Phosphinoalkyne Additions to $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)$: Facile Conversion of Coordinated Phosphinoalkynes to Phosphino−Enone Ligands on a Rh−Rh Bond

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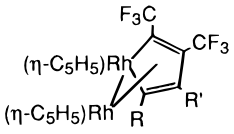
The phosphinoalkynes $Ph_2PC{\equiv}CR$ (R = H, Me, CF_3, Bu^t, Ph, and PPh_2) behave as tertiary phosphines in their reactions with the dirhodium complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)$ (**1**). All six addition products $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)(\eta^1\text{-}Ph_2PC{\equiv}CR)$ (**4**) have been isolated and fully characterized. The bis(diphenylphosphino)alkyne $Ph_2PC{\equiv}CPPh_2$ also forms a tetranuclear complex (**5**) in which each phosphorus coordinates to a dirhodium unit. With the exception of **4** when R = H, the solid complexes are relatively stable. However, when solutions of two of the complexes (R = Me, Ph) are left in the presence of both silica and oxygen, there is oxygen transfer to an alkyne carbon accompanied by an intramolecular condensation reaction to generate a phosphino−enone ligand. The structure of one of these oxidation products, $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}C(CF_3)C(CF_3)C\{C(O)R\}PPh_2)$ (**6**, R = Ph), has been established by X-ray crystallography. Prior oxidation of the phosphinoalkynes to give $Ph_2P(O)C{\equiv}CR$ and subsequent reaction with **1** leads to the formation of typical alkyne addition products.

Introduction

A wide variety of ligands and some transient species have been added coordinatively to the dirhodium complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)$ (**1**).[1] For example, the reactions with tertiary phosphanes, PR_3, give the inert products $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(PR_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$.[2] In other reactions, the added substrate reacts further with the existing ligands to form condensed ligands. This occurs, for instance, in the reactions between **1** and various alkynes, which give products containing bridging metallacyclopentadiene (**2**) or dimetallacycloheptadienone (**3**) units.[3−5] Recently, we



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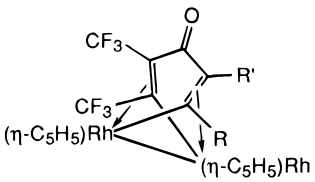

(3)

investigated some reactions of **1** with phosphinoalkynes $Ph_2P(CH_2)_nC{\equiv}CR$. In these systems, coordination occurs exclusively from phosphorus.[6]

In other studies, phosphinoalkynes of the type $Ph_2PC{\equiv}CR$ have been shown to react with mononuclear and polynuclear complexes in a number of ways. Coordination can be from phosphorus only[7−10] or from phosphorus and the alkyne,[11−14] but in other cases, these ligands undergo cleavage of the P−C(alkyne) bond to generate separate phosphido and acetylide fragments.[15,16] An example of this type of behavior is found in the reactions of $Ph_2PC{\equiv}CR$ (R = Ph, Pr^i, Bu^t) with $M_3(CO)_{12}$ (M = Fe, Ru, Os) where the substituted cluster $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$ is formed initially, but oxidative insertion into the P−C bond accompanied by cluster fragmentation then gives the binuclear products $M_2(CO)_6(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CR)(\mu_2\text{-}PPh_2)$.[17]

The bis(diphenylphosphino)alkyne $Ph_2PC{\equiv}CPPh_2$ is potentially even more versatile in its coordination behavior. This compound often coordinates exclusively from one or both phosphorus atoms. Even with $Co_2(CO)_8$, which is especially prone to form μ-alkyne complexes,[18] $Ph_2PC{\equiv}CPPh_2$ gives phosphane substitution products.[19] The complex $W(CO)(S_2CNEt_2)_2(\eta^2\text{-}Ph_2PC{\equiv}CPPh_2)$ provides a rare example of coordination from the alkyne function of $Ph_2PC{\equiv}CPPh_2$.[20] There are also examples of P−C bond cleavage in some reactions of bis(phosphino)alkynes and clusters.[21]

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This diversity in coordination behavior demonstrated by phosphinoalkynes, plus the extensive and interesting reaction chemistry reported for P−coordinated phosphinoalkynes,[7,8,22] prompted us to explore the reactions between these ligands and **1**. In this paper, we describe the results of our investigations.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified nitrogen in oven-dried Schlenk flasks. Purification of some products was achieved by preparative-scale thin layer chromatography (TLC), which was carried out on 20 cm by 20 cm glass plates with a 1:1 silica gel G-HF_{254} mixture (type 60, Merck) as the adsorbent. All separations were achieved on deactivated plates, obtained by drying at room temperature only. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Melting points were determined on a Buchi melting point apparatus using analytically pure samples and are uncorrected.

Instrumentation. Solution infrared spectra (KBr windows) were obtained using a Perkin Elmer 1600 Fourier transform spectrometer. NMR spectra were measured on a Bruker AC 200, AM 300, or RDX 400 spectrometer. Deuterated solvents ($CDCl_3$, toluene-d_8) were used as internal locks. Chemical shifts are in parts per million from internal Me_4Si for ^1H and ^{13}C, from CCl_3F for ^{19}F, and from external 85% H_3PO_4 for ^{31}P; in all cases, a positive chemical shift denotes a resonance downfield from the reference. Electron impact mass spectra were obtained by using a TRIO-1 GCMS spectrometer operating at 70 eV and a 200 °C inlet temperature.

Materials. Acetone was analytical-grade reagent; hydrocarbons and dichloromethane were purified by distillation under nitrogen from the appropriate drying agent.[23] All solvents were stored in the dark over activated 4 Å molecular sieves and were purged with nitrogen prior to use. (η^5-C_5H_5)$_2$-Rh_2(μ-CO)(μ-η^2:η^2-$CF_3C_2CF_3$) was prepared as described in ref 24.

The alkynes $Ph_2PC{\equiv}CR$ (R = H, Ph, PPh_2) were prepared by the dropwise addition of PPh_2Cl to the appropriate alkynyl−Grignard RC≡CMgX following the method described by Charrier.[25] The other alkynes $Ph_2PC{\equiv}CR$ (R = Bu^t, Me, CF_3) were prepared in similar manner from the alkynyl−lithium reagent and PPh_2Cl by the method described by Carty.[26] Treatment of $Ph_2PC{\equiv}CR$ (R = Me, Ph) with H_2O_2 in glacial acetic acid gave the phosphine oxides $Ph_2P(O)C{\equiv}CR$.[25] All of the phosphinoalkynes and the oxides were spectroscopically characterized by MS and IR and multinuclear NMR spectroscopies.

Reactions of (η^5-C_5H_5)$_2$$Rh_2$($\mu$-CO)($\mu$-$\eta^2$:$\eta^2$-$CF_3C_2CF_3$) (1) with Phosphinoalkynes. $Ph_2PC{\equiv}CBu^t$. A solution of $Ph_2PC{\equiv}CBu^t$ (36 mg, 0.135 mmol) in dichloromethane (2.0 mL) was added dropwise to a stirred solution of **1** (61 mg, 0.116 mmol) in dichloromethane (5.0 mL). The green solution immediately turned to a dark orange color. The solvent was removed under reduced pressure, and the red residue was purified by TLC with a 3:1 mixture of petroleum ether and dichloromethane as the eluent. A major orange band developed and was extracted with dichloromethane. Removal of the solvent under reduced pressure gave (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CBu^t$) (**4**, R = Bu^t; 72 mg, 78%) as red-orange crystals. Anal. Calcd for $C_{33}H_{29}F_6OPRh_2$: C, 50.0; H, 3.7; F, 14.4; P, 3.9. Found: C, 50.2; H, 3.6; F, 14.1; P, 3.8. MS, *m*/*z*: 792 (4, $[M]^+$), 764 (20, $[M - CO]^+$), 233 (80, $[C_{10}H_{10}Rh]^+$), 168 (40, $[C_5H_5Rh]^+$), 57 (100, $[C_2H_2P]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1985 (vs), ν(C≡C) 2208 (w) and 2169 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 9H, CH_3), 5.10 (s, 5H, C_5H_5), 5.14 (d, $^2J_{RhH}$ = 1.7 Hz, 5H, C_5H_5), 7.3−7.5 (m , 8H, *ortho*- and *meta*-H of C_6H_5), 7.92 (m, 2H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 282 MHz): two isomers were evident in the ratio 95:5; major isomer δ −51.7 (q, $^5J_{FF}$ = 11.4 Hz, 3F, CF_3), −55.0 (qdd, $^5J_{FF}$ = 11.4 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.3 Hz, 3F, CF_3); minor isomer δ −51.1 (qd, $^5J_{FF}$ = 11.3 Hz, $^3J_{RhF}$ = 3.0 Hz, 3F, CF_3), −55.0 (qdd, $^5J_{FF}$ = 11.3 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.3 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 297 K): δ 28.3 (br m, PPh_2).

$Ph_2PC{\equiv}CCF_3$. Upon dropwise addition of a solution of $Ph_2PC{\equiv}CCF_3$ (44 mg, 0.158 mmol) in dichloromethane (5 mL) to a stirred solution of **1** (82 mg, 0.156 mmol) in dichloromethane (25 mL), there was an instant color change from green to orange. The solvent was removed under reduced pressure to give (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CCF_3$) (**4**, R = CF_3; 126 mg, 100%) as orange crystals. Anal. Calcd for $C_{30}H_{20}F_9OPRh_2$: C, 44.8; H, 2.5; F, 21.3; P, 3.9. Found: C, 44.5; H, 2.5; F, 21.0; P, 3.8. MS, *m*/*z*: 804 (<1, $[M]^+$), 776 (6, $[M - CO]^+$), 526 (11, $[M - Ph_2PC_2CF_3]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 168 (29, $[C_5H_5Rh]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1993 (vs), ν(C≡C) 2218 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.10 (s, 5H, C_5H_5), 5.25 (d, $^2J_{RhH}$ = 1.5 Hz, 5H, C_5H_5), 7.3−7.6 (m, 8H, *ortho*- and *meta*-H of C_6H_5), 7.83 (m, 2H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 376.5 MHz): two isomers were evident in the ratio 93:7; major isomer δ −51.8 (s, 3F, CF_3), −52.0 (q, $^5J_{FF}$ = 11.2 Hz, 3F, CF_3), −56.0 (m, 3F, CF_3); minor isomer δ −51.6 (q, $^5J_{FF}$ = 10.8 Hz, 3F, CF_3), −52.6 (s, 3F, CF_3), −55.5 (m, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 297 K): δ 36.9 (d, $^1J_{RhP}$ = 194 Hz, PPh_2)—the signal emerges from a broader doublet centered at δ 35.2.

$Ph_2PC{\equiv}CPPh_2$. The dropwise addition of $Ph_2PC{\equiv}CPPh_2$ (36 mg, 0.135 mmol) dissolved in dichloromethane (2 mL) to a stirred solution of **1** (77 mg, 0.146 mmol) in dichloromethane (15 mL) resulted in an instant color change from green to orange. Removal of the solvent under reduced pressure gave a red residue. Workup by TLC with a 3:1 mixture of petroleum ether and dichloromethane as the eluent gave two major bands. An orange band was extracted with dichloromethane, and the solvent was removed under reduced pressure to yield orange crystals of (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CPPh_2$) (**4**, R = PPh_2; 69 mg, 51%). Anal. Calcd for $C_{41}H_{30}F_6OP_2Rh_2$: C, 53.5; H, 3.3; F, 12.4; P, 6.8. Found: C, 53.7; H, 3.3; F, 12.5; P, 6.4. MS, *m*/*z*: 920 (<1, $[M]^+$), 892 (<1, $[M - CO]^+$), 526 (6, $[M - Ph_2PC{\equiv}CPPh_2]^+$), 498 (<1, $[M - Ph_2PC{\equiv}CPPh_2 - CO]^+$), 394 (30, $[Ph_2PC{\equiv}CPPh_2]^+$), 233 (62, $[C_{10}H_{10}Rh]^+$), 168 (100, $[C_5H_5Rh]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1987 (vs), ν(C≡C) 2111 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.00 (s, 5H, C_5H_5), 5.18 (dd, $^2J_{RhH}$ = 1.6 Hz, $^3J_{PH}$ = 0.3 Hz, 5H, C_5H_5), 7.2−7.6 (m, 16H, *ortho*- and *meta*-H of C_6H_5), 7.83 (m, 4H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −52.0 (q, $^5J_{FF}$ = 10.7 Hz, 3F, CF_3), −55.3 (m, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 297 K): δ 27.6 (br d, $^1J_{RhP}$ = 189 Hz, 1P, PPh_2), −30.8 (s, 1P, uncoordinated PPh_2).

Similar workup of a second orange band gave an orange solid, which was characterized spectroscopically as [(η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)]$_2$($\eta^1$:$\eta^1$-$Ph_2PC{\equiv}CPPh_2$) (31 mg, 15%). IR ($CH_2Cl_2$), cm^{-1}: ν(CO) 1991 (vs), ν(C≡C) 2116 (w) . ^1H NMR ($CDCl_3$, 400 MHz): δ 4.92 (s, 5H, C_5H_5), 4.95 (s, 5H, C_5H_5), 5.23 (d, $^2J_{RhH}$ = 1.2 Hz, 5H, C_5H_5), 5.25 (d, $^2J_{RhH}$ = 1.3 Hz, 5H, C_5H_5), 7.3−7.7 (m, 20H, C_6H_5). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −52.3 (m, 3F, CF_3), −55.3 (br m, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 297 K): δ 17.6 (br d, PPh_2).

$Ph_2PC{\equiv}CPh$. In similar manner, a mixture of $Ph_2PC{\equiv}CPh$ (45 mg, 0.157 mmol) and **1** (82 mg, 0.155 mmol) in dichloromethane (20 mL) was stirred for a few minutes. The green solution immediately turned to a reddish color. The reaction

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mixture was filtered, and the solvent was then removed from the filtrate under reduced pressure. The residue was washed with cold pentane. This gave orange crystals of (η^5-C_5H_5)$_2$-Rh_2(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(η^1-$Ph_2PC{\equiv}CPh$) (**4,** R = Ph; 123 mg, 97%). Anal. Calcd for $C_{35}H_{25}F_6OPRh_2$: C, 51.8; H, 3.1; F, 14.0. Found: C, 52.3; H, 3.3; F, 13.5. MS, *m*/*z*: 812 (5, $[M]^+$), 784 (100, $[M - CO]^+$), 233 (10, $[C_{10}H_{10}Rh]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1986 (vs), ν(C≡C) 2176 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.11 (s, 5H, C_5H_5), 5.21 (d, $^2J_{RhH}$ = 1.5 Hz, 5H, C_5H_5), 7.3−7.5 (m , 13H, *ortho*- and *meta*-H of C_6H_5), 7.99 (m, 2H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 376.5 MHz): two isomers were evident in the ratio 96:4; major isomer δ −51.7 (q, $^5J_{FF}$ = 11.2 Hz, 3F, CF_3), −55.2 (qdd, $^5J_{FF}$ = 11.2 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.5 Hz, 3F, CF_3); minor isomer δ −51.6 (poorly resolved m, 3F, CF_3), −54.7 (poorly resolved m, 3F, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 297 K): δ 30.8 (d, $^1J_{RhP}$ = 170 Hz, PPh_2).

$Ph_2PC{\equiv}CMe$. When a solution of $Ph_2PC{\equiv}CMe$ (39 mg, 0.174 mmol) in dichloromethane (8 mL) was added dropwise to a stirred solution of **1** (90 mg, 0.171 mmol) in dichloromethane (20 mL), the green solution instantly turned to a reddish color. After filtration of the reaction mixture and removal of the solvent under reduced pressure, the residue was washed with cold pentane. This gave (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CCH_3$) (**4,** R = Me; 129 mg, 100%) as orange crystals. Anal. Calcd for $C_{30}H_{23}F_6OPRh_2$: C, 48.0; H, 3.1; F, 15.2; P, 4.1. Found: C, 47.9; H, 2.9; F, 15.1; P, 4.2. MS, *m*/*z*: 750 (10, $[M]^+$), 722 (60, $[M - CO]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 168 (22, $[C_5H_5Rh]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1985 (vs), ν(C≡C) 2205 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.04 (d, $^4J_{PH}$ = 3.5 Hz, 3H, CH_3), 5.09 (s, 5H, C_5H_5), 5.17 (d, $^2J_{RhH}$ = 1.7 Hz, 5H, C_5H_5), 7.2−7.5 (m , 8H, *ortho*- and *meta*-H of C_6H_5), 7.93 (m, 2H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 376.5 MHz): two isomers were evident in the ratio 96:4; major isomer δ −52.0 (qd, $^5J_{FF}$ = 11.5 Hz, $^3J_{RhF}$ = 1.6 Hz, 3F, CF_3), −55.1 (qdd, $^5J_{FF}$ = 11.5 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.5 Hz, 3F, CF_3); minor isomer δ −51.9 (qd, $^5J_{FF}$ = 11.4 Hz, $^3J_{RhF}$ = 3.0 Hz, 3F, CF_3), −54.7 (qdd, $^5J_{FF}$ = 11.4 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.6 Hz, 3F, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 297 K): δ 30.9 (d, $^1J_{RhP}$ = 188 Hz, PPh_2).

$Ph_2PC{\equiv}CH$. $Ph_2PC{\equiv}CH$ (21 mg, 0.100 mmol) was dissolved in dichloromethane (5 mL) and added dropwise to a stirred solution of **1** (53 mg, 0.101 mmol) in dichloromethane (10 mL). The green solution instantly changed to a red color. Immediate removal of the solvent under reduced pressure left a red-brown residue. NMR results indicated that the product was not pure, but attempts to purify it by recrystallization or TLC resulted in further decomposition. The orange complex was characterized spectroscopically as (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CH$). MS, *m*/*z*: 736 (<1, $[M]^+$), 708 (<2, $[M - CO]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1988 (s), ν(C≡C) 2057 (w). ^{1}H NMR (toluene-d_8, 300 MHz): δ 4.30 (s, 1H, C≡C−H), 4.95 (s, 5H, C_5H_5), 5.04 (d, $^2J_{RhH}$ = 1.7 Hz, 5H, C_5H_5), 6.9−7.8 (m, 10H, C_6H_5). ^{19}F NMR (toluene-d_8, 282 MHz): δ −49.6 (q, $^5J_{FF}$ = 11.3 Hz, 3F, CF_3), −53.5 (qdd, $^5J_{FF}$ = 11.3 Hz, $^3J_{RhF}$ = $^4J_{PF}$ = 3.3 Hz, 3F, CF_3). ^{31}P{^{1}H} NMR (toluene-d_8, 162 MHz, 297 K): δ 31.4 (br d, $^1J_{RhP}$ = 181 Hz, PPh_2).

Conversion of (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CR$) (4) to ($\eta^5$-$C_5H_5$)$_2$$Rh_2$($\mu$-C($CF_3$)C($CF_3$)C{C(O)R}-$PPh_2$) (6). R = Me. A spectroscopically pure sample of (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CMe$) (**4**, R = Me) (97 mg, 0.129 mmol) was chromatographed by TLC with a 3:1 mixture of petroleum ether and dichloromethane as the eluent. The chromatogram was left to develop for 1 h; this separated three bands from an immobile base band containing decomposition material. A minor purple band was rejected. The two major bands were individually extracted with dichloromethane, and solvent was removed under reduced pressure. The first extract (orange) was identified as unchanged **4** (4 mg). The infrared spectrum of the second extract (87 mg) indicated it was a mixture of **4** and a new compound with an acyl carbonyl absorption near 1660 cm^{-1}. This extract was dissolved in dichloromethane to which some silica gel (ca. 0.3 g) was added. The suspension was then stirred at room temperature for 18 h without protection from the air. Periodic monitoring by infrared spectroscopy indicated a gradual increase in the intensity of the acyl carbonyl absorption near 1660 cm^{-1}. Further TLC of the material with a 3:1 mixture of petroleum ether and dichloromethane as the eluent separated two orange bands. Each was extracted with dichloromethane. The infrared spectrum of the first extract indicated it was still a mixture of **4** and the new product. Evaporation of solvent gave 8 mg of residue. Evaporation of solvent from the second extract gave an orange crystalline solid, which was identified as (η^5-C_5H_5)$_2$$Rh_2$($\mu$-C($CF_3$)C($CF_3$)C{C(O)Me}$PPh_2$) (**6,** R = Me; 57 mg, 60%), mp 280 °C. Anal. Calcd for $C_{29}H_{23}F_6OPRh_2$: C, 47.2; H, 3.1; F, 15.4; P, 4.2. Found: C, 47.0; H, 3.2; F, 15.5; P, 4.4. MS, *m*/*z*: 738 (100, $[M]^+$), 661 (60, $[M - Ph]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1661 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.08 (d, $^4J_{PH}$ = 1.6 Hz, 3H, CH_3), 5.17 (d, $^2J_{RhH}$ = 1.0 Hz, 5H, C_5H_5), 5.46 (d, $^2J_{RhH}$ = 0.8 Hz, 5H, C_5H_5), 7.2−7.5 (m , 8H, *ortho*- and *meta*-H of C_6H_5), 7.74 (m, 2H, *para*-H of C_6H_5). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −46.4 (qdd, $^5J_{FF}$ = 12.4 Hz, $^4J_{PF}$ = $^3J_{RhF}$ = 3.4 Hz, 3F, CF_3), −51.0 (qd, $^5J_{FF}$ = 12.4 Hz, $^3J_{RhF}$ = 1.0 Hz, 3F, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 297 K): δ 62.0 (d, $^1J_{RhP}$ = 153 Hz, PPh_2).

R = Ph. A similar experiment was performed with (η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($\eta^1$-$Ph_2PC{\equiv}CPh$) (**4**, R = Ph). TLC of the complex (40 mg, 0.129 mmol) with a 3:1 mixture of petroleum ether and dichloromethane as the eluent separated a major orange band from trace amounts of yellow and orange compounds, which were rejected. After 2.5 h, the major orange band was extracted with dichloromethane and the solvent was removed under reduced pressure. This gave dark orange crystals of (η^5-C_5H_5)$_2$$Rh_2$($\mu$-C($CF_3$)C($CF_3$)C{C(O)Ph}-$PPh_2$) (**6**, R = Ph; 36 mg, 91%), mp ∼210 °C. Anal. Calcd for $C_{34}H_{25}F_6OPRh_2$: C, 51.0; H, 3.2; F, 14.2. Found: C, 50.8; H, 3.2; F, 14.1. MS, *m*/*z*: 800 (28, $[M]^+$), 723 (20, $[M - Ph]^+$). IR (CH_2Cl_2), cm^{-1}: ν(CO) 1660 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.13 (d, $^2J_{RhH}$ = 1.5 Hz, 5H, C_5H_5), 5.49 (d, $^2J_{RhH}$ = 0.8 Hz, 5H, C_5H_5), 6.8−7.7 (m, 15H, C_6H_5). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −45.9 (q, $^5J_{FF}$ = 14.7 Hz, 3F, CF_3), −49.6 (qd, $^5J_{FF}$ = 14.7 Hz, $^3J_{RhF}$ = 2.5 Hz, 3F, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 297 K): δ 60.2 (dd, $^1J_{RhP}$ = 153 Hz, $^2J_{RhP}$ = 3.2 Hz, PPh_2).

Further Investigation of Factors Affecting the Conversion of 4 to 6, R = Ph; O_2. Oxygen was bubbled through a solution of **4** (3 mg) in dichloromethane for 1 h. The reaction solution was stirred at room temperature for a further 15 h. An infrared spectrum of the solution showed that **4** was the only species present.

H_2O. The complex **4** (4 mg) was dissolved in dichloromethane (10 mL) containing some added water (0.5 mL). Nitrogen was bubbled through the mixture, and it was then stirred at room temperature for 15 h. The mixture was dried over calcium chloride and filtered. An infrared spectrum of the filtrate established that only unchanged **4** was present.

SiO_2. Oven dried silica (0.5 g) was added to a solution of **4** (4 mg) in dichloromethane (10 mL). The solution was stirred for 15 h under a nitrogen atmosphere. The silica was removed by filtration. An infrared spectrum of the filtrate revealed only unchanged **4**.

SiO_2 + H_2O. A slurry containing **4** (4 mg), silica (0.5 g), dichloromethane (10 mL), and water (0.5 mL) was stirred under nitrogen for 15 h. Filtration followed by infrared examination showed that no reaction had occurred.

SiO_2 + O_2. Oxygen was bubbled through a slurry containing **4** (5 mg) and silica (0.5 g) in dichloromethane (10 mL). The slurry was stirred for 15 h under an oxygen atmosphere and was then filtered. An infrared spectrum of the filtrate showed the presence of **6** (R = Ph, medium intensity ν(CO) absortion at 1661 cm^{-1}) and a trace of unchanged **4** (weak ν-(CO) absortion at 1985 cm^{-1}).

Comparison of Extent of Conversion of 4 with R = Ph and 4 with R = Me. Samples of **4** with R = Ph (6 mg) and **4** with R = Me (6 mg) were applied to separate halves of a

Table 1. Crystal Data and Experimental Details

formula	$Rh_2C_{34}H_{25}F_6OP$
fw	800.4
cryst syst	triclinic
space group	$P\bar{1}$
cell dimens	
a	14.165(2) Å
b	11.707(1) Å
c	9.522(1) Å
α	71.893(5)°
β	83.693(4)°
γ	86.801(8)°
cell vol, *Z*	1491.4(3) Å^3, 2
density (calcd, obs)	1.78, 1.78(1) g cm^{-3}
F(000)	792
abs coeff	1.21 mm^{-1}
Mo Kα radiation	(λ = 0.7107 Å)
temp	20(1) °C

single TLC plate. The complexes were slowly eluted with a 3:1 mixture of petroleum ether and dichloromethane without protection from the air. After 60 min, the plate was removed from the eluent mix. The chromatogram for **4** with R = Me showed three orange bands which were extracted together. Analysis of the combined extract by ^{19}F NMR spectroscopy established that the mixture contained 20% **4** and 80% **6**. For **6**, R = Ph, the chromatogram showed one major orange band and several minor bands, which were rejected. Extraction of the orange band followed by ^{19}F NMR analysis showed that it contained only **6**.

Reactions of 1 with $Ph_2P(O)C{\equiv}CR$. $Ph_2P(O)C{\equiv}CPh$. $Ph_2P(O)C{\equiv}CPh$ (31 mg, 0.103 mmol) was dissolved in dichloromethane (3 mL) and added dropwise to a stirred solution of **1** (24 mg, 0.045 mmol) in dichloromethane (5 mL). The green solution was stirred for 24 h; during this time, the color of the solution changed to a red-brown color. The solvent was removed under reduced pressure, and the residue was purified by TLC with a 1:1:1 mixture of petroleum ether, acetone, and diethyl ether as the eluent. After the major red-orange band was extracted with acetone and the solvent was removed under reduced pressure, $(\eta^5\text{-}C_5H_5)_2Rh_2[\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_4(CF_3)_2\{P(O)Ph_2\}(Ph)CO]$ (**2**, 17 mg, 45%) was obtained as red-brown crystals. MS, m/z: 828 (12, $[M]^+$), 800 (14, $[M - CO]^+$), 751 (8, $[M - Ph]^+$). IR (CH_2Cl_2) cm^{-1}: ν(CO) 1712 (m), ν (P=O) 1184 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.49 (s, 5H, C_5H_5), 5.71 (s, 5H, C_5H_5), 7.0−7.95 (m, 15H, C_6H_5). ^{19}F NMR ($CDCl_3$,): δ −48.9 (q, $^5J_{FF}$ = 11.3 Hz, 3F, CF_3), −54.9 (q, $^5J_{FF}$ = 11.3 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 31.6 (s, $Ph_2P{=}O$).

$Ph_2P(O)C{\equiv}CMe$. $Ph_2P(O)C{\equiv}CMe$ (20 mg, 0.083 mmol) was dissolved in dichloromethane (4 mL) and added dropwise to a stirred solution of **1** (21 mg, 0.040 mmol) in dichloromethane (5 mL). The green solution was stirred for 4 days; the color of the final solution was orange. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, and hexane was added to precipitate out excess $Ph_2P(O)C{\equiv}CMe$, which was removed by filtration. The red filtrate was evaporated to dryness, yielding red crystals of $(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C_4(CF_3)_2\{P(O)Ph_2\}Me\}$ (**3**, 14 mg, 49%). MS, *m*/*z*: 729 (42, $[M]^+$), 723 (3, $[M - Me]^+$), 710 (6, $[M - F]^+$), 673 (30, $[C_{24}H_{18}R_2F_6PO]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 168 (48, $[C_5H_5Rh]^+$). IR (CH_2Cl_2) cm^{-1}: ν(P=O) 1198 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (d, $^4J_{PH}$ = 2.1 Hz, 3H, CH_3), 4.68 (s, 5H, C_5H_5), 5.77 (d, $^2J_{RhH}$ = 0.6 Hz, 5H, C_5H_5), 7.42−7.87 (m, 10H, C_6H_5). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −48.1 (q, $^5J_{FF}$ = 13.6 Hz, 3F, CF_3), −50.1 (q, $^5J_{FF}$ =13.6 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 32.9 (s, $Ph_2P{=}O$).

X-ray Structure Determination. Crystals of **6** (R = Ph) were grown by slow evaporation of the solvent from a solution in dichloromethane. A representative dark red tabular crystal of approximate dimensions (0.16 × 0.18 × 0.26 mm) was used for data collection. Intensity measurements were made on a Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation with 6° < 2θ ≤ 60°, operating in an ω scan mode with a symmetric scan range of ±(0.75 + 0.15 tan θ) from the calculated Bragg scattering angle at a scan rate of 0.05° s^{-1}. A total of 8699 unique data were collected, (±*h*,±*k*,+*l*), 5458 of which were considered to be observed ($I \geq 3\sigma(I)$) and used in the final refinement. Three standard reflections monitored every 4 h showed no significant variation in intensity over the data collection period. Crystal data are given in Table 1. The cell parameters were determined from 24 accurately centered reflections measured in the range 18° < 2θ ≤ 40° and were refined by least-squares methods using the standard Philips program.

Intensity data were processed as described previously.[27] A face-indexed numerical absorption correction was applied[28] on six crystal faces, the maximum and minimum transmission factors being 0.844 and 0.778, respectively. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion.[29] All calculations were performed on a VAX 6250 computer. The program used for least-squares refinement was SHELX-76.[28]

The structure was solved by conventional Patterson and Fourier methods. Final refinement was by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms and a single isotropic thermal parameter for hydrogen (which refined to 0.070(3) Å^2) positioned in geometrically idealized positions (d(C−H) = 0.96 Å). At convergence (398 variables, 5458 observed data), R was 0.039 and R_w = 0.039, where $R_w = \sum|F_o - F_c|)w^{1/2}/\sum|F_o|w^{1/2}$ and $w = [\sigma^2(F_o)]^{-1}$. The goodness of fit value ($[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$) was 1.31. The highest peak in the difference Fourier synthesis was 0.94 e·Å^{-3}.

Final atomic parameters are given in the Supporting Information, selected bond lengths in Table 2 and selected bond angles in Table 3. Figure 1 shows the atomic labeling scheme used.

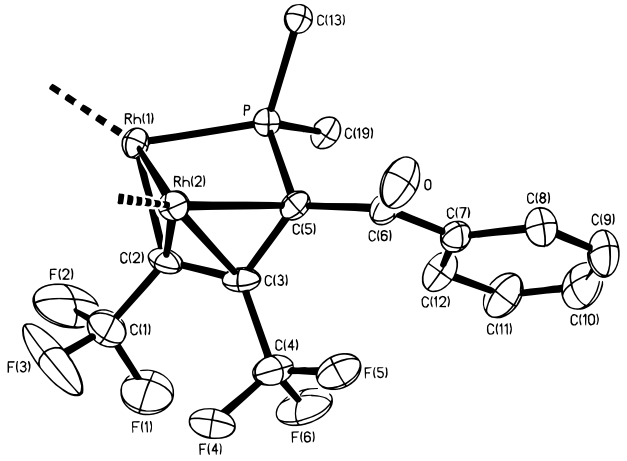


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}C(CF_3)C(CF_3)C\{C(O)Ph\}PPh_2)$ (**6**; R = Ph) showing the atom labeling scheme; the cyclopentadienyl rings (C(25)−C(29)) and (C(30)−C(34)) are omitted for clarity.

Table 2. Selected Bond Lengths (Å) for 6 (R = Ph), with Esd Values in Parentheses

Rh(1)−P	2.187(1)	C(2)−C(3)	1.385(7)
Rh(1)−C(2)	2.037(4)	C(3)−C(5)	1.468(6)
Rh(1)−Rh(2)	2.6751(4)	C(5)−C(6)	1.524(7)
Rh(2)−C(2)	2.105(4)	C(6)−O	1.207(5)
Rh(2)−C(3)	2.047(4)	C(6)−C(7)	1.493(6)
Rh(2)−C(5)	2.148(4)	P−C(5)	1.815(4)
Rh(2)···P	2.941(1)	P−C(13)	1.828(4)
		P−C(19)	1.836(4)

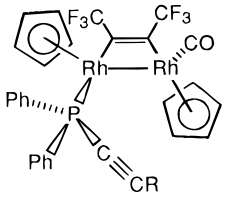
(27) Fallon, G. D.; Gatehouse, B. M. *J. Solid State Chem.* **1980**, *34*, 193.
(28) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; Cambridge University: Cambridge, England, 1975.
(29) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 3. Selected Bond Angles (deg) for 6 (R = Ph), with Esd Values in Parentheses

C(2)−Rh(1)−P	83.0(1)	C(5)−P−Rh(1)	100.0(1)
C(2)−Rh(1)−Rh(2)	50.9(1)	C(13)−P−C(19)	103.0(2)
P−Rh(1)−Rh(2)	73.7(0)	C(13)-P-Rh(1)	115.4(1)
C(3)−Rh(2)−C(2)	39.0(2)	C(19)−P−Rh(1)	118.9(2)
C(3)−Rh(2)−C(5)	40.9(2)	C(2)−C(3)−C(5)	115.4(3)
C(3)−Rh(2)−Rh(1)	77.2(1)	C(3)−C(5)−C(6)	125.0(3)
C(2)−Rh(2)−C(5)	69.1(2)	C(3)−C(5)−P	110.1(3)
C(2)−Rh(2)−Rh(1)	48.7(1)	C(6)−C(5)−P	120.9(3)
C(5)−Rh(2)−Rh(1)	78.4(1)	O−C(6)−C(7)	120.4(4)
C(5)−P−C(13)	110.6(2)	O−C(6)−C(5)	120.4(4)
C(5)−P−C(19)	108.8(2)	C(7)−C(6)−C(5)	119.2(3)

Results

Formation of the Complexes (η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(η^1-$Ph_2PC{\equiv}CR$), R = Bu^t, CF_3 or PPh_2. When $Ph_2PC{\equiv}CBu^t$ was added to **1** in dichloromethane, the color of the solution changed immediately from green to red. Chromatographic workup yielded (η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(η^1-$Ph_2PC{\equiv}CBu^t$), which was isolated as red-orange crystals in almost 80% yield. Formation of this complex occurs without the loss of ligands from **1** and involves the well-established 90° rotation of the alkyne.[1] The product has been fully characterized by elemental analysis and various spectroscopic techniques, which indicate that the phosphinoalkyne is attached exclusively from phosphorus. Thus, the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet resonance at δ 28.3 with a rhodium−phosphorus coupling of 188 Hz, and there is a free alkyne stretching absorption in the IR spectrum at 2169 cm^{-1}. The IR spectrum also shows a terminal carbonyl absorption at 1985 cm^{-1}. These and other spectroscopic results are consistent with the structure of **4** with R = Bu^t, which is analogous to those established for other complexes of the type (η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(L).[2,30] In these complexes, the preferred orientation of CO and



4

L is *trans*, but in the present case, the ^{19}F NMR spectrum shows that a small amount of the corresponding *cis* isomer is also present, with the ratio of *trans:cis* being 95:5. We have not previously seen evidence for both *cis* and *trans* isomers of the complexes (η^5-C_5H_5)$_2$-Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(L) when L is a tertiary phosphane. However, when L = CO, the two isomers can be separated by TLC and the *cis* isomer transforms to the *trans* isomer when left in solution.[31]

The $^{31}P\{^1H\}$ NMR spectrum of **4** (R = Bu^t) showed an unusual temperature dependence, which is illustrated in Figure 2. The doublet is sharp and well-resolved at low temperature (−83 °C) but is broad and unresolved near room temperature. When the solution is warmed further, the peaks begin to sharpen again. We suggest that these changes can be related to rotation

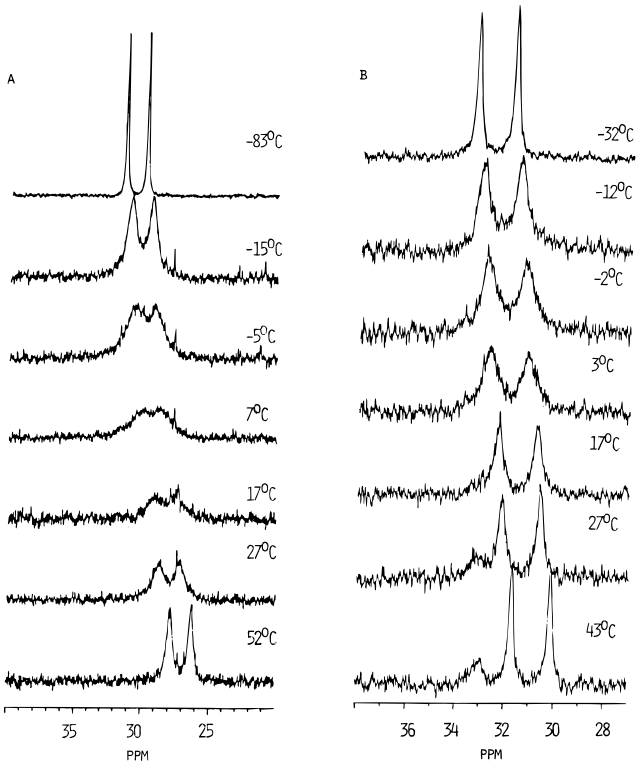


Figure 2. Variable temperature $^{31}P\{^1H\}$ NMR spectra for (η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(η^1-$Ph_2PC{\equiv}CR$): (a) R = Bu^t, (b) R = Me.

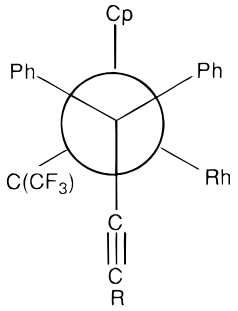


Figure 3. Fischer projection down the P−Rh bond of one rotamer of complex **4**.

of the coordinated phosphinoalkyne about the Rh−P bond. From steric considerations, three orientations of the phosphinoalkyne would be favored. One of these is represented in Figure 3; the others are generated by 120° rotations of one set of ligands. At elevated temperatures, rotation would be rapid, leading to a sharp doublet in the NMR spectrum. At reduced temperature, one conformer could be frozen out, again generating a sharp doublet. The doublet would be broad and poorly resolved at intermediate temperatures. It is interesting to note that restricted rotation about Rh−P bonds has been observed previously for the complexes (η^5-C_5Me_5)-Rh{P(*p*-tolyl)$_3$}(C_6F_5)Br[32] and (η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$){P(*p*-tolyl)$_3$}.[33]

An analogous complex (**4**, R = CF_3) was obtained in quantitative yield when $Ph_2PC{\equiv}CCF_3$ was added to **1**. Spectroscopic results indicated a 93:7 ratio of *trans* to *cis* isomer for this orange complex.

When $Ph_2PC{\equiv}CPPh_2$ was added to **1**, the complex **4** with R = PPh_2 was formed as orange crystals in greater than 50% yield. Again, the spectroscopic results (see

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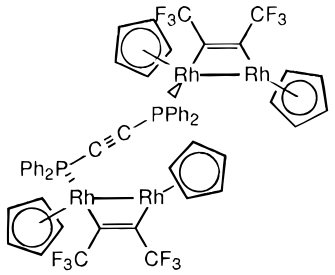
Experimental Section) were consistent with the proposed structure. At −50 °C, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at δ 27.6, with Rh−P coupling of 189 Hz, and a singlet at δ −30.8. This clearly indicates that only one phosphorus atom is coordinated to rhodium. Again, the doublet broadens significantly as the temperature of the solution is raised toward room temperature, but the resonance for the uncoordinated phosphorus remains sharp.

A second product is isolated from this reaction, and it has been characterized spectroscopically as $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\eta^1\text{:}\eta^1\text{-}Ph_2PC{\equiv}CPPh_2)$ (**5**). The $^{31}P\{^1H\}$ NMR spectrum of this

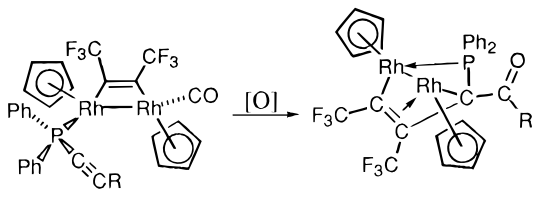


5

product shows a single broad doublet at δ 17.6, but other spectroscopic properties are similar to those of **4** with R = PPh_2. The isolated yield of **5** was 15%. The complex **5** is presumably formed by the further reaction of **4** (R = PPh_2) with **1**. Similar reactions have been observed with $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)(L)$, where L is a bis(phosphine) of the type $Ph_2P(CH_2)_n\text{-}PPh_2$.[34]

Reaction of 1 with $Ph_2PC{\equiv}CR$ (R = Ph, Me, H). Each of the phosphinoalkynes $Ph_2PC{\equiv}CR$ (R = Ph, Me, H) adds coordinatively to **1** to give the appropriate addition product **4**. The complex **4** with R = H could not be obtained analytically pure because it decomposed when kept in solution during attempted recrystalization and chromatography. The spectroscopic results for these complexes (see Experimental Section) are similar to those previously discussed for **4** with R = Bu^t. The $^{31}P\{^1H\}$ NMR spectra for the complexes **4** with R = Ph and Me display the same type of temperature dependence as described previously for **4** with R = Bu^t and PPh_2). However, the extent of line broadening at intermediate temperatures depends on the mass of the alkyne substituent. The spectra for **4** with R = Bu^t and **4** with R = Me are compared in Figure 2. Presumably, there is a shallower energy well for the rotation when the substituent has a lower mass.

When the complexes **4** with R = Ph and Me are stirred in solution in the presence of chromatographic silica and oxygen, there is a transformation to new complexes of the formula $(\eta^5\text{-}C_5H_5)Rh_2(\mu\text{-}C(CF_3)C(CF_3)C\{C(O)R\}PPh_2)$ (**6**). A molecular ion is observed for these



4 **6**

complexes in the mass spectrum. In the infrared spectra, no absorptions are observed for a terminal carbonyl or a free C≡C bond; there is however, an absorption within the region of 1660−1695 cm^{-1} which is attributed to a ketonic carbonyl. In the ^1H and ^{19}F NMR spectra, there are two cyclopentadienyl and two trifluoromethyl resonances consistent with an unsymmetrical structure. There is a doublet resonance near δ 61−64 in the $^{31}P\{^1H\}$ NMR spectra with rhodium−phosphorus couplings of 127 (R = H) and 167 (R = Ph) Hz. These chemical shifts are moved about 30 ppm downfield from those for the initial complexes **4**.

At face value, these data are consistent with the formal loss of C in the conversion of **4** to **6**. This probably arises through the loss of CO and the gain of O. However, the precise nature of the new ligand in **6** is difficult to visualize. Since it was not possible to deduce the structure of **6** from the spectroscopic evidence, determination of the molecular structure of one of the complexes (R = Ph) was undertaken by X-ray crystallography. Figure 1 shows a molecular core diagram of the structure of the complex (**6**, R = Ph). It demonstrates that components of the phosphinoalkyne and the fluorinated alkyne have condensed to form a unit of the type $C(CF_3){=}C(CF_3)C\{C(=O)R\}PPh_2$. The new ligand is attached to the Rh−Rh bond as shown in Figure 4. The P and C(2) ends of the ligand are σ-attached to one rhodium atom, and there is an $\eta^2\text{:}\eta^1$-linkage of C(2)−C(3)−C(5) to the second rhodium atom. The incorporation of a ketonic function in the new ligand is of particular interest; the ketonic oxygen is not involved in the attachment. Although the source of the oxygen in the ligand has not been determined, we favor a concerted pathway involving the loss of the terminal carbonyl in **4**, transfer of an oxygen atom from the oxygenated silica surface to the β-carbon of the phosphinoalkyne, and condensation of the phosphino−ketone and hexafluorobut-2-yne units. The overall process is outlined in Figure 5.

It is known that the uncoordinated triple bonds in coordinated phosphinoalkynes are susceptible to nucleophilic attack. For example, phosphino−enolates are formed by the controlled hydrolysis of complexes of the type *cis*-$[MCl_2(Ph_2PC{\equiv}CCF_3)_2]$, where M = Pd or Pt.[7,8] We have also previously reported the transfer of oxygen atoms from silica to ligand atoms during the chromatographic workup of the complex $(\eta^5\text{-}C_5H_5)_2Rh_2\{\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)C(H)C(Bu^t)\}$; in this case, the product incorporates an unsaturated keto−ether.[35] There are also many examples of condensation reactions between hexafluorobut-2-yne and transient species coordinated to the Rh−Rh bond in intermediates derived from **1**.[36] An alternative pathway involving cleavage of the P−C and/or C≡C bonds and CO insertion is much less likely because it involves the need for elimination of one of the alkyne carbons.

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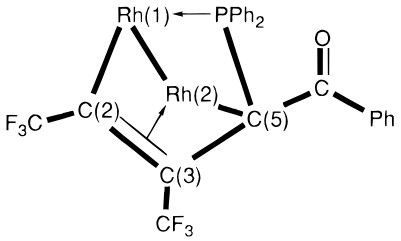

Figure 4. Representation of the bonding in complex **6** (R = Ph).

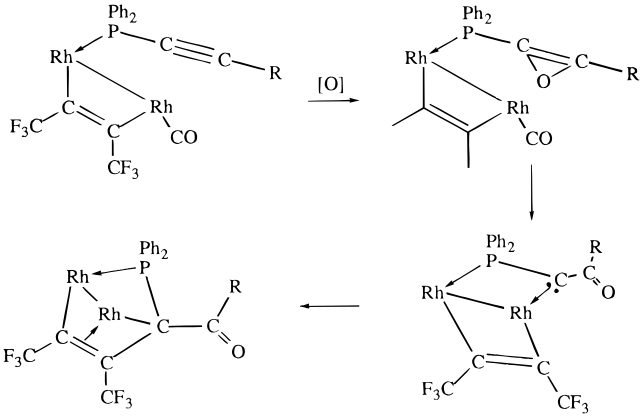

Figure 5. Pathway for the conversion of **4** to **6**; cyclopentadienyl groups omitted for clarity.

We are aware of several examples of metal complexes containing related phosphino-enolato ligands. These are formed by reaction of nickel complexes with phenacylidenetriphenylphosphoranes, $Ph_3P{=}CHC(=O)R$,[37] or of rhodium complexes with β-keto phosphines, $Ph_2PCH(R)C(=O)R'$,[38] and in each case, there is a three-electron P−O chelation of the ligand to the metal. It is interesting that some phosphino−enolato ruthenium(II) complexes react with alkynes to form ligands of the type $C(H){=}C(R)CR'\{C{=}O)R''\}PPh_2$, which are closely related to the one in our complex. However, in the ruthenium complex, the new ligand is η^3-coordinated with attachments from P, C, and a ketonic oxygen.[39]

Reactions of 1 with $Ph_2P(O)C{\equiv}CR$. Before the structure of **6** was established, it seemed possible that oxygen addition was to the phosphorus atom. To help assess this idea, the reactions of **1** with two phosphine oxides $Ph_2P(O)C{\equiv}CR$ (R = Ph, Me) were investigated. These reactions occurred slowly at room temperature, and the phosphine oxides behaved as alkynes. Different products were obtained for the two systems.

The reactions with $Ph_2P(O)C{\equiv}CPh$ yielded the dimetallapentadienone product $(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_4(CF_3)_2(Ph_2PO)(Ph)CO\}$ in 45% yield. Spectroscopic data indicates that this has the structure of **2** (R, R′ = Ph_2PO, Ph). The cyclometallabutadiene complex $(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^2{:}\eta^4\text{-}C_4(CF_3)_2(Ph_2PO)(Me)\}$ was obtained in 49% yield from the reaction with $Ph_2P(O){\equiv}CMe$.

Acknowledgment. We thank the Australian Research Council for financial support.

Supporting Information Available: Tables of atomic positional coordinates, anisotropic thermal parameters, bond lengths, and bond angles, as well as a complete structural diagram for **6** (R = Ph) (13 pages). Ordering information is given on any current masthead page.

OM960830E

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