Organometallics 1985, *4*, 1445–1451

Metal–Metal Interactions in Binuclear Complexes. Structural Characterization of Isomers Resulting from Apparent Internal Oxidative Addition of a Platinum–Chlorine Bond to a Rhodium(I) Center

Alan L. Balch,* Rosalvina R. Guimerans, John Linehan, Marilyn M. Olmstead, and Douglas E. Oram

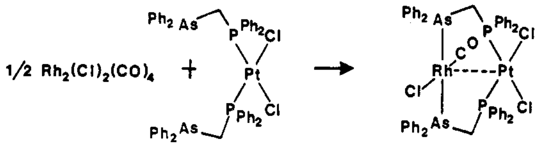
Department of Chemistry, University of California, Davis, California 95616

Received December 10, 1984

The face-to-face complex *trans*-$Rh(CO)Cl(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*cis*-$PtCl_2$, **1**, isomerizes to *trans*-$Rh(CO)Cl_2(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*trans*-PtCl upon heating in chloroform or upon treatment with a small amount of $Ph_2AsCH_2PPh_2$. Metathesis of **1** with iodide produces *trans*-$Rh(CO)I_2(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*trans*-PtI, and the bromo analogue has been prepared similarly. *trans*-$Rh(CO)Cl_2(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*trans*-$PtCl{\cdot}2CH_2Cl_2$, **2**, crystallizes in the monoclinic space group $P2_1/c$ with a = 17.563 (4) Å, b = 14.995 (4) Å, c = 21.338 (4) Å, β = 105.90 (2)°, V = 5404 (2) Å^3, and Z = 4, at 140 K. The structure was refined to a conventional R value of 0.051 using 6017 unique reflections and 334 parameters. *trans*-$Rh(CO)I_2(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*trans*-$PtI{\cdot}CH_2Cl_2{\cdot}2CHCl_3$, **4**, crystallizes in the orthorhombic space group *Pbca* with a = 17.808 (8) Å, b = 19.488 (8) Å, c = 35.228 (15) Å, V = 12225.6 (9) Å^3, and Z = 8 at 140 K. The structure was refined to a conventional R value of 0.092 using 5001 unique data and 344 parameters. Both structures are similar with a six-coordinate rhodium atom (ligands: two As, CO, two Cl or two I, Pt) and a four-coordinate platinum (ligands two P, Rh, Cl or I) joined by a Pt–Rh bond (2.692 (1) Å in **2** and 2.737 (3) Å in **4**). The carbonyl group in both complexes displays a subtle tilting toward the platinum atom. This results in a significant lowering (20–40 cm^{-1}) of the carbonyl stretching frequency.

Introduction

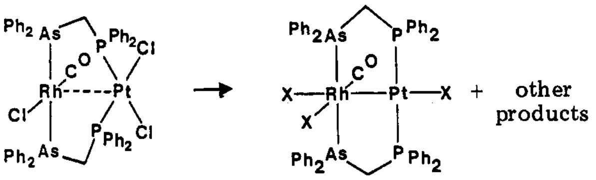
Metal–metal interaction lie at the heart of the unique aspects of binuclear complexes and the study of their nature accounts for some of the current interest in this area.[1] Here we describe an unusual example of an isomerization in which the metal–metal interaction in a heterobinuclear complex is significantly altered. The complex involved is *trans*-$Rh(CO)Cl(\mu\text{-dapm})_2$-*cis*-$PtCl_2$, **1** (dapm is (diphenylarsino)(diphenylphosphino)methane), which has been prepared via the addition of $Rh_2(CO)_4(\mu\text{-}Cl)_2$ to $Pt(dapm)_2Cl_2$ as shown in eq 1. The face-to-face complex **1** contains two planar d^8 metal ions in an arrangement which does not require a formal Rh–Pt bond. Indeed the observed Rh···Pt separation, 3.043 (1) Å, is considerably longer than that expected for a single bond.[2] However, the metal ions are sufficiently close to allow some orbital interaction of the type found for a number of face-to-face rhodium(2) dimers.[3-5]



(1)

Results

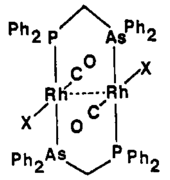
Preparative Studies. Under a variety of conditions **1** undergoes conversion into several products, the most interesting of which is its isomer **2**. The simple thermal reaction (eq 2) is readily monitored by ^{31}P NMR spectroscopy. The changes accompanying heating a sample of **1** in chloroform at 60 °C for 2 h are shown in Figure 1. Trace I shows the spectrum of pure **1** (peaks labeled A) while trace II and inset III show the sample after being heated. The products have been identified by comparison with authentic material prepared independently. The high field triplet C (δ −53.3 (^1J(PtP) = 3129 Hz)) results from the chelate $Pt(dapm)Cl_2$.[6] The doublets D and E are the face-to-face rhodium dimers **5** and **6**.[7,8] The triplet B is due to **2**, which has been separated from the reaction mixture and purified by fractional crystallization. The ^{31}P NMR and infrared data which characterize this and other new compounds along with some reference compounds are given in Table I. Treatment of **1** with dapm yields a



(2)

1

2, X = Cl
3, X = Br
4, X = I



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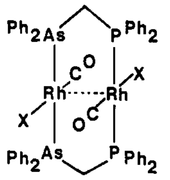

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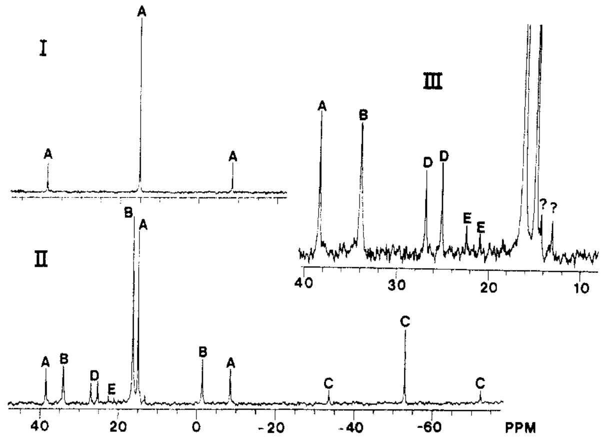


Figure 1. ^{31}P NMR spectra of a sample of *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$, 1, in chloroform solution: trace I, sample before heating; trace II, sample after heating to 60 °C for 2 h; trace III, expansion of the low field region of trace II.

Table I. Spectroscopic Data

compd	^{31}P NMR^a δ	^1J(Pt,P), Hz	infrared^b ν(CO), cm^{-1}
1, *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$^{a}	15.0	3826	1987 s
2, *trans*-Rh(CO)Cl$_2$(μ-dapm)$_2$-*trans*-PtCl	16.4	2880	2006 w
3, *trans*-Rh(CO)Br$_2$(μ-dapm)$_2$-*trans*-PtBr	15.1	2849	2004 w
4, *trans*-Rh(CO)I$_2$(μ-dapm)$_2$-*trans*-PtI	10.4	2764	1985 w
trans-Pt(dapm)$_2$I$_2$^{c}	1.3	2380	
cis-Pt(dapm)$_2$I$_2$^{c}	7.1	3553	
cis-Pt(dapm)$_2$Cl$_2$^{c}	6.1	3875	
7, Rh(CO)Cl$_2$(μ-Ph$_2$Ppy)$_2$PdCl^d			2053 s
8, Rh(CO)Cl$_2$(μ-Ph$_2$Ppy)$_2$PtCl^e			2055 s
Mo(CO)$_2$(μ-CO)(μ-Ph$_2$Ppy)$_2$PtCl^f	34.4	3064	1749 s
11, Rh$_2$(μ-dpm)$_2$(μ-CO)(μ-Cl)-(CO)$_2$$^{+g}$			1865 s

[a] In dichloromethane-d_2 solution at 25 °C. [b] Nujol mull. [c] Data from ref 2b. [d] Data from ref 12. [e] Data from ref 13. [f] Data from ref 15. [g] Data from ref 16.

similar mixture of compounds from which 2 has been separated in low yield.

Metathesis reactions of 1 with other halide ions have been examined. Treatment of 1 with excess sodium bromide yields RhPt(μ-dapm)$_2$(CO)Br$_3$ which we presume to have structure 3 (vide infra). Back-metathesis of RhPt(dapm)$_2$(CO)Br$_3$ with excess sodium chloride yields 2. This set of two metatheses represents the best route for the synthesis of 2. However, it should be noted that treatment of 1 with chloride ion under the conditions used for the preceding metathesis reactions does not result in isomerization to give 2, rather 1 is recovered unchanged. Treatment of 1 with sodium iodide yields 4, the iodide analogue of 2. Since the spectroscopic data (Table I) for these complexes did not serve unambiguously to define their gross structure, X-ray diffraction studies of 2 and 4 were undertaken.

X-ray Structural Results. Compound 2 crystalizes with one molecule of 2 and two molecules of dichloromethane in the asymmetric unit and no unusual intermolecular contacts. Compound 4 crystallizes with one molecule of 4, one of dichloromethane, and two of chloroform in the asymmetric unit. The structure of 4 suffers from disorder in which 16.5% of the molecules have undergone a 180° rotation so that the Pt and Rh positions are reversed (see Experimental Section). Final atomic postional and thermal parameters for 2 and 4 are listed in Tables II and III, respectively. Table IV contains selected interatomic distances for both complexes, and Table V contains selected interatomic angles. A drawing of 2 is shown in Figure 2 while 4 is shown in Figure 3. It is apparent that 2 and 4 have similar structures. Neither molecule has crystallographically imposed symmetry. However, both have approximate C_s symmetry with a near mirror plane passing through the PtRh(CO)X$_3$ core.

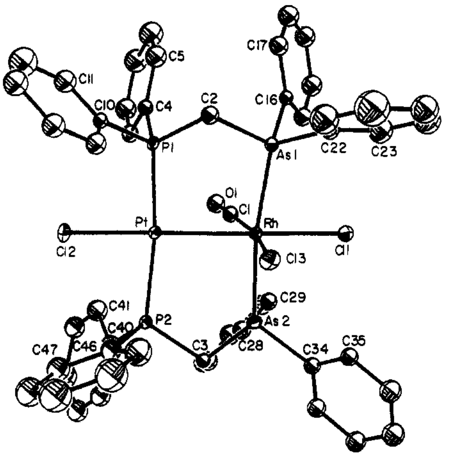


Figure 2. A drawing of *trans*-Rh(CO)Cl$_2$(μ-dapm)$_2$-*trans*-PtCl, 2.

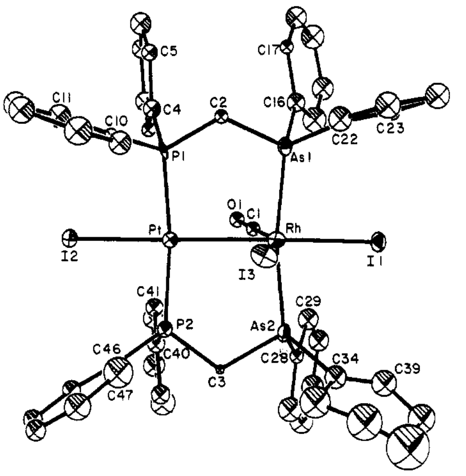


Figure 3. A drawing of *trans*-Rh(CO)I$_2$(μ-dapm)$_2$-*trans*-PtI, 4.

In both structures the rhodium atom is six-coordinate while the platinum atom is four-coordinate and planar. A Pt–Rh bond connects the two metals. The bridging ligands are trans to one another and are arranged in a head-to-head fashion.

It is instructive to compare the structural parameters for the isomers 1 and 2. The inner cores of both are shown in Figure 4. The isomerization has resulted in the transfer of one chloride ligand from platinum to rhodium and a shortening of the rhodium–platinum separation by 0.35 Å. These changes are the result of oxidative addition of the Pt–Cl bond to the rhodium atom. In formal terms the original isomer 1 contains a Rh(I) and a Pt(II) center while 2 contains Rh(II) and Pt(I) joined by a metal–metal bond. As a result of the chloride transfer the two phosphine ligands on platinum assume a trans orientation. Thus the platinum atom in both complexes 1 and 2 is in a planar environment, but the orientation of that plane relative to the rhodium atom has shifted. The rhodium atom, on the other hand, has gone from four-coordination in 1 to six-coordination in 2.

Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for *trans*-Rh(CO)Cl_2(μ-$Ph_2AsCH_2PPh_2$)$_2$-*trans*-PtCl, 2

atom	*x*	*y*	*z*	*U*
Pt	2863 (1)	1877 (1)	3013 (1)	13 (1)[a]
Rh	1844 (1)	3088 (1)	3249 (1)	12 (1)[a]
As(1)	2861 (1)	4208 (1)	3594 (1)	16 (1)[a]
As(2)	730 (1)	2086 (1)	3011 (1)	14 (1)[a]
Cl(1)	894 (2)	4275 (2)	3386 (2)	26 (1)[a]
Cl(2)	3766 (2)	889 (2)	2728 (2)	26 (1)[a]
Cl(3)	2154 (2)	2523 (2)	4334 (1)	25 (1)[a]
Cl(4)	3559 (2)	1835 (2)	800 (2)	37 (1)[a]
Cl(5)	4698 (3)	522 (3)	660 (2)	61 (2)[a]
Cl(6)	2964 (3)	977 (3)	5908 (2)	71 (2)[a]
Cl(7)	1966 (3)	−151 (3)	4923 (2)	66 (2)[a]
P(1)	3983 (2)	2653 (2)	3546 (1)	14 (1)[a]
P(2)	1888 (2)	866 (2)	2570 (1)	13 (1)[a]
O(1)	1719 (5)	3443 (5)	1850 (4)	26 (2)
C(1)	1765 (6)	3294 (7)	2380 (5)	19 (3)
C(2)	3848 (6)	3632 (6)	4006 (5)	13 (2)
C(3)	1080 (6)	858 (7)	2948 (5)	21 (3)
C(4)	4585 (7)	3062 (7)	3039 (5)	24 (3)
C(5)	4309 (7)	2982 (8)	2363 (6)	32 (3)
C(6)	4771 (7)	3339 (8)	1990 (7)	35 (3)
C(7)	5466 (8)	3760 (9)	2265 (7)	45 (4)
C(8)	5743 (8)	3838 (8)	2922 (6)	36 (3)
C(9)	5310 (7)	3479 (8)	3324 (6)	30 (3)
C(10)	4633 (7)	1960 (8)	4165 (6)	27 (3)
C(11)	4429 (9)	1755 (9)	4706 (7)	46 (4)
C(12)	4905 (9)	1198 (11)	5200 (8)	63 (5)
C(13)	5594 (9)	896 (11)	5119 (8)	59 (4)
C(14)	5822 (9)	1084 (9)	4579 (7)	49 (4)
C(15)	5343 (8)	1617 (8)	4088 (7)	36 (3)
C(16)	3007 (7)	4967 (7)	2914 (6)	25 (3)
C(17)	3731 (7)	5151 (7)	2978 (6)	28 (3)
C(18)	3116 (7)	6066 (8)	1886 (6)	33 (3)
C(19)	3798 (7)	5716 (8)	2295 (6)	32 (3)
C(20)	2383 (7)	5910 (8)	1997 (6)	33 (3)
C(21)	2335 (7)	5345 (7)	2505 (5)	24 (3)
C(22)	2800 (6)	5059 (7)	4269 (5)	20 (3)
C(23)	3230 (7)	5858 (7)	4321 (6)	26 (3)
C(24)	3237 (7)	6444 (8)	4821 (6)	31 (3)
C(25)	2818 (7)	6253 (8)	5255 (7)	36 (3)
C(26)	2396 (7)	5473 (8)	5205 (6)	33 (3)
C(27)	2388 (7)	4877 (7)	4711 (5)	22 (3)
C(28)	−104 (6)	2296 (7)	2222 (5)	15 (2)
C(29)	−621 (7)	1629 (8)	1937 (6)	26 (3)
C(30)	−1204 (7)	1792 (8)	1369 (6)	33 (3)
C(31)	−1311 (8)	2621 (8)	1075 (6)	34 (3)
C(32)	−782 (7)	3295 (8)	1381 (6)	35 (3)
C(33)	−175 (7)	3157 (8)	1938 (5)	24 (3)
C(34)	132 (6)	2019 (7)	3652 (5)	21 (3)
C(35)	226 (9)	1336 (10)	4085 (7)	52 (4)
C(36)	−221 (10)	1305 (12)	4540 (9)	75 (5)
C(37)	−720 (8)	1987 (9)	4557 (7)	46 (4)
C(38)	−823 (8)	2675 (10)	4129 (7)	46 (4)
C(39)	−392 (8)	2674 (9)	3678 (7)	41 (4)
C(40)	1443 (6)	969 (7)	1708 (5)	16 (2)
C(41)	1814 (7)	1477 (7)	1332 (5)	22 (3)
C(42)	1486 (8)	1578 (8)	677 (6)	35 (3)
C(43)	787 (8)	1187 (9)	368 (7)	44 (4)
C(44)	401 (9)	702 (9)	734 (7)	47 (9)
C(45)	726 (7)	563 (8)	1387 (6)	33 (3)
C(46)	2206 (6)	−293 (7)	2705 (5)	14 (2)
C(47)	2119 (7)	−897 (8)	2218 (6)	32 (3)
C(48)	2341 (9)	−1779 (10)	2352 (8)	53 (4)
C(49)	2698 (7)	−2047 (8)	2973 (6)	36 (3)
C(50)	2818 (7)	−1446 (8)	3469 (6)	31 (3)
C(51)	2574 (7)	−569 (8)	3337 (6)	26 (3)
C(80)	1999 (8)	773 (10)	5432 (7)	50 (4)
C(81)	4188 (9)	982 (11)	1165 (8)	60 (5)

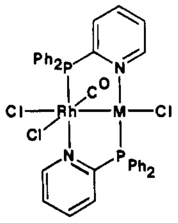
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The interatomic distances show really rather small differences between the two isomers. The platinum-rhodium contraction is the largest change. The shortening is consistent with the formation of a single bond between the two metals. The expansion of the Pt-P bonds upon isomerization is probably as much a reflection of the change in trans ligands as it is of a change in oxidation state of platinum. For planar group 8-10[21] metal ions, P-M bonds trans to a phosphorus atom are generally ca. 0.05 Å longer than P-M bonds trans to a chloride ligand.[10,11] The Rh-As and Rh-C bonds show no significant change upon isomerization. Likewise the Rh-Cl(3) bond has undergone minor elongation upon isomerization. The new Rh-Cl(1) bond however is unusually long.

Detailed comparison of 2 and 4 is readily made by examining Tables IV and V. The largest difference involves the slight elongation of the Rh-Pt bond in the iodide complex 4 probably as a result of the trans effect of the iodide ligands. Otherwise analogous bond lengths have comparable values.

A feature common to the structures of both 2 and 4 is the elongation of the Rh-X bond trans to platinum relative to the Rh-X bond trans to carbon mononoxide. It has been noted previously[12] that metal-metal single bonds between group 8-10 metals have high structural trans effects. The Pt-X bond shows much less elongation. In particular in comparison to the parameters in 1, the Pt-Cl bond in 2 is only very slightly lengthened.

The structures of 2 and 4 may be compared to that of a related rhodium palladium complex, 7.[12] The platinum analogue 8 is also known but has not been structurally characterized by X-ray diffraction.[13] These complexes differ from 2 and 4 in the nature of the bridging ligand. Additionally the bridging ligands are arranged in a head-to-tail fashion in 7 and 8. However, they both contain the six-coordinate rhodium(II)/four-coordinate Pd(I) or Pt(I) unit which is valence isoelectronic with the core of 2 and 4. The bridging ligands in 7 and 8, 2-(diphenylphosphino)pyridine, are more rigid than dapm. As a consequence the Rh-Pd distance in 7 (2.594 (1) Å) is shorter than the Rh-Pt distances in 2 and 4. (These distances are directly comparable since the atomic and ionic radii of palladium and platinum are similar due to the lanthanide contraction.) Another consequence of the rigidity of Ph_2Ppy is the twisting of the N-Rh-Pd-P dihedral angles. These angles are 21.1° and 21.1° in 7. In 2 and 4 there is much less of a comparable twist. For 2 the P-Pt-Rh-As dihedral angles are 10.7° and 13.6° while for 4 they are 3.7° and 3.2°.



7, M = Pd
8, M = Pt

Discussion

The structural characterization of 1 and 2 demonstrates a novel form of isomerization in binuclear complexes. The

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Table III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for *trans*-Rh(CO)I$_2$(μ-Ph$_2$AsCH$_2$PPh$_2$)$_2$-*trans*-PtI, 4

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
PtA	330 (1)	6813 (1)	6042 (1)	15 (1)^a	C(15)	-1164 (16)	5310 (17)	6379 (9)	31 (9)
PtB	1387 (1)	6873 (1)	6605 (1)	20	C(16)	207 (16)	7611 (16)	7372 (9)	25 (9)
I(1)	2481 (1)	7056 (1)	7140	24 (1)^a	C(17)	-478 (15)	7627 (15)	7602 (8)	13 (8)
I(2)	-687 (1)	6979 (1)	5492 (1)	22 (1)^a	C(18)	-682 (17)	8140 (19)	7804 (10)	34 (9)
I(3A)	1257 (1)	5504 (1)	6549 (1)	29 (1)^a	C(19)	-271 (19)	8727 (19)	7800 (11)	45 (11)
I(3B)	635 (7)	5478 (7)	6184 (4)	20	C(20)	425 (18)	8775 (18)	7584 (10)	40 (10)
RhA	1387 (1)	6873 (1)	6605 (1)	16 (1)^a	C(21)	634 (18)	8192 (19)	7378 (10)	45 (11)
KhB	330 (1)	6813 (1)	6042 (1)	20	C(22)	764 (14)	6253 (14)	7550 (8)	11 (7)
As(1A)	497 (2)	6811 (2)	7116 (1)	17 (1)^a	C(23)	1174 (15)	6478 (15)	7854 (9)	18 (8)
As(1B)	-662 (3)	6668 (3)	6467 (2)	20	C(24)	1431 (15)	6163 (15)	8145 (8)	15 (8)
As(2A)	2440 (2)	6792 (2)	6176 (1)	19 (1)^a	C(25)	1320 (17)	6463 (18)	8143 (10)	35 (10)
As(2B)	1218 (6)	6793 (4)	5555 (2)	20	C(26)	907 (17)	5125 (18)	7852 (10)	36 (10)
Cl(1)	2532 (6)	766 (5)	2220 (3)	63 (4)^a	C(27)	642 (17)	5584 (17)	7553 (10)	34 (10)
Cl(2)	3133 (5)	-227 (5)	2741 (4)	67 (5)^a	C(28)	2990 (15)	7613 (15)	6056 (9)	15 (8)
Cl(3)	7055 (5)	1058 (6)	301 (3)	59 (5)^a	C(29)	2819 (17)	8224 (19)	6273 (10)	35 (9)
Cl(4)	5800 (6)	903 (6)	-195 (3)	66 (5)^a	C(30)	3305 (18)	8807 (18)	6175 (10)	37 (10)
Cl(5)	5688 (5)	455 (6)	580 (3)	55 (1)^a	C(31)	3775 (19)	8779 (19)	5878 (11)	45 (11)
Cl(6)	8233 (6)	2251 (7)	1008 (4)	60	C(32)	3932 (19)	8249 (21)	5667 (11)	47 (11)
Cl77)	9547 (7)	2209 (7)	1404 (4)	60	C(33)	3520 (19)	7621 (19)	5730 (11)	45 (11)
Cl(8)	9417 (6)	3053 (7)	782 (4)	60	C(34)	3274 (10)	6103 (12)	6285 (7)	33 (10)
P(1A)	-662 (3)	6668 (3)	6467 (2)	12 (3)^a	C(35)	3170 (10)	5444 (13)	4111 (7)	41 (13)
P(1B)	497 (2)	6811 (2)	7116 (1)	20	C(36)	3720 (10)	5019 (12)	6308 (7)	78 (15)
P(2A)	1218 (3)	6793 (4)	5555 (2)	26 (4)^a	C(37)	4409 (10)	5117 12)	6403 (7)	120 (22)
P(2B)	2440 (2)	6792 (2)	6176 (1)	20	C(38)	4513 (10)	5953 (12)	6548 (7)	52 (12)
O(1)	940 (11)	8321 (12)	6403 (6)	17 (6)	C(39)	3885 (10)	6346 (12)	6499 77)	43 (11)
C(1)	1149 (17)	7776 (17)	6480 (10)	14 (9)	C(40)	1394 (16)	7634 (16)	5329 (9)	23 (9)
C(2)	-447 (15)	6351 (14)	6950 (8)	12 (7)	C(41)	1031 (15)	8224 (17)	5451 (9)	25 (8)
C(3)	2134 (14)	6413 (14)	5684 (8)	5 (7)	C(42)	1205 (18)	8819 (18)	5313 (10)	34 (10)
C(4)	-1201 (16)	7479 (16)	6565 (10)	22 (8)	C(43)	1785 (18)	8901 (19)	5037 (11)	41 (11)
C(5)	-1808 (15)	7469 (16)	6839 (9)	19 (8)	C(44)	2235 (19)	8358 (20)	4947 (11)	51 (12)
C(6)	-2228 (17)	7960 (17)	6919 (10)	35 (10)	C(45)	2009 (16)	7682 (17)	5072 (10)	28 (9)
C(7)	-1990 (17)	8642 (17)	6754 (9)	26 (9)	C(46)	1012 (15)	6219 (16)	5165 (8)	14 (8)
C(8)	-1366 (16)	8658 (16)	6491 (9)	27 (9)	C(47)	1043 (20)	5503 (22)	5257 (11)	56 (12)
C(9)	-1011 (14)	8067 (15)	6400 (8)	15 (8)	C(48)	937 (19)	4973 (19)	4965 (11)	42 (11)
C(10)	-1331 (14)	6009 (14)	6320 (8)	10 (7)	C(49)	803 (16)	5175 (16)	4604 (9)	26 (9)
C(11)	-2008 (17)	6165 (17)	6134 (10)	33 (10)	C(50)	747 (17)	5918 (16)	4508 (9)	25 (9)
C(12)	-2507 (20)	5695 (18)	6011 (9)	37 (9)	C(51)	872 (16)	6387 (16)	4792 (9)	24 (9)
C(13)	-2349 (18)	5001 (18)	6082 (10)	39 (10)	C(52)	2725 (18)	-127 (19)	2272 (10)	44 (11)
C(14)	-1637 (18)	4774 (18)	6280 (11)	43 (11)	C(53)	6060 (17)	1076 (18)	270 (10)	32 (10)

^{a}Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

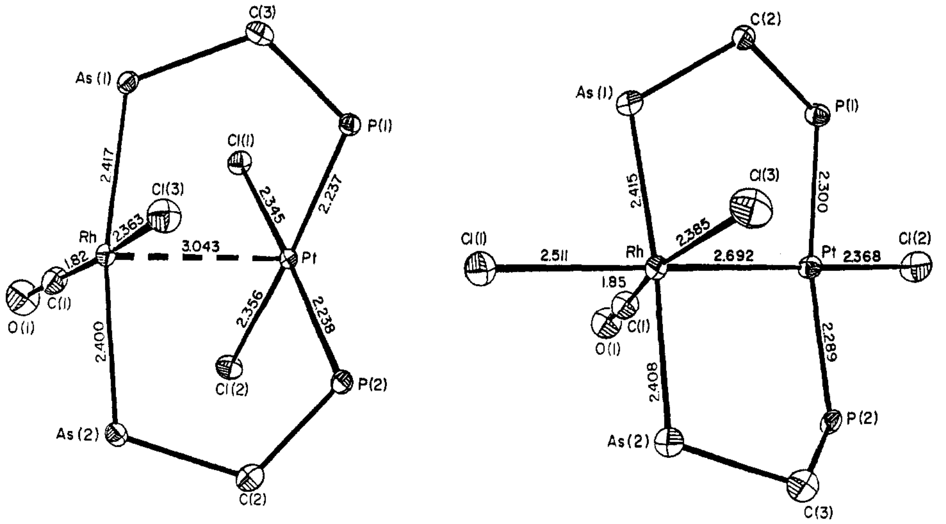

Figure 4. A comparison of the inner cores of A, *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$, 1, and B, *trans*-Rh(CO)Cl$_2$(μ-dapm)$_2$-*trans*-PtCl, 2. Phenyl groups are ommitted.

ability of dapm to form the isomeric pair 1 and 2 is a direct consequence of its flexibility. This allows for expansion or contraction of the metal–metal separation that it spans.[1,2] In contrast Ph$_2$Ppy is a constraining ligand which in many cases forces oxidative addition of one metal–halogen bond on to a second metal center,[9,12,13] so that the products obtained from the synthesis of binuclear complexes using this ligand generally have metal–metal single bonds.

We are aware of no isomers totally analogous to 1 and 2. However, there is one pair of complexes which is related to our work. Mazany and Fackler[14] have isolated and structurally characterized 9 and 10. These differ by an internal Au–I oxidative addition as well as by a head-to-head/head-to-tail isomerization. The Au···Au distance

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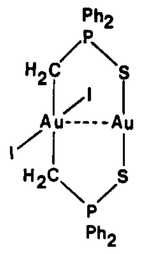
[14] Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801.



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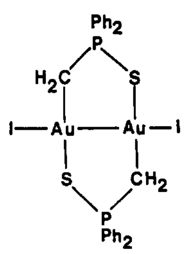


10

decreases by 0.44 Å on going from **9** to **10**. Notice that this decrease is comparable to the decrease noted on transforming **1** into **2**. Interconversion of these isomers has not as yet been reported.

The spectroscopic data in Table I were not sufficient to provide definitive structural identification of **2**, **3**, and **4**. The ^{31}P NMR spectra are consistent with the presence of a trans P–Pt–P unit,[9] but the carbonyl stretching frequencies occur at unusually low energies. In addition they are relatively weak and broad. Because of this **2** was initially misidentified as a trans/trans face-to-face isomer of cis/trans **1**.[2] The weak carbonyl band of **2** was obscurred in the original (impure) preparation of **2** by carbonyl absorbtions from **5** and **6** which had not been completely removed.

Generally terminal carbonyl groups bound to Rh(I) have stretching frequencies in the range 1950–2000 cm^{-1}.[4,5] Oxidative addition usually raises the carbonyl stretch to values above 2020 cm^{-1}. For example ν(CO) in Rh(CO)I$_2$(PPh$_3$)$_2$ is 2085 cm^{-1},[4] for **7** it is 2053 cm^{-1},[12] and for **8** it is 2055 cm^{-1}.[13] For **2**, **3**, and **4**, the observed carbonyl stretches approach and enter the Rh(I) range. For this reason X-ray crystallographic studies were undertaken on both **2** and **4** to be sure that these structures were well established. By analogy with these structures we infer that **3** has similar geometry but the spectroscopic information is not definitive.

The cause for the low carbonyl stretching energies in **2**, **3**, and **4** can be attributed to a tilting of the carbonyl group toward the platinum atom. Both structures **2** and **4** show this tilting. In contrast in **7** there is no tilt of the carbonyl and ν(CO) occurs within the expected range. Relevant parts of these structures are compared in Figure 5. In all three structures the carbonyl groups are nearly linear. However the Pt–Rh–C angles in **2** (78.2 (3)°) and in **4** (73.3 (1)°) deviate significantly from the ideal 90°. Moreover these are the largest deviations from 90° for any pair of cis ligands in these complexes. We find no intermolecular contacts which might be responsible for this tilting. It appears to be an intrinsic aspect of the bonding. In contrast in **7** the Pd–Rh–C angle is 89°.

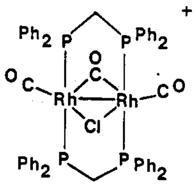
The tilting of the carbonyl group in **2** and **4** results in a shortening of the distance from the carbonyl carbon to the remote metal atom from 3.14 (1) Å in **7** to 2.94 (1) Å in **2** to 2.83 (3) Å in **4**. Thus we conclude that the carbonyl groups in **2** and **4** are interacting with the remote platinum atoms probably as very weak π-donors. The perturbation is significant enough to lower ν(CO) by 20–40 cm^{-1}. As a consequence the infrared spectra of such binuclear complexes are much less diagnostic of structure than we originally believed, and considerable care must be given using spectroscopic criteria to elucidate bond connectivities in these molecules. A much more pronounced example of a bridging carbonyl acting as a π-donor toward a PtP$_2$Cl unit is seen in Mo(CO)$_3$(μ-CO)(μ-Ph$_2$Ppy)$_2$-*trans*-PtCl where the corresponding Pt–C distance is 2.218 (17) Å.[15] Finally we point out that **2** and **4** are valence isoelectronic with **11** which has a longer Rh–Rh distance 2.838 (1) Å, and a symmetrically bridging carbonyl.[16] Through the presence of the bridging chloride and carbonyl groups, this cation achieves an 18-electron count at both rhodium atoms,

Table IV. Selected Interatomic Distances (Å) for *trans*-Rh(CO)Cl$_2$(μ-dapm)$_2$-*trans*-PtCl (2) and *trans*-Rh(CO)I$_2$(μ-dapm)$_2$-*trans*-PtI (4)

	2 (X = Cl)	4 (X = I)
Rh–Pt	2.692 (1)	2.737 (3)
Rh–C(1)	1.848 (12)	1.864 (34)
Rh–As(1)	2.415 (1)	2.400 (4)
Rh–As(2)	2.408 (1)	2.414 (4)
Rh–X(1)	2.511 (3)	2.731 (3)
Rh–X(3)	2.385 (3)	2.686 (3)
Pt–P(1)	2.300 (3)	2.333 (6)
Pt–P(2)	2.289 (3)	2.333 (7)
Pt–X(2)	2.368 (3)	2.673 (2)
As(1)–C(2)	1.920 (9)	1.993 (27)
As(2)–C(3)	1.957 (11)	1.961 (27)
P(1)–C(2)	1.819 (11)	1.849 (29)
P(2)–C(3)	1.814 (13)	1.849 (26)
As(1)···P(1)	3.073 (6)	3.093 (9)
As(2)···P(2)	3.068 (6)	3.087 (9)

Table V. Selected Interatomic Angles (deg) for *trans*-Rh(CO)Cl$_2$(μ-dapm)$_2$-*trans*-PtCl (2) and *trans*-Rh(CO)I$_2$(μ-dapm)$_2$-*trans*-PtI (4)

	2 (X = Cl)	4 (X = I)
Pt–Rh–X(1)	175.5 (1)	174.4 (1)
As(1)–Rh–As(2)	171.3 (1)	168.2 (2)
C(1)–Rh–X(3)	165.6 (3)	154.3 (10)
Pt–Rh–C(1)	78.2 (3)	73.3 (10)
Pt–Rh–X(3)	87.4 (1)	81.1 (1)
Pt–Rh–As(1)	93.0 (1)	95.0 (1)
Pt–Rh–As(2)	94.7 (1)	94.4 (1)
X(1)–Rh–As(1)	86.1 (1)	87.8 (1)
X(1)–Rh–As(2)	86.5 (1)	83.5 (1)
X(1)–Rh–C(1)	97.4 (3)	101.7 (10)
X(1)–Rh–X(3)	96.9 (1)	104.0 (1)
As(1)–Rh–C(1)	92.1 (3)	94.3 (10)
As(1)–Rh–X(3)	89.9 (1)	87.0 (1)
As(2)–Rh–C(1)	93.3 (3)	95.1 (10)
As(2)–Rh–X(3)	86.5 (1)	87.5 (1)
Rh–Pt–X(2)	175.0 (1)	170.6 (1)
P(1)–Pt–P(2)	168.9 (1)	169.4 (2)
Rh–Pt–P(1)	95.1 (1)	93.5 (2)
Rh–Pt–P(2)	93.7 (1)	93.9 (2)
X(2)–Pt–P(1)	84.3 (1)	88.1 (2)
X(2)–Pt–P(2)	87.6 (1)	85.8 (2)
Pt–P(1)–C(2)	117.1 (3)	118.2 (9)
Pt–P(2)–C(3)	114.1 (4)	115.0 (9)
Rh–As(1)–C(2)	109.0 (3)	111.1 (8)
Rh–As(2)–C(3)	110.4 (3)	111.2 (7)
P(1)–C(2)–As(1)	110.5 (5)	107.2 (13)
P(2)–C(3)–As(2)	108.9 (6)	108.2 (13)
Rh–C(1)–O(1)	178.2 (10)	174.3 (28)



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(15) Farr, J. P.; Olmstead, M. M.; Rutherford, N. M.; Wood, F. E.; Balch, A. L. *Organometallics* **1983**, *2*, 1758.

(16) Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organometal. Chem.* **1979**, *179*, 289.

(17) Garrou, P. E.; Hartwell, G. E. *Inorg. Chem.* **1976**, *15*, 646.

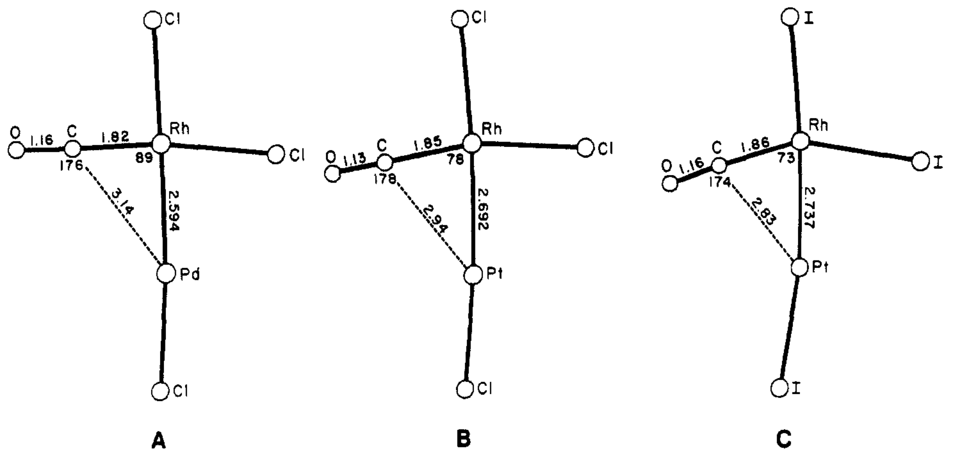

Figure 5. A comparison of planar sections of A, *trans*-Rh(CO)Cl(μ-Ph_2Ppy)$_2$-*trans*-PdCl, B, *trans*-Rh(CO)Cl_2(μ-dapm)$_2$-*trans*-PtCl, and C, *trans*-Rh(CO)I_2(μ-dapm)$_2$-*trans*-PtI.

whereas 2 and 4 each have an electron-deficient platinum center.

We have termed the conversion 1 → 2 an apparent intramolecular oxidative addition in order to emphasize the fact that mechanistic information on this reaction has not been obtained. The geometry of 1 appears unfavorable for a simple, direct transfer of chloride from platinum to rhodium. There is no vacant coordination site on rhodium that is adjacent to the Pt–Cl bonds. The complexity of the reaction, which gives 2 in only modest yield along with other products, does not encourage further study. It is not feasible to monitor the 1 → 2 conversion through a double-label experiment using different halide ligands because of the ease of intermolecular halide exchange in molecules of this sort.[20]

Experimental Section

Preparation of Compounds. The ligand dapm[18] and complex 1[2] were prepared as described previously.

***trans*-Rh(CO)Cl_2(μ-dapm)$_2$-*trans*-PtCl (2). Method 1.** An orange solution of 0.147 g (0.114 mmol) of *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2$ in 20 mL of chloroform was heated under reflux for 2 h. The volume of the red solution was reduced to 2 mL through the use of a rotary evaporator. Methanol was added dropwise until precipitation of cream crystals of Pt(dapm)Cl_2 was complete. These were removed by filtration. The volume of the filtrate was again reduced by $^2/_3$. Methanol was added dropwise until precipitation of the red-orange product was complete. The product was removed by filtration. It was purified by recrystallization from dichloromethane/ethyl ether to give 28 mg (19%) of the product after vacuum drying. Anal. Calcd for $C_{51}H_{44}As_2Cl_3OP_2PtRh$: C, 47.52; H, 3.44. Found: C, 47.00; H, 3.71.

Method 2. A solution of 7.2 mg (0.017 mmol) of dapm in 1 mL of dichloromethane was added to a solution of 229 mg (0.177 mmol) of *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2$ 1 in 15 mL of dichloromethane. The solution was allowed to stand for 8 h during which it changed from orange to red-orange. The solution was then evaporated to 2 mL, and the workup followed that in method 1 to give 48 mg (21%) of the product which was identified by its spectroscopic properties.

Method 3. An excess of sodium chloride (1.27 g, 22 mmol) dissolved in a mixture of 15 mL of methanol and 2 mL of water was added to a solution of 0.122 g (0.086 mmol) of *trans*-Rh(CO)Br_2(μ-dapm)$_2$-*trans*-PtBr (3) in 5 mL of dichloromethane. The mixture was stirred for 2 h after which the organic solvents were removed by use of a rotary evaporator. The red solid was removed from the water by filtration, washed with more water, and washed with methanol. The product was recrystallized from dichloromethane/ethyl ether and vacuum dried to give 47 mg (38%) of the product. The ^{31}P NMR and infrared spectra of this material were identical with those of the material prepared by method 1.

***trans*-Rh(CO)Br_2(μ-dapm)$_2$-*trans*-PtBr·CH_2Cl_2 (3).** A solution of 0.20 g (2.0 mmol) of sodium bromide in a mixture of 8 mL of acetone and 2 mL of water was added to a solution of 0.133 g (0.103 mmol) of 1 in 10 mL of dichloromethane. The mixture was stirred for 30 min, and then the organic solvents were removed by rotary evaporation. The red solid was removed from the water layer by filtration and washed with water and methanol. It was recrystallized successively from dichloromethane/methanol and from dichloromethane/ethyl ether to yield 0.11 g (76%). Anal. Calcd for $C_{52}H_{46}As_2Br_3OP_2PtRh$: C, 41.43; H, 3.01. Found: C, 41.63; H, 3.00. The presence of dichloromethane in the solid was verified by ^1H NMR spectroscopy.

***trans*-Rh(CO)I_2(μ-dapm)$_2$-*trans*-PtI (4).** This was obtained by metathesis using sodium iodide in the fashion described for 3. Burgundy needles were obtained in 92% yield.

Physical Measurements. The instrumentation and methodology has been described previously.[9] All ^{31}P NMR spectra were run at 81 MHz and were proton decoupled.

X-ray Data Collection. *trans*-Rh(CO)Cl_2(μ-dapm)$_2$-*trans*-PtCl·2CH_2Cl_2 (2). Bright red-orange hexagonal based needles of 2 were formed by diffusion of diethyl ether into a dichloromethane solution of the compound. The crystals were taken from the diffusion tube and immediately covered with epoxy resin to reduce loss of solvent from the crystal lattice. A suitable crystal was mounted on a glass fiber and placed on a Syntex $P2_1$ diffractometer with the principal axis of the crystal parallel to the ϕ axis. The temperature of the crystal was maintained at 140K by using a modified LT-1 low-temperature apparatus. Unit cell parameters were obtained from a least-squares refinement of 19 reflections with $30° < 2\theta < 35°$. The crystal lattice was found to be monoclinic P by the presence of symmetry in the *b*-axial photo and the automatic indexing routine of the diffractometer software. Quick scans of the space group-determining reflections showed the conditions h0l, l=2n; 0k0, k=2n. Therefore, the space group was $P2_1/c$ (No. 14). The usual corrections for Lorentz and polarization effects were applied to the intensity data. Data collection parameters are summarized in Table 6.

***trans*-Rh(CO)I_2(μ-dapm)$_2$-*trans*-PtI·CH_2Cl_2·2$CHCl_3$ (4).** Crystals suitable for X-ray data collection were obtained by diffusion of methanol into a solution of the above compound in a 6:4 mixture of CH_2Cl_2 and $CHCl_3$. The dark red parallelpipeds are fairly stable in air, but some loss of crystallinity occurs with standing. The crystal selected was coated with epoxy resin to retard deterioration. The procedure for data collection and reduction was as described for the chloride species. The space group Pbca (No. 61) is uniquely determined by the observed conditions 0kl, k=2n; h0l, l=2n; and hk0, h=2n. No decay in the intensities of three standard reflections occurred.

Solution and Refinement of Structure. *trans*-Rh(CO)Cl_2(μ-dapm)$_2$-*trans*-PtCl·2CH_2Cl_2 (2). All structure determination calculations were done on a Data General Eclipse computer using the SHELXTL Version 4 software package. The position

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(18) Appel, R.; Geisler, K.; Scholer, H. F. *Chem. Ber.* **1979**, *112*, 648.

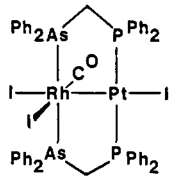
Table VI. Crystal Data for *trans*-Rh(CO)Cl_2(μ-dapm)$_2$-*trans*-PtCl • 2CH_2Cl_2 (2) and *trans*-Rh(CO)I_2(μ-dapm)$_2$*trans*-PtI • CH_2Cl_2 • 2$CHCl_3$ (4)

	2	4
formula	$PtRhAs_2P_2Cl_7O$-$C_{53}H_{48}$	$PtRhAs_2P_2I_3Cl_8O$-$C_{54}H_{48}$
fw, g·mol^{-1}	1288.99	1887.11
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbca*
a, Å	17.563 (4)	17.808 (8)
b, Å	14.995 (4)	19.488 (8)
c, Å	21.338 (4)	35.228 (15)
β, deg	105.90 (2)	
V, Å^3	5404 (2)	12225.6 (9)
Z	4	8
d(calcd) (140 K), g·cm^{-3}	1.60	2.05
cryst dimens, mm	0.75 × 0.47 × 0.62	0.13 × 0.37 × 0.62
diffractometer	Syntex $P2_1$	Syntex $P2_1$
radiatn(graphite monochromated)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
μ(Mo Kα), cm^{-1}	48.0	55.5
temp, K	140	140
range of transmissn factors	0.082–0.179	0.17–0.55
scan type	ω	ω
2θ max, deg	50	45
scan speed, deg·min^{-1}	60	60
scan range, deg	1.8	1
ω bkgd offset, deg	1.5	1
octants collected	$+h,+k,+l$	$+h,+k,+l$
R(MERGE)^a	0.022	0.001
no. of unique data	9510	7994
unique data used	6017 [$F_o > 6\sigma(F_o)$]	5001 [$F_o > 4\sigma(F_o)$]
no. of parameters refined	334	344
check reflctn interval no.	2 measd every 200 reflctn	3 measd every 200 reflctn
R	0.051	0.092
R_w	0.052	0.081

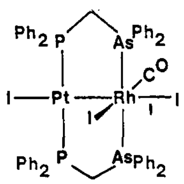
^{a} $R(\text{MERGE}) = (\sum(N\sum(\text{weight}(F(\text{mean}) - F)^2))/\sum((N - 1)\sum(\text{weight}\cdot R^2)))^{1/2}$, where the inner summations are over the *N* equivalent reflections averaged to give *F*(mean) and the outer summations are over all unique observed reflections.

of the platinum atom was found from the Patterson map, assuming the space group $P2_1/c$. Other atom positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to platinum, rhodium, arsenic, phosphorus, and chlorine while isotropic thermal parameters were used for the remaining non-hydrogen atoms. Refinement of these atom converged at 0.083. The final stages of refinement included an absorption correction[19] and fixing all hydrogen atoms at calculated positions by using a riding model in which the C–H vector is fixed at 0.96 Å and the *U* value for each hydrogen atom is set to 1.2 times the *U* value for the carbon atom to which it is bonded. The final *R* value of 0.051 was computed from 334 least-squares parameters and 6017 reflections. This yielded a goodness-of-fit of 1.25 and a mean shift/esd of 0.019 for overall scale on the last cycle of refinement. A value of 0.45 e Å^3 (less than that expected for a hydrogen atom) was found as the largest feature on the final difference Fourier map. The weighting scheme used was $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$. Corrections for anomalous dispersion are applied to all atoms.[20a] Neutral atom scattering factors were those of Cromer and Waber.[20b]

***trans*-Rh(CO)I_2(μ-dapm)$_2$-*trans*-PtI (4).** The positions of three iodines, the platinum, and the rhodium were generated from FMAP 8, the Patterson-solving routine of SHELXTL, version 4. Refinement of these five atoms yielded an *R* of 33%. It was noted that the thermal parameter for Rh was anomalously small. However, a difference map clearly showed most of the remaining atoms. Structure solution proceeded normally except for a persistent anomaly in several thermal parameters, namely, those for Pt, I(3), As(1), and As(2) were larger than average while those for Rh, P(1), and P(2) were smaller than average. After all non-hydrogen atoms were accounted for, a difference map computed at *R* = 16% revealed a peak approximately $^1/_5$ the size of iodine in the same relative position as I(3) but bonded to platinum. In view of these facts the following model for disorder was tried.



A



B

Initially, an 83.5%/16.5% A/B disorder was determined by allowing the occupancy of I(3)A to refine as *k* and that of I(3)B to refine as 1 − *k*. Next, the rest of molecule B was included, such that the positional parameters of PtA and RhB, ..., P(2)A and As(2)B were tied together, and the thermal parameters of all the affected atoms were fixed at *U* = 0.02 Å^2. Further refinement converged at *R* = 0.105 with *k* = 0.835 (*k* was allowed to vary, thus confirming the original estimate). A difference map computed at this stage did not reveal the positions of the carbon monoxide molecule in molecule B. Since these atoms would be small (ca. 1 e Å^{-3}), this was not unexpected, but their presence can be inferred. It can be seen that molecules A and B are related by a 180° rotation of the molecule about an axis perpendicular to the Pt–Rh bond. The effect on packing of substituting molecule B for molecule A is minor. The interior iodines I(3)A and I(3)B are located in a pocket of phenyl rings. The carbon atoms of the ligands seem relatively unaffected except for those of the ring C(34)–C(39), which displays large thermal motion. Two reflections which were affected by extinction (0,2,0 and 0,2,1) were suppressed from the data at this stage. The heavier atoms (I, Pt, Rh, As, and P) of molecule A were assigned anisotropic thermal parameters. No attempt was made to include hydrogens. Final blocked-cascade least-squares refinement converged with *R* = 0.092 using 5001 reflections and 344 parameters; goodness-of-fit, 2.47; mean shift/esd of 0.008 with the largest 0.036 for *x* of C(29); largest feature 4.5 e Å^{-3} probably representing a partial chlorine in place of one of the hydrogens in CH_2Cl_2. Absorption correction, scattering factors, and corrections for anomalous dispersion were as for the chlorine analogue above.[18,19]

Acknowledgment. We thank the National Science Foundation (Grant CHE 8217954) for financial support and Alan Fossett for experimental assistance.

Registry No. 1, 88867-59-8; 2, 97112-55-5; 3, 97112-56-6; 4, 97112-58-8; Pt, 7440-06-4; Rh, 7440-16-6.

Supplementary Material Available: Tables of calculated hydrogen coordinates, anisotropic thermal parameters, and structure factors (76 pages). Ordering information is given on any current masthead page.

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(19) XABS, a program which produces an empirical absorption tensor from an expression relating F_o and F_c: Hope, H.; Moezzi, B., Department of Chemistry, University of California, Davis, CA 95616, unpublished results.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 149–150; (b) pp 99–101.

(21) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)