Studies of Dirhodium(II) Tetrakis(trifluoroacetate). 6. The First Structural Characterization of Axial Alkyne Complexes, $Rh_2(O_2CCF_3)_4(Ph_2C_2)_n$ (n = 1, 2): Diphenylacetylene as a Bifunctional Ligand

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The solid-state reactions of $Rh_2(O_2CCF_3)_4$ with diphenylacetylene (Ph_2C_2) have produced the first two dirhodium(II,II) carboxylate complexes with coordinated alkynes having overall compositions of 1:2 (**1**) and 1:1 (**2**). Compounds **1** and **2** have been characterized by elemental analysis and IR and mass spectroscopy, and their structures have been determined by X-ray diffraction. The bisadduct **1** has two alkyne groups coordinating to axial positions of the dirhodium tetrakis(trifluoroacetate) molecule. In the crystal structure of **2** the diphenylacetylene is acting as a bifunctional ligand, binding one dirhodium unit through the carbon−carbon triple bond while coordinating to another one via its phenyl group, thus forming an extended polymeric structure. The alkyne coordination in both complexes is an η^2-type without disruption of the triple-bond system (the C≡C distances are 1.204(6) Å (**1**) and 1.206(8) Å (**2**); the average C≡C−C angles are 168.3(4)° (**1**) and 169.2(6)° (**2**)). The axial $Rh-C_{alkyne}$ contacts are averaged to 2.530(4) Å in **1** and to 2.494(5) Å in **2**. The coordination of Rh to one of the phenyl groups of Ph_2C_2 in (**2**) is off-centered (3,4), with the two closest $Rh-C_{arene}$ distances being 2.696(5) and 2.750(6) Å.

Introduction

It is well-known that $Rh_2(O_2CCF_3)_4$ has a great ability to bond axially many types of donor ligands.[1,2] The study of the binding of unsaturated hydrocarbons is of fundamental interest, owing to wide application of their catalytic reactions in modern chemistry and industry. Olefin complex formation with $Rh_2(O_2CCF_3)_4$ has been detected in solutions by UV−vis spectroscopy, and equilibrium constants for the 1:1 adducts with a series of alkenes have been calculated.[3] It was shown that increasing alkyl substitution of the carbon−carbon double bond favors coordination, while arylethylenes exhibit no detectable interaction in solution. Later the crystal structure of the bis(olefin) adduct of $Rh_2(O_2CCF_3)_4$ with (−)-*trans*-caryophyllene was reported.[4] Not long ago we isolated the first example of a dirhodium(II) carboxylate complex with an arene in the form of the one-dimensional coordination copolymer $[Rh_2(O_2CCF_3)_4(C_6Me_6)]_\infty$.[5a] However, up to now there has been still one class of interactions missing: coordination of alkyne carbon−carbon triple bonds by the dirhodium unit.

Recently we have found a facile route to $Rh_2(O_2CCF_3)_4$ adducts based on the co-deposition of solid sublimable reactants from the vapor phase ("solventless" technique),[5] which offers an efficient alternative over complexation in solutions. The great advantage of this method is the absence of solvent molecules, which very often compete with weak donors for axial coordination. Another gain is the ability to effectively regulate the concentrations of different species in the vapor phase, which leads to the deposition of products with different compositions or structures. Here we have attempted to apply this technique to study the interactions between $Rh_2(O_2CCF_3)_4$ and the solid volatile ligand diphenylacetylene (Ph_2C_2). We have succeeded in isolating both a discrete bisadduct complex of the composition $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (**1**) and a monoadduct with an extended polymeric structure, $[Rh_2(O_2CCF_3)_4(Ph_2C_2)]_\infty$ (**2**). These two complexes are the first ones structurally characterized having an alkyne C≡C bond coordinated to the dirhodium unit. In addition, the one-dimensional polymer **2** affords an interesting example of the bifunctionality of the Ph_2C_2 ligand.

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993.
(2) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73.
(3) (a) Doyle, M. P.; Colsman, M. R.; Chinn, M. S. *Inorg. Chem.* **1984**, *23*, 3684. (b) Doyle, M. P.; Mahapatro, S. N.; Caughey, A. C.; Chinn, M. S.; Colsman, M. R.; Harn, N. K.; Redwine, A. E. *Inorg. Chem.* **1987**, *26*, 3070.
(4) Cotton, F. A.; Falvello, L. R.; Gerards, M.; Snatzke, G. *J. Am. Chem. Soc.* **1990**, *112*, 8979.
(5) (a) Part 2: Cotton, F. A.; Dikarev, E. V.; Stiriba, S.-E. *Organometallics* **1999**, *18*, 2724. (b) Part 3: Cotton, F. A.; Dikarev, E. V.; Stiriba, S.-E. *Inorg. Chem.* **1999**, *38*, 4877. (c) Part 4: Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Organomet. Chem.* **2000**, *596*, 130. (d) Part 5: Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Stiriba, S.-E. *Inorg. Chem.*, in press. (e) Part 8: Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Stiriba, S.-E. *Polyhedron*, submitted for publication.

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Table 1. Principal Dimensions (Distances in Å, Angles in deg) of Axial Coordination to $Rh_2(O_2CCF_3)_4$ Molecules by Diphenylacetylene (1, 2) and Hexamethylbenzene

	Rh−Rh	Rh−C_{al}[a]	∠Rh−Rh−C_{al}	C≡C	∠C−C≡C	Rh−C_{ar}[b,c]	∠Rh−Rh−C_{ar}	C···C	∠C···C···C
$Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (**1**)	2.4316(6)	2.550(4) 2.510(4)	166.2(1) 166.3(1)	1.204(6)	168.5(4) 168.1(4)				
$[Rh_2(O_2CCF_3)_4(Ph_2C_2)]_\infty$ (**2**)	2.4256(6)	2.499(5) 2.489(5)	166.8(1) 165.2(1)	1.206(8)	169.2(6) 169.3(6)	2.696(5) 2.750(6)	165.1(1) 164.7(1)	1.369(9)	119.7(5) 120.5(5)
$[Rh_2(O_2CCF_3)_4(C_6Me_6)]_\infty$[d]	2.422(1)					2.770(6) 2.787(6)	165.4(1) 164.1(1)	1.40(1)	121.3(6) 118.9(6)

[a] C_{al} = alkyne carbon atom. [b] C_{ar} = arene carbon atom. [c] Two closest contacts. [d] From ref 5a.

Results and Discussion

Here we have again applied a solventless synthesis technique,[5] which makes it possible to examine weak interactions unobservable in solutions, for studying the system $Rh_2(O_2CCF_3)_4-Ph_2C_2$. Under the conditions of low temperatures (65−80 °C) and high concentration of ligand in the initial mixture (1:2) we obtained crystals of a volatile bisadduct, $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (**1**). At higher temperatures (120−140 °C) and lower concentration of diphenylacetylene (1:1) we isolated crystals of a monoadduct, $Rh_2(O_2CCF_3)_4(Ph_2C_2)$ (**2**), in moderate yield. Thus, we have found that the two complexes can be selectively prepared under different experimental conditions. The obvious explanation for that is based on the variation of concentrations of different species in the vapor phase. At low temperature and high concentration of ligand we can preserve dirhodium molecules in the gas phase in the form of the volatile bisadduct, which then condenses exclusively in the cold temperature zone. At higher temperatures the bisadduct apparently loses one ligand and the monoadduct molecules become the predominant Rh-containing species in the gas phase and then crystallize upon condensation to give **2**. At temperatures higher than 200 °C the monoadduct starts to lose another ligand, resulting in the separate deposition of dirhodium tetrakis(trifluoroacetate) and diphenylacetylene.

Both products **1** and **2** have been examined by X-ray crystallography and IR and mass spectroscopy. The fragmentation patterns in the mass spectra are similar for **1** and **2**, starting with the parent peak $[Rh_2(O_2CCF_3)_4]^+$. The main fragments result from the loss of one, two, three, and four trifluoroacetate groups. The dominant IR peaks in spectra of **1** and **2** are broad C−O stretching vibrations of trifluoroacetate groups at 1660 and 1190 cm^{-1}. The carbon−carbon stretching vibrations of the C≡C triple bonds are generally fairly weak and appear at 2200−1900 cm^{-1}. There are no infrared active bands observed in this region in either case, except for a very weak band at 2170 cm^{-1} in **1**.

The structure of **1** consists of discrete neutral molecules, $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (Figure 1), which have crystallographic inversion symmetry, and there are no significant close contacts. The two diphenylacetylene groups coordinate to the dirhodium unit in axial positions through two alkyne C atoms so that the alkyne is disposed approximately perpendicular to the metal−metal axis. The two Rh−C distances are slightly different: 2.510(4) and 2.550(4) Å (Table 1). Although it exceeds the limits of statistical significance, this difference is most probably a consequence of crystal packing effects. There is no significant lengthening of the C≡C triple bond (1.204(6) Å) in **1** compared to the value found in the free ligand (1.200(3) Å).[6] This implies a weak interaction preserving triple-bond character, a conclusion confirmed by the fact that the phenylacetylene moiety is not significantly bent at C(5) and C(6); the angles C≡C−C are 168.5(4) and 168.1(4)°, respectively.

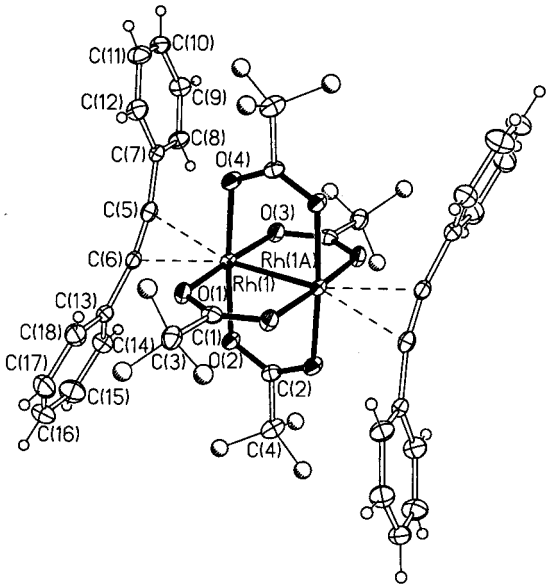

Figure 1. Perspective drawing of the molecule $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (**1**). Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and hydrogen atoms are shown as spheres of arbitrary radii and are not labeled for clarity. Axial contacts to Rh atoms are drawn by dashed lines.

The structure of complex **2** is particularly interesting, as both arene and alkyne functions of the starting ligand are involved in coordination with the dirhodium units, so as to form a one-dimensional polymeric chain (Figure 2). One rhodium atom of each Rh_2 unit coordinates to the acetylene bond of a Ph_2C_2 molecule with two very similar Rh−C bond distances, which average to 2.494(5) Å. The C≡C distance is 1.206(8) Å, which, again, does not significantly differ from the value in the free ligand.[6] Both angles C≡C−C in the Ph_2C_2 group are the same (169.2(6)°). The other rhodium atom of the Rh_2 unit has an off-centered coordination to a phenyl ring (3,4) of a Ph_2C_2 molecule with the two closest Rh−C distances being 2.696(5) and 2.750(6) Å. The distances adjacent to the alkyne linkage, C(9)−C(11) = 1.443(8) Å and C(10)−C(17) = 1.430(8) Å, were found to be different for noncoordinated and coordinated phenyl groups. Within these two phenyl rings of the

(6) Zanin, I. E.; Antipin, M. Yu.; Struchkov, Yu. T. *Sov. Phys. Crystallogr.* **1991**, *36*, 219.

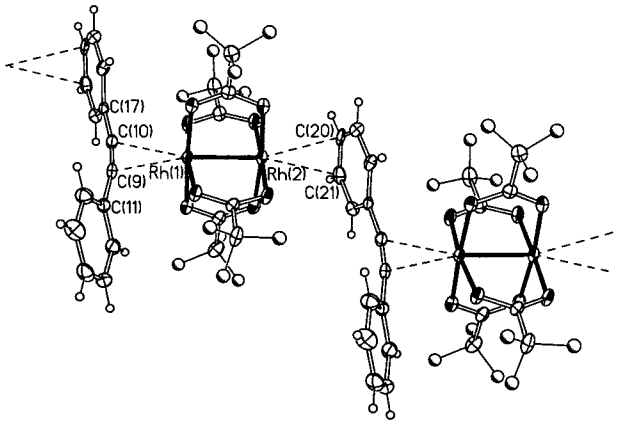

Figure 2. Fragment showing the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and Ph_2C_2 in the chain structure of **2**. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Only atoms involved in axial interactions (drawn by dashed lines) are labeled for clarity.

diphenylacetylene moiety, the mean C−C bond lengths (1.381(9) and 1.384(8) Å, respectively) and angles averaged to 120° appeared to be the same. The Rh−Rh bonds in **1** and **2** of 2.4316(6) and 2.4256(6) Å, respectively, are each within the expected range for the dirhodium unit bearing axially coordinated ligands.

The axial coordination to dirhodium units in **2** can be compared with what has been observed in related complexes (Table 1) in two ways: with the C≡C coordination in **1** and with the arene interaction in $[Rh_2(O_2CCF_3)_4(C_6Me_6)]_\infty$.[5a] For the former, the only difference is the Rh−C contacts averaged 2.530(4) Å in **1** and 2.494(5) Å in **2**. The explanation for that might stem from additional packing forces in the polymeric structure **2** or from the weaker interaction on the other end of the Rh_2 unit in **2**. These axial interactions are apparently weak in both **1** and **2**. There is no significant elongation of the acetylene C≡C bond upon coordination, and the deviations of the C≡C−C angles from 180° are among the smallest known for Ph_2C_2 complexes. With regard to the $Rh-C_{arene}$ interaction in **2**, we can compare it with that in the dirhodium polymer containing C_6Me_6 in which the same off-centered coordination of an arene has been observed. The Rh−C distances are a bit shorter in **2** (2.723(6) Å) than those (2.779(6) Å) in the C_6Me_6 complex, in which each arene group coordinates two Rh_2 units in contrast to **2.** More important, however, is the fact that in neither case is there any disruption of the aromatic system of the phenyl rings.

The two coordination modes of the Ph_2C_2 group found in **2** stem from the bifunctionality offered by the diphenylacetylene ligand, with metal−carbon interactions occurring through both its alkyne and arene functions. Another example of this type of bifunctionality was clearly observed in the mixed metal−carbonyl complex $Cr(CO)_3(\eta^6{:}\eta^2\text{-}PhC_2Ph)Co_2(CO)_6$, which consists of a $Cr(CO)_3(\eta^6$-arene) unit and the $Co_2(CO)_6$ fragment bound to the triple bond of diphenylacetylene in the $\mu_2{:}\ \eta^2$ mode.[7] There was a significant inequivalence in the $Cr-C_{ar}$ distances over the range 2.205(3)−2.263(3) Å and a typical elongation of the C−C bonds in the complexed phenyl ring (mean C−C distance of 1.405(4) Å). In the $Co_2(CO)_6(\mu_2{:}\eta^2\text{-}PhC{\equiv}CPh)$ unit the alkyne C−C vector lies perpendicular to the Co−Co axis and has a bond distance of 1.341(4) Å, which is much longer than those in complexes **1** and **2**, and indicates the loss of triple bond character. Despite the fact that Ph_2C_2 coordinates to metal complexes overwhelmingly by its alkyne part, there are some other examples of using its second function, which include $[(Cr(CO)_3)_2(\eta^6{:}\eta^6\text{-}PhC{\equiv}CPh)]$[8] and $[(Cp^*Ru)_2(\eta^6{:}\eta^6\text{-}PhC{\equiv}CPh)](CF_3SO_3)_2$[9] compounds. In both of these molecules two fragments, $Cr(CO)_3$ or Cp*Ru, respectively, are centrosymmetrically bonded to two phenyl rings of a diphenylacetylene molecule, each in an η^6-mode.

Table 2. Axial Coordination of $Rh_2(O_2CCF_3)_4$ to Different Types of Unsaturated Hydrocarbons

	C−C bond character	Rh−C (Å)	C−C (Å)	ref
$Rh_2(O_2CCF_3)_4(C_6H_6)$	C⋯C	2.646(6) 2.678(6)	1.39(1)	5e
$Rh_2(O_2CCF_3)_4$-(p-$C_6H_4Me_2$)	C⋯C	2.598(7) 2.770(7)	1.39(1)	5e
$Rh_2(O_2CCF_3)_4(C_6Me_6)$	C⋯C	2.770(6) 2.787(6)	1.40(1)	5a
$Rh_2(O_2CCF_3)_4(Ph_2C_2)$	C⋯C	2.696(5) 2.750(6)	1.369(9)	this work
$Rh_2(O_2CCF_3)_4$-((−)-*trans*-caryophyllene)$_2$	C=C	2.46(1) 2.63(1)	1.40(2)	4
$Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$	C≡C	2.550(4) 2.510(4)	1.204(6)	this work
$Rh_2(O_2CCF_3)_4(Ph_2C_2)$	C≡C	2.499(5) 2.489(5)	1.206(8)	this work

With regard to rhodium chemistry, there are a number of acetylene bridging complexes of Rh(0) of the type $Rh_2(PF_3)_4L_2$(alkyne) (L = PR_3, AsR_3) known, including $Rh_2(PF_3)_4(PPh_3)_2(Ph_2C_2)$, for which an X-ray structural analysis was performed.[10] In the latter complex the C≡C bond lies above and approximately normal to the Rh−Rh axis. There are two sets of Rh−C distances averaged to 2.093(5) and 2.125(5) Å, indicating that the Ph_2C_2 group is not precisely normal to the Rh−Rh axis. The acetylene C−C distance in the bridging Ph_2C_2 group of 1.369(7) Å is significantly longer than that in the free ligand and in the complexes **1** and **2**, again indicating the reduction of carbon−carbon bond order.

To recapitulate, in this work two novel compounds isolated by employing solventless synthesis, namely $Rh_2(O_2CCF_3)_4(\eta^2\text{-}PhC{\equiv}CPh)_2$ (**1**) and $[Rh_2(O_2CCF_3)_4(\eta^2{:}\eta^2\text{-}PhC{\equiv}CPh)]_\infty$ (**2**) are the first compounds of the dirhodium core bearing axially coordinated alkyne groups. We can now compare the axial coordination of three types of unsaturated hydrocarbons to dirhodium tetra(trifluoroacetate). The data for these types of carbon−carbon bonds, namely aromatic, double, and triple, are listed in Table 2. Two types of coordination, symmetrical and unsymmetrical, are observed when comparing contacts of rhodium atoms with two C atoms of carbon−carbon bonds. Despite the fact that these

(7) Tunik, S. P.; Vlasov, A. V.; Nikol'skii, A. B.; Starova, G. L.; Ooi, S.; Nakai, H.; Sato, T. *J. Organomet. Chem.* **1994**, *464*, 71.

(8) Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607.

(9) He, X. D.; Chaudret, B.; Dahan, F.; Huang, Y.-S. *Organometallics* **1991**, *10*, 970.

(10) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97.

interactions are definitely affected by steric factors and substituents, we can state that coordinations to double and triple bonds are about the same magnitude, while the interaction with the aromatic bond is considerably weaker.

Experimental Section

General Information. All the experimental manipulations involving the synthesis of the starting materials were carried out under dry, oxygen-free argon by employing Schlenk techniques. The anhydrous form of $Rh_2(O_2CCF_3)_4$ was prepared using literature procedures.[11c] Diphenylacetylene (Ph_2C_2) was purchased from Aldrich and sublimed before use. The IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer using KBr pellets. The EI/DP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Elemental analysis was done by Canadian Microanalytical Services, Ltd.

Synthesis of $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (1). Compound **1** was prepared by heating a mixture of unligated dirhodium(II) tetrakis(trifluoroacetate) (0.066 g, 0.10 mmol) and diphenylacetylene (0.036 g, 0.20 mmol) at 65−85 °C for 3 days in a sealed evacuated Pyrex ampule. Dark green block crystals were grown in both "hot" and "cold" zones of the tube. Yield: 0.058 g, 57.2%. Anal. Calcd for $Rh_2O_8F_{12}C_{36}H_{20}$: C, 42.62; H, 1.99. Found: C, 42.48; H, 2.00. IR (KBr, cm^{-1}): 2169.7 (w), 1662.2 (s), 1498.9 (w), 1458.6 (w), 1443.4 (w), 1225.6 (s), 1191.0 (s), 1166.0 (s), 1070.2 (w), 1026.9 (w), 917.9 (w), 860.2 (s), 840.3 (w), 806.1 (w), 784.7 (m), 757.1 (s), 739.6 (s), 689.9 (m), 536.6 (m), 525.8 (w), 511.4 (w). MS (EI/DP, 300 °C, *m*/*z*): 657 [$(Rh_2(O_2CCF_3)_4^+$], 544 [$(Rh_2(O_2CCF_3)_3^+$], 431 [$(Rh_2(O_2CCF_3)_2^+$], 318 [$(Rh_2(O_2CCF_3)^+$].

Synthesis of $[Rh_2(O_2CCF_3)_4(Ph_2C_2)]_\infty$ (2). Compound **2** was prepared by heating a mixture of $Rh_2(O_2CCF_3)_4$ (0.066 g, 0.10 mmol) and Ph_2C_2 (0.018 g, 0.10 mmol) at 120 °C overnight in a sealed evacuated ampule. Light green crystals of **2** were collected from the "cold" zone of the tube, where the temperature was set about 5 °C lower. Yield: 0.045 g, 54.1%. Anal. Calcd for $Rh_2O_8F_{12}C_{22}H_{10}$: C, 31.60; H, 1.21. Found: C, 31.69; H, 1.23. IR (KBr, cm^{-1}): 1664.2 (s), 1559.6 (w), 1540.3 (w), 1522.0 (w), 1507.5 (w), 1457.9 (w), 1310.9 (w), 1193.8 (s), 1165.2 (s), 1077.4 (w), 1025.7 (w), 859.0 (m), 804.7 (w), 785.6 (m), 738.5 (s), 697.8 (m), 571.2 (w), 546.3 (m), 527.3 (w). MS (EI/DP, 300 °C, *m*/*z*): 657 [$(Rh_2(O_2CCF_3)_4^+$], 544 [$(Rh_2(O_2CCF_3)_3^+$], 431 [$(Rh_2(O_2CCF_3)_2^+$], 318 [$(Rh_2(O_2CCF_3)^+$].

X-ray Structure Determination. Single crystals of compounds **1** and **2** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details concerning data collection have been fully described elsewhere.[11] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (−60 °C) of a low-temperature controller. Fifty reflections were used in cell indexing and more than 200 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[12] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[13]

All calculations were done on a DEC Alpha running VMS. The coordinates of rhodium and oxygen atoms for the structures were found in direct method *E* maps using the structure solution program SHELXTL.[14] The positions of the remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps.[15] The fluorine atoms of all CF_3 groups were found to be disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine atoms. Hydrogen atoms of the diphenylacetylene ligand were refined (**1**) or included in the structure factor calculations at idealized positions (**2**). Relevant crystallographic data for complexes **1** and **2** are summarized in Table 3.

Table 3. Crystallographic Data and Structure Refinement Details for $Rh_2(O_2CCF_3)_4(Ph_2C_2)_2$ (1) and $[Rh_2(O_2CCF_3)_4(Ph_2C_2)]_\infty$ (2)

	1	**2**
formula	$Rh_2O_8F_{12}C_{36}H_{20}$	$Rh_2O_8F_{12}C_{22}H_{10}$
fw	1014.34	836.12
cryst syst	monoclinic	triclinic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	24.700(1)	9.3030(4)
b, Å	9.7055(5)	9.5423(9)
c, Å	18.5448(4)	16.3049(6)
α, deg		76.795(4)
β, deg	124.368(2)	84.240(5)
γ, deg		68.653(4)
V, Å^3	3669.6(3)	1312.2(1)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.836	2.116
μ, mm^{-1}	1.012	1.390
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (°C)	−60	−60
R1[a], wR2[b] ($I > 2\sigma(I)$)	0.036, 0.085	0.038, 0.094
R1[a], wR2[b] (all data)	0.038, 0.087	0.041, 0.097

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

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Supporting Information Available: X-ray structural data for **1** and **2**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (c) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19.

(12) Pflugrath, J.; Messerschmitt, A. MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

(13) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67. (b) *Ibid.* **1988**, *21*, 916.

(14) SHELXTL V.5; Siemens Industrial Automation Inc., Madison, WI, 1994.

(15) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.