(21′)	0.6271 (19)	0.1878 (12)	0.2857 (24)
C(22′)	0.7291 (20)	0.1888 (13)	0.3373 (31)

the reaction but is obtained when **3** is chromatographed on activated supports. Several of the products are analogous to those obtained[5] from other reactions of alkynes with $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, but three of the compounds have structures that have not been encountered previously. We have characterized these crystallographically. The known[7] dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is also formed in the reaction.

The Dimetallacycloheptadienone Complexes 1 and 2. Two isomers of the bridging dienone complex $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$ can be separated. The major and minor isomers are obtained in 10 and 5% yields, respectively. They are fully characterized by elemental analysis, mass spectroscopy which shows a parent ion and loss of CO from the parent, and infrared spectroscopy which reveals ketonic carbonyl bands near 1675 cm^{-1}. The individual isomers are readily distinguished from their NMR spectra. For the major isomer, the resonance for the hydrogen atom on the dienone unit is observed as a poorly resolved "triplet" at δ 4.51; it is a doublet of doublets at δ 9.97 for the minor isomer. The configurations shown in Scheme I have been established by comparison with the NMR spectra of related complexes, including $(\eta^5\text{-}C_9H_7)_2Rh_2(C_4H_4CO)$[11] and $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2Me_2CO\}$,[12,13] and by lanthanide shift experiments performed on **1** and **2**; **1** is the major isomer.

The Metallacyclopentadiene Complex 3 and Its Oxidation to 4. The major product of the reaction is the

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[11] Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.

[12] Dickson, R. S.; Gatehouse, B. M. and Johnson, S. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 319.

[13] Dickson, R. S.; Johnson, S. H.; Rae, I. D. *Aust. J. Chem.* **1975**, *28*, 1681.

Table IV. Final Positional Parameters for Complex 6, (η-C_5H_5)$_2$$Rh_2$($C_2H$-*t*-Bu){$C_4(CF_3)_2H$-*t*-BuCO} (Esd Values in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.4157 (1)	0.0877 (1)	0.4545 (1)
Rh(2)	0.5713 (1)	0.0886 (1)	0.5194 (1)
F(1)	0.3821 (8)	−0.0863 (10)	0.7742 (13)
F(2)	0.3920 (7)	0.0564 (10)	0.7859 (11)
F(3)	0.2939 (6)	−0.0015 (9)	0.6821 (12)
F(4)	0.2743 (5)	−0.0745 (8)	0.4618 (14)
F(5)	0.3493 (7)	−0.1877 (8)	0.4948 (18)
F(6)	0.3470 (8)	−0.1277 (10)	0.3121 (14)
C(1)	0.3737 (13)	−0.0106 (15)	0.7101 (22)
C(2)	0.4300 (10)	−0.0109 (11)	0.5961 (15)
C(3)	0.4215 (11)	−0.0546 (12)	0.4775 (16)
C(4)	0.3483 (12)	−0.1097 (15)	0.4408 (21)
C(5)	0.5045 (9)	−0.0916 (13)	0.4436 (19)
C(6)	0.5638 (11)	−0.0589 (13)	0.5382 (18)
C(7)	0.5184 (11)	−0.0123 (12)	0.6333 (19)
C(8)	0.6433 (11)	−0.1139 (13)	0.5582 (20)
C(9)	0.6982 (12)	−0.1090 (15)	0.4417 (21)
C(10)	0.6915 (13)	−0.0807 (17)	0.6782 (20)
C(11)	0.6151 (15)	−0.2122 (17)	0.5826 (24)
C(12)	0.5185 (10)	0.0696 (12)	0.3533 (18)
C(13)	0.5509 (12)	0.0569 (13)	0.2404 (20)
C(14)	0.5154 (11)	0.0401 (13)	0.1083 (21)
C(15)	0.4198 (17)	0.0519 (18)	0.1070 (25)
C(16)	0.5456 (14)	0.1185 (15)	0.0198 (24)
C(17)	0.5437 (16)	−0.0455 (18)	0.0578 (26)
C(18)	0.2816 (11)	0.1266 (13)	0.4596 (20)
C(19)	0.3249 (11)	0.1795 (14)	0.5531 (20)
C(20)	0.3876 (11)	0.2309 (13)	0.4930 (19)
C(21)	0.3822 (13)	0.2152 (14)	0.3599 (20)
C(22)	0.3170 (14)	0.1527 (15)	0.3388 (22)
C(23)	0.6679 (14)	0.1804 (17)	0.4480 (24)
C(24)	0.6001 (14)	0.2318 (17)	0.4908 (24)
C(25)	0.5959 (16)	0.2209 (16)	0.6228 (24)
C(26)	0.6560 (18)	0.1609 (20)	0.6656 (28)
C(27)	0.6987 (14)	0.1370 (16)	0.5575 (25)
O	0.5168 (8)	−0.1435 (9)	0.3589 (14)

binuclear metalladiene complex (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H$-*t*-Bu} (**3**), which is obtained in almost 30% yield. Again, this has been fully characterized from elemental analysis and spectroscopic data. Two isomers are possible for this product, but only one is obtained. NMR results are consistent with the configuration **3** shown in Scheme I. This assignment is based on spectroscopic data for some related complexes, including (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H_2$},[14] and on theoretical predictions.[15,16]

Complex **3** is isolated only when chromatography of the reaction products is done on supports that have not been activated by ovendrying. When activated plates are used, another complex of formula (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H$-*t*-$BuO_2$} (**4**) is obtained instead. It is also possible to quantitatively convert pure **3** to **4** by chromatography on activated plates.

The molecular formula of **4** is based on elemental analysis and mass spectral data. The results of IR and NMR investigation are listed in the Experimental Section, but they are not particularly helpful in structure elucidation. Consequently, the crystal and molecular structure of **4** was determined from X-ray diffraction data.

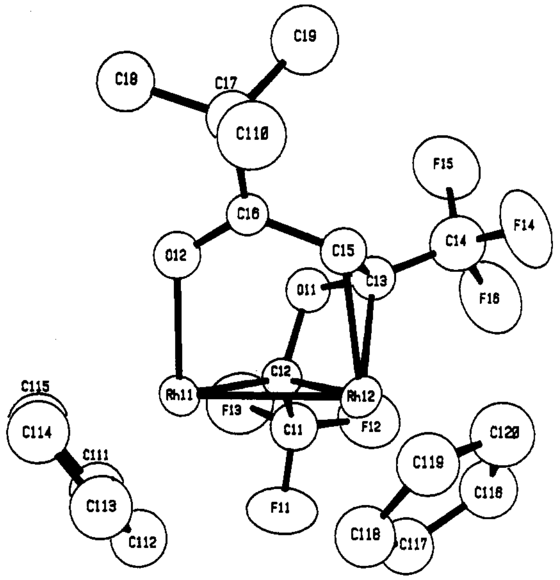

Figure 1. Molecular structure of complex 4, (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H$-*t*-$BuO_2$}.

Table V. Selected Bond Length (Å) and Esd's for Complex 4, (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H$-*t*-$BuO_2$}

	(a) Molecule 1		
Rh(11)–Rh(12)	2.662 (1)	C(12)–O(11)	1.45 (1)
Rh(11)–C(12)	1.953 (8)	C(13)–O(11)	1.42 (1)
Rh(11)–O(12)	2.098 (6)	C(13)–C(15)	1.45 (1)
Rh(12)–C(12)	2.047 (7)	C(15)–C(16)	1.45 (1)
Rh(12)–C(15)	2.123 (9)	C(16)–O(12)	1.24 (1)
Rh(12)–C(13)	2.019 (9)		
	(b) Molecule 2		
Rh(21)–Rh(22)	2.675 (1)	C(22)–O(21)	1.47 (1)
Rh(21)–C(22)	1.949 (7)	C(23)–O(21)	1.42 (1)
Rh(21)–O(22)	2.109 (7)	C(23)–C(25)	1.43 (1)
Rh(22)–C(22)	2.039 (6)	C(25)–C(26)	1.44 (1)
Rh(22)–C(25)	2.123 (10)	C(26)–O(22)	1.25 (1)
Rh(22)–C(23)	2.012 (9)		

Table VI. Selected Interatomic Angles (deg) with Esd's for Complex 4, (η-C_5H_5)$_2$$Rh_2${$C_4(CF_3)_2H$-*t*-$BuO_2$}

	(a) Molecule 1		
Rh(12)–Rh(11)–C(12)	49.8 (2)	Rh(12)–C(13)–C(15)	73.4 (4)
Rh(12)–Rh(11)–O(12)	88.1 (1)	Rh(12)–C(13)–O(11)	101.6 (5)
		C(15)–C(13)–O(11)	118.2 (7)
Rh(11)–Rh(12)–C(12)	46.8 (2)	Rh(12)–C(15)–C(13)	65.7 (4)
Rh(11)–Rh(12)–C(13)	91.1 (2)	Rh(12)–C(15)–C(16)	118.9 (5)
Rh(11)–Rh(12)–C(15)	84.1 (2)	C(13)–C(15)–C(16)	120.2 (7)
Rh(11)–C(12)–Rh(12)	83.4 (3)	O(12)–C(16)–C(15)	123.6 (7)
Rh(11)–C(12)–O(11)	118.2 (5)	O(12)–C(16)–C(17)	117.6 (7)
Rh(12)–C(12)–O(11)	99.0 (4)	C(15)–C(16)–C(17)	118.7 (7)
C(12)–O(11)–C(13)	96.0 (5)	Rh(11)–O(12)–C(16)	120.8 (5)
	(b) Molecule 2		
Rh(22)–Rh(21)–C(22)	49.3 (2)	Rh(22)–C(23)–C(25)	74.0 (5)
Rh(22)–Rh(21)–O(22)	87.7 (1)	Rh(22)–C(23)–O(21)	102.5 (5)
		C(25)–C(23)–O(21)	118.9 (6)
Rh(21)–Rh(22)–C(22)	46.4 (2)		
Rh(21)–Rh(22)–C(23)	91.0 (2)	Rh(22)–C(25)–C(23)	65.6 (5)
Rh(21)–Rh(22)–C(25)	83.9 (2)	Rh(22)–C(25)–C(26)	120.4 (6)
		C(23)–C(25)–C(26)	118.9 (5)
Rh(21)–C(22)–Rh(22)	84.2 (3)	O(22)–C(26)–C(25)	123.4 (8)
Rh(21)–C(22)–O(21)	119.4 (6)	O(22)–C(26)–C(27)	116.3 (7)
Rh(22)–C(22)–O(21)	99.3 (4)	C(25)–C(26)–C(27)	120.3 (7)
C(22)–O(21)–C(23)	94.8 (5)	Rh(21)–O(22)–C(26)	121.6 (5)

Crystal and Molecular Structure of Complex 4. In the crystal structure, there are two molecules per asymmetric unit. The structure of molecule 1 is shown in Figure 1, which also indicates the labeling of the atoms. Molecule 2 has the same gross stereochemistry except that one C_5H_5 ring and the *tert*-butyl group are both disordered. The atom-labeling scheme for molecule 2 is similar to that depicted for molecule 1 in the sense that Rh(21) in molecule 2 and Rh(11) in molecule 1 are related, as are C(22) and C(12), F(25) and F(15), etc. Selected intramolecular distances and angles for each molecule are collected in

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[14] Dickson, R. S.; Nesbit, R. J., unpublished results.
[15] Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.
[16] Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.

Table VII. Dihedral Angles between Planes for Complex 4

(a) Planes and Atoms in Plane

1	Rh(11), Rh(12), C(15), C(16), O(12)
2	Rh(11), Rh(12), C(12)
3	Rh(12), C(13), C(15)
4	Rh(12), C(13), O(11), C(12)

(b) Angles (deg) between Planes

1-2, 85.0	2-4, 119.6
1-3, 99.4	3-4, 61.7
1-4, 56.8	

Tables V and VI. Other ligand bond parameters are deposited as supplementary material (Table SUP-IV).

The molecular structure shows that the diene ligand of 3 has become an unsaturated keto–ether, with a ketonic oxygen attached to the C-*t*-Bu unit and an ether oxygen inserted between the two CCF_3 groups. The ligand is attached to Rh(11) via bonds from the ketonic oxygen O(12) and an ether carbon C(12) and to Rh(12) through C(12) and the alkene unit C(13)=C(15). A representation of this attachment of the bridging ligand is given in 4 (Scheme I). We are not aware of other complexes with ligands of this type.

The bond parameters for molecules 1 and 2 are identical within experimental error. When the molecular geometry is discussed, the parameters used will be those for molecule 1. There is a normal single-bond distance of 2.662 (1) Å between the two rhodium atoms. The carbon atom C(12) is attached to both metal atoms, but there is some asymmetry in the bonding. Thus, the Rh(11)–C(12) and Rh(12)–C(12) distances are 1.953 (8) and 2.047 (7) A, respectively, and the Rh(11)–C(12)–O(11) and Rh(12)–C(12)–O(11) angles are 118.2 (5) and 99.0 (4)°, respectively. It seems reasonable to compare the Rh(11)–C(12)–Rh(12) system in 4 with that in some Rh_2–(μ-alkylidene) complexes. Appropriate parameters for such complexes are tabulated in a recent review,[17] and the Rh–C distances fall within the range 2.03–2.12 Å. The corresponding distances for 4 are toward or beyond the lower end of this range, and this may be due to the presence of the electron-withdrawing CF_3 and OR groups.

The distances from Rh(12) to C(13) and C(15) are 2.019 (9) and 2.123 (9) Å, respectively, and the C(13)–C(15) bond length is 1.45 (1) Å. These distances are similar to those found in other binuclear rhodium complexes where the alkene part of a bridging ligand bonds to one rhodium atom (see, for example, ref 6, 18, and 19). The asymmetry in the alkene–rhodium bonding in 4 is presumably due to differing electronic effects caused by the presence of CF_3 and OCF_3 substituents on C(13) but H and OC-*t*-Bu on C(15).

As expected, the ether C—O distances (1.42 (1) and 1.45 (1) Å) are significantly longer than the ketonic C=O distance (1.24 (1) Å). The ketonic oxygen is coordinated to a rhodium atom, and the Rh(11)–O(12) distance of 2.098 (6) Å is similar to Rh–O single-bond distances found in other complexes, including $Rh(CO)_2(acac)$[20] and $Rh(CO)(PPh_3)(acac)$.[21] This coordination has little effect on the ketonic C=O distance, which is only 0.01–0.03 Å longer than the "free" ketonic C=O distance found in complexes such as $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2RR'CO\}$.[6,13] In contrast, for the complex $Mo_2(CO)_3(C_4Ph_4)(\mu\text{-}C_2Ph)(\mu\text{-}C_4Ph_4CO)$, in which a bridging cyclopentadienone ligand is coordinated to one molybdenum through the ketonic oxygen atom,[22] the C=O distance is lengthened to 1.38 (2) A.

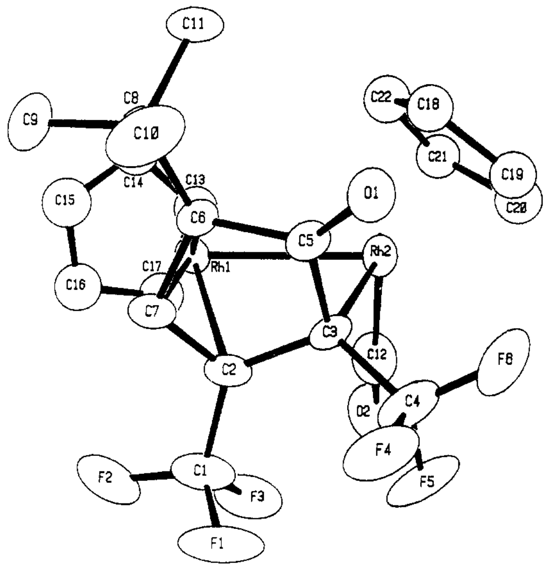

Figure 2. Molecular structure of complex 5, $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(HC_2\text{-}t\text{-}Bu)(CF_3C_2CF_3)$.

Table VIII. Selected Bond Distances (Å) and Esd's for Complex 5, $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$

Rh(1)–Rh(2)	2.674 (1)	C(2)–C(3)	1.50 (1)
		C(2)–C(7)	1.43 (1)
Rh(1)–C(2)	2.108 (7)	C(3)–C(5)	1.53 (1)
Rh(1)–C(6)	2.302 (6)	C(5)–C(6)	1.48 (1)
Rh(1)–C(7)	2.078 (7)	C(5)–O(1)	1.22 (1)
Rh(2)–C(3)	2.131 (7)	C(6)–C(7)	1.42 (1)
Rh(2)–C(12)	1.846 (11)	C(12)–O(2)	1.13 (1)

Table IX. Selected Angles (deg) and Esd's for Complex 5

Rh(2)–Rh(1)–C(2)	76.3 (2)	C(3)–C(5)–O(1)	126.0 (7)
Rh(2)–Rh(1)–C(6)	88.5 (2)	C(6)–C(5)–O(1)	127.2 (7)
Rh(2)–Rh(1)–C(7)	104.7 (2)	C(3)–C(5)–C(6)	106.7 (6)
C(2)–Rh(1)–C(6)	62.7 (3)		
C(2)–Rh(1)–C(7)	39.7 (3)		
C(6)–Rh(1)–C(7)	37.4 (3)		
Rh(1)–Rh(2)–C(3)	67.4 (2)	C(5)–C(6)–Rh(1)	99.3 (4)
Rh(1)–Rh(2)–C(12)	91.1 (3)	C(5)–C(6)–C(7)	105.9 (6)
C(3)–C(2)–C(7)	110.3 (6)	Rh(1)–C(7)–C(2)	71.3 (4)
C(3)–C(2)–Rh(1)	95.4 (4)	Rh(1)–C(7)–C(6)	79.9 (4)
		C(2)–C(7)–C(6)	107.9 (7)
C(2)–C(3)–Rh(2)	109.3 (4)	Rh(2)–C(12)–O(2)	173.7 (9)
C(2)–C(3)–C(5)	102.0 (6)		

Equations for several best-fit planes, the deviations of atoms from these planes, and dihedral angles between the planes have been calculated; appropriate detail is collected in Table SUP-V (supplementary material). The dihedral angles help to define the geometry of 4 and are summarized in Table VII.

Knowledge of the structure of 4 enables rationalization of some of the unusual spectroscopic results observed for this complex. These include loss of the fragments *t*-BuCO and CF_3CO from the molecular ion in the mass spectrum, the low ketonic carbonyl stretch at 1608 cm^{-1} in the infrared spectrum, and the two high-field *singlets* for the CF_3 groups in the ^{19}F NMR spectrum.

Complex 5, $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(HC_2\text{-}t\text{-}Bu)(CF_3C_2CF_3)$. Another major product was obtained in 17%

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yield and is formulated as $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(HC_2\text{-}t\text{-}Bu)(CF_3C_2CF_3)$ (5) from elemental analyses and spectral data. The infrared spectrum indicates that one carbonyl is terminal (ν(CO) at 2000 cm^{-1}) and the other ketonic (ν(CO) at 1670 and 1655 cm^{-1}). The mass spectrum does not show a parent ion; the highest mass fragment observed corresponds to loss of a carbonyl, and there is subsequent loss of the second carbonyl. The NMR results add little to our knowledge of the molecular structure of this complex, and consequently it was completely characterized by X-ray crystallography.

Crystal and Molecular Structure of Complex 5. Figure 2 shows the molecular structures and the atom-labelling scheme. Tables VIII and IX present selected intramolecular distances and angles. Other ligand bond parameters are deposited as Table SUP-VI (supplementary material). Inspection of the structure shows that there is an unusual η^1,η^3-attachment of a bridging cyclopentadienone ligand to the Rh–Rh bond. A terminal carbonyl is attached to one rhodium and a cyclopentadienyl ring to each rhodium atom. This bonding arrangement is shown more clearly in **5** (Scheme I).

Within the cyclopentadienone ring, there are two adjacent short bonds (C(2)–C(7) and C(6)–C(7) = 1.42–1.43 Å); the remaining three C–C bonds are long (1.48–1.53 Å). The carbon atom C(3) is σ-bonded to Rh(2), with a normal Rh–C single bond distance of 2.131 (7) Å, and there is an allyl-type attachment of C(2)┄C(7)┄C(6) to Rh(1). Some variation in the three Rh-C(allyl) distances is noted with the Rh(1)–C(6)(*tBu*) distance (2.302 (6) Å) being significantly longer than the other two (Rh(1)–C(2) = 2.108 (7) Å; Rh(1)–C(7) = 2.078 (7) Å). These bond distances span those found in the methylallyl–rhodium complex $(\eta\text{-}C_4H_7)_2RhCl_2(AsPh_3)_2$;[23] in this complex, the Rh–C(allyl) distances range from 2.23 to 2.27 (2) Å.

The equation for the plane through the ring carbons C(2), C(3), C(5), C(6), and C(7), and displacements of atoms from this plane, has been calculated, and the information is in Table SUP-VII (supplementary material). All substituent atoms except the *tert*-butyl carbon C(8) are displaced away from the metal atoms with the largest displacement (0.92 Å) found for the trifluoromethyl carbon C(4).

The Rh(1)–Rh(2) distance of 2.674 (1) Å is typical of a Rh–Rh single bond. There is linear attachment of a terminal carbonyl to Rh(2), and the Rh(2)–C(12) and C(12)–O(2) distances are 1.846 (11) and 1.13 (1) Å, respectively.

Complex 6, $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2\text{-}t\text{-}Bu)_2$. The final major product was isolated in 19% yield and is formulated as $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2\text{-}t\text{-}Bu)_2$ (6) from analytical and mass spectral results. A ketonic carbonyl group is indicated by a strong absorption at 1710 cm^{-1} in the infrared spectrum. In the NMR spectra, there are resonances for two CF_3, two C_5H_5, and two *t*-Bu groups plus single proton peaks at δ 6.37 and 5.23. As shown in the Experimental Section, there are small changes in the spectroscopic properties of **6** after it has been chromatographed, and these presumably indicate isomerization of the product. It is difficult to deduce a structure for **6** on the basis of the available spectroscopic data. It was necessary, therefore, to use X-ray diffraction results to determine the structure of the compound.

Crystal and Molecular Structure of Complex 6. Figure 3 shows a drawing of the structure, and bond distances and selected angles are collected in Tables X and XI. Other ligand bond parameters are collected in Table SUP-VIII (supplementary material). There are two interesting bridging groups within the structure. One is a cyclopentadienone ring $[C_4(CF_3)_2H\text{-}t\text{-}BuCO]$ which is attached in η^2,η^2 manner to the Rh–Rh bond. The second is a vinylidene group C=CH-*t*-Bu which has a $\mu\text{-}\eta^1$-attachment to the Rh–Rh bond. The coordination geometry about each rhodium atom is completed by an η^5-cyclopentadienyl group. The coordination of the bridging ligands is indicated more clearly in **6** (Scheme I).

The bond parameters for the cyclopentadienone ligand show the expected features. The two coordinated C=C bonds (average 1.43 (3) Å) are shorter than the three C—C single bonds (average 1.49 (3) Å), and the C=O distance (1.20 (2) Å) is similar to that found in other coordinated cyclopentadienones. One of the Rh–C(diene) distances is longer (2.22 (2) Å) than the other three (2.11 (2), 2.11 (2),

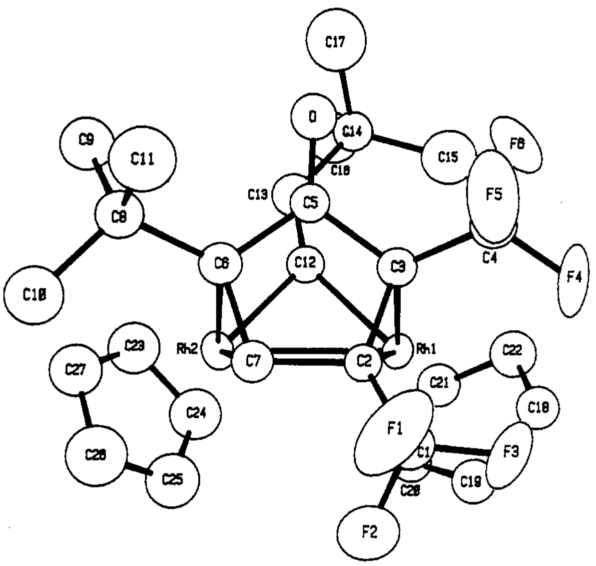

Figure 3. Molecular structure of complex 6, $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}\{C{=}CH\text{-}t\text{-}Bu\}$.

Table X. Selected Bond Distances (Å) and Esd's for Complex 6, $(\eta\text{-}C_5H_5)_2Rh_2(C_2H\text{-}t\text{-}Bu)\{C_4(CF_3)_2H\text{-}t\text{-}BuCO\}$

Rh(1)–Rh(2)	2.625 (2)	C(2)–C(3)	1.42 (2)
Rh(1)–C(2)	2.11 (2)	C(2)–C(7)	1.49 (2)
Rh(1)–C(3)	2.14 (2)	C(3)–C(5)	1.50 (2)
Rh(1)–C(12)	2.00 (2)	C(5)–C(6)	1.47 (3)
Rh(2)–C(6)	2.22 (2)	C(6)–C(7)	1.43 (3)
Rh(2)–C(7)	2.11 (2)	C(12)–C(13)	1.32 (3)
		C(13)–C(14)	1.53 (3)
Rh(2)–C(12)	1.98 (2)	C(5)–O	1.20 (2)

Table XI. Selected Angles (deg) with Esd's for Complex 6

C(2)–Rh(1)–C(3)	39.0 (6)	C(3)–C(5)–O	124.4 (15)
Rh(2)–Rh(1)–C(2)	73.3 (4)	C(6)–C(5)–O	127.6 (15)
Rh(2)–Rh(1)–C(3)	86.2 (5)	C(3)–C(5)–C(6)	107.8 (15)
Rh(2)–Rh(1)–C(12)	48.3 (5)	Rh(2)–C(6)–C(7)	66.9 (10)
C(2)–Rh(1)–C(12)	101.1 (7)	Rh(2)–C(6)–C(5)	107.8 (12)
C(3)–Rh(1)–C(12)	83.7 (7)	C(5)–C(6)–C(7)	107.5 (15)
C(6)–Rh(2)–C(7)	38.4 (7)		
Rh(1)–Rh(2)–C(6)	88.0 (5)	Rh(2)–C(7)–C(2)	103.5 (12)
Rh(1)–Rh(2)–C(7)	75.6 (5)	Rh(2)–C(7)–C(6)	74.7 (11)
Rh(1)–Rh(2)–C(12)	49.2 (5)	C(2)–C(7)–C(6)	108.7 (16)
C(6)–Rh(2)–C(12)	85.0 (7)	Rh(1)–C(12)–Rh(2)	82.5 (7)
C(7)–Rh(2)–C(12)	103.1 (7)	Rh(1)–C(12)–C(13)	146.7 (15)
Rh(1)–C(2)–C(3)	71.6 (10)	Rh(2)–C(12)–C(13)	130.7 (14)
Rh(1)–C(2)–C(7)	107.6 (11)	C(12)–C(13)–C(14)	134.2 (18)
C(3)–C(2)–C(7)	108.7 (15)		
Rh(1)–C(3)–C(2)	69.4 (10)		
Rh(1)–C(3)–C(5)	112.2 (12)		
C(2)–C(3)–C(5)	107.0 (15)		

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2.14 (2) Å); the long bond is to the ring carbon with a *tert*-butyl substituent. The equation for the plane through the cyclopentadienone ring carbons and the displacement of atoms from this plane have been calculated and are given in Table SUP-IX (supplementary material). All substituent atoms, including the ketonic oxygen, are significantly displaced away from the metal. The displacements are similar to those observed for complex **5**.

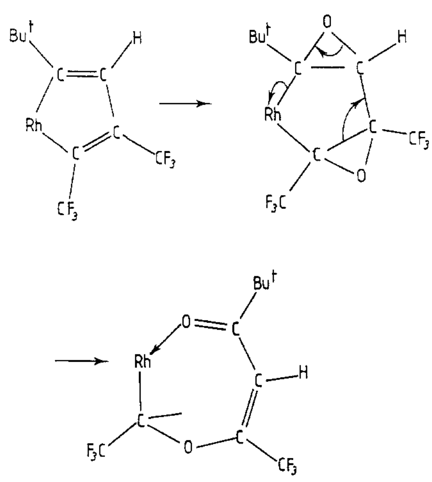
The μ-carbon of the vinylidene group is symmetrically bonded to the Rh–Rh bond with Rh–C distances of 1.98 (2) and 2.00 (2) Å. The Rh(1)–C(12)–C(13) and Rh(2)–C(12)–C(13) angles of 146.7 (15) and 130.7 (14)°, coupled with the C(12)–C(13)–C(14) angle of 134.2 (10)°, indicate that the large *tert*-butyl group forces some displacement of the rest of the vinylidene from its most symmetrical position. The C(12)═C(13) and C(13)—C(14) distances (1.32 (3) and 1.53 (3) Å, respectively) are normal double- and single-bond distances and are similar to those found in other binuclear vinylidene complexes.[24,25] There is a good best-fit plane through the atoms Rh(1), Rh(2), C(12), C(13), C(14) (see Table SUP-IX), and the dihedral angle between this plane and the cyclopentadienone ring plane is 21.9°.

It is possible to contemplate two changes to the molecular structure of **6** to account for the observed isomerization during chromatography. One is an interchange of the positions of H and *t*-Bu within the vinylidene system. The other is a 180° "flip" of the cyclopentadienone ring.

Discussion of Possible Interrelationships between the Complexes. Formation of complexes **1**–**3** is interesting in comparison with other reactions we have investigated involving $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and HC≡CR[14] or MeC≡CBu.[6] *tert*-Butylacetylene is the only terminal acetylene to give dimetallacycloheptadienone complexes, with all other terminal acetylenes forming metallacyclopentadiene complexes selectively. This difference in behavior probably has steric origins and may be due to the relative rates of formation of intermediates that lead to the two complex types. With MeC≡C-*t*-Bu, a dimetallacycloheptadienone complex is formed preferentially, and two isomers are obtained. As with HC≡C-*t*-Bu, the major isomer has *t*-Bu on the ring carbon nearest the rhodium atoms.

When the metallacyclopentadiene complex **3** is chromatographed on activated supports, there is quantitative conversion to the keto–ether complex **4**. This is an unusual oxidation reaction, and we have attempted to elucidate the reaction pathway. We observe there is no conversion when oxygen is bubbled into solutions of **3**. Hence the silica surface must play a key role, but it is not easy to define that role. The Si–O–Si links of the silica are not a likely source of [O]. If the terminal Si–OH bonds provided the [O], "deactivated" silica should be a better [O] source than "activated" silica; the reverse is observed. If acidic sites on the silica surface catalyze the uptake of [O] from the atmosphere, it is difficult to see why the water content of the support should be so significant. Moreover, we observe no conversion to **4** when oxygen is bubbled through acidified solutions of **3** in dichloromethane. Whatever the source of oxygen, the most likely pathway to **4** would seem to be epoxidation of the metalladiene double bonds in **3**; a possible mechanism is shown in Scheme II. With this in mind we treated solutions of **3** with *m*-chloroperoxybenzene acid, a known epoxidation reagent. Although there was an immediate reaction, intractable brown products were formed that contained no **4**. Thus, we can offer no clarification of the reaction pathway for the conversion of **3** to **4**.

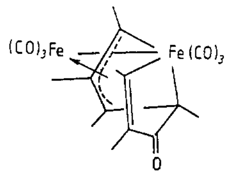
Scheme II. Possible Pathway for Conversion of 3 to 4



Comparison of the proposed structure of **2** and the known structure of **5** indicates that the former complex might be an intermediate in the formation of the latter. We have attempted this conversion by treating a solution of **2** with CO at atmospheric pressure, but no reaction was observed. Conversely, conversion of **5** to **2** by removal of CO looked feasible. We attempted to achieve this by treatment of **5** with Me_3NO, which might be expected[26] to oxidize the terminal CO to the nonligating CO_2. This reaction failed in acetone at room temperature but proceeded smoothly in refluxing dichloromethane. More than 80% conversion to **5** was achieved. Although rhodium compounds are known[27] to assist ring-opening reactions, we are not aware of previous examples where cleavage of a cyclopentadienone ring has been achieved.

Complex **2** has an open pentadienone unit bridging the Rh–Rh bond. In **5**, there is a cyclopentadienone ring plus a terminal carbonyl. Addition of HC≡C-*t*-Bu to **2**, or replacement of CO in **5** by HC≡C-*t*-Bu, is each a possible route to **6**. However, we find that neither complex converts to **6** upon attempted reaction with excess HC≡C-*t*-Bu.

In previous work,[28] we isolated the complexes $(\eta\text{-}C_5H_5)_2Co_2(RC_2R')_3(CO)$ from reactions of $(\eta\text{-}C_5H_5)Co(CO)_2$ with the diynes RC≡CR′ (R = Me, Ph; R′ = C≡CR). The formula of these complexes is similar to that of **6**. At the time, we assigned structures to these cobalt complexes on the basis of the known structure[29] (see **7**) of the related diiron complexes $Fe_2(CO)_5\{(PhC_2H)_3CO\}$. For the cobalt complexes, this required one cyclopentadienyl ring to be η^3-attached to a metal. It now seems likely that these complexes should be reformulated as (μ-cyclopentadienone)(μ-vinylidene)dicobalt complexes. Again,



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two isomers of these complexes were separated and identified spectroscopically.

Summary and Conclusions

The behavior of the $\{(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3) + HC{\equiv}C\text{-}t\text{-}Bu\}$ system is reminiscent of iron carbonyl–acetylene chemistry.[30] A large range of products is obtained, with a variety of cyclic ligands being constructed from the alkyne units and CO. It is unlike that observed in reactions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ with other alkynes where high specificity in product formation is generally observed. It seems likely that the different behavior of HC≡C-*t*-Bu is due to a combination of steric (*t*-Bu) and kinetic (H vs. *t*-Bu) effects that permit several alternative reaction pathways to develop simultaneously.

One feature of the set of products obtained in the present work is the variety of coordination modes observed for the pentadienone unit $C(CF_3){=}C(CF_3){-}C(O){-}C(R){=}C(R')$ (R, R′ = H or *t*-Bu). The fairly common "flyover bridge" attachment of an acyclic pentadienone is observed in two of the complexes (**1** and **2**). A closed cyclopentadienone ring is found in two other products. In one, it is attached in η^1,η^3 manner (complex **5**); in the other, there is an η^2,η^2 attachment (complex **6**). These are most unusual bonding modes for this type of ligand.

Perhaps the most unexpected feature of the reaction systems is the strange oxygenation of the metalladiene ring in complex **3**. Such ring systems are generally very inert in binuclear complexes, although a variety of additions to mononuclear metalladiene rings have been reported.[31] We are not aware of previous observations of oxygenation of metalladiene rings involving either mononuclear or binuclear systems. Another novel feature of this reaction system is the cyclopentadienone ring opening that occurs when **5** is decarbonylated to give **2**.

Acknowledgment. We are grateful to the Australian Research Grants Scheme for financial support and to Johnson Matthey for the loan of rhodium trichloride. Mr. Wayne Baimbridge and Dr. Ian Grayson helped with various aspects of the experimental work.

Registry No. **1**, 105969-35-5; **2**, 105969-36-6; **3**, 105945-01-5; **4**, 105945-02-6; **5**, 105945-03-7; **6**, 105945-04-8; $(\eta\text{-}C_5H_5)_2Rh_5(CO)(CF_3C_2CF_3)$, 71844-53-6; HC≡C-*t*-Bu, 917-92-0; $(\eta\text{-}C_5H_5)_2Rh_2(W)_2(CF_3C_2CF_3)$, 57872-13-6; Rh, 7440-16-6.

Supplementary Material Available: Tables of thermal parameters, ligand geometries, and equations for planes for complexes **4**, **5**, and **6** (12 pages); listing of structure factor amplitudes for complexes **4**, **5**, and **6** (69 pages). Ordering informtion is given on any current masthead page.

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Reactions of Carbon Dioxide with the Electron-Rich Polyhydride Complex [Mo(dmpe)$_2$H$_4$]

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The electron-rich polyhydride complex $[Mo(dmpe)_2H_4]$ (**1**), formed by reduction of $[Mo(dmpe)_2Cl_2]$ under H_2, reacts with CO_2 to give a complex manifold of products containing formate, carbon dioxide, and carbonate ligands. The final product of the reaction is $[Mo(dmpe)_2(CO_3)H_2]$ (**2**), in which reductive disproportionation of CO_2 has led to formation of a carbonate ligand. Two other products have been identified in which only two of the initial hydrides have been retained, one of which is the crystallographically characterized bis(formate) $[Mo(dmpe)_2(OCHO)_2]$ (**3**). The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.842$ (8) Å, $b = 13.830$ (4) Å, $c = 9.910$ (3) Å, $\beta = 104.45$ (2)°, $\rho_{calcd} = 1.38$ g cm^{-1}, $Z = 4$, and $R_w = 3.96\%$ and has an octahedral geometry with trans η^1-formate ligands. A precursor to **3** containing an η^2-CO_2 ligand has been spectroscopically characterized as $[Mo(dmpe)_2(CO_2)(OCHO)H]$ (**4**). Two complexes formed early in the reaction sequence, before elimination of H_2, have been spectroscopically identified as $[Mo(dmpe)_2(CO_2)(OCHO)H_3]$ (**5**) and $[Mo(dmpe)_2(OCHO)_2H_2]$ (**6**). The characteristic absorptions between 1600 and 2800 cm^{-1} of the formate, carbonate, hydride, and carbon dioxide ligands in these molecules have been assigned on the basis of ^{13}C and deuterium-labeling studies.

Introduction

Two of the characteristic reactions of carbon dioxide with transition-metal complexes are reversible insertion into a transition-metal hydride bond and reductive disproportion into carbonate and carbon monoxide by electron-rich transition-metal complexes.[1] While examining[2] the chemistry of molybdenum complexes with the strongly σ-donating bis(chelate) phosphane $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (dmpe), we have prepared an electron-rich polyhydride complex ($[Mo(dmpe)_2H_4]$ (**1**)) which could a priori exhibit either of these reactions when treated with CO_2.

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