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Synthesis, Structure, and Reactions of the Clusters $(\eta\text{-}C_5H_5)_2(\text{chel})Rh_3(CO)(CF_3C_2CF_3)$. The First 46-Electron Alkyne–M_3 Clusters with a Parallel Attachment of the Alkyne

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Treatment of the binuclear complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ with chelate complexes of the type $(\text{chel})Rh(CO)_2$ gives the trinuclear clusters $(\eta\text{-}C_5H_5)_2(\text{chel})Rh_3(CO)(CF_3C_2CF_3)$. Clusters have been prepared with chel = acetylacetonato and other substituted β-diketonates, 8-hydroxyquinolate, *N*-*p*-tolylsalicylaldimine, and other Schiff bases. The structure of the complex $(\eta\text{-}C_5H_5)_2(\text{thd})Rh_3(CO)(CF_3C_2CF_3)$, where thd is 2,2,6,6-tetramethyl-3,5-heptanedionate, has been determined by X-ray crystallography. Crystal data: $C_{26}H_{29}F_6O_3Rh_3$, M_r 812.2, triclinic, $P\bar{1}$, a = 10.905 (2) Å, b = 11.170 (2) Å, c = 13.3869 (15) Å, Z = 2, final R = 0.050 for 6588 "observed" reflections. The molecular structure establishes that the hexafluorobut-2-yne adopts a parallel bonding mode rather than the perpendicular attachment normally observed for 46-electron alkyne–M_3 clusters. It also reveals a very unsymmetrical attachment of the face-bridging carbonyl. Spectroscopic results show that two isomers coexist in acetone solution, with the major isomer exhibiting fluxional behavior. In chlorinated solvents ($CHCl_3$, CH_2Cl_2), only one isomer is present. Various addition reactions have been investigated. Cluster fragmentation occurs in the reactions with CO, CN-*t*-Bu, PhC≡CH, and $PHPh_2$. New complexes isolated from these reactions include $(\eta\text{-}C_5H_5)_2Rh_2(CN\text{-}t\text{-}Bu)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)[\mu\text{-}\eta^1,\eta^2\text{-}C(CF_3)C(CF_3)H]$. Cluster retention is observed in the reactions with SO_2 and tri-*p*-tolylphosphine; the cluster derivatives isolated from these additions are $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(\mu\text{-}SO_2)(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(\mu\text{-}CO)[P(p\text{-tolyl})_3](CF_3C_2CF_3)$. There is chelate ligand exchange in the reaction with 1,10-phenanthroline to give the cationic cluster $[(\eta\text{-}C_5H_5)_2(\text{phen})Rh_3(CO)(CF_3C_2CF_3)]^+$. Removal of the acac ligand from $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ by treatment with $Si(CH_3)_3Cl$ in the presence of other ligands has given the cluster products $(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(\text{dppm-H})$ and $(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)[P(p\text{-tolyl})_3]Cl$.

Introduction

Alkyne–M_3 clusters can be divided into two groups, one with 48- and the other with 46-electron counts.[1] In 48-electron alkyne–M_2M' clusters, the alkyne invariably adopts the μ_3-(η^2-∥) bonding mode,[2,3] shown in Figure 1A, but there can be variation in the metals to which the alkyne σ and π bonds.[4] Recent work by several groups[1,3-5] demonstrates that there is little difference in energy of the possible isomers of such clusters. Some of the factors that influence the precise mode of attachment of the alkyne have been recognized,[3,6,7] and this was also the focus of our previous paper.[8] In all of the known 46-electron alkyne–M_2M' clusters, the alkyne adopts the μ_3-(η^2-⊥) bonding mode,[7,9] displayed in Figure 1B. The relationship between cluster electron count and alkyne bonding mode is now firmly entrenched and has been given theoretical backing.[4,10]

In the present paper, we report the characterization of some alkyne–M_3 clusters which violate the established pattern. In $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ and some related clusters, the electron count is 46 but the alkyne is coordinated in the μ_3-(η^2-∥) mode.

Experimental Section

The general experimental procedures and instrumental techniques are described in a previous paper.[8] Literature methods were used to prepare $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$,[11] the various Schiff base ligands,[12] and the following $(\text{chel})Rh(CO)_2$ compounds: chel = acetylacetonate (acac),[13] trifluoroacetylacetonate (tfac),[13] hexafluoroacetylacetonate (hfac),[13] 2,2,6,6-tetramethyl-3,5-heptanedionate (thd),[14] 8-hydroxyquinolate (oxine),[15] *N*-*p*-tolylsalicylaldimine (Sal=NC_6H_4Me-*p*),[16] *N*-(*p*-methoxyphenyl)salicylaldimine (Sal=$NC_6H_4OCH_3$-*p*),[16] and 2-(*p*-tolylimino)-3-penten-4-olato (tipo).[16] Commercial samples of the following reagents were used without purification: CO (Matheson); 1,10-phenanthroline (phen), phenylacetylene, trimethylsilyl chloride (Aldrich); bis(diphenylphosphino)methane, diphenylphosphine, tri-*p*-tolylphosphine (Strem); sulfur dioxide (BDH). All reactions and manipulation were done under purified nitrogen with use of standard Schlenk techniques.

Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) with $(\text{chel})Rh(CO)_2$. $(\text{acac})Rh(CO)_2$. A solution of 1 (0.125 g, 0.239 mmol) and $(\text{acac})Rh(CO)_2$ (0.063 g, 0.244 mmol) in a 5:1 mixture of hexane–dichloromethane (20 mL) was stirred at 0 °C for 20 h. The color of the solution changed from green to brown, and

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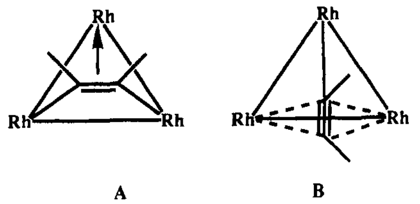

Figure 1. Representations of the parallel (A) and perpendicular (B) bonding modes of alkynes on the Rh_3 face of clusters.

a black precipitate deposited. A syringe was used to separate the solution from the precipitate. TLC of the solution separated trace products from $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.030 g, 23%), which was identified[11,17] from its IR spectrum and R_f value. The solid dissolved in polar organic solvents, but the solutions obtained were very air sensitive. Adsorption onto chromatographic grade silica or alumina also resulted in decomposition. The solid was washed thoroughly with cold hexane and dried under vacuum. This gave $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ (0.0957 g, 55%), mp 152 °C dec. Anal. Calcd for $C_{20}H_{17}F_6O_3Rh_3$: C, 33.0; H, 2.4; F, 15.7. Found: C, 32.9; H, 2.3; F, 16.0. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1750 (w) cm^{-1}, ν(acac) at 1560 (m), 1510 (m) and 1420 (m br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (s, 10 H, $2C_5H_5$), 5.37 (s, 1 H, CH), 2.07 (s, 6 H, $2CH_3$); ^{19}F NMR ($CDCl_3$) δ −50.3 (m, 3 F, CF_3), −52.3 (m, 3 F, CF_3); MS [m/z ion (relative intensity)] 728 $[M]^+$ (18), 700 $[M - CO]^+$ (23), 601 $[M - CO - acac]^+$ (24), 233 $[C_{10}H_{10}Rh]^+$ (100).

(tfac)Rh(CO)$_2$. A solution containing **1** (0.105 g, 0.199 mmol) and (tfac)Rh(CO)$_2$ (0.065 g, 0.208 mmol) dissolved in a 5:2 mixture of hexane–dichloromethane (20 mL) was stirred at room temperature. Within 10 min, the color of the solution had changed from green to brown. After 1 h, the reaction temperature was lowered from room temperature to 0 °C, and the mixture was stirred for a further 48 h to ensure complete reaction. With the aid of a syringe, the reaction solution was separated from a dark brown precipitate, which was washed thoroughly with cold hexane. The combined solution and washings were concentrated and chromatographed by TLC with a 1:1 mixture of hexane–dichloromethane as eluent. This separated $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (yellow, first band; 0.028 g, 25%)[11,17] and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (purple, fifth band; 0.004 g, 3%)[18] from several trace bands and decomposed material which remained in the base band.

The brown solid decomposed when left in the air. Solutions of the compound in polar organic solvents were very air sensitive, and decomposition also occurred on attempted chromatography under nitrogen. The well-washed solid was dried under vacuum. This gave $(\eta\text{-}C_5H_5)_2(tfac)Rh_3(CO)(CF_3C_2CF_3)$ (0.0634 g, 41%), mp 187 °C. Anal. Calcd for $C_{20}H_{14}F_9O_3Rh_3$: C, 30.7; H, 1.8; F, 21.9. Found: C, 30.7; H, 2.0; F, 22.0. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1760 (m) cm^{-1}, ν(tfac) at 1615 (m) and 1420 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.74 (s, 1 H, CH), 5.54 (s, 10 H, $2C_5H_5$), 2.19 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −50.4 (m, 3 F, CF_3), −52.7 (m, 3 F, CF_3), −72.25 (s, 3 F, CF_3); MS [m/z ion (relative intensity)] 782 $[M]^+$ (25), 754 $[M - CO]^+$ (32), 601 $[M - CO - tfac]^+$ (34), 233 $[C_{10}H_{10}Rh]^+$ (100).

(thd)Rh(CO)$_2$. Solutions of **1** (0.100 g, 0.190 mmol) and (thd)Rh(CO)$_2$ (0.070 g, 0.210 mmol) in hexane (20 mL) were mixed and stirred at room temperature for 3 h and then at 0 °C for a further 18 h. During this time, a black solid precipitated. This was filtered, washed with cold hexane, and dried under vacuum. The solid was identified as $(\eta\text{-}C_5H_5)_2(thd)Rh_3(CO)(CF_3C_2CF_3)$ (0.066 g, 43%), mp 188 °C. Anal. Calcd for $C_{26}H_{29}F_6O_3Rh_3$: C, 38.4; H, 3.6; F, 14.0. Found: C, 38.2; H, 3.5; F, 14.1. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1760 (m) cm^{-1}, ν(thd) at 1535 (m br) and 1400 (w br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.73 (s, 1 H, CH), 5.50 (s, 10 H, $2C_5H_5$), 1.16 (s, 18 H, $2C(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −50.6 (m, 3 F, CF_3), −52.1 (m, 3 F, CF_3); MS [m/z ion (relative intensity)] 812 $[M]^+$ (30), 784 $[M - CO]^+$ (15), 727 $[M - CO - Bu^t]^+$ (20), 629 $[M - 2CO - 2Bu^t - CH]^+$ (12), 601 $[M - CO - thd]^+$ (50), 233 $[C_{10}H_{10}Rh]^+$ (100).

The combined filtrate and washings were concentrated and chromatographed by TLC with a 2:1 mixture of hexane–dichloromethane as eluent. The major species separated were $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.0185 g, 18%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.0168 g, 13%).

(oxine)Rh(CO)$_2$. **1** (0.113 g, 0.215 mmol) and (oxine)Rh(CO)$_2$ (0.060 g, 0.198 mmol) in a 2:1 mixture of dichloromethane–hexane (20 mL) were stirred at room temperature. Over 1 h, a solution color change from green to brown was observed. The reaction mixture was then cooled to 0 °C and stirred for a further 24 h. Black-brown crystals deposited, and were isolated by removal of the solution with a syringe. The crystals were washed thoroughly with cold hexane. The solution and washings were concentrated under reduced pressure and chromatographed by TLC with a 2:1 mixture of hexane–dichloromethane as eluent; $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.033 g, 30%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.002 g, 2%) were separated from the decomposition material in the base band.

The solid product was reasonably stable to air. It dissolved readily in common organic solvents, and the solutions decomposed slowly upon exposure to air. This product was characterized as $(\eta\text{-}C_5H_5)_2(oxine)Rh_3(CO)(CF_3C_2CF_3)$ (0.103 g, 67%), mp 238 °C. Anal. Calcd for $C_{24}H_{16}F_6NO_2Rh_3$: C, 37.3; H, 2.1; F, 14.7; N, 1.8. Found: C, 37.5; H, 2.1; F, 14.4; N, 1.9. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1735 (m br) cm^{-1}; ^1H NMR (acetone-d_6) δ 9.07 (d, 1 H, $J_{H_1-H_2}$ = 4.9 Hz, H_1), 8.49 (dd, 1 H, $J_{H_2-H_3}$ = 8.2 Hz and $J_{H_1-H_3}$ = 1.3 Hz, H_3), 7.74 (dd, 1 H, $J_{H_2-H_3}$ = 8.2 Hz and $J_{H_1-H_2}$ = 4.9 Hz, H_2), 7.44 (t, 1 H, $J_{H_4-H_5} = J_{H_5-H_6}$ = 7.9 Hz, H_5), 7.10 (dd, 1 H, $J_{H_4-H_5}$ = 7.9 Hz and $J_{H_4-H_6}$ = 0.7 Hz, H_4), 6.93 (d, 1 H, $J_{H_5-H_6}$ = 7.9 Hz, H_6) 5.64 (s br, 10 H, $2C_5H_5$); ^{19}F NMR (acetone-d_6) δ −48.3 (m, 3 F, CF_3), −50.1 (m, 3 F, CF_3); MS [m/z ion (relative intensity)] 773 $[M]^+$ (7), 745 $[M - CO]^+$ (10), 233 $[C_{10}H_{10}Rh]^+$ (12), 145 $[C_9H_7NO]^+$ (25), 69 $[CF_3]^+$ (100).

Sal═N(C$_6$H$_4$CH$_3$-*p*)Rh(CO)$_2$. A solution of Sal═N(C$_6$H$_4$CH$_3$-*p*)Rh(CO)$_2$ (0.070 g, 0.180 mmol) in dichloromethane (10 mL) was added to **1** (0.100 g, 0.190 mmol). The resulting solution was stirred for 6 h; during this time the color of the solution changed from green to brown. Heptane (15 mL) was added, and stirring was continued for a further 18 h. With a syringe, solution was removed from a black solid that had precipitated, and the latter was washed thoroughly with cold heptane. TLC of the solution and washings with a mixture of hexane and diethyl ether as eluent separated several trace products from unchanged **1** (0.006 g), $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.050 g, 51%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.004 g, 3%). Decomposition material was evident in the base band.

The black solid decomposed relatively quickly in the air, and solutions of the compound in polar organic solvents were rapidly decomposed by air. The black solid was characterized as $(\eta\text{-}C_5H_5)_2[Sal{=}N(C_6H_4CH_3\text{-}p)]Rh_3(CO)(CF_3C_2CF_3)$ (0.041 g, 27%), mp 212 °C. Anal. Calcd for $C_{29}H_{22}F_6NO_2Rh_3$: C, 41.5; H, 2.6; F, 13.6; N, 1.7. Found: C, 41.3; H, 2.8; F, 13.6; N, 1.8. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1695 (m br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07 (d, 1 H, J = 2.5 Hz), 7.40 (dd, 1 H, J = 6.8 and 1.8 Hz), 7.39 (dd, 1 H, J = 6.8 and 1.8 Hz), 7.28 (m, 1 H), 7.23 (d, 1 H, J = 1.8 Hz), 7.20 (m, 1 H), 7.17 (m, 1 H), 7.07 (dd, 1 H, J = 6.7 and 1.8 Hz), 6.71 (ddd, 1 H, J = 6.8, 6.7 and 1.8 Hz), 5.26 (s, 10 H, $2C_5H_5$), 2.39 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −49.5 (m, 3 F, CF_3), −52.5 (m, 3 F, CF_3); MS [m/z ion (relative intensity)] 839 $[M]^+$ (2), 811 $[M - CO]^+$ (10), 692 $[M - 2CO - C_6H_5]^+$ (10), 666 $[C_{19}H_{15}F_6Rh_3]^+$ (14), 233 $[C_{10}H_{10}Rh]^+$ (100).

Preparation of Additional (η-C$_5$H$_5$)$_2$(chel)Rh$_3$(CO)(CF$_3$C$_2$CF$_3$) Complexes. Experimental detail for the complexes with chel = hfac, sal═N(C$_6$H$_4$OCH$_3$-*p*), and tipo is submitted as supplementary material.

Crystallography. Single crystals of $(\eta\text{-}C_5H_5)_2(thd)Rh_3(CO)(CF_3C_2CF_3)$ were grown from a methylcyclohexane–tetrahydrofuran solvent mixture. A red-brown tabular crystal was mounted and sealed under nitrogen in a Lindeman capillary. Intensity measurements were made on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation at 293 K. The unit cell parameters were determined by a least-squares fit of 26 reflections in the range $3.5 < 2\theta < 60°$. Pertinent crystallographic data are summarized in Table I. Three standard

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Table I. Summary of Crystal Structure Data for the Complex (η-$C_5H_5)_2$(thd)Rh_3(CO)($CF_3C_2CF_3$)

(a) Crystal Data	
formula	$C_{26}H_{29}F_6O_3Rh_3$
mol wt	812.2
cryst syst	triclinic
space syst	$P\bar{1}$
a, Å	10.905 (2)
b, Å	11.170 (2)
c, Å	13.3869 (15)
V, Å^3	1405.8 (4)
Z	2
D(calcd), g cm^{-3}	1.919
abs coeff, mm^{-1}	1.779
F(000)	796
μ(Mo, Kα), cm^{-1}	17.8
(b) Data Collection	
cryst dimens, mm	0.35 × 0.39 × 0.12
2θ limits, deg	3.5–60
ω scan range, deg	variable; 3.00–15.63
total no. of data	8528
independent reflns., R int = 1.40%	8206
data $F > 6\sigma(F)$	6588
final R and R_w	0.050 and 0.051
weighting scheme	$\omega^{-1} = \sigma^2(F)$

Table II. Non-Hydrogen Atom Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)[a]

	x	y	z	U(eq)
Rh(1)	1508 (1)	3212 (1)	3586 (1)	33 (1)
Rh(2)	1700 (1)	4365 (1)	1539 (1)	32 (1)
Rh(3)	−609 (1)	5316 (1)	2667 (1)	27 (1)
O(1)	−1190 (4)	7397 (4)	2126 (3)	39 (1)
O(2)	−2636 (4)	5664 (4)	2751 (3)	38 (1)
O(3)	1512 (5)	6113 (5)	2958 (4)	45 (1)
F(1)	2924 (5)	1162 (5)	1607 (5)	98 (3)
F(2)	1569 (8)	470 (5)	2711 (6)	138 (5)
F(3)	1011 (7)	1575 (7)	1205 (6)	130 (5)
F(4)	−1847 (5)	3192 (5)	4288 (4)	69 (2)
F(5)	−1891 (5)	2711 (5)	2868 (5)	80 (3)
F(6)	−453 (5)	1309 (5)	3987 (5)	97 (3)
C(1)	−3471 (9)	10655 (9)	2408 (8)	79 (3)
C(2)	−2991 (9)	10381 (9)	586 (7)	79 (3)
C(3)	−1069 (10)	9843 (10)	1626 (9)	97 (4)
C(4)	−2445 (7)	9788 (7)	1654 (6)	44 (2)
C(5)	−2361 (6)	8316 (6)	2063 (5)	34 (1)
C(6)	−3565 (7)	8063 (7)	2306 (5)	44 (2)
C(7)	−3630 (6)	6783 (6)	2615 (5)	36 (1)
C(8)	−5042 (7)	6673 (7)	2817 (6)	47 (2)
C(9)	−5871 (8)	7561 (8)	1878 (6)	56 (2)
C(10)	−5749 (11)	7162 (11)	3772 (9)	105 (4)
C(11)	−4893 (10)	5237 (10)	2975 (8)	92 (3)
C(12)	1658 (8)	1523 (8)	1958 (7)	55 (2)
C(13)	1079 (6)	2829 (6)	2273 (5)	34 (1)
C(14)	−100 (6)	3323 (6)	2941 (5)	32 (1)
C(15)	−1078 (8)	2627 (8)	3523 (6)	52 (2)
C(16)	3197 (9)	1503 (9)	4338 (7)	69 (2)
C(17)	1993 (9)	1472 (9)	4950 (7)	70 (3)
C(18)	1389 (9)	2682 (9)	5306 (7)	70 (3)
C(19)	2213 (9)	3402 (10)	4935 (8)	74 (3)
C(20)	3338 (10)	2647 (9)	4394 (7)	72 (3)
C(22)	2050 (18)	6054 (17)	254 (13)	50 (5)
C(23)	1644 (15)	5257 (18)	−190 (11)	42 (4)
C(24)	2552 (22)	4014 (23)	−60 (16)	55 (5)
C(25)	3553 (16)	3750 (17)	485 (12)	45 (4)
C(211)	3655 (17)	4279 (20)	591 (12)	43 (5)
C(221)	2682 (21)	5796 (20)	517 (14)	50 (5)
C(231)	1718 (19)	5770 (21)	−31 (15)	50 (5)
C(241)	2095 (27)	4487 (29)	−162 (20)	72 (8)
C(251)	3093 (28)	3622 (30)	180 (21)	84 (9)
C(26)	1132 (6)	5370 (6)	2769 (5)	34 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Occupancies of rings C21–C25 and C211–C251 are 0.53 (3) and 0.47 (3), respectively.

reflections were measured every 197 reflections to monitor crystal decay. During data collection, no decay of intensity was observed.

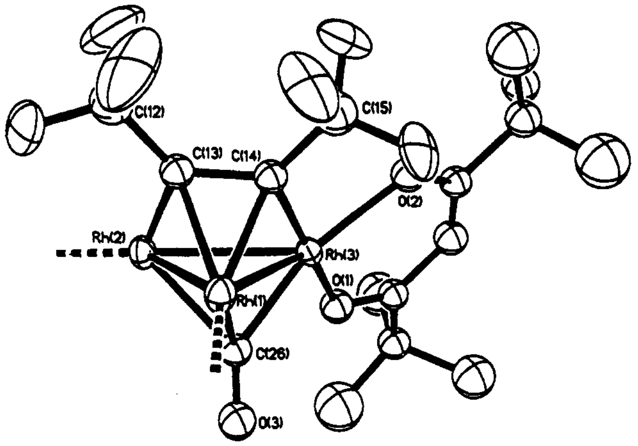

Figure 2. Molecular structure of the complex (η-$C_5H_5)_2$(thd)-Rh_3(CO)($CF_3C_2CF_3$). The C_5H_5 ligands on Rh(1) and Rh(2) have been omitted for clarity.

Table III. Important Bond Lengths (Å) and Angles (deg) for (η-$C_5H_5)_2$(thd)Rh_2(CO)($CF_3C_2CF_3$)

(a) Bond Lengths			
Rh(1)–Rh(2)	2.654 (1)	C(13)–C(14)	1.413 (8)
Rh(1)–Rh(3)	2.692 (1)		
Rh(2)–Rh(3)	2.635 (1)	Rh(1)–C(26)	2.219 (6)
		Rh(2)–C(26)	2.119 (7)
Rh(1)–C(13)	2.111 (18)	Rh(3)–C(26)	1.958 (8)
Rh(1)–C(14)	2.052 (8)	C(26)–O(3)	1.176 (11)
Rh(2)–C(13)	2.008 (7)		
Rh(3)–C(14)	1.988 (5)	Rh(3)–O(1)	2.064 (4)
		Rh(3)–O(2)	2.064 (5)
(b) Bond Angles			
Rh(2)–Rh(1)–Rh(3)	59.1 (1)	C(12)–C(13)–C(14)	128.7 (7)
Rh(1)–Rh(2)–Rh(3)	61.2 (1)	C(13)–C(14)–C(15)	128.0 (7)
Rh(1)–Rh(3)–Rh(2)	59.8 (1)		
		Rh(2)–Rh(1)–C(26)	50.6 (2)
Rh(2)–Rh(1)–C(13)	48.2 (2)	Rh(1)–Rh(2)–C(26)	54.0 (2)
Rh(3)–Rh(1)–C(14)	47.2 (2)	Rh(1)–Rh(3)–C(26)	54.3 (2)
Rh(2)–Rh(1)–C(14)	71.4 (2)	Rh(3)–Rh(2)–C(26)	47.1 (2)
Rh(3)–Rh(1)–C(13)	69.0 (1)	Rh(2)–Rh(3)–C(26)	52.5 (2)
Rh(1)–Rh(2)–C(13)	51.6 (2)	Rh(1)–C(26)–Rh(2)	75.4 (2)
Rh(1)–Rh(3)–C(14)	49.2 (2)	Rh(1)–C(26)–Rh(3)	80.0 (3)
		Rh(2)–C(26)–Rh(3)	80.4 (3)
Rh(3)–Rh(2)–C(13)	71.5 (2)		
Rh(2)–Rh(3)–C(14)	72.7 (2)		
Rh(1)–C(13)–Rh(2)	80.2 (3)	Rh(1)–C(26)–O(3)	128.4 (5)
Rh(1)–C(14)–Rh(3)	83.5 (3)	Rh(2)–C(26)–O(3)	132.6 (5)
		Rh(3)–C(26)–O(3)	137.1 (4)
Rh(1)–C(13)–C(14)	67.9 (4)	Rh(1)–Rh(3)–O(1)	137.1 (2)
Rh(1)–C(14)–C(13)	72.5 (4)	Rh(1)–Rh(3)–O(2)	132.9 (1)
Rh(2)–C(13)–C(14)	108.0 (5)	Rh(2)–Rh(3)–O(1)	103.5 (1)
Rh(3)–C(14)–C(13)	107.4 (5)	Rh(2)–Rh(3)–O(2)	141.2 (1)
C(13)–Rh(1)–C(14)	39.6 (2)	O(1)–Rh(3)–O(2)	86.1 (2)
		O(1)–Rh(3)–C(14)	170.1 (2)
		O(2)–Rh(3)–C(14)	91.4 (2)

Data were corrected for Lorentz–polarization effects. A face-indexed numerical absorption correction was applied. The structure was solved by Patterson methods using SHELXTL PLUS[19] and difference Fourier methods. Only the observed reflections with $F > 6.0\sigma(F)$ were used in the final full-matrix least-squares refinement, the function minimized being $\sum w(F_o - F_c)^2$. Anisotropic thermal parameters were introduced for Rh and F. All other atoms were allowed to refine isotropically. Hydrogen atoms were included at calculated positions (C–H = 0.97 Å), with a riding model single-variable isotropic thermal parameter which refined to 0.12 (2) Å. The cyclopentadienyl rings C(21)–C(25) and C(211)–C(251) were disordered and were refined with site occupancy factors of 0.53 and 0.47, respectively. All calculations were carried

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(19) Sheldrick, G. M. *Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.

out on a Micro-VAXII computer with the SHELXTL PLUS system of programs. Scattering factors used for all atoms as well as anomalous dispersion corrections were those stored in SHELXTL PLUS.

The atomic labeling scheme used is shown in Figure 2. Final positional parameters are given in Table II, and selected bond lengths and angles, in Table III. The supplementary material contains listings of hydrogen atom coordinates, structure factor amplitudes, thermal parameters, ligand geometries, and equations for planes.

Addition Reactions to the Rh_3 Clusters. $(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)(CF_3C_2CF_3)$ + CO. Carbon monoxide was bubbled through a solution of $(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)(CF_3C_2CF_3)$ (0.040 g, 0.051 mmol) in CH_2Cl_2 (20 mL). Over 30 min, the color of the solution changed from brown to yellow. The mixture was evaporated to dryness. TLC of the residue with a 2:1 mixture of hexane–dichloromethane as eluent separated six bands. The three major bands were collected. These gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.020 g, 71%; yellow, second band), $(\text{hfac})Rh(CO)_2$ (0.004 g, 25%; red, third band), and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.002 g, 6%; purple, sixth band).

$(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ + CN-*t*-Bu. *tert*-Butyl isocyanide (0.01 mL, 0.097 mmol) was added to a solution of $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ (0.060 g, 0.082 mmol) in a 1:1 mixture of hexane and dichloromethane (20 mL). After 5 days, the solution was evaporated to dryness. A solution of the residue in dichloromethane was chromatographed by TLC with a 2:1 mixture of hexane–dichloromethane as eluent. Seven bands developed, leaving a large amount of intractable material in the base band. Five of the bands were very faint and were rejected. The second, orange band was characterized spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(\text{CN-}t\text{-Bu})_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.017 g, 31%), mp 159 °C dec. Spectroscopic data: IR (CH_2Cl_2) ν(CN) at 2125 (vs) and 2075 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.26 (s, 10 H, $2C_5H_5$), 1.35 (s, 18 H, $2C(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −54.4 (s, CF_3); MS [*m/z* ion (relative intensity)] 664 $[M]^+$ (<5), 645 $[M - F]^+$ (5), 581 $[M - \text{CN-}t\text{-Bu}]^+$ (6), 562 $[M - F - \text{CN-}t\text{-Bu}]^+$ (5), 525 [na] (10), 498 $[M - 2\text{CN-}t\text{-Bu}]^+$ (5), 479 $[M - F - 2\text{CN-}t\text{-Bu}]^+$ (5), 460 $[M - 2F - 2\text{CN-}t\text{-Bu}]$ (5), 334 $[(C_5H_5)Rh(\text{CN-}t\text{-Bu})_2]^+$ (60), 278 [na] (45), 233 $[C_{10}H_{10}Rh]^+$ (100). The fifth purple band was characterized spectroscopically as $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.001 g, 2%).

$(\eta\text{-}C_5H_5)_2(\text{oxine})Rh_3(CO)(CF_3C_2CF_3)$ + $PHPh_2$. To a solution of $(\eta\text{-}C_5H_5)_2(\text{oxine})Rh_3(CO)(CF_3C_2CF_3)$ (0.041 g, 0.053 mmol) in dichloromethane (20 mL) was added neat $PHPh_2$ (0.03 mL, 0.164 mmol) from a syringe. No immediate reaction was apparent. IR monitoring of the reaction solution indicated consumption of the starting material over 19 h. Concentration of the red reaction solution and subsequent TLC with a 1:1 mixture of hexane–dichloromethane as eluent separated four bands from the decomposition material in the base band. Extraction of products from the major bands gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (band 1, orange; 0.0043 g, 15%), $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)[\mu\text{-}\eta^1,\eta^2\text{-}C(CF_3)C(CF_3)H]$[20] (band 2, red; 0.0113 g, 32%), and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (band 3, purple; 0.003 g, 8%). The remaining band was very faint and was not collected.

$(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ + PhC≡CH. Phenylacetylene (0.01 mL, 0.078 mmol) was added from a syringe to a stirred solution of $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ (0.040 g, 0.055 mmol) in dichloromethane (15 mL). On complete addition, the color of the solution had changed from brown to orange. TLC with a 8:3 mixture of hexane–dichloromethane as eluent separated five minor products from $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}\eta^2,\eta^4\text{-}C_4(CF_3)_2HPh]$ (0.0135 g, 41%), which was identified from spectroscopic data.[21]

$(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ + SO_2. Sulfur dioxide gas was bubbled through a solution of $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ (0.050 g, 0.069 mmol) in benzene (30 mL) for ca. 2 h. During this time, the color of the solution changed from green to orange. Solvent was removed under reduced pressure, and the residue was well washed with heptane. This gave an orange solid, $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(\mu\text{-}SO_2)(CF_3C_2CF_3)$ (0.027 g, 50%), mp <100 °C dec. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 2050 (s) cm^{-1}, ν(SO) and/or ν(CF) at 1235 (m), 1190 (vs), and 1130 (m br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (s, 5 H, C_5H_5), 5.66 (s, 5 H, C_5H_5), 5.27 (s, 1 H, CH), 2.01 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −51.9 (q, 3 F, J_{F-F} = 10 Hz, CF_3), −54.5 (qd, 3 F, J_{F-F} = 10 Hz and J_{Rh-F} = 0.7 Hz, CF_3); MS [*m/z* ion (relative intensity)] 728 $[M - SO_2]^+$ (35), 700 $[M - SO_2 - CO]^+$ (30), 601 $[M - SO_2 - CO - \text{acac}]^+$ (28), 267 $[C_5H_5Rh\text{hacac}]^+$ (10), 233 $[C_{10}H_{10}Rh]^+$ (100).

TLC of the washings, with a 3:1 mixture of hexane–dichloromethane as eluent, separated $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.005 g, 13%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.003 g, 5%).

$(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ + P(*p*-tolyl)$_3$. Solid tri-*p*-tolylphosphine (0.050 g, 0.164 mmol) was added to a solution of $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)$ (0.112 g, 0.153 mmol) in dichloromethane (30 mL). IR monitoring of the reaction solution showed no further change after 72 h. Concentration of the solution and addition of heptane (10 mL) resulted in the precipitation of a crimson solid. This was isolated by filtration and washed with heptane until the washings were clear. The filtrate and washings were set aside. Recrystallization of the solid from dichloromethane–heptane at 0 °C gave a crimson solid, $(\eta\text{-}C_5H_5)_2(\text{acac})Rh_3(CO)(CF_3C_2CF_3)[P(p\text{-}C_6H_4CH_3)_3]$ (0.058 g, 37%), mp 172 °C. Anal. Calcd for $C_{41}H_{38}F_6O_3PRh_3$: C, 47.7; H, 3.7; F, 11.0; P, 3.0. Found: C, 47.9; H, 4.0; F, 10.8; P, 3.4. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1725 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 6 H, C_6H_4), 7.10 (m, 6 H, C_6H_4), 5.43 (s, 5 H, C_5H_5), 4.97 (s, 5 H, C_5H_5), 4.57 (s, 1 H, CH(acac)), 3.25 (s, 9 H, CH_3 (*p*-tolyl)), 1.68 (s, 3 H, CH_3(acac)), 1.56 (s, 3 H, CH_3(acac)); ^{19}F NMR ($CDCl_3$) δ −44.7 (qd, 3 F, J_{F-F} = 10.6 Hz and $J_{P-F} \approx$ 10 Hz, CF_3), −52.3 (q, 3 F, J_{F-F} = 10.6 Hz, CF_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 39.3 (dd, J_{Rh-P} = 180 Hz, the additional coupling constant was difficult to determine from this spectrum); FAB MS (CH_2Cl_2, NOBA, positive ion) [*m/z* ion] 933 $[M - \text{acac}]^+$, 905 $[M - CO - \text{acac}]^+$, 841 $[M - \text{acac} - C_7H_8]^+$, 814 $[M - CO - \text{acac} - C_7H_7]^+$, 723 $[M - CO - \text{acac} - 2C_7H_7]^+$, 632 $[C_{14}H_{10}F_6PRh_3]^+$, 601 $[C_{14}H_{10}F_6Rh_3]^+$, 472 $[C_{26}H_{26}PRh]^+$, 304 $[C_{21}H_{21}P]^+$, 233 $[C_{10}H_{10}Rh]^+$.

Under reduced pressure, solvent was removed from the combined filtrate and washings. TLC of the residue with a 1:1 mixture of hexane–dichloromethane as eluent separated seven bands from the decomposition material in the base band. The first band was yellow and yielded $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.040 g, 47%). The red product obtained from the second band was identified spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2[P(C_6H_4CH_3\text{-}p)_2(C_6H_3CH_3)](C(CF_3)C(CF_3)H)$ (0.0025 g, 2%). Spectroscopic data: IR no ν(CO) evident; ^1H NMR ($CDCl_3$) δ 7.34 and 7.17 (2 m, 9 H, C_6H_4/C_6H_3), 6.60 (m, 1 H, meta H of C_6H_3), 6.15 (dd, 1 H, ortho H of C_6H_3), 5.40 (s, 5 H, C_5H_5), 4.78 (s, 5 H, C_5H_5), 2.41 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 1.75 (m, 1 H, CH); ^{19}F NMR ($CDCl_3$) δ −49.5 (q, 3 F, J_{F-F} = 12.5 Hz, CF_3), −51.65 (qd, 3 F, J_{F-F} = 12.5 Hz and J_{F-H} = 11.8 Hz, $C(CF_3)H$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 13.9 (dd, $^1J_{Rh-P}$ = 146 Hz, $^3J_{Rh-P}$ = 8 Hz); MS [*m/z* ion (relative intensity)] 802 $[M]^+$ (1), 634 $[M - C_5H_5Rh]^+$ (21), 304 $[C_{21}H_{21}P]^+$ (2), 233 $[C_{10}H_{10}Rh]^+$ (100). The purple cluster compound $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.008 g, 7.5%) was isolated from band 6. All other bands were very faint and were rejected.

$(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)(CF_3C_2CF_3)$ + phen. Solutions of $(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)(CF_3C_2CF_3)$ (0.100 g, 0.120 mmol) and phen (0.025 g, 0.135 mmol) in acetone (50 mL) were thoroughly mixed, and NH_4PF_6 (0.024 g, 0.140 mmol) was then added. The reaction mixture was stirred for 24 h; over this time, the color of the solution changed gradually from green to red-brown. Concentration of the mixture and the addition of heptane caused a red-brown solid to precipitate. This was isolated by filtration. Thorough washing of the solid with heptane and benzene, and several recrystallizations from acetone/benzene failed to remove the last traces of NH_4PF_6 and some minor C_5H_5Rh impurities from the major product $[(\eta\text{-}C_5H_5)_2(\text{phen})Rh_3(CO)(CF_3C_2CF_3)]^+PF_6^-$ (0.03 g, ~26%), mp >250 °C. Spectroscopic data: FAB MS (CH_2Cl_2, NOBA, positive ion) [*m/z* ion (relative intensity)] 809 $[M]^+$ (95), 781 $[M - CO)]^+$ (55), 601 $[M - CO - \text{phen}]^+$ (<10), 348 $[C_5H_5Rh\text{phen}]^+$ (20); IR (CH_2Cl_2) ν(CO) at 1710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.0–7.0 (series of multiplets, ~8 H, phen), 5.63 (s br,

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[20] Dickson, R. S.; Paravagna, O. M. Unpublished results. This compound is formed as a major product in the reaction of $PHPh_2$ with $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ and will be described in detail in a later paper.

[21] Dickson, R. S.; McLure, F. I.; Nesbit, R. J. *J. Organomet. Chem.* **1988**, *349*, 413.

5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −49.2 (m, 3 F, CF_3), −51.5 (m, 3 F, CF_3), −73.0 (d, >6 F, J_{P-F} = 713 Hz, PF_6^-).

The combined filtrate and washings obtained above were concentrated and subjected to TLC. Elution with a 1:1 mixture of hexane and dichloromethane separated small amounts of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ from the decomposition material in the base band.

$(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ + $Si(CH_3)_3Cl$/dppm. Addition of $Si(CH_3)_3Cl$ (0.02 mL, 0.184 mmol) and dppm (0.060 g, 0.154 mmol) to a solution of $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ (0.120 g, 0.165 mmol) in benzene (30 mL) resulted in the color of the solution changing from emerald green to dark olive green. The reaction mixture was left for 3 h. Subsequent TLC of the reaction mixture with a 3:1:1 mixture of heptane–dichloromethane–diethyl ether as eluent separated three major bands from the decomposition material in the base band. The first two bands yielded compounds that were identified spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (yellow; 0.006 g, 7%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (purple; 0.003 g, 3%). The third band gave an olive green solid, $(\eta\text{-}C_5H_5)_2Rh_3(CO)$(dppm-H)$(CF_3C_2CF_3)$ (0.097 g, 61%), mp 160 °C dec. Anal. Calcd for $C_{40}H_{31}F_6OP_2Rh_3$: C, 47.5; H, 3.1; F, 11.3; P, 6.1. Found: C, 47.2; H, 3.25; F, 11.5; P, 6.0. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 2010 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (m, 11 H, $C_6H_{4/5}$) 6.99 (m, 6 H, C_6H_5), 6.70 (ddd, 2 H, J = 7.8, 7.8, and 2.2 Hz, C_6H_4) 5.51 (s, 5 H, C_5H_5), 5.50 (s, 5 H, C_5H_5), 4.54 (td, 1 H, J_{P-H} = 11.3 Hz and J_{H-H} = 12.3 Hz, CH), 4.23 (m, 1 H, CH); ^{19}F NMR ($CDCl_3$) −48.1 (q, 3 F, J_{F-F} = 10 Hz, CF_3), −53.8 (q, 3 F, J_{F-F} = 10 Hz, CF_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 10.5 (dd, 1 P, $^3J_{P-P}$ = 29 Hz and $^1J_{Rh-P}$ = 181 Hz, P^2), 1.5 (ddd, 1 P, $^3J_{P-P}$ = 29 Hz, $^1J_{Rh-P}$ = 133 Hz, and $^3J_{Rh-P}$ = 11 Hz, P^1); FAB MS [m/z ion] 1012 $[M]^+$, 984 $[M - CO]^+$, 867 $[M - CO - CH_2]^+$, 731 [na], 601 $[(C_5H_5)_2Rh_3(C_4F_6)]^+$, 568 $[(C_5H_5)Rh(CO)(dppm)]^+$.

$(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ + $Si(CH_3)_3Cl$/P(*p*-tolyl)$_3$. $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ (0.087 g, 0.120 mmol) was dissolved in benzene (20 mL), and $Si(CH_3)_3Cl$ (0.02 mL, 0.140 mmol) and then P(*p*-tolyl)$_3$ (0.070 g, 0.230 mmol) were added to this solution. There was an immediate change in the color of the solution from brown to crimson. Solvent was removed under reduced pressure, and the residue was extracted with hexane; some solid material remained undissolved. TLC of the extracts, with a 9:1 mixture of hexane–diethyl ether as eluent, separated three bands from decomposition material in the base band. The first band gave orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)$[P(*p*-tolyl)$_3$]$(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.008 g, 8%), mp 138 °C. Anal. Calcd for $C_{36}H_{31}F_6OPRh_2$: C, 52.1; H, 3.8. Found: C, 52.4; H, 3.7. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1985 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 7.13 (m, 12 H, C_6H_5), 5.15 (d, 5 H, J_{Rh-H} = 1.4 Hz, C_5H_5), 4.97 (s, 5 H, C_5H_5), 2.43 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −52.8 (q, 3 F, J_{F-F} = 11 Hz, CF_3), −55.6 (qt, 3 F, J_{F-F} = 11 Hz, J_{Rh-F} = 3 Hz, and J_{P-F} = 3 Hz, CF_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 36.0 (d, J_{Rh-P} = 184 Hz); MS [m/z ion (relative intensity)] 802 $[M - CO]^+$ (22), 634 $[M - CO - C_5H_5Rh]^+$ (16), 472 $[C_5H_5RhP(C_6H_4CH_3)_3]^+$ (19), 233 $[C_{10}H_{10}Rh]^+$ (100). The second band gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ (0.005 g, 8%). There was too little material in the third band for identification.

The solid residue remaining after extraction was recrystallized from dichloromethane–heptane to give a crimson solid. This was identified as $(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)$[P(*p*-tolyl)$_3$]Cl (0.043 g, 37%), mp 155 °C dec. Anal. Calcd for $C_{36}H_{31}ClF_6OPRh_3$: C, 44.6; H, 3.2; Cl, 3.7; F, 11.8; P, 3.2. Found: C, 43.4; H, 3.6; Cl, 4.1; F, 11.5; P, 3.2. Spectroscopic data: IR(CH_2Cl_2) ν(CO) at 1740 (m br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27 (m, 7 H, C_6H_4), 7.15 (m, 5 H, C_6H_4), 5.23 (s br, 10 H, C_5H_5), 2.36 (s br, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −48.5 (m, 3 F, CF_3), −53.5 (m, 3 F, CF_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 39.3 (d, J_{Rh-P} = 183 Hz); FAB MS (CH_2Cl_2, NOBA, positive ion) [m/z ion (relative intensity)] 949 $[M - F]^+$ (12), 921 $[M - F - CO]^+$ (15).

Results and Discussion

Formation and Spectroscopic Properties of the Clusters. Chelate complexes of the type $(acac)Rh(CO)_2$ and (Sal=NR)$Rh(CO)_2$ undergo a variety of ligand replacement reactions,[22] but to the best of our knowledge the dicarbonyl compounds have not been used previously in cluster synthesis. Their behavior might differ from that of complexes like $(\eta\text{-}C_5H_5)Rh(CO)_2$ because the metal has a 16-electron count in the chelate compounds but the electron count is 18 for the cyclopentadienyl species. Moreover, the cyclopentadienyl ligand is generally inert in clusters whereas the chelate ligands might be induced to undergo a range of reactions.

A slow reaction does occur when solutions of $(acac)Rh(CO)_2$ and $(\eta\text{-}C_5H_5)_2$ $Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) are stirred together at 0 °C, and a cluster complex $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$ is isolated in 55% yield. Similar reactions occur between 1 and other $(chel)Rh(CO)_2$ compounds, where the chelate ligand includes β-diketonates and Schiff bases. Yields of the clusters obtained vary from 27% (Sal=N($C_6H_4CH_3$-*p*)) to 63% (hfac). The clusters are brown or black solids that are reasonably stable in the air, but solutions of the clusters need to be kept under N_2 to avoid decomposition.

The formulas of the clusters are deduced from elemental analysis and mass spectral data. Retention of just one carbonyl means that these are "unsaturated" clusters with a 46-electron count. Since 46-electron alkyne–trimetal clusters are much less common than the 48-electron counterparts, it was of interest to pursue some structural information.

Spectroscopic data indicate that the chelate clusters exist predominantly as a single isomer when dissolved in chlorinated solvents at room temperature. Infrared results for solutions in dichloromethane are consistent with a face-bridging carbonyl. The ^1H NMR spectra ($CDCl_3$ solutions) show a broad singlet resonance for the cyclopentadienyl protons, and two poorly resolved multiplets of equal intensity are generally observed for the trifluoromethyl groups in the ^{19}F NMR spectra. There is one exception; in the ^{19}F NMR spectrum of the Sal=N(C_6H_4OMe-*p*) derivative, only a single broad trifluoromethyl multiplet is revealed. The spectra of the thd derivative were further investigated a low temperatures. In the ^1H spectrum, the cyclopentadienyl resonance is resolved into two sharp singlets of equal intensity at −40 °C. At the same temperature, the trifluoromethyl multiplets in the ^{19}F spectrum are seen as well-resolved quartets with J_{F-F} = 10 Hz.

Some interesting differences in the spectra were revealed when the solvent was changed to acetone. The infrared spectra of the derivatives with chel = thd, hfac, and Sal=N(C_6H_4R) (R=OMe-*p* or Me-*p*) were measured in this solvent, and each shows a strong carbonyl absorption in the edge-bridging region (eg. at 1848 cm^{-1} for the thd cluster). There is presumably a further carbonyl absorption in the face-bridging region, but this is masked by strong solvent absorptions. The NMR data provide convincing evidence that two isomers do coexist in acetone solutions for all the cluster complexes except that with chel = oxine. In the room-temperature spectra of the latter derivative, there is a single broad singlet in the C_5H_5 region of the ^1H NMR spectrum and two CF_3 multiplets in the ^{19}F NMR spectrum; the spectra closely resemble those discussed above for chloroform solutions of the various clusters. However, the spectra of the other derivatives incorporate additional peaks. The spectra of the thd derivative in acetone-d_6 are representative and are discussed below.

The room-temperature ^1H NMR spectrum contains one broad cyclopentadienyl resonance at δ 5.61 and two sharp

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[22] Dickson, R. S. *Organometallic Chemistry of Rhodium and Iridium*; Academic Press: London, 1983; Chapter III, pp 107–114.

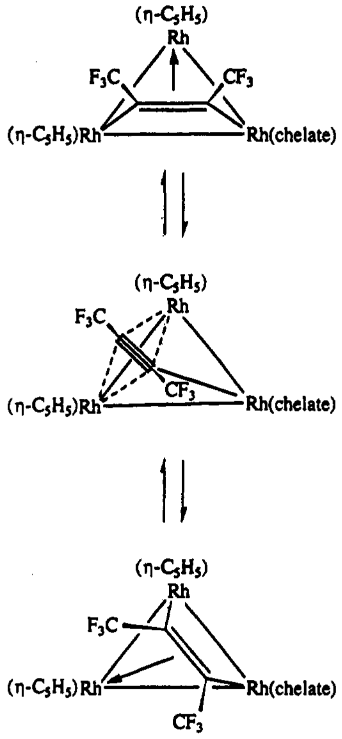


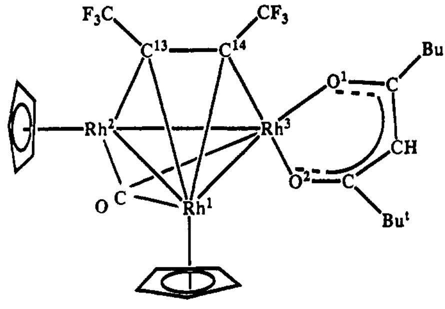
Figure 3. Windshield-wiper motion of the alkyne in the clusters $(\eta\text{-}C_5H_5)_2(chel)Rh_3(CO)(CF_3C_2CF_3)$.

cyclopentadienyl singlets at δ 5.78 and 5.76. The relative areas are 10:1:1, indicating that two isomers are present in the ratio of 5:1. There are also resonances for the CH-(thd) protons in this region at δ 5.83 (major isomer) and δ 5.97 (minor isomer). The ^{19}F NMR spectrum exhibits two broad multiplets at δ 48.9 and ca. 50.7 together with two well-resolved quartets of lesser intensity; one of the latter is partially obscured by the multiplet at δ 50.7, and the other is seen at δ 54.0; it is actually a quartet of doublets with $^5J_{F-F}$ = 9.5 Hz and $^3J_{Rh-F}$ = 2.7 Hz. The profiles of these spectra changed as the temperature was lowered. In the ^1H spectrum, the broad cyclopentadienyl resonances of the major isomer gradually resolved and at −60 °C had split into two sharp singlets of equal intensity. Resonances corresponding to the minor isomer remain sharp over the entire temperature range. The ^{19}F spectrum reveals similar behavior. The two broad CF_3 multiplets of the major isomer resolve into two quartets of equal intensity, and at −60 °C a F–F coupling constant of 10.5 Hz was determined. Again, peaks associated with the minor isomer remain sharp. There is also separation of the two multiplets that were overlapping at room temperature.

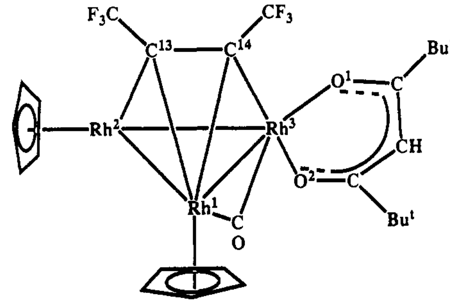
For the oxine derivative in acetone-d_6, the only cyclopentadienyl resonance detected at room temperature is a broad peak. As the temperature is lowered to −40 °C, this is gradually resolved into two sharp singlets of equal intensity. A value of 52 kJ mol^{-1} has been determined for the fluxional process. In the ^{19}F spectrum, only two CF_3 resonances are observed. They are broad multiplets, which resolve into two quartets (J_{F-F} = 10.3 Hz) of equal intensity at −43 °C.

The cumulative data indicate that an unsymmetrical μ_3-(η^2-‖) attachment of the alkyne unit (Figure 1A) is the most stable configuration for both the major and minor isomers of the clusters in both solvents. The variable-temperature NMR results for the major isomer indicate dynamic behavior and are best interpreted in terms of a "windshield-wiper" motion of the bridging alkyne, as shown in Figure 3. This renders the C_5H_5 but not the CF_3 groups equivalent in the fast-exchange limit. Other workers[23,24] have proposed this mechanism to explain related NMR observations. The minor isomer detected in acetone solutions is static on the NMR time scale over all temepratures investigated. For the Sal=N(C_6H_4OMe-*p*) derivative in $CDCl_3$, it is conceivable that the observed equivalence of the pairs of C_5H_5 and CF_3 groups is due to free rotation of the alkyne unit over the trirhodium face.

Static structures for the major and minor isomers in solution are shown in **2a** and **2b**, respectively. Since all previously reported 46-electron trinuclear alkyne clusters have a μ_3-(η^2-⊥) attachment of the alkyne (Figure 1B) and since this bonding mode is essentially the transition state in the fluxional process, it seemed important to determine the solid-state structure of one of the complexes by X-ray crystallography. It proved extremely difficult to grow crystals suitable for X-ray diffraction of any of the eight complexes isolated, and this is the principal reason for preparing so many related compounds. Eventually, satisfactory crystals of the thd complex were obtained by slow crystallization from a mixture of methylcyclohexane and tetrahydrofuran.



2a



2b

Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)_2(thd)Rh_3(CO)(CF_3C_2CF_3)$. The molecular structure is shown in Figure 2; clearly, the alkyne has adopted the parallel bonding mode (Figure 1A); it lies parallel to the (η-C_5H_5)Rh(2)Rh(3)(thd) edge of the Rh_3 triangle, with an angle of 4.4° between the C(13)–C(14) and Rh(2)–Rh(3) bond axes. The observed geometry is consistent with σ attachment of the alkyne to Rh(2) and Rh(3) and π bonding to Rh(1). This is the only 46-electron cluster known where the alkyne has adopted this bonding mode rather than lying perpendicular to an edge of the M_3 triangle.[1] As predicted from infrared results, the carbonyl is face-bridging.

Within the Rh_3 triangle, the Rh(1)–Rh(2), Rh(1)–Rh(3), and Rh(2)–Rh(3) distances all fall within the range nor-

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(23) Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519.

(24) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7385.

mally associated with the Rh–Rh single bond; there is a 0.06 Å difference between the shortest and longest Rh–Rh bonds. Parameters within the Rh_3–$CF_3C_2CF_3$ unit are similar to those found in related complexes, including $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-t-Bu})_3]^+$.[8] For the present complex, the dihedral angle between the Rh_3 and C_4 (of hexafluorobut-2-yne) planes is 68.6°. There is some asymmetry in the attachment of the carbonyl to the Rh_3 face, with the shortest Rh–C distance to Rh(3) (1.96 Å) and the longest to Rh(1) (2.22 Å). The short Rh(3)–C(26) distance is similar to that observed for carbonyls that edge-bridge a Rh–Rh bond, whereas the other two Rh–C(O) bond lengths are close to the longer and shorter distances found in semi-face-bridging carbonyls.[25] It is unusual to find such a large difference in the three M–C distances for a face-bridging carbonyl. There are no π-acid ligands attached to Rh(3) apart from the bridging CO, and consequently there is substantial back-donation from Rh(3) to CO. In contrast, the cyclopentadienyl ligands on Rh(1) and Rh(2) and the π bonding of the alkyne to Rh(1) would reduce the extent of back-donation from these metals to CO. Thus, the different Rh–C(O) distances can be attributed to the nature of the subsidiary ligands. Bond parameters for the Rh(3)(thd) fragment indicate a normal attachment of the β-diketonate to the rhodium atom. There is a dihedral angle of 61.9° between the Rh_3 and O(1)–C(5)–C(6)–C(7)–O(2) planes.

Addition Reactions to the Clusters. The (η-C_5H_5)$_2$(chel)$Rh_3(CO)(CF_3C_2CF_3)$ clusters are formally coordinatively unsaturated, and it was therefore of interest to determine if additional ligands could be added to the clusters. Two different reaction pathways were revealed in the addition reactions tried. One resulted in cluster fragmentation to form substituted binuclear compounds based on the (η-C_5H_5)$_2Rh_2$ unit. In the other, trinuclear cluster integrity was retained upon ligand addition.

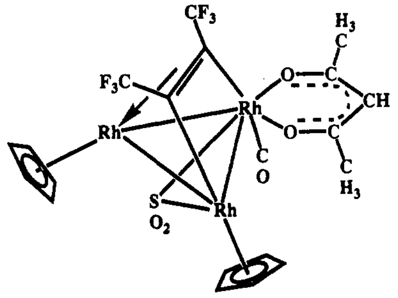
The addition of CO to (η-C_5H_5)$_2$(hfac)$Rh_3(CO)(CF_3C_2CF_3)$ is a good example of the first type of reaction. The major products isolated after workup of this reaction mixture were (η-C_5H_5)$_2Rh_2(CO)_2$(μ-η^1-$CF_3C_2CF_3$) and (hfac)$Rh(CO)_2$. A possible cluster fragmentation pathway is shown in eq 1. Although the proposed dicarbonyl cluster intermediate was not detected, an analogous phosphine cluster (η-C_5H_5)$_2$(acac)Rh_3(CO)L($CF_3C_2CF_3$) (L = tri-p-tolylphosphine) has been isolated (vide infra). Further carbonylation of the dicarbonyl intermediate results in cluster fragmentation to regenerate (hfac)$Rh(CO)_2$ and (η-C_5H_5)$_2Rh_2$(μ-CO)(μ-η^2-$CF_3C_2CF_3$). The binuclear monocarbonyl complex is known[17] to add CO readily to form (η-C_5H_5)$_2Rh_2(CO)_2$(μ-η^1-$CF_3C_2CF_3$). It is likely that this ability of CO to cleave the clusters will have affected the yields of the clusters obtained in the original syntheses. The reaction between *tert*-butyl isocyanide and (η-C_5H_5)$_2$(acac)$Rh_3(CO)(CF_3C_2CF_3)$ presumably follows a similar pathway to give (acac)Rh(CO)(CN-t-Bu) and (η-C_5H_5)$_2Rh_2$(CN-t-Bu)$_2$(μ-η^1-$CF_3C_2CF_3$). The monomeric complex was not detected; complexes of this type have not been reported and we suspect they are unstable under the workup conditions used. However, the binuclear complex was obtained in good yield. This compound has not been described previously. We were not able to purify it adequately for elemental analysis, but it has been well characterized spectroscopically. A parent ion is detected in the mass spectrum, and the infrared spectrum indicates a trans arrangement of the isocyanide groups analogous to that found[18] for the carbonyls in (η-C_5H_5)$_2Rh_2(CO)_2$(μ-η^1-$CF_3C_2CF_3$).

$$
\begin{aligned}
&(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)(CF_3C_2CF_3) \xrightarrow{+CO} \\
&\qquad [(\eta\text{-}C_5H_5)_2(\text{hfac})Rh_3(CO)_2(CF_3C_2CF_3)] \xrightarrow{+CO} \\
&\qquad \mathbf{(hfac)Rh(CO)_2} + \\
&\qquad (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3) \xrightarrow{+CO} \\
&\qquad\qquad \boldsymbol{(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)} \quad (1)
\end{aligned}
$$

Reactions with phosphines might be expected to proceed similarly. With tertiary phosphines there is cluster retention (vide infra), but secondary phosphines do give a binuclear product. Thus, the major product obtained from the reaction between $PHPh_2$ and (η-C_5H_5)$_2$(oxine)$Rh_3(CO)(CF_3C_2CF_3)$ is (η-C_5H_5)$_2Rh_2$(μ-PPh_2)[μ-η^1,η^2-C(CF_3)-C(CF_3)H].[20] We suggest that this is formed from (η-C_5H_5)$_2Rh_2$(CO)($PHPh_2$)(μ-η^1-$CF_3C_2CF_3$) by an intramolecular proton shift accompanied by decarbonylation. The liberated CO is used to generate (η-C_5H_5)$_2Rh_2(CO)_2$(μ-η^1-$CF_3C_2CF_3$) according to the last step in eq 1.

A binuclear metalladiene complex (η-C_5H_5)$_2Rh_2$[μ-η^2,η^4-$C_4(CF_3)_2$PhH] was the only major product obtained from the reaction between (η-C_5H_5)$_2$(acac)$Rh_3(CO)(CF_3C_2CF_3)$ and phenylacetylene. This complex has been prepared previously[21] from the rapid reaction between PhC≡CH and (η-C_5H_5)$_2Rh_2$(μ-CO)(μ-η^2-$CF_3C_2CF_3$). In the present case, it again seems likely that ligand addition precedes cluster fragmentation, and that the mononuclear fragment (acac)Rh(CO)(PhC_2H) is unstable and decomposes.

One reaction that resulted in retention of the Rh_3-cluster framework was that between SO_2 and (η-C_5H_5)$_2$(acac)$Rh_3(CO)(CF_3C_2CF_3)$. The addition product (η-C_5H_5)$_2$(acac)Rh_3(CO)(μ-SO_2)($CF_3C_2CF_3$) was isolated from this reaction in 50% yield. It was an orange solid which changed its composition when kept in the solid state under N_2 but which remained unchanged if left in solution for several days. We have been unable to determine the nature of the solid-state transformation, and it prevented us from obtaining reproducible microanalytical results. The analyses always showed a higher than expected sulfur content whereas the mass spectrum indicated ready loss of SO_2. The spectroscopic results for solutions of the complex are consistent with the structure 3 in which the CO and SO_2 ligands are attached in terminal and edge-bridging bonding modes, respectively. The η^1-edge-bridging mode is relatively common for SO_2 in cluster complexes,[26] and in the present context it enables each metal in the cluster to attain an 18-electron count. The same electron count could have been attained with a terminally bound SO_2 and an edge-bridging CO, but there is no evidence for the formation of this isomer. Recently, attention has been drawn[26] to the fact that no clusters are



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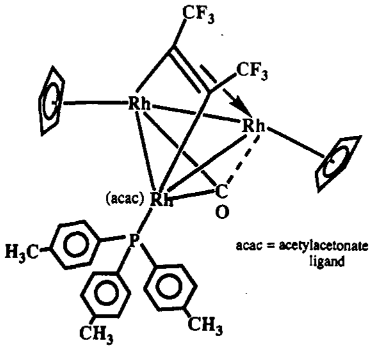
[25] Trin-Toan; Broach, R. W.; Gardner, S. A.; Rausch, M. D.; Dahl, L. F. *Inorg. Chem.* **1977**, *16*, 279.

[26] Ewing, P.; Farrugia, L. J. *Organometallics* **1989**, *8*, 1665 and references therein.

known with a terminally attached SO_2 ligand.

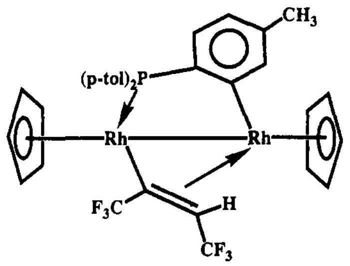
The tertiary phosphine, P(*p*-tolyl)$_3$, also adds to (η-C_5H_5)$_2$(acac)Rh_3(CO)($CF_3C_2CF_3$) with retention of cluster integrity. The product (η-C_5H_5)$_2$(acac)Rh_3(CO)($CF_3C_2CF_3$)[P(*p*-tolyl)$_3$] is obtained as a crimson solid in 37% yield. The phosphine is presumably bound to the Rh(acac) site. The observed Rh–P coupling constant of 180 Hz in the $^{31}P\{^1H\}$ NMR spectrum is similar to that found[17,27] for numerous other phosphine–rhodium complexes. Terminal attachment of the phosphine forces the carbonyl into a bridging position, and the observed infrared stretching frequency at 1725 cm^{-1} is consistent with a face-bridging or semi-face-bridging attachment. Two CF_3 resonances are detected in the ^{19}F NMR spectrum. One is a quartet with a F–F coupling of 10.6 Hz, but the other is a quartet of doublets. We assign the doublet coupling of 10 Hz to $^4J_{F-P}$. Long-range P–F couplings of this magnitude have been observed previously[17,28,29] for some binuclear complexes in which hexafluorobut-2-yne is attached to a Rh–phosphine site. The combined spectroscopic data indicate the structure 4.



acac = acetylacetonate ligand

4

Three other products were isolated from this reaction. One was the dicarbonyl compound (η-C_5H_5)$_2Rh_2$(CO)$_2$(μ-η^1-$CF_3C_2CF_3$) and another the trinuclear cluster (η-C_5H_5)$_3Rh_3$(CO)($CF_3C_2CF_3$). The remaining species was a minor product (2% yield), but the spectroscopic results indicated the unusual and interesting binuclear structure 5. A weak parent ion in the mass spectrum, the absence of a carbonyl absorption in the infrared spectrum, and the multinuclear data support the proposed structure. The ^1H chemical shift at δ 1.75 and the coupling of this proton to a trifluoromethyl group are consistent[30] with the presence of the alkylidene group. The ortho-metalation of one *p*-tolyl ring locks the phosphine into a fixed orientation, thus generating three inequivalent ring–methyl environments; three methyl signals are detected in the ^1H NMR spectrum. The proposed ortho-metalation is also supported by the appearance of the phenyl region in the ^1H NMR spectrum and by the ^{31}P NMR spectrum where a strong (146 Hz) and a weak (8 Hz) coupling of phosphorus to the rhodium atoms is revealed.



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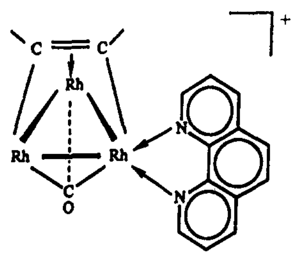
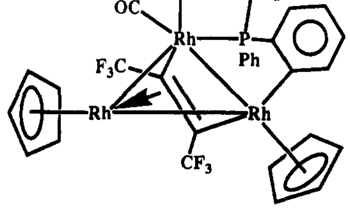
Replacement of the Chelate Ligand. Treatment of (η-C_5H_5)$_2$(hfac)Rh_3(CO)($CF_3C_2CF_3$) with 1,10-phenanthroline in the presence of ammonium hexafluorophosphate resulted in the exchange of chelate ligands to produce [(η-C_5H_5)$_2$(phen)Rh_3(CO)($CF_3C_2CF_3$)]$^+$ PF_6^-. The cluster is charged because a neutral ligand has replaced an anionic ligand. The infrared and NMR data indicate there has been no change in the mode of attachment of the carbonyl and hexafluorobut-2-yne ligands. The structure 6 is therefore proposed. In contrast to the neutral (η-C_5H_5)$_2$(chel)Rh_3(CO)($CF_3C_2CF_3$) complexes, two C_5H_5 resonances are observed for 6 in the ^1H NMR spectrum at room temperature. This implies a much higher barrier to alkyne rearrangement in the cationic complex. This idea was tested by running the spectrum at higher temperature. Although the resonances broadened, the fast-exchange limiting spectrum was not observed due to thermal decomposition of the complex above about 60 °C.



6

We developed another strategy, which should be quite general, for removing the β-diketonate from the clusters. This involves the addition of trimethylchlorosilane, Si(CH_3)$_3$Cl, in the presence of another ligand. After completing some experiments of this type, we noted a very recent publication[31] describing a similar approach related to some acac–Fe complexes.

Treatment of (η-C_5H_5)$_2$(acac)Rh_3(CO)($CF_3C_2CF_3$) with Si(CH_3)$_3$Cl and dppm did give a Rh_3 cluster devoid of the acac ligand. The olive green solid was obtained in 61% yield. Spectroscopic results are consistent with the unusual structure 7, in which the bidentate phosphine chelates to one rhodium and there is ortho-metalation of one of the phenyl rings to a neighboring rhodium. The terminal carbonyl is indicated by an intense stretching frequency at 2010 cm^{-1} in the infrared spectrum. The unusual attachment of the deprotonated dppm ligand is inferred from multinuclear NMR data. The relatively high field chemical



7

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(27) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* 1981, *14*, 266.

(28) Dickson, R. S.; Jenkins, S. M. Unpublished results. For a series of complexes of the type (η-C_5H_5)$_2Rh_2$(CO)($CF_3C_2CF_3$)($P\frown P$), where $P\frown P$ is a bidentate phosphine, $J_{Rh-P} \approx$ 175–180 and $J_{P-F} \approx$ 3–10 Hz.

(29) Mague, J. T.; Deuries, S. H. *Inorg. Chem.* 1982, *21*, 1632.

(30) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M. *J. Organomet. Chem.* 1986, *314*, 333. Dickson, R. S.; Jenkins, S. M.; Skelton, B. W.; White, A. H. *Polyhedron* 1988, *7*, 857.

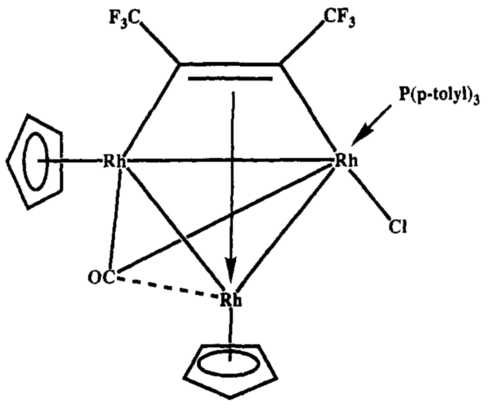
(31) Paciello, R. A.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* 1990, *9*, 260.

shifts for the phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectrum are consistent[27] with the presence of a four-membered chelate ring. The resonance at δ 10.5 is a doublet of doublets, but that at δ 1.5 is a doublet of doublets of doublets. For each resonance, there is a large ^1J(Rh–P) coupling (181 or 133 Hz) and a normal ^3J(P–P) coupling (29 Hz). For the higher field peak, we assign the additional coupling of 11 Hz to through-bond Rh–P coupling involving the ortho-metalated ring. The fate of the [H] which is lost to achieve ortho-metalation has not been determined explicitly. It has not been transferred to the hexafluorobut-2-yne ligand; the ^1H and ^{19}F NMR results would readily reveal the formation of an alkenyl unit of the type $Rh_2\{\mu\text{-}\eta^1,\eta^2\text{-}C(CF_3)C(CF_3)H\}$.[30] In the sense of eq 2, it does seem reasonable to suggest that [H] is lost formally as HCl; this could well react with other species in solution. Without the loss of H^+ (as HCl), a cationic cluster would have been generated, as was the case in the reaction between $(\eta\text{-}C_5H_5)_2(hfac)Rh_3(CO)(CF_3C_2CF_3)$ and 1,10-phenanthroline.

$$[Rh]\text{–}acac + Si(CH_3)_3Cl + dppm \rightarrow [Rh]\text{–}[dppm(\text{–}H)] + acac\text{–}Si(CH_3)_3 + \mathbf{HCl} \quad (2)$$

A similar reaction involving $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$, $Si(CH_3)_3Cl$, and 2 equiv of P(*p*-tolyl)$_3$ was attempted. Two phosphine-containing products were obtained. One was the binuclear complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)[P(p\text{-tolyl})_3](\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$, isolated in 8% yield. As mentioned earlier, analogous complexes with other phosphine ligands have been formed previously[17] from the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ and tertiary phosphines. We subsequently prepared $(\eta\text{-}C_5H_5)_2Rh_2(CO)[P(p\text{-tolyl})_3](\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ by this route and found its NMR spectra to be identical with those of the compound obtained from the cluster degradation reaction. An unusual feature in the ^1H NMR spectrum of this compound was the detection of three distinct *p*-tolyl methyl resonances. Restricted rotation about the Rh–P bond would account for this feature of the spectrum. While the phenominon of restricted rotation about M–P bonds is not common, there is a thoroughly studied example in the literature.[32] For the complex $(\eta\text{-}C_5Me_5)Rh[P(p\text{-tolyl})_3](C_6F_5)Br$, the ^1H NMR spectrum at 285 K revealed three singlets in the tolyl methyl region, and these signals coalesced into a single resonance at 378 K. A similar high-temperature NMR study was conducted on $(\eta\text{-}C_5H_5)_2Rh_2(CO)[P(p\text{-tolyl})_3](\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$. As the temperature was increased, the three tolyl methyl resonances broadened and partially merged and at 324 K were observed as a broad multiplet centered at δ 2.0. At this temperature, no changes were apparent in the C_5H_5 region of the spectrum. On further heating, significant decomposition occurred; this was evident from NMR and TLC results.

The other complex was a trinuclear cluster, $(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)[P(p\text{-tolyl})_3]Cl$, and spectroscopic data indicate the structure 8. In the formation of this complex, [Cl] from the $Si(CH_3)_3Cl$ and one phosphine have replaced the acac– ligand. The structure 8 is indicated by spectroscopic data. Formally, this is a 46-electron cluster that could have a perpendicular (Figure 1B) rather than the parallel attachment of the alkyne shown in 8. Our spectroscopic results do not enable us to distinguish between the alternative bonding modes, but we prefer the parallel attachment, since this has been unequivocally established for the parent cluster $(\eta\text{-}C_5H_5)_2(thd)Rh_3(CO)(CF_3C_2CF_3)$. The room-temperature ^1H NMR spectrum of 8 shows a single broad C_5H_5 resonance. This suggests fluxional behavior in solution, as was observed for $(\eta\text{-}C_5H_5)_2(acac)Rh_3(CO)(CF_3C_2CF_3)$.



8

Conclusions

Two bonding modes are known for alkyne–M_3 clusters. The parallel and perpendicular bonding modes shown in Figure 1 are usually associated with clusters having 48- and 46-electron counts, respectively. Characterization of the complexes $(\eta\text{-}C_5H_5)_2(chel)Rh_3(CO)(CF_3C_2CF_3)$ has provided the first example of a 46-electron cluster with a parallel alkyne attachment. These new 46-electron clusters are formally coordinatively unsaturated and do add various ligands. In some instances, ligand addition generates a 48-electron cluster, but cluster fragmentation and other rearrangements can occur. This study and that described in a previous paper[8] emphasize that there is only a small difference in stability of the various possible alkyne attachments in such complexes. It seems that the balance is tipped in the present case by the influence of the strongly electron withdrawing trifluoromethyl groups which enhance σ bonding from the alkyne carbons.

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Supplementary Material Available: A diagram of the molecular structure of 2 with the complete atom-labeling scheme, tables of hydrogen atom coordinates and isotropic displacement coefficients, anisotropic displacement coefficients, ligand geometries, and equations for planes, and a textual presentation of experimental detail on the preparation of other $(\eta\text{-}C_5H_5)_2(chel)Rh_3(CO)(CF_3C_2F_3)$ complexes (12 pages); a listing of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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[32] Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.