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Synthesis and Structure of the Unusual 30-Electron Homobinuclear Vinylidene-Bridged Complexes $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHR)(CO)_2(PCy_3)_2]BF_4$

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*Summary: The alkynyl complexes $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph (**1**), CO_2CH_3 (**3**), $SiMe_3$ (**6**)) react with $HBF_4{\cdot}OEt_2$ to give the vinylidene-bridged rhodium derivatives $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHR)(CO)_2(PCy_3)_2]BF_4$ (R = Ph (**2**), CO_2CH_3 (**4**), H (**5**)). The molecular structure of complex **2** has been determined; crystals of **2** are monoclinic, space group $P2_1/n$ with a = 10.377(12) Å, b = 28.526(2) Å, c = 17.155(2) Å, β = 91.53(1)°, and Z = 4. On the basis of X-ray analysis, the cation of **2** can be described as a dinuclear species of 30 valence electrons, which contains a single rhodium–rhodium bond (d(Rh–Rh) = 2.6557(5) Å). Additionally, the metal centers are bridged by a vinylidene ligand and a carboxylate group.*

Introduction

Vinylidene complexes have been shown to be useful intermediates in the synthesis of novel organic compounds.[1] Furthermore, it has been suggested that they can play an important role in Fischer–Tropsch chemistry,[2] in carbon–carbon bond formation, in the condensation of alkynes with other substrates,[3] and in reactions such as the hydrogenation,[4] hydrosilylation,[5] disproportionation,[4] and polymerization[6] of alkynes.

Although the majority of vinylidene complexes are mononuclear, dinuclear vinylidene-bridged compounds are attracting recent interest. In that sense, it should be pointed out that the homobinuclear vinylidene-bridged complexes previously reported are species of 32 or 34 valence electrons.[7]

Following our previous work,[8] we have recently reported the synthesis and structural characterization of μ-acetylide compounds of the type $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph, CO_2H_3, $SiMe_3$).[9] We have now observed that these complexes react with $HBF_4{\cdot}OEt_2$ to give $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHR)(CO)_2(PCy_3)_2]BF_4$ derivatives (R = Ph, CO_2CH_3, H),[10] which are the first examples of cationic vinylidene-bridged rhodium compounds and, furthermore, have 30 valence electrons.

Results and Discussion

Treatment of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (**1**) with 1 equiv of $HBF_4{\cdot}OEt_2$ in diethyl ether at room temperature gives a red solution from which the compound $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$ (**2**) is afforded as a red solid in 60% yield. Under similar conditions, the complex $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2CO_2CH_3)(CO)_2(PCy_3)_2]$ (**3**) leads to $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHCO_2CH_3)(CO)_2(PCy_3)_2]BF_4$ (**4**) in 82% yield.

A single-crystal X-ray diffraction analysis of **2** demonstrates the presence of the vinylidene-bridged ligand in these complexes. Figure 1 shows an ORTEP drawing of the molecular structure of the cation of **2**. Selected bond distances and angles are listed in Table I.

This cation can be described as a dinuclear species of 30 valence electrons, which contains a single rhodium–rhodium bond. The Rh–Rh distance (2.6557(5) Å) compares well with those found for the vinylidene-bridged compounds $[Rh_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\eta^4\text{-}C_4(CF_3)_2H\text{-}t\text{-}BuCO\}(\mu\text{-}C{=}CH\text{-}t\text{-}Bu)]$ (2.625(2) Å),[11] $[Rh_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}C{=}CH_2)(CO)_2]$ (2.691(1) Å)[12] and $[Rh_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}C{=}C(CH_3)_2)(CO)_2]$ (2.684(0) Å).[13] The μ-carbon of the vinylidene group is nearly symmetrically bonded to metals with Rh–C distances of 1.984(5) and 2.015(5) Å. The C(5)–C(6) distance (1.318(7) Å) is a normal double bond distance, similar to those found in other binuclear vinylidene complexes.[7] Interestingly, the Rh(1)–C(5)–Rh(2) angle (83.2(2)°) agrees well with the related parameter involving the bridging carbonyl ligands in $[Rh_4(\mu\text{-}OOCCH_3)_4(\mu\text{-}$

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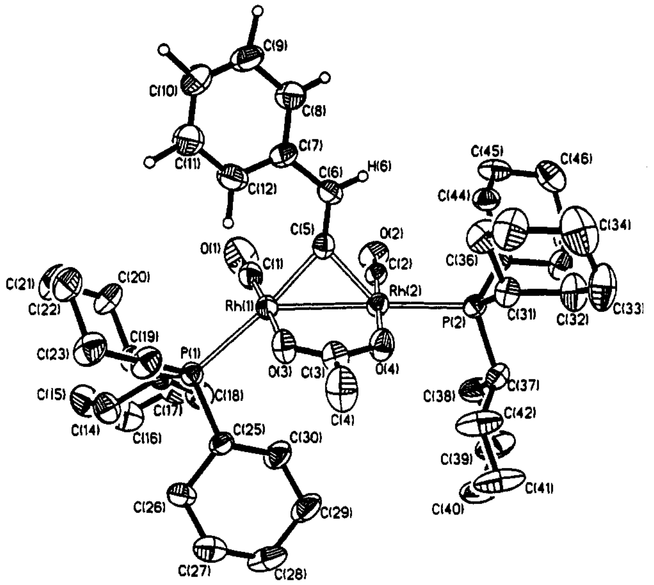

Figure 1. ORTEP diagram of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$ (**2**); 50% thermal ellipsoids are shown.

Table I. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$ (2)

Rh(1)–Rh(2)	2.6557(5)	Rh(2)–P(2)	2.329(1)
Rh(1)–P(1)	2.396(1)	Rh(2)–O(4)	2.062(3)
Rh(1)–O(3)	2.065(3)	Rh(2)–C(2)	1.812(5)
Rh(1)–C(1)	1.806(6)	Rh(2)–C(5)	1.984(5)
Rh(1)–C(5)	2.015(5)	O(2)–C(2)	1.145(6)
O(1)–C(1)	1.141(7)	O(4)–C(3)	1.261(6)
O(3)–C(3)	1.256(6)	C(5)–C(6)	1.318(7)
C(3)–C(4)	1.487(7)		
Rh(2)–Rh(1)–P(1)	139.30(4)	Rh(1)–Rh(2)–P(1)	171.99(4)
Rh(2)–Rh(1)–O(3)	82.5(1)	Rh(1)–Rh(2)–O(4)	85.8(1)
Rh(2)–Rh(1)–C(1)	99.2(2)	Rh(1)–Rh(2)–C(2)	95.7(2)
Rh(2)–Rh(1)–C(5)	49.9(1)	Rh(1)–Rh(2)–C(5)	48.4(1)
P(1)–Rh(1)–O(3)	85.8(1)	P(2)–Rh(2)–O(4)	86.3(1)
P(1)–Rh(1)–C(1)	93.2(2)	P(2)–Rh(2)–C(2)	92.2(2)
P(1)–Rh(1)–C(5)	171.3(2)	P(2)–Rh(2)–C(5)	130.5(1)
O(3)–Rh(1)–C(1)	178.2(2)	O(4)–Rh(2)–C(2)	177.7(2)
O(3)–Rh(1)–C(5)	91.2(2)	O(4)–Rh(2)–C(5)	94.1(2)
C(1)–Rh(1)–C(5)	89.6(2)	C(2)–Rh(2)–C(5)	88.3(2)
Rh(1)–C(1)–O(1)	179.9(5)	Rh(2)–C(2)–O(2)	177.8(4)
Rh(1)–O(3)–C(3)	125.1(3)	Rh(2)–O(4)–C(3)	121.2(3)
Rh(1)–C(5)–C(6)	132.8(4)	Rh(2)–C(5)–C(6)	143.9(4)
Rh(1)–C(5)–Rh(2)	83.2(2)	C(5)–C(6)–C(7)	124.7(5)

$CO)_4(NC_5H_4CH{=}NC_6H_4OC_{14}H_{29})_4]$ (84.6(3)° and 85.1(3)°).[8c]

Each rhodium atom is five-coordinate, and four of the five atoms directly bonded to the metals are arranged in a slightly distorted square planar disposition with the fifth atom located about 1.5 Å outside the plane. The atoms C(1), C(5), O(3), and P(1) form the square planar environment around the Rh(1) atom, while C(2), P(2), O(4), and Rh(1) form the square planar environment around Rh(2). This asymmetric disposition leads to a situation where the two phosphines exhibit different Rh–P distances (Rh(1)–P(1) 2.396(1) Å and Rh(2)–P(2) 2.329(1) Å) and consequently behave as nonequivalent chemical centers. Thus, consistently the $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ shows an ABXY splitting pattern (Figure 2a). The $^{31}P\{^1H\}$ NMR spectrum of **4** also shows an ABXY splitting pattern (for more details, see Experimental Section), suggesting that **4** has the same structure as **2**.

The $^{31}P\{^1H\}$ NMR spectrum of the complex $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CH_2)(CO)_2(PCy_3)_2]BF_4$ (**5**) shows a second-order AA′XX′ spin system, suggesting that its structure, in contrast to the structures of **2** and **4**, is symmetrical (Figure 2b). **5** was prepared similarly to **2** and **4** by treatment of the alkynyl compound $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2SiMe)(CO)_2(PCy_3)_2]$ (**6**) with $HBF_4{\cdot}OEt_2$. Furthermore, this reaction involves the cleavage of a Si–C bond. There are precedents in related processes. The vinylidene ligand $C{=}CH_2$ of the mononuclear compound $[OsI(\eta^6\text{-}C_6H_6)(C{=}CH_2)(PMe^tBu_2)]PF_6$ is produced from the reaction of $[OsI_2(\eta^6\text{-}C_6H_6)(PMe^tBu_2)]$ with $AgPF_6$ in the presence of (trimethylsilyl)acetylene.[14] The same alkyne and the complex $IrCl(P^iPr_3)_2$ have been used to prepare $[IrCl(C{=}CH_2)(P^iPr_3)_2]$.[15] The formation of the carbyne complex $[OsHCl_2(CCH_3)(P^iPr_3)_2]$ involves as intermediate the dihydrogen vinylidene compound $[OsCl_2(\eta^2\text{-}H_2)(C{=}CH_2)(P^iPr_3)_2]$, which is produced by reaction of $[OsH_2Cl_2(P^iPr_3)_2]$ with (trimethylsilyl)acetylene.[16]

In summary, the reactions of the alkynyl compounds $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph, CO_2CH_3, $SiMe_3$) with $HBF_4{\cdot}OEt_2$ have allowed us to prepare the first examples of cationic vinylidene-bridged rhodium derivatives; these complexes, $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHR)(CO)_2(PCy_3)_2]BF_4$ (R = Ph, CO_2CH_3, H), are also the first examples of homobinuclear vinylidene-bridged compounds with 30 valence electrons.

Experimental Section

All reactions were carried out by using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL 200 or Varian UNYT 300 spectrometer. Infrared spectra were run on a Perkin-Elmer 783 spectrometer using Nujol mulls on polyethylene sheets. The starting materials $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph (**1**), CO_2CH_3 (**3**), $SiMe_3$ (**6**)) were prepared by published methods.[9]

Preparation of $[Rh(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$ (2). A suspension of **1** (100 mg, 0.12 mmol) in 15 mL of diethyl ether was treated with $HBF_4{\cdot}OEt_2$ (16 μL, 0.12 mmol) resulting in an almost immediate color change to red. After the mixture was stirred for ca. 2 h, the resulting dark red solid was removed by filtration, washed with cold diethyl ether, and then dried under vacuum; yield 76 mg (60%). Anal. Calcd for $C_{48}H_{75}BF_4O_4P_2Rh_2$: C, 53.86; H, 7.01. Found: C, 53.41; H, 7.63. IR (cm^{-1}): ν(CO) = 2037, 1999; $\nu(C{=}C)$ = 1600; $\nu(OCOCH_3)_{asym}$ = 1545; $\nu(OCOCH_3)_{sym}$ = 1425. ^1H NMR ($CDCl_3$): δ 7.5 (Ph); 6.5 (d, C=CH, J_{Rh-H} = 1 Hz); 2.2–1.2 (Cy); 1.9 (s, O_2CCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 186.9–185.4 complicated signal (*C*=CHPh, 2CO, O_2CCH_3); 131.7 (s, C=*C*HPh); 128.5 (s, Ph); 127.7 (s, Ph); 127.4 (s, Ph); 34.8 (d, CH_2CHP, J_{P-C} = 20 Hz); 34.0 (d, CH_2CHP, J_{P-C} = 19 Hz); 30.4 (s, CH_2); 30.3 (s, CH_2); 30.1 (s, CH_2); 29.9 (s, CH_2); 27.5 (d, CH_2CHP, J_{P-C} = 10 Hz); 27.2 (d, CH_2CHP, J_{P-C} = 10 Hz); 26.0 (s, CH_2); 25.9 (s, CH_2); 22.9 (s, $OCCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_A 50.9 and δ_B 40.4 (ABXY system, J_{X-A} = 126 Hz, J_{Y-A} = 11 Hz, J_{B-A} = 11 Hz, J_{Y-B} = 115 Hz, J_{X-B} = 0, J_{A-B} = 11 Hz).

Preparation of $[Rh(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHCO_2CH_3)(CO)_2(PCy_3)_2]BF_4$ (4). The complex was prepared using the procedure described for **2** but starting from **3** (100 mg, 0.10 mmol) and $HBF_4{\cdot}OEt_2$ (14 μL, 0.10 mmol), the yield of the resulting dark

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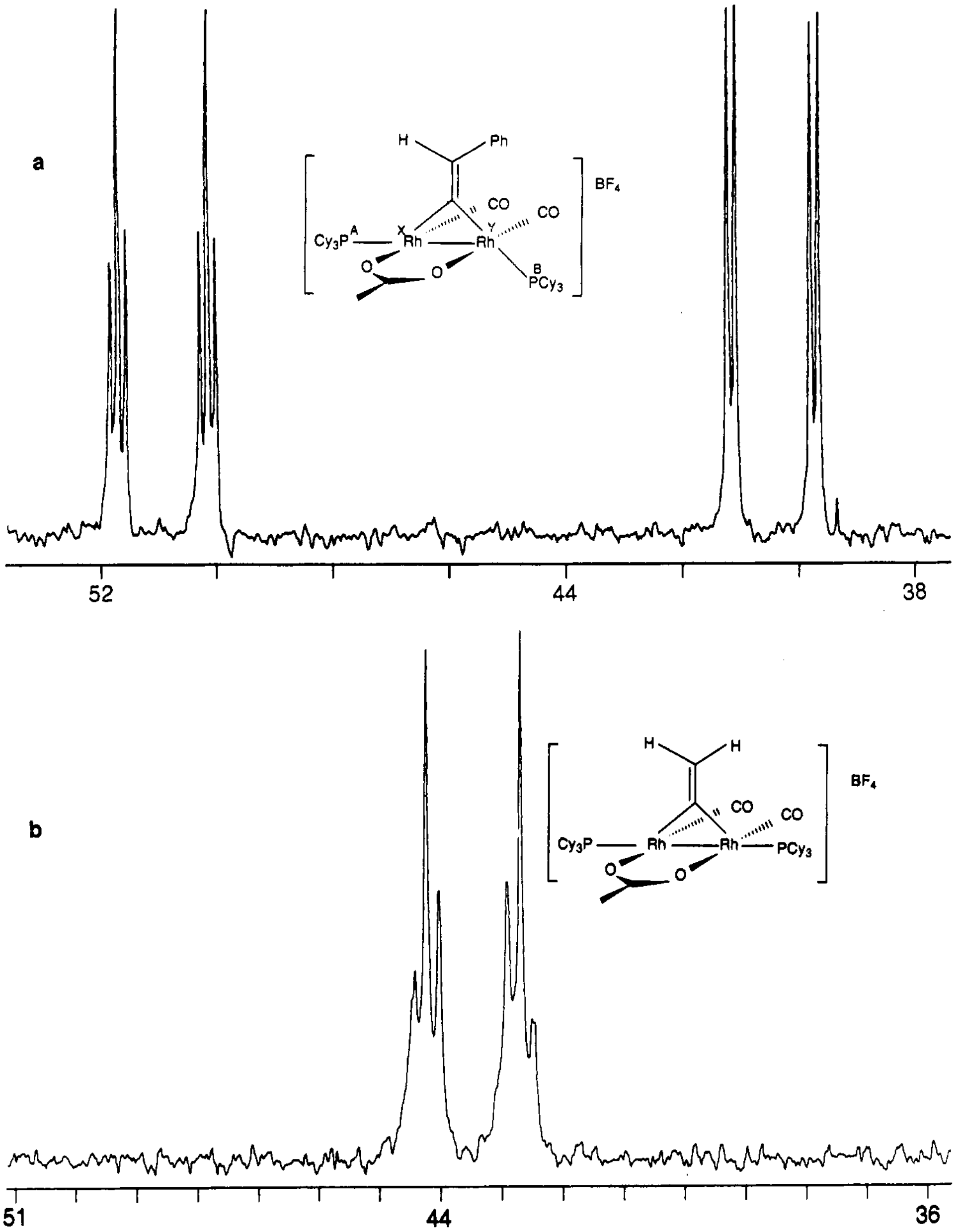

Figure 2. $^{31}P\{^1H\}$ NMR $CDCl_3$ spectra of (a) $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$ (**2**) δ_A 50.9 and δ_B 40.4 (ABXY system, $J_{X\text{-}A} = 126$ Hz, $J_{Y\text{-}A} = 11$ Hz, $J_{B\text{-}A} = 11$ Hz, $J_{Y\text{-}B} = 115$ Hz, $J_{X\text{-}B} = 0$, $J_{A\text{-}B} = 11$ Hz) and (b) $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CH_2)(CO)_2(PCy_3)_2]BF_4$ (**5**) δ 43.5 (AA′XX′ system, $J_{A\text{-}A'} = 35$ Hz, $J_{A\text{-}X} = J_{A\text{-}X'} = 140$ Hz).

orange solid was 87 mg (82%). Anal. Calcd for $C_{44}H_{73}BF_4O_4P_2Rh_2$: C, 51.80; H, 7.16. Found: C, 51.87; H, 7.50. IR (cm^{-1}): ν(CO)= 2050, 1990; $\nu(CO_2CH_3)$ = 1720; ν(C=C) = 1575; $\nu(OCOCH_3)_{asym}$ = 1545; $\nu(OCOCH_3)_{sym}$ = 1425. ^1H NMR ($CDCl_3$): δ 5.4 (br, C=CH); 3.7 (s, $OCOCH_3$); 2.4–1.1 (Cy); 1.9 (s, O_2CCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 187.1–185.3 complicated signal (*C*=$CHCO_2CH_3$, 2CO, O_2CCH_3); 159.7 (s, O*C*OMe); 125.4 (s, C=*C*HCO_2CH_3); 51.8 (s, OMe); 34.9 (d, CH_2*C*HP, $J_{P\text{-}C} = 22$ Hz); 34.4 (d, CH_2*C*HP, $J_{P\text{-}C} = 20$ Hz); 30.4 (s, CH_2); 30.2 (s, CH_2); 30.0 (s, CH_2); 29.7 (s, CH_2); 27.6 (d, *C*H_2CHP, $J_{P\text{-}C} = 8$ Hz); 27.4 (d, *C*H_2CHP, $J_{P\text{-}C} = 8$ Hz); 26.0 (s, CH_2); 25.9 (s, CH_2); 23.3 (s, OCCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_A 48.7 and δ_B 39.2 (ABXY system, $J_{X\text{-}A} = 124$ Hz, $J_{Y\text{-}A} = 15$ Hz, $J_{B\text{-}A} = 15$ Hz, $J_{Y\text{-}B} = 115$ Hz, $J_{X\text{-}B} = 0$, $J_{A\text{-}B} = 15$ Hz).

Preparation of $[Rh(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CH_2)(CO)_2(PCy_3)_2]BF_4$ (5). The complex was prepared using the procedure described for **2** but starting from **6** (100 mg, 0.10 mmol) and $HBF_4\cdot OEt_2$ (14 μL, 0.10 mmol) the yield of the resulting orange solid was 70 mg (69%). Anal. Calcd for $C_{42}H_{71}BF_4O_4P_2Rh_2$: C, 50.72; H, 7.10. Found: C, 50.35; H, 7.22. IR (cm^{-1}): ν(CO)= 2020, 2000; ν(C=C) = 1615; $\nu(OCOCH_3)_{asym}$ = 1545; $\nu(OCOCH_3)_{sym}$ = 1425. ^1H NMR ($CDCl_3$): δ 4.6 (br, C=CH_2); 2.3–1.1 (Cy); 2.1 (s, O_2CCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 187.5–186.0 complicated signal (*C*=CH_2, 2CO, O_2*C*CH_3); 114.1 (s, C=*C*H_2); 34.4 (d, CH_2*C*HP, $J_{P\text{-}C} = 18$ Hz); 29.9 (s, CH_2); 29.8 (s, CH_2); 27.7 (d, *C*H_2CHP, $J_{P\text{-}C} = 10$ Hz); 25.6 (s, CH_2); 23.3 (s, OCCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.5 (AA′XX′ system, $J_{A\text{-}A'} = 35$ Hz, $J_{A\text{-}X} = J_{A\text{-}X'} = 140$ Hz).

X-ray Structure Analysis of 2. Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of diethyl ether into a concentrated solution of **2** in CH_2Cl_2. Atomic coordinates and U_{eq} values are listed in Table II. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table III. The irregular crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 58 reflections in the range $20 \le 2\theta \le 35°$. The 7070 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by an empirical method (max and min correct fact: 1.147, 0.848).[17]

The structure was solved by Patterson (Rh atoms) and conventional Fourier techniques. Refinement was carried out

Table II. Atomic Coordinates (×10⁴; ×10⁵ for Rh Atoms) and Equivalent Isotropic Displacement Coefficients (Å² × 10⁴) for the Compound $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Rh(1)	9986(4)	13703(1)	28084(2)	319(1)
Rh(2)	44(4)	22197(1)	25921(2)	309(1)
P(1)	497(1)	570(1)	2507(1)	307(4)
P(2)	−734(1)	2962(1)	2233(1)	296(4)
O(1)	481(5)	1252(1)	4478(2)	819(20)
O(2)	−850(3)	2325(1)	4213(2)	495(14)
O(3)	1402(3)	1437(1)	1641(2)	425(12)
O(4)	550(3)	2149(1)	1451(2)	442(13)
C(1)	681(5)	1298(2)	3831(3)	456(20)
C(2)	−540(5)	2290(2)	3580(3)	336(17)
C(3)	1129(5)	1787(2)	1225(3)	396(18)
C(4)	1491(6)	1766(2)	393(3)	652(24)
C(5)	1700(5)	2016(2)	3035(3)	333(16)
C(6)	2728(5)	2249(2)	3285(3)	379(19)
C(7)	4000(5)	2032(2)	3475(3)	372(17)
C(8)	4872(5)	2279(2)	3938(3)	447(19)
C(9)	6090(5)	2086(2)	4100(3)	526(21)
C(10)	6433(5)	1666(2)	3794(3)	552(22)
C(11)	5569(6)	1417(2)	3347(4)	627(24)
C(12)	4366(5)	1600(2)	3174(3)	556(22)
C(13)	−297(5)	226(2)	3277(3)	356(17)
C(14)	−343(5)	−308(2)	3151(3)	491(20)
C(15)	−883(6)	−555(2)	3871(3)	599(24)
C(16)	−2183(6)	−357(2)	4082(3)	678(26)
C(17)	−2153(6)	160(2)	4186(3)	630(24)
C(18)	−1648(5)	412(2)	3468(3)	456(19)
C(19)	1975(4)	238(2)	2290(3)	352(17)
C(20)	2866(5)	236(2)	3017(3)	463(19)
C(21)	4127(5)	−40(2)	2855(3)	611(24)
C(22)	4795(5)	145(2)	2149(3)	528(22)
C(23)	3874(5)	130(2)	1439(3)	521(21)
C(24)	2673(5)	422(2)	1590(3)	460(19)
C(25)	−488(4)	591(2)	1597(3)	335(16)
C(26)	−945(5)	121(2)	1265(3)	416(18)
C(27)	−1552(5)	198(2)	451(3)	504(21)
C(28)	−2643(5)	552(2)	465(3)	641(24)
C(29)	−2215(6)	1014(2)	820(3)	577(23)
C(30)	−1620(5)	944(2)	1637(3)	481(20)
C(31)	332(5)	3240(2)	1536(3)	367(17)
C(32)	−93(5)	3728(2)	1274(3)	492(20)
C(33)	741(6)	3914(2)	627(3)	645(25)
C(34)	2158(7)	3905(2)	858(4)	766(28)
C(35)	2596(6)	3435(2)	1134(4)	653(25)
C(36)	1766(5)	3242(2)	1793(3)	504(21)
C(37)	−2313(5)	2899(2)	1721(3)	363(17)
C(38)	−3304(5)	2687(2)	2238(3)	547(21)
C(39)	−4606(5)	2642(3)	1796(3)	703(26)
C(40)	−4509(6)	2363(2)	1059(4)	749(28)
C(41)	−3505(6)	2566(3)	555(3)	862(31)
C(42)	−2211(6)	2606(3)	975(3)	716(27)
C(43)	−1031(4)	3332(2)	3091(3)	302(16)
C(44)	210(5)	3424(2)	3585(3)	408(18)
C(45)	−161(5)	3611(2)	4384(3)	504(20)
C(46)	−964(6)	4055(2)	4297(3)	552(22)
C(47)	−2127(6)	3980(2)	3772(3)	519(21)
C(48)	−1772(5)	3792(2)	2967(3)	417(18)
B	9016(8)	1236(3)	8514(5)	622(30)
F(1)	8419(4)	1619(1)	8811(3)	1143(21)
F(2)	9705(4)	1017(2)	9102(2)	1087(20)
F(3)	8093(4)	937(1)	8243(3)	1211(23)
F(4)	9815(5)	1353(2)	7945(3)	1427(27)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *Uij* tensor.

Table III. Crystal Data and Data Collection and Refinement for $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}C{=}CHPh)(CO)_2(PCy_3)_2]BF_4$

	Crystal Data
formula	$C_{48}H_{75}BF_4O_4P_2Rh_2$
mol wt	1070.68
color and habit	dark red wine, transparent, irregular block
crystal size, mm	0.409 × 0.570 × 0.576
crystal syst	monoclinic
space gp	$P2_1/n$ (No. 14)
a, Å	10.377(1)
b, Å	28.526(2)
c, Å	17.155(2)
β, deg	91.53(1)
V, Å³	5076.3(9)
Z	4
D(calcd), g cm⁻³	1.401
temp (K)	233
	Data Collection and Refinement
diffractometer	four-circle Siemens-STOE AED
λ(Mo Kα) radiation, Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm⁻¹	0.754
scan type	$\omega/2\theta$
2*θ* range, deg	$3 \leq 2\theta \leq 45$
no. of data collect	7070
no. of unique data	6633
no. of unique obsd data	5183 ($F_o \geq 4.0\sigma(F_o)$)
no. of params refined	555
R, R_w[a]	0.0356, 0.0343

[a] $w^{-1} = \sigma^2(F_o) + 0.000169(F_o)^2$.

by a full-matrix least-squares method with initial isotropic thermal parameters. Hydrogen atoms were partially located from difference Fourier maps and included in the refinement (some of them in calculated positions; C–H = 0.96 Å) riding on carbon atoms with a common isotropic thermal parameter. The vinylic hydrogen H(6) was refined as a free isotropic atom. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Atomic scattering factors, corrected for anomalous dispersion for Rh and P, were taken from ref 18. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight defined as $w^{-1} = \sigma^2(F_o) + 0.000169F_o^2$. Final *R* and R_w values were 0.0356 and 0.0343, respectively. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[19]

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (20 pages). Ordering information is given on any current masthead page.

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