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Retention of dinitrogen in the reactions of some diazoalkanes with a dirhodium complex. Crystal and molecular structures of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CRR'\}$, RR′ = MePh and $(\text{t-Bu})_2$

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Abstract

Upon treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**1**) with the diazo compounds N_2CRR' ($RR' = Ph_2$, MePh, Me(CF_3), Ph(CF_3)), the complexes $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CRR'\}$ (**2a**–**2d**) are formed. They do not lose nitrogen upon attempted thermolysis or photolysis. The crystal structure of the complex **2b** (RR′ = MePh) was determined by X-ray crystallography: orthorhombic, *Pbca*, $Z = 8$, $a = 25.28(1)$, $b = 19.84(1)$, $c = 9.031(7)$ Å. The molecular structure shows that there has been end-to-end condensation of the components $CF_3C_2CF_3$, CO and N_2CMePh to produce a single bridging ligand, $C(CF_3){=}C(CF_3)C({=}O)N\{N{=}C(Ph)Me\}$. It is attached to one Rh atom from a terminal alkene-carbon and a nitrogen lone pair; the same nitrogen atom is covalently bonded to the second Rh atom which is also π-bonded to the alkene function Spectroscopic results indicate that the other complexes have analogous structures. The reaction of **1** with $N_2C(\text{t-Bu})_2$ gives a related product $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\ CO\cdot N_2C(\text{t-Bu})_2\}$ (**5**), but crystal structure determination reveals a vastly different ligand arrangement The crystals are orthorhombic, *Pbca*, $Z = 8$, $a = 27.679(3)$, $b = 11.560(1)$, $c = 15.924(1)$ Å. This complex incorporates a cyclic ligand C–N–N–C(t-Bu)$_2$–O with the first ring carbon incorporated into an allylic group $C{-}C(CF_3){-}C(CF_3)$. The allylic side chain is σ–π attached to the Rh–Rh bond; a ring nitrogen also forms a dative bond with one Rh atom. A minor product $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{CF_3C_2CF_3\ CMePh\}$ (**3**) is also formed in the reaction with N_2CMePh, this undergoes decarbonylation during chromatography to give $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CMePh\}$ (**4**).

Introduction

Diazo compounds, N_2CRR', are commonly used as a source of carbenes in both organic [1] and organometallic chemistry [2]. The reactions with binuclear organometallic compounds usually lead to the formation of μ-alkylidene complexes. However, new C–C bonds are sometimes formed as a consequence of interactions involving the alkylidene and other substrates within the complex. The importance of coupling reactions between alkylidenes and coordinated alkenes or vinylidenes has been emphasized in numerous recent papers [3–7] due to the likely involvement of such reactions in the mechanism of carbon homologation in Fischer-Tropsch chemistry. However, few studies have demonstrated how the nature of the substituents on the alkylidene group can affect the course of such coupling reactions. Our previous investigations [8, 9] with the complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**1**) has shown clearly that the rate of the C–C bond forming reaction in eqn. (1) is markedly affected by the substituents.

$$\begin{aligned}&1 + N_2CHR \longrightarrow\\&\quad(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CHR)(\mu\text{-}CF_3C_2CF_3) \longrightarrow\\&\quad(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CHR\} \qquad (1)\end{aligned}$$

The final step in this reaction sequence is extremely rapid when $R = SiMe_3$ or $CH{=}CH_2$, but takes several days when $R = CO_2Et$ and does not occur (even in refluxing solvents) when $R = CF_3$. An even more dramatic effect was found [8] in the corresponding reaction between **1** and $N_2C(CO_2Et)_2$ where the coupling reaction involved formation of a new C–O (eqn. (2)) rather than a C–C (eqn. (1)) bond.

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$$\mathbf{1} + N_2C(CO_2Et)_2 \longrightarrow$$
$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(CO_2Et)_2\}(\mu\text{-}CF_3C_2CF_3) \longrightarrow$$
$$(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}C(CF_3)C(CF_3)OC(OEt)C(CO_2Et)\} \quad (2)$$

Some of our observed substituent effects were not readily explained, and we decided to extend our investigations to include a greater range of disubstituted diazo compounds. This has revealed several alternative reaction pathways which we describe and discuss in this paper. A surprising feature of many of these new reactions is that the diazo-nitrogens are retained in the products.

Experimental

General procedures

All reactions were carried out under an atmosphere of purified nitrogen in oven-dried Schlenk flasks [10]. The progress of the slower reactions was monitored by IR spectroscopy and/or analytical thin layer chromatography (Mackery-Nagel, Polygram SIL G/UV$_{254}$). Purification was generally achieved by preparative-scale thin layer chromatography which was carried out on 20 by 20 cm plates with a 1:1 silica gel G-HF$_{254}$ mixture (Type 60, Merck) as adsorbent. In some instances, better product separation was achieved using preparative radial chromatography which was carried out on a 'Chromatotron' model 7924T with Merck silica gel plus gypsum (60PF/UV$_{254}$ No. 7749) as adsorbent. All separations were achieved on deactivated plates, obtained by drying at room temperature only. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, Australia or Analytical Laboratories, Engelskirchen, Germany. Melting points were determined on a Buchi melting point apparatus using analytically pure samples and are uncorrected.

Instrumentation

Solution IR spectra (KBr windows) were obtained using a Digilab FTS-60 Fourier transform spectrometer. NMR spectra were measured on Bruker AC 200 or AM 300 spectrometers. The ^{1}H NMR spectra were measured at 200 or 300 MHz, ^{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$_4$Si for ^{1}H and ^{13}C and from CCl$_3$F for ^{19}F; in all cases, a positive chemical shift denotes a resonance downfield from the reference. In the ^{13}C spectra, Cr(acac)$_3$ was added to reduce T_1 relaxation times. Electron impact mass spectra were obtained by using a VG Micromass 70/70-F spectrometer operating at 70 eV and 200 °C inlet temperature.

Materials

Acetone was analytical grade reagent; hydrocarbons and dichloromethane were purified by standard procedures [11]. '×4' refers to petroleum fraction of boiling point range 30–60 °C. All solvents were stored in the dark over activated 4 Å molecular sieves and were purged with nitrogen prior to use. $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ was prepared as described in ref. 12. The following diazo compounds were prepared by literature procedures: N$_2$CPh$_2$ [13], N$_2$CMePh [14], N$_2$CMe(CF$_3$) [15], N$_2$CPh(CF$_3$) [16] and N$_2$C(t-Bu)$_2$ [17]. Most diazo reagents were not isolated as pure products but were used *in situ*. The amounts used in subsequent reactions were calculated on the basis of published yields with sufficient solution being added to provide a slight excess of the diazo compound; generally, the mole ratio of reactants was estimated to be *c.* 1.1:1.0.

Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) with N_2CRR'

N_2CPh_2

An excess of diphenyldiazomethane in hexane was added at 0 °C to a solution of **1** (0.110 g) in hexane (10 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. During this time, red–brown crystals deposited from an orange–brown solution. The crystals were isolated by filtration and recrystallized from dichloromethane/hexane to give dark orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CPh_2\}$ (**2a**). A further amount of **2a** was obtained from the filtrate by evaporation of some solvent and preparative radial chromatography of the concentrated solution with dichloromethane as eluent. Total yield 0.150 g, 100%; m.p. 272 °C. *Anal.* Calc. for C$_{28}$H$_{20}$F$_6$N$_2$ORh$_2$: C, 46.7; H, 2.8; F, 15.8; N, 3.9. Found: C, 47.0; H, 2.9; F, 15.4: N, 4.0%. Spectroscopic data: IR (CH$_2$Cl$_2$): ν(CO) 1660 m cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.41 (m, 10H, 2×C$_6$H$_5$), 5.64 (s, 5H, C$_5$H$_5$), 4.83 (s, 5H, C$_5$H$_5$); ^{19}F NMR (CDCl$_3$): δ −47.2 (q (br), 3F, J(F–F) = 13 Hz, CF$_3$), −57.5 (q, 3F, J(F–F) = 13 Hz, CF$_3$); MS, m/z (relative intensity): 720 (7, M^+), 692 (1, $M^+ -$CO), 526 (6, $M^+ -$N$_2$CPh$_2$), 233 (100, C$_{10}$H$_{10}$Rh$^+$).

N_2CMePh

A solution of **1** (0.120 g) in diethyl ether (10 cm^3) was cooled to 0 °C, and excess 1-phenyldiazomethane in diethyl ether was added with stirring. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 20 min. Evaporation of some solvent from the deep red solution and subsequent TLC with a 4:1 mixture of dichloromethane/X$_4$ as eluent separated several minor bands from one major crimson band (R_f = 0.2). The latter was extracted with dichloromethane. Removal of solvent and recrystallization from dichloromethane/X_4 gave dark orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CMePh\}$ (**2b**). Yield 0.072 g, 48%; m.p. 242 °C. *Anal.* Calc. for $C_{23}H_{18}F_6N_2ORh_2$: C, 42.0; H, 2.8; F, 17.3; N, 4.3. Found: C, 41.9; H, 2.8; F, 17.1; N, 4.3%. Spectroscopic data: IR (CH_2Cl_2): ν(CO) 1685sh, 1675vs cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.59 (dm, 2H, J(H–H) = 8.3 Hz, C_6H_5), 7.38 (m, 3H, C_6H_5), C_6H_5), 5.67 (d, 5H, J(Rh–H) = 0.7 Hz, C_5H_5), 5.25 (s, 5H, C_5H_5), 2.12 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$): δ −47.9 (qm, 3F, J(F–F) = 12 Hz, CF_3), −57.4 (q, 3F, J(F–F) = 12 Hz, CF_3); MS, m/z (relative intensity): 658 (10, M^+), 630 (1, M^+-CO), 526 (6, M^+-N_2CMePh), 233 (100, $C_{10}H_{10}Rh^+$).

Only one of the minor products ($R_f = 0.9$) could be isolated in reasonable yield (0.014 g, 10%). It was obtained as a yellow–brown solid and was characterized spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{CF_3C_2CF_3\cdot CMePh\}$ (**3**). IR (CH_2Cl_2): ν(CO) 1840vs, ν(C=C) 1590m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.49 (m (br), 2H, C_6H_5), 7.19 (tm, 2H, J(H–H) = 7.4 Hz, C_6H_5), 7.02 (tm, 1H, J(H–H) = 7.4 Hz, C_6H_5), 5.56 (s, 5H, C_5H_5), 4.83 (s, 5H, C_5H_5), 1.69 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$): δ −49.3 (m, 3F, CF_3), −56.4 (q, 3F, J(F–F) = 7 Hz, CF_3); MS, m/z (relative intensity): 630 (<10, M^+), 602 (35, M^+-CO), 600 (26, $M^+-CO-2H$), 233 (100, $C_{10}H_{10}Rh^+$).

When attempts were made to purify **3** by repeated TLC with a mixture of dichloromethane/X_4 as eluent, decarbonylation occurred to give a new compound ($R_f = 0.8$), spectroscopically characterized as $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CMePh\}$ (**4**), m.p. 190 °C. Spectroscopic data: accurate mass MS, calc. for $C_{22}H_{18}F_6Rh_2$: 601.942, found: 601.942 ± 0.005; IR (CH_2Cl_2): no absorptions assigned to ν(CO) or ν(C=C); ^{1}H NMR (acetone-d_6): δ 7.39 (dm, 1H, J(H–H) = 7.8 Hz, C_6H_5), 7.14 (m, 1H, C_6H_5), 6.54 (m, 3H, C_6H_5), 5.59 (d, 5H, J(Rh–H) = 1.4 Hz, C_5H_5), 4.69 (s, 5H, C_5H_5), 1.97 (q, 3H, J(H–H) = 2.2 Hz, CH_3); ^{19}F NMR ($CDCl_3$): δ −50.4 (q, 3F, J(F–F) = 12 Hz, CF_3), −51.5 (q, 3F, J(F–F) = 12 Hz, CF_3); MS, m/z (relative intensity): 602 (35, M^+), 600 (25, M^+-2H), 433 (10, $C_{10}H_{10}Rh_2^+$), 233 (100, $C_{10}H_{10}Rh^+$).

$N_2CMe(CF_3)$

To a stirred solution of **1** (0.065 g) in diethyl ether (5 cm^3) was added excess 1,1,1-trifluoro-2-diazopropane in diethyl ether. The reaction mixture was stirred at room temperature for 80 min. Concentration of the red solution and subsequent TLC with a 1:1 mixture of dichloromethane/X_4 as eluent separated numerous trace bands and a yellow–orange band ($R_f = 0.8$) containing $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.22 g, 32%) from a red band ($R_f = 0.1$). Extraction of the material in the latter and purification by recrystallization from dichloromethane/X_4 gave dark red–brown crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CMe(CF_3)\}$ (**2c**). Yield 0.020 g, 25%; m.p. 230 °C. *Anal.* Calc. for $C_{18}H_{13}F_9N_2ORh_2$: C, 33.2; H, 2.0; F, 26.3; N, 4.3. Found: C, 33.0; H, 1.7; F, 26.2; N, 4.3%. Spectroscopic data: IR (CH_2Cl_2): ν(CO) 1690s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.66 (d, 5H, J = 0.8 Hz, C_5H_5), 5.27 (d, 5H, J = 0.5 Hz, C_5H_5), 1.87 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$): δ −48.1 (qm, 3F, J(F–F) = 12 Hz, CF_3), −57.5 (q, 3F, J = 12 Hz, CF_3), −72.9 (s, 3F, $N_2CMe(CF_3)$; MS, m/z (relative intensity): 650 (12, M^+), 631 (1, M^+-F), 581 (3, M^+-CF_3), 526 (3, $M^+-N_2CMeCF_3$), 498 (3, $(C_5H_5)_2Rh_2(CF_3C_2CF_3)^+$), 233 (100, $C_{10}H_{10}Rh^+$).

$N_2CPh(CF_3)$

An excess of 1-phenyl-2,2,2-trifluorodiazomethane in diethyl ether was added to a stirred solution of **1** (0.240 g) in diethyl ether (10 cm^3), and the reaction mixture was stirred at room temperature for 16 h. Concentration of the deep red reaction solution and subsequent preparative radial chromatography with a 1:1 mixture of dichloromethane/X_4 as eluent developed one major crimson band. Evaporation of solvent and subsequent recrystallization of the residue from dichloromethane/X_4 gave dark orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CPh(CF_3)\}$ (**2d**). Yield 0.305 g, 94%; m.p. 240 °C. *Anal.* Calc. for $C_{23}H_{15}F_9N_2ORh_2$: C, 38.8; H, 2.1; F, 24.0; N, 3.9. Found: C, 38.6; H, 2.3; F, 24.2; N, 4.0%. Spectroscopic data: IR (CH_2Cl_2): ν(CO) 1700m, sh, 1670 vs cm^{-1}; ^{1}H NMR (acetone-d_6): δ 7.58 (m, 5H, C_6H_5), 5.75 (d, 5H, J(Rh–H) = 0.8 Hz, C_5H_5), 5.13 (s, 5H, C_5H_5); ^{19}F NMR (acetone-d_6): δ −46.0 (qd, 3F, J(F–F) = 13 Hz and J(Rh–F) = 2Hz, CF_3), −56.2 (q, 3F, J(F–F) = 13 Hz, CF_3), −66.4 (s, 3F, $N_2CPh(CF_3)$); MS, m/z (relative intensity): 712 (8, M^+), 684 (<1, M^+-CO), 643 (4, $M^+-CO-CF_3$), 526 (4, $M^+-N_2CPhCF_3$), 233 (100, $C_{10}H_{10}Rh^+$).

$N_2C(t\text{-}Bu)_2$

A solution of **1** (0.220 g) in hexane (15 cm^3) was treated with excess 2,2,4,4-tetramethyl-3-diazopentane dissolved in hexane. A dark orange solution was obtained after stirring the reaction mixture for 30 min at room temperature. Concentration of the solution and subsequent TLC with a 3:8 mixture of dichloromethane/X_4 as eluent separated trace bands from one major dark orange band ($R_f = 0.4$). Extraction of the latter with dichloromethane and removal of solvent gave dark orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2C(t\text{-}Bu)_2\}$ (**5**). Yield 0.284 g, 100%; m.p. 184 °C. *Anal.* Calc. for $C_{24}H_{28}F_6N_2ORh_2$: C, 42.4; H, 4.2; F, 16.8; N, 4.1. Found: C, 42.3; H, 4.0; F, 16.9; N, 4.2%. Spectroscopic data: IR (CH_2Cl_2): no ν(CO) absorptions in the region 2100–1600 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.40 (s, 5H,

C_5H_5), 5.33 (s, 5H, C_5H_5), 1.09 (s, 9H, t-Bu), 0 92 (s, 9H, t-Bu); ^{19}F NMR ($CDCl_3$): δ −48.8 (qd, 3F, J(F–F) = 12 Hz and J(Rh–F) = 2 Hz, CF_3), −54.1 (q, 3F, J(F–F) = 12 Hz, CF_3); MS, m/z (relative intensity): 680 (5, M^+), 662 (<1, M^+-2H-O), 624 (15, $M^+-C_4H_8$), 623 (77, $M^+-C_4H_9$), 233 (100, $C_{10}H_{10}Rh^+$).

Attempted thermolysis and photolysis of (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CRR'\}$ complexes

Reactions with the complex (η-$C_5H_5)_2Rh_2$-$\{CF_3C_2CF_3\cdot CO\cdot N_2CPh_2\}$ (**2a**) are typical. A solution of **2a** (0.051 g) in xylene (15 cm^3) was tranferred to a Carius tube. The tube was evacuated and then heated at 135 °C for 3 weeks. TLC workup revealed only the starting compound, which was recovered in near quantitative yield.

A solution of **2a** (0.080 g) in toluene (20 cm^3) was irradiated with a medium pressure mercury lamp for 2 h. Unchanged starting compound was recovered in quantitative yield after workup.

Carbonylation of (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3$ CO $N_2C(t\text{-}Bu)_2\}$ (5)

Carbon monoxide was bubbled for 10 min through a solution of **5** (0.045 g) in hexane (15 cm^3) containing some dichloromethane (0.5 cm^3). The reaction vessel was then sealed, and the solution was exposed to Pyrex filtered sunlight for 4 days. During this time, dark brown crystals had deposited from an orange solution. The crystals were isolated by filtration and washed with hexane. This gave (η-$C_5H_5)_2Rh_2(CO)\{CF_3C_2CF_3\cdot CO\cdot N_2C(t\text{-}Bu)_2\}$ (**6**). Yield 0.018 g, 38%; m.p. 112 °C. *Anal.* Calc. for $C_{25}H_{28}F_6N_2O_2Rh_2$: C, 42.4; H, 4.0; F, 16 1; N, 4.0. Found: C, 42.3; H, 3.9; F, 16.2; N, 4.1%. Spectroscopic data: IR (CH_2Cl_2): ν(CO) 1900m, 1610 s cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.69 (s, 5H, C_5H_5), 5.49 (s, 5H, C_5H_5), 1.27 (s, 9H, t-Bu), 1.22 (s, 9H, t-Bu); ^{19}F NMR ($CDCl_3$): δ −46.9 (q, 3F, J(F–F) = 14 Hz, CF_3), −58.3 (q, 3F, J(F–F) = 14 Hz, CF_3); MS, m/z (relative intensity): 680 (<10, M^+-CO), 624 (12, $M^+-CO-C_4H_8$), 623 (50, $M^+-CO-C_4H_9$), 233 (100, $C_{10}H_{10}Rh^+$).

Workup of the filtrate yielded unchanged **5** (50%).

Crystallography

Well formed single crystals of (η-$C_5H_5)_2Rh_2$-$\{CF_3C_2CF_3\cdot CO\cdot N_2CMePh\}$ (**2b**) were grown from dichloromethane/hexane. A prism of dimensions 0.20×0.17×0.16 mm was selected. A unique data set was measured at 295 K using an Enraf-Nonius CAD-4 four circle diffractometer in conventional $2\theta/\theta$ scan mode. Data are summarized in Table 1. 'Observed' data were used in the full matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were used for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values. Residuals R, R' on $|F|$ at convergence were 0.041, 0.036, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0002\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed [18]; computation used the XTAL 2.4 program system [19] implemented by Hall. Non-hydrogen atom coordinates are given in Table 2, and selected bond distances and angles in Table 3. Figure 1 shows the molecule in projection.

TABLE 1 Summary of crystal structure data for the complexes (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3$ CO $N_2CRR'\}$, RR′ = MePh (**2b**), t-Bu_2 (**5**)

	2b	**5**
Crystal data		
RR′	MePh	t-Bu_2
Formula	$C_{23}H_{18}F_6N_2ORh_2$	$C_{24}H_{28}F_6N_2ORh_2$
Molecular weight	658.2	680 3
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca* (D_{2h}^{15}, No 61)	*Pbca* (D_{2h}^{15}, No. 61)
a (Å)	25.28(1)	27.679(3)
b (Å)	19.84(1)	11 560(1)
c (Å)	9.031(7)	15 924(1)
U ($Å^3$)	4529	5095.2
Z	8	8
D_{calc} (g cm^{-3})	1.93	1 77
D_{meas} (g cm^{-3})		1 76(1)
F(000)	2576	2704
μ(Mo Kα) (cm^{-1})	13.7	13 4
A^* min , max.	1 20, 1 29	1.16, 1 22
Data collection		
2θ (max) (°)	50	50
Total data	3932	4478
Data $I > 3\sigma(I)$	1972	2678
Final R, R_w	0.041, 0 036	0.057, 0.057

Dark red prisms of (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2C(t\text{-}Bu)_2\}$ (**5**) were also grown from dichloromethane/hexane. Dimensions of the selected crystal were 0.20×0.16×0.16 mm. A unique data set was measured using a Philips PW1100 diffractometer in conventional ω scan mode, with a symmetric scan range of $(\pm 0.65 + 0.2 \tan\theta)°$, at a scan rate of 0.04° s^{-1}. Other crystal data are summarized in Table 1. Intensity data were processed as described previously [20]. A numerical absorption correction was applied. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion [18]. All calculations were performed on a Monash University DEC/VAC 11/780 computer. The program used for least-squares refinement was that due to Sheldrick [21]. The structure was solved by conventional heavy atom methods. Anisotropic thermal parameters were refined for Rh and F and isotropic thermal parameters for all other non-hydrogen atoms. R, R' on $|F|$ at convergence were 0.057, 0.057, statistical weights $\omega = [\sigma^2|F_o|]^{-1}$ being used. Final atomic

TABLE 2. Non-hydrogen atom coordinates for the complex $(\eta$-$C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2C(Me)Ph\}$ (**2b**)

Atom	x	y	z
Rh(1)	0.08943(3)	0.09968(4)	−0.03558(9)
Rh(2)	0.18903(3)	0.07851(4)	0.02560(8)
C(101)	0.0581(5)	0.1979(5)	0.020(2)
C(102)	0.0243(5)	0.1680(7)	−0.081(1)
C(103)	0.0027(4)	0.1087(6)	−0.018(2)
C(104)	0.0252(5)	0.1039(6)	0.126(2)
C(105)	0.0590(5)	0.1590(7)	0.150(1)
C(201)	0.2279(6)	0.0531(8)	0.237(2)
C(202)	0.2130(5)	0.1199(8)	0.240(1)
C(203)	0.2383(5)	0.1549(6)	0.127(2)
C(204)	0.2703(4)	0.1085(9)	0.052(1)
C(205)	0.2641(5)	0.0469(8)	0.118(2)
C(1)	0.1586(4)	0.1061(5)	−0.172(1)
C(11)	0.1763(4)	0.1671(6)	−0.254(1)
F(111)	0.2202(3)	0.1944(4)	−0.1990(8)
F(112)	0.1874(3)	0.1555(3)	−0.3949(7)
F(113)	0.1411(3)	0.2168(3)	−0.2557(9)
C(2)	0.1211(4)	0.0597(5)	−0.236(1)
C(21)	0.0931(5)	0.0644(6)	−0.382(1)
F(211)	0.1217(3)	0.0384(4)	−0.4907(6)
F(212)	0.0824(3)	0.1287(4)	−0.4208(7)
F(213)	0.0477(3)	0.0326(3)	−0.3838(7)
C(3)	0.1173(4)	−0.0073(5)	−0.160(1)
O(3)	0.1009(3)	−0.0597(3)	−0.2052(8)
N(4)	0.1315(3)	0.0087(4)	−0.0098(8)
N(5)	0.1150(3)	−0.0384(4)	0.0991(9)
C(6)	0.1408(4)	−0.0930(5)	0.110(1)
C(60)	0.1892(4)	−0.1113(5)	0.020(1)
C(61)	0.1213(5)	−0.1400(6)	0.224(1)
C(62)	0.1300(6)	−0.2072(7)	0.216(2)
C(63)	0.1045(9)	−0.252(1)	0.315(2)
C(64)	0.0745(9)	−0.226(1)	0.422(3)
C(65)	0.0673(6)	−0.159(1)	0.436(2)
C(66)	0.0897(5)	−0.1141(7)	0.339(1)

TABLE 3. Selected interatomic distances (Å) and angles (°) for the complex $(\eta$-$C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2C(Me)Ph\}$ (**2b**)

Distances	
Rh(1)–Rh(2)	2.611(2)
Rh(1)–C(101)	2.16(1)
Rh(1)–C(102)	2.17(1)
Rh(1)–C(103)	2.21(1)
Rh(1)–C(104)	2.19(1)
Rh(1)–C(105)	2.19(1)
Rh(1)–C(1)	2.141(9)
Rh(1)–C(2)	2.13(1)
Rh(1)–N(4)	2.108(7)
Rh(2)–C(201)	2.21(1)
Rh(2)–C(202)	2.19(1)
Rh(2)–C(203)	2.16(1)
Rh(2)–C(204)	2.15(1)
Rh(2)–C(205)	2.17(1)
Rh(2)–C(1)	2.016(9)
Rh(2)–N(4)	2.033(7)
C(1)–C(11)	1.49(1)
C(1)–C(2)	1.44(1)
C(2)–C(21)	1.50(2)
C(2)–C(3)	1.50(1)
C(3)–O(3)	1.19(1)
C(3)–N(4)	1.44(1)
N(4)–N(5)	1.42(1)
N(5)–C(6)	1.27(1)
C(6)–C(60)	1.51(1)
C(6)–C(61)	1.47(2)
Angles	
C(1)–Rh(1)–C(2)	39.5(4)
C(1)–Rh(1)–N(4)	72.7(3)
C(2)–Rh(1)–N(4)	65.5(3)
C(1)–Rh(2)–N(4)	76.9(3)
Rh(1)–C(1)–Rh(2)	77.8(3)
Rh(1)–C(1)–C(11)	125.4(7)
Rh(1)–C(1)–C(2)	69.9(5)
Rh(2)–C(1)–C(11)	123.2(7)
Rh(2)–C(1)–C(2)	115.6(7)
C(11)–C(1)–C(2)	121.0(8)
Rh(1)–C(2)–C(1)	70.6(5)
Rh(1)–C(2)–C(21)	123.1(7)
Rh(1)–C(2)–C(3)	85.3(6)
C(1)–C(2)–C(21)	128.5(9)
C(1)–C(2)–C(3)	115.1(8)
C(21)–C(2)–C(3)	115.3(9)
C(2)–C(3)–O(3)	129.7(9)
C(2)–C(3)–N(4)	102.7(8)
O(3)–C(3)–N(4)	127.1(9)
Rh(1)–N(4)–Rh(2)	78.2(3)
Rh(1)–N(4)–C(3)	87.6(5)
Rh(1)–N(4)–N(5)	119.5(5)
Rh(2)–N(4)–C(3)	118.5(6)
Rh(2)–N(4)–N(5)	123.3(5)
C(3)–N(4)–N(5)	115.8(7)
N(4)–N(5)–C(6)	117.6(8)
N(5)–C(6)–C(60)	125.5(9)
N(5)–C(6)–C(61)	114.9(9)
C(60)–C(6)–C(61)	119.5(9)

parameters are given in Table 4, and selected bond lengths and angles in Table 5. The atomic labelling scheme used is shown in Fig. 2.

Results and Discussion

Formation of the complexes

When solutions of $(\eta$-$C_5H_5)_2Rh_2(\mu$-$CO)(\mu$-η^2-$CF_3C_2CF_3)$ (**1**) are treated at 25 °C with the diazo compounds N_2CRR' ($RR' = Ph_2$, MePh, Me(CF_3), Ph(CF_3)), addition products of the type $(\eta$-$C_5H_5)_2Rh_2\{CF_3C_2CF_3\cdot CO\cdot N_2CRR'\}$ (**2a**–**2d**) are formed. The reactions with N_2CPh_2 and $N_2CPh(CF_3)$ are relatively slow, but the addition products **2a** ($RR' = Ph_2$) and **2d** ($RR' = PhCF_3$) are obtained in essentially quantitative yields. With the methyl substituted diazo compounds N_2CMePh and $N_2CMe(CF_3)$, the reactions are rapid but more than one type of product is formed and consequently the yields of **2b** ($RR' = MePh$) and **2c** ($RR' = MeCF_3$) are lower. The other major product formed in the reaction with $N_2CMe(CF_3)$ is $(\eta$-$C_5H_5)_2Rh_2(CO)_2(\mu$-$\eta^1\eta^1$-CF_3C_2-

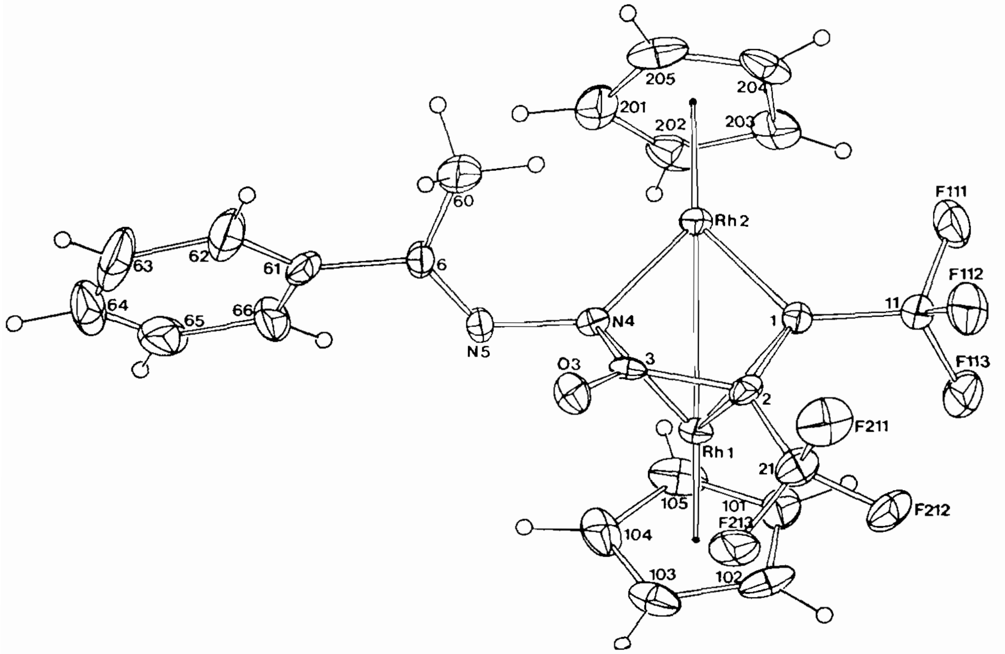


Fig. 1. ORTEP projection showing the atom arrangement in (η-C_5H_5)$_2$$Rh_2${$CF_3C_2CF_3$ CO N_2CMePh} (**2b**). The non-hydrogen atoms are shown as 20% thermal ellipsoids, hydrogen atoms have arbitrary radii of 0.1 Å.

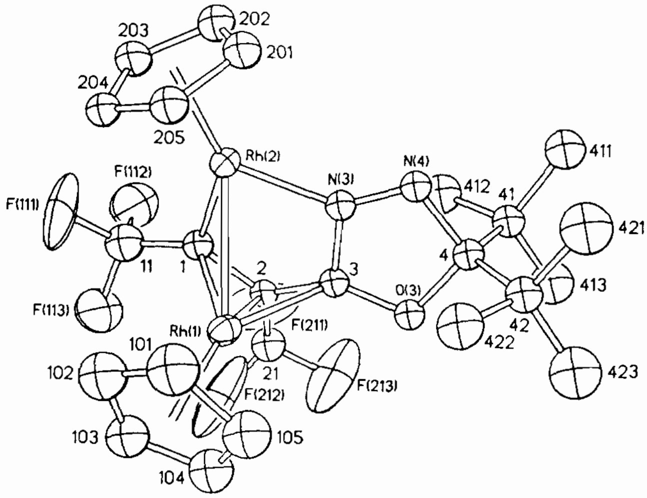


Fig 2. ORTEP projection showing the atom arrangement in (η-C_5H_5)$_2$$Rh_2${$CF_3C_2CF_3$ CO·$N_2C(t\text{-}Bu)_2$} (**5**), 40% thermal envelopes are shown.

CF_3). With N_2CMePh, the second product is of the type (η-C_5H_5)$_2$$Rh_2$($\mu$-CO)($CF_3C_2CF_3$·CMePh) (**3**); the nature and behaviour of this complex are discussed later.

The products (η-C_5H_5)$_2$$Rh_2${$CF_3C_2CF_3$·CO·$N_2CRR'$} are air stable, dark orange solids. The retention of nitrogen in these complexes is surprising given the facile loss of N_2 in the corresponding reactions with N_2CHR compounds [9]. Moreover, the compounds show no tendency to eliminate nitrogen when they are heated or photolyzed in solution. The product **2a** (RR′ = Ph_2), for example, survives unchanged when heated at 135 °C in xylene for 3 weeks. The same compound is also unaffected when a toluene solution is irradiated for 2 h with a 250 W medium pressure mercury lamp.

Spectroscopic data are not particularly helpful in deducing the structure of the complexes **2a**–**2d**. The IR spectra do establish that the carbonyl has become ketonic with ν(CO) observed between 1660 (for **2a**) and 1690 (for **2c**) cm^{-1}, and an unsymmetrical structure is indicated by the NMR spectra. In the ^{19}F NMR spectra, the two CF_3 chemical shifts are found near δ −47 and −57 ppm, consistent with quite different environments for these groups. The mass spectra generally show a molecular ion and loss of CO and N_2CRR' fragments. We decided to determine the crystal structure of one of these complexes to establish how the CO, $CF_3C_2CF_3$ and N_2CRR' units have interacted.

Description of the structure of (η-C_5H_5)$_2$$Rh_2$-{$CF_3C_2CF_3$·CO·$N_2CMePh$} (2b)

The ORTEP diagram (Fig. 1) shows the atom arrangement. Each of the units $CF_3C_2CF_3$, CO and N_2CMePh has retained its integrity but all have coupled to form a new ligand of the type [−C(CF_3)=C(CF_3)-C(=O)-N-N=C(Me)Ph]. This is attached to Rh(2) through a σ-bond from C(1) and a dative bond from N(4). The bonding to Rh(1) involves a π-interaction with C(1)=C(2) and a σ-bond from

TABLE 4. Non-hydrogen atom coordinates for the complex (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3 \cdot CO \cdot N_2C(t\text{-}Bu)_2\}$ (**5**)

Atom	*x*	*y*	*z*
Rh(1)	0.08938(3)	0.39263(8)	0.36788(6)
Rh(2)	0.18233(3)	0 43246(7)	0.33101(5)
F(111)	0.1821(5)	0.1649(7)	0.3906(6)
F(112)	0.1997(3)	0.2228(7)	0.5101(6)
F(113)	0.1306(3)	0.1631(7)	0 4845(7)
F(211)	0.1355(3)	0.3623(13)	0.6217(5)
F(212)	0.0739(5)	0.3019(11)	0.5709(6)
F(213)	0.0794(5)	0.4715(10)	0.6021(6)
C(11)	0.1661(5)	0.2275(12)	0.4523(9)
C(1)	0.1528(4)	0.3460(9)	0.4288(7)
C(2)	0.1238(4)	0.4158(9)	0.4835(6)
C(21)	0.1022(5)	0.3872(12)	0.5688(8)
C(3)	0.1180(4)	0.5317(9)	0.4468(6)
C(4)	0 1219(4)	0.7262(9)	0.4486(7)
C(41)	0 1504(4)	0.7791(10)	0.5271(7)
C(411)	0.1842(5)	0.8788(11)	0.4995(8)
C(412)	0.1816(5)	0.6816(12)	0.5664(9)
C(413)	0.1161(5)	0.8214(14)	0.5961(10)
C(42)	0.0855(4)	0.7993(10)	0.3930(7)
C(421)	0.1103(6)	0 8982(14)	0 3438(10)
C(422)	0.0648(5)	0 7198(12)	0.3260(9)
C(423)	0.0421(6)	0.8464(15)	0.4442(11)
C(101)	0.0561(6)	0.3658(14)	0.2445(10)
C(102)	0.0632(5)	0.2572(14)	0.2800(9)
C(103)	0.0352(5)	0 2501(12)	0.3526(8)
C(104)	0.0101(5)	0.3551(12)	0.3660(9)
C(105)	0.0209(5)	0.4331(13)	0.2989(9)
C(201)	0.2236(4)	0 5086(10)	0.2227(7)
C(202)	0 2576(4)	0 4582(10)	0 2833(7)
C(203)	0.2471(4)	0 3358(10)	0.2890(7)
C(204)	0.2073(4)	0 3111(9)	0.2347(7)
C(205)	0.1930(4)	0.4166(10)	0 1915(7)
N(4)	0.1588(3)	0 6762(7)	0.3906(5)
N(3)	0.1558(3)	0.5685(7)	0.3937(5)
O(3)	0.0954(2)	0.6247(6)	0 4801(4)

TABLE 5. Selected interatomic distances (Å) and angles (°) for the complex (η-$C_5H_5)_2Rh_2\{CF_3C_2CF_3$ $CO \cdot N_2C(t\text{-}Bu)_2\}$ (**5**)

Distances			
Rh(1)–Rh(2)	2.679(1)	C(3)–O(3)	1.35(1)
Rh(1)–C(1)	2.08(1)	C(3)–N(3)	1.41(1)
Rh(1)–C(2)	2.09(1)	C(4)–O(3)	1.47(1)
Rh(1)–C(3)	2.19(1)	C(4)–N(4)	1.49(1)
Rh(1)–C(101)	2 19(2)	C(4)–C(42)	1.58(2)
Rh(1)–C(102)	2.22(2)	C(4)–C(41)	1.60(2)
Rh(1)–C(104)	2.24(1)	C(41)–C(413)	1.53(2)
Rh(1)–C(105)	2 24(1)	C(41)–C(411)	1.55(2)
Rh(1)–C(103)	2.24(1)	C(41)–C(412)	1 55(2)
Rh(2)–N(3)	2.00(1)	C(42)–C(422)	1.52(2)
Rh(2)–C(1)	2.02(1)	C(42)–C(421)	1.55(2)
Rh(2)–C(204)	2.19(1)	C(42)–C(423)	1.55(2)
Rh(2)–C(203)	2.21(1)	C(42)–C(4)	1.58(2)
Rh(2)–C(202)	2 24(1)	N(4)–N(3)	1.25(1)
Rh(2)–C(201)	2.25(1)	N(4)–C(4)	1.49(1)
Rh(2)–C(205)	2.25(1)		
C(11)–C(1)	1.47(2)		
C(1)–C(2)	1.43(1)		
C(2)–C(3)	1 47(1)		
C(2)–C(21)	1.52(2)		
Angles			
C(1)–Rh(1)–C(2)	40 2(4)		
C(1)–Rh(1)–C(3)	67.5(4)		
C(2)–Rh(1)–C(3)	40.1(4)		
N(3)–Rh(2)–C(1)	81 7(4)		
Rh(2)–C(1)–Rh(1)	81.6(4)		
C(2)–C(1)–C(11)	120 7(10)		
C(1)–C(2)–C(3)	109.5(9)		
C(1)–C(2)–C(21)	129.9(10)		
C(3)–C(2)–C(21)	120.6(9)		
O(3)–C(3)–N(3)	109 8(8)		
O(3)–C(3)–C(2)	128.3(9)		
N(3)–C(3)–C(2)	115.5(9)		
O(3)–C(4)–N(4)	104.1(8)		
O(3)–C(4)–C(42)	107 4(8)		
O(3)–C(4)–C(41)	106.5(8)		
N(4)–C(4)–C(42)	107.1(8)		
N(4)–C(4)–C(41)	107 1(8)		
C(42)–C(4)–C(41)	123.1(9)		
N(3)–N(4)–C(4)	108.4(8)		
N(4)–N(3)–C(3)	111.9(8)		
C(3)–O(3)–C(4)	105 5(7)		

N(4). Another schematic of the molecule, which emphasizes these bonding interactions, is presented in Fig. 3.

The Rh(1)–Rh(2) distance of 2.611(2) Å is consistent with a single bond between the metals. With this bridging arrangement, each metal attains an electron count of eighteen valence electrons. Only one nitrogen of the diazo unit is involved in bonding to the metals. The dative bond to Rh(2) is significantly shorter (2.033(7) Å) than the σ-bond to Rh(1) (2.108(7) Å). As a consequence of these N–Rh interactions and the coupling of N(4) to C(3), there is a single bond interaction between N(4) and N(5) (distance 1.42(1) Å). The bent N(4)–N(5)–C(6) angle of 117.6(8)° and the short distance between N(5) and C(6) (1.27(1) Å, cf. N(4)–C(3) = 1.44(1) Å) indicates a N(5)=C(6) double bond interaction. All the remaining molecular parameters are unexceptional.

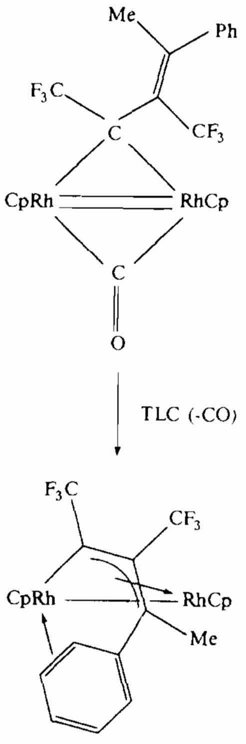
Knowledge of the structure indicates that initial attack of the diazo compound on the dirhodium species is probably a 1,2-dipolar addition to a Rh–CO bond. This is represented schematically in Fig. 4.

Additional products formed in the reactions with N_2CMePh and $N_2CMe(CF_3)$

The dicarbonyl complex (η-$C_5H_5)_2Rh_2(CO)_2(\mu$-$\eta^1\eta^1$-$CF_3C_2CF_3)$ was obtained in 32% yield from the reaction between **1** and $N_2CMe(CF_3)$. While this is a fairly common product from reactions between **1** and various ligands [22], this is the only instance in the present series where it is detected. It is likely that the dicarbonyl complex is formed as a result of carbonyl loss from some unstable species which is also formed but not recognized in this reaction. This CO would readily be trapped by unreacted **1**. The relatively low yield (25%) of **2c** is consistent with this idea.

In the reaction between **1** and N_2CMePh, **2b** was the major product, but again the yield was relatively low (48%). Other products were evident on the TLC plate, but only one of these could be extracted in reasonable yield (10%). Based on spectroscopic data, we believe this compound has the structure **3**. An analogous compound is obtained in the corresponding reaction with N_2CMe_2 which will be discussed in detail in a subsequent paper [23].

When attempts were made to purify compound **3** by repeated TLC, decarbonylation occurred to produce a new compound which was spectroscopically characterized as **4**. The ^1H NMR spectrum provides support for the η^2-coordination of the phenyl substituent. Thus, two of the phenyl protons are deshielded (δ 7.39 and 7.14) relative to the other three (δ 6.54).



3

4

The structurally different product 5 formed with $N_2C(t\text{-}Bu)_2$

The reaction between **1** and $N_2C(t\text{-}Bu)_2$ was complete within 30 min at room temperature, and an essentially quantitative yield of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3 \cdot CO \cdot N_2C(t\text{-}Bu)_2\}$ (**5**) was obtained. However, the spectroscopic data for this complex differed in several respects from that for the other $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3 \cdot CO \cdot N_2CRR'\}$ complexes. The absence of ν(CO) in the IR spectrum and the absence of a peak corresponding to $[M^+ - CO]$ in the mass spectrum seemed particularly significant. To gain insight into the nature of this compound, the crystal and molecular structure was determined from X-ray diffraction data. A preliminary account of this part of the work has been published [24].

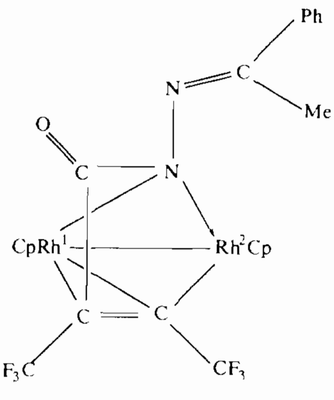


Fig. 3. A representation of the structure of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3\ CO \cdot N_2CMePh\}$ (**2b**) which emphasizes the ligand–metal bonding interactions.

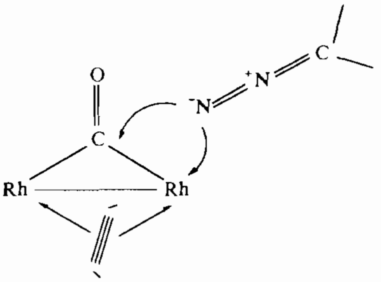


Fig. 4. Proposed 1,2-dipolar addition of a diazoalkane to a Rh–CO bond in $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**1**).

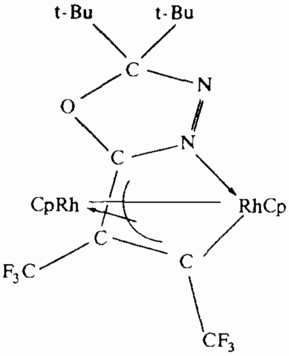


Fig. 5. A representation of the structure of $(\eta\text{-}C_5H_5)_2Rh_2\{CF_3C_2CF_3 \cdot CO \cdot N_2C(t\text{-}Bu)_2\}$ (**5**) which emphasizes the ligand–metal bonding interactions

An ORTEP view of the molecular structure of **5** is given in Fig. 2, and the bonding interactions are shown in Fig. 5. Comparison of Figs. 5 and 3 establishes clearly the different forms and modes of attachment of the ligands.

Again the ligand is constructed from the condensation of $CF_3C_2CF_3$, CO and N_2CR_2 units, but this time a five-membered N=N–C(t-Bu)$_2$–O–C ring is formed, and there is a $\overset{\cdot}{-}$C(CF_3)$\overset{\cdot}{-}$C(CF_3) side chain attached to one carbon. An end carbon atom (C(1)) is σ-bonded to Rh(2), and one ring nitrogen (N(3)) forms a dative bond to Rh(2). The N(3)–Rh(2) distance (2.00(1) Å) is similar to that in (η-C_5H_5)$_2$Rh$_2${$CF_3C_2CF_3$·CO·N_2CMePh}. The attachment at Rh(1) involves three adjacent carbon atoms which form an allylic arrangement C(1)$\overset{\cdot}{-}$C(2)$\overset{\cdot}{-}$C(3). The allyl–rhodium attachment is slightly asymmetric, with the Rh(1)–C(3) bond being slightly longer (2.19(1) Å) than the other two Rh–C distances (2.08(1), 2.09(1) Å). The usual picture in allyl–metal structures is to have slightly longer M–C bonds to the two terminal carbon atoms. The short Rh(1)–C(1) distance in the present complex is probably a consequence of C(1) being also attached to Rh(2). The parameters within the N–N–C–O–C ring are consistent with the representation shown in Fig. 5. Double bond character is indicated for N(3)–N(4) by the short interatomic distance of 1.25(1) Å; this can be compared with the N(4)–N(5) single bond distance of 1.42 Å for the complex in Fig. 1. The N(3)→Rh(2) dative bond distance of 2.00(1) Å is similar to that (2.033(7) Å) for the complex in Fig. 1. The remaining molecular parameters show no unusual features.

The heterocyclic fragment of the ligand is presumably formed by a [3+2] cycloaddition of $^-$N=N–C$^+$(t-Bu)$_2$ to the polar μ-C$^+$=O$^-$ bond in complex **1**; this is represented in Fig. 6. Further interaction with the coordinated hexafluorobut-2-yne would complete ligand formation. A similar [3+2] cycloaddition has been proposed to account for the formation of epoxides from reactions between diazo compounds and organic ketones. An example is shown in eqn. (3).

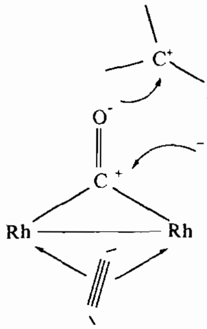
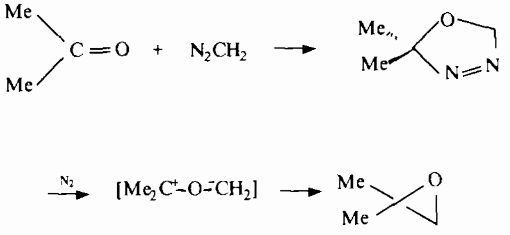


Fig. 6. Proposed [3+2] cycloaddition of the diazoalkane to the bridging carbonyl in the dirhodium complex **1**.

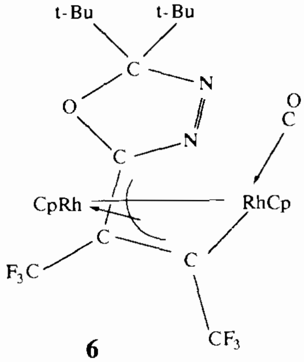


(3)

To the best of our knowledge, there is no direct evidence for the proposed cyclic intermediate in these systems. There is ready elimination of nitrogen from the intermediate in this organic reaction. In contrast, the rhodium complex is remarkably stable with respect to nitrogen loss. It melts without decomposition at 184 °C, and is unchanged when kept in refluxing toluene for 24 h. Moreover, the mass spectrum does not indicate loss of N_2 from the molecular ion.

Photolytic carbonylation of (η-C_5H_5)$_2$Rh$_2${$CF_3C_2CF_3$·CO·N_2C(t-Bu)$_2$} (5)

A solution containing **5** was saturated with CO and exposed to sunlight for several days. Dark brown crystals deposited from the solution, and these were shown by elemental analysis and spectroscopic results to be the carbonyl addition product (η-C_5H_5)$_2$Rh$_2$(CO)-{$CF_3C_2CF_3$·CO·N_2C(t-Bu)$_2$}. A terminal carbonyl was indicated by an absorption at 1900 cm^{-1} in the IR spectrum; other spectroscopic data were similar to that for the starting complex **5**. It seems reasonable to postulate a structure **6** in which the dative N→Rh bond has been displaced by the incoming carbonyl.



6

General comments on binuclear complexes with ligands derived from diazoalkanes

There are few other binuclear complexes that incorporate intact N_2CRR′ units. In two recent examples, diazoalkanes are η^1-coordinated from the terminal nitrogen to one atom of a metal–metal bond [25, 26]. In another case [27], a complete diazoalkane condenses with the bridging aminoalkyne group in a di-iron complex. The two examples that have been structurally characterized in the present study represent quite different modes of reaction and indicate substantially different attachments of the ligands formed. In most other studies of reactions between dinuclear complexes and diazoalkanes, there is facile loss of nitrogen and initial formation of an alkenyl group.

The wide range of products formed in these reactions emphasizes just how sensitive such systems are to stereoelectronic effects. The investigations so far do not establish a clear correlation between substituent type and chemical behaviour, and clearly more work is needed. We shall report some further investigations of the reactions between **1** and diazoalkanes in a subsequent paper [23]; these reveal some further types of reaction.

Supplementary material

Material deposited with the Cambridge Crystallographic Data Centre for both structures comprises structure factor amplitudes, thermal and hydrogen atom parameters, and all bonding distances and angles.

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