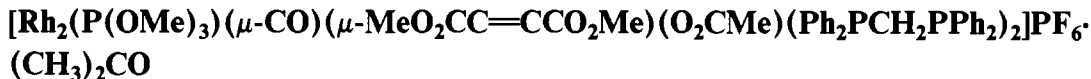


## Binuclear Cationic Complexes of Rhodium. 7. Crystal and Molecular Structure of the Dimetalated Olefin A-Frame Derivative



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The complex  $[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]\text{PF}_6 \cdot (\text{CH}_3)_2\text{CO}$  crystallizes in the space group  $P2_1/n$  with  $a = 10.697$  (6) Å,  $b = 15.679$  (7) Å,  $c = 39.961$  (9) Å,  $\beta = 97.353$  (2)°,  $V = 6647$  Å<sup>3</sup>, and  $Z = 4$ . Diffraction data ( $2\theta = 42^\circ$ , Mo K $\alpha$  radiation) were collected on an Enraf-Nonius CAD-4 automated diffractometer, and the structure was solved by conventional methods. Discrepancy indices are  $R_F = 0.054$  and  $R_w = 0.066$  for 4567 data with  $I \geq 2\sigma(I)$ . The two rhodium atoms are bridged by the two bis(diphenylphosphino)methane ligands, which occupy axial positions. In the equatorial plane the rhodium atoms are additionally bridged by the carbonyl group and the dimethyl acetylenedicarboxylate moiety, which is bound as a *cis*-dimetalated olefin. The coordination in the equatorial plane is completed by the trimethyl phosphite ligand on one rhodium and an unsymmetrically bidentate acetate ligand on the other. The rhodium-rhodium distance is 3.386 (1) Å, indicating negligible direct metal-metal interaction.

### Introduction

There is considerable current interest in the chemistry and catalytic properties of binuclear complexes bridged by bis-(diphenylphosphino)methane (DPM).<sup>1-11</sup> In the course of our studies on  $[\text{Rh}_2(\text{CO})_2(\mu\text{-O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6$  and its arsine analogue, we found it to react readily with electro-negatively substituted acetylenes.<sup>1</sup> From spectroscopic data, it appeared that the acetylene moieties were symmetrically bound as dimetalated olefins. To confirm this formulation, we have undertaken a crystallographic investigation of one member of this series and report here the results of that study, which confirms the proposed mode of binding of the acetylene.

### Experimental Section

**Collection and Processing of X-ray Diffraction Data.** Bright yellow crystals of the title compound prepared as described previously<sup>1</sup> were grown by slow diffusion of diethyl ether into an acetone solution of the complex containing a small quantity of trimethyl phosphite. A well-formed parallelepiped was mounted in a thin-walled glass capillary and oriented such that the long dimension was parallel to the  $\phi$  axis of the diffractometer. Final lattice parameters as determined from a least-squares refinement of  $((\sin \theta)/\lambda)^2$  values for 15 reflections ( $\theta > 15^\circ$ ) accurately centered on the diffractometer are given in Table I together with other data pertinent to the data collection. From these and the systematic absences observed during data collection, the space group is uniquely determined to be  $P2_1/n$ .

A unique quadrant of data was collected on an Enraf-Nonius CAD-4 diffractometer (Table I), with the stability being monitored by three check reflections measured every 40 reflections. Only a random  $\pm 3\%$  variation was noted. As described earlier,<sup>12</sup> this method of data collection gives calculated standard deviations that are very nearly equal. The intensities were corrected for Lorentz and polarization effects but not for absorption.

**Solution and Refinement of the Structure.**<sup>13</sup> Standard heavy-atom

Table I. Summary of Crystal Data and Intensity Collection

compd	$[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6 \cdot (\text{CH}_3)_2\text{CO}$
fw	1530.97
formula	$\text{C}_{65}\text{H}_{68}\text{P}_6\text{O}_{11}\text{F}_6\text{Rh}_2$
cell parameters	
<i>a</i>	10.697 (6) Å
<i>b</i>	15.679 (7) Å
<i>c</i>	39.961 (9) Å
$\beta$	97.353 (2)°
<i>V</i>	6647 Å <sup>3</sup>
<i>Z</i>	4
<i>d</i> (calcd)	1.53 g cm <sup>-3</sup>
systematic absences	$h0l, h + l = 2n + 1; 0k0, k = 2n + 1$
space group	$P2_1/n$
cryst dimens	0.035 × 0.040 × 0.062 cm
temp	24 °C
radiation	Mo K $\alpha$ ( $\lambda = 0.7107$ Å), graphite monochromated
scan mode	$\omega$ - $2\theta$
takeoff angle	3.0°
scan range	(1.0 + 0.20 tan $\theta$ )°
scan speed	0.2-7.0° min <sup>-1</sup>
total bkgd time/scan time	0.5
2 $\theta$ range	2.8-42.0°
$\mu$	7.02 cm <sup>-1</sup>
unique data used ( $I \geq 2\sigma(I)$ ) <sup>a</sup>	4567
final no. of parameters varied	561
error in observn of unit weight	1.276
<i>R</i>	0.054
<i>R<sub>w</sub></i>	0.066

<sup>a</sup>  $\sigma(I) = [(C + 4B) + (0.03(C + 4B))^2]^{1/2}$  ( $C$  = total scan count,  $B$  = total background count).

methods were used to solve the structure, and it was refined by a block-diagonal least-squares process. Scattering factors for neutral Rh, P, F, O, and C were those tabulated by Cromer and Waber<sup>14</sup> while the values given by Stewart et al.<sup>15</sup> were used for hydrogen.

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- All computations were performed on a Digital Equipment Corp. 2060 computer at the Tulane University Computer Laboratory using the LOKI Crystallographic Computing System by C. J. Fritchie, Jr., B. L. Trus, J. L. Wells, C. A. Langhoff, Jr., M. Guise, W. Lamia, M. Krieger, J. T. Mague, and R. Jacobs. Other programs used were local versions of MGEOM (J. S. Wood; distance and angle calculations), PACK (C. J. Fritchie, Jr.; molecular packing), RANGER (J. A. Ibers; analysis of weighting scheme), SFTBL2 (J. T. Mague; preparation of structure factor table for publication), and ORTEP (C. K. Johnson; graphical illustrations).

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Table III. Atomic Coordinates<sup>a</sup>

atom <sup>b</sup>	x	y	z	atom	x	y	z	atom	x	y	z
Rh <sub>1</sub>	2607.3 (9)	2360.2 (6)	3444.3 (3)	O <sub>3</sub> DD	-1086 (9)	2886 (8)	3630 (3)	C <sub>213</sub>	1298 (12)	-442 (8)	4232 (3)
Rh <sub>2</sub>	2692.4 (9)	1578.1 (7)	4236.7 (3)	O <sub>4</sub> DD	-62 (9)	2855 (6)	3181 (2)	C <sub>223</sub>	60 (13)	-663 (9)	4156 (3)
P <sub>1</sub>	1865 (3)	993 (2)	3251.8 (8)	O <sub>1</sub> AC	4130 (6)	1032 (6)	4634 (2)	C <sub>233</sub>	-539 (15)	-1162 (10)	4384 (4)
P <sub>2</sub>	2757 (3)	3723 (2)	3693.2 (9)	O <sub>2</sub> AC	2154 (8)	1195 (6)	4718 (2)	C <sub>243</sub>	104 (16)	-1428 (12)	4680 (4)
P <sub>3</sub>	2186 (3)	244 (2)	3984.6 (8)	C <sub>1</sub> AC	3280 (13)	966 (9)	4826 (4)	C <sub>253</sub>	1341 (16)	-1253 (11)	4751 (4)
P <sub>4</sub>	3066 (3)	2990 (2)	4431.0 (8)	C <sub>2</sub> AC	3558 (18)	606 (12)	5182 (4)	C <sub>263</sub>	1979 (14)	-757 (10)	4527 (4)
P <sub>5</sub>	4190 (3)	2566 (2)	3090 (1)	C <sub>1</sub> S	1432 (19)	1793 (14)	545 (5)	C <sub>113</sub>	3467 (12)	-470 (8)	3909 (3)
P <sub>6</sub>	6535 (4)	3163 (3)	1759 (1)	C <sub>2</sub> S	2729 (19)	1441 (11)	680 (4)	C <sub>123</sub>	4706 (13)	-282 (9)	4017 (3)
F <sub>1</sub>	6670 (20)	3600 (10)	2102 (2)	C <sub>3</sub> S	3596 (19)	1965 (12)	925 (5)	C <sub>133</sub>	5662 (13)	-857 (9)	3956 (4)
F <sub>2</sub>	6197 (11)	2328 (7)	1928 (3)	OS	3076 (15)	731 (8)	596 (3)	C <sub>143</sub>	5357 (14)	-1588 (10)	3791 (4)
F <sub>3</sub>	7969 (10)	2930 (8)	1819 (3)	C <sub>1</sub> BR	1218 (12)	339 (8)	3577 (3)	C <sub>153</sub>	4132 (14)	-1778 (10)	3676 (4)
F <sub>4</sub>	5150 (11)	3414 (10)	1688 (5)	C <sub>2</sub> BR	2332 (11)	3761 (8)	4123 (3)	C <sub>163</sub>	3148 (13)	-1229 (9)	3731 (3)
F <sub>5</sub>	6869 (11)	4024 (7)	1594 (3)	C <sub>114</sub> <sup>c</sup>	4697 (12)	3349 (8)	4536 (3)	C <sub>111</sub>	2895 (12)	221 (8)	3080 (3)
F <sub>6</sub>	6479 (16)	2742 (10)	1408 (4)	C <sub>124</sub>	5716 (13)	2806 (9)	4539 (3)	C <sub>121</sub>	4164 (12)	252 (8)	3179 (3)
O <sub>1</sub> P	4263 (9)	3539 (6)	2998 (2)	C <sub>134</sub>	6935 (13)	3134 (9)	4612 (4)	C <sub>131</sub>	4985 (13)	-354 (9)	3074 (4)
O <sub>2</sub> P	5684 (10)	2409 (10)	3179 (3)	C <sub>144</sub>	7126 (14)	3973 (10)	4679 (4)	C <sub>141</sub>	4466 (14)	-993 (10)	2855 (4)
O <sub>3</sub> P	3812 (12)	2104 (7)	2750 (2)	C <sub>154</sub>	6134 (13)	4520 (9)	4681 (4)	C <sub>151</sub>	3221 (14)	-1047 (10)	2760 (4)
C <sub>1</sub> P	5251 (14)	4042 (10)	2874 (4)	C <sub>164</sub>	4920 (13)	4217 (9)	4616 (3)	C <sub>161</sub>	2394 (13)	-432 (9)	2872 (4)
C <sub>2</sub> P	6482 (14)	1796 (12)	3280 (5)	C <sub>112</sub>	4223 (12)	4329 (8)	3722 (3)	C <sub>211</sub>	554 (12)	1055 (8)	2917 (3)
C <sub>3</sub> P	4438 (22)	2209 (14)	2444 (4)	C <sub>122</sub>	5371 (13)	3933 (9)	3770 (3)	C <sub>221</sub>	772 (15)	1492 (11)	2624 (4)
CCO	3616 (11)	1861 (8)	3849 (3)	C <sub>132</sub>	6509 (14)	4383 (10)	3796 (4)	C <sub>231</sub>	-177 (16)	1545 (11)	2347 (4)
OCC	4731 (7)	1742 (5)	3854 (2)	C <sub>142</sub>	6461 (15)	5234 (11)	3772 (4)	C <sub>241</sub>	-1311 (15)	1164 (11)	2369 (4)
C <sub>1</sub> DD	-53 (12)	1918 (9)	4179 (3)	C <sub>152</sub>	5348 (16)	5661 (11)	3723 (4)	C <sub>251</sub>	-1549 (15)	754 (11)	2644 (4)
C <sub>2</sub> DD	1077 (11)	1992 (8)	3991 (3)	C <sub>162</sub>	4198 (14)	5222 (10)	3701 (4)	C <sub>261</sub>	-600 (13)	678 (9)	2923 (3)
C <sub>3</sub> DD	1010 (11)	2325 (8)	3680 (3)	C <sub>214</sub>	2436 (12)	3235 (8)	4819 (3)	C <sub>212</sub>	1611 (12)	4437 (9)	3468 (3)
C <sub>4</sub> DD	-1144 (15)	3252 (11)	2968 (4)	C <sub>224</sub>	1347 (13)	3692 (10)	4842 (4)	C <sub>222</sub>	677 (14)	4850 (10)	3611 (4)
C <sub>5</sub> DD	-159 (12)	2699 (9)	3506 (3)	C <sub>234</sub>	951 (15)	3857 (10)	5160 (4)	C <sub>232</sub>	-172 (16)	5386 (11)	3422 (4)
C <sub>6</sub> DD	-1978 (13)	1138 (12)	4195 (4)	C <sub>244</sub>	1619 (14)	3556 (10)	5444 (4)	C <sub>242</sub>	-100 (15)	5520 (10)	3088 (4)
O <sub>1</sub> DD	-794 (8)	1278 (6)	4047 (2)	C <sub>254</sub>	2677 (15)	3112 (11)	5434 (4)	C <sub>252</sub>	851 (16)	5126 (11)	2938 (4)
O <sub>2</sub> DD	-264 (9)	2361 (7)	4410 (2)	C <sub>264</sub>	3124 (13)	2946 (9)	5120 (3)	C <sub>262</sub>	1709 (15)	4579 (11)	3132 (4)

<sup>a</sup> The standard deviations of the least significant figure(s) are given in parentheses. Positional parameters are  $\times 10^4$ . <sup>b</sup> The atom labeling is that of Figure 1. <sup>c</sup> The labeling scheme C<sub>*i*jk</sub> indicates that carbon atom *j* is part of ring *i* attached to P<sub>*k*</sub>. Atom C<sub>*i*1*k*</sub> is that attached to phosphorus.

Those for Rh, P, and F included both the real and imaginary parts of the correction for the effects of anomalous dispersion. The function minimized was  $\sum w\Delta^2$ , where  $\Delta = K|F_o| - G|F_c|$ ,  $F_o$  and  $F_c$  are respectively the observed and calculated structure factors, and  $K$  and  $G$  are scale factors ( $G = 1.0$ ) and  $w = 1/\sigma^2(F_o)$ . The standard deviation in  $F_o$ ,  $\sigma(F_o)$ , was taken as  $\sigma(F_o^2)/F_o$ . The conventional and weighted residuals,  $R_F$  and  $R_wF$ , are defined as  $R_F = \sum|\Delta|/\sum|F_o|$  and  $R_wF = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ .

Following isotropic refinement to  $R_F = 0.132$ , anisotropic thermal parameters of the form  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$  were introduced for all non-hydrogen atoms except the carbon atoms of the DPM ligands. In the final stages of refinement a difference Fourier synthesis revealed reasonable locations for all the hydrogen atoms of the DPM ligands. These were included in fixed positions ( $C-H = 0.95 \text{ \AA}$ ;  $B = 1.0 \text{ \AA}^2$  greater than that of the attached carbon atom), and refinement of the non-hydrogen atoms was continued, with the hydrogen atom parameters being updated every two cycles.

At this point, concern developed over the large thermal parameters for the fluorine atoms and for some of the carbon and oxygen atoms of the phosphite ligand. However, difference Fourier syntheses calculated with the contributions of these atoms to the structure factors omitted showed no firm evidence for disorder in either set. Refinement was therefore continued with these groups considered to be ordered until no parameter changed by more than 10% of its estimated standard deviation. A final difference Fourier synthesis showed no features larger than  $\pm 0.4 e \text{ \AA}^{-3}$ . An analysis of the residuals over various ranges of  $F_o$ ,  $(\sin \theta)/\lambda$ , and Miller indices showed no unusual features. The final  $R$  factors are given in Table I while Table II (supplementary material) lists the final values of  $F_o$  and  $F_c$ . The atomic coordinates obtained from the last cycle of least-squares refinement are presented in Table III together with the associated standard deviations as estimated from the inverse least-squares matrix. In similar fashion, the thermal parameters of all atoms refined are presented in Table IV while Tables VIII and IX present nonessential metrical parameters (supplementary material).

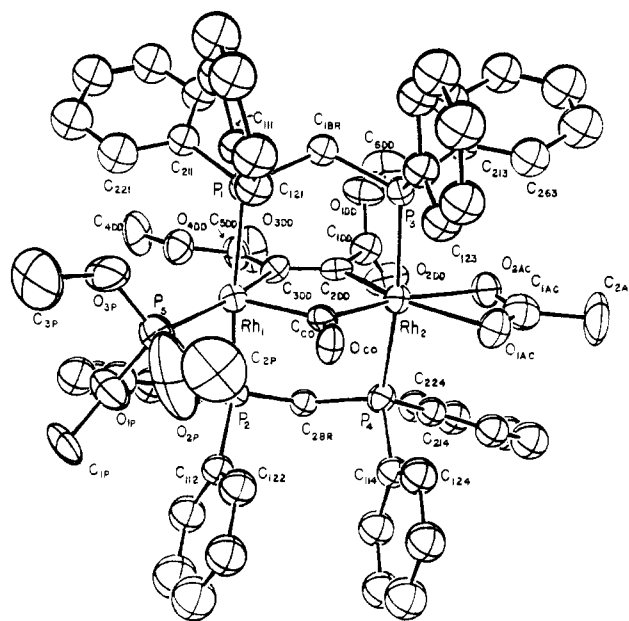
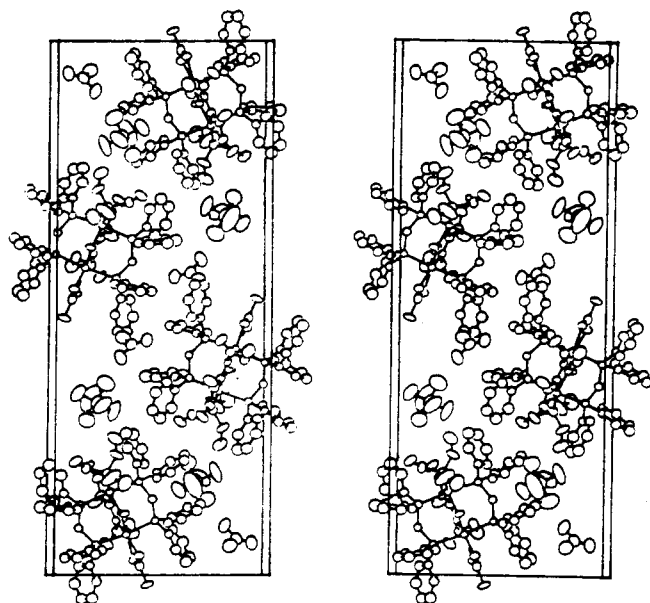


Figure 1. Perspective view of the  $[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]^+$  cation with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 50% probability. The numbering of the phenyl carbons continues around the ring as indicated with the second subscript as the running index.

#### Description of the Structure and Discussion

The structure consists of discrete binuclear cations,  $[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]^+$ , and hexafluorophosphate anions interspersed with molecules of acetone. There are no unusually short intermolecular contacts. A perspective view of the cation is given in Figure 1 while Figure 2 depicts the contents of the unit cell. No crystallographic symmetry is imposed. Interatomic dis-



**Figure 2.** Stereoview of the unit cell contents for  $[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6 \cdot (\text{CH}_3)_2\text{CO}$ . The view is along  $a$  with the positive direction away from the viewer.  $b$  runs from left to right, and  $c$  from top to bottom. Thermal ellipsoids are drawn at 50% probability.

**Table V.** Interatomic Distances ( $\text{\AA}$ )<sup>a</sup>

$\text{Rh}_1\text{-P}_1$	2.379 (4)	$\text{P}_1\text{-C}_{1\text{BR}}$	1.858 (13)
$\text{Rh}_1\text{-P}_2$	2.353 (4)	$\text{P}_1\text{-C}_{111}$	1.829 (13)
$\text{Rh}_1\text{-P}_5$	2.364 (4)	$\text{P}_1\text{-C}_{211}$	1.814 (13)
$\text{Rh}_1\text{-C}_{\text{CO}}$	1.985 (11)	$\text{P}_2\text{-C}_{3\text{BR}}$	1.832 (12)
$\text{Rh}_1\text{-C}_{3\text{DD}}$	2.053 (12)	$\text{P}_2\text{-C}_{112}$	1.825 (13)
$\text{Rh}_2\text{-P}_3$	2.354 (4)	$\text{P}_2\text{-C}_{212}$	1.813 (14)
$\text{Rh}_2\text{-P}_4$	2.362 (4)	$\text{P}_3\text{-C}_{1\text{BR}}$	1.820 (13)
$\text{Rh}_2\text{-C}_{\text{CO}}$	1.992 (11)	$\text{P}_3\text{-C}_{113}$	1.825 (13)
$\text{Rh}_2\text{-C}_{2\text{DD}}$	1.985 (12)	$\text{P}_3\text{-C}_{213}$	1.811 (13)
$\text{Rh}_2\text{-O}_{1\text{AC}}$	2.236 (8)	$\text{P}_4\text{-C}_{3\text{BR}}$	1.831 (13)
$\text{Rh}_2\text{-O}_{2\text{AC}}$	2.160 (8)	$\text{P}_4\text{-C}_{114}$	1.831 (13)
$\text{C}_{2\text{DD}}\text{-C}_{3\text{DD}}$	1.342 (17)	$\text{P}_4\text{-C}_{214}$	1.810 (13)
		$\text{C}_{\text{CO}}\text{-O}_{\text{CO}}$	1.204 (14)

<sup>a</sup> Estimated standard deviations in the least significant digit(s) are given in parentheses.

tances and interbond angles within the asymmetric unit are presented in Tables V and VI, respectively.

The study confirms the conclusions drawn from the spectroscopic data with respect to the structure of the cation, in particular that the acetylenic moiety has become bound as a dimetalated olefin. The only unexpected feature is the bidentate coordination of the acetate ligand, which was not clearly indicated by the infrared spectrum.

Inspection of Figure 1 and Tables V and VI shows that the coordination about  $\text{Rh}_1$  can be considered as a rather distorted square pyramid with  $\text{C}_{\text{CO}}$  at the apex while  $\text{Rh}_2$  is in a distorted octahedral environment. The  $\text{Rh}_1\text{-Rh}_2$  separation of 3.386 (1)  $\text{\AA}$  is significantly longer than the distance of 3.3542 (9)  $\text{\AA}$  found in the closely related neutral complex  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{DPM})_2]^5$  and appears to be the largest such separation yet encountered in DPM-bridged dirhodium species. Because of the large metal-metal separation it is unlikely that there is any direct metal-metal bonding, and this together with the observed diamagnetism suggests that the metal atoms be considered as formally  $\text{Rh}(\text{III})$  (also *vide infra*). The  $\text{Rh-P}$  distances to the DPM ligands are comparable to those found in related DPM-bridged dimers (2.303 (2)–2.367 (8)  $\text{\AA}$ ),<sup>5</sup> and although the  $\text{Rh}_1\text{-P}_1$  distance is not significantly longer than the top end of this range, it is significantly longer than the other three in the present molecule. There is no obvious explanation for this although it may be

**Table VI.** Interbond Angles (Deg)<sup>a</sup>

$\text{P}_1\text{-Rh}_1\text{-P}_2$	163.0 (1)	$\text{C}_{1\text{BR}}\text{-P}_1\text{-Rh}_1$	114.2 (4)
$\text{P}_1\text{-Rh}_1\text{-P}_5$	99.5 (1)	$\text{C}_{111}\text{-P}_1\text{-C}_{211}$	101.8 (6)
$\text{P}_1\text{-Rh}_1\text{-C}_{\text{CO}}$	91.8 (3)	$\text{C}_{111}\text{-P}_1\text{-Rh}_1$	121.7 (4)
$\text{P}_1\text{-Rh}_1\text{-C}_{3\text{DD}}$	82.0 (4)	$\text{C}_{211}\text{-P}_1\text{-Rh}_1$	112.6 (4)
$\text{P}_2\text{-Rh}_1\text{-P}_5$	96.5 (1)	$\text{C}_{3\text{BR}}\text{-P}_2\text{-C}_{112}$	103.8 (6)
$\text{P}_2\text{-Rh}_1\text{-C}_{\text{CO}}$	90.8 (3)	$\text{C}_{3\text{BR}}\text{-P}_2\text{-C}_{212}$	102.3 (6)
$\text{P}_2\text{-Rh}_1\text{-C}_{3\text{DD}}$	81.2 (4)	$\text{C}_{3\text{BR}}\text{-P}_2\text{-Rh}_1$	114.5 (4)
$\text{P}_5\text{-Rh}_1\text{-C}_{\text{CO}}$	100.6 (3)	$\text{C}_{112}\text{-P}_2\text{-C}_{212}$	103.3 (6)
$\text{P}_5\text{-Rh}_1\text{-C}_{3\text{DD}}$	168.4 (4)	$\text{C}_{112}\text{-P}_2\text{-Rh}_1$	120.7 (4)
$\text{C}_{\text{CO}}\text{-Rh}_1\text{-C}_{3\text{DD}}$	90.8 (5)	$\text{C}_{212}\text{-P}_2\text{-Rh}_1$	110.2 (4)
$\text{P}_3\text{-Rh}_2\text{-P}_4$	173.1 (1)	$\text{C}_{1\text{BR}}\text{-P}_3\text{-C}_{113}$	104.7 (6)
$\text{P}_3\text{-Rh}_2\text{-C}_{\text{CO}}$	88.5 (3)	$\text{C}_{1\text{BR}}\text{-P}_3\text{-C}_{213}$	105.0 (6)
$\text{P}_3\text{-Rh}_2\text{-C}_{2\text{DD}}$	86.6 (4)	$\text{C}_{1\text{BR}}\text{-P}_3\text{-Rh}_2$	112.6 (4)
$\text{P}_3\text{-Rh}_2\text{-O}_{1\text{AC}}$	93.6 (2)	$\text{C}_{113}\text{-P}_3\text{-C}_{213}$	100.6 (6)
$\text{P}_3\text{-Rh}_2\text{-O}_{2\text{AC}}$	93.5 (2)	$\text{C}_{113}\text{-P}_3\text{-Rh}_2$	118.6 (4)
$\text{P}_4\text{-Rh}_2\text{-C}_{\text{CO}}$	88.2 (3)	$\text{C}_{213}\text{-P}_3\text{-Rh}_2$	113.7 (4)
$\text{P}_4\text{-Rh}_2\text{-C}_{2\text{DD}}$	87.5 (4)	$\text{C}_{2\text{BR}}\text{-P}_4\text{-C}_{114}$	105.3 (6)
$\text{P}_4\text{-Rh}_2\text{-O}_{1\text{AC}}$	93.1 (2)	$\text{C}_{2\text{BR}}\text{-P}_4\text{-C}_{214}$	105.2 (6)
$\text{P}_4\text{-Rh}_2\text{-O}_{2\text{AC}}$	91.2 (2)	$\text{C}_{2\text{BR}}\text{-P}_4\text{-Rh}_2$	111.0 (4)
$\text{C}_{\text{CO}}\text{-Rh}_2\text{-C}_{2\text{DD}}$	91.6 (5)	$\text{C}_{114}\text{-P}_4\text{-C}_{214}$	100.8 (6)
$\text{C}_{\text{CO}}\text{-Rh}_2\text{-O}_{1\text{AC}}$	105.9 (4)	$\text{C}_{114}\text{-P}_4\text{-Rh}_2$	118.7 (4)
$\text{C}_{\text{CO}}\text{-Rh}_2\text{-O}_{2\text{AC}}$	165.8 (4)	$\text{C}_{214}\text{-P}_4\text{-Rh}_2$	114.5 (4)
$\text{C}_{2\text{DD}}\text{-Rh}_2\text{-O}_{1\text{AC}}$	162.4 (4)	$\text{O}_{\text{CO}}\text{-C}_{\text{CO}}\text{-Rh}_1$	120.6 (8)
$\text{C}_{2\text{DD}}\text{-Rh}_2\text{-O}_{2\text{AC}}$	102.5 (4)	$\text{O}_{\text{CO}}\text{-C}_{\text{CO}}\text{-Rh}_2$	122.7 (8)
$\text{O}_{1\text{AC}}\text{-Rh}_2\text{-O}_{2\text{AC}}$	59.9 (3)	$\text{Rh}_1\text{-C}_{\text{CO}}\text{-Rh}_2$	116.7 (6)
$\text{C}_{1\text{BR}}\text{-P}_1\text{-C}_{111}$	101.2 (6)	$\text{C}_{3\text{DD}}\text{-C}_{2\text{DD}}\text{-Rh}_2$	121.7 (9)
$\text{C}_{1\text{BR}}\text{-P}_1\text{-C}_{211}$	102.9 (6)	$\text{C}_{2\text{DD}}\text{-C}_{3\text{DD}}\text{-Rh}_1$	119.1 (9)

<sup>a</sup> Estimated standard deviations in the least significant digit(s) are given in parentheses.

due in part to a rather short nonbonded contact (2.76  $\text{\AA}$ ) between  $\text{H}_{121}$  (attached to  $\text{C}_{121}$ ) and  $\text{C}_{2\text{p}}$ . The presence of the relatively bulky trimethyl phosphite ligand between  $\text{P}_1$  and  $\text{P}_2$  may also explain the significant bending of these two atoms away from  $\text{P}_5$ . The extent and direction of this distortion may be seen from an inspection of the angles that these two atoms make with the three equatorial atoms  $\text{P}_5$ ,  $\text{C}_{\text{CO}}$ , and  $\text{C}_{3\text{DD}}$  about  $\text{Rh}_1$  (Table VI). It is also evident from the fact that  $\text{Rh}_1$  lies 0.33  $\text{\AA}$  out of the best plane containing  $\text{P}_1\text{-P}_4$ .<sup>16</sup> In this connection we also note that, while the atoms  $\text{Rh}_1$ ,  $\text{Rh}_2$ ,  $\text{C}_{\text{CO}}$ ,  $\text{C}_{2\text{DD}}$ , and  $\text{C}_{3\text{DD}}$  are not rigorously planar, they are not far from being so and the best plane through these five atoms is virtually perpendicular to that containing  $\text{P}_1\text{-P}_4$ . The corresponding angles about  $\text{Rh}_2$  indicate that the bending of the  $\text{P}_3\text{-Rh}_2\text{-P}_4$  moiety is considerably less and is directed much more closely parallel to the metal-metal vector. This also is evident from the fact that  $\text{Rh}_2$  lies only 0.06  $\text{\AA}$  out of the  $\text{P}_1\text{-P}_4$  plane. This is to be expected since the acetate ligand is much less bulky than trimethyl phosphite, and moreover, the orientation of the carbomethoxy group adjacent to  $\text{Rh}_2$  is such as to oppose a displacement of  $\text{P}_3$  in the same direction as observed for  $\text{P}_1$ . The phenyl rings are in the usual staggered arrangement, which serves to minimize intramolecular contacts. All are planar within experimental error. The methylene carbons of the DPM ligands are displaced toward the more crowded side of the molecule so as to allow the phenyl rings on the opposite side to avoid too many close contacts.

The acetate ligand is coordinated in an unsymmetrical bidentate fashion since both oxygen atoms are within bonding distance of the rhodium atom. The two  $\text{Rh-O}$  distances are significantly different, with the longer one being that trans to the  $\text{Rh-C}$  bond of the metalated olefin ( $\text{Rh}_2\text{-O}_{1\text{AC}}$ ). The lengthening of this bond indicates a significant trans influence of the latter ligand. Similar long  $\text{Rh-O}$  bonds (2.241 (8) and

(16) The equation of the plane is  $0.988X - 0.147Y - 0.045Z + 0.480 = 0$ , where  $X$ ,  $Y$ , and  $Z$  are the orthogonal coordinates (in  $\text{\AA}$ ), which are related to the fractional coordinates ( $x$ ,  $y$ ,  $z$ ) by the transformations  $X = ax + cz \cos \beta$ ,  $Y = by$ , and  $Z = cz \sin \beta$ . The four atoms  $\text{P}_1\text{-P}_4$  deviate from the plane by  $-0.005$ ,  $0.005$ ,  $0.005$ , and  $-0.005$   $\text{\AA}$ , respectively.

2.220 (8) Å) have been found in the ortho-metalated azobenzene complex  $[\text{Rh}(\text{C}_6\text{H}_4\text{N}=\text{NPh})_2(\text{O}_2\text{CMe})]$ ,<sup>17</sup> where the acetate oxygens are both trans to the Rh–C bonds. Also a very similar unsymmetrically bidentate acetate ligand has been found in  $[\text{Ru}(\text{CO})(\text{CH}=\text{NC}_6\text{H}_4\text{Me})(\text{O}_2\text{CMe})(\text{PPh}_3)_2]$ ,<sup>18</sup> with Ru–O distances of 2.279 (8) Å (trans to the formamidoyl ligand) and 2.173 (8) Å (trans to the carbonyl group). The other dimensions of the  $\text{RhO}_2\text{C}$  ring compare very closely with those found in the two structures mentioned. In particular, the two C–O distances are identical, indicating that the difference in the Rh–O distance is a result of the high trans influence of the olefinic ligand and not a tendency toward monodentate coordination.

We have earlier characterized the acetylenic ligand as a cis-dimetalated olefin. This is evident from the fact that the  $\text{C}_{2\text{DD}}-\text{C}_{3\text{DD}}$  vector is less than  $2^\circ$  from being parallel to the metal–metal vector whereas coordination of the acetylene in the more usual  $\eta^2-\mu$  fashion would have positioned the C–C vector approximately perpendicular to the metal–metal vector.<sup>19–29</sup> Also the  $\text{C}_{2\text{DD}}-\text{C}_{3\text{DD}}$  distance of 1.342 (17) Å is comparable to that for a normal carbon–carbon double bond while the  $\text{Rh}_1-\text{C}_{3\text{DD}}$  and  $\text{Rh}_2-\text{C}_{2\text{DD}}$  distances, although significantly different, are both in the range of Rh–C  $\sigma$  bonds to  $\text{sp}^2$ -hybridized carbon atoms.<sup>30,31</sup> The lengthening of the  $\text{Rh}_1-\text{C}_{3\text{DD}}$  bond relative to  $\text{Rh}_2-\text{C}_{2\text{DD}}$  can be ascribed to the expected significant trans influence of the trimethyl phosphite ligand. Finally, the angles about  $\text{C}_{2\text{DD}}$  and  $\text{C}_{3\text{DD}}$  do not differ drastically from the  $120^\circ$  angles expected for  $\text{sp}^2$ -hybridized carbon atoms. The remaining metrical parameters of this ligand are normal (Tables VIII and IX). One feature of the present molecule that contrasts with what was found in  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{DPM})_2]$ <sup>5</sup> is that the two carbomethoxy groups are oriented nearly perpendicular to one another while in the latter complex they are more nearly parallel. The dihedral angle between the planes of the two carbomethoxy groups is approximately  $70^\circ$  while the “upright” group ( $\text{C}_{1\text{DD}}, \text{O}_{1\text{DD}}, \text{O}_{2\text{DD}}, \text{C}_{6\text{DD}}$ ) makes an angle of ca.  $74^\circ$  with the equatorial plane of the dimer. This orientation is undoubtedly due to the presence of the acetate ligand since, if this carbomethoxy group were to become more nearly coplanar with this latter plane, a severe interaction of  $\text{O}_{1\text{DD}}$  or  $\text{O}_{2\text{DD}}$  with  $\text{O}_{2\text{AC}}$  would result. The significantly different orientations of the two carbomethoxy groups explain the considerable differences in chemical shifts observed for the carbonylmethyl protons.<sup>1</sup> Since  $\text{C}_{4\text{DD}}$  appears sandwiched between the phenyl rings built on  $\text{C}_{211}$  and  $\text{C}_{212}$ , we suggest that it is the protons on this carbon that are responsible for the higher field resonance since they would be in the dia-

magnetic shielding regions of these two rings.

The Rh–P<sub>5</sub>(phosphite) distance of 2.364 (4) Å also reflects the high trans influence of the olefinic ligand as it is significantly longer than those found in  $[\text{HRh}(\text{P}(\text{OMe})_3)_2]_3$ ,<sup>32</sup> *mer*- $[\text{RhCl}_3(\text{P-}n\text{-Bu}_3)_2\text{P}(\text{OMe})_3]$ ,<sup>33</sup> and  $[\text{HRh}(\text{P}(\text{O-}i\text{-Pr})_3)_2]_2$ ,<sup>34</sup> which fall in the range 2.155 (7)–2.202 (8) Å. It is shorter than that found in  $[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{P}(\text{OMe})_3)_2]$  (2.437 (5) Å),<sup>35</sup> but in these Rh(II) dimers it is established that the axial ligands are only weakly coordinated. The various distances and angles associated with the methoxy groups  $\text{O}_{1\text{P}}, \text{C}_{1\text{P}}$  and  $\text{O}_{3\text{P}}, \text{C}_{3\text{P}}$  (Tables VIII and IX) are unexceptional and fall well within the ranges observed in a variety of trimethyl phosphite complexes<sup>32–42</sup> (e.g., P–O = 1.539 (9)–1.636 (8) Å, O–C = 1.376 (12)–1.489 (9) Å, M–P–O =  $108.2(2)$ – $128.1(4)^\circ$ , P–O–C =  $113(1)$ – $134.2(6)^\circ$ , O–P–O =  $90.7(4)$ – $111(1)^\circ$ ). On the other hand, while the P<sub>5</sub>–O<sub>2P</sub> distance of 1.611 (12) Å is not unusual when compared to the above range or to P<sub>5</sub>–O<sub>1P</sub> and P<sub>5</sub>–O<sub>3P</sub>, the O<sub>2P</sub>–C<sub>2P</sub> distance is significantly less than the values found for O<sub>1P</sub>–C<sub>1P</sub> and O<sub>3P</sub>–C<sub>3P</sub>. Also, the  $\text{Rh}_1-\text{P}_5-\text{O}_{2\text{P}}$  and  $\text{P}_5-\text{O}_{2\text{P}}-\text{C}_{2\text{P}}$  angles are at the high end and outside the corresponding ranges, respectively. It is evident from Figure 1 that the thermal ellipsoids for C<sub>2P</sub> and O<sub>2P</sub> are considerably larger than those for the other two methoxy groups, and it was mentioned earlier that we had been concerned about possible disorder in this group. There is at least one report of apparent disorder in one methoxy group of a coordinated trimethyl phosphite ligand<sup>40</sup> although it appeared that refinement of two equally populated sites was not an adequate model. In the present case, if any such disorder is in fact present, it is not severe enough to enable us to define separate sites for this group. We therefore elected to consider this group to be ordered while recognizing that the model used may not be completely satisfactory. We also note that the O<sub>2P</sub>–C<sub>2P</sub> distance is in fact not significantly shorter than the low end of the range quoted above ( $\Delta/\sigma = 2.7$ ) and in addition a C–O distance of 1.299 (16) Å has been found in  $[\text{Ag}(\text{P}(\text{OMe})_3)_2\text{NO}_3]_2$ .<sup>43</sup> In any event, any deficiencies in the treatment of this one methoxy group will not significantly affect any of the important features of the structure. This leaves the P<sub>5</sub>–O<sub>2P</sub>–C<sub>2P</sub> angle as the only unusual dimension of the phosphite ligand. A possible explanation could be the rather close contact of C<sub>2P</sub> with H<sub>121</sub> mentioned earlier, which would tend to open this angle (see Figure 1).

This structure provides an additional example of a growing number of complexes in which there is a bridging carbonyl but no accompanying metal–metal bond. The two Rh–C distances are equivalent and significantly shorter than those found in the more conventional situation, e.g.,  $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{DPM})_2]^+$ , where these distances are 2.034 (7) and 2.104 (7) Å.<sup>44</sup> The most striking feature is the  $\text{Rh}_1-\text{C}_{\text{CO}}-\text{Rh}_2$

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**Table VII.** Comparison of the Structures of  $[\text{Rh}_2\text{L}(\mu\text{-CO})(\mu\text{-DMAD})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6$  and  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMAD})(\text{DPM})_2]^a$ 

parameter <sup>b</sup>	$[\text{Rh}_2\text{L}(\mu\text{-CO})(\mu\text{-DMAD})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6$	$[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMAD})(\text{DPM})_2]$
Rh <sub>1</sub> -P <sub>1</sub> , Rh <sub>2</sub> -P <sub>4</sub>	2.379 (4), 2.362 (4)	2.348 (2)
Rh <sub>1</sub> -P <sub>2</sub> , Rh <sub>2</sub> -P <sub>3</sub>	2.353 (4), 2.354 (4)	2.346 (2)
Rh <sub>1</sub> -C <sub>CO</sub> , Rh <sub>2</sub> -C <sub>CO</sub>	1.985 (11), 1.992 (11)	1.977 (4)
Rh <sub>1</sub> -C <sub>3DD</sub> , Rh <sub>2</sub> -C <sub>2DD</sub>	2.053 (12), 1.985 (12)	2.004 (6)
C <sub>2DD</sub> -C <sub>3DD</sub>	1.342 (17)	1.32 (1)
C <sub>1DD</sub> -C <sub>2DD</sub> , C <sub>3DD</sub> -C <sub>5DD</sub>	1.507 (17), 1.472 (17)	1.494 (9)
C <sub>CO</sub> -O <sub>CO</sub>	1.20 (1)	1.16 (1)
Rh <sub>1</sub> -Rh <sub>2</sub>	3.386 (1)	3.3542 (9)
P <sub>1</sub> -Rh-P <sub>2</sub> , P <sub>3</sub> -Rh-P <sub>4</sub>	163.0 (1), 173.1 (1)	170.63 (5)
P <sub>1</sub> -Rh <sub>1</sub> -C <sub>CO</sub> , P <sub>4</sub> -Rh <sub>2</sub> -C <sub>CO</sub>	91.8 (3), 88.2 (3)	91.31 (5)
P <sub>2</sub> -Rh <sub>1</sub> -C <sub>CO</sub> , P <sub>3</sub> -Rh <sub>2</sub> -C <sub>CO</sub>	90.8 (3), 88.5 (3)	87.0 (2)
P <sub>1</sub> -Rh <sub>1</sub> -C <sub>3DD</sub> , P <sub>4</sub> -Rh <sub>2</sub> -C <sub>2DD</sub>	82.0 (4), 87.5 (4)	83.7 (2)
P <sub>2</sub> -Rh <sub>1</sub> -C <sub>3DD</sub> , P <sub>3</sub> -Rh <sub>2</sub> -C <sub>3DD</sub>	81.2 (4), 86.6 (4)	87.50 (4)
Rh <sub>1</sub> -C <sub>CO</sub> -Rh <sub>2</sub>	116.7 (6)	116.0 (4)
P <sub>1</sub> -Rh <sub>1</sub> -P <sub>5</sub> , P <sub>2</sub> -Rh <sub>1</sub> -P <sub>5</sub>	99.5 (1), 96.5 (1)	91.58 (5) <sup>c</sup>
P <sub>3</sub> -Rh <sub>2</sub> -O <sub>1AC</sub> , P <sub>4</sub> -Rh <sub>2</sub> -O <sub>1AC</sub>	93.6 (2), 93.1 (2)	97.66 (5) <sup>c</sup>

<sup>a</sup> Distances are in angstroms; angles are in degrees. Dimensions for  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMAD})(\text{DPM})_2]$  are from ref 5. L = P(OMe)<sub>3</sub>; DMAD = dimethyl acetylenedicarboxylate. <sup>b</sup> The labeling system is that of Figure 1. The corresponding symmetry-equivalent pairs of dimensions are quoted for the neutral complex. <sup>c</sup> These represent the two independent P-Rh-Cl angles.

angle of 116.7 (6)°, which is much greater than the usual values, ranging from ca. 70 to 90°,<sup>45</sup> and which is even larger than the Cl-C-Cl angle of 111.3 (1)° reported<sup>46</sup> for Cl<sub>2</sub>C=O. Thus the carbonyl group is best considered as a "ketonic" carbonyl and as such leads to the rhodium atoms being formally Rh(III). This formalism has been suggested by Hoffmann<sup>47</sup> and is in accord with the very low C-O stretching frequency (1712 cm<sup>-1</sup>) observed for this ligand.<sup>1</sup> It is also in agreement with the value of 2046 cm<sup>-1</sup> observed<sup>1</sup> for the stretching frequency of the terminal carbonyl group in  $[\text{Rh}_2(\text{CO})(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})-$

$(\text{DPM})_2]\text{PF}_6$ , which was used to prepare the present complex and which, from the virtually identical spectroscopic data, should have the same structure. Considering the metal atoms as formally Rh(III) leads to the assignment of a 16-electron configuration for Rh<sub>1</sub> and an 18-electron configuration for Rh<sub>2</sub>. This latter situation is achieved by having the acetate group function as a bidentate ligand and is presumably the reason for its coordinating in this fashion. On the assumption that  $[\text{Rh}_2(\text{CO})(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6$  has the same structure, the assignment of a 16-electron configuration to the rhodium atom bearing the terminal carbonyl group also explains the apparent associative nature of the substitution reaction<sup>1</sup> by which the present complex is prepared from the dicarbonyl complex.

The hexafluorophosphate anion and the solvent acetone occupy voids between the cations and apart from rather large amplitudes of thermal motion do not exhibit any unusual geometrical features.

It is of interest to compare the details of this structure with those of the closely related neutral complex  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{DPM})_2]$ , whose structure was reported<sup>5</sup> while this work was in progress. This comparison is presented in Table VII. Apart from some modest differences in bond lengths and angles, which are undoubtedly due to the fact that the present complex is less symmetrical, the major contrasts are the bend of P<sub>1</sub> and P<sub>2</sub> away from the phosphite ligand and the orientation of the carbomethoxy group attached to C<sub>2DD</sub>. As discussed above, these differences can be traced to steric constraints of the present molecule, which are absent in the neutral complex.

## Conclusions

This study has confirmed that the title compound contains the acetylenic moiety bound as a cis-dimetalated olefin and a ketonic carbonyl group. Direct metal-metal bonding is absent.

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**Registry No.**  $[\text{Rh}_2(\text{P}(\text{OMe})_3)(\mu\text{-CO})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{O}_2\text{CMe})(\text{DPM})_2]\text{PF}_6 \cdot (\text{CH}_3)_2\text{CO}$ , 83350-14-5.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes, atomic thermal parameters, interatomic distances, and interbond angles (Tables II, IV, VIII, and IX) (20 pages). Ordering information is given on any current masthead page.

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