Synthesis, Structures, and Reactions of Dirhodium Complexes Bearing a 1,2-Diphenyl-3,4-diphosphinidenecyclobutene Ligand (DPCB)

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A di-μ-hydroxo-dirhodium complex bearing a low-coordinate phosphorus ligand, $[Rh_2(\mu\text{-}OH)_2(DPCB)_2]$ (**2**; DPCB = 1,2-diphenyl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutene), is prepared from $[Rh_2(\mu\text{-}Cl)_2(DPCB)_2]$ (**1**) and KOH. Complex **2** serves as a good precursor for hydrido complexes, affording $[Rh_2(\mu\text{-}H)(\mu\text{-}OH)(DPCB)_2]$ (**3**) and $[Rh_2(\mu\text{-}H)_2(DPCB)_2]$ (**7**) by the reactions with $HSiMe_2Ph$ and HCO_2H, respectively. Although complex **7** is too unstable to be isolated, its formation is evidenced by a trapping experiment using 1,3-cyclohexadiene to give $[Rh(\eta^3\text{-}C_6H_9)(DPCB)]$ (**8**). Complex **2** reacts with CO to afford $[Rh_2(\mu\text{-}\kappa P,P;\kappa P,C\text{-}DPCB)(CO)_4]$ (**9**) and $[Rh_2(\mu\text{-}CO)_2(DPCB)_2]$ (**10**), which are interconvertible in solution. Complex **9** is the stable form under a CO atmosphere even in the presence of free DPCB, but readily converted to **10** by purging the CO gas from the solution. The X-ray structures of **2**, **3**, **9**, **10**, and related $[Rh_2(\mu\text{-}H)(\mu\text{-}OMe)(DPCB)_2]$ (**4**) are reported. Two Rh(DPCB) moieties in **10** are oriented orthogonal to each other in the crystal; namely, one of the Rh centers has a square-planar configuration, whereas the other is in a tetrahedral arrangement with the μ-CO and DPCB ligands, showing flexible electronic properties of DPCB.

Introduction

There has been considerable recent interest in the coordination chemistry of low-coordinate phosphorus compounds due to their unique ligand properties, differing significantly from common tertiary phosphanes.[1] Phosphaalkenes having a P=C double bond are among the central subjects in such chemistry.[2] The MO calculations on carbon monoxide (C≡O), phosphaethene ($H_2C{=}PH$), imine ($H_2C{=}NH$), and phosphane (PH_3) have shown that the π^* orbital level of the C=P bond is much lower than those of C≡O and C=N bonds.[3] On the other hand, the lone-pair orbital of phosphaethene is situated at a comparable level to that of phosphane. Accordingly, phosphaalkenes undergo strong σ-donation and π-back-donation interactions with transition metals. We have demonstrated using 1,2-diphenyl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes (DPCB-Y; Y stands for the *p*-substituents of 1,2-diphenyl groups) that this ligand property is useful for catalysis, leading to highly efficient organic transformations in conjunction with group 8 and 10 metals.[4,5]

In this study, we synthesized several organorhodium complexes bearing DPCB ligand (Y = H) and examined their structures and reactivities. A particular interest has been focused on hydridorhodium complexes, because hydrido species have often been observed as key intermediates in DPCB-Y complex-catalyzed reactions.[4] For their preparation, we employed the rhodium hydroxide $[Rh_2(\mu\text{-}OH)_2(DPCB)_2]$ as a common precursor. In the past several decades, a great deal of attention has been focused on hydroxo complexes of late transition metals, because of their interesting reactivities and potential relevance to catalytic reactions.[6] For example, M-OH species often react with organic compounds with acidic nature, along with only by-production of H_2O. Thus, hydroxo complexes may serve as clean and versatile precursors of a variety of complexes.[7] The synthesis and reactions of rhodium hydroxides have been

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examined with tertiary phosphanes as ancillary ligands.[8−11] However, most of them are highly air-sensitive even in the solid state, probably due to high electron density of the metal centers. Accordingly, despite their utility, the study of hydroxorhodium complexes has remained insufficiently explored. On the other hand, we found that the DPCB ligand successfully stabilizes rhodium hydroxide without notable loss of the reactivity.

Results and Discussion

Synthesis of [$Rh_2(\mu\text{-}OH)_2(DPCB)_2$] (2). DPCB was introduced to rhodium by ligand displacement with [$Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$] in toluene at room temperature (Scheme 1). Treatment of **1** with aqueous KOH in toluene at 80 °C formed [$Rh_2(\mu\text{-}OH)_2(DPCB)_2$] (**2**), which was isolated in 98% yield as a dark yellow solid, fairly stable in air. The $^{31}P\{^1H\}$ NMR signal appeared at δ 164.1 as a doublet with the $^1J_{RhP}$ coupling of 244 Hz. The ^1H NMR spectrum exhibited a singlet signal at δ −1.66, assignable to μ-OH protons; the chemical shift is comparable to those of tertiary phosphane analogues.[8c,9i,10,11a] The signal instantly disappeared upon treatment with D_2O.

Scheme 1

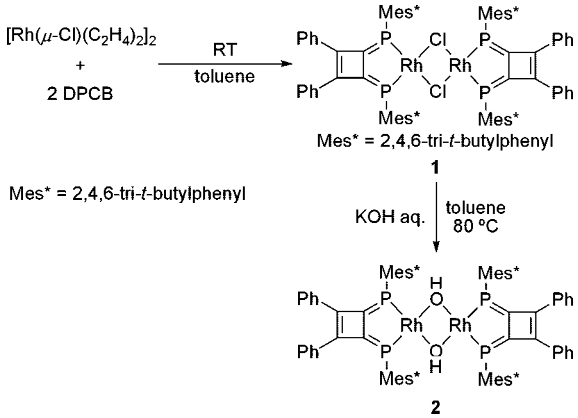

Figure 1 shows the crystal structure of **2**, which has a center of symmetry at the intersection of Rh−Rh* and O−O* vectors. Each rhodium center takes a square-planar geometry. The Rh−P (Rh−P1 = 2.1879(12), Rh−P2 = 2.1863(12) Å) and Rh−O (Rh−O = 2.077(3), Rh−O* = 2.082(3) Å) distances are comparable to those of phosphane analogues (Rh−P = 2.185−2.241 Å, Rh−O = 2.064−2.127 Å).[8e,11a] The interatomic distance of Rh···Rh* is 3.273 Å, showing the absence of bonding interaction.

Reaction of 2 with $HSiMe_2Ph$. We have recently found that the ruthenium chloride [$Ru_2Cl_2(\mu\text{-}Cl)_2(CO)_2(DPCB\text{-}OMe)_2$] is cleanly reduced to hydride by the treatment with $HSiMe_2Ph$ and water, where an Ru-OH species undergoes metathesis with $HSiMe_2Ph$ to give an Ru−H species and $HOSiMe_2Ph$.[5a] Thus, the reaction of **2** with $HSiMe_2Ph$ was examined as the first attempt to synthesize hydridorhodium complexes (eq 1). Complex **2** was treated with excess $HSiMe_2Ph$ (3 equiv/Rh) in THF at room temperature for 27 h. After removal of volatiles, the residue was washed with pentane and dried under vacuum, giving a dark red powder of [$Rh_2(\mu\text{-}H)(\mu\text{-}OH)(DPCB)_2$] (**3**) in 84% yield.

X-ray diffraction analysis of **3** revealed the dirhodium structure bearing μ-H and μ-OH ligands (Figure 2). The rhodium atoms adopt slightly distorted square-planar configurations and

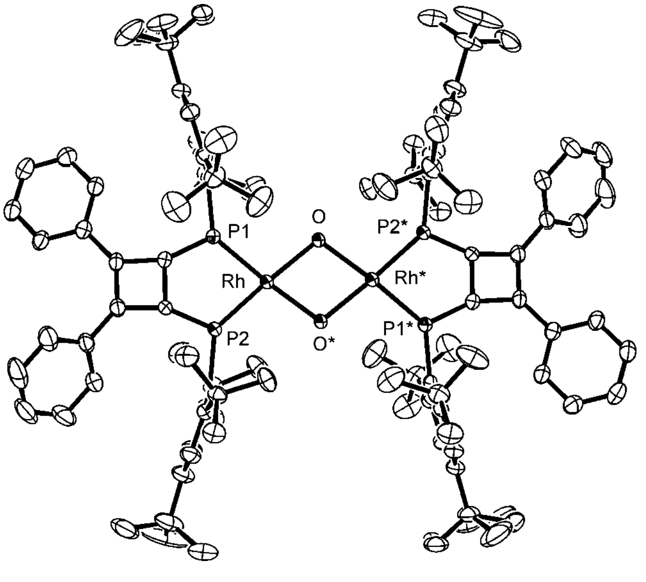

Figure 1. ORTEP drawing of $\mathbf{2}\cdot 2(C_5H_{12})$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms and pentane molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−P1 = 2.1879(12), Rh−P2 = 2.1863(12), Rh−O = 2.077(3), Rh−O* = 2.082(3), P1−Rh−P2 = 82.59(4), O−Rh−O* = 76.19(12), P1−Rh−O = 100.24(8), P2−Rh−O* = 100.92(8). Asterisks indicate atoms generated by the symmetric operation (−*x*, −*y*, −*z*).

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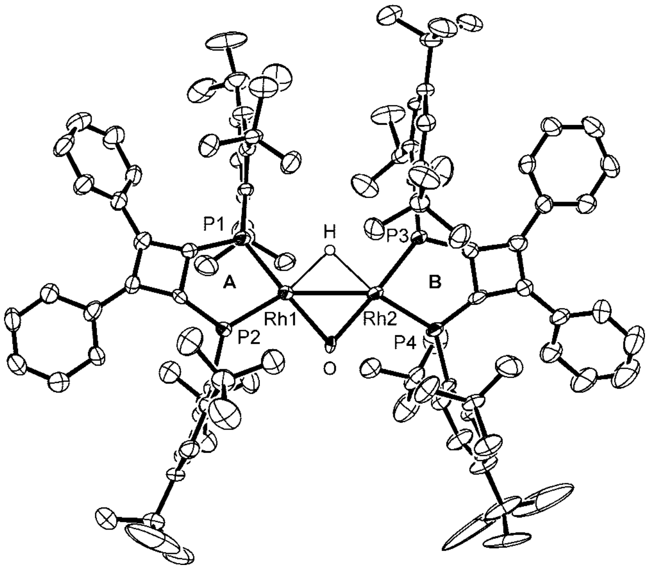
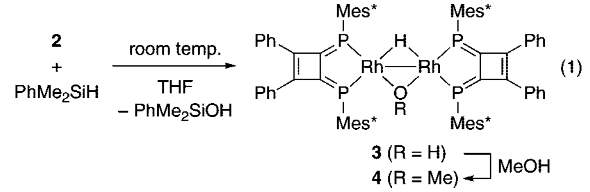


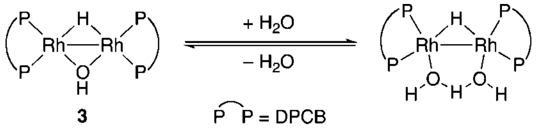
Figure 2. ORTEP drawing of $\mathbf{3}\cdot Et_2O$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms except for the μ-H ligand and a Et_2O molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1−Rh2 = 2.7486(12), Rh1−P1 = 2.1660(19), Rh1−P2 = 2.2178(19), Rh2−P3 = 2.174(2), Rh2−P4 = 2.202(2), Rh1−H = 1.87(5), Rh2−H = 1.90(5), Rh1−O = 2.087(4), Rh2−O = 2.098(4), P1−Rh1−P2 = 83.79(7), P3−Rh2−P4 = 83.36(7), Rh1−O−Rh2 = 82.11(16). Dihedral angel (deg): **A**−**B** = 23.2(2).



(1)

are connected with each other by a metal−metal bond (2.7486(12) Å). Reflecting the higher trans influence of hydrido ligand than hydroxo ligand, the Rh1−P2 (2.2178(19) Å) and Rh2−P4 (2.202(2) Å) bonds are clearly longer than the Rh1−P1 (2.1660(19) Å) and Rh2−P3 (2.174(2) Å) bonds, respectively.

The ^1H NMR signal of the μ-hydrido ligand appeared at δ −9.34 as a triplet of triplets of triplets, due to the couplings with ^{31}P nuclei at the trans and cis positions ($^2J_{PH}$ = 85, 28 Hz) and with ^{103}Rh nuclei ($^1J_{RhH}$ = 15 Hz), showing the occurrence of a tight connection among the μ-hydrido ligand and rhodium centers. On the other hand, the $^{31}P\{^1H\}$ NMR signal at δ 156.1 (d, $^1J_{RhP}$ = 244 Hz) assignable to the phosphorus trans to the μ-OH ligand was significantly broadened, while the other at δ 175.6 (dd, $^1J_{RhP}$ = 208 Hz, $^1J_{PP}$ = 12 Hz) remained as a sharp signal. Since the OH proton signal was broadened as well, it is likely that complex **3** undergoes a rapid exchange of the μ-OH ligand with residual water in solution, probably via the process given in eq 2. Actually, the μ-OH ligand in **3** was readily replaced by MeOH to give **4**, having a μ-OMe ligand, in 67% yield after isolation as dark brown crystals (eq 1).



(2)

As seen from the ORTEP drawing given in Figure 3, complex **4** has a structure very similar to **3**, while the Rh−Rh bond

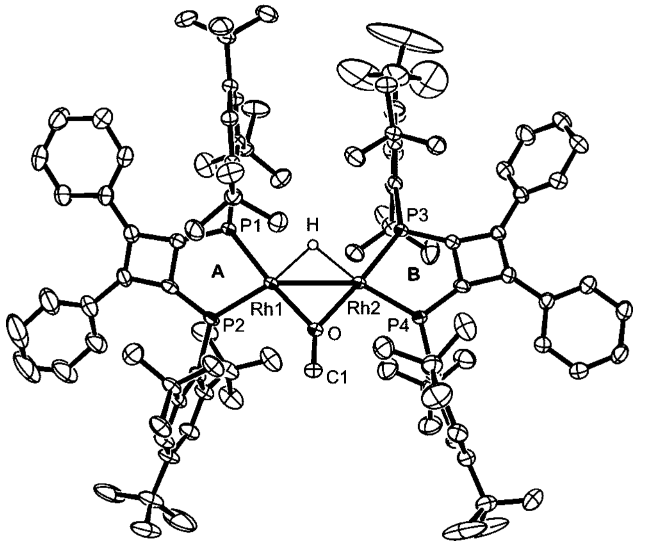
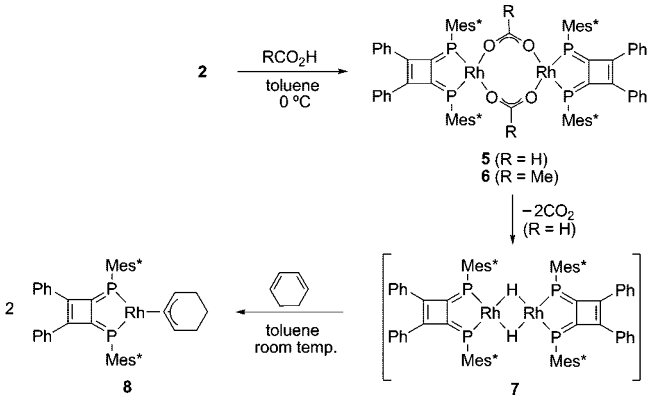


Figure 3. ORTEP drawing of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms expect for the μ-H ligand are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1−Rh2 = 2.7682(5), Rh1−P1 = 2.1705(9), Rh1−P2 = 2.2229(9), Rh2−P3 = 2.1769(9), Rh2−P4 = 2.2177(10), Rh1−H = 1.79(4), Rh2−H = 1.88(4), Rh1−O = 2.022(3), Rh2−O = 2.017(3), O−C1 = 1.397(5), P1−Rh1−P2 = 83.18(4), P3−Rh2−P4 = 83.08(4), Rh1−O−Rh2 = 86.52(10), Rh1−O−C1 = 129.5(2), Rh2−O−C1 = 133.8(3), **A**−**B** = 10.0(1).

Scheme 2



(2.7682(5) Å) is somewhat longer, and the Rh−O bonds (2.022(3), 2.017(3) Å) are clearly shorter than **3**.

Reaction of 2 with HCO_2H. The reaction of **2** with $HSiMe_2Ph$ formed mono-μ-hydrido complex **3** exclusively, and no further reduction took place even in the presence of a large excess of $HSiMe_2Ph$ (>20 equiv/Rh). Since stronger reducing agents such as $NaBH_4$ and EtLi provided complex mixtures, we next examined the reaction with formic acid to synthesize di-μ-hydrido complex **7** (Scheme 2).

When **2** was treated with HCO_2H (1 equiv/Rh) at 0 °C in toluene, the $^{31}P\{^1H\}$ NMR signal at δ 164.1 (d, $^1J_{RhP}$ = 244 Hz) instantly disappeared, and a new broad signal, assignable to di-μ-formato complex **5**, appeared at δ 163.2 (d, $^1J_{RhP}$ = 262 Hz). Although this complex was too unstable to be isolated, the related di-μ-acetato complex **6** could be obtained in 98% yield, using $MeCO_2H$ instead of HCO_2H. The ^1H NMR data of both complexes were almost identical to each other, except for the signals of bridging ligands. Complex **5** readily decomposed with liberation of CO_2 at room temperature. In the presence of 1,3-cyclohexadiene, η^3-cyclohexenyl complex **8** was formed, as confirmed by NMR spectroscopy. This observation is

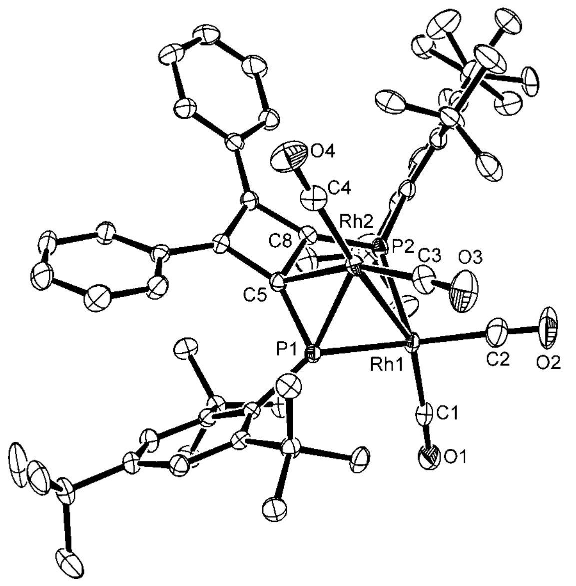
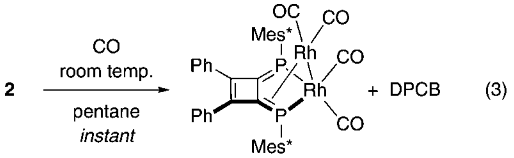


Figure 4. ORTEP drawing of $\mathbf{9}\cdot C_5H_{12}$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms and a pentane molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1−Rh2 = 2.7452(6), Rh1−P1 = 2.2592(8), Rh1−P2 = 2.4180(9), Rh2−P1 = 2.3909(8), Rh1−C1 = 1.881(3), Rh1−C2 = 1.905(3), Rh2−C3 = 1.877(3), Rh2−C4 = 1.912(3), Rh2−C5 = 2.203(2), P1−C5 = 1.743(2), P2−C8 = 1.696(2), P1−Rh1−P2 = 85.84(2), C1−Rh1−C2 = 95.00(11), P1−Rh1−C1 = 101.84(7), P2−Rh1−C2 = 106.36(9), Rh1−Rh2−C5 = 80.45(6), C3−Rh2−C4 = 97.10(11), Rh1−Rh2−C3 = 87.93(8), C4−Rh2−C5 = 96.53(10), Rh1−Rh2−P1 = 51.63(2), P1−Rh2−C5 = 44.37(6).

consistent with the formation of $[Rh_2(\mu\text{-}H)_2(DPCB)_2]$ (**7**), which undergoes the insertion of 1,3-cyclohexadiene to give **8**.

Reaction of 2 with CO. Next, complex **2** was treated with CO. It has been documented that hydroxycarbonyl complexes formed by the insertion of CO into a Rh−OH bond undergo decarboxylation to give hydrido complexes.[12] However, the reaction of **2** with CO in pentane afforded the novel dirhodium complex $[Rh_2(\mu\text{-}\kappa P,P;\kappa P,C\text{-DPCB})(CO)_4]$ (**9**) instead, along with dissociation of one of the DPCB ligands (eq 3). Slow evaporation of the solvent under the flow of CO gas provided dark brown crystals with the composition $\mathbf{9}\cdot C_5H_{12}$ in 55% yield, suitable for X-ray diffraction analysis.



(3)

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Figure 4 shows the X-ray crystal structure. There are two nonequivalent rhodium centers, connected by a metal−metal bond (2.7452(6) Å). One (Rh1) adopts a significantly distorted five-coordinate structure having P1, P2, C1, C2, and Rh2 as coordination atoms. On the other hand, the other rhodium atom (Rh2) is combined with the Rh1−P1−C5 moiety in η^3-fashion.[13] Thus, the partial structure around Rh2 may be regarded as a π-allyl complex bearing two carbonyl ligands. The C3−Rh2−C4 angle (97.10(11)°) is within the range of π-allyl complexes having a d^8 metal center.

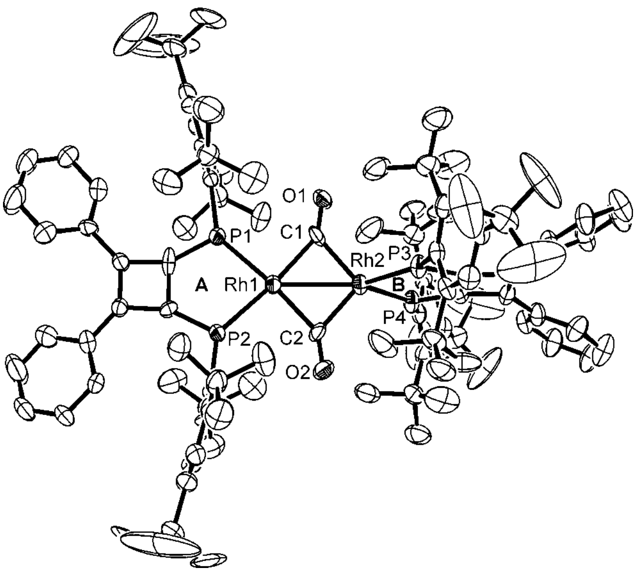
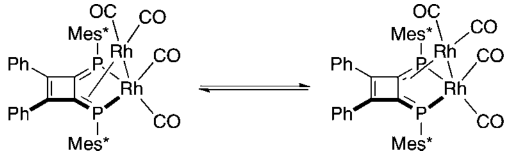


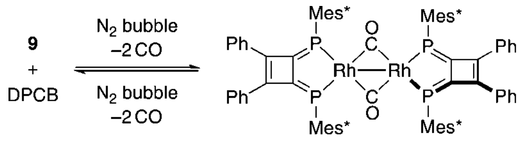
Figure 5. ORTEP drawing of **10** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1−Rh2 = 2.6802(11), Rh1−P1 = 2.282(2), Rh1−P2 = 2.279(2), Rh1−C1 = 2.008(8), Rh1−C2 = 2.028(8), Rh2−P3 = 2.329(2), Rh2−P4 = 2.325(2), Rh2−C1 = 1.975(9), Rh2−C2 = 1.986(10), C1−O1 = 1.179(10), C2−O2 = 1.167(10), P1−Rh1−P2 = 82.93(8), C1−Rh1−C2 = 94.6(4), P3−Rh2−P4 = 85.78(8), C1−Rh2−C2 = 97.0(3), Rh1−C1−O1 = 145.8(7), Rh2−C1−O1 = 129.4(7), Rh1−C2−O2 = 145.7(7), Rh2−C2−O2 = 130.2(7), **A**−**B** = 80.6(4).

Unlike the crystal structure, two phosphorus nuclei of the DPCB ligand were observed equivalently at δ 152.9 (dd, $^1J_{RhP}$ = 151, 44 Hz) in toluene at room temperature, showing the occurrence of a rapid migration of the $Rh(CO)_2$ moiety between the P=C bonds (eq 4). The fractional behavior did not freeze even at −90 °C.



(4)

Complex **9** is stable in solution under a CO atmosphere even in the presence of free DPCB, but readily converted to $[Rh_2(\mu\text{-}CO)_2(DPCB)_2]$ (**10**) when the CO gas was purged from the solution (eq 5). The IR and NMR data were consistent with the dirhodium structure having two μ-CO ligands. A strong ν_{CO} absorption band appeared in a typical region of bridging carbonyls (1766 cm^{-1}). The $^{13}C\{^1H\}$ NMR signal of μ-CO ligands (δ 172.1) was observed as a triplet due to the coupling with two ^{103}Rh nuclei ($^1J_{RhC}$ = 28 Hz).



(5)

10

Figure 5 shows the X-ray structure of **10**. Although the quality of diffraction data was low (R_1 = 0.170), an interesting structural

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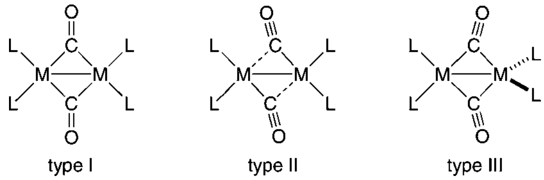
[12] (a) Johansson, R.; Wendt, O. F. *Organometallics* **2007**, *26*, 2426. (b) Torresan, I.; Michelin, R. A.; Marsella, A.; Zanardo, A.; Pinna, F.; Strukul, G. *Organometallics* **1991**, *10*, 623. (c) Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1.

[13] A similar coordination mode of DPCB has been reported for a tungsten complex: Yoshifuji, M.; Ichikawa, Y.; Yamada, N.; Toyota, K. *Chem. Commun.* **1998**, 27.

Scheme 3



feature emerged.[14] Complex **10** is a 30-electron dimer having a rhodium−rhodium bond (2.6802(11) Å). The Rh1 center has a square-planar geometry,[15a] whereas the Rh2 atom is in a distorted tetrahedral configuration.[15b] Two Rh(DPCB) units are oriented orthogonal to each other with the dihedral angle of 80.6(4)°. Reflecting the highly unsymmetrical dirhodium framework, both μ-CO ligands are tilted toward the Rh2 atom by 8.2 (C1−O1) and 7.8° (C2−O2), respectively. Furthermore, the Rh2−C1 and Rh2−C2 bonds (1.975(9), 1.986(10) Å) are shorter than the Rh1−C1 and Rh1−C2 bonds (2.008(8), 2.028(8) Å), respectively.

The crystal structures of [$L_2M(\mu\text{-CO})_2ML'_2$] type complexes have been rationalized by Cotton (Scheme 3).[16,17] When two metal centers bear the same or very similar ancillary ligands (L = L′), they form symmetrical structures of type I or II. On the other hand, when the ancillary ligands with significantly different electronic properties are bound to each metal (L ≠ L′; typically those in donor and acceptor relations), the complexes adopt unsymmetrical structures of type III, involving square-planar and tetrahedral geometries of metal centers and asymmetric bridging of CO ligands. In this context, the X-ray structure of **10** is quite unique, being categorized into type III despite the coordination of the same DPCB ligands to both rhodium atoms.

The highly distorted coordination structure of **10** should be attributed principally to steric repulsion between DPCB ligands. The orthogonal arrangement of Rh(DPCB) units most effectively relieves the steric congestion. In this case, the nonequivalent rhodium centers with square-planar and tetrahedral configurations must bear electronic conditions quite distinct from each other. Actually, DFT calculations suggested that the Rh1 atom is much more negatively charged than the Rh2 atom,[18] and this is an important reason that the complexes of type III commonly have ancillary ligands with significantly different properties at each metal center. As described in the introductory part, DPCB serves not only as a strong π-acceptor but also as an effective σ-donor toward transition metals. Therefore, it is likely that this highly flexible ligand property of DPCB compensates for the imbalance of charge distribution between rhodium atoms, leading to the unusual structural feature of **10**.

Conclusion

It has been found that the di-μ-hydroxo-dirhodium complex bearing DPCB ligands (**2**) serves as a versatile starting material for organorhodium complexes. Complex **2** is stable in air, but sufficiently reactive toward a variety of substrates including $HSiMe_2Ph$ and CO, affording complexes with unique structural features. The carbonyl complexes **9** and **10** are of particular interest. DPCB undergoes the μ-$\kappa P,P$;$\kappa P,C$-coordination with two rhodium atoms in **9** and forms a novel $Rh_2(\mu\text{-CO})_2$ framework with square-planar and tetrahedral rhodium centers in **10**. Both structures demonstrate highly flexible electronic ligand properties of DPCB.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Toluene and pentane were distilled from sodium benzophenone ketyl. Chloroform-*d* was purified by passing successively through alumina and activated MS4A columns and degassed by freeze−pump−thaw cycles prior to use. Benzene-d_6 and dichloromethane-d_2 were dried over $LiAlH_4$ and CaH_2, respectively, and stored over activated MS4A. Dehydrated diethyl ether, tetrahydrofuran, and dichloromethane were obtained from commercial sources. The compounds [$Rh_2(\mu\text{-Cl})_2(C_2H_4)_4$][19] and DPCB[3] were synthesized by the literature methods. Other chemicals were purchased and used as received.

NMR spectra were recorded on a Bruker Avance 400 spectrometer at 20 °C unless otherwise noted. Chemical shifts are reported in δ, referenced to ^1H (of residual protons) and ^{13}C signals of deuterated solvents as internal standard or to the ^{31}P signal of 85% H_3PO_4 as an external standard. IR spectra were recorded on a JASCO FT/IR-410 instrument. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

Preparation of [$Rh_2(\mu\text{-Cl})_2(DPCB)_2$] (1). To a solution of DPCB (827.0 mg, 1.095 mmol) in toluene (10 mL) was added [$Rh_2(\mu\text{-Cl})_2(C_2H_4)_4$] (216.4 mg, 0.556 mmol) at room temperature. The color of the solution immediately turned from yellow to dark brown. After 1 h, insoluble materials were removed by filtration through a Celite pad, and volatiles were removed under reduced pressure. The residue was washed with diethyl ether at 0 °C and dried under vacuum, giving a dark brown microcrystalline powder of **1** (878.7 mg, 90%). Mp: 225 °C (dec). ^1H NMR ($CDCl_3$): δ 1.40 (s, 36H, *p*-*t*Bu), 1.76 (s, 72H, *o*-*t*Bu), 6.63 (d, J = 7.7 Hz, 8H, *o*-Ph), 6.79 (t, J = 7.8 Hz, 8H, *m*-Ph), 7.02 (t, J = 7.4 Hz, 4H, *p*-Ph), 7.46 (s, 8H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.5, 34.6, 35.3, 39.1, 122.7, 126.5, 127.2, 128.0, 128.1 (d, J = 7.5 Hz), 132.9, 142.1 (m, J = 62, 33 Hz), 152.0, 156.4, 157.9 (dd, J = 88, 10 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 160.6 (d, J = 250 Hz). Anal. Calcd for $C_{104}H_{136}Cl_2P_4Rh_2$: C, 69.91; H, 7.67. Found: 69.97; H, 7.84.

Preparation of [$Rh_2(\mu\text{-OH})_2(DPCB)_2$] (2). To a dark brown solution of **1** (372.2 mg, 0.208 mmol) in toluene (15 mL) was added an aqueous solution (9 mL) of KOH (2.5 g, 44.6 mmol) at room temperature. The resulting mixture was stirred at 80 °C for 10 h. The dark yellow organic layer was separated, washed with H_2O, and transferred to another Schlenk tube through a cotton-tipped cannula. After volatiles were removed under reduced pressure, the residue was washed with pentane at 0 °C and dried under vacuum to give an analytically pure sample of **2** as a dark yellow microcrystalline powder (266.8 mg, 73%). Evaporation of the

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[14] The poor R_1 value is mainly due to insufficient disorder treatment for *tert*-butyl groups. Based on the standard deviations, it has been concluded that the structural data on the $P_2Rh(CO)_2RhP_2$ core deserve discussion.

[15] (a) The sum of the four angles around Rh1: 360.2°. (b) The sum of the four angles around Rh2: 405.2°.

[16] (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. (b) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

[17] For examples of di-μ-carbonyl-dirhodium complexes, see: (a) Singh, P.; Dammann, C. B.; Hodgson, D. J. *Inorg. Chem.* **1973**, *12*, 1335. (b) Burch, R. R.; Muetterties, E. L.; Schultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5517. (c) James, B. R.; Mahajan, D.; Rettig, S. J.; Williams, G. M. *Organometallics* **1983**, *2*, 1452. (d) Freeman, M. A.; Young, D. A. *Inorg. Chgem.* **1986**, *25*, 1556. (e) Shulman, P. M.; Burkhardt, E. D.; Lundquist, E. G.; Pilato, R. S.; Geoffroy, G. L. *Organometallics* **1987**, *6*, 101. (f) Cecconi, F.; Chilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P.; Heaton, B. T.; Huang, L.; Iggo, J. A.; Bordoni, S. *J. Organomet. Chem.* **1988**, *353*, C5. (g) Douglas, S.; Lowe, J. P.; Mahon, M. F.; Warren, J. E.; Whittlesey, M. K. *J. Organomet. Chem.* **2005**, *690*, 5027.

[18] DFT calculations for [$Rh(\mu\text{-CO})(DPCB)]_2$ were carried out with the Gaussian 98 program (Revision A.9, Gaussian, Inc., 1998) using B3LYP in conjunction with the standard LanL2DZ basis set and effective core potentials for Rh and 6-31G(d) basis set for other atoms. This examination showed the Mulliken atomic charges of Rh1 (−0.14) and Rh2 (+0.38).

[19] Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

Table 1. Details of the X-ray Structure Determinations of 2·2(C_5H_{12}), 3·Et_2O, 4, 9·C_5H_{12}, and 10

	2·2(C_5H_{12})	**3**·Et_2O	**4**	**9**·C_5H_{12}	**10**
formula	$C_{114}H_{162}O_2P_4Rh_2$	$C_{108}H_{148}O_2P_4Rh_2$	$C_{105}H_{140}OP_4Rh_2$	$C_{61}H_{80}O_4P_2Rh_2$	$C_{106}H_{136}O_2P_4Rh_2$
fw	1894.14	1807.96	1747.87	1145.01	1771.85
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	16.318(6)	15.134(4)	15.1401(15)	12.783(4)	23.782(5)
b, Å	16.990(6)	19.251(6)	19.3117(19)	23.929(7)	28.125(6)
c, Å	19.833(7)	20.244(6)	20.181(2)	18.804(6)	34.019(8)
α, deg	90	71.59(2)	71.572(11)	90	90
β, deg	104.493(6)	67.53(2)	68.830(9)	97.609(5)	110.534(3)
γ, deg	90	68.04(2)	68.024(10)	90	90
Z	2	2	2	4	8
V, Å^3	5324(3)	4951(3)	4989.7(9)	5701(3)	21309(8)
F(000)	2024	1924	1856	2392	7504
μ, mm^{-1}	0.417	0.445	0.439	0.679	0.413
θ range, deg	3.25 to 27.48	3.05 to 27.48	3.00 to 27.48	3.00 to 27.48	3.09 to 27.48
no. of reflns collected	41 918	40 250	40 137	45 351	80 384
no. of indep reflns (R_{int})	12 123 (0.0564)	21 705 (0.0616)	21 779 (0.03411)	13 005 (0.0350)	24 235 (0.0903)
no. of data/restraints/params	12 123/0/602	21 705/0/1062	21 779/ 0/1050	13 005/0/673	24 235/0/1063
goodness of fit on F^2	1.242	1.205	1.082	1.068	1.338
final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0812$ $wR_2 = 0.1462$	$R_1 = 0.1221$ $wR_2 = 0.1961$	$R_1 = 0.0586$ $wR_2 = 0.1667$	$R_1 = 0.0347$ $wR_2 = 0.0811$	$R_1 = 0.1700$ $wR_2 = 0.3018$
R indices (all data)	$R_1 = 0.0979$ $wR_2 = 0.1544$	$R_1 = 0.1573$ $wR_2 = 0.2142$	$R_1 = 0.0718$ $wR_2 = 0.1795$	$R_1 = 0.0399$ $wR_2 = 0.0843$	$R_1 = 0.2073$ $wR_2 = 0.3222$
largest diff peak and hole, e Å^{-3}	0.812 and −0.545	0.904 and −1.000	3.321 and −0.912	1.371 and −1.166	1.013 and −0.528

pentane washings gave additional product of **2** (89.3 mg, 25%; totally 98%). Mp: 140 °C (dec). ^{1}H NMR (C_6D_6): δ −1.66 (s, 2H, μ-OH), 1.23 (s, 36H, *p*-*t*Bu), 2.00 (s, 72H, *o*-*t*Bu), 6.74 (t, $J = 7.4$ Hz, 8H, *m*-Ph), 6.84 (t, $J = 7.4$ Hz, 4H, *p*-Ph), 7.00 (d, $J = 7.1$ Hz, 8H, *o*-Ph), 7.44 (s, 8H, *m*-PAr). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.5, 34.6, 35.2, 39.2, 122.4, 125.6, 126.6, 127.2, 129.3 (d, $J = 6$ Hz), 134.1, 142.2 (m), 151.9, 156.6, 157.6 (m). ^{31}P{^{1}H} NMR (C_6D_6): δ 164.1 (d, $J = 244$ Hz). Anal. Calcd for $C_{104}H_{138}O_2P_4Rh_2$: C, 71.38; H, 7.95. Found: C, 70.99; H, 8.22.

Preparation of [Rh_2(μ-H)(μ-OH)(DPCB)$_2$] (3). To a solution of **2** (251.8 mg, 0.143 mmol) in THF (8.0 mL) was added $HSiMe_2Ph$ (135 μL, 0.881 mmol) at room temperature. The solution gradually changed from dark yellow to dark red. After 27 h, volatiles were removed under reduced pressure, and the residue was washed with pentane at 0 °C and dried under vacuum to give a dark red powder of **3** (208.7 mg, 84%). Mp: 120 °C (dec). ^{1}H NMR (C_6D_6): δ −9.34 (ttt, $J = 85, 28, 15$ Hz, 1H, μ-H), 1.42 (s, 36H, *p*-*t*Bu), 1.83 (s, 36H, *o*-*t*Bu), 1.90 (s, 36H, *o*-*t*Bu), 6.77 (t, $J = 6.9$ Hz, 4H, *m*-Ph), 6.80 (t, $J = 6.6$ Hz, 4H, *m*-Ph), 6.88 (m, 4H, *p*-Ph), 7.07 (d, $J = 7.2$ Hz, 4H, *o*-Ph), 7.09 (d, $J = 7.5$ Hz, 4H, *o*-Ph), 7.60 (s, 2H, *m*-PAr), 7.61 (s, 2H, *m*-PAr), 7.65 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.6, 31.7, 34.0, 35.2, 35.4, 35.5, 39.2, 39.4, 122.4, 122.8, 122.9, 126.8, 127.4, 127.3, 128.5, 132.2, 134.0, 134.3, 134.4 (d, $J = 5$ Hz), 134.5 (d, $J = 5$ Hz), 141.7 (dd, $J = 56, 30$ Hz), 144.9 (dd, $J = 57, 29$ Hz), 151.8, 152.2, 155.7, 156.9, 159.0 (m), 162.5 (m). ^{31}P{^{1}H} NMR (C_6D_6): δ 175.6 (dd, $J = 208, 12$ Hz), 156.1 (d, $J = 244$ Hz). Anal. Calcd for $C_{104}H_{138}OP_4Rh_2$: C, 72.04; H, 8.02. Found: C, 71.74; H, 8.18.

Preparation of [Rh_2(μ-H)(μ-OMe)(DPCB)$_2$] (4). A solution of **3** (113.9 mg, 0.0657 mmol) in THF (1.5 mL) was prepared, layered with MeOH (6.0 mL), and allowed to stand at room temperature for 2 days to give dark brown crystals of **4** (96.1 mg, 67%). ^{1}H NMR (C_6D_6): δ −9.80 (ttt, $J = 84, 26, 15$ Hz, 1H, μ-H), 1.37 (s, 18H, *p*-*t*Bu), 1,41 (s, 18H, *p*-*t*Bu), 1.81 (s, 36H, *o*-*t*Bu), 1.92 (s, 36H, *o*-*t*Bu), 3.88 (s, 3H, OMe), 6.77 (t, $J = 7.2$ Hz, 4H, *m*-Ph), 6.79 (t, $J = 7.5$ Hz, 4H, *m*-Ph), 6.87 (t, 2H, $J = 6.9$ Hz, *p*-Ph), 6.89 (t, 2H, $J = 7.2$ Hz, *p*-Ph), 7.04 (t, $J = 8.1$ Hz, 4H, *o*-Ph), 7.12 (t, $J = 8.1$ Hz, 4H, *o*-Ph), 7.59 (s, 2H, *m*-PAr), 7.60 (s, 2H, *m*-PAr), 7.67 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR (C_6D_6): δ 32.0, 32.0, 32.1, 34.4, 35.5, 35.6, 35.7, 35.8, 35.8, 39.6, 39.7, 39.8, 39.8, 69.6, 122.8, 122.8, 123.2, 123.2, 123.3, 127.2, 127.5, 127.7, 127.8, 128.9, 128.9, 132.6, 134.4, 134.4, 134.6, 134.8, 134.9 (m), 142.1 (m), 145.3 (m), 152.1, 152.2, 152.5, 156.1, 157.0, 157.3, 158.2 (m), 162.8 (m). ^{31}P{^{1}H} NMR (C_6D_6): δ 174.6 (dd, $J = 220, 31$ Hz), 156.9 (d, $J = 266$ Hz). Anal. Calcd for $C_{105}H_{140}OP_4Rh_2$: C, 72.15; H, 8.07. Found: C, 71.92; H, 8.09.

Preparation of [Rh_2(μ-HCO_2)$_2$(DPCB)$_2$] (5). To a solution of **2** (12.5 mg, 0.00741 mmol) in toluene-d_8 (0.5 mL) was added formic acid (0.6 μL, 0.0159 mmol) at 0 °C. After 10 min, complex **5** was exclusively formed, as confirmed by NMR spectroscopy. ^{1}H NMR (toluene-d_8): δ 1.36 (s, 36H, *p*-*t*Bu), 1.93 (s, 72H, *o*-*t*Bu), 6.74 (t, $J = 7.5$ Hz, 8H, *m*-Ph), 6.87 (t, $J = 7.5$ Hz, 4H, *p*-Ph), 6.91 (d, $J = 8.4$ Hz, 8H, *o*-Ph), 7.61 (s, 8H, *m*-PAr). ^{31}P{^{1}H} NMR (toluene-d_8): δ 163.2 (d, $J = 262$ Hz).

Preparation of [Rh_2(μ-$MeCO_2$)$_2$(DPCB)$_2$] (6). To a suspension of **2** (100.0 mg, 0.0571 mmol) in pentane (1.0 mL) was added acetic acid (6.9 μL, 0.120 mmol) at 0 °C. The color of the suspension immediately turned from dark yellow to dark brown. After 1 h, the precipitate was collected by filtration, washed with pentane at 0 °C, and dried under vacuum to give a dark brown power of **6** (102.2 mg, 98%). Mp: 197 °C (dec). IR (KBr): 1595, 1449 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.39 (s, 36H, *p*-*t*Bu), 1.71 (s, 6H, O_2CMe), 2.01 (s, 72H, *o*-*t*Bu), 6.78 (t, $J = 7.5$ Hz, 8H, *m*-Ph), 6.88 (t, $J = 7.5$ Hz, 4H, *p*-Ph), 7.00 (d, $J = 7.5$ Hz, 8H, *o*-Ph), 7.63 (s, 8H, *m*-PAr). ^{13}C{^{1}H} NMR (C_6D_6): δ 24.4, 31.5, 34.5, 35.5, 39.1, 122.6, 126.9, 128.1, 128.6, 129.6 (m), 133.3, 143.4 (m), 153.1, 157.2, 158.9 (m), 191.6 (m). ^{31}P{^{1}H} NMR (C_6D_6): δ 165.9 (d, $J = 263$ Hz). Anal. Calcd for $C_{108}H_{142}O_4P_4Rh_2$: C, 70.73; H, 7.80. Found: C, 70.54; H, 8.10.

Preparation of [Rh(η^3-C_6H_9)(DPCB)] (8). To a suspension of **2** (49.9 mg, 0.0285 mmol) in toluene (2.5 mL) containing 1,3-cyclohexadiene (5.5 μL, 0.0577 mmol) was added formic acid (2.2 μL, 0.0583 mmol) at room temperature. The solution immediately turned dark reddish-brown. After 0.5 h, volatiles were removed under reduced pressure, and the residue was washed with pentane at 0 °C and dried under vacuum to give a dark reddish-brown powder of **8** (27.3 mg, 51%). Slow diffusion of a concentrated THF solution into MeOH gave analytically pure crystals with the composition **8**·MeOH. Mp: 220 °C (dec). ^{1}H NMR (C_6D_6): δ 1.41 (s, 18H, *p*-*t*Bu), 1.71 (s, 18H, *o*-*t*Bu), 1.91 (s, 18H, *o*-*t*Bu), 2.26 (br, 4H, CHCH_2CH_2), 4.79 (m, 2H, allyl H_{syn}), 5.69 (td, $J = 6.5, 2.6$ Hz, 1H, allyl $H_{central}$), 6.81 (t, $J = 7.4$ Hz, 4H, *m*-Ph), 6.90 (t, $J = 7.4$ Hz, 2H, *p*-Ph), 7.05 (d, $J = 7.2$ Hz, 4H, *o*-Ph), 7.65 (s, 2H, *m*-PAr), 7.70 (s, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (C_6D_6): δ 23.0, 29.8, 31.7, 33.6, 34.4, 35.4, 39.1, 39.1, 68.6 (dd, $J = 36, 9$ Hz), 101.2 (m, $J = 3$ Hz), 122.5, 122.8, 127.5, 128.5, 134.0, 135.4 (m), 144.7 (dd, $J = 55, 32$ Hz), 151.5, 156.0, 156.1, 167.5 (ddd, $J = 34, 30, 5$ Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 165.4 (d, $J = 241$ Hz).

Anal. Calcd for $C_{59}H_{81}OP_2Rh$ (**8**·MeOH): C, 72.97; H, 8.41. Found: C, 72.70; H, 8.24.

Preparation of [Rh_2(μ-κP,P;κP,C-DPCB)$(CO)_4$] (9). A suspension of **2** (71.2 mg, 0.0411 mmol) in pentane (8.0 mL) was degassed by freeze−pump−thaw cycles, and carbon monoxide (1 atm) was introduced from a CO balloon. The dark red suspension changed to a dark brown solution. Slow evaporation of the solvent under the flow of CO gas at room temperature for 2 days formed dark brown crystals with the composition **8**·C_5H_{12} (24.0 mg, 55%). Mp: >300 °C. IR (KBr): 2033, 2008, 1977, 1962 cm^{-1}. ^1H NMR (toluene-d_8): δ 1.27 (s, 18H, *p*-*t*Bu), 1.77 (s, 18H, *o*-*t*Bu), 1.85 (s, 18H, *o*-*t*Bu), 6.71−6.81 (m, 10H, Ph), 7.33 (s, 2H, *m*-PAr), 7.47 (s, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 31.3, 35.2, 35.3, 39.9, 40.0, 123.1, 123.6, 127.2, 128.0, 128.3, 131.3 (td, J = 13, 5 Hz), 132.3, 133.0 (dd, J = 8, 7 Hz), 144.4 (t, J = 8 Hz), 152.4, 157.6, 158.5, 194.7 (dt, J = 74, 28 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 152.9 (dd, J = 151, 44 Hz). Anal. Calcd for $C_{61}H_{80}O_4P_2Rh_2$ (**8**·C_5H_{12}): C, 63.98; H, 7.04. Found: C, 63.60; H, 6.86.

Preparation of [Rh_2(μ-CO)$_2$(DPCB)$_2$] (10). A solution of **2** (150.8 mg, 0.086 mmol) in THF (4.0 mL) was degassed by freeze−pump−thaw cycles, and carbon monoxide (1 atm) was introduced from a CO balloon. The solution immediately turned dark brown. The mixture was stirred for 30 min at room temperature under a CO atmosphere. After purging the CO gas from the solution, volatiles were removed under vacuum, and the residue was washed with Et_2O at 0 °C and dried under vacuum to give a dark brown powder of **10** (111.8 mg, 73%). Recrystallization from THF and MeOH formed single crystals, suitable for X-ray structural analysis. IR (KBr): 1766 cm^{-1}. ^1H NMR (C_6D_6): δ 1.35 (s, 36H, *p*-*t*Bu), 1.82 (s, 72H, *o*-*t*Bu), 6.80 (m, 12H, *m*- and *p*-Ph), 6.96 (d, J = 6.9 Hz, 4H, *o*-Ph), 7.61 (s, 8H, *m*-PAr). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 31.6, 34.5, 35.3, 39.3, 122.8, 128.1, 128.5, 132.6, 148.6 (m), 151.7, 156.8, 172.1 (t, J = 28 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 173.9 (d, J = 235 Hz).

X-ray Diffraction Studies. All measurements were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The intensity data were collected at 173 K and corrected for Lorentz and polarization effects and absorption (numerical). The structures were solved by DIRDIF99 and refined on F^2 for all reflections (SHELXL-97).[20] All non-hydrogen atoms were refined anisotropically. The μ-H ligands in **3** and **4** were located from the differential Fourier maps and refined isotropically. The other hydrogen atoms were placed using AFIX instructions. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 671945 (**2**·(2C_5H_{12})), 671947 (**3**·Et_2O), 671948 (**4**), 671949 (**9**·C_5H_{12}), 671950 (**10**). A summary of the crystallographic data is given in Table 1.

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Supporting Information Available: Crystallographic data of **2**·(2C_5H_{12}), **3**·Et_2O, **4**, **9**·C_5H_{12}, and **10** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Sheldrick, G. M. *SHELX-97*; University of Göttingen: Germany, 1997.