Acetylene Binding to Triphosphine-Bridged, Trirhodium Chains. The Preparation and X-ray Crystal Structure of the Dimetalated Olefin Complex $[Rh_3(\mu\text{-}(Ph_2PCH_2)_2PPh)_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$

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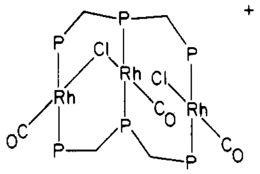
Received April 29, 1985

$[Rh_3(dpmp)_2(CO)_3Cl_2][BPh_4]$ (dpmp = bis[(diphenylphosphino)methyl]phenylphosphine) reacts with dimethyl acetylenedicarboxylate ($CH_3O_2CC{\equiv}CCO_2CH_3$) to yield major, brown and minor, violet isomers of $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$. A similar reaction with diethyl acetylenedicarboxylate ($CH_3CH_2O_2CC{\equiv}CCO_2CH_2CH_3$) yields only the brown form of $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3CH_2O_2CC{=}CCO_2CH_2CH_3)][BPh_4]$. With $[Rh_3(dpma)_2(CO)_3Cl_2][BPh_4]$ (dpma = bis[(diphenylphosphino)methyl]phenylarsine) and $CH_3O_2CC{\equiv}CCO_2CH_3$, the brown form of $[Rh_3(dpma)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ is obtained. Spectroscopic data (^1H, ^{13}C, and ^{31}P NMR and infrared) indicate that the brown complexes contain a dimetalated olefin, two terminal carbon monoxide ligands, and nonequivalent ends to the triphosphine ligand: a structure with the dimetalated olefin spanning the Rh–Rh bond is proposed. $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ undergoes stepwise substitution with iodide without major structural change. The minor, violet isomer of $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ has been structurally characterized by X-ray crystallography. $[Rh_3[\{(C_6H_5)_2PCH_2\}_2PC_6H_5]_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl(\mu\text{-}CH_3O_2C_4O_2CH_3)][B(C_6H_5)_4]\cdot 3CH_2Cl_2$ crystallizes from dichloromethane/ethyl ether in the triclinic space group $P\bar{1}$ (no. 2) with two molecules per unit cell of dimensions a = 12.667 (8) Å, b = 16.787 (6) Å, c = 23.417 (6) Å, α = 75.60 (2)°, β = 81.95 (4)°, and γ = 86.31 (4)° at 140 K. Least-squares refinement of 578 parameters using 7758 reflections yields R = 0.073. The structure consists of a triphosphine-bridged, trirhodium chain with a carbon monoxide and a dimetalated olefin bridging a nonbonded pair of rhodium ions (Rh···Rh = 3.410 (1) Å). This unit is linked to the third rhodium through the phosphine bridge and through a bridging chloride.

Introduction

In recent years a substantial body of information has been assembled regarding the reactivity and structural forms of binuclear, phosphine-bridged complexes of the late transition metals.[1,2] Through the utilization of the small-bite, linear triphosphine, bis[(diphenylphosphino)methyl]phenylphosphine (dpmp),[3] we have begun to explore the consequences of extending this area to trinuclear complexes with a nearly linear array of metal centers.[4-12] The development of this area results from the synthesis and structural characterization of the trirhodium complex 1, which represents the entry point from which all other trirhodium complexes of this type have been derived.[4] The Rh_3P_6 cores in these complexes are subject to facile reaction of the ligands lying in the plane perpendicular to the P–Rh–P bonds. For example, substituting different anions (Br^-, I^-, $S_2CNR_2^-$) for chloride can lead to major structural rearrangements.[4,8] Complex 1 undergoes both reversible addition and reversible loss of a carbon monoxide ligand.[8,11] The oxidative addition behavior of the Rh_3 core has been examined primarily for $[Rh_3(dpmp)_2(CO)_3I_2][BPh_4]$.[8,12] As part of our systematic investigation of the reactivity of these trinuclear complexes toward small molecules, we have examined their interaction with acetylenes. Here we describe the products obtained by the reaction of 1 with acetylenes (dimethyl acetylenedicarboxylate ($CH_3O_2CC{\equiv}CCO_2CH_3$) and diethyl acetylenedicarboxylate ($CH_3CH_2O_2CC{\equiv}CCO_2CH_2CH_3$)) that are activated by electron withdrawing groups.



1 (phenyl groups omitted)

A number of studies of the interaction of such activated acetylenes with binuclear, phosphine-bridged complexes of group VIII (8–10[30]) metals have established that these reactions produce dimetalated olefins[13] which are bound in the plane perpendicular to the M_2P_4 unit. Originally, this laboratory demonstrated that acetylenes could be inserted into the Pd–Pd bond of $Pd_2(\mu\text{-dpm})_2Cl_2$ (dpm =

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Table I. Infrared Spectral Data (cm^{-1}) for Acetylene Adducts

compound	carbon monoxide ligands	ester carbonyl	olefin
2a, $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$	2027, 1991	1691, 1672	1577
3, $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3CH_2O_2CC{=}CCO_2CH_2CH_3)][BPh_4]$	2028, 1993	1707, 1675, 1663	1577
4, $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$	2010 sh, 1988	1691, 1681	1574
5a, $[Rh_3(dpmp)_2(CO)_2ClI(\mu\text{-}CH_2O_2CC{=}CCO_2CH_3)][BPh_4]$	2012, 2003, 1976	1702, 1682, 1668	1571
6, $[Rh_3(dpmp)_2(CO)_2I_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$	2011, 1988	1693, 1672	1568
2b, $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$	2032, 1680[a]	1702, 1693, 1677	1569
5b, $[Rh_2(dpmp)_2(CO)_2ClI(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)]I$	1996, 1688[b]	1674, 1682	1572

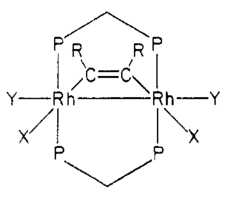
[a] Shifts to 1641 cm^{-1} on ^{13}CO labeling. [b] Shifts to 1646 cm^{-1} on ^{13}CO labeling.

Table II. NMR Data for Acetylene Adducts[a]

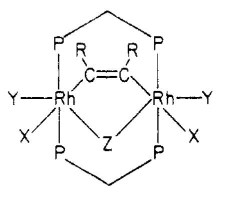
	^{31}P		^{13}C			^1H	
	δ	$^1J(P,Rh)$, Hz	δ	$^1J(C,Rh)$, Hz	$^2J(P,C)$, Hz	$\delta(CH_3)$	$\delta(CH_2)$
$[Rh_3(dpmp)_2(CO)_2Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2a**)	14.6	121.6	189.6	81.4	11	3.45	3.7 (m), 3.1 (d)
	8.4	103	188.7	81.4	13	2.24	3.8 (m), 3.0 (d)
	~8.5						
$[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3CH_2O_2CC{=}CCO_2CH_2CH_3)][BPh_4]$ (**3**)	14.3	121	185.4	82.9	15.4	0.05 (t)[b]	3.6 (m), 3.2 (d)
	8.4	103	163.0	62		0.85 (t)[b]	3.5 (m), 3.1 (d)
	~8.5						
$[Rh_3(dpma)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**4**)	26.3	112.5	186.6	81.4			
	8.2	124.5	166.7	63			
$[Rh_3(dpmp)_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**5a**)	16.6	115.8				3.35	3.7 (d), 3.3 (m)
	11.6	89.6				2.42	3.5 (d), 3.1 (m)
	5.2	114.9					
$[Rh_3(dpmp)_2(CO)_2I_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**6**)	17.1	100.3	193.4	92.5	11	3.54	3.8, 3.3 (d)
	10.3	90.2	182.5	62.9	16	2.31	3.6 (m), 3.0 (m)
	2.3	113.6					
$[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2b**)	14.1	139				3.95	4.3 (m), 3.8 (d)
	13.8	130				1.75	3.9 (m), 3.1 (d)
	8.7	120					
$[Rh_3(dpmp)_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**5b**)	17.1	140					
	6.7	85					
	~7						

[a] In dichloromethane solution at 23 °C: d, doublet; m, multiplet, t, triplet. [b] CH_2CH_3 at 2.90 and 3.95 ppm.

bis(diphenylphosphino)methane).[14,15] Subsequent studies with dinuclear rhodium complexes established the existence to two types of complexes.[16-22] Those of type A contained a dimetalated olefin and a Rh–Rh bond (typical distances 2.70–2.97 Å).[16-18] The coordination of each rhodium is completed by one or two additional in-plane ligands (X and/or Y). Those of type B lack the Rh–Rh bond (typical distances ~3.4 Å) but have a second, in-plane bridging ligand (Z = CO or CH_2) across from the olefin and additional terminal ligands X (which may be a chelating bidentate ligand).[19-21]



A



B

Results

Synthetic and Spectroscopic Studies. Treatment of a dichloromethane solution of 1 with $CH_3O_2CC{\equiv}CCO_2CH_3$ produces a mixture of two isomeric complexes of composition $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$. They are readily separated by fractional crystallization. The more soluble, brown complex **2a** is the major product (yield 56%) while the less soluble, violet isomer **2b** is a decidedly minor product (15% yield). Under similar conditions $CH_3CH_2O_2CC{\equiv}CCO_2CH_2CH_3$ reacts with 1 to form the brown complex $[Rh_3(dpmp)_2(CO)_2Cl_2(\mu\text{-}CH_3CH_2O_2CC{=}CCO_2CH_2CH_3)][BPh_4]$ (**3**) in 85% yield. The properties of **3** correspond closely to those of **2a**. No analogue of **2b** appears to be formed in this reaction. Treatment of $[Rh_3(dpma)_2(CO)_3Cl_2][BPh_4]$ (dpma = bis[(diphenylphosphino)methyl]phenylarsine)[23] with $CH_3O_2CC{\equiv}CCO_2CH_3$ yields brown $[Rh_3(dpma)_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**4**) which has properties similar to those of **2a** and **3**. Again no analogue of **2b** has been found.

Infrared spectral data for the new compounds are given in Table I. The infrared spectra of **2a**, **3**, and **4** show terminal carbon monoxide absorptions, along with characteristic bands due to the ester functions and bands at ca. 1575 cm^{-1} due to the stretch of the dimetalated olefin. In contrast, the infrared spectrum for **2b** shows both terminal and bridging carbonyl absorptions in addition to the bands of the dimetalated olefin. It is important to note that the presence of the bridging carbon monoxide absorption in **2b** has been distinguished from the ester absorptions by labeling with ^{13}CO. Similar labeling of **2a**,

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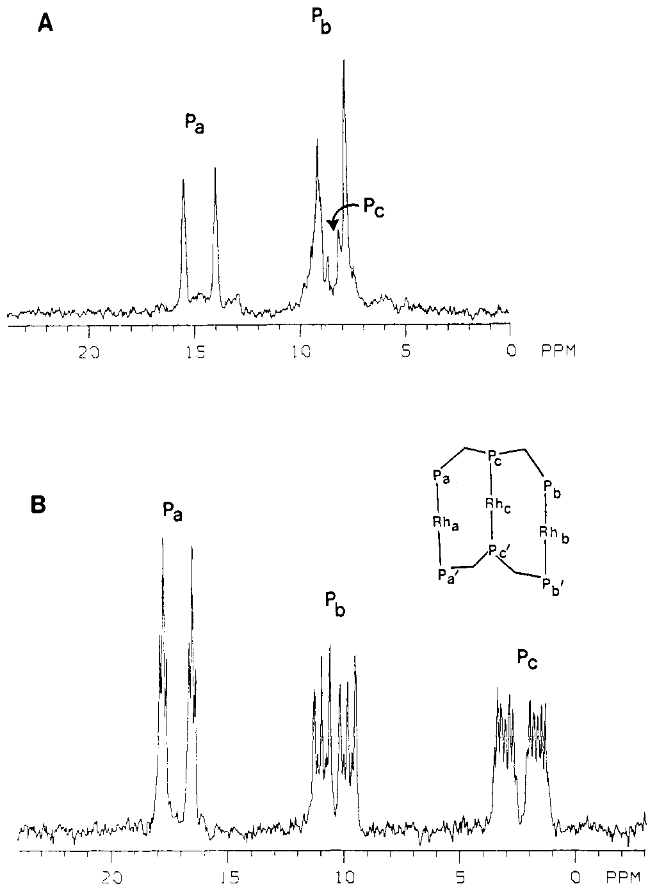


Figure 1. The ^{31}P NMR spectra of A, $[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2a**), and B, $[Rh_3(\mu\text{-dpmp})_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**5a**).

3, and 4 reveals the lack of any absorption due to bridging carbon monoxide groups.

NMR data for the new complexes are given in Table II. The ^{31}P NMR spectra of **2a** and **3** are not well resolved even at 145.8 MHz. This is shown in Figure 1. The doublet of one terminal PPh_2 unit overlaps severely with the resonance of the central PPh unit. This spectrum is shown as an example of how poorly resolved the ^{31}P NMR spectra of these complexes can be in some cases. With the simplification of the spectrum resulting from the use of dpma, it is clear that for **4** the environments of the two terminal PPh_2 groups are unique. Likewise the ^{31}P NMR spectrum of **2b** shows three distinct resonances, each with coupling to rhodium. Consequently, the two ends of the phosphine ligand in this complex are different. The ^{13}C NMR spectra of **2a**, **3**, and **4** reveal the presence of two terminal carbonyl groups, each in a unique environment. The low solubility of **2b** precluded the acquisition of a ^{13}C NMR spectrum under reasonable conditions. The ^1H NMR spectra show that there are four methylene proton environments in **2a**, **2b**, **3**, and **4**. The methylene groups are diastereotopic in the free ligand. Consequently, the presence of four methylene resonances in these complexes indicates that the two ends of each triphosphine are unique. The ^1H NMR spectra also indicate that the two ends of the dimetalated olefin are distinct, since two methyl resonances are seen for **2a**, **2b**, and **4** and two sets of ethyl resonances are observed for **3**.

Since the structure of **1** undergoes significant changes upon the substitution of chloride by other anions,[5,9] the reactivity of **2a** and **2b** toward iodide was investigated. The reaction of **2a** in dichloromethane with sodium iodide in methanol proceeds stepwise with significant rate differences so that the monosubstituted brown $[Rh_3(dpmp)_2(CO)_2ClI(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**5a**) and the disubstituted, purple $[Rh_3(dpmp)_2(CO)_2I_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**6**) can be isolated after short and long reaction times, respectively. The spectral data suggest that the basic structure of the complex remains intact during these transformations. The ^{31}P NMR spectrum of **5a** is shown in trace B of Figure 1 in order to offer a comparison with the less well-resolved spectrum of **2a**. In particular, there is no conversion of a terminal carbon monoxide into a bridging one, and the dimetalated olefin remains bound. Treatment of **2b** in dichloromethane with iodide in methanol produces violet $[Rh_3(dpmp)_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)]I$ (**5b**). The spectroscopic properties indicate again that substitution has occurred without isomerization. Complex **5b** is distinctly different from isomeric **5a**. The infrared spectrum of **5b** shows features which are similar to those of **2b**: both terminal and bridging carbon monoxide ligands are present.

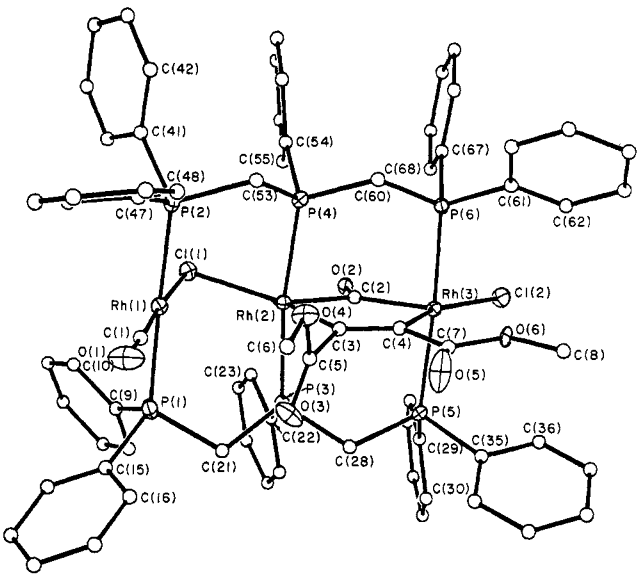


Figure 2. A perspective view of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)]^+$ (**2b**) showing 50% probability thermal ellipsoids for anisotropic atoms and uniform, arbitrarily sized circles for carbon atoms.

Isomers **2a** and **2b** have different affinities for adding ligands. While **2a** shows no evidence for a reaction with carbon monoxide, dichloromethane solutions of **2b** change color from violet to red-brown when exposed to one atmosphere of carbon monoxide. New infrared absorptions appear at 2046 and 1753 cm^{-1} in the carbon monoxide treated solution. Both the color change and the appearance of the new infrared absorptions are reversed when the solution is purged with dinitrogen. We attribute these changes to reversible carbon monoxide binding.

The X-ray Crystal Structure of 2b, $[Rh_3(dpmp)_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]\cdot 3CH_2Cl_2$. The solid consists of the cation, a normal tetraphenylborate anion, and three molecules of dichloromethane. There are no unusual contacts between these units. A drawing which shows the atomic numbering scheme of the cation is presented in Figure 2. Atomic positional parameters are given in Table III. Tables IV and V give selected interatomic distances and angles.

While there is no crystallographically required symmetry in the cation, there is a virtual mirror symmetry with regard to the plane passing through the $Rh_3(CO)_2Cl_2(C\text{-}C{=}CC)$ section. Notice that even the arrangement of the phenyl rings on the triphosphine ligands bear this near

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Rh_3(\mu\text{-}(Ph_2PCH_2)_2PPh)_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3][BPh_4]\bullet 3CH_2Cl_2$

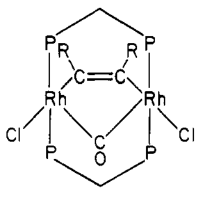
atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Rh(1)	1147 (1)	1681 (1)	1463 (1)	14 (1)[a]	C(40)	6075 (11)	2409 (9)	3002 (7)	34 (4)
Rh(2)	1898 (1)	1271 (1)	2625 (1)	11 (1)[a]	C(41)	−206 (10)	−268 (7)	1666 (5)	17 (3)
Rh(3)	3455 (1)	683 (1)	3743 (1)	12 (1)[a]	C(42)	−210 (11)	−1094 (8)	1686 (6)	25 (3)
Cl(1)	8 (2)	1572 (2)	2384 (1)	17 (1)[a]	C(43)	−1137 (11)	−1515 (9)	1814 (6)	29 (4)
Cl(2)	3355 (3)	499 (2)	4817 (1)	20 (1)[a]	C(44)	−2123 (13)	−1106 (10)	1917 (7)	41 (4)
Cl(3)	2343 (4)	3253 (3)	8590 (2)	50	C(45)	−2112 (11)	−279 (8)	1902 (6)	26 (3)
Cl(4)	3355 (4)	3939 (3)	7381 (2)	50	C(46)	−1181 (10)	148 (8)	1770 (5)	23 (3)
Cl(5)	6655 (4)	4156 (4)	3920 (2)	50	C(47)	1632 (9)	50 (7)	795 (5)	14 (3)
Cl(6)	6617 (4)	4092 (4)	5069 (2)	50	C(48)	2594 (10)	−362 (8)	709 (6)	22 (3)
Cl(7)	5984 (4)	3310 (3)	490 (2)	50	C(49)	3009 (12)	−471 (9)	148 (6)	33 (4)
Cl(8)	7379 (4)	2000 (3)	1027 (2)	50	C(50)	2473 (10)	−139 (8)	−331 (6)	24 (3)
P(1)	1407 (3)	3079 (2)	1383 (1)	17 (1)[a]	C(51)	1514 (11)	270 (8)	−259 (6)	25 (3)
P(2)	1049 (3)	271 (2)	1495 (1)	14 (1)[a]	C(52)	1077 (11)	373 (8)	298 (6)	24 (3)
P(3)	2329 (3)	2619 (2)	2577 (1)	14 (1)[a]	C(53)	1841 (9)	−385 (7)	2042 (5)	10 (3)
P(4)	1659 (3)	−130 (2)	2753 (1)	12 (1)[a]	C(54)	418 (9)	−561 (7)	3175 (5)	14 (3)
P(5)	3928 (3)	2072 (2)	3514 (1)	14 (1)[a]	C(55)	−187 (9)	−107 (7)	3544 (5)	13 (3)
P(6)	3088 (3)	−683 (2)	3793 (1)	12 (1)[a]	C(56)	−1061 (10)	−484 (8)	3922 (5)	20 (3)
O(1)	2655 (8)	1809 (6)	363 (4)	36 (4)[a]	C(57)	−1358 (11)	−1241 (8)	3912 (6)	24 (3)
O(2)	1320 (6)	1197 (5)	3821 (3)	15 (3)[a]	C(58)	−773 (10)	−1672 (8)	3535 (6)	25 (3)
O(3)	4165 (7)	1940 (5)	1542 (4)	27 (3)[a]	C(59)	119 (10)	−1335 (8)	3170 (5)	20 (3)
O(4)	4104 (7)	596 (5)	1571 (4)	22 (3)[a]	C(60)	2689 (10)	−832 (8)	3102 (5)	17 (3)
O(5)	5768 (7)	640 (7)	2337 (4)	36 (4)[a]	C(61)	4223 (10)	−1402 (8)	3902 (6)	23 (3)
O(6)	5531 (6)	249 (5)	3338 (4)	19 (3)[a]	C(62)	4815 (10)	−1381 (8)	4345 (5)	20 (3)
C(1)	2088 (10)	1761 (8)	791 (6)	20 (3)	C(63)	5666 (10)	−1929 (8)	4472 (6)	21 (3)
C(2)	2074 (9)	1078 (7)	3488 (5)	11 (3)	C(64)	5946 (12)	−2517 (9)	4144 (6)	35 (4)
C(3)	3466 (9)	1021 (7)	2453 (5)	13 (3)	C(65)	5334 (12)	−2540 (10)	3684 (7)	42 (4)
C(4)	4041 (9)	758 (7)	2886 (5)	15 (3)	C(66)	4487 (11)	−1990 (8)	3571 (6)	30 (4)
C(5)	3960 (9)	1244 (7)	1811 (5)	14 (3)	C(67)	2035 (10)	−1166 (7)	4366 (5)	17 (3)
C(6)	4784 (11)	747 (9)	988 (6)	32 (4)	C(68)	1397 (9)	−709 (8)	4700 (5)	15 (3)
C(7)	5196 (10)	548 (8)	2792 (6)	22 (3)	C(69)	590 (10)	−1073 (8)	5133 (5)	20 (3)
C(8)	6622 (11)	−12 (9)	3363 (6)	29 (4)	C(70)	432 (10)	−1900 (8)	5239 (6)	22 (3)
C(9)	188 (10)	3616 (8)	1592 (5)	18 (3)	C(71)	1086 (10)	−2374 (8)	4909 (6)	25 (3)
C(10)	−768 (10)	3349 (8)	1472 (5)	21 (3)	C(72)	1878 (10)	−1997 (8)	4467 (6)	24 (3)
C(11)	−1739 (11)	3741 (8)	1617 (6)	30 (4)	C(73)	−3533 (11)	4250 (8)	−1749 (6)	29 (3)
C(12)	−1784 (12)	4388 (9)	1889 (6)	32 (4)	C(71)	−4047 (11)	4675 (9)	−2229 (6)	31 (4)
C(13)	−821 (11)	4653 (9)	2000 (6)	31 (4)	C(75)	−4773 (12)	5330 (9)	−2184 (6)	34 (4)
C(14)	142 (11)	4281 (8)	1852 (6)	25 (3)	C(76)	−5012 (12)	5625 (9)	−1676 (7)	37 (4)
C(15)	1923 (10)	3697 (7)	657 (5)	15 (3)	C(77)	−4486 (11)	5219 (9)	−1178 (6)	32 (4)
C(16)	3001 (11)	3602 (8)	423 (6)	27 (3)	C(78)	−3753 (11)	4545 (9)	−1219 (6)	31 (4)
C(17)	3392 (11)	4050 (8)	−123 (6)	25 (3)	C(79)	−1977 (11)	3195 (8)	−1235 (6)	27 (3)
C(18)	2751 (11)	4628 (8)	−461 (6)	28 (3)	C(80)	−1416 (13)	3808 (10)	−1113 (7)	46 (4)
C(19)	1713 (12)	4731 (10)	−252 (7)	38 (4)	C(81)	−604 (14)	3614 (11)	−741 (8)	52 (5)
C(20)	1287 (11)	4260 (8)	309 (6)	29 (3)	C(82)	−363 (13)	2807 (10)	−472 (7)	43 (4)
C(21)	2432 (10)	3263 (7)	1814 (5)	16 (3)	C(83)	−920 (12)	2177 (9)	−589 (7)	35 (4)
C(22)	1450 (10)	3232 (8)	2993 (5)	17 (3)	C(84)	−1731 (11)	2380 (9)	−962 (6)	30 (4)
C(23)	418 (10)	2996 (8)	3236 (5)	17 (3)	C(85)	−3719 (11)	2652 (8)	−1561 (6)	27 (3)
C(24)	−267 (11)	3515 (8)	3485 (5)	21 (3)	C(86)	−4411 (11)	2603 (9)	−1006 (6)	34 (4)
C(25)	72 (11)	4257 (8)	3530 (6)	27 (3)	C(87)	−5223 (12)	2018 (9)	−811 (6)	34 (4)
C(26)	1110 (11)	4491 (9)	3315 (6)	27 (3)	C(88)	−5358 (11)	1483 (9)	−1163 (6)	34 (4)
C(27)	1797 (11)	3971 (8)	3039 (5)	21 (3)	C(89)	−4708 (12)	1498 (9)	−1693 (6)	34 (4)
C(28)	3662 (9)	2684 (7)	2773 (5)	13 (3)	C(90)	−3898 (10)	2088 (8)	−1876 (6)	24 (3)
C(29)	3378 (9)	2739 (7)	3994 (5)	12 (3)	C(91)	−2128 (11)	3401 (8)	−2392 (6)	27 (3)
C(30)	3870 (11)	3495 (8)	3945 (6)	26 (3)	C(92)	−1012 (11)	3389 (9)	−2471 (6)	32 (4)
C(31)	3419 (11)	4022 (9)	4282 (6)	35 (4)	C(93)	−415 (13)	3417 (10)	−3040 (7)	44 (4)
C(32)	2497 (11)	3826 (9)	4671 (6)	31 (4)	C(94)	−928 (13)	3444 (10)	−3525 (7)	48 (4)
C(33)	2031 (10)	3089 (8)	4720 (5)	19 (3)	C(95)	−2057 (12)	3458 (10)	−3473 (7)	42 (4)
C(34)	2459 (10)	2543 (8)	4383 (5)	18 (3)	C(96)	−2669 (12)	3435 (10)	−2908 (7)	41 (4)
C(35)	5369 (10)	2083 (8)	3509 (5)	20 (3)	C(97)	3542 (16)	3478 (13)	8140 (9)	50
C(36)	5775 (9)	1700 (7)	4036 (5)	14 (3)	C(98)	6394 (17)	3555 (14)	4545 (10)	50
C(37)	6853 (10)	1631 (8)	4063 (6)	24 (3)	C(99)	7138 (16)	2746 (12)	360 (9)	50
C(38)	7560 (11)	1945 (8)	3558 (6)	28 (3)	B	−2844 (12)	3381 (10)	−1732 (7)	24 (4)
C(39)	7180 (11)	2331 (8)	3036 (6)	30 (4)					

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

mirror symmetry. The major deviation from this mirroring is the ester group on C(3). This group is oriented nearly perpendicular to the virtual mirror plane. In solution normal motion, including free rotation about the C(5)–C(3) bond, renders the two phosphine ligands equivalent.

The complex cation consists of a nearly linear array of three rhodium ions with the two triphosphine bridges lying in trans positions above and below the plane containing the $Rh_3(CO)_2Cl_2$(C—C═C—C) unit. The P–Rh–P angles at each rhodium fall in the range 169.9–174.6°. There is little twisting of the P–Rh···Rh–P dihedral angles.

The overall geometry of the complex contains units analogous to those encountered in binuclear, phosphine bridged rhodium chemistry. Thus, the portion of the structure including Rh(2) and Rh(3) and their directly bonded ligands closely resembles the binuclear complex, $Rh_2(\mu\text{-dpm})_2(\mu\text{-CO})(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)Cl_2$ (7).[19] The similarity is best appreciated by comparing the planar sections shown in Figure 3. Not only are the Rh_2C_3 rings very similar in all of the dimensions, but the placements



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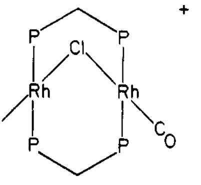
of the chloro substituents, even the bridging chloride Cl(1), are similar. Moreover, the orientations of the bridging methylene groups, which lie on the side over the dimetalated olefin, are similar in both complexes. The unit comprised of Rh(1) and its ligands and Rh(2) and the phosphine bound to it resembles the chloro-bridged A-frame unit exemplified by $[Rh_2(\mu\text{-dpm})_2(\mu\text{-Cl})(CO)_2]^+$ (**8**).[24]



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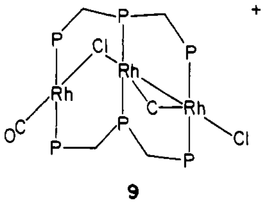

9

A similar structural element is also found in **1** and $[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2]^+$ (**9**). The Rh–C–Rh angle in **2b**, 72.6 (1)°, is smaller than the corresponding angles in **1**, 82.8 (1)°,[4] **8**, 82.38 (5)°,[24] and **9**, 75.8 (1)°.[11] Correspondingly, the Rh···Rh separation in **2b**, 2.915 (1) Å, is less than in **1**, 3.164 (3),[4] **8**, 3.1520 (8),[24] and **9**, 2.966 (1) Å.[11] One cause for this shortening may be the constraints offered by the triphosphine ligand which is required to span two relatively long, nonbonded Rh···Rh groups. Another difference between the chloro-bridged A-frame unit in **2b** and these other examples is the orientation of the methylene groups of the phosphine backbone. In **2b** they both lie on the side away from the chloro bridge, while in **1**, **8**, and **9** the corresponding methylene groups lie directly over the Rh–Cl–Rh bridge.

The $CH_3O_2CC{\equiv}CCO_2CH_3$-derived unit that spans Rh(3) and Rh(2) has clearly undergone major transformation in bonding to the chain. It now has all of the structural characteristics of an olefin. The bond angles about both C(3) and C(4) are all close to the ideal 120°. That and the planarity of the Rh_2C_4 unit are indicative of sp^2 hybridization at C(3) and C(4). The C(3)–C(4) distance, 1.30 (2) Å, is within the range expected for an olefin and considerably longer than that of an acetylene, ~1.20 Å. The structural characteristics of the ester functions are normal.

The Rh(2)···Rh(3) separation in **2b**, 3.410 (1) Å, is slightly longer than in **7**, 3.3542 (9) Å,[19] or in the closely related $[Rh_2(\mu\text{-dpm})_2(\mu\text{-CO})(\mu\text{-CH}_3O_2CC{=}CCO_2CH_3)(O_2CCH_3)(P(OCH_3)_3)][PF_6]$, 3.386 (1) Å,[21] and is clearly much longer than the bonded Rh–Rh separations found in dimetalated olefin complexes in class A. However, this Rh···Rh separation is somewhat shorter than that found in the less constrained complex $Pd_2(\mu\text{-dpm})_2(\mu\text{-CF}_3C{=}CCF_3)Cl_2$, 3.492 (1) Å,[14] or in $Rh_2(\mu\text{-dpm})_2(\mu\text{-CH}_2)(\mu\text{-CF}_3C{=}CCF_3)Cl_2$, 3.464 (1) Å.[20]

The bridging carbon monoxide ligand falls into the relatively rare class of "ketonic carbonyls" in which the ligand spans two metals that are unconnected by a metal–metal bond. While the three other structurally characterized complexes incorporating this entity have similar parameters, **2b** does have the longest M···M separation, 3.410 (1) Å, and the widest M–C–M angle, 119.0 (6)° within the group. For comparison, in **7** these values are 3.3542 (9) Å and 116.0 (4)°;[19] in $Pt_2(\mu\text{-dam})_2(\mu\text{-CO})Cl_2$ (dam = bis(diphenylarsino)methane) they are 3.162 (4) Å and 106 (1)°[25] and in $Pd_2(\mu\text{-dam})_2(\mu\text{-CO})Cl_2$ they are 3.274 (8) Å and 119 (3)°.[26]

Table IV. Selected Interatomic Distances (Å) for $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl(\mu\text{-CH}_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (2b)

At Rh(1)			
Rh(1)–P(1)	2.349 (4)	Rh(1)–P(2)	2.359 (4)
Rh(1)–C(1)	1.818 (13)	Rh(1)–Cl(1)	2.394 (3)
Rh(1)···Rh(2)	2.915 (1)		
At Rh(2)			
Rh(2)–P(3)	2.333 (4)	Rh(2)–P(4)	2.330 (3)
Rh(2)–C(2)	2.006 (12)	Rh(2)–C(3)	2.008 (11)
Rh(2)–Cl(1)	2.528 (3)	Rh(2)···Rh(3)	3.410 (1)
Rh(2)···Rh(1)	2.915 (1)		
At Rh(3)			
Rh(3)–P(5)	2.355 (3)	Rh(3)–P(6)	2.340 (4)
Rh(3)–C(2)	1.951 (12)	Rh(3)–C(4)	2.015 (12)
Rh(3)–Cl(2)	2.443 (3)	Rh(3)···Rh(2)	3.410 (1)
At Carbon Monoxide			
C(1)–O(1)	1.136 (16)	C(2)–O(2)	1.186 (13)
Within Dimetalated Olefin			
C(3)–C(4)	1.30 (2)	C(3)–C(5)	1.51 (2)
C(4)–C(7)	1.48 (2)	O(3)–C(5)	1.208 (14)
O(4)–C(5)	1.34 (2)	O(4)–C(6)	1.482 (15)
O(5)–C(7)	1.184 (15)	O(6)–C(7)	1.367 (15)
O(6)–C(8)	1.428 (15)		
At Phosphorus			
P(1)–C(9)	1.807 (13)	P(1)–C(15)	1.814 (11)
P(1)–C(21)	1.836 (14)	P(2)–C(41)	1.826 (13)
P(2)–C(47)	1.817 (13)	P(2)–C(53)	1.837 (11)
P(3)–C(21)	1.835 (11)	P(3)–C(22)	1.816 (13)
P(3)–C(28)	1.828 (13)	P(4)–C(53)	1.802 (12)
P(4)–C(54)	1.824 (12)	P(4)–C(60)	1.839 (12)
P(5)–C(28)	1.847 (11)	P(5)–C(29)	1.821 (13)
P(5)–C(35)	1.825 (13)	P(6)–C(60)	1.840 (14)
P(6)–C(61)	1.821 (13)	P(6)–C(67)	1.825 (11)
P(1)···P(3)	3.082 (7)	P(3)···P(5)	3.125 (7)
P(2)···P(4)	3.052 (7)	P(4)···P(6)	3.157 (7)

Discussion

The structural results for **2b** show that trinuclear **1** has reacted with the acetylene $CH_3O_2CC{\equiv}CCO_2CH_3$ so that only a binuclear portion of the complex is affected. The remaining rhodium, Rh(1), appears largely unaltered by the bonding of the acetylene. This behavior contrasts sharply with the oxidative addition chemistry previously described. There, where addition of iodine to $[Rh_3(dpmp)_2(CO)_3I_2]^+$ was studied, the oxidation affected the entire cluster.[9,12]

Each rhodium in **2b** is an unsaturated 16-electron center. Rh(1) is part of a typical $Rh^I(CO)ClP_2$ unit. In counting both the dimetalated olefin and the bridging carbon monoxide units as dianions,[13] Rh(2) and Rh(3) become formally Rh^{III} centers. No rhodium–rhodium bonding is required, and indeed the Rh···Rh separations within **2b** are all longer than normal Rh–Rh single bonds (range 2.6–2.8 Å). The fact that each rhodium is coordinatively unsaturated readily accounts for the ease with which **2b** binds additional carbon monoxide and other bases. We suspect that Rh(3) is the most likely site for nucleophilic attack, but there are no data available to substantiate this.

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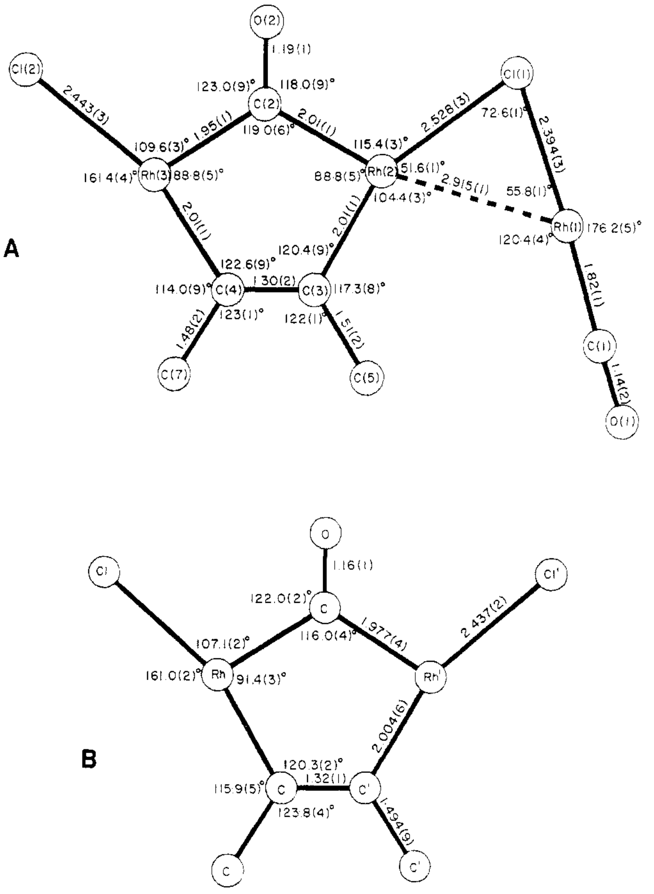
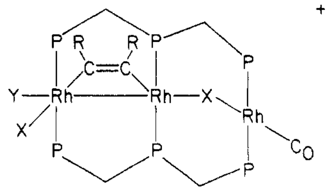
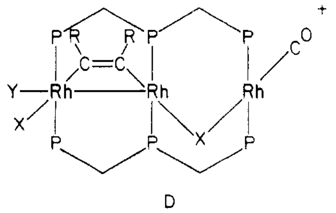


Figure 3. Planar sections through A, $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)]^+$ (**2b**) and B, $Rh_2(\mu\text{-dpm})_2(\mu\text{-CO})(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)Cl_2$ (**7**) (from ref 24).

Unfortunately, crystals suitable for X-ray diffraction of the major isomer **2a** or of any of its analogues or substitution products have not been obtained. On the basis of the available spectroscopic data, we propose that the complexes **2a**, **3**, **4**, **5a**, and **6** are built around the basic Rh_3P_6 core present in **1**. For the in-plane set of ligands, the arrangements C and D are the most likely possibilities.



C



D

Table V. Selected Interatomic Angles (deg) for $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})(CO)(\mu\text{-Cl})Cl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3]\text{-}[BPh_4]$ (2b)

	At Rh(1)		
Rh(2)–Rh(1)–Cl(1)	55.8 (1)	Rh(2)–Rh(1)–P(1)	89.6 (1)
Cl(1)–Rh(1)–P(1)	91.3 (1)	Rh(2)–Rh(1)–P(2)	90.7 (1)
Cl(1)–Rh(1)–P(2)	93.3 (1)	P(1)–Rh(1)–P(2)	174.6 (1)
Rh(2)–Rh(1)–C(1)	120.4 (4)	Cl(1)–Rh(1)–C(1)	176.2 (5)
P(1)–Rh(1)–C(1)	87.9 (4)	P(2)–Rh(1)–C(1)	87.3 (4)
	At Rh(2)		
Rh(1)–Rh(2)–Cl(1)	51.6 (1)	Rh(1)–Rh(2)–P(3)	94.3 (1)
Cl(1)–Rh(2)–P(3)	97.5 (1)	Rh(1)–Rh(2)–P(4)	92.5 (1)
Cl(1)–Rh(2)–P(4)	89.9 (1)	P(3)–Rh(2)–P(4)	172.1 (1)
Rh(1)–Rh(2)–C(2)	166.7 (3)	Cl(1)–Rh(2)–C(2)	115.4 (3)
P(3)–Rh(2)–C(2)	84.2 (4)	P(4)–Rh(2)–C(2)	90.1 (4)
Rh(1)–Rh(2)–C(3)	104.4 (3)	Cl(1)–Rh(2)–C(3)	155.5 (4)
P(3)–Rh(2)–C(3)	87.9 (4)	P(4)–Rh(2)–C(3)	86.6 (4)
C(2)–Rh(2)–C(3)	88.8 (5)		
	At Rh(3)		
Cl(2)–Rh(3)–P(6)	95.2 (1)	Cl(2)–Rh(3)–P(5)	94.6 (1)
Cl(2)–Rh(3)–C(2)	109.6 (3)	P(5)–Rh(3)–P(6)	169.9 (1)
P(6)–Rh(3)–C(2)	92.1 (4)	P(5)–Rh(3)–C(2)	87.2 (4)
P(5)–Rh(3)–C(4)	83.6 (4)	Cl(2)–Rh(3)–C(4)	161.4 (4)
C(2)–Rh(3)–C(4)	88.8 (5)	P(6)–Rh(3)–C(4)	86.3 (4)
	At Carbon Monoxide		
Rh(1)–C(1)–O(1)	178.2 (13)	Rh(2)–C(2)–Rh(3)	119.0 (6)
Rh(2)–C(2)–O(2)	118.0 (9)	Rh(3)–C(2)–O(2)	123.0 (9)
	At Cl(1)		
Rh(1)–Cl(1)–Rh(2)	72.6 (1)		
	Within μ-$CH_3O_2CC{=}CCO_2CH_3$		
Rh(2)–C(3)–C(4)	120.4 (9)	Rh(2)–C(3)–C(5)	117.3 (8)
C(4)–C(3)–C(5)	121.9 (11)	Rh(3)–C(4)–C(3)	122.6 (9)
Rh(3)–C(4)–C(7)	114.0 (9)	C(3)–C(4)–C(7)	123.3 (11)
O(3)–C(5)–O(4)	124.0 (11)	O(3)–C(5)–C(3)	123.1 (12)
O(4)–C(5)–C(3)	112.8 (9)	O(5)–C(7)–O(6)	123.9 (11)
O(5)–C(7)–C(4)	128.1 (12)	O(6)–C(7)–C(4)	107.9 (10)
C(5)–O(4)–C(6)	114.6 (9)	C(7)–O(6)–C(8)	118.4 (9)
	Methylene Carbons		
P(1)–C(21)–P(3)	114.1 (6)	P(3)–C(28)–P(5)	116.5 (6)
P(2)–C(53)–P(4)	114.0 (6)	P(4)–C(60)–P(6)	118.2 (7)
	At Phosphorus		
Rh(1)–P(1)–C(9)	112.3 (4)	Rh(1)–P(1)–C(15)	117.2 (5)
C(9)–P(1)–C(15)	104.3 (5)	Rh(1)–P(1)–C(21)	114.0 (4)
C(9)–P(1)–C(21)	108.5 (6)	C(15)–P(1)–C(21)	99.2 (6)
Rh(1)–P(2)–C(41)	122.9 (4)	Rh(1)–P(2)–C(47)	111.2 (4)
C(41)–P(2)–C(47)	103.3 (6)	Rh(1)–P(2)–C(53)	112.3 (4)
C(41)–P(2)–C(53)	101.3 (5)	C(47)–P(2)–C(53)	103.8 (5)
Rh(2)–P(3)–C(21)	112.0 (5)	Rh(2)–P(3)–C(22)	119.7 (4)
C(21)–P(3)–C(22)	102.8 (5)	Rh(2)–P(3)–C(28)	112.5 (4)
C(21)–P(3)–C(28)	102.1 (5)	C(22)–P(3)–C(28)	106.0 (6)
Rh(2)–P(4)–C(53)	110.0 (4)	Rh(2)–P(4)–C(54)	117.9 (4)
C(53)–P(4)–C(54)	109.0 (6)	Rh(2)–P(4)–C(60)	116.4 (5)
C(53)–P(4)–C(60)	98.4 (6)	C(54)–P(4)–C(60)	103.3 (5)
Rh(3)–P(5)–C(28)	115.2 (5)	Rh(3)–P(5)–C(29)	120.5 (4)
C(28)–P(5)–C(29)	102.3 (5)	Rh(3)–P(5)–C(35)	107.2 (4)
C(28)–P(5)–C(35)	105.7 (5)	C(29)–P(5)–C(35)	104.6 (6)
Rh(3)–P(6)–C(60)	113.4 (4)	Rh(3)–P(6)–C(61)	114.7 (5)
C(60)–P(6)–C(61)	101.9 (6)	Rh(3)–P(6)–C(67)	117.3 (5)
C(60)–P(6)–C(67)	103.7 (6)	C(61)–P(6)–C(67)	103.9 (5)

In these X is halide and Y is carbon monoxide. The positions of the two terminal ligands on the left most rhodium may be interchanged so that either halide or carbon monoxide is trans to the Rh–Rh bond. Such arrangements incorporate the dimetalated olefin unit whose presence is suggested by the infrared spectroscopy and produce inequivalence in the opposite ends of both the triphosphine ligands and of the dimetalated olefin. Both arrangements utilize the unit A which has been established as a structural type in binuclear rhodium chemistry through several X-ray crystallographic studies.[16–18]

Experimental Section

Preparation of Compounds. Dpmp[3] and **1**[4] were prepared as described previously. All complexes reported here have excellent stability to a normal laboratory atmosphere, and so no precautions were taken to work under an inert atmosphere or to use specially dried solvents.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (Isomers 2a and 2b). A solution of 360 mg (0.200 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_3Cl_2][BPh_4]$ and 1.0 mL (8.1 mmol) of dimethyl acetylenedicarboxylate in 25 mL of dichloromethane was allowed to slowly evaporate over a 24-h period. The brown oil which remained was filtered to give a brown filtrate (containing **2a**) and a fine black powder (**2b**). The filtrate was treated dropwise with ethyl ether until precipitation of brown crystals of **2a** was complete. The solid was collected by filtration and washed with ether. Purification was achieved by dissolution in dichloromethane, filtration, and reprecipitation with ether. This procedure was repeated to give 213 mg (56%) of fine brown crystals of **2a** which were then vacuum dried. Anal. Calcd for $C_{96}H_{84}BCl_2O_6P_6Rh_3$: C, 60.37; H, 4.43; P, 9.73; Cl, 3.71. Found: C, 59.68; H, 4.39; P, 9.82; Cl, 3.78. The black powder was rapidly washed with 1 mL of dichloromethane. Purification was achieved by extracting the powder with dichloromethane in which it slowly dissolves to form a violet solution. The extract was concentrated to ca. 20 mL, and diethyl ether was added dropwise to give dark violet crystals of **2b**, yield 57 mg (15%).

$[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3CH_2O_2CC{=}CCO_2CH_2CH_3)][BPh_4]$ (3). This was prepared by the procedure described for **2a** in 85% yield using diethyl acetylenedicarboxylate. Anal. Calcd for $C_{98}H_{88}BCl_2O_6P_6Rh_3$: C, 60.67; H, 4.68; Cl, 3.65; P, 9.58. Found: C, 60.04; H, 4.61; Cl, 3.65; P, 9.36.

$[Rh_3(\mu\text{-dpma})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (4). A sample of 143 mg (0.076 mmol) of $[Rh_3(\mu\text{-dpma})_2(CO)_3Cl_2][BPh_4]$ and 1 mL (8.1 mmol) of dimethyl acetylenedicarboxylate in 30 mL of dichloromethane was allowed to evaporate over a 24-h period. The brown oil was dissolved in 2 mL of dichloromethane and filtered. A small amount (0.5 mL) of methanol was added to the filtrate, and then ethyl ether was added dropwise. Brown crystals of the product slowly formed. These were collected by filtration and washed with ethyl ether. Purification was achieved by dissolving the solid in dichloromethane/methanol (10:1 v/v), filtering, and adding ethyl ether slowly. The brown crystalline product (100 mg, 66%) was collected by filtration, washed with ethyl ether, and vacuum dried. Anal. Calcd for $C_{96}H_{84}As_2BCl_2O_6P_4Rh_3$: C, 57.71; H 4.24; Cl, 3.46. Found: C, 57.87; H, 4.15; Cl, 3.46.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (5a). A solution of 240 mg (0.126 mmol) of $[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2a**) in 15 mL of dichloromethane was treated with 1 mL of a saturated methanol solution of sodium iodide. The brown solution was filtered, and 70 mL of methanol was added to the solution within 5 min of the initial mixing. The dark brown solid (largely the iodide salt of the desired cation) was separated by filtration from the violet solution. The solid was suspended in 10 mL of dichloromethane, and 1 mL of a saturated methanol solution of sodium tetraphenylborate was added. The green-brown solution was filtered, and 70 mL of methanol was added. The fine brown crystalline product was collected and washed with methanol. Purification was accomplished by dissolving the solid in dichloromethane, filtering the solution, and slowly crystallizing the product through the gradual addition of ethyl ether. The yield was 180 mg (72%). Anal. Calcd for $C_{96}H_{84}BClIO_6P_6Rh_3$: C, 57.61; H, 4.23; P, 9.29; I, 6.34. Found: C, 57.35; H, 4.15; P, 9.30; I, 6.28.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2I_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (6). A solution of 158 mg (0.083 mmol) of $Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2a**) in 5 mL of dichloromethane was treated with 2 mL of a saturated methanol solution of sodium iodide. On standing for 2 h, the solution gradually turned from brown to violet. The solution was filtered, and 70 mL of methanol was gradually added. After the solution was cooled to 5 °C, the violet-black crystalline product was collected by filtration and washed with methanol. Purification was effected by dissolving the product in a minimum of dichloromethane, filtering the solution, and adding ethyl ether dropwise to precipitate the product, yield 122 mg (70%). Anal. Calcd for $C_{96}H_{84}BI_2O_6P_6Rh_3$: C, 55.09; H, 4.05; P, 8.88; I, 12.13. Found: C, 55.01; H, 3.84; P, 8.64; I, 11.5.

$[Rh_3(\mu\text{-dpmp})_2(CO)_2ICl(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)]I$ (5b). One milliliter of a saturated methanol solution of sodium iodide was added to a slurry of 143 mg of $[Rh_3(\mu\text{-dpmp})_2(CO)_2Cl_2(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]$ (**2b**) in 15 mL of dichloromethane. The solid immediately dissolved to produce a rich purple solution. The solution was filtered, and 60 mL of methanol was gradually added. The black crystalline solid was collected by filtration and washed with ethanol. The solid was purified by dissolving it in a minimum volume of dichloromethane, filtering, and precipitating the product through the slow addition of ethyl ether; yield 110 mg (81%). Anal. Calcd for $C_{72}H_{64}ClI_2O_6P_6Rh_3$: C, 47.80; H, 3.56; Cl, 1.96; I, 14.03. Found: C, 47.00; H, 3.42; Cl, 1.68; I, 14.03.

Table VI. Crystal Data for $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)(Cl)(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)][BPh_4]\cdot 3CH_2Cl_2$

formula	$C_{99}H_{90}BCl_8O_6P_6Rh_3$
fw including	2164.80
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
cryst dimens, mm	0.27 × 0.25 × 0.10
color and habit	red brown parallelpipeds
unit cell dimens (140 K)	
a, Å	12.667 (8)
b, Å	16.787 (6)
c, Å	23.417 (6)
α, deg	75.60 (2)
β, deg	81.95 (4)
γ, deg	86.31 (4)
V, Å^3	4773 (4)
ρ(calcd), g cm^{-3} (at 140 K)	1.51
Z	2
radiatn λ, Å (graphite monochromator)	Mo K$\bar{\alpha}$, 0.71069
μ(Mo Kα) cm^{-1}	8.8
range of absorptn correctn factors	1.07–1.22
scan type, 2θ(max), deg	ω, 45
scan range, deg	1.2
octants	$h,\pm k,\pm l$
scan speed, deg min^{-1}	8
check reflctn, interval no.	3 measured ever 200 reflctns
no. of unique data	12479
no. of data $I > 2\sigma(I)$	7758
R	0.073
R_w	0.075
no. of parameters	578

Spectroscopic Measurements. The ^{31}P spectra were recorded with proton decoupling on a Nicolet NT-200 Fourier transform spectrometer operating at 81 MHz or on a Nicolet NT-360 spectrometer at 145.8 MHz. The ^1H and ^{13}C NMR spectra were recorded at 360 and 90.5 MHz, respectively, on a Nicolet NT-360 FT spectrometer. The references were as follows: ^{31}P, external 85% phosphoric acid; ^1H and ^{13}C, internal tetramethylsilane. The high-frequency positive convention, recommended by IUPAC, has been used in reporting all chemical shifts. Infrared spectra were recorded from mineral oil mulls by using a Perkin-Elmer 180 spectrometer.

X-ray Data Collection, Solution, and Refinement. Well-formed red-brown parallelpipeds were grown by slow vapor diffusion of diethyl ether into a dichloromethane solution of **2b**. Crystal data, data collection procedures, and refinement of the structure are summarized in Table VI. The lattice was found to be triclinic by standard procedures using the software associated with the Syntex P2$_1$ diffractometer. The data were collected at 140 K using a locally modified LT-1 low-temperature apparatus on the Syntex P2$_1$ diffractometer. Printer plots of several reflections using ω scans revealed small satellite peaks separate from but within 2° of the main peaks. Since many of the reflections would have had unsymmetrical backgrounds, the data were collected by scanning the main peak but without making a background measurement. At the end of the data collection, the crystallographic axes were doubled, and background counts were recorded as a function of 2θ using odd-numbered indices. These data were curve fit, and a correction was applied to the intensity data in the same manner as a crude absorption correction (as a function of 2θ only). In our experience, this method gives satisfactory results in cases such as this or in the instance of cracked crystals.[27] The data were also corrected for Lorentz and polarization effects.

The structure was solved by locating the three rhodium atoms using the Patterson method (FMAP 8 routine of SHELXTL, version 4, 1984 (Nicolet Instrument Corporation, Madison, WI)). Other atoms were located from successive difference Fourier maps. Final cycles of refinement were made with anisotropic thermal

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(27) Wood, F. E.; Hvoslef, J.; Hope, H.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 4309.

Organometallics **1986**, *5*, 698–707

parameters for rhodium, phosphorus, chlorine and oxygen and isotropic thermal parameters for all remaining atoms. Hydrogen atoms were not located. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[28] An absorption correction (XABS) was applied.[29] The atoms of the three dichloromethane molecules were assigned isotropic U values of 0.05 and were allowed to refine with variable occupancy. The final occupancies were 0.824 (6) for Cl(3)C(97)Cl(4), 0.774 (6) for Cl(5)C(98)Cl(6), and 0.859 (6) for Cl(7)C(99)Cl(8). Two low-angle reflections suffering from extinction were removed from the data set for the final cycles of refinement. A conventional R factor of 0.073 was obtained. The final difference map showed some residual electron density in the vicinity of the dichloromethane molecules, but otherwise no significant features were present.

Acknowledgment. We thank the National Science Foundation (CHE8217954) for financial support.

Registry No. 1·BPh4, 84774-75-4; **2a**, 100082-53-9; **2b**, 100082-55-1; **2b**·3CH$_2$Cl$_2$, 100164-67-8; **3**, 100082-57-3; **4**, 100082-59-5; **5a**, 100082-63-1; **5b**, 100102-33-8; **6**, 100082-65-3; [Rh$_3$(dpma)$_2$(CO)$_3$Cl$_2$]BPh$_4$, 100082-61-9; dimethyl acetylenedicarboxylate, 762-42-5; diethyl acetylenedicarboxylate, 762-21-0; rhodium, 7440-16-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positions, and structure factor amplitudes (53 pages). Ordering information is given on any current masthead page.

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(28) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(29) The method obtains 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.

(30) In this paper the periodic group notation (in parentheses) 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.)

Transposition—A New Rearrangement of α-Silylsilylenes Involving Disilene Intermediates

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Received August 28, 1985

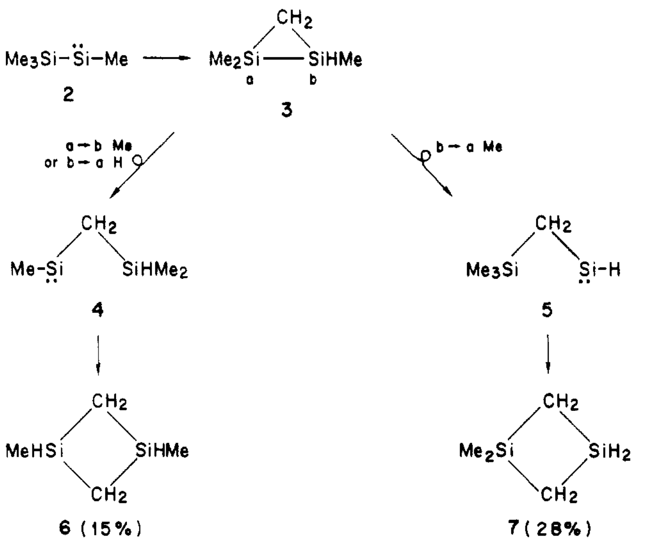
Evidence has been found for the rearrangement of Me$_3$Si—$\ddot{\text{Si}}$—H to Me$_2$HSi—$\ddot{\text{Si}}$—Me and for the formation of a Me$_2$Si═SiHMe intermediate. Me$_3$Si—$\ddot{\text{Si}}$—H also rearranges to two isomeric β-silylsilylenes Me$_2$HSiCH$_2$—$\ddot{\text{Si}}$—H and Me—$\ddot{\text{Si}}$—CH$_2$SiH$_2$Me, the latter having been previously overlooked. The question whether methyl shifts occur in the ring opening of disiliranes $\overline{\text{Me}_2\text{Si-SiHR-CH}_2}$ (R = H, Me) is discussed in light of these findings. An experimental value of 29 kcal/mol is derived for the activation energy for intramolecular C–H insertion by a divalent silicon center to form 1-methyl-1,3-disilacyclobutane.

Introduction

Reinvestigation of the gas-phase chemistry of (trimethylsilyl)silylene was prompted by the belated recognition that our previous observations on the rearrangements of Me$_3$Si-$\ddot{\text{Si}}$-H (1) underscored a nagging mechanistic question concerning the isomerization of alkylated α-silyl- to β-silylsilylenes.[2,3]

In 1978 Wulff, Goure and Barton both enlivened and revolutionized the study of divalent silicon species by a daring suggestion: that intramolecular C–H insertion by the divalent silicon center of methyl(trimethylsilyl)silylene (**2**) forms a disilirane, **3**, whose ring opening by competing hydrogen and methyl shifts completes the conversion of an α-silylsilylene **2** to a pair of isomeric β-silylsilylenes, **4** and **5**.[4] Further intramolecular C–H insertions by **4** and **5** can explain the formation of the stable 1,1- and 1,3-dimethyl-1,3-disilacyclobutanes **6** and **7**, obtained as end products of Scheme I.

Scheme I



While α-eliminations of acyclic disilanes forming silylenes and monosilanes by migration of hydrogen, halogen, and alkoxy groups are well-known,[5] Davidson and co-

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(1) Mo, S.-H.; Holten, J. D., III; Konieczny, S.; Ma, E. C.-1; Gaspar, P. P. *J. Am. Chem. Soc.* **1982**, *104*, 1424.

(2) Boo, B. H.; Gaspar, P. P.; Ghosh, A. K.; Holten, J. D.; Kirmaier, C. R.; Konieczny, S. "Transposition-A New Silylene Rearrangement, and the Laser Photolysis of Polysilanes", 17th Organosilicon Symposium, North Dakota State University, Fargo, ND, June 1983, abstracts, p 12.

(3) Boo, B. H.; Gaspar, P. P. 187th National Meeting of American Chemical Society, St. Louis, MO, 1984; American Chemical Society: Washington, D.C., 1984; ORGN 227.

(4) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

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