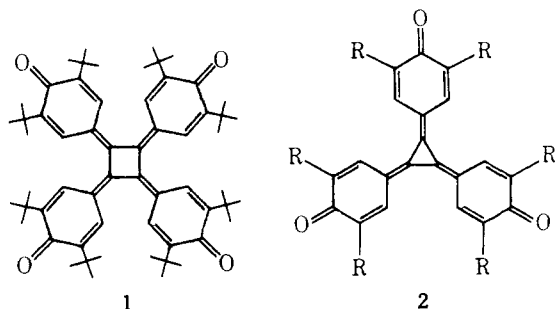# Catalyzed Dimerization of a Diquinoethylene and Formation of Diquinoethylene–Rhodium Complexes

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Abstract: Dimerization of diquinoethylene (dqe) **3a** to tetraquinocyclobutane **4** is catalyzed by the nickel complexes Ni-(PPh₃)₂(CO)₂ and Ni(diphos)(CO)₂, and also by a mixture of Ni(COD)₂ and triphenylphosphine. Triphenylphosphine alone catalyzes the same dimerization but more slowly. With tris(triphenylphosphine)chlororhodium, compounds **3a** and **3b** form complexes Rh(Ph₃P)₂(dqe). Single-crystal X-ray diffraction of the Rh(PPh₃)₂Cl(dqe) complex from **3a** shows that the central double bond of the cumulene system is bonded to the rhodium; the diquinoethylene moiety is almost planar but is significantly bent at the central carbon atoms.

The synthesis and properties of the tetraquinocyclobutane **1** [tetrakis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutane] were reported earlier from our laboratories.[1] Compound **1** is the four-membered ring analogue of the triquinocyclopropanes (**2**) which are useful as organic semi-

conductors and photosensitizers.[2,3] Even though models indicate that it cannot be planar, **1** similarly shows photoconductive and semiconductive behavior.

In our earlier studies **1** was obtained by thermal [2 + 2] dimerization of the diquinoethylene (dqe) **3**. This reaction produces **1** in a maximum yield of 25%, and isolation of the product from the reaction mixture is difficult. In attempts to improve the preparation we have investigated the effect of catalysts on the dimerization of **3a**.

3a, R = *tert*-butyl
b, R = isopropyl
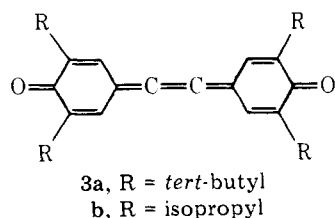
Although there seems to be no previous report of catalyzed dimerization of cumulenes, the transition metal catalyzed oligomerization of alkenes and allenes is well-known.[4,5] We therefore tried initially some of the metal complexes which are known to oligomerize olefins. Later results led us to try phosphines and other electron-donor molecules as catalysts.

Results and Discussion

Catalyst Evaluation. A standard reaction procedure, described in the Experimental Section, was used to evaluate catalysts and conditions. The yield of **1** was determined by measuring the absorbance of the product solution at 575 nm.[1] The results of these experiments are shown in Table I.

Although bis(1,5-cyclooctadiene)nickel [Ni(COD)₂] is a good catalyst for the cyclodimerization of certain alkenes and also readily trimerizes allenes, it is not an active catalyst for

the cyclodimerization of cumulene **3a**.[6,7] The tetrakis(triphenylphosphine) derivatives of nickel, palladium, and platinum as well as Rh(PPh₃)₃Cl all show some catalytic activity, with the nickel complex being the most effective. Bis(triphenylphosphine)dicarbonylnickel was the best catalyst tried, producing **1** in 95% yield, and bis(1,2-diphenylphosphinoethane)dicarbonylnickel worked nearly as well.

Because many of the active metal complexes contained phosphine ligands, triphenylphosphine itself was tried as a catalyst. To our surprise it was found to have moderate catalytic activity for dimerization of **3a** (Table I). Related compounds were then tried as catalysts, but none were effective. Diphenylmethylphosphine, 1,2-bis(diphenylphosphine)-ethane, triethoxyphosphine, and tri-*n*-butylphosphine all catalyzed decomposition of **3a** to unidentified products, but no **1** was formed in any case. Triphenylarsine and triphenylstibine also led to slow decomposition of **3a** but did not catalyze dimerization. With *N,N*-diisopropylaniline no reaction of **3a** was observed. The catalytic action of triphenylphosphine thus appears to be quite specific.

Catalysis of dimerization by triphenylphosphine is apparently unprecedented. The mechanism of this catalyst is not known, but may involve nucleophilic attack on one of the central carbon atoms of the cumulene system. The behavior of PPh₃ as a catalyst perhaps explains the activity of the M(PPh₃)₄ complexes, which may work simply by liberating triphenylphosphine to the solution. The most active nickel complexes, Ni(PPh₃)₂(CO)₂ and Ni(diphos)(CO)₂, catalyze dimerization of **3a** much more rapidly than does PPh₃, presumably via a mechanism involving coordination of the diquinoethylene to the metal. These phosphine–carbonyl complexes may be especially active because the CO ligands can dissociate and leave the solution, thereby providing free coordination sites on the nickel atom.

The results with bis(1,5-cyclooctadiene)nickel (Table I) provide support for the concept of duality of mechanism for the dimerization. Ni(COD)₂ alone is ineffective as a catalyst, but a mixture of Ni(COD)₂ and PPh₃ acts as a good catalyst, far more effective than PPh₃ alone.

Isolation of Complexes 4a and 4b. Although Rhᴵ catalysts have been shown to be effective for the oligomerization of various allenes to trimers and tetramers,[8] tris(triphenylphosphine)chlororhodium proved to be a rather poor catalyst for dimerization of **3a** (Table I). However, when this rhodium complex was heated with **3a**, formation of a new compound was observed by TLC of the reaction mixture. When the reaction was carried out using a stoichiometric amount of tris(triphenylphosphine)chlororhodium a complex (**4a**) containing **3a** and rhodium was isolated. The same reaction using **3b** gave a similar complex **4b**. These complexes, the first to be obtained from diquinoethylene or related polyquinone molecules, are

Table I. Catalytic Dimerization of **3a** to **1** in Benzene

catalyst	mol %	temp, °C	time, h	yield, % (UV)
none		80	48	0
Ph₃P	40	80	24	68
Ph₃P	20	80	18	33
Ph₃P	20	25	18	0
Ni(PPh₃)₄	20	80	18	64 (50[b])
Pd(PPh₃)₄	20	80	18	37
Pt(PPh₃)₄	20	80	18	33
Rh(PPh₃)₃Cl	20	80	18	24
Rh(PPh₃)₂Cl·**3a**	20	80	18	<5
Ni(PPh₃)₂(CO)₂	20	80	4	92
Ni(PPh₃)₂(CO)₂	5	80	4	97 (95[b])
Ni(PPh₃)₂(CO)₂	5	100[a]	18	34
Ni(diphos)(CO)₂	5	80	4	78
Ni(COD)₂	20	80	18	<5
Ni(COD)₂ + 2PPh₃	20	80	18	23
Ni(COD)₂ + 2PPh₃	20	25	18	56

[a] In toluene. [b] Isolated yields.

bright red, crystalline compounds inert to air both as solids and in solution.

The mass spectra and elemental analyses of the complexes indicated structures containing one cumulene, two triphenylphosphines, and a chlorine bonded to the Rh metal. Four possibilities (A–D) were considered for the cumulene–metal bonding.
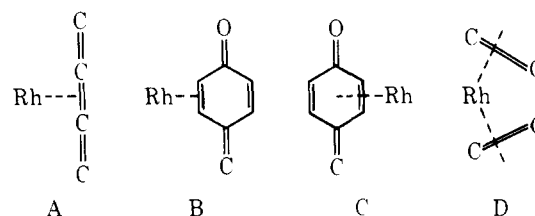
Structure D is unlikely on stoichiometric grounds, because the known structures for Rh–diene complexes from tris(triphenylphosphine)chlororhodium(I) contain only one triphenylphosphine ligand whereas both **4a** and **4b** contain two.[9] The same objection applies to π-bonded quinone structures like C.

Structures A and B are consistent with the composition of **4a** and **4b**, and analogues for both are known. An example of type B is the complex bis(triphenylphosphine)nitrosyl-1-4-benzoquinonerhodium(I) in which the quinone is bonded to the metal using only one of the carbon–carbon double bonds.[10]

Analogues to structure A are provided by the complexes formed from tris(triphenylphosphine)chlororhodium(I) and certain alkenes (ethene,[11] tetrafluoroethene,[12] and trifluorochloroethene)[12] and allenes (allene itself and trifluoromethylallene).[13] However, these ligands are much smaller than the cumulenes **3a,b**, and tris(triphenylphosphine)chlororhodium(I) will not form isolable complexes with alkenes even as large as propene. To determine the structure of the complexes, a sin-

Table II. Atom Parameters for **4a**

| atom	X	Y	Z	atom	X	Y	Z
Rh	2324.3(3)	1862.4(2)	4516.8(3)	C(5C)	3404(6)	3726(3)	2430(7)
P(1)	1073.0(9)	1857.3(5)	5389.7(9)	C(6C)	3180(5)	3097(3)	2404(5)
P(2)	3380.9(10)	1900.0(6)	3410.1(11)	C(1D)	4665(4)	1427(2)	3880(4)
Cl	2066.1(11)	794.2(5)	3769.8(11)	C(2D)	4887(4)	960(2)	4708(5)
C(1)	3078(3)	2496(2)	5742(4)	C(3D)	5874(4)	611(3)	5084(5)
C(2)	2339(3)	2820(2)	4875(4)	C(4D)	6615(4)	712(3)	4644(6)
C(1A)	3841(4)	2447(2)	6829(4)	C(5D)	6386(5)	1167(3)	3818(7)
C(2A)	4307(4)	1829(2)	7282(4)	C(6D)	5415(5)	1525(3)	3432(5)
C(3A)	5038(4)	1756(3)	8366(4)	C(1E)	2667(4)	1627(2)	1910(4)
C(4A)	5354(5)	2351(3)	9089(5)	C(2E)	3132(5)	1206(3)	1264(5)
C(5A)	4859(4)	2988(3)	8651(5)	C(3E)	2506(6)	999(3)	126(5)
C(6A)	4146(4)	3013(2)	7564(5)	C(4E)	1481(6)	1217(3)	−346(5)
C(7A)	5133(6)	3593(4)	9457(7)	C(5E)	1017(5)	1626(3)	294(5)
C(8A)	4905(10)	3575(6)	10530(9)	C(6E)	1617(4)	1830(3)	1429(4)
C(9A)	6231(9)	3677(6)	9881(12)	C(1F)	−238(4)	2059(2)	4334(4)
C(10A)	4511(9)	4196(4)	8882(9)	C(2F)	−1042(4)	2390(3)	4642(5)
C(11A)	5527(4)	1097(3)	8865(5)	C(3F)	−2042(4)	2510(3)	3823(6)
C(12A)	5375(9)	1026(5)	9982(8)	C(4F)	−2224(5)	2289(3)	2674(6)
C(13A)	6679(6)	1011(4)	9064(9)	C(5F)	−1441(5)	1962(3)	2363(5)
C(14A)	5039(7)	553(3)	8043(7)	C(6F)	−447(4)	1842(3)	3174(4)
O(A)	6092(5)	2312(3)	10025(5)	C(1G)	992(4)	1095(2)	5967(4)
C(1B)	1866(4)	3394(2)	4382(4)	C(2G)	53(4)	911(3)	5917(4)
C(2B)	2209(4)	4003(2)	4942(5)	C(3G)	37(5)	346(3)	6426(5)
C(3B)	1818(4)	4572(2)	4451(5)	C(4G)	946(6)	−32(3)	6971(5)
C(4B)	986(5)	4578(3)	3276(6)	C(5G)	1872(5)	146(3)	7012(5)
C(5B)	577(4)	3962(2)	2709(5)	C(6G)	1905(4)	705(2)	6505(5)
C(6B)	1010(4)	3413(2)	3265(4)	C(1H)	1237(3)	2441(2)	6621(4)
C(7B)	−273(5)	3973(3)	1489(5)	C(2H)	1799(4)	2248(2)	7743(4)
C(8B)	−652(6)	3315(4)	1099(6)	C(3H)	2015(5)	2706(3)	8675(4)
C(9B)	161(8)	4155(5)	597(7)	C(4H)	1679(5)	3344(3)	8489(5)
C(10B)	−1187(6)	4462(4)	1405(8)	C(5H)	1130(4)	3546(2)	7386(5)
C(11B)	2158(6)	5218(3)	5054(7)	C(6H)	913(4)	3097(2)	6448(4)
C(12B)	3005(7)	5118(3)	6257(9)	SC(1)	9265(7)	118(5)	9007(8)
C(13B)	2626(9)	5563(4)	4368(12)	SC(2)	9293(11)	694(7)	10673(12)
C(14B)	1233(7)	5643(4)	5229(10)	SC(3)	9701(12)	293(7)	10220(13)
O(B)	659(5)	5085(2)	2769(5)	SC(4)	8661(13)	2845(8)	7780(14)
C(1C)	3717(4)	2711(2)	3317(4)	SC(5)	8330(18)	2108(11)	7624(18)
C(2C)	4507(5)	2954(3)	4261(5)	SC(6)	7348(17)	2728(10)	6729(18)
C(3C)	4738(6)	3576(4)	4275(8)	SC(7)	7134(20)	2245(12)	7124(22)
C(4C)	4178(7)	3955(3)	3350(9)				
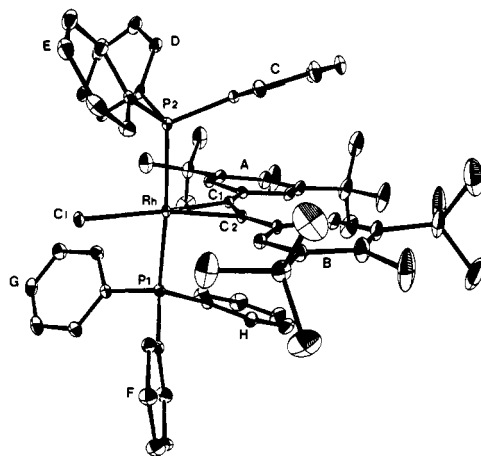
Figure 1. ORTEP drawing of complex **4a**. Ellipsoids of 10% probability are used.

gle-crystal X-ray diffraction investigation of **4a** was undertaken.

Crystal Structure of 4a·1.5C₃H₆O. The results from X-ray diffraction, shown in Figures 1 and 2 and Tables II and III, confirm that the structure is of type A, with the central double bond of the diquinoethylene bonded to the rhodium atom. Two acetone molecules are present in the crystal lattice, but neither one is bonded to the metal complex.

As seen from Figure 1 the coordination about the Rh atom can be regarded as square planar, with the triphenylphosphine ligands occupying trans positions. The diquinoethylene moiety is nearly planar and is essentially perpendicular to the RhP₂Cl plane. The perpendicular arrangement may be required by the presence of the bulky triphenylphosphine groups, which are situated above and below the diquinoethylene in a conformation which minimizes steric interaction between the rings C, H and A, B. The angle between the plane containing RhP₂Cl and the RhC(1)C(2) is 92°. There is a slight T₂ distortion of the ligands around the Rh, such that the P(1)–Rh–P(2) angle is 172.21 (4) and the Cl–Rh–C(1)–C(2) midpoint is 171° (Table III).

There is an increase in the C═C internuclear distance (Figure 2) on complexation, as well as considerable cis bending of the attached carbon atoms. For uncomplexed butatrienes, the central and outer C═C internuclear distances are normally 1.26 and 1.33 Å.¹⁴ For the complexed diquinoethylene these values increase to 1.34 and 1.37 Å. The cis bending of the substituents is 26 and 30°. The distortions of the diquinoethylene moiety in **4a** are similar to those observed in other cumulene–metal complexes.¹⁴,¹⁵ This cis bending of the ligand can be understood in terms of rehybridization of the central atoms from sp to a value intermediate between sp and sp².¹⁶ The bond lengths elsewhere in the diquinoethylene moiety are also slightly longer than normal for quinones, suggesting that some delocalization of positive charge takes place over the entire ligand.

The diquinoethylene is slightly distorted from planarity resulting from small twists of 4 and 1° about the C(1)–C(1A) and C(2)–C(1B) bonds and a 13° twist about the C(1)–C(2) bond, but the maximum deviation of atoms out of the Rh–Cl–C(1)–C(2)–C(1A)–C(2A) planes is only 0.027 Å. The bond distances from the Rh to the coordinated P(1), P(2), Cl, C(1), and C(2) are very similar to those previously reported in the literature.¹⁷,¹⁸

Preparation of Complexes Rh(C₂H₄)(acac)(dqe). In the oligomerization of allene, intermediates have been isolated containing two allene molecules π bonded to the metal.¹⁹ We also attempted to prepare rhodium(bisdiquinoethylene) complexes from Rh(C₂H₄)(acac) and **3a,b**. However, in this case only one
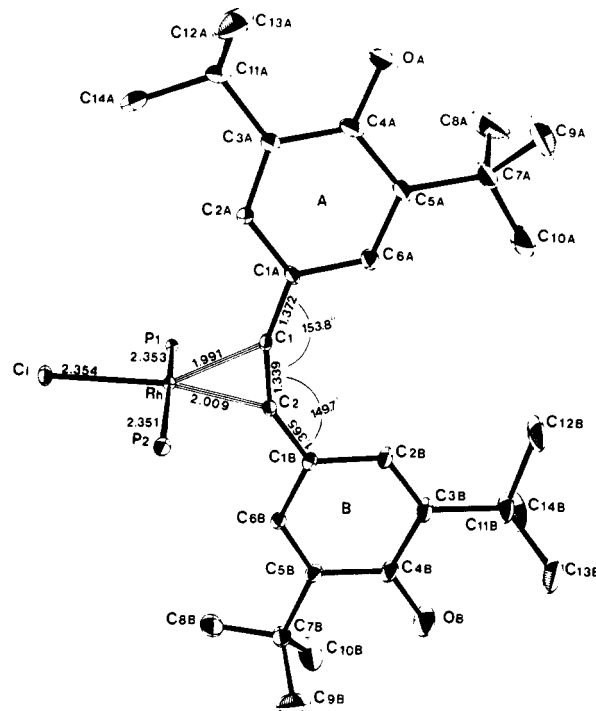

Figure 2. ORTEP drawing of complex **4a**. Phenyl rings have been omitted for clarity.

of the ethylene ligands was displaced and the complexes isolated had the composition Rh(C₂H₄)(acac)·**3a** and Rh(C₂H₄)(acac)·**3b**. A similar result occurred in the reaction of Rh(C₂H₄)₂(acac) with bis(trifluoromethyl)acetylene.²⁰ All attempts to drive the reaction further by heating or flowing nitrogen over the reaction mixture resulted in decomposition of the complexes. The complexes are unstable in solution and decompose after standing for a few hours in solvents such as CHCl₃, CH₂Cl₂, and acetone, to unidentified products.

Experimental Section

The following catalysts were prepared by literature methods: Rh(Ph₃P)₃Cl,²¹ Ni(PPh₃)₄,²² Ni(COD)₂,²³ Pt(PPH₃)₄,²⁴ Pd(Ph₃P)₄,²⁵ (C₂H₄)Rh(acac),²⁶ and C₆H₅N(i-Pr)₂.²⁷ Both Ni(PPh₃)₂(CO)₂ and Ni(diphos)(CO)₂ were purchased from Alfa Division, Ventron CORP. Tri-*n*-butylphosphine and triethyl phosphite were obtained from Aldrich Chemical Co., Ph₃P from Mallinckrodt Chemical Co., Ph₃As from K&K Laboratories, and Ph₃Sb from Columbia Organic Chemicals Co. Ph₂PMe and (Ph₂PCH₂)₂ were samples kindly donated by Professor P. M. Treichel. Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)ethylene (**3a**) and bis(3,5-diisopropyl-4-oxo-2,5-cyclohexadien-1-ylidene)ethylene (**3b**) were prepared as previously reported.²⁸

Cyclodimerization of 3a. Catalyst Evaluation. In a typical reaction, 100 mg (0.23 mmol) of **3a** was placed in a dry, argon-purged 50-mL Schlenk flask. After addition of 20 mol % catalyst and 20 mL of benzene the reaction mixture was refluxed for the desired length of time. The Schlenk flask was cooled to room temperature, the contents transferred to a 25-mL volumetric flask, and the volumetric flask diluted to the mark with benzene. Standard dilution techniques provided a solution which was used for the UV–visible determination of percent yield. This was done by comparing the degree of absorbance at 575 nm with a standard curve prepared from pure **1**.

Preparation of Tetraquinocyclobutane (1) by Cyclodimerization of 3a. A solution of 500 mg (1.7 mmol) of **3a**, 5 mol % Ni(PPh₃)₂(CO)₂,

Table III. Significant Interatomic Distances (Å) and Angles (deg) in **4a**

Rh-P(1)	2.353(1)	SC(4)-SC(5)	1.634(22)	Rh-P(1)-C(1H)	113.6(1)
Rh-P(2)	2.351(1)	SC(5)-SC(7)	1.535(26)	C(1F)-P(1)-C(1G)	104.1(2)
Rh-Cl	2.354(1)	SC(6)-SC(7)	1.271(26)	C(1F)-P(1)-C(1H)	106.6(2)
Rh-C(1)	1.991(4)	C(1C)-P(2)-C(1D)	102.0(2)	C(1G)-P(1)-C(1H)	103.8(2)
Rh-C(2)	2.009(4)	C(1C)-P(2)-C(1E)	105.7(2)	Rh-P(2)-C(1C)	114.7(2)
P(1)-C(1F)	1.824(4)	C(1D)-P(2)-C(1E)	107.2(2)	Rh-P(2)-C(1D)	117.8(2)
P(1)-C(1G)	1.834(4)	Rh-C(1)-C(2)	71.2(3)	Rh-P(2)-C(1E)	108.5(2)
P(1)-C(1H)	1.826(4)	Rh-C(1)-C(1A)	134.7(3)	C(12A)-C(11A)-C(13A)	109.7(7)
P(2)-C(1C)	1.837(5)	C(2)-C(1)-C(1A)	153.8(4)	C(12A)-C(11A)-C(14A)	106.9(7)
P(2)-C(1D)	1.831(5)	Rh-C(2)-C(1)	69.7(3)	C(13A)-C(11A)-C(14A)	107.3(6)
P(2)-C(1E)	1.829(5)	Rh-C(2)-C(1B)	140.4(3)	C(2)-C(1B)-C(2B)	121.3(4)
C(1)-C(2)	1.339(6)	C(1)-C(2)-C(1B)	149.7(4)	C(2)-C(1B)-C(6B)	121.2(4)
C(1)-C(1A)	1.372(6)	C(1)-C(1A)-C(2A)	120.7(4)	C(2B)-C(1B)-C(6B)	117.5(4)
C(2)-C(1B)	1.365(6)	C(1)-C(1A)-C(6A)	120.8(4)	C(1B)-C(2B)-C(3B)	123.2(5)
C(1A)-C(2A)	1.429(6)	C(2a)-C(1A)-C(6A)	118.3(4)	C(2B)-C(3B)-C(4B)	118.5(5)
C(1A)-C(6A)	1.433(6)	C(1A)-C(2A)-C(3A)	122.8(4)	C(2B)-C(3B)-C(11B)	123.3(5)
C(2A)-C(3A)	1.356(6)	C(2A)-C(3A)-C(4A)	117.4(5)	C(4B)-C(3B)-C(11B)	118.2(5)
C(3A)-C(4A)	1.478(8)	C(2A)-C(3A)-C(11A)	123.3(5)	C(3B)-C(4B)-C(5B)	119.4(4)
C(3A)-C(11A)	1.526(7)	C(4A)-C(3A)-C(11A)	119.4(4)	C(3B)-C(4B)-O(B)	120.2(6)
C(4A)-C(5A)	1.465(8)	C(3A)-C(4A)-C(5A)	120.4(5)	C(5B)-C(4B)-O(B)	120.5(6)
C(4A)-O(A)	1.229(7)	C(3A)-C(4A)-O(A)	119.5(6)	C(4B)-C(5B)-C(6B)	118.2(5)
C(5A)-C(6A)	1.342(7)	C(5A)-C(4A)-O(A)	119.8(6)	C(4B)-C(5B)-C(7B)	118.9(4)
C(5A)-C(7A)	1.534(8)	C(4A)-C(5A)-C(6A)	118.1(5)	C(6B)-C(5B)-C(7B)	122.8(5)
C(7A)-C(8A)	1.476(15)	C(4A)-C(5A)-C(7A)	119.3(5)	C(1B)-C(6B)-C(5B)	123.1(4)
C(7A)-C(9A)	1.442(12)	C(6A)-C(5A)-C(7A)	122.5(6)	C(5B)-C(7B)-C(8B)	111.2(5)
C(7A)-C(10A)	1.502(12)	C(1A)-C(6A)-C(5A)	122.9(5)	C(5B)-C(7B)-C(9B)	110.4(6)
C(11A)-C(12A)	1.492(10)	C(5A)-C(7A)-C(8A)	112.9(8)	C(5B)-C(7B)-C(10B)	113.1(6)
C(11A)-C(13A)	1.508(9)	C(5A)-C(7A)-C(9A)	113.3(8)	C(8B)-C(7B)-C(9B)	106.8(6)
C(11A)-C(14A)	1.505(9)	C(5A)-C(7A)-C(10A)	111.9(6)	C(8B)-C(7B)-C(10B)	109.3(6)
C(1B)-C(2B)	1.440(6)	C(8A)-C(7A)-C(9A)	103.7(9)	C(9B)-C(7B)-C(10B)	105.8(7)
C(1B)-C(6B)	1.450(6)	C(8A)-C(7A)-C(10A)	105.3(9)	C(3B)-C(11B)-C(12B)	110.8(5)
C(2B)-C(3B)	1.338(7)	C(9A)-C(7A)-C(10A)	109.2(9)	C(3B)-C(11B)-C(13B)	111.0(7)
C(3B)-C(4B)	1.484(8)	C(3A)-C(11A)-C(12A)	111.1(6)	C(3B)-C(11B)-C(14B)	110.3(6)
C(3B)-C(11B)	1.524(7)	C(3A)-C(11A)-C(13A)	110.2(5)	C(12B)-C(11B)-C(13B)	106.6(7)
C(4B)-C(5B)	1.482(7)	C(3A)-C(11A)-C(14A)	111.5(4)	C(12B)-C(11.B)-C(14B)	107.5(8)
C(4B)-O(B)	1.226(7)	P(1)-Rh-P(2)	172.21(4)	C(13B)-C(11B)-C(14B)	110.6(7)
C(5B)-C(6B)	1.343(6)	P(1)-Rh-Cl	90.77(4)	P(2)-C(1C)-C(2C)	117.7(4)
C(5B)-C(7B)	1.533(7)	P(1)-Rh-C(1)	90.8(1)	P(2)-C(1C)-C(6C)	123.2(4)
C(7B)-C(8B)	1.508(9)	P(1)-Rh-C(2)	89.5(1)	SC(3)-SC(1)-SC(3)'	61.9(11)
C(7B)-C(9B)	1.529(11)	P(2)-Rh-Cl	88.13(4)	SC(1)-SC(3)-SC(1)'	118.1(11)
C(7B)-C(10B)	1.494(10)	P(2)-Rh-C(1)	93.8(1)	SC(1)-SC(3)-SC(2)	122.7(15)
C(11B)-C(12B)	1.528(11)	P(2)-Rh-C(2)	90.2(1)	SC(1)-SC(3)-SC(3)'	64.1(10)
C(11B)-C(13B)	1.513(13)	Cl-Rh-C(1)	151.4(1)	SC(1)'-SC(3)-SC(2)	119.0(15)
C(11B)-C(14B)	1.530(12)	Cl-Rh-C(2)	169.5(1)	SC(1)'-SC(3)-SC(3)'	54.0(9)
SC(1)-SC(3)	1.428(16)	C(1)-Rh-C(2)	39.1(2)	SC(2)-SC(3)-SC(3)'	171.9(20)
SC(1)-SC(3)'	1.586(16)	Rh-P(1)-C(1F)	110.2(2)	SC(4)-SC(5)-SC(7)	100.4(17)
SC(3)-SC(3)'	1.556(29)	Rh-P(1)-C(1G)	117.5(2)	SC(5)-SC(7)-SC(6)	82.1(19)
SC(2)-SC(3)	1.163(17)				

and 125 mL of benzene was heated to reflux for 4 h. After removal of most of the solvent the reaction mixture was chromatographed on 50 g of silica gel using 20% benzene in pentane as the eluant. The only product obtained was 476 mg (95%) of purple solid identified by its NMR, IR, and UV-visible spectra as **1**.

Preparation of Complex Rh(Ph₃P)₂Cl(dqe) (4a). A solution of 618 mg (0.66 mmol) of Rh(PPh₃)₃Cl, 288 mg (0.66 mmol) of **3a**, and 20 mL of benzene was stirred under argon. The brown solution rapidly turned bright red and at the end of 5 h the solvent was removed under vacuum. The solid remaining was chromatographed on 50 g of silica gel, eluting with a mixture of 20% CHCl₃ in CCl₄ to remove the Ph₃P and a mixture of 30% CHCl₃ in CCl₄ to remove the Rh complex. The resulting red solid was dried under vacuum overnight to give 638 mg (87%) of **4a:** mp 254-255 °C dec; IR (CCl₄) 1595 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) a pair of singlets at δ 1.23 and 1.32 (36 H), doublet 6.26 (2 H, *J* = 3 Hz), multiplet 7.50 (30 H), doublet 7.94 ppm (2 H, *J* = 3 Hz); UV-visible (CHCl₃) 540 nm (log ε 4.55), 510, 345, 263; Ms no parent peak, peaks at *m/e* 662 and 434. Anal. Calcd for C₆₆H₇₀P₂O₂ClRh: C, 72.36; H, 6.44; P, 5.65. Found: C, 72.39; H, 6.40; P, 5.76.

Complex Rh(Ph₃P)₂Cl(dqe) (4b). Complex **4b** was prepared in similar fashion from **3b** and Rh(PPh₃)₃Cl yielding 421 mg (75%) of

product: mp 225-230 °C dec; IR (CCl₄) 1590 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) overlapping doublets at δ 1.02 and 1.10 (24 H, *J* = 3 Hz), septet 3.02 (4 H, *J* = 3 Hz), doublet 6.22 (2 H, *J* = 2 Hz), multiplet 7.40 (30 H), doublet 7.86 ppm (2 H, *J* = 2 Hz); UV-Visible (CHCl₃) λ 547 nm (log ε 4.53), 525, 350, 265; MS exact mass 1038.296 20 (calcd, 1038.296 14). Anal. Calcd for C₆₂H₆₂P₂O₂ClRh: C, 71.64; H, 6.01; P, 5.96. Found: C, 71.43; H, 6.03; P, 6.51.

Complex Rh(C₂H₄)(acac)(dqe) (5a). A solution of 100 mg (0.39 mmol) of (C₂H₄)₂Rh(acac), 167 mg (0.39 mmol) of **3a**, and 20 mL of benzene was stirred under argon. The purple-brown solution turned bright red almost immediately and at the end of 1 h the solution was filtered. Removal of most of the solvent under vacuum followed by filtration gave 198 mg (77%) of product **5a:** mp 212-214 °C dec; IR (CCl₄) 1600 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) a pair of singlets at δ 1.38 and 1.44 (36 H), a pair of singlets at 2.06 and 2.16 (6 H), a broad singlet 3.54 (4 H), singlet 5.50 (1 H), doublet 7.30 (2 H, *J* = 3 Hz), doublet 8.10 ppm (2 H, *J* = 3 Hz). Anal. Calcd for C₃₇H₅₁O₄Rh: C, 67.06; H, 7.76. Found: C, 67.66; H, 7.88.

Complex Rh(C₂H₄)(acac)(dqe) (5b). This complex was prepared as above to give 127 mg (63%) of product: mp 200-210 °C dec; IR (CCl₄) 1595 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) multiplet δ 1.28 (24 H), a pair of singlets 2.04 and 2.20 (6 H), septet 3.34 (4 H, *J* = 3 Hz),

broad singlet 3.64 (4 H), singlet 5.60 (1 H), doublet 7.40 (2 H, J = 2 Hz), doublet 8.14 ppm (2 H, J = 2 Hz). Anal. Calcd for $C_{33}H_{43}O_4Rh$: C, 65.34; H, 7.15. Found: C, 65.06; H, 7.24.

Crystal Structure of 4a·1.5C_3H_6O. A crystal of the compound was cut from a large crystal obtained by seeding a saturated solution of the compound in acetone. The seed crystal was obtained from evaporation of a tetrahydrofuran solution. Larger crystals obtained from THF tended to split and to lose solvent on exposure to air. The crystal chosen for the X-ray study had dimensions 0.60 × 0.45 × 0.45 cm, and was sealed in a glass capillary and placed on a Syntex PĪ autodiffractometer equipped with a graphite monochromated Mo K_2 source. After careful crystal alignment 15 diffraction maxima were used to obtain orientation and cell parameters. The compound is triclinic with a = 13.830 Å, b = 20.862 Å, c = 12.350 Å, α = 95.181°, β = 111.563°, γ = 82.455°. For Z = 2 the calculated density is 1.197 g/mL.

Data numbering 9233 were collected from 3° ≤ 2θ ≤ 45° and merged to give 8386 unique reflections of which 6820 had $I \geqslant 26(I)$[29] and were used in the structure analysis. The data were treated in the usual fashion for Lorentz–polarization with P = 0.055. The data were not corrected for absorption, because with μ 3.864 cm^{-1} for the block-like crystal the effect of absorption was negligible. Also there was no evidence of radiation damage during the collection of the data.

The structure was determined from heavy-atom methods in space group $P\bar{1}$ and refined isotropically via block diagonal least squares[30] to R_1 = 11.3, R_2 = 15.8. Refinement was continued with anisotropic thermal parameters for all nonhydrogen atoms and converged to R_1 = 7.1, R_2 = 12.1. At this stage a difference map clearly revealed the location of two molecules of acetone. The first was located on the center of symmetry in a well-defined disorder. The second was located in a general position in a cavity in the crystal and was not well resolved. A partial refinement of the multiplicity factors for the second solvent molecule indicated an occupancy factor of 90% at this site. The final refinement series allowed anisotropic thermal parameters for all nonhydrogen atoms in the complex but only isotropic refinement for the seven atoms defining the crystallized solvent molecule. The refinement also included terms for the anomalous dispersion of Rh, P, and Cl and idealized positions for hydrogen atoms of the complex (C–H 95 Å, β_{iso} = 8 Å). The refinement converged with R_1 = 4.56 and R_2 = 6.3, with the standard deviation of observation at unit weight of 1.63. A final full-matrix least-squares cycle was performed on coordinates only to verify convergence and to calculate the variance–covariance matrix for error analysis. In the final cycle the average shift per error was 0.04 and the data to parameter ratio was 10.0:1. Final atomic parameters are given in Table II. Bond lengths and angles are given in Table III.

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(29) The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_R] T_R$, where S is the scan counts, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time (B_R = 0.67 for this data set), and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R[S + (B_1 + B_2)/B_R^2 + q(I)^2]^{1/2}$, where q in this case was set equal to 0.003. All crystallographic programs used in structural determination and least-squares refinement were written by one of us (J.C.C.). The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).
(30) All least-squares refinement were based on the minimization of $\sum W_i\|$ $- F_o| - \|F_c\|^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040. Those for the hydrogen atoms are from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.