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THE ADDITION OF SMALL MOLECULES TO $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$

I. THE COORDINATIVE-ADDITION OF CO, CNR, AND SOME GROUP V DONOR LIGANDS

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Summary

Treatment of the $\mu(\eta^1)$-alkyne complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ with trimethylamine-*N*-oxide results in mono-decarbonylation to give the $\mu(\eta^2)$-alkyne complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CF_3C_2CF_3)$. Coordinative addition of a variety of ligands L to the monocarbonyl complex has been achieved at room temperature, and stable adducts $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(CF_3C_2CF_3)$ (L = CO, $CNBu^t$, PPh_3, $PMePh_2$, $P(OMe)_3$, $AsPh_3$, PF_3 and $PF_2(NEt_2)$) have been fully characterized by infrared and NMR spectroscopy. In each complex, there is a $\mu(\eta^1)$-attachment of the hexafluorobut-2-yne and a *trans*-arrangement of CO and L. The spectroscopic data establish that there is rapid scrambling of CO and L when L = $CNBu^t$. An unstable adduct is formed when $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CF_3C_2CF_3)$ is dissolved in pyridine.

Introduction

In a preliminary communication [1], we described the conversion of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ by treatment with Me_3NO in dry acetone at room temperature. The crystal and molecular structures of both complexes have been determined from X-ray diffraction data [2,3], and representations of these structures are given in I and II. It can be seen that decarbonylation is accompanied by a 90° twist of the coordinated alkyne and a shift of the intact carbonyl from a terminal to a bridging position. This fascinating intramolecular transformation re-establishes an 18-electron count at each rhodium atom. We have found [1] that a range of ligands L will add coordinatively to the monocarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ to give adducts of the type $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(CF_3C_2CF_3)$. In this paper, we report details of our investigations with the π-acceptor ligands CO, CNR, PR_3, AsR_3, PF_3, $PF_2(NEt_2)$, and pyridine.

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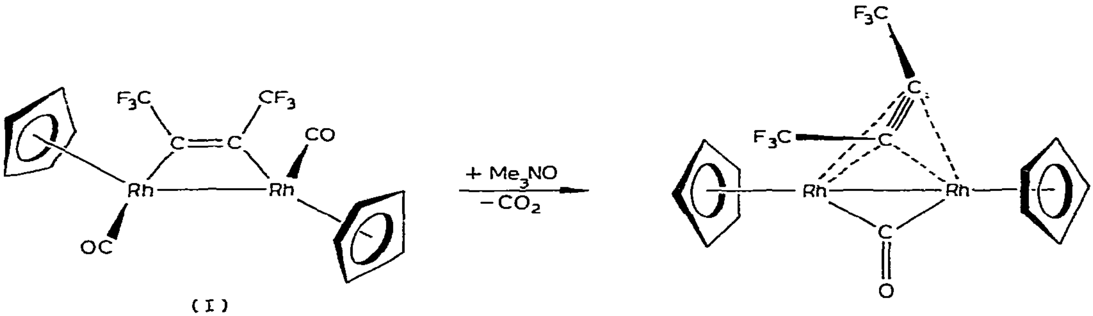


(I) (II)

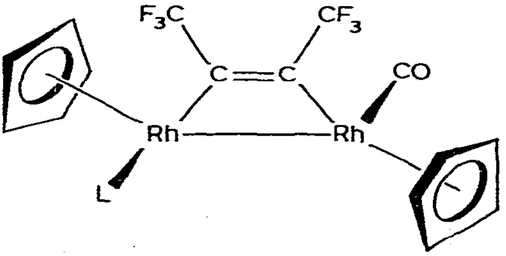
Results and discussion

1. Reactions with C-donors

Both the *cis*- and *trans*-isomers of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ are formed when CO is added to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$; the yields are 20% and 80% respectively. Preparation of the *trans*-dicarbonyl complex from $(\eta\text{-}C_5H_5)Rh(CO)_2$ [4] or $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ [5] and $CF_3C{\equiv}CCF_3$ at 100°C has been reported previously, and the *cis*-complex is obtained, together with *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2$-$(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2\{COCF_3C_2CF_3\}$, when $(C_5H_5)Tl$ is added to the intractable products of the reaction between $[Rh(CO)_2Cl]_2$ and $CF_3C{\equiv}CCF_3$ [6]. A detailed description of the spectroscopic properties of *cis*- and *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ has been presented elsewhere [5]. The interconversion is stoichiometric in each direction, and this provides a convenient procedure for obtaining a ^{13}CO-enriched dicarbonyl complex.

$$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3) \underset{+CO}{\overset{+Me_3NO}{\rightleftharpoons}} (\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$$

The reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and the isonitrile $CNBu^t$ gives $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNBu^t)(CF_3C_2CF_3)$ quantitatively. This complex is very stable in solution and it can be chromatographed without decomposition. The TLC and spectroscopic results are consistent with the formation of just one isomer. We assume that this is the conformer with a *trans*-arrangement of the CO and CNR groups (III; L = $CNBu^t$) because previous investigations [5] have



(III)

established that *cis*-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ transforms to the *trans*-isomer in solution.

In the infrared spectrum of (η-$C_5H_5)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)$ strong absorptions at 2154 and 1974 cm^{-1} are assigned to ν(C≡N) and ν(C≡O), respectively. The NMR spectra are consistent with rapid scrambling of the CO and CNR groups between the two Rh sites. The ^1H spectrum at 28°C shows two singlets at δ 5.40 and 1.41 ppm which are assigned to the C_5H_5 and Bu^t groups, respectively. At —88°C, the C_5H_5 resonance is split into two singlets at δ 5.49 and 5.37 ppm. On warming the solution, these two resonances merge and coalesce at —18°C. The Bu^t resonance is unaffected by these changes in temperature. The ^{19}F spectrum shows a broad unresolved multiplet at room temperature. Although this resonance broadens considerably when the solution is cooled, it does not separate into the two quartets expected for two inequivalent CF_3 groups. Presumably, the two CF_3 chemical shifts are almost identical in the static molecule. The ^{13}C spectrum of a ^{13}CO-enriched sample shows a 1 : 2 : 1 triplet at δ 191.8 ppm (*J*(Rh—C) 41.2 Hz) at room temperature, and this is consistent with the terminal carbonyl scrambling rapidly from one rhodium atom to the other. As the sample is cooled, the central peak of the triplet broadens and decreases in height relative to the sharp outermost peaks, and finally it merges into the background leaving a doublet at δ 192.0 ppm (*J*(Rh—C) 82.4 Hz) (Fig. 1). This behavior resembles very closely that observed [5] in the variable temperature ^{13}C NMR spectra of *trans*-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$. A difference with ($\eta$-$C_5H_5)_2Rh_2(CO)(CNBu^t)(CF_3C_2CF_3)$ is that the static structure possesses inequivalent C_5H_5 groups, and this is reflected in the ^{13}C NMR spectrum (and the ^1H NMR spectrum). Thus, at room temperature, all C_5H_5 carbons are observed at δ 88.5 ppm as a sharp singlet; this broadens on cooling the solution, and at —60°C it separates into two peaks at δ 89.4 and 87.1 ppm. Unfortunately, the terminal carbon of $CNBu^t$ was not observed in the ^{13}C NMR experiments. It seems likely that scrambling of the CO and CNR ligands in this complex occurs by the pairwise bridge closing and opening mechanism proposed [5] for *trans*-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$.

2. *Reactions with Group V donor ligands*

Addition of the Group V donor ligands PPh_3, $PMePh_2$, $P(OMe)_3$, and $AsPh_3$ to (η-$C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ gives the appropriate (η-$C_5H_5)_2Rh_2(CO)L$-$(CF_3C_2CF_3)$ complex in 90—100% yield. Only one isomer of each complex was isolated, and again this is probably the one with a *trans*-arrangement of CO and L (III, L = PR_3 or $AsPh_3$). The tertiary phosphine complexes are particularly stable in solution, and they could be extracted quantitatively from chromatographic supports. The spectroscopic properties of the $AsPh_3$ adduct indicate that there is some dissociation of the arsine ligand in solution. TLC of a solution that had been aged for several days separated (η-$C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, ($\eta$-$C_5H_5)_2Rh_2(CO)(AsPh_3)(CF_3C_2CF_3)$, and a small amount of Ph_3AsO. The arsine oxide does not form an adduct with (η-$C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$.

In the infrared spectra of the complexes (η-$C_5H_5)_2Rh_2(CO)L(CF_3C_2CF_3)$, ν(CO) is observed at 1989 (L = PPh_3), 1988 ($AsPh_3$), 1981 ($P(OMe)_3$) or 1979 ($PMePh_2$), and ν(C═C) is within the range 1623—1609 cm^{-1}. The NMR spectra are unremarkable. Thus, the ^1H spectra show two C_5H_5 resonances (e.g. at

δ 5.19 and 4.98 ppm, L = PPh_3), and there are two CF_3 resonances in the ^{19}F spectra (e.g. at δ 52.9 and 55.7 ppm, L = PPh_3).

In some instances, the C_5H_5 resonances showed coupling to rhodium of about 1 Hz. The two CF_3 resonances were mutually coupled with ^5J(F—F) in the range 11.5 to 12.2 Hz and this is consistent with the *cis*-arrangement of the CF₃ groups about the C═C bond. In some cases, it is possible to assign the C_5H_5 and CF_3 resonances at higher field to the groups adjacent to L. The $P(OMe)_3$ complex, for example, exhibits two C_5H_5 resonances at δ 5.5 and 5.4 ppm, and the latter shows a coupling of 2.9 Hz which is attributed to P—H coupling. The ^{19}F spectrum of this complex contained two resonances at δ 53.66 and 55.60 ppm. The low field resonance was a quartet of doublets with J(F—F) = 11.8 and J(Rh—F) = 3 Hz. The high field resonance was a quartet of doublets (qdd), showing an additional coupling of 28 Hz which is assigned to ^4J(P—F).

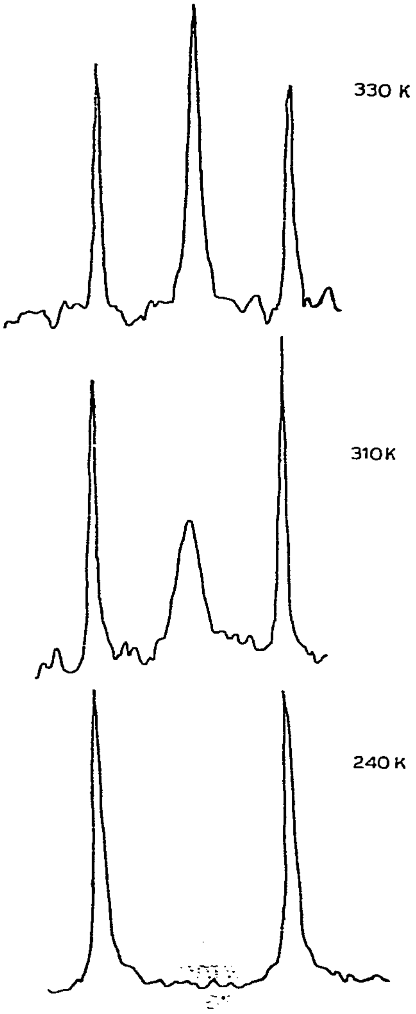


Fig. 1. Variable temperature ^{13}C magnetic resonance spectra of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNBu^t)(CF_3C_2CF_3)$; changes in profile of the CO resonance.

The complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PF_3)(CF_3C_2CF_3)$ is obtained in 97% yield when PF_3 is bubbled into $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. For this complex, $\nu(CO)$ is observed at 2018 cm^{-1} (cf. $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$, $\nu(CO)$ at 1994 cm^{-1}). The high carbonyl stretching frequency for the PF_3 adduct is consistent with the view that PF_3 is a stronger π-acceptor than CO [7,8]. Three strong bands at 880, 870, and 860 cm^{-1} are assigned to $\nu(P—F)$. The free ligand exhibits peaks at 891 and 860 cm^{-1}. It has been found that coordination reduces the symmetry so that for complexes containing one PF_3 ligand, three bands are commonly observed [7,8]. Rhodium(III) complexes often show $\nu(P—F)$ at higher frequency than the free ligand, whereas rhodium(I) complexes tend to show $\nu(P—F)$ at lower frequency [7,8]. The complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PF_3)(CF_3C_2CF_3)$, in which each rhodium has a formal oxidation state of II, exhibits $\nu(P—F)$ close to the average of those of the free ligand. These observations are consistent with stronger $d[Rh] \rightarrow \pi^*[P—F]$ back-bonding in the order $Rh^I > Rh^{II} > Rh^{III}$.

Some unusual effects are revealed in the NMR spectra of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PF_3)(CF_3C_2CF_3)$. In the ^1H spectrum, the two resonances expected for inequivalent C_5H_5 groups were not clearly separated. Under high resolution, a shoulder emerged from the singlet at δ 5.55 ppm, but the relative intensities of the two lines were far from equal. There was no change in the appearance of the spectrum when the solution was cooled to —60°C. The ^{19}F spectrum shows two resonances of relative intensity 1 : 2 which can be assigned to the PF_3 and CF_3 groups. The PF_3 resonance is observed at δ 8.22 ppm, and there is coupling to phosphorus ($J(F—P) = 1340$ Hz) and to one rhodium ($J(F—Rh) = 27.5$ Hz). The observation of only one CF_3 resonance at δ 55.62 ppm is unexpected, and it raises the possibility of some sort of fluxional process which averages the CF_3 environments. It seems unlikely that CO and PF_3 groups could be scrambling rapidly between the two rhodium sites by a pairwise bridge closing and opening mechanism because PF_3 does not normally act as a bridging group. The further possibility of a dissociative exchange mechanism is negated by our ^{31}P NMR results. Thus, the PF_3 resonance is observed as a quartet of doublets with $J(P—Rh)$ and $J(P—F) = 360$ and 1338 Hz, respectively.

In an attempt to resolve these problems, we have studied the spectroscopic properties of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PF_2NEt_2)(CF_3C_2CF_3)$, which has a slightly modified fluorophosphine ligand. In the infrared spectrum, structurally significant absorptions were observed at 1996 ($\nu(CO)$), 1627 ($\nu(C{=}C)$), 843 and 820 ($\nu(P—F)$) cm^{-1}. The ^{31}P NMR spectrum of the complex shows a triplet of doublets with $J(P—F) = 1145$ and $J(P—Rh) = 300$ Hz. Thus, the P-donor atom is attached to a single rhodium atom as in the PF_3 complex. In the ^1H NMR spectrum, the two resonances for the C_5H_5 hydrogens are well resolved and occur as a singlet at δ 5.49 ppm and a doublet at δ 5.45 ppm. The H—P coupling constant of 2.9 Hz is similar to that of other phosphinecyclopentadienyl complexes of transition metals [9], including rhodium. The ^{19}F spectrum confirms that the PF_2 group is attached to one rhodium only. The two F-atoms in the PF_2NEt_2 ligand become inequivalent upon coordination to the chiral rhodium, and the resonance for each F atom is a doublet of triplets. For the resonance at δ 28.0 ppm, $J(F—P) = 1144$ and $J(F—F') \approx J(F—Rh) \approx 25$ Hz; the resonance at δ 38.4 ppm has $J(F'—P) = 1144$ and $J(F'—F) \approx J(F'—Rh) \approx 19$ Hz.

The F—Rh coupling constant is similar to that for the PF_3 complex. The resonances for the CF_3 groups are resolved and appear as two quartets with an F—F coupling constant of 12.2 Hz. The observation of two CF_3 resonances confirms that no fluxional process is occurring in *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)\{PF_2(NEt_2)\}(CF_3C_2CF_3)$.

These results for the $PF_2(NEt_2)$ complex enable us to re-interpret the spectroscopic data for the PF_3 complex as follows. We believe that the molecule is stereochemically rigid, and that the CF_3 resonances in the ^{19}F spectrum are accidentally degenerate. In the ^1H spectrum, the smaller of the two observed lines is probably one line of a doublet due to coupling to phosphorus. The remaining line of the doublet is obscured by the singlet resonance for the other cyclopentadienyl ring.

When $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ is dissolved in pyridine, an orange adduct of formula $(\eta\text{-}C_5H_5)_2Rh_2(CO)(py)(CF_3C_2CF_3)$ is formed. This complex is not particularly stable, and it loses pyridine slowly at room temperature, and very rapidly under high vacuum, to reform the monocarbonyl species. Attempts to obtain adducts with other N-base ligands such as Et_3N failed.

Experimental

(a) General

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ was prepared from $(\eta\text{-}C_5H_5)Rh(CO)_2$ and hexafluorobut-2-yne at 100°C [4]. Trimethylamine-*N*-oxide dihydrate was obtained from Ega-Chemie; sublimation under vacuum at 120°C gave anhydrous Me_3NO. Commercial samples of PPh_3, $PMePh_2$, $P(OMe)_3$ and $AsPh_3$ were used without purification. PF_3 was purchased from Research Organic/Inorganic Chemical Company and was purified before use by passing the gas through two dry-ice/acetone traps to remove any HF. The reaction between anhydrous NaF and PCl_2NEt_2 [10] in dry sulfolane gave PF_2NEt_2 [11]. Bu^tNC was prepared from t-butylformamide by dehydration with $POCl_3$ in the presence of pyridine [12]. All solvents were dried by standard procedures.

Column chromatography was carried out under nitrogen on dry packed supports; deactivated alumina or Florisil was used. Thin layer chromatography was performed on 20 by 20 cm plates with 1/1 silica gel G-HF_{254} mixture as adsorbent.

Infrared spectra were recorded with a Perkin-Elmer 521 spectrometer. A Bruker WH-90 spectrometer was used to obtain the nuclear magnetic resonance spectra; the ^1H chemical shifts are reported as δ values, the ^{19}F chemical shifts are reported upfield from trichlorofluoromethane internal reference, the ^{13}C chemical shifts are downfield from tetramethylsilane ($Cr(acac)_3$ was added as a relaxation agent), and the ^{31}P chemical shifts are downfield from phosphoric acid (all ^{31}P spectra were broad-band ^1H decoupled). Mass spectra were recorded on a V.G. Micromass 7070-F spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

(b) Conversion of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.37 g) and Me_3NO (0.056 g, mol ratio 1/1) in dry acetone (15 ml) were stirred under nitrogen at 20°C for 7 h. The solution was concentrated by evaporation of solvent under reduced pressure. Column chromatography on Florisil with petroleum spirit (b.p. 30—40°C) as eluent developed a green band. This yielded green dichroic crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.25 g; 70%) m.p. 136°C (Found: C, 34.2; H, 2.1; F, 22.0. $C_{15}H_{10}F_6ORh_2$ calcd.: C, 34.2; H, 1.9; F, 21.7%). Infrared absorption (KBr): $\nu(CO)$ 1841s, $\nu(C{\equiv}C)$ 1592s cm^{-1}. A sample prepared from ^{13}CO-enriched $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ showed $\nu(^{13}CO)$ at 1800 cm^{-1}. NMR spectra ($CDCl_3$): ^1H (301 K); δ 5.79 (s) ppm. ^{19}F (301 K); δ 52.16 ppm (dd, J(Rh—F) 2.0 and 1.9 Hz). ^{13}C (312 K); δ 205.1 ppm (t, J(Rh—C) 41.5 Hz, CO) and 90.4 (s, C_5H_5). Mass spectrum: 526 (75%, M), 507 (<1%, M — F), 498 (9%, M — CO), 479 (7%, M — CO — F), 233 (100%, $C_{10}H_{10}Rh^+$). A metastable peak was observed at 471—472 (calcd. for 526 → 498, 471.5).

Continued elution with 1/1 pentane/dichloromethane mixture as eluent separated an orange band which gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CO)_2(CF_3C_2CF_3)$ (0.17 g, 25%), and a purple band which yielded $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (0.023 g, 3%).

(c) Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ with L

(i) L = CO. CO gas was bubbled through a solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ in $CHCl_3$ for 5 min at 20°C. Concentration of the solution and TLC separated two orange bands. These were identified spectroscopically as *trans*- and *cis*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (ca. 80% and 20% yields, respectively).

(ii) L = CNBu^t. A slight excess of $CNBu^t$ (0.013 g) was added dropwise to a solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.077 g; mol ratio ca. 1/1) in CH_2Cl_2 (10 ml). The color of the solution changed immediately from green to orange. Solvent and excess $CNBu^t$ were removed under vacuum leaving an orange solid. TLC with a 1/1 hexane/CH_2Cl_2 mixture as eluent gave one orange band which yielded orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNBu^t)(CF_3C_2CF_3)$ (0.088 g, 99%), m.p. 110°C (Found: C, 39.6; H, 3.3; F, 18.7. $C_{20}H_{19}F_6NORh_2$ calcd.: C, 39.4; H, 3.1; F, 18.7%). Infrared absorption (KBr): $\nu(C{\equiv}N)$ 2154vs, $\nu(CO)$ 1974vs, $\nu(C{=}C)$ 1631s cm^{-1}. ^1H NMR spectrum ($CDCl_3$, 301 K): δ 5.38 (s, 10 H, C_5H_5) and 1.41 ppm (s, 9 H, $C(CH_3)_3$). ^{19}F NMR spectrum ($CDCl_3$ — $CFCl_3$): δ 54.9 ppm (br.s, CF_3). ^{13}C NMR spectrum (CD_2Cl_2): δ 191.8 (t, J(Rh—C) 41.2 Hz, CO), 88.5 (s, C_5H_5), and 31.1 ppm (s, Bu^t). Mass spectrum: 609 (2%, M), 581 (6%, M — CO), 526 (<1%, M — $CNBu^t$), 279 (32%, $C_{11}H_{14}ONRh^+$), 233 (100%, $C_{10}H_{10}Rh^+$), ...

(iii) L = PPh$_3$. A solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.026 g) in $CHCl_3$ (10 ml) was treated with a slight excess of PPh_3 (0.013 g; mol ratio ca. 1/1). Removal of solvent under reduced pressure produced a red solid which was recrystallized from $CHCl_3$/hexane to give red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_3)(CF_3C_2CF_3)$ (0.036 g, 92%), m.p. 164°C (Found: C, 50.1; H, 3.4; F, 14.1. $C_{33}H_{25}OF_6PRh_2$ calcd.: C, 50.3; H, 3.2; F, 14.5%). Infrared absorption (KBr): $\nu(CO)$ 1989vs, $\nu(C{=}C)$ 1611s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.36 (m, 15 H, PPh_3), 5.19 (d, J(P—H) 1.2 Hz, 5 H, C_5H_5), and 4.98 ppm (s, 5 H, C_5H_5). ^{19}F NMR spectrum ($CDCl_3$): δ 52.9 (m, J(F—F) 11.5 Hz, 3 F) and 55.7 ppm (qdd, J(F—H) 11.5 and J(P—F) ≈ J(Rh—F) ≈ 3.5 Hz, 3 F). Mass spectrum: 760

(1%, $M - CO$), 592 (6%, $M - CO - C_5H_5Rh$), 526 (24%, $M - PPh_3$), 498 (2%, $M - CO - PPh_3$), 458 (9%, $C_{24}H_{20}OPRh^+$), 430 (57%, $C_{23}H_{20}PRh^+$), 330 (5%, $C_9H_5F_6Rh^+$), 286 (32%, n.a.), 262 (72%, $C_{18}H_{15}P^+$), 233 (100%, $C_{10}H_{10}Rh^+$), ...

(iv) $L = PMePh_2$. The above reaction (iii) was repeated with $PMePh_2$ in place of PPh_3. TLC of the orange product with a 1/1 mixture of hexane/CH_2Cl_2 as eluent separated two minor bands from the main orange-red band. The solid from the latter band was recrystallized from pentane/$CHCl_3$ to give red-orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PMePh_2)(CF_3C_2CF_3)$ (95% yield) m.p. 167°C (Found: C, 46.2; H, 3.5; F, 15.4; mol. wt. (M^+, m/e) 726. $C_{28}H_{23}F_6OPRh_2$ calcd.: C 46.3; H, 3.2; F, 15.7%, mol. wt. 726). Infrared absorption (KBr): ν(CO) 1979vs, ν(C=C) 1621s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 (m, 10 H, C_6H_5), 5.11 (d, J 1.2 Hz, 5 H, C_5H_5), 5.07 (s, 5 H, C_5H_5) and 1.65 ppm (dd, J(P—H) 9.2 and J(Rh—H) 1.3 Hz, 3 H, CH_3). ^{19}F NMR ($CDCl_3$): δ 51.7 (qd, J(Rh—F) ≈ 3 and J(F—F) ≈ 11.7 Hz, 3 F) and 55.6 ppm (qdd, J(Rh—F) ≈ J(P—F) = 3 and J(F—F) ≈ 11.7 Hz, 3 F).

(v) $L = P(OMe)_3$. Repetition of reaction (iii) with $P(OMe)_3$ in place of PPh_3, and TLC of the reaction product with 1/1 hexane/CH_2Cl_2 as eluent, separated a major orange band from some minor bands. Recrystallization of the orange product from n-pentane gave orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{P(OMe)_3\}(CF_3C_2CF_3)$ (97% yield) m.p. 158°C (Found: C, 33.4; H, 2.9; F, 17.4; mol. wt. (M, m/e) 650. $C_{18}H_{19}F_6O_4PRh_2$ calcd.: C, 33.3; H, 3.0; F, 17.5%; mol. wt. 650). Infrared absorptions (KBr): ν(CO) 1981vs, ν(C=C) 1623m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.5 (s, 5 H, C_5H_5), 5.4 (d, J(P—H) 2.9 Hz, 5 H, C_5H_5) and 3.6 ppm (d, J(P—H) 11.3 Hz, 9 H, CH_3). ^{19}F NMR ($CDCl_3$): δ 53.7 (qd, J(F—F) ≈ 11.8 and J(Rh—F) ≈ 2.8 Hz, 3 F) and 55.6 ppm (qdd, J(F—F) ≈ 11.8, J(Rh—F) ≈ 3, J(P—F) ≈ 2.8 Hz, 3 F).

(vi) $L = AsPh_3$. Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.018 g) with $AsPh_3$ (0.011 g, mole ratio 1/1.05) in $CHCl_3$ (5 ml) immediately produced a red solution. TLC of the reaction mixture with a 1/1 mixture of hexane/CH_2Cl_2 as eluent separated a major red band from two minor orange bands which were not characterized. Recrystallization of the red solid from pentane/CH_2Cl_2 gave red crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(AsPh_3)(CF_3C_2CF_3)$ (0.028 g, 99% yield) m.p. 164°C (Found: C, 47.8; H, 3.2; F, 13.7. $C_{33}H_{25}AsF_6ORh_2$ calcd.: C, 47.6; H, 3.0; F, 13.7%). Infrared (KBr): ν(CO) 1988vs, ν(C=C) 1609m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.37 (m, 15 H, C_6H_5), 5.22 (s, 5 H, C_5H_5), and 5.01 ppm (s, 5 H, C_5H_5). ^{19}F ($CDCl_3$): δ 53.3 (qd, J(F—F) 11.8 and J(Rh—F) ≈ 2.9 Hz, 3F) and 55.3 ppm (qd, J(F—F) 11.8 and J(Rh—F) ≈ 3.7 Hz). Mass spectrum: 526 (15%, $M - AsPh_3$), 498 (1%, $M - CO - AsPh_3$), 479 (<1%, $C_{14}H_{10}F_5Rh_2^+$), 306 (26%, $C_{18}H_{15}As^+$), 233 (100%, $C_{10}H_{10}Rh^+$), 168 (10%, $C_5H_5Rh^+$) ....

(vii) $L = PF_3$. PF_3 was bubbled through a solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.023 g) in pentane (10 ml) for 2—4 min. Concentration of the solution and TLC with 5/3 hexane/CH_2Cl_2 as eluent separated a major orange band from minor products. This yielded orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PF_3)(CF_3C_2CF_3)$ (0.026 g, 97%) m.p. 155°C (dec.). (Found: C, 29.8; H, 1.8; F, 28.1. $C_{15}H_{10}F_9OPRh_2$ calcd.: C, 29.3; H, 1.6; F, 27.9%). Infrared absorptions (KBr): ν(CO) 2018vs, ν(C=C) 1621s, ν(PF) 880vs, 870vs, 860vs cm^{-1}. ^1H NMR ($CDCl_3$, 301 K): δ 5.56 ppm (this appears to be a singlet at 5.55 overlapping a doublet with one observable component at 5.57, J(H—P) < 3 Hz). ^{19}F NMR ($CDCl_3$):

δ 8.22 (dd, J(F—P) 1340 and J(F—Rh) 27.5 Hz, 3 F, PF_3) and 55.6 ppm (s, 6 F, CF_3). ^{31}P NMR ($CDCl_3$): δ 124.9 ppm (qd, J(P—F) 1338 and J(P—Rh) 360 Hz). Mass spectrum: 614 (<1%, M), 586 (4%, $M - CO$), 526 (17%, $M - PF_3$), 507 (1%, $C_{15}H_{10}F_5ORh_2^+$), 498 (39%, $M - CO - PF_3$), 479 (2%, $C_{14}H_{10}F_5Rh_2^+$), 330 (5%, $C_9H_5F_6Rh^+$), 284 (12%, $C_6H_5F_3OPRh^+$), 233 (100%, $C_{10}H_{10}Rh^+$), 168 (56%, $C_5H_5Rh^+$) ....

A minor orange band afforded orange crystals (0.001 g) m.p. 123°C. Infrared (KBr): ν(CO) 2000vs, ν(C=C) 1637s cm^{-1}. Mass spectrum: 614 (<1%, M), 586 (3%, $M - CO$), 526 (14%, $M - PF_3$) .... 233 (100%, $C_{10}H_{10}Rh^+$) ....

(viii) L = $PF_2(NEt_2)$. A slight excess of $PF_2(NEt_2)$ (0.014 g) was distilled under high vacuum directly onto $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.050 g, mole ratio 1/1) in pentane (10 ml). The mixture was allowed to warm to room temperature and was stirred for 5 min. Removal of solvent gave an orange solid, $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{PF_2(NEt_2)\}(CF_3C_2CF_3)$ (ca. 100% yield), m.p. 138—140°C (dec) (Found: C, 34.75; H, 3.0; F, 23.1. $C_{19}H_{20}F_8NOPRh_2$ calcd.: C, 34.2; H, 3.0; F, 22.8%). Infrared absorptions (hexane solution) ν(CO) 1996vs, ν(C=C) 1627s, ν(P—F) 843vs, 820vs cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.48 (t, $J(H—H_{vic})$ 7.2 Hz, 6 H, CH_3), 2.9—3.4 (m, 4 H, CH_2), 5.45 (d, J(H—P) 2.9 Hz, 5 H, C_5H_5RhP), 5.49 ppm (s, 5 H, C_5H_5RhCO). ^{19}F NMR spectrum ($CDCl_3$): δ 28.0 (dt, J(F—P) 1144 and $J(F—F') \approx J(F—Rh) \approx$ 25 Hz, 1 F, PF), 38.4 (dt, J(F'—P) 1144 and $J(F'—F) \approx J(F—Rh) \approx$ 19 Hz, 1 F, PF'), 54.5 (q, ^5J(F—F) 12.2 Hz, 3 F, CF_3), 55.7 ppm (q, ^5J(F—F) 12.2 Hz, 3 F, CF_3). ^{31}P NMR spectrum ($CDCl_3$): δ 157.0 ppm (td, J(P—F) 1145 and J(P—Rh) 300 Hz). Mass spectrum: 667 (<1%, M), 639 (5%, $M - CO$), 568 (14%, $M - CO - NC_4H_9$), 530 (11%, $M - CO - NC_4H_9F_2$), 526 (23%, $M - PF_2NEt_2$), 498 (6%, $M - CO - PF_2NEt_2$).... 233 (100%, $C_{10}H_{10}Rh^+$) ....

(ix) L = pyridine. An orange solution was obtained by dissolving $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ in pyridine. Removal of excess pyridine under reduced pressure yielded an unstable orange-red solid. Infrared absorption (Nujol): ν(CO) 1972vs and 1845s, ν(C=C) 1616m and 1596m cm^{-1}. The orange-red solid decomposed slowly at room temperature, and more rapidly on heating or under vacuum to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ which was identified from its color and infrared spectrum.

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