The Addition of Small Molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. 3.[1] The Formation of a Bridging Acrylamide Ligand on a Dirhodium Center by the Cycloaddition of Nitrenes, Carbon Monoxide, and an Alkyne. X-ray Crystal Structure of $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}\eta^3\text{-}C(CF_3)C(CF_3)C(O)N(Ph)]$

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Received April 4, 1985

Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) with organic azides (N_3R) in diethyl ether at 0 °C results in the immediate formation of the complexes $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(O)N(R)]$ (2, R = Ph, PhCO, $p\text{-}MeOC_6H_4SO_2$, $(MeO_2C)CH{=}C(CO_2Me)$). The related complexes 2 (R = *i*-Pr, Cy) are formed, together with the isocyanide complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)$ (3), when 1 is treated with the appropriate carbodiimide (RNCNR) in dichloromethane at room temperature. Another route to the complexes 2 involves the addition of organic isocyanates to 1; this has been achieved with RNCO (R = Me, *t*-Bu, $p\text{-}MeC_6H_4$) at 70–80 °C for several days. Finally, the complex 2 (R = *t*-Bu) is obtained by the oxidation with trimethylamine *N*-oxide of the isocyanide complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$. Determination of the crystal and molecular structure of the complex 2 (R = Ph) reveals that the bridging group is a substituted acrylamide of the form $-C(CF_3){=}C(CF_3)C({=}O)N(Ph)-$. Crystal data: $C_{21}H_{15}F_6NORh_2$, $M_r = 617.2$, tetragonal $I4_1/a$, $a = 24.49(1)$ Å, $c = 14.298(4)$ Å, $Z = 16$, final $R = 0.046$, for 2559 "observed" reflections.

Introduction

In preceding papers, we have shown that a variety of small molecules will add to the dirhodium compound $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1). For example, phosphines and related ligands[2] add coordinately to give the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(CF_3C_2CF_3)$. In the reactions with alkynes[3] and carbenes,[1] the initial coordinative addition of the ligand is followed by intramolecular interactions on the Rh–Rh bond to form new C–C or C–O bonds. We now describe some reactions in which nitrenes, carbodiimides, and isocyanates are added to 1. We find that each of these addition reactions, as well as the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$ and the mild oxidant trimethylamine *N*-oxide, gives a product of formula $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(O)N(R)]$ (2). The structure of the complex 2 (R = Ph) has been determined from X-ray diffraction data. Some of these results have been reported in a preliminary communication.[4]

Experimental Section

A. General Data. Infrared absorption spectra were measured with a Perkin-Elmer 521 spectrometer using matched 0.1-mm NaCl cells. NMR spectra were obtained on a Brüker WH-90 Fourier transform spectrometer at 90 MHz for ^1H, 22.62 MHz for ^{13}C, and 84.66 MHz for ^{19}F; deuterated solvents ($CDCl_3$, acetone-d_6) were used as internal locks. Chemical shifts are in parts per million from internal Me_4Si for ^1H and ^{13}C and from CCl_3F for ^{19}F. In all cases, a positive chemical shift denotes a resonance downfield from the reference. A V.G. Micromass 7070-F spectrometer was used to record the mass spectra; the spectrometer was operated at 70 eV and 200 °C inlet temperature. Microanalyses (C, H, F, N, S) were performed by the Australian Microanalytical Service, Melbourne. Melting or decomposition points were determined with a Büchi SMP-20 apparatus and are uncorrected.

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk or high-vacuum line techniques.[5] 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.

B. Solvents, Ligands, and Reagents. Acetone and dichloromethane were purified by standard procedures[6] and stored over molecular sieves. Ether was distilled from $LiAlH_4$ immediately before use. Toluene (AR grade) and X4 (petroleum fraction of bp 30–60 °C) were stored over molecular sieves.

The following ligands were obtained commercially and were used without purification: *t*-BuNC, MeNCO, *t*-BuNCO, *i*-PrNCN-*i*-Pr, and CyNCNCy. Trimethylamine *N*-oxide was dehydrated by sublimation at 100°C under vacuum. Literature procedures were used to prepare the following compounds: $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$,[2] $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$,[2] PhN_3,[7] $PhCON_3$,[8] $p\text{-}MeC_6H_4SO_2N_3$,[9] *cis*- and *trans*-$(MeO_2C)CH{=}C(CO_2Me)N_3$,[10] and $p\text{-}MeC_6H_4NCO$.[11]

C. Reactions of 1 with Organic Azides, RN_3 (R = Ph, PhCO, $p\text{-}MeOC_6H_4SO_2$, and $(MeO_2C)CH{=}C(CO_2Me)$). The reaction with phenyl azide is typical and is described in detail.

A slight excess of phenyl azide in diethyl ether was added to a solution of 1 (0.082 g) in diethyl ether at 0 °C. The color of the solution changed rapidly from green to dark red-brown. The solution was concentrated in a stream of N_2 and then chromatographed by TLC with a 16:12:3 mixture of CH_2Cl_2/X4/ether as eluent. This separated unchanged azide and numerous trace bands from a major crimson band. The latter yielded crimson crystals of $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(O)NPh]$ (0.080 g, 83%), **2a**, mp >200 °C. Anal. Calcd for $C_{21}H_{15}F_6NORh_2$: C, 40.9; H, 2.5; F, 18.5; N, 2.3. Found: C, 40.6; H, 2.7; F, 18.6; N, 2.1. Spectroscopic data: IR (CH_2Cl_2) (1680 vs (br), 1592 m, 1488 m,

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1390 s cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.1 (m, 5 H, C_6H_5), 5.92 (d, 5 H, J = 0.9 Hz, C_5H_5), 5.17 (d, 5 H, J = 0.6 Hz, C_5H_5); ^{19}F NMR (acetone-d_6) quartets (J = 12 Hz) of equal intensity at δ −46.9 and −56.2; MS, m/e 617 [M]$^+$, 498 [M − PhNCO]$^+$.

Benzoyl azide and 1 (0.075 g) gave crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)NCOPh] (0.089 g, 95%), **2b**, mp >200 °C. Anal. Calcd for $C_{22}H_{15}F_6NO_2Rh_2$: C, 41.0; H, 2.3; F, 17.7; N, 2.2. Found: C, 41.2; H, 2.6; F, 17.4; N, 2.4. Spectroscopic data: IR (CH_2Cl_2) 1680 vs (br), 1385 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.3 (m, 5 H, C_6H_5), 5.76 (s, 5 H, C_5H_5), 5.11 (s, 5 H, C_5H_5); ^{19}F NMR ($CDCl_3$) quartets (J = 12 Hz) of equal intensity at δ −48.4 and −57.4; ^{13}C NMR ($CDCl_3$, sample enriched in ^{13}CO, Cr(acac)$_3$ added) δ 178.5 (s, Ph*C*(O)N), 166.4 (s, N*C*(O)C(CF_3)), 133.6, 131.5, 130.5, 128.3 (C_6H_5), 85.2 (d, J = 5.9 Hz, C_5H_5), 82.8 (d, J = 5.9 Hz, C_5H_5); MS, m/e 645 [M]$^+$, 626 [M − F]$^+$, 498 [M − PhCONCO]$^+$.

p-Toluenesulfonyl azide and 1 (0.054 g) gave crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)N$SO_2C_6H_4$Me] (0.060 g, 84%), **2c**, mp >200 °C. Anal. Calcd for $C_{22}H_{17}F_6NO_3Rh_2S$: C, 38.0; H, 2.5; F, 16.4; N, 2.0; S, 4.6. Found: C, 38.3; H, 2.8; F, 16.2; N, 2.1; S, 4.3. Spectroscopic data: IR (CH_2Cl_2) 1710 vs (br), 1595 m, 1388 s, 1340 m cm^{-1}. ^{1}H NMR (acetone-d_6) δ 7.91 and 7.41 (m with AA′BB′ pattern, 4 H, J = 9 Hz, C_6H_4), 5.88 (s, 5 H, C_5H_5), 5.58 (s, 5 H, C_5H_5), 2.43 (s, 3 H, Me); ^{19}F NMR (acetone-d_6) quartets (J = 12 Hz) of equal intensity at δ −47.3 and −56.2;MS, m/e 695 [M]$^+$, 676 [M − F]$^+$, 498 [M − $MeC_6H_4SO_2NCO$]$^+$.

1 (0.087 g), plus a mixture of the azidomaleate *cis*-(MeO_2C)-CH=C(CO_2Me)N_3 and the azidofumarate *trans*-(MeO_2C)CH=C(CO_2Me)N_3 gave crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C-($CF_3$)C(O)NC($CO_2Me$)=CH($CO_2Me$)] (0.046 g, 41%), **2d**, mp >200 °C. This complex is derived from the maleate; no product was formed from the fumarate. Anal. Calcd for $C_{21}H_{17}F_6NO_5Rh_2$: C, 36.9; H, 2.5; F, 16.7; N, 2.1. Found: C, 37.1; H, 2.6; F, 16.4; N, 2.1. Spectroscopic data: IR (CH_2Cl_2) 1724 s, 1706 sh, 1633 m, 1390 s, 1345 m (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.65 (d, 5 H, J = 0.6 Hz, C_5H_5), 5.63 (s, 1 H, C=CH), 5.29 (s, 5 H, C_5H_5), 3.80 (s, 3 H, Me), 3.70 (s, 3 H, Me); ^{19}F NMR ($CDCl_3$) quartets (J = 12 Hz) of equal intensity at δ −49.0 and −57.3; MS, m/e 683 [M]$^+$, 652 [M − OMe]$^+$, 624 [M − CO_2Me]$^+$, 498 [M − (MeO_2C)CH=C(CO_2Me)NCO]$^+$.

D. Reactions of 1 with Carbodiimides, RNCNR (R = *i*-Pr and Cy). 1 (0.130 g) and excess *N,N*′-dicyclohexylcarbodiimide (0.159 g, mole ratio 1:4) in dichloromethane (30 mL) were kept at 25 °C for 2 h. The color of the solution changed from green to crimson. TLC with 2:3 mixture of CH_2Cl_2/X4 separated two major products. The first was isolated as a bright yellow oil, identified spectroscopically as (η-C_5H_5)$_2$$Rh_2$(CO)(CNCy)-($CF_3C_2CF_3$) (0.040 g, 32%). The second band yielded deep crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)NCy] (0.079 g, 65%), **2e**, mp 246 °C dec. Anal. Calcd for $C_{21}H_{21}F_6NORh_2$: C, 40.5; H, 3.4; N, 2.3; F, 18.3. Found: C, 40.5; H, 3.7; N, 2.3; F, 18.2. Spectroscopic data: IR (CH_2Cl_2) 1674 vs, 1379 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.58 (d, 5 H, J = 0.9 Hz, C_5H_5), 5.33 (s, 5 H, C_5H_5), 2.91 (m, 1 H, CH), 1.38 (m, 10 H, C_6H_{10}) ^{19}F NMR ($CDCl_3$) quartets (J = 13 Hz) at δ −48.5 and −57.3; *MS, m/e* 623 [M]$^+$, 498 [M − CyNCO]$^+$.

In similar manner, 1 was treated with *N,N*′-diisopropylcarbodiimide. TLC separated (η-C_5H_5)$_2$$Rh_2$(CO)(CN-*i*-Pr)-($CF_3C_2CF_3$) (0.031 g, 32%), which was identified spectroscopically, from (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)N-*i*-Pr], which was obtained as crimson crystals (0.050 g, 53%), **2f**, mp 265 °C dec. Anal. Calcd for $C_{18}H_{17}F_6NORh_2$: C, 37.0; H, 3.1; N, 2.4; F, 19.6. Found: C, 36.6; H, 2.8; N, 2.2; F, 19.3. Spectroscopic data: IR (CH_2Cl_2) 1690 sh, 1675 s, 1492 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.57 (s, 5 H, C_5H_5), 5.35 (s, 5 H, C_5H_5), 3.34 (sept, 1 H, J = 7 Hz, CH), 1.14 (d, 3 H, J = 7 Hz, CH_3), 1.01 (d, 3 H, J = 7 Hz, CH_3); ^{19}F NMR ($CDCl_3$) quartets (J = 12 Hz) of equal intensity at δ −48.5 and −57.2; MS, m/e 583 [M]$^+$, 498 [M − *i*-PrNCO]$^+$.

E. Reactions of 1 with Organic Isocyanates, RNCO (R = Me, *t*-Bu, and *p*-MeC_6H_4). MeNCO. 1 (0.080 g) and a slight excess of methyl isocyanate in toluene (20 mL) were kept at 80 °C for 3 days. The color of the solution changed slowly from green to crimson. TLC with a 4:2:1 mixture of CH_2Cl_2/X4/ether separated (η-C_5H_5)$_2$$Rh_2(CO)_2$($CF_3C_2CF_3$) (0.009 g, 11%) and ($\eta$-$C_5H_5$)$_3$$Rh_3$(CO)($CF_3C_2CF_3$) (0.005 g, 7%) from a major crimson band. The latter yielded crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)NMe] (0.065 g, 77%), **2g**, mp 230 °C. Anal. Calcd for $C_{16}H_{13}F_6NORh_2$: C, 34.6; H, 2.4; F, 20.5; N, 2.5. Found: C, 33.9; H, 2.1; F, 20.5; N, 2.5. Spectroscopic data: IR (CH_2Cl_2) 1690 vs, 1680 vs, 1665 sh, 1392 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.55 (d, 5 H, J = 0.4 Hz, C_5H_5), 5.29 (s, 5 H, C_5H_5), 2.99 (s, 3 H, Me); ^{19}F NMR ($CDCl_3$) quartets (J = 13 Hz) of equal intensity at δ −48.6 and −57.5; MS, m/e 555 [M]$^+$, 498 [M-MeNCO]$^+$.

Table I. Summary of Crystal Structure Data for Complex 2

(a) Crystal Data	
formula	$C_{21}H_{15}F_6NORh_2$
mol wt	617.2
cryst system:	tetragonal, space group $I4_1/a$ (C_{4h}^6, No. 88)
a = 24.49 (1) Å	D_{calcd} = 1.91 g cm^{-3}
c = 14.298 (4) Å	D_{measd} = 1.91 (1) g cm^{-3}
U = 8577 (6) Å^3	$F(000)$ = 4800
Z = 16	μ(Mo Kα) = 28.4 cm^{-1}
(b) Data Collection	
radiation:	graphite-monochromated Mo Kα (λ = 0.71069 Å)
temp:	295 K
scan mode:	$2\theta/\theta$
2θ max:	50°
ω scan angle (min):	0.8°
scan rate:	variable
total data:	3555
data $I > 3\sigma(I)$:	2559
final R and R_w:	0.046 and 0.058
weight w:	$(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$

Reactions with ***t*-BuNCO** (75 °C, 4 days) and ***p*-MeC_6H_4NCO** (70 °C, 2 days) were done in similar manner.

tert-Butyl isocyanate gave unchanged (η-C_5H_5)$_2$$Rh_2$(CO)-($CF_3C_2CF_3$) (52%), ($\eta$-$C_5H_5$)$_2$$Rh_2(CO)_2$($CF_3C_2CF_3$) (20%), ($\eta$-$C_5H_5$)$_3$$Rh_3$(CO)($CF_3C_2CF_3$), (7%), and crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)N-*t*-Bu] (8%), **2h**, mp 263 °C. Anal. Calcd for $C_{19}H_{19}F_6NORh_2$: C, 38.2; H, 3.2; N, 2.3; F, 19.1. Found: C, 37.8; H, 3.4; N, 2.2; F, 18.9. Spectroscopic data: IR (CH_2Cl_2) 1700 vs, 1408 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.59 (d, 5 H, J = 0.9 Hz, C_5H_5), 5.32 (s, 5 H, C_5H_5), 1.23 (s, 9 H, *t*-Bu); ^{19}F NMR ($CDCl_3$) quartets (J = 12 Hz) of equal intensity at δ −49.9 and −56.8; MS, m/e 597 [M]$^+$, 498 [M-*t*-BuNCO]$^+$.

p-Tolyl isocyanate gave unchanged (η-C_5H_5)$_2$$Rh_2$(CO)-($CF_3C_2CF_3$) (44%), ($\eta$-$C_5H_5$)$_2$$Rh_2(CO)_2$($CF_3C_2CF_3$) (27%), and red crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C($CF_3$)C(O)N$C_6H_4$Me] (25%), **2i**, mp >200 °C. Anal. Calcd for $C_{22}H_{17}F_6NORh_2$: C, 41.9; H, 2.7; N, 2.2; F, 18.1. Found: C, 42.1; H, 3.1; N, 2.0; F, 17.9. Spectroscopic data: IR (CH_2Cl_2) 1680 vs, 1392 s cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.97 (s, 4 H, C_6H_4), 5.90 (d, 5 H, J = 0.9 Hz, C_5H_5), 5.17 (s, 5 H, C_5H_5); ^{19}F NMR (acetone-d_6) quartets (J = 12 Hz) of equal intensity at δ −47.0 and −56.1; MS, m/e 631 [M]$^+$, 498 [M − MeC_6H_4NCO]$^+$.

F. Treatment of (η-C_5H_5)$_2$$Rh_2$(CO)(CN-*t*-Bu)($CF_3C_2CF_3$) with Me_3NO. A solution of (η-C_5H_5)$_2$$Rh_2$(CO)(CN-*t*-Bu)-($CF_3C_2CF_3$) (0.052 g) in dry acetone (30 mL) was stirred under N_2 for several minutes. After the addition of anhydrous trimethylamine *N*-oxide (0.013 g, mole ratio 1:1.9), the mixture was refluxed for 2 h to give a deep red solution. The evolution of CO_2 was indicated by bubbling the N_2 outflow through a trap containing saturated aqueous barium hydroxide solution. The reaction mixture was cooled and the solvent removed with a stream of N_2. TLC with CH_2Cl_2 as eluent separated unchanged (η-C_5H_5)$_2$$Rh_2$(CO)(CN-*t*-Bu)($CF_3C_2CF_3$) (0.036 g, 69%) from a second band which gave crimson crystals of (η-C_5H_5)$_2$$Rh_2$[C($CF_3$)C-($CF_3$)C(O)N-*t*-Bu], **2h** (0.012 g, 24%). The compound was identified from its melting point and spectroscopic properties.

G. Crystallography. Well-formed single crystals of **2a** were grown from hexane/dichloromethane. A crystal of dimensions 0.40 × 0.22 × 0.08 mm was mounted on a Syntex P2$_1$ four-circle diffractometer. Data are summarized in Table I.

The "observed" data were used in the block diagonal (four blocks) least-squares refinement after analytical absorption correction[11] and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were included constrained at idealized values.

Table II. Non-Hydrogen Atom Coordinates

atom	*x*	*y*	*z*
Rh(1)	0.40221 (2)	0.51342 (3)	0.21649 (4)
Rh(2)	0.47579 (2)	0.44862 (3)	0.28843 (4)
C(11)	0.3366 (4)	0.5546 (4)	0.1337 (7)
C(12)	0.3142 (3)	0.5138 (4)	0.1828 (6)
C(13)	0.3378 (4)	0.4618 (4)	0.1551 (8)
C(14)	0.3780 (5)	0.4747 (6)	0.0874 (7)
C(15)	0.3796 (5)	0.5329 (6)	0.0753 (6)
C(21)	0.4607 (4)	0.3601 (4)	0.2655 (9)
C(22)	0.4731 (5)	0.3672 (5)	0.3558 (8)
C(23)	0.5288 (5)	0.3932 (4)	0.3588 (9)
C(24)	0.5464 (4)	0.3988 (5)	0.2681 (10)
C(25)	0.5049 (7)	0.3800 (6)	0.2095 (8)
C(31)	0.3913 (3)	0.4747 (3)	0.4362 (5)
C(32)	0.4147 (4)	0.4712 (5)	0.5245 (6)
C(33)	0.3837 (5)	0.4510 (5)	0.5984 (6)
C(34)	0.3307 (4)	0.4341 (3)	0.5858 (6)
C(35)	0.3092 (3)	0.4365 (3)	0.4997 (7)
C(36)	0.3379 (3)	0.4556 (3)	0.4235 (6)
C(1)	0.4890 (3)	0.5230 (4)	0.2317 (5)
C(2)	0.4608 (3)	0.5682 (3)	0.2757 (5)
C(3)	0.4356 (3)	0.5535 (3)	0.3664 (5)
O(3)	0.4230 (2)	0.5828 (2)	0.4303 (4)
N(3)	0.4228 (2)	0.4974 (3)	0.3614 (4)
C(16)	0.5289 (3)	0.5327 (5)	0.1523 (6)
F(11)	0.5078 (3)	0.5522 (3)	0.0745 (4)
F(12)	0.5665 (3)	0.5678 (4)	0.1752 (5)
F(13)	0.5539 (3)	0.4873 (4)	0.1269 (5)
C(26)	0.4632 (5)	0.6278 (4)	0.2525 (7)
F(21)	0.4694 (4)	0.6388 (3)	0.1644 (4)
F(22)	0.5028 (4)	0.6529 (3)	0.3010 (6)
F(23)	0.4196 (3)	0.6547 (2)	0.2762 (5)

R and R' (on $|F|$) were 0.046 and 0.058. Neutral complex scattering factors were used; computation used the X-RAY 76 program system[12] implemented on a Perkin-Elmer 3240 computer. Final positional parameters are presented in Table II. Material deposited comprises structure factor amplitudes, thermal parameters, and least-squares planes.

Results

Crimson-red crystalline products of formula $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(O)NR]$ (**2**) can be prepared from $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (**1**) by four different methods.

(a) The addition of organic azides RN_3 (R = Ph, PhCO, and $p\text{-}MeOC_6H_4SO_2$) to solutions of **1** in diethyl ether gave **2** in yields of 83–95%. These reactions occur exceedingly quickly at 0 °C; there was an immediate color change from green to red when the reactants were mixed, and workup of the reaction solution could proceed without any delay. When a mixture of the azidomaleate *cis*-$(MeO_2C)CH{=}C(CO_2Me)N_3$ and the azidofumarate *trans*-$(MeO_2C)CH{=}C(CO_2Me)N_3$ was added to **1**, reaction occurred only with the maleate. Consequently, a high yield of the product was obtained only if a large excess of ligand was added.

(b) Complex **2** can also be obtained from the direct reaction between **1** and organic isocyanates, RNCO (R = Me, *t*-Bu, and $p\text{-}MeC_6H_4$). These reactions require more forcing conditions (70–80 °C, 2–4 days), and the yields of **2** were markedly dependent on the nature of R. With MeNCO, the yield of **2** was almost 80% after 3 days; in contrast, less than 10% yield of **2** was obtained from *t*-BuNCO after 4 days. Other products formed in these reactions were the dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and the trinuclear complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$. These compounds are commonly formed in reactions where **1** is heated.

(c) The reactions of **1** with carbodiimides, RNCNR (R = *i*-Pr and Cy), occurred readily in CH_2Cl_2 at room temperature, and two major products were separated. These were identified as **2** and $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)$ (**3**). The formation of these particular compounds indicates that the carbodiimide has split into [RN] and [CNR] fragments during the course of the reaction. The yield of **2** was approximately twice that of the isocyanide adduct **3** when the reactions were done with an excess of the ligand; for example, the yields were 65% and 32%, respectively, when R = *i*-Pr.

(d) A final procedure used to form **2** (R = *t*-Bu) involves the treatment of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$[2] with trimethylamine *N*-oxide. This reaction was achieved in refluxing acetone, and the yield of **2** was 24% after 2 h; about 70% of the starting material was recovered unchanged. Related reactions occur with other isocyanide adducts $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)$, but these systems are complicated by interconversion reactions involving the initial isocyanide complexes. A detailed report on these isocyanide complexes and their solution behavior will be published subsequently.

Spectroscopic data was obtained on all of the complexes **2** (R = Me, *i*-Pr, *t*-Bu, Cy, Ph, $p\text{-}MeC_6H_4$, PhCO, $p\text{-}MeC_6H_4SO_2$, and $(MeO_2C)CH{=}C(CO_2Me)$). The mass spectra showed a prominent molecular ion and then a fragment corresponding to the loss of RNCO from the parent. In the IR spectra, a band near 1700 cm^{-1} (e.g., at 1674 cm^{-1} (R = Cy) and 1700 (R = Ph)) was assigned to a ketonic carbonyl absorption. The ^1H NMR spectra showed two C_5H_5 environments. Two CF_3 chemical shifts were observed in the ^{19}F NMR spectra; these were each well defined quartets with $J_{F,F} \approx 12$ Hz, and this is consistent with a mutually cis arrangement of the two CF_3 groups. One of the CF_3 resonances was at much higher field than the other (e.g., at −46.8 and −57.5 ppm (R = Me)). This phenomenon has been observed in other systems[13-15] where one of the $C{-}CF_3$ units is adjacent to a ketonic carbonyl. ^{13}C NMR spectra were obtained for the complex **2** (R = PhCO). The natural abundance spectrum showed only peaks due to the C_6H_5 and C_5H_5 carbon atoms in the usual regions. When the complex **2** was obtained from a ^{13}CO-enriched sample of **1**, an additional peak at δ 166.4 was observed. This is assigned to the ketonic CO in the RNCO part of the ligand. If $Cr(acac)_3$ was added as a relaxation reagent to a solution of the ^{13}CO-enriched sample, a further peak of low intensity was detected at δ 178.5 and is assigned to the benzoyl CO. The combined spectroscopic results are consistent with the existence of a bridging group of the type $-C(CF_3){=}C(CF_3)C({=}O)N(R)-$ within the compounds **2**. However, doubt remains about the precise mode of attachment of this new ligand to the Rh–Rh bond and consequently the crystal and molecular structures were determined from X-ray diffraction results.

Discussion

Molecular Structure of $(\eta\text{-}C_5H_5)_2Rh_2[C(CF_3)C(CF_3)C(O)NPh]$. The molecular structure is shown in Figure 1, which also specifies the atom labeling scheme. Intramolecular distances and angles are indicated in Tables III (rhodium atom geometries) and IV (other nonhydrogen atom geometries). The mode of attachment of the bridging unit to the metal atoms is represented in Figure 2 — the

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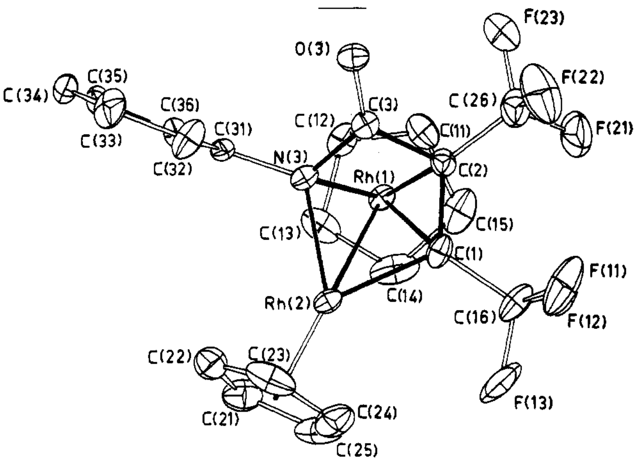

Figure 1. A projection of the molecule down the line from Rh(1) to the centroid of its associated cyclopentadienyl ring. The 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with atom labeling.

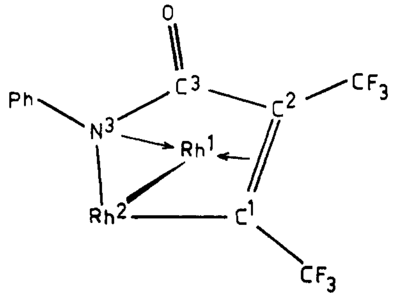

Figure 2. Representation of the coordination of the bridging ligand in the complex.

bonding picture is based on the coordination geometry and the discussion of bond parameters presented below.

There is a difference in the formal oxidation states of the two metal atoms within this arrangement. We represent Rh(1) as rhodium(I) (d^8) and Rh(2) as rhodium(III) (d^6). To satisfy the EAN formalism for each metal atom, it is necessary to represent the metal–metal interaction as a dative bond of the type Rh(1)→Rh(2). A similar representation is applied to the binuclear metalladiene complexes $(\eta\text{-}C_5H_5)_2Rh_2(C_4R_4)$, M = Co or Rh. The observed Rh–Rh distance of 2.612 (1) Å is at the lower limit of the range found for some related compounds with Rh^{II}–Rh^{II}[15-17] Rh^{III}–Rh^{I}[18,19] single bonds.

The bridging group can be viewed as a substituted acrylamide; there are trifluoromethyl groups on carbon atoms C(1) and C(2) and a phenyl ring is attached to N(3). This ligand is attached to Rh(2) by σ-bonds from C(1) and N(3) and to Rh(1) by a π-bond from C(1)=C(2) plus a dative bond from N(3). [Preliminary structural data on this complex was reported earlier.[4] We draw attention to the fact that the symbols Rh(1) and Rh(2) should be interchanged in the *caption* to Figure 1 in the preliminary communication]. The geometry around each rhodium atom is completed by a cyclopentadienyl group.

The Rh(2)–N(3) distance is 0.12 Å shorter than that for Rh(1)–N(3); similarly, the Rh(2)–C(1) σ-bonding distance

Table III. Rhodium Atom Geometries[a]

	Rh(1)				
atoms	*r*	C(10)	C(1)	C(2)	N(3)
Rh(2)	2.612 (1)	135.83 (-)	49.0 (2)	76.3 (2)	49.7 (2)
C(10)	1.830 (-)		141.3 (-)	143.3 (-)	145.1 (-)
C(11)	2.236 (10)	32.3 (-)	135.7 (3)	114.1 (3)	139.0 (3)
C(12)	2.209 (8)	32.4 (-)	170.7 (3)	137.6 (3)	115.9 (3)
C(13)	2.205 (10)	33.7 (-)	144.2 (3)	175.9 (3)	116.3 (3)
C(14)	2.159 (11)	34.1 (-)	113.9 (4)	143.0 (4)	143.3 (4)
C(15)	2.148 (10)	34.5 (-)	109.0 (4)	114.0 (4)	177.1 (5)
C(1)	2.148 (8)	141.3 (-)		39.5 (3)	72.1 (3)
C(2)	2.138 (8)	143.3 (-)	39.5 (3)		65.1 (3)
N(3)	2.169 (6)	145.1 (-)	72.1 (3)	65.1 (3)	

	Rh(2)			
atoms	*r*, Å	C(20)	C(1)	N(3)
Rh(1)	2.612 (1)	145.77 (-)	53.4 (2)	53.8 (2)
C(20)	1.810 (-)		142.3 (-)	139.6 (-)
C(21)	2.225 (11)	32.5 (-)	147.8 (4)	122.6 (3)
C(22)	2.216 (11)	33.1 (-)	172.3 (4)	106.5 (4)
C(23)	2.130 (12)	34.2 (-)	131.9 (4)	121.1 (4)
C(24)	2.136 (11)	34.5 (-)	109.4 (4)	156.2 (4)
C(25)	2.146 (14)	33.1 (-)	116.3 (4)	159.1 (4)
C(1)	2.020 (9)	142.3 (-)		77.3 (3)
N(3)	2.049 (6)	139.6 (-)	77.3 (3)	

Also Rh(1)–C(1)–Rh(2) = 77.6 (3)° and Rh(1)–N(3)–Rh(2) = 76.5 (2)°

[a] Selected distances and angles are given for each rhodium atom. Entries in the first column in each case are the rhodium–other atom distances (Å); other entries are the angles (deg) subtended by the relevant atoms at the head of each row and column. C(10) and C(20) are the centroids of the two Cp rings.

Table IV. Other Non-Hydrogen Atom Geometry

Distances (Å)

C(1)–C(16)	1.52 (1)	C(16)–F(11)	1.31 (1)
C(1)–C(2)	1.45 (1)	C(16)–F(12)	1.30 (1)
C(2)–C(3)	1.48 (1)	C(16)–F(13)	1.32 (1)
C(2)–C(26)	1.50 (1)	C(26)–F(21)	1.30 (1)
C(3)–O(3)	1.20 (1)	C(26)–F(22)	1.34 (1)
C(3)–N(3)	1.41 (1)	C(26)–F(23)	1.30 (1)
N(3)–C(31)	1.43 (1)		

Angles (deg)

C(1)–C(16)–F(11)	115.9 (7)	C(2)–C(1)–Rh(2)	116.0 (5)
C(1)–C(16)–F(12)	111.9 (8)	C(1)–C(2)–C(3)	113.1 (7)
C(1)–C(16)–F(13)	111.8 (9)	C(1)–C(2)–C(26)	129.0 (8)
F(11)–C(16)–F(12)	104.6 (9)	C(1)–C(2)–Rh(1)	70.6 (4)
F(11)–C(16)–F(13)	104.7 (8)	C(3)–C(2)–C(26)	116.6 (7)
F(12)–C(16)–F(13)	107.2 (8)	C(3)–C(2)–Rh(1)	85.1 (5)
C(2)–C(26)–F(21)	115.0 (8)	C(26)–C(2)–Rh(1)	123.4 (6)
C(2)–C(26)–F(22)	111.2 (8)	C(2)–C(3)–O(3)	128.9 (7)
C(2)–C(26)–F(23)	113.7 (8)	C(2)–C(3)–N(3)	106.5 (6)
F(21)–C(26)–F(22)	108.8 (9)	O(3)–C(3)–N(3)	124.2 (7)
F(21)–C(26)–F(23)	104.1 (9)	C(3)–N(3)–C(31)	117.4 (6)
F(22)–C(26)–F(23)	103.0 (8)	C(3)–N(3)–Rh(1)	85.6 (4)
C(16)–C(1)–C(2)	120.7 (8)	C(3)–N(3)–Rh(2)	116.9 (5)
C(16)–C(1)–Rh(1)	125.4 (6)	C(31)–N(3)–Rh(1)	131.2 (5)
C(16)–C(1)–Rh(2)	123.1 (6)	C(31)–N(3)–Rh(2)	119.7 (5)
C(2)–C(1)–Rh(1)	69.9 (4)		

Also: Cp and Phenyl Geometries: distances are given in order from C(*n*1) around each ring and angles are given at each atom in order

Ring 1. Distances (Å): 1.34 (1), 1.45 (1), 1.42 (2), 1.44 (2), 1.45 (2)
Angles (deg): 109.1 (9), 110.3 (8), 105.6 (9), 108.7 (10), 106.0 (9)

Ring 2. Distances (Å): 1.34 (2), 1.51 (2), 1.37 (2), 1.40 (2), 1.43 (2)
Angles (deg): 108.9 (10), 106.7 (10), 107.4 (11), 107.8 (11), 109.1 (10)

Ring 3. Distances (Å): 1.39 (1), 1.39 (1), 1.38 (2), 1.34 (1), 1.38 (1), 1.40 (1)
Angles (deg): 118.8 (7), 119.2 (8), 121.5 (8), 118.4 (8), 122.9 (8), 119.1 (7)
N(3)–C(31)–C(32,36): 118.7 (7), 122.4 (6)

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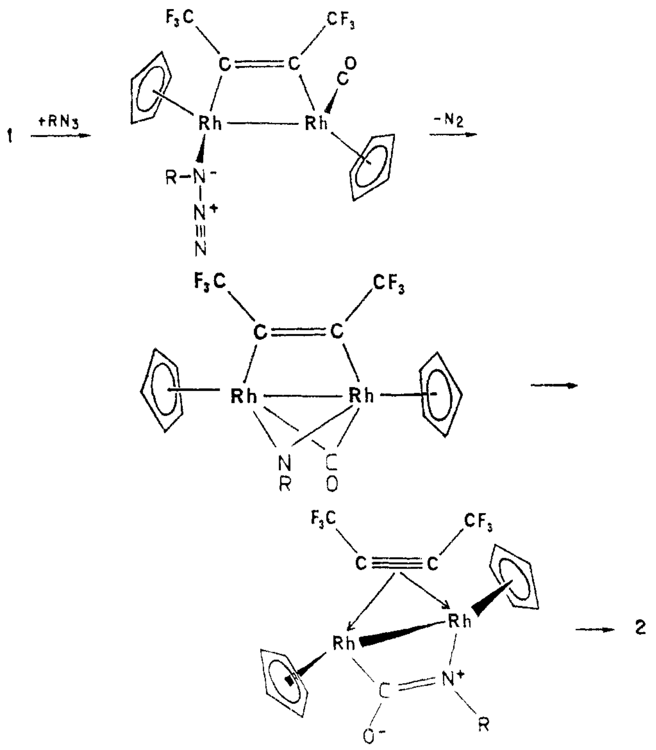
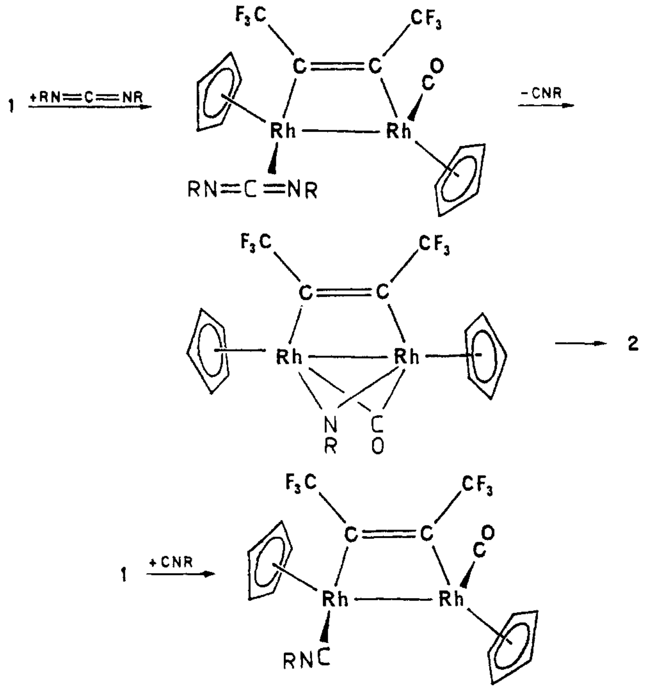
Scheme I



is 0.12 Å shorter than the average of the Rh(1)–C(1) and Rh(1)–C(2) distances. Within the ligand–Rh(2) chelate ring, the bond distances are consistent with relatively low C–C and C–N bond orders. Although there are some distortions from ideal geometry about the nitrogen and the three carbon atoms within this ring, the ring itself is substantially planar. There is a good least-squares plane defined by the carbon atoms C(16), C(1), C(2), and C(26), (the deviation of the individual atoms in this plane are 0.004, -0.009, 0.009, and -0.004 Å), and the atoms Rh(2), N(3), C(31) and C(3) deviate from this by only 0.084, -0.070, -0.007, and 0.361 Å, respectively. Thus, the ring conformation is substantially that of a normal five-membered envelope with C(3) the deviant atom to the opposite side of Rh(1) (deviation -1.763 Å) and with O(3) deviating further (0.806 Å). Dihedral angles from the C(16), C(1), C(2), C(26) plane to the cyclopentadienyl rings 1 and 2 are 5.9 and 76.9°, respectively, while that to the phenyl ring 3 is 86.8°.

There has been recent interest in distortions within cyclopentadienyl–metal interactions.[20] For the present complex, the bond distances in Table III give some hint of distortions from fivefold symmetry. For the ring attached to Rh(1), the range of C–C and Rh–C distances is 1.34 (1)–1.45 (1) and 2.148 (10)–2.236 (10) Å, respectively; the corresponding ranges for the C_5H_5–Rh(2) system are 1.34 (2)–1.51 (2) and 2.130 (12)–2.225 (11) Å. Since the rings are essentially planar (Table S3), the best interpretation of the Rh–C bond distance data is in terms of a slight tilting of each C_5H_5 ring plane so that it is not perpendicular to the vector from rhodium to the center of the ring. Presumably this arises from differences in the electronic influences of the donor atoms on the opposite face of the model. It would be unwise to predicate any conclusions concerning variations *within* the cyclopentadienyl ring C–C distances in the present data without a further study at lower temperature.

Scheme II



Formation of the Bridging Ligand. In two of the preparative procedures studied, it is suggested that nitrenes are formed transiently. These are the reactions of 1 with organic azides and with carbodiimides.

The generation of nitrenes from organic azides has been exploited in a number of organometallic syntheses.[21-26] In some of these reactions, free or coordinated isocyanates are formed by interaction of the azide (or nitrene) with a carbonyl ligand; examples are given in eq 1 and 2. The

$$\mathrm{Ir(CO)ClL_2 + RN_3 \rightarrow Ir(N_2)ClL_2 + RNCO} \qquad (1)$$

$$\mathrm{R = Ph}$$

$$\mathrm{Ru(CO)_3(PPh_3)_2 + RN_3 \rightarrow Ru(CO)_2(PPh_3)_2(RNCO) + N_2} \qquad (2)$$

$$\mathrm{R} = p\text{-}\mathrm{MeC_6H_4}$$

likely sequence of steps in the formation of 2 from 1 and RN_3 is shown in Scheme I. Intermediates incorporating coordinated RN_3, μ-NR, and μ-RNCO are suggested. However, the reaction is exceedingly rapid, even at 0 °C, and no evidence is obtained for these proposed intermediates.

In the reactions with carbodiimides, it seems likely that coordination of the intact RNCNR unit is followed by ligand fragmentation to give RN and CNR. This type of behavior has been established previously in the reaction between $Fe(CO)_5$ and unsymmetrical carbodiimides.[27] The pathway shown in Scheme II is probably followed in

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the reaction with the dirhodium complex **1**. Again, the key intermediate has not been detected. Some support for this proposed pathway comes from the observed product distribution. When an excess of RNCNR is used, complex **2** is the major product (— the ratio of **2**:**3** is approximately 2:1). However, if an excess of **1** is present in the reaction mixture, compounds **2** and the CNR adduct **3** are obtained in approximately equal amounts. This indicates that both fragments of the RN–CNR molecules are coordinated to an equal extent provided there is sufficient **1** in the reaction system. If there is excess ligand, however, there is competition between the free isocyanide and carbodiimide ligands for the remaining molecules of **1**.

The idea that there is initial interaction between the coordinated groups RN and CO to produce RNCO in these reactions (Schemes I and II) prompted an investigation of reactions between **1** and RNCO. There are relatively few examples in the literature of the formation of complexes containing an intact RNCO ligand. Some mononuclear compounds of Ru,[24] Rh,[28,29] Ir,[23] and Ni[30,31] are among the known compounds of this type. In some reactions between RNCO and metal carbonyl or organometallic species, other types of organic ligands are generated. The examples in eq 3–6 illustrate some of these reactions.

$$Fe(CO)_5 + ArNCO \rightarrow Fe(CO)_4(CNAr) + CO_2 \qquad (3)^{32}$$

$$PtL_4 + RNCO \rightarrow L_2\overline{Pt—N(R)C(O)N}(R) \qquad (4)^{33}$$

$$L = PPh_3,\ R = p\text{-}MeC_6H_4SO_2$$

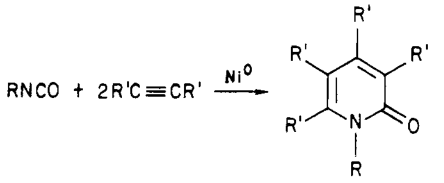
$$LNi + 2RNCO \rightarrow L\overline{NiN(R)C(O)N(R)C}(O) \qquad (5)^{34}$$

$$L = TMEDA,\ R = Ph$$

$$Ru_3(CO)_{12} + RNCO \rightarrow Ru_3(CO)_{10}(NR) + 2CO \qquad (6)^{35}$$

Although **1** does react directly with RNCO compounds to form **2**, the reactions are rather sluggish relative to those that involve nitrenes. Indeed the comparison between the formation of **2** (R = Ph) in 85% yield from **1** and PhN_3 at 0 °C in seconds, and formation of the closely related complex **2** (R = p-MeC_6H_4) in 27% yield from **1** and RNCO at 120 °C in 24 h could hardly be more dramatic. This may indicate that the interaction between NR, CO, and $CF_3C_2CF_3$ is a concerted [1 + 1 + 2] cycloaddition rather than a stepwise reaction. [However (as pointed out by a reviewer), the {**1** + NR} and {**1** + RNCO} systems differ in that the latter incorporates an additional CO. If the carbonyl ligand in **1** is retained after coordination of the RNCO, it may block formation of the $C(CF_3)$–C(O)NR bond; alternatively, the carbonyl ligand may inhibit the initial coordination of the RNCO. Either way, the harsh conditions required could reflect the need to dissociate this carbonyl ligand.]

There are some other examples in the literature of metal assisted reactions between RNCO and R′C≡CR′. Perhaps the best documented[36–38] are those involving Ni^0 compounds leading to 2-pyridones (eq 7). These reactions proceed through intermediates of the types **4** and **5**. With activated alkynes such as $MeO_2CC{\equiv}CCO_2Me$, formation of the pyridones is achieved at room temperature, but more forcing conditions (80 °C) are required with alkynes such as PhC≡CPh.



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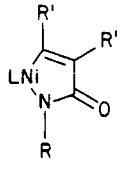

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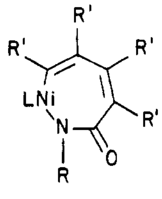

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A totally different approach to the synthesis of **2** involves the reaction between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CN\text{-}t\text{-}Bu)(CF_3C_2CF_3)$ (**3**) and Me_3NO. In attempting this reaction, we were uncertain whether to expect oxidation of the coordinated CO or CNR ligand (see eq 8 and 9). The first reaction would be analogous to that we have investigated previously[2] between $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and Me_3NO; this reaction gives **1**. We are not aware of any examples of the oxidation of bound CNR by Me_3NO, but the similarity between the ligands CO and CNR suggests that there should be no electronic barrier to the reaction. In the event, it seems that both ligands are oxidized. Thus, there is evolution of CO_2 and formation of RNCO which is retained within the complex.

$$\mathbf{3} + Me_3NO \rightarrow (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CN\text{-}t\text{-}Bu)(CF_3C_2CF_3) + CO_2 \qquad (8)$$

$$\mathbf{3} + Me_3NO \rightarrow (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CF_3C_2CF_3) + RNCO \qquad (9)$$

Summary and Conclusion

The complex **1** proves to be a very useful "trap" for nitrenes that are generated by the metal-assisted decomposition of organic azides or carbodiimides. A concerted [1 + 1 + 2] cycloaddition involving NR, CO, and $CF_3C_2CF_3$ occurs on the Rh–Rh bond and generates an acrylamide group $-C(CF_3){=}C(CF_3)C({=}O)N(R)-$ which is strongly retained within the complex. Although the same ligand can be made on the Rh–Rh bond of **1** by the direct addition of RNCO and by the oxidation of bound CNR in the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)$, these systems require more forcing conditions and give lower yields of the products.

Crystal structure analysis has revealed that the ligand is bound to the Rh–Rh bond in **2** via both "alkene" carbons and the amine nitrogen. This mode of attachment gives each metal a formal 18-electron count and confers high thermal and chemical stability on the complex.

In many of the systems studied, new C–C and C–N bonds are being formed rapidly at room temperature on a Rh–Rh bond. The ease and specificity of formation of

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the acrylamide ligand in these systems is an excellent illustration of the potential usefulness of binuclear complexes in organic synthesis.

Acknowledgment. We gratefully acknowledge support of this work by grants (R.S.D., A.H.W.) from the Australian Research Grants Scheme.

Registry No. 1, 98395-25-6; **2a**, 90860-67-6; **2b**, 90883-06-0; **2c**, 90860-68-7; **2d**, 98395-26-7; **2e**, 90860-73-4; **2f**, 90860-72-3; **2g**, 90860-65-4; **2h**, 90860-66-5; **2i**, 90883-05-9; **3** (R = Cy), 98464-04-1; **3** (R = *i*-Pr), 98464-05-2; **3** (R = *t*-Bu), 71853-17-3; (η-C_5H_5)-$Rh_2(CO)_2(CF_3C_2CF_3)$, 57872-13-6; (η-C_5H_5)$_3$$Rh_3(CO)(CF_3C_2CF_3)$, 37343-45-6; *cis*-($MeO_2C$)CH=C($CO_2Me$)$N_3$, 36875-40-8; *trans*-($MeO_2C$)CH=C($CO_2Me$)$N_3$, 36875-41-9; phenyl azide, 622-37-7; benzoyl azide, 582-61-6; *p*-toluenesulfonyl azide, 941-55-9; *N*,*N*′-dicyclohexylcarbodiimide, 538-75-0; *N*,*N*′-diisopropylcarbodiimide, 693-13-0; methyl isocyanate, 624-83-9; *tert*-butyl isocyanate, 1609-86-5; *p*-tolyl isocyanate, 622-58-2.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters, hydrogen atom parameters, ring planes, and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

A Kinetic Study of the Generation of Terminal Phosphinidene Complexes from 7-Phosphanorbornadiene Complexes. X-ray Crystal Structure Analysis of the Dimers of Terminal Phosphinidene Complexes

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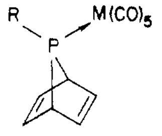
Received December 28, 1985

A kinetic study of the thermal decomposition of a 7-phenyl-7-phosphanorbornadiene P—W(CO)$_5$ complex in the presence of aniline, tolan, and cyclooctene has been performed at 105, 115, 117, and 125 °C. The kinetics of this decomposition are first order in the concentration of the phosphanorbornadiene complex and do not depend on the concentration and nature of the trapping reagent. These results give additional support to the intermediacy of a terminal phosphinidene complex, [PhP=W(CO)$_5$], in such a decomposition. The activation energy of the process is calculated to be 33 ± 1 kcal mol^{-1}. The thermolysis of the same 7-phosphanorbornadiene at 55 °C in the presence of CuCl as a catalyst gives a dimeric complex, [PhP=PPh][W(CO)$_5$]$_3$, in which both the phosphorus atoms and the P=P double bond are complexed by the three W(CO)$_5$ units as shown by X-ray crystal structure analysis.

Recently, we have studied the thermal reactions of 7-phosphanorbornadiene complexes 1 with a variety of organic and inorganic reagents including primary and secondary amines,[2] alcohols,[2] water,[2] alkenes,[3] conjugated dienes,[3] enamines,[4] alkynes,[5] etc. In each case, the products of the reactions were best explained by assuming the intermediacy of a terminal phosphinidene complex, 2, resulting from the collapse of the phosphorus bridge of the 7-phosphanorbornadiene skeleton. Since then, other authors have attempted to stabilize such terminal phosphinidene complexes but they have been unsuccessful as of yet.[6,7] Thus, the existence of terminal phosphinidene complexes so far relies only on a range of successful trapping reactions. In view of the theoretical importance of such species (they are the phosphorus analogues of carbene and nitrene complexes) and of their highly diversified suspected reactivity,[2-5] we thought that it would be interesting to provide additional evidence in favor of their (at least) transient existence. We thus decided to study the kinetics of the reactions of 7-phosphanorbornadiene complexes with a selection of efficient trapping reagents and to establish what were the products of the thermal decomposition of 7-phosphanorbornadienes when no trapping reagent was added to the reaction medium.



1

R—P=M(CO)$_5$

2

M = Cr, W

Results and Discussion

All our experiments were performed with the readily available tungsten complex 3. We selected three representative trapping reagents, aniline, tolan, and cyclooctene. In the first two cases, the reaction with 3 is quantitative and no by-product is formed according to ^{31}P NMR studies. In the third case, the reaction was normally run in the presence of CuCl as a catalyst around 55 °C. Thus, in order to get comparable data, it was first necessary to check whether or not the same reaction could be run without catalyst at higher temperature. Since we suspected that previous failures were due to the thermal instability of phosphiranes, we decided to repeat our attempts with the most stable phosphiranes at the lowest possible temperatures. In so doing, we found that it was

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0276-7333/85/2304-2134$01.50/0