ORGANOMETALLICS

Synthesis, structure, and fluxional properties of the cationic rhodium clusters [(.eta.-C5H5)2Rh3(CO)(CF3C2CF3)(CNR)3]+PF6- (R = iso-Pr, tert-Bu). Unexpected attachment of the alkyne in the crystal structure

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Synthesis, Structure, and Fluxional Properties of the Cationic Clusters $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CNR)_3]^+PF_6^-$ (R = *i*-Pr, *t*-Bu). Unexpected Attachment of the Alkyne in the Crystal Structure

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The cationic cluster complexes $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CNR)_3]^+PF_6^-$ are formed when $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is treated with $[Rh(CNR)_4]^+PF_6^-$ (R = *i*-Pr, *t*-Bu). The structure of the complex with R = *t*-Bu and one solvent molecule (CH_2Cl_2) has been determined by X-ray crystallography. Crystal data: $C_{31}H_{39}Cl_2F_{12}N_3OPRh_3$, M_r 1108.25, monoclinic, $P2_1/m$, $a = 17.509$ (2) Å, $b = 12.360$ (2) Å, $c = 10.154$ (1) Å, $Z = 2$, final $R = 0.064$ for 1635 "observed" reflections. The molecular structure confirms loss of one CNR ligand in the addition reaction and reveals a symmetrical structure with an edge-bridging CO and a face-bridging $CF_3C_2CF_3$. The CO is attached to the two $(\eta\text{-}C_5H_5)Rh$ sites, and the alkyne is σ-attached to these two rhodium atoms and π-bonded to the metal of the $Rh(CNR)_3$ unit. This is contrary to expectation; π-bonding is normally to the least electron attracting metal center. All CNR ligands are terminal. Spectroscopic results indicate that two isomers coexist in solution for each of the clusters (R = *t*-Bu, *i*-Pr). The symmetrical solid-state structure is preserved for the minor isomer in solution, and the NMR spectra of this isomer are not temperature-dependent. Variable-temperature NMR results show that the major isomer is fluxional at room temperature; the limiting spectra at low temperature are consistent with an unsymmetrical structure in which the alkyne is σ-attached to one $(\eta\text{-}C_5H_5)Rh\text{-}Rh(CNR)_3$ bond and π-bonded to the remaining $(\eta\text{-}C_5H_5)Rh$. The CO adopts a semi-face-bridging location with the weakest interaction to $Rh(CNR)_3$.

Introduction

The chemistry of alkyne metal clusters has been the subject of two recent reviews.[1,2] A major reason for the considerable interest in these compounds relates to their possible use as models for the behavior of small unsaturated molecules on catalytic metal surfaces. This cluster–surface analogy has been expounded in several review articles, particularly by Muetterties.[2-6] In a recent paper by Puddephatt,[7] a quite explicit link has been developed between an alkyne–Pt_3 cluster and the Pt(111) surface with chemisorbed acetylene. Alkyne cluster chemistry is intriguing also in terms of the diversity of coordination modes displayed by the alkyne ligands.

There are several approaches to the synthesis of (alkyne)metal clusters.[1,2] One that we have exploited recently involves construction of the cluster from a mononuclear metal complex and a binuclear alkyne complex.[8,9] The reaction between $Pt(COD)_2$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ provides an example and is shown in eq 1. In

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3) + Pt(COD)_2 \rightarrow (\eta\text{-}C_5H_5)_2Rh_2Pt(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)(COD) \quad (1)$$

this reaction, dissociation of the labile 1,5-cyclooctadiene ligand creates a coordinatively unsaturated platinum center, which adds to the Rh–Rh bond. This prompted us to seek other mononuclear complexes that might add in a similar manner.

The square-planar cations $[Rh(CNR)_4]^+$ have vacant coordination sites and readily undergo coordinative and oxidative-addition reactions.[10,11] They also show a strong tendency to oligomerize to form dimers or trimers linked by Rh–Rh bonds.[10,12] Moreover, the cations $[Rh(CNR)_4]^+$ associate with some $[Rh(CNR)_4X_2]^+$ species to give $[Rh_2(CNR)_8X_2]^{2+}$, which are thought to have a direct Rh–Rh bond.[10,13] It therefore seemed worthwhile to determine if interaction would occur between $[Rh(CNR)_4]^+$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$. We have investigated such reactions using cationic complexes with R = isopropyl and *tert*-butyl, and we describe our results in this paper.

Experimental Section

General Procedures. All preparations and manipulations were performed under an atmosphere of purified nitrogen with use of standard Schlenk techniques. 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. All separations were achieved on plates that had been dried at room temperature only. The reported microanalyses were performed by the National Analytical Laboratories Pty. Ltd., Victoria, Australia.

Instrumentation. Infrared absorption spectra were recorded on a Jasco IRA-1 spectrometer. The variable-temperature solution infrared spectra were kindly recorded by D. Bogsanyi, Australian National University; a PE1800 FTIR spectrophotometer controlled through a PE7500 computer running CDS under the Idris operating system was used. Spectral subtractions were carried out interactively. NMR spectra were measured on a Bruker AM-300 spectrometer. The ^1H NMR spectra were measured at 300 MHz,

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^{19}F at 282.4 MHz, and ^{13}C at 75.5 MHz; deuterated solvents ($CDCl_3$, acetone-d_6) were used as internal locks. Chemical shifts are in parts per million from internal Me_4Si for ^{1}H and ^{13}C and from CCl_3F for ^{19}F; in all cases, a positive chemical shift denotes a resonance downfield from the reference. In ^{13}C NMR spectra, $Cr(acac)_3$ was added to reduce T_1 relaxation times for carbonyl-containing compounds. The FAB mass spectra were kindly provided by M. J. Liddell, University of Adelaide: the spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, with a current of 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as 0.5 M solutions in dichloromethane, a drop was added to a drop of matrix, and the mixture was applied to the FAB probe tip.

Solvents, Ligands, and Reagents. Reagent-grade solvents were purified by standard procedures[14] and were stored in the dark over activated 4A molecular sieves (CH_2Cl_2) or Na wire (hexane); they were degassed and saturated with nitrogen before use. The ligands *i*-PrNC and *t*-BuNC were commercial samples (Strem) and were used without purification. The following complexes were prepared by literature methods: $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$[15] and $[Rh(CNR)_4]^+PF_6^-$ (R = *i*-Pr, *t*-Bu).[11]

Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) with $[Rh(CNR)_4]^+$. $[Rh(CN\text{-}t\text{-}Bu)_4]^+PF_6^-$. A slight excess of 1 (58.3 mg, 0.111 mmol) and $[Rh(CN\text{-}t\text{-}Bu)_4]^+PF_6^-$ (59.9 mg, 0.103 mmol) were dissolved in a 5:1 mixture of hexane–dichloromethane (30 mL), and the solution was stirred at 0 °C for 8 h. During this time, the color of the solution changed from green to orange, and some crimson solid precipitated. A syringe was used to remove the solution from the precipitate, which was washed thoroughly with cold hexane. Examination of the product under the microscope showed a mixture of crimson (major) and yellow (minor) crystals. The yellow material was difficult to remove because the product is unstable on chromatographic supports and decomposes slowly in solution. Nonetheless, a homogeneous sample of the crimson material was obtained after several recrystallizations. On the basis of analytical and spectroscopic data, the crimson crystals are formulated as $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-$ (55.6 mg, 53%), mp >140 °C. Anal. Calcd for $C_{30}H_{37}F_{12}N_3OPRh_3$: C, 35.2; H, 3.6; F, 22.3; N, 4.1; P, 3.0. Found: C, 35.4; H, 3.7; F, 22.2; N, 4.3; P, 3.2. Spectroscopic data: FAB MS (CH_2Cl_2, NOBA, positive ion) *m/e* 878 $[M]^+$ (6), 850 $[M - CO]^+$ (85), 795 $[M - CNR]^+$ (35), 767 $[M - CO - CNR]^+$ (100), 684 $[M - CO - 2CNR]^+$ (<10), 628 [not assigned] (15), 601 $[M - CO - 3CNR]^+$ (<10), 435 [not assigned] (40), 233 $[C_{10}H_{10}Rh]^+$ (<10) (high-mass peaks of low intensity observed at 1077, 994, and 911 were not assigned); FAB MS (negative ion) *m/e* 145 $[PF_6]^-$; IR (Nujol) ν(CNR) at 2195 sh, 2150 s cm^{-1}, ν(CO) at 1840 m, 1760 w cm^{-1} (see Table IV for solution IR spectra); ^{1}H NMR ($CDCl_3$) δ 5.57 (s br, 10 H, C_5H_5), 1.55 (s br, 32 H, *t*-Bu + H_2O); ^{1}H NMR (acetone-d_6) δ 5.74 (s br, 10 H, C_5H_5), 5.65 (s, 2 H, C_5H_5), 1.58 (s br, 33 H, *t*-Bu + H_2O); ^{19}F NMR ($CDCl_3$) δ −52.2 (s br, 6 F, CF_3), −73.8 (d, 6 F, J_{P-F} = 711 Hz, PF_6); ^{19}F NMR (acetone-d_6) δ −50.9 (s br, 6 F, CF_3), −52.3 (s, 1 F, CF_3), −71.5 (d, 7 F, J_{P-F} = 708 Hz, PF_6); see text for low-temperature ^{1}H and ^{19}F NMR data; ^{13}C NMR ($CDCl_3$) δ 221.0 (td, J_{Rh-C} = 41.7, 17.3 Hz, CO), 91.8 (d, J_{Rh-C} = 5 Hz, C_5H_5), 58.6 (s, $C(CH_3)_3$), 30.2 (s, $C(CH_3)_3$).

The solution that had been removed from the precipitate was chromatographed by TLC with a 3:1 mixture of hexane–dichloromethane as eluent. This separated three majors bands from decomposition material retained in the base band. Yellow crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$[15,16] (4.3 mg, 7.5%), the orange product $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$[16,17] (10.6 mg, 17%), and the purple cluster compound $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$[18] (3.0 mg, 4%) were isolated from the first, second, and third bands, respectively. Each product was identified spectroscopically.

Table I. Summary of Crystal Structure Data for the Complex $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-\bullet CH_2Cl_2$

(a) Crystal Data	
formula	$C_{31}H_{39}Cl_2F_{12}N_3OPRh_3$
mol wt	1108.25
cryst syst	monoclinic
space group	$P2_1/m$
a, Å	17.509 (2)
b, Å	12.360 (2)
c, Å	10.154 (1)
β, deg	105.47 (3)
V, Å^3	2118
Z	2
D(calcd), g cm^{-3}	3.46
D(measd), g cm^{-3}	3.47
F(000)	1092
Mo Kα radiation, λ, Å	0.710 73
μ(Mo Kα), cm^{-1}	13.82
(b) Data Collection	
2θ limits, deg	6–60
ω-scan angle, deg	$\pm(1.40 + 0.3 \tan \theta)$
scan rate, deg s^{-1}	0.06
total no. of data	6442
no. of data, $I > 3\sigma(I)$	1635
abs cor	0.588 (min), 1.118 (max)
h	−24 to +23
k	0–17
l	0–14
final R and R_w	0.064 and 0.058
weight w	$1.6153/[\sigma^2(F)]$

$[Rh(CN\text{-}i\text{-}Pr)_4]^+PF_6^-$. In a similar manner, 1 (52.0 mg, 0.098 mmol) and $[Rh(CN\text{-}i\text{-}Pr)_4]^+PF_6^-$ (46.0 mg, 0.088 mmol) gave an orange solution and dark crimson-black crystals. The latter were well washed with cold hexane to give $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}i\text{-}Pr)_3]^+PF_6^-$ (58 mg, 67%), mp 193 °C. Although spectroscopic data showed no significant amounts of impurities and the compound appeared homogeneous when viewed under a microscope, there was some discrepancy between analytical data obtained from several different microanalysis laboratories. (The analysts suggest there is a problem with the analytical technique when applied to the compound rather than inhomogeneity within the sample.) Spectroscopic data: FAB MS (CH_2Cl_2, NOBA, positive ion) *m/e* 836 $[M]^+$ (6), 808 $[M - CO]^+$ (60), 767 $[M - CNR]^+$ (25), 739 $[M - CO - CNR]^+$ (100), 698 $[M - 2CNR]^+$ (20), 629 $[M - 3CNR]^+$ (<10), 601 $[M - CO - 3CNR]^+$ (20), 233 $[C_{10}H_{10}Rh]^+$ (60) (a high-mass peak of low intensity at 878 was not assigned); FAB MS (negative ion) *m/e* 145 $[PF_6]^-$; IR (Nujol) ν(CNR) at 2210 vs, 2185 vs cm^{-1}, ν(CO) at 1835 vs cm^{-1}; IR (CH_2Cl_2) 2200 vs, 2175 vs, 1840 w, 1760 s br cm^{-1}; IR (acetone) 2225 vs, 2175 vs, 1845 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.57 (s br, 10 H, C_5H_5), 5.45 (s, 1 H, C_5H_5), 4.39 (m, 0.4 H, $CH(CH_3)_2$), 4.22 (m, 4 H, $CH(CH_3)_2$), 1.55 (partly obscured), 1.48 (d, ~21 H, J = 6.4 Hz, $CH(CH_3)_2$; ^{1}H NMR (acetone-d_6) δ 5.74 (s br, 20 H, C_5H_5), 5.66 (s, 5 H, C_5H_5), 4.50 (m, 1.5 H, $CH(CH_3)_2$), 4.32 (sept, 6 H, J = 6.5 Hz, $CH(CH_3)_2$), 1.56 (d, ~10 H, J = 6.4 Hz, $CH(CH_3)_2$), 1.48 (d, ~40 H, J = 6.5 Hz, $CH(CH_3)_2 + H_20$); ^{19}F NMR ($CDCl_3$) δ −52.3 (s br, 6 F, CF_3), −54.1 (s, 0.6 F, CF_3), −73.5 (d, 6.6 F, J_{P-F} = 712 Hz, PF_6); ^{19}F NMR (acetone-d_6) δ −50.9 (s br, 6 F, CF_3), −52.6 (s, 1.5 F, CF_3), −71.4 (d, 7.5 F, J_{P-F} = 707 Hz, PF_6).

A sample prepared from ^{13}CO-enriched 1 showed infrared bands (CH_2Cl_2) at 2200 vs, 2175 vs, 1840 w, 1760 s br, and 1730 sh cm^{-1} and $^{13}C\{^1H\}$ NMR signals at ($CDCl_3$) δ 221.6 (td, J_{Rh-C} = 42, 17 Hz, CO), 91.6 (d, J_{Rh-C} = 5 Hz, C_5H_5), 89.9 (m, C_5H_5), 42.9 (s, $CH(CH_3)_2$), 23.1 (s, $CH(CH_3)_2$), and 23.0 (s, $CH(CH_3)_2$).

The combined filtrate and washings from the original reaction solution were chromatographed by TLC with a 1:1 mixture of hexane–dichloromethane as eluent. This separated $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$[15,16] (orange, 5 mg, 9%) and $(\eta\text{-}C_5H_5)_2Rh_2\{CO\cdot CF_3C_2CF_3\cdot CN\text{-}i\text{-}Pr\}$[18] (red, 17 mg, 29%) from three

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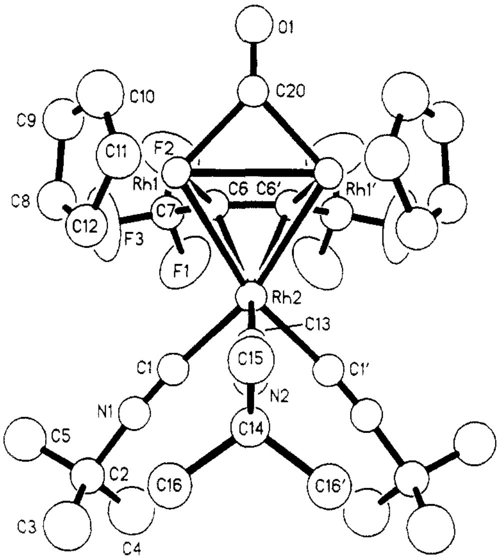

Figure 1. Molecular structure of the cationic cluster $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+$.

minor bands, which were not collected.

Crystallography. Single crystals of $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-$ were grown from heptane-dichloromethane. A red tabular crystal was used for data collection. The crystal was taken directly from solution and mounted and sealed in a 0.5-mm capillary tube as a precaution against solvent loss. Intensity measurements were made on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation at 22 °C. Cell parameters were determined from 25 accurately centered reflections and were calculated by the standard Philips program. Other crystal data are summarized in Table I. Three standard reflections were monitored every 4 h, and a decay correspoonding to 8% over 6442 reflections was observed and corrected for.

Intensity data were processed as described previously.[19] The intensity data revealed the extinctions (*hkl*) 0*k*0, $k = 2n$, consistent with either of the space groups $P2_1$ or $P2_1/m$. The presence of a center of symmetry was suggested from the distribution of $|E|$ values (average $|E^2 - 1| = 0.908$, cf. 0.968 if centrosymmetric). The space group $P2_1/m$ was verified by the subsequent successful refinement of the structure. An absorption (DIFABS[20]) correction was applied. The atomic scattering factors for neutral atoms were taken from ref 21 and were corrected for anomalous dispersion by using values from ref 21. All calculations were performed on a VAX 11/780 computer. The program used for least-squares refinement was that written by Sheldrick.[22]

The structure was solved by conventional Patterson and Fourier techniques and refinement effected by full-matrix least-squares methods. Anisotropic thermal parameters were introduced for Rh, Cl, F, P, and the carbon of the solvent molecule, dichloromethane. Isotropic thermal parameters were assigned to all other atoms. Hydrogen atoms were included at calculated positions (C–H = 0.97 Å), with a single variable isotropic thermal parameter, which was refined to 0.12 (2) Å. Final positional parameters are given in Table II. Figure 1 shows the atomic labeling scheme used, and selected bond lengths and angles are listed in Table III. The supplementary material contains listings of structure factor amplitudes, thermal parameters, and ligand geometries.

Table II. Non-Hydrogen Atom Coordinates

atom	*x*	*y*	*z*
Rh(1)	0.2007 (1)	0.3576 (1)	0.2196 (1)
Rh(2)	0.2566 (1)	$^1/_4$	0.0449 (2)
Cl(1)	0.6275 (7)	$^1/_4$	0.8056 (10)
Cl(2)	0.6452 (8)	$^1/_4$	0.5361 (11)
P(1)	0.8754 (6)	$^1/_4$	0.2008 (9)
F(1)	0.4435 (6)	0.3546 (10)	0.2285 (13)
F(2)	0.4160 (7)	0.3797 (11)	0.4130 (12)
F(3)	0.3711 (6)	0.4779 (9)	0.2492 (16)
F(4)	0.8451 (11)	$^1/_4$	0.3305 (18)
F(5)	0.9104 (10)	$^1/_4$	0.0717 (17)
F(6)	0.9611 (13)	$^1/_4$	0.2893 (19)
F(7)	0.7930 (10)	$^1/_4$	0.1099 (21)
F(8)	0.8796 (10)	0.1256 (11)	0.2036 (18)
C(17)	0.5830 (20)	$^1/_4$	0.6372 (31)
N(1)	0.3221 (7)	0.4221 (10)	−0.1207 (13)
N(2)	0.0978 (11)	$^1/_4$	−0.1854 (19)
O(1)	0.2068 (9)	$^1/_4$	0.4817 (17)
C(1)	0.2992 (8)	0.3640 (13)	−0.0556 (15)
C(2)	0.3514 (10)	0.4929 (14)	−0.2161 (17)
C(3)	0.2821 (12)	0.5128 (17)	−0.3357 (20)
C(4)	0.4187 (12)	0.4313 (18)	−0.2449 (22)
C(5)	0.3806 (11)	0.5921 (15)	−0.1374 (21)
C(13)	0.1570 (13)	$^1/_4$	−0.0985 (23)
C(14)	0.0239 (14)	$^1/_4$	−0.3027 (25)
C(15)	−0.0490 (18)	$^1/_4$	−0.2447 (27)
C(16)	0.0327 (9)	0.1482 (14)	−0.3865 (17)
C(6)	0.3131 (8)	0.3064 (10)	0.2453 (14)
C(7)	0.3856 (11)	0.3805 (15)	0.2825 (20)
C(8)	0.1856 (10)	0.5249 (14)	0.1589 (18)
C(9)	0.1783 (11)	0.5176 (14)	0.2910 (19)
C(10)	0.1160 (12)	0.4588 (16)	0.2845 (22)
C(11)	0.0787 (10)	0.4294 (15)	0.1546 (20)
C(12)	0.1209 (10)	0.4746 (14)	0.0712 (19)
C(20)	0.2009 (12)	$^1/_4$	0.3600 (23)

Table III. Some Important Bond Lengths (Å) and Angles (deg) for $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-$

(a) Bond Lengths

Rh(1)–Rh(1′)	2.660 (3)	C(6)–C(6′)	1.39 (3)
Rh(1)–Rh(2)	2.608 (2)	C(20)–O(1)	1.21 (2)
Rh(1)–C(6)	2.02 (1)	C(1)–N(1)	1.12 (2)
Rh(1)–C(20)	1.95 (2)	C(13)–N(2)	1.17 (3)
Rh(2)–C(6)	2.13 (1)		
Rh(2)–C(1)	2.00 (2)		
Rh(2)–C(13)	1.95 (2)		

(b) Bond Angles

Rh(1′)–Rh(1)–Rh(2)	59.3 (0)	C(1)–Rh(2)–Rh(1)	165.1 (5)
Rh(1′)–Rh(1)–C(6)	71.7 (4)	C(6)–Rh(2)–C(13)	143.9 (7)
Rh(1′)–Rh(1)–C(20)	47.0 (5)	C(6)–Rh(2)—C(6′)	38.2 (7)
C(6)–Rh(1)–Rh(2)	53.0 (4)	C(6′)–Rh(2)–C(1)	125.3 (5)
C(6)–Rh(1)–C(20)	83.1 (7)	C(6′)–Rh(2)–Rh(1)	71.3 (4)
C(20)–Rh(1)–Rh(2)	102.8 (6)	Rh(2)–C(1)–N(1)	174.3 (14)
Rh(1)–Rh(2)–Rh(1′)	61.3 (1)	Rh(1)–C(6)–Rh(2)	77.9 (4)
Rh(1)–Rh(2)–C(1)	104.3 (5)	Rh(1)–C(6)–C(6′)	108.3 (4)
Rh(1)–Rh(2)–C(6)	49.1 (4)	Rh(1)–C(6)–C(7)	124.2 (10)
Rh(1)–Rh(2)–C(13)	94.9 (6)	Rh(2)–C(6)–C(6′)	70.9 (3)
Rh(1)–Rh(2)–C(6′)	71.3 (4)	Rh(2)–C(6)–C(7)	125.1 (12)
Rh(1)–Rh(2)–C(1′)	165.1 (5)	C(6′)–C(6)–C(7)	126.8 (8)
C(1)–Rh(2)–C(13)	90.0 (6)	Rh(2)–C(13)–N(2)	179.3 (23)
C(1)–Rh(2)–C(6)	96.6 (5)	C(13)–N(2)–C(14)	177.1 (25)
C(1)–Rh(2)–C(6′)	125.3 (5)	Rh(1)–C(20)–Rh(1′)	86.1 (9)
C(1)–Rh(2)–C(1′)	89.7 (9)	Rh(1)–C(20)–O(1)	136.8 (5)
C(1)–N(1)–C(2)	175.5 (15)		

Results and Discussion

Formation of the Cluster Complexes. When solutions of 1 and $[Rh(CNR)_4]^+PF_6^-$ (R = *t*-Bu, *i*-Pr) in a mixture of hexane and dichloromethane are stirred at 0 °C, crystalline products are slowly deposited. Microanalysis of the *tert*-butyl product indicates that addition has occurred with loss of one isocyanide group. This is supported by FAB mass spectral data, which show a parent cation, $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+$, and stepwise loss of three isocyanide groups; in an alternative fragmentation pathway, there is loss of CO and then three CN-*t*-Bu groups. The isopropyl product proved difficult to analyze, but the FAB mass spectrum and other spec-

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troscopic data discussed below clearly indicate that an analogous product has been formed. The major reaction in each case is therefore described by eq 2. There is some

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)] + [Rh(CNR)_4]^+PF_6^- \rightarrow [(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CNR)_3]^+PF_6^- + CNR \quad (2)$$

further interaction between 1 and the CNR released to form the known binuclear complexes $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)]$ and $[(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(N\text{-}i\text{-}Pr)C(CF_3)C(CF_3)\}]$.

We observed some unusual features in the NMR spectra of the trinuclear products. Of particular concern was the indication from relative intensity data that the major species in solution might contain more than three isocyanide groups. To make absolutely certain of the formula, and to determine the precise ligand arrangement within the solid complexes, a crystal structure determination was undertaken on the *tert*-butyl complex.

Crystal and Molecular Structure of $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-\cdot CH_2Cl_2$. The crystal structure consists of well-separated solvent molecules, PF_6^- anions, and cationic clusters. The trinuclear cluster is composed of a $Rh(CN\text{-}t\text{-}Bu)_3$ unit symmetrically attached to the Rh–Rh bond of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$. The hexafluorobut-2-yne and carbonyl groups remain attached to the two rhodium atoms that bear cyclopentadienyl rings, with the alkyne and carbonyl adopting face- and edge-bridging positions, respectively. The cation is bisected by a mirror plane at $y = {}^1/_4$. The plane contains Rh(2), one CN-*t*-Bu, the bridging CO, and the midpoints of the $(C_5H_5)Rh\text{–}Rh(C_5H_5)$ and $(CF_3)C\text{–}C(CF_3)$ bonds. The atoms P(1), F(4), F(5), F(6), and F(7) of the PF_6^- anion are also bisected by the mirror plane at $y = {}^1/_4$.

The Rh(1)–Rh(1′) distance is similar to that found in several other $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CF_3C_2CF_3)$ systems,[17,23,24] but the Rh(1)–Rh(2) distances are significantly shorter (0.05-Å difference). This reflects the localization of positive charge on Rh(2) and its consequent smaller radius.

The isocyanide groups on Rh(2) are mutually perpendicular. The central isocyanide is essentially linear, but there is slight bending of the other CN-*t*-Bu ligands at both carbon and nitrogen, presumably to relieve steric interactions between the three bulky *tert*-butyl groups.

The carbonyl and alkyne ligands are arranged on the same side of the Rh_3 plane. This is a situation analogous to that found for the complex $(\eta\text{-}C_5H_5)_3Rh_3(\mu_2\text{-}CO)(\mu\text{-}C_6F_5C_2C_6F_5)$;[25] in contrast, the CO and alkyne ligands occupy opposite faces in the related complex $(\eta\text{-}C_5H_5)_3Rh_3(\mu_3\text{-}CO)(\mu\text{-}C_6H_5C_2C_6H_5)$. In the present complex, the dihedral angle between the Rh(1)–Rh(1′)–Rh(2) and Rh(1)–Rh(1′)–C(20) planes is 25°. That between the Rh(1)–Rh(1′)–Rh(2) and Rh(1)–C(6)–C(6′)–Rh(1′) planes is 57°, and this is similar to that in numerous other (alkyne)trimetal complexes.[26]

The attachment of the carbonyl ligand to the Rh(1)–Rh(1′) bond is symmetrical, and the Rh—C and C═O bond parameters are as expected[23,24] for an edge-bridging carbonyl. The carbonyl is bent away from Rh(2). Within the Rh_3–alkyne unit, there are no unusual bond parameters. The observed geometry is consistent with σ-attachments of the alkyne carbon to Rh(1) and Rh(1′) and with π-attachment to Rh(2); the C(6)–C(6′) and Rh(1)–Rh(1′) bonds are parallel. Thus, the alkyne is face-bridging in the "$\mu_3\text{-}\eta^2\text{-}\|$" mode commonly found for 48-electron trinuclear clusters.[1,2,27] The π-attachment to Rh(2) is an unexpected feature of the structure. Generally, the π-interaction for this bonding mode is to the metal atom with the least electron-withdrawing ligands.[26-29] Since isocyanides are stronger π-acids than the cyclopentadienyl ring, this is clearly Rh(1/1′) in the present situation. As discussed below, there is evidence that a structure with σ-bonding to Rh(1) and Rh(2) and π-bonding to Rh(1′) is preferred in solution.

Table IV. Isocyanide and Carbonyl Absorptions (cm^{-1}) in the Infrared Spectra of $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CN\text{-}t\text{-}Bu)_3]^+PF_6^-$

	temp, °C	
solvent	+20	−70
CH_2Cl_2	2204 + 2180 (10)[a] 1854 (0.1) 1768 (3.1)	2210 + 2186 (10) 1848 (0.1) 1760 (3.6)
acetone	2204 + 2180 (10) 1852 (0.5)	2210 + 2186 (10) 1852 (0.6)
THF	2204 + 2182 (10) 1852 (0.4) 1768 (2.2) 1716 (0.3)	2210 + 2186 (10) 1846 (0.4) 1762 (2.6) 1714 (0.4)

[a] Numbers in parentheses refer to relative areas, with the area under the combined CNR absorptions taken as 10.

Spectroscopic Results and Structures in Solution. Infrared solution spectral data for the CN-*t*-Bu complex at two temperatures are summarized in Table IV. Spectra were also measured at −25 and −50 °C, but they differ little from the −70 °C spectra. For the CN-*i*-Pr complex, spectra were measured at room temperature only. Generally, these spectra are similar to the 20 °C spectra for the CN-*t*-Bu compound.

There are two regions of interest in these spectra. The CNR absorptions occur in the terminal region between 2150 and 2210 cm^{-1}. For samples in the solid state, two frequencies are observed and the pattern is typical of a *fac*-$(RNC)_3ML_3$ system. This is consistent with the local geometry around Rh(2) in the molecular structure (Figure 1). Two absorptions are also observed for samples in solution. It is worth noting that a more complex four-line spectrum ($2a_1 + b_1 + b_2$) would be expected if four CNR groups were attached to the rhodium. The CO absorptions are generally observed in the bridging region between 1760 and 1850 cm^{-1}. The results indicate that two isomers can coexist, one with an edge-bridging and the other with a face-bridging carbonyl. A similar phenomenon has been reported previously for the related trimeric complexes $(\eta\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)(\mu\text{-}RC_2R)$ (R = Ph, C_6F_5,[25,30] CF_3[18]).

There is little variation in the amounts of the various isomers as the temperature is changed from +20 to −70 °C. It is clear that the face-bridging isomer is dominant in dichloromethane and tetrahydrofuran at all temperatures. For the solution in acetone, there is greater difficulty in

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interpreting the spectra. Only the edge-bridging carbonyl is readily detected. However, its intensity is very weak compared to the total intensity of bridging carbonyl absorptions in the other solvents. It seems likely that the face-bridging isomer is also present (and probably dominant), but it is not detected due to the beam energy absorbed by the intense solvent peak in this region. This idea is supported by the NMR results discussed below.

The NMR data shed further light on the isomer distribution but raise some new questions. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of the CN-*i*-Pr complex ($CDCl_3$ solution) shows only one carbonyl resonance at δ 221.6. The signal is a triplet of doublets with a significant difference in the two Rh–C coupling constants. The triplet and doublet couplings are 42 and 17 Hz, respectively, consistent with a relatively weaker interaction with the unique rhodium. This indicates that the face-bridging isomer should really be designated as *semi*-face-bridging.

The ^1H and ^{19}F NMR spectra have been measured in two solvents for both complexes. The room-temperature ^1H NMR spectrum of the CN-*t*-Bu compound in $CDCl_3$ shows two broad singlets, one at δ 5.57 due to the cyclopentadienyl protons and another at δ 1.55 attributed to the *tert*-butyl protons. The relative intensity of the higher field signal is somewhat greater than expected for a $\{(C_5H_5)_2 + (CN\text{-}t\text{-}Bu)_3\}$ system, and we believe this is due to coincidence of a water peak and the *tert*-butyl peak. This view is reinforced by subtracting the spectrum of the solvent used.

When the solution of the CN-*t*-Bu complex is cooled, the broad C_5H_5 resonance splits into two singlet resonances separated by 0.17 ppm. At lower temperature, the *tert*-butyl resonance becomes three resonances at δ 1.60, 1.59, and 1.54, with the central resonance being of higher intensity than the other two. This is due to coincidence of this central peak and the water resonance. Thus, we believe that the limiting spectrum contains three individual *tert*-butyl resonances of equal intensity.

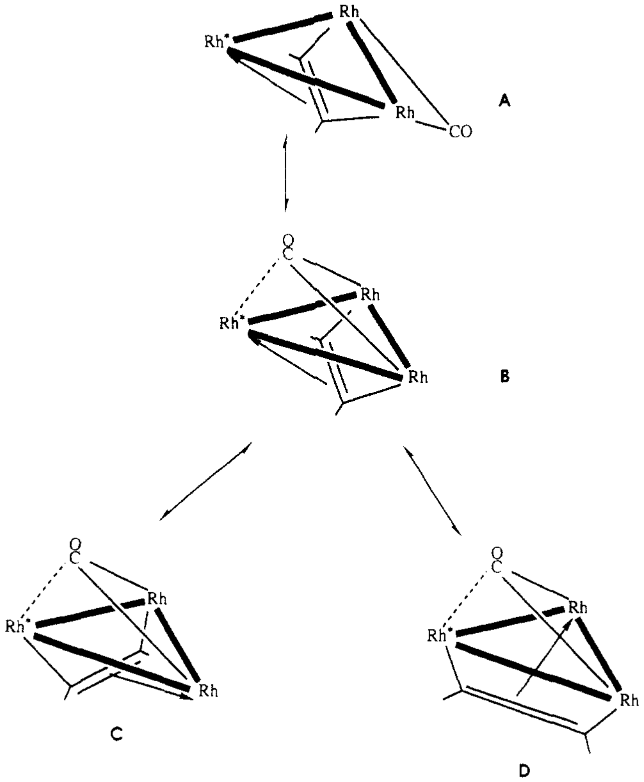
At room temperature, the ^{19}F NMR spectrum of the CN-*t*-Bu compound in $CDCl_3$ shows a single broad CF_3 signal plus a doublet with J_{P-F} = 711 Hz for the PF_6^- anion. When the temperature of the solution is lowered, the CF_3 resonance splits into two well-resolved quartets (J_{F-F} = 12 Hz) of equal intensity.

For the CN-*i*-Pr compound in $CDCl_3$, the ^1H NMR spectrum at room temperature is more detailed in that the isopropyl groups generate methine plus methyl signals and there is evidence for two isomers in the ratio 10:1. At room temperature, the spectrum of each isomer consists of a single cyclopentadienyl resonance, a poorly resolved methine multiplet, and a methyl doublet; the last is difficult to observe for the minor isomer because it is partly obscured by the signal for the major isomer. The ^{19}F NMR spectrum is very similar to that for the CN-*t*-Bu compound except that an extra singlet is observed at δ −54.1.

On the basis of these results, we suggest that the major species existing in these solutions are C and D, shown in Scheme I. At room temperature, C and D equilibrate via the symmetrical intermediate B.

More informtaion about the minor isomer is obtained from the spectra of samples dissolved in acetone. In this solvent at room temperature, the CN-*t*-Bu compound gives a spectrum with two cyclopentadienyl resonances of relative intensity 6:1. The more intense signal is broad, but it splits into two singlets as the temperature of the solution is lowered. This behavior is analogous to that observed for $CDCl_3$ solutions. The cyclopentadienyl signal of lower intensity is a sharp singlet that is unaffected by decreasing the temperature. In the *tert*-butyl region of the spectrum, several overlapping signals are apparent in a narrow chemical shift region. The ^{19}F NMR spectrum shows a broad CF_3 signal for the major isomer, a sharp singlet for the CF_3 group of the minor isomer, and a doublet at δ −71.5 assigned to PF_6^-. At low temperature, the broad CF_3 signal splits into two well-resolved quartets with J_{F-F} = 12 Hz, but the other signals are not altered.

Scheme I. Interconversion between Isomers of the Cationic Clusters[a]



[a] Rh represents (η-C_5H_5)Rh, Rh* represents $Rh(CNR)_3$, and CF_3 groups are omitted for clarity.

Similar behavior is found for the CN-*i*-Pr compound in acetone, except that the isomer ratio is 4:1. In the isopropyl region of the ^1H NMR spectrum, well-defined methine septets and methyl doublets are observed for each isomer. The less intense peaks attributed to the minor isomer are unaffected on lowering the temperature, but the signals for the major isomer become more complex. At −82 °C, the methyl signal appears to consist of several overlapping doublets, and the methine resonance is a poorly resolved and complex multiplet. These results indicate that the major isomer in acetone is analogous to that in chloroform and that the minor isomer has a symmetrical structure such as A in Scheme I. The structures A and B are closely related to those previously established[25] for the complexes $(\eta\text{-}C_5H_5)_3Rh_3(CO)(RC_2R)$ (R = Ph, C_6F_5).

Attempts To Prepare Related Heteronuclear Cluster Cations. An investigation of the corresponding reaction between **1** and the isocyanide–iridium compound $[Ir(CNC_6H_4CH_3)_4]^+PF_6^-$ was not rewarding. Photoinduced dissociation of the iridium oligomer[31] followed by stirring with a solution of **1** did result in a color change. However, NMR and TLC examination of the reaction solution indicated the presence of a large number of minor products and substantial decomposition material. A variety of

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products was formed also when 1 was treated with the isocyanide–platinum dication $[Pt(CNCy)_4]^{2+}$.[32] Most of the products identified from this reaction were known polynuclear rhodium compounds. These included $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (34% yield), $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNCy)(CF_3C_2CF_3)$ (three isomers, total yield 20%), and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (6%). No Rh_2Pt clusters could be identified.

Conclusions. The sites of attachment of the hexafluorobut-2-yne and carbonyl ligands to the isosceles Rh_3 triangle in $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CNR)_3]^+$ are dependent on the phase. The alkyne always adopts the $\mu_3\text{-}\eta^2\text{-}\|$ bonding mode characteristic of 48-electron clusters. However, in the solid state, π-bonding is to the most electron-attracting rhodium center, in contrast with theory and most previous observations. The CO is edge-bridging in the solid state. In solution, two isomers coexist, but in the predominant form, the alkyne has twisted to the predicted position with π-bonding to one or the other of the $(\eta\text{-}C_5H_5)Rh$ centers. The CO has also shifted to a semi-face-bridging position. It is clear that the stabilities of the isomers are very similar. Small differences in the relative electronegativities of the metal centers and weak coordination of solvent molecules can affect the preferred orientation of the ligands in these complexes. These results, and recently published work[29] on the $[FeCo_2(CO)_9(EtC_2Et)]$ cluster, establish that the alkyne orientation in asymmetric trinuclear clusters is extremely sensitive to a range of extraneous factors.

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Supplementary Material Available: Listings of thermal parameters, bond distances and angles for the ligands, equations of least-squares planes and dihedral angles, and H atom positional parameters (7 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis of (1*RS*,2*RS*,5*SR*)-3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]-oct-2-yl Acetate and the Chemo- and Stereoselective Coordination of Its Butadiene Functions with Rhodium and Iron Moieties[1]

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The title compound (**6**) has been derived from 7,8-epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane. Treatment of **6** with tris(μ_2-carbonyl)tris(η^5-indenyl)-*triangulo*-trirhodium gave first μ-carbonyl(Rh–Rh)bis(η^5-indenyl)[(1*RS*,2*RS*,5*SR*,6*SR*,7*RS*)-*C*,6,7,*C*-η-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]dirhodium(I)(*Rh–Rh*) (**13**) and then [*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*SR*,7*RS*)-*C*,3,4,*C*-η(*Rh*):*C*,6,7,*C*-η(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](indenylrhodium) (**16**) with high chemo- and stereoselectivity. Treatment of **13** with $Fe_2(CO)_9$ gave first [*trans*-μ-[(1*RS*,2*RS*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,4-η^2(*Fe*):*C*,6,7,*C*-η^4(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](tetracarbonyliron) (**17**) and then [*cis*-μ[1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η^4(*Fe*):*C*,6,7,*C*-η^4(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl((Rh–*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](tricarbonyliron) (**18**) with good regio- and stereoselectivity. The ketone function in the unstable tetraenone **6** is probably responsible for the selectivities observed in the formation of the rhodium polymetallic complexes.

Introduction

2,3,6,7-Tetramethylidenebicyclo[3.2.1]octane (**1**)[3] and its derivatives[4] are potential synthetic intermediates for the preparation of naphthocyclinones[5] and analogues via tandem Diels–Alder additions.[6] In 1980, Gabioud et al.[7] developed a quick access to 7,8-epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**2**). Since bicyclo[2.2.2]oct-2-yl ester[8] and halide derivatives[9] are known to

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(1) Preliminary communication: Autumn meeting of the Swiss Chemistry Society, Bern, Switzerland, Oct 20, 1989.

(2) Part of the planned Ph.D. thesis of F. Claret, University of Lausanne.

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