

I and II summarize the physical, analytical, and NMR spectroscopic data.

**Preparation of Vinylphosphoranimes 3-15.** In a typical experiment, a 250-mL, 3-necked flask, equipped with a magnetic stirrer, N<sub>2</sub> inlet, and a rubber septum, was charged with Me<sub>3</sub>SiN=P(OCH<sub>2</sub>CF<sub>3</sub>)(Me)(CH<sub>2</sub>SiMe<sub>3</sub>) (2) (12.8 g, 40 mmol) and Et<sub>2</sub>O (100 mL). The solution was cooled to -78 °C and stirred for 30 min, and then *n*-BuLi (16.0 mL of 2.5 M hexane solution, 40 mmol) was added via syringe. After the mixture was stirred for 1 h, benzaldehyde (4.2 g, 40 mmol) was added via syringe and the mixture was stirred for ca. 3 h at -78 °C before being quenched with chlorotrimethylsilane (5.1 mL, 40 mmol). The solution was allowed to warm to room temperature, and the salts were allowed to settle. The supernatant solution was transferred by cannula to a 1-neck flask, and the salts were washed with hexane. The ether-hexane solvent mixture was removed under reduced pressure. Distillation through a 10-cm column afforded 3 as a colorless liquid (Tables I and II). Compounds 4-7 and 10-15 were prepared according to the same procedure by using the appropriate aldehyde or ketone in place of benzaldehyde. In the case of 9,

the *P*-phenoxyphosphoranime 8 was used as the starting material.

**Acknowledgment.** We thank the U. S. Army Research Office and the Robert A. Welch Foundation for generous financial support of this work.

**Registry No.** 2, 106821-78-7; (*E*)-3, 121231-24-1; (*Z*)-3, 121231-25-2; (*E*)-4, 121231-26-3; (*Z*)-4, 121231-27-4; 5, 121231-28-5; 6, 121231-29-6; (*E,E*)-7, 121231-30-9; (*Z,E*)-7, 121231-31-0; 8, 121231-32-1; 9, 121231-33-2; (*E*)-10, 121252-66-2; (*Z*)-10, 121252-67-3; (*E*)-11, 121231-34-3; (*Z*)-11, 121231-35-4; 12, 121231-36-5; (*E,E*)-13, 121231-37-6; (*Z,E*)-13, 121231-38-7; 14, 121231-39-8; 15, 121231-40-1; PhC(=O)H, 100-52-7; Me<sub>2</sub>N-*p*-C<sub>6</sub>H<sub>4</sub>C(=O)H, 100-10-7; *t*-BuC(=O)H, 630-19-3; C<sub>6</sub>F<sub>5</sub>C(=O)H, 653-37-2; MeCH=CHC(=O)H, 123-73-9; MeC(=O)H, 75-07-0; PhC(=O)Me, 98-86-2; PhC(=O)*n*-Pr, 495-40-9; PhC(=O)CF<sub>3</sub>, 434-45-7; Me<sub>3</sub>SiN=PMe<sub>2</sub>(OPh), 121231-41-2; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; 2,6-dimethyl-2,5-heptadien-4-one, 504-20-1; 9*H*-fluoren-9-one, 486-25-9.

## Chemistry of Metallacyclobutan-3-one ( $\eta^3$ -Oxodimethylenemethane) Complexes. 6.<sup>1</sup> The Synthesis, Structure, and Bonding in Pt[ $\eta^3$ -CH<sub>2</sub>C(O)CH<sub>2</sub>](PPh<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>

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David R. Russell,<sup>†</sup> Brenda Lam,<sup>‡</sup> Sung Kwon Kang,<sup>§</sup> and Thomas A. Albright<sup>\*†</sup>

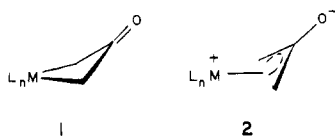
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Received January 17, 1989

The synthesis of Pt[ $\eta^3$ -CH<sub>2</sub>C(O)CH<sub>2</sub>](PPh<sub>3</sub>)<sub>2</sub> (5) was accomplished by the reaction of Pt( $\eta^2$ -*trans*-stilbene)(PPh<sub>3</sub>)<sub>2</sub> with an excess of 3-chloro-1-(trimethylsilyl)propan-2-one or by reaction of an excess of sodium amalgam with *cis*-PtCl[CH<sub>2</sub>C(O)CH<sub>2</sub>Cl](PPh<sub>3</sub>)<sub>2</sub>. The X-ray structure of 5·CH<sub>2</sub>Cl<sub>2</sub> is comparable to other oxodimethylenemethane-ML<sub>2</sub> complexes and bears a much closer resemblance to  $\pi$ -allyl complexes than to metallacyclobutanones. The crystal data were as follows: *a* = 13.835 (4) Å, *b* = 17.560 (9) Å, *c* = 15.42 (3) Å,  $\beta$  = 109.7 (1)°, monoclinic *P*2<sub>1</sub>/*c*, *Z* = 4, *R*' = 0.0532. The geometry of Pd[CH<sub>2</sub>C(O)CH<sub>2</sub>](PH<sub>3</sub>)<sub>2</sub> was optimized at the ab initio SCF level and found to be in good agreement with that of 5 and other complexes in this series. The computations reveal a low-energy reaction path for isomerization to a metallacyclobutanone. The energy difference between this optimized transition state and the ground state was found to be 7.9 kcal/mol at the MP(2) level. This is in moderately good agreement with the value of  $\Delta G^\ddagger$  = 9.2 kcal/mol found for exchange of the syn and anti protons of 5 by <sup>1</sup>H NMR. The ring inversion process in oxodimethylenemethane complexes is compared to an analogous reaction observed for Cp<sub>2</sub>M(butadiene) compounds.

### Introduction

We have recently shown that a number of metallacyclobutan-3-one complexes contain highly puckered four membered rings<sup>1-6</sup> and bonding descriptions 1 and 2 have



been used to rationalize the structural features. These complexes, described hereafter as  $\eta^3$ -oxodimethylenemethane complexes, display a variation of ring puckering

that depends upon the metal, auxiliary ligands, and the substituents on the ring carbons. As a continuation of these studies we wished to examine the parent, unsubstituted  $\eta^3$ -oxodimethylenemethane ligand. Mononuclear examples up to this time were unknown; however, a bridging  $\eta^4$ -oxodimethylenemethane complex has recently been described.<sup>7</sup> In view of our success with push-pull

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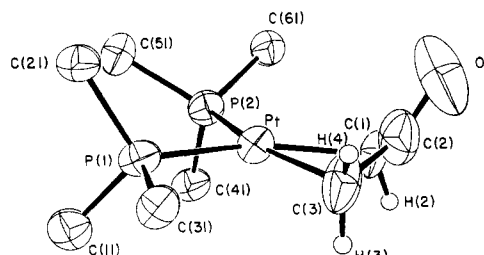
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**Figure 1.** The molecular structure of  $\text{Pt}[\text{CH}_2\text{C}(\text{O})\text{CH}_2](\text{PPh}_3)_2$  (**5**). Only the carbon atoms attached to the phosphorus are shown for the phenyl groups.

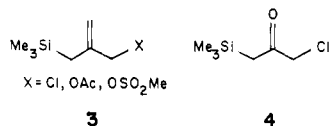
**Table I.** Selected Bond Lengths (Å) for  $5 \cdot \text{CH}_2\text{Cl}_2$

P(1)–Pt	2.292 (3)	O(1)–C(2)	1.257 (15)
P(2)–Pt	2.296 (3)	C(21)–P(1)	1.831 (5)
C(1)–Pt	2.145 (11)	C(31)–P(1)	1.808 (6)
C(2)–Pt	2.422 (12)	C(11)–P(1)	1.815 (6)
C(3)–Pt	2.119 (14)	C(41)–P(2)	1.825 (6)
C(2)–C(3)	1.496 (19)	C(51)–P(2)	1.819 (6)
C(1)–C(2)	1.473 (20)	C(61)–P(2)	1.818 (6)

**Table II.** Selected Bond Angles (deg) for  $5 \cdot \text{CH}_2\text{Cl}_2$

P(2)–Pt–P(1)	103.6 (1)	C(3)–Pt–P(2)	162.0 (4)
C(1)–Pt–P(1)	161.9 (3)	C(3)–Pt–C(1)	68.4 (5)
C(1)–Pt–P(2)	93.6 (4)	C(3)–Pt–C(2)	37.7 (5)
C(2)–Pt–P(1)	128.8 (4)	C(3)–C(2)–C(1)	107.7 (10)
C(2)–Pt–P(2)	125.8 (3)	O(1)–C(2)–C(1)	124.8 (12)
C(2)–Pt–C(1)	37.0 (5)	O(1)–C(2)–C(3)	123.8 (14)
C(3)–Pt–P(1)	94.3 (4)		

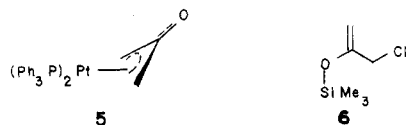
precursors, **3**, in the synthesis of  $\eta^4$ -trimethylenemethane complexes,<sup>8</sup> we decided to investigate the use of reagent **4** in the synthesis of  $\eta^3$ -oxodimethylenemethane complexes.



In this paper, we describe the synthesis and structure of an  $\eta^3$ -oxodimethylenemethane complex of platinum together with theoretical calculations at the *ab initio* and extended Hückel levels. A portion of this work has been reported in a preliminary communication.<sup>6</sup>

### Results and Discussion

Treatment of  $\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2$  with an excess of 3-chloro-1-(trimethylsilyloxy)propan-2-one (**4**)<sup>9</sup> in diethyl ether afforded complex **5** in 60% yield as an air-stable

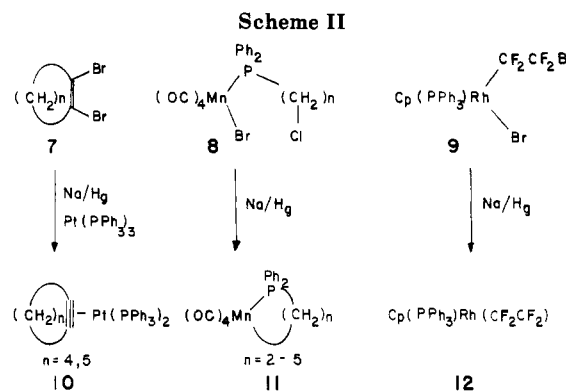
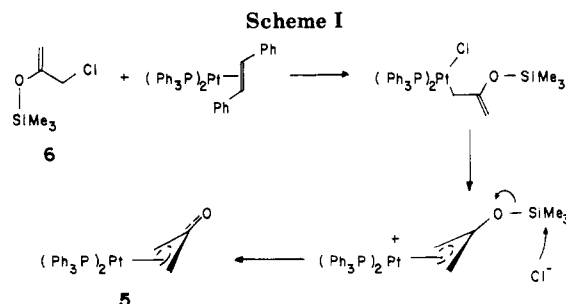


white microcrystalline solid. The formation of **5** is accompanied by a Brooke rearrangement of the ketone to 3-chloro-2-(trimethylsilyloxy)prop-1-ene (**6**) as has been previously reported.<sup>9</sup> The mechanism of this reaction has not been established with certainty, but it may involve oxidative addition of **4** to  $\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2$  followed by elimination of  $\text{Me}_3\text{SiCl}$  to afford **5**. However, since **5** catalyzes the isomerization of **4** to **6**,<sup>9</sup> formation of the  $\eta^3$ -oxodimethylenemethane complex can then proceed via oxidative addition of **6** as shown in Scheme I. The

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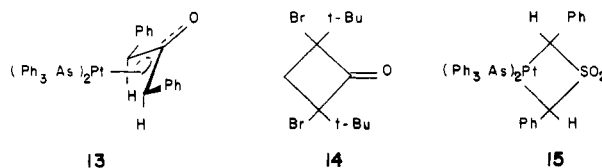
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dehalogenation of *cis*- $\text{PtCl}[\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{Cl}](\text{PPh}_3)_2$  with an excess of sodium amalgam in THF can also be used to prepare **5**. A number of dehalogenation reactions have previously been used in an analogous manner, as shown in Scheme II. For example, dehalogenation of **7**, **8**, and **9** has been shown to afford **10**,<sup>10</sup> **11**,<sup>11</sup> and **12**,<sup>12</sup> respectively.

In order to gain further insight into the factors which control structural variations for oxodimethylenemethane complexes, a single-crystal X-ray diffraction study has been carried out on **5**. The molecular architecture of **5** is illustrated in Figure 1, and selected bond lengths and angles are given in Tables I and II, respectively. Many structural features of **5** are similar to those previously observed for oxodimethylenemethane complexes of  $\text{Pt}(\text{II})$ ,<sup>1,2,3,5</sup>  $\text{Pd}(\text{II})$ ,<sup>4</sup> and  $\text{Ir}(\text{III})$ .<sup>5</sup> The metal, C(1), C(2), and C(3) markedly deviate from planarity. This ring puckering is quantified by  $\theta$ , the fold angle between the C(1)–Pt–C(3) and C(1)–C(2)–C(3) planes. In **5**,  $\theta$  is  $51.0^\circ$ , which is within the range of  $48.0$ – $53.3^\circ$  observed for oxodimethylenemethane complexes of  $\text{Pt}(\text{II})$  and  $\text{Pd}(\text{II})$ .<sup>3–5</sup> We have recently shown<sup>1</sup> that the *syn,syn*-diphenyl complex **13** is even more highly puckered with  $\theta = 56.7^\circ$ . Such a large degree of nonplanarity is not a feature of cyclobutanones or platinacyclobutanes. For example,  $\theta$  is  $10^\circ$  in the cyclobutanone **14**.<sup>13</sup> Platinacyclobutanes typically have  $\theta$  in the range of  $0$ – $30^\circ$ ,<sup>14–16</sup> for example,  $\theta$  is  $24.5^\circ$  in the substituted platinathietane-3,3-dioxide complex **15**.<sup>17</sup>



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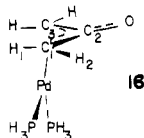
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The ring puckering in **5** is highly reminiscent of that observed in  $\eta^3$ -allyl complexes of Pt(II) and Pd(II). In these compounds,  $\theta$  ranges from  $61^\circ$  to  $72^\circ$ .<sup>18,19</sup> Likewise, the local coordination at the metal is very close to being square-planar for theoretical reasons presented elsewhere.<sup>20</sup> In **5**, the twist between the C(1)-Pt-C(3) and P(1)-Pt-P(2) planes is  $5.5^\circ$ . These structural features suggest that a  $\pi$ -allyl formulation like **2** is important in the bonding of these complexes. Also consistent with this is that the average oxodimethylenemethane C-C distance in **5** (1.48 (2) Å) is shortened from that observed in platinacyclobutanes. For example, the average C-C bond length in Pt-[CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>](PEt<sub>3</sub>)<sub>2</sub> is 1.535 (10) Å.<sup>15</sup> However, in  $\eta^3$ -allyl-ML<sub>2</sub> complexes the C-C distances are somewhat shorter than in **5**, typically 1.40 Å.<sup>18,19</sup> A further ramification of **2** is that there is a lengthening of the C(2)-O bond in **5** to 1.26 Å, as compared to a "normal" C-O double bond distance of 1.21 Å in cyclobutanone **14**. Of course there must be considerable back delocalization into the  $\pi$ -allyl portion since a normal C-O single bond distance is 1.36 Å. Nevertheless, the oxygen atom in oxodimethylenemethane complexes is quite basic, as witnessed by the fact that a variety of metals coordinate to it.<sup>21,22</sup>

A delocalized view of the bonding in oxodimethylenemethane-ML<sub>2</sub> complexes is most conveniently described in terms of interacting the  $\pi$  orbitals of an oxodimethylenemethane(2-) ligand<sup>23</sup> with an ML<sub>2</sub><sup>2+</sup> unit.<sup>24</sup> This is done for Pd(CH<sub>2</sub>COCH<sub>2</sub>)(PH<sub>3</sub>)<sub>2</sub> (**16**) at the ex-



tended Hückel level in Figure 2. The parameters are given in the Computational Details section. The reader should note that in the ensuing discussion the molecular orbitals of **16** are constructed at  $\theta = 53^\circ$  and not at  $\theta = 90^\circ$ , where the PdP<sub>2</sub> and oxodimethylenemethane planes are perpendicular to each other. Nevertheless, because of our choice of partitioning the two fragments, there are four purely  $\pi$ -type orbitals on the oxodimethylenemethane(2-) ligand (for simplicity we have neglected any hybridization changes caused by puckering the methylene hydrogens, the details of which we shall return to). Basically, there is a very strong interaction between the b<sub>1</sub> orbital on Pd-(PH<sub>3</sub>)<sub>2</sub><sup>2+</sup> and  $\pi_3$  to produce a filled bonding and empty antibonding level. The 1a<sub>1</sub> and 3a<sub>1</sub> levels combine with  $\pi_2$  to produce three molecular orbitals, the lower two of which are filled. The remaining fragment orbitals are left nonbonding. The electronic structure is then quite similar to that given previously<sup>25-27</sup> for the isoelectronic tri-

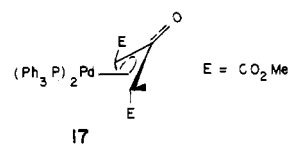
Table III. A Comparison of Computed versus Experimental Geometrical Parameters in Oxodimethylenemethane Complexes

structural parameter <sup>e</sup>	5	17 <sup>a</sup>	16	18
M-P	2.294 (3) <sup>b</sup>	2.330 (2) <sup>b</sup>	2.57	2.59
P-M-P	103.6 (1)	102.2 (1)	98.0	95.8
M-C(1)	2.132 (14) <sup>b</sup>	2.138 (5) <sup>b</sup>	2.11	2.07
M-C(2)	2.422 (12)	2.384 (6)	2.49	2.65
$\theta^c$	51.0	53.3	50.5	0
C(1)-C(2)	1.484 (20) <sup>b</sup>	1.480 (9) <sup>b</sup>	1.49	1.51
C(2)-O	1.257 (15)	1.224 (8)	1.22	1.21
C(1)-C(2)-C(3)	107.7 (10)	109.5 (6)	101.9	102.6
$\tau^d$	16.9	12.2	11.2	0
H(1)-C(1)-C(2)	106 (7) <sup>b</sup>	115 (3) <sup>b</sup>	113.5	112.7
H(2)-C(1)-C(2)	107 (8) <sup>b</sup>	119 (5) <sup>b</sup>	116.9	112.7
H(2)-C(1)-C(2)-C(3)	163 <sup>b</sup>	170 <sup>b</sup>	159.7	117.1
H(1)-C(1)-C(2)-C(3)	66 <sup>b</sup>	54 <sup>b</sup>	64.7	117.1

<sup>a</sup> See ref. 4. <sup>b</sup> Average of two values. <sup>c</sup> Dihedral angle between the MP<sub>2</sub> and C(1)-C(2)-C(3) planes. <sup>d</sup> Inclination between the C(2)-O bond and the C(1)-C(2)-C(3) plane. <sup>e</sup> Distances in Å and angles in deg.

methylenemethane-Pd(PR<sub>3</sub>)<sub>2</sub> system, a proposed intermediate in the palladium-catalyzed cycloaddition of trimethylenemethane with olefins.<sup>28</sup> Here, the better bonding capacity of the b<sub>1</sub> fragment orbital by virtue of its hybridization and closeness in energy to  $\pi_3$  causes the ML<sub>2</sub> unit to shift away from  $\eta^4$  toward a  $\pi$ -allyl,  $\eta^3$  geometry. This is identical with the situation for trimethylenemethane-Pd(PH<sub>3</sub>)<sub>2</sub>.<sup>25-27</sup> However, there are important differences that stem from the greater electronegativity of oxygen compared to a CH<sub>2</sub> group. In trimethylenemethane  $\pi_2$  and  $\pi_3$  are degenerate. Furthermore, in  $\pi_2$  the atomic coefficient at C(2) is zero. Thus,  $\pi_2$  interacts primarily with b<sub>2</sub> on the ML<sub>2</sub> fragment and  $\pi_1$  interacts with 1a<sub>1</sub> and 3a<sub>1</sub>. In oxodimethylenemethane, as was previously mentioned,  $\pi_2$  interacts with 1a<sub>1</sub> and 3a<sub>1</sub>. The  $\pi_1$  orbital lies at a considerably lower energy and electronically resembles a carbonyl  $\pi$  orbital. Thus, the ring puckering,  $\theta$ , in trimethylenemethane-Pd(PH<sub>3</sub>)<sub>2</sub> is expected to be larger than in the isoelectronic oxodimethylenemethane complexes. An optimum value of  $\theta = 84^\circ$  was found from Fenske-Hall calculations.<sup>26</sup>

We have also carried out an optimization of ( $\eta^3$ -CH<sub>2</sub>COCH<sub>2</sub>)Pd(PH<sub>3</sub>)<sub>2</sub> (**16**) at the ab initio SCF level. Specifications regarding the basis sets and effective core potentials used on Pd and P are given in the Computational Details section. The geometry was fully optimized within a C<sub>s</sub> symmetry constraint except that the P-H distances were fixed at 1.42 Å and the Pd-P-H angles at 123.1°. The optimized geometrical values for **16** are listed in Table III along with a comparison to the experimental values for **5** and Pd[CH(CO<sub>2</sub>Me)COCH(CO<sub>2</sub>Me)](PPh<sub>3</sub>)<sub>2</sub> (**17**). The agreement between the computed values and the experimental geometry for **5** and **17** is quite good, with the exception of the Pd-P distances. The computed value



is 0.24 Å longer than the experimental value in **17**. This effect has been noted elsewhere,<sup>29</sup> and the addition of

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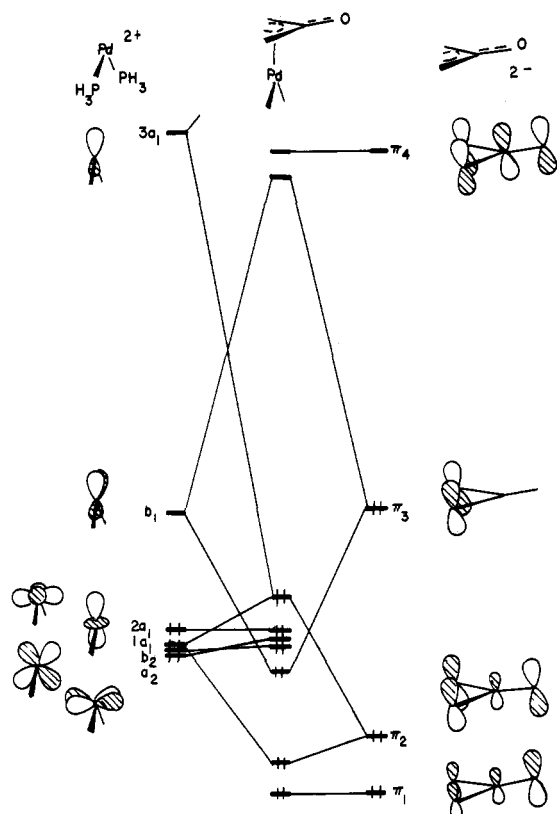
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**Figure 2.** An orbital interaction for 16 at the ground-state geometry.

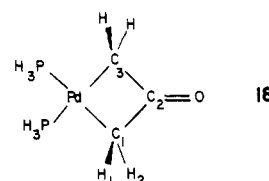
electron correlation would remove most of the discrepancy, based on analogous situations observed for Pd-CO<sup>30</sup> and Pd-H<sup>31</sup> distances. Interestingly, the computed Pd-C(1) distance in 16 is very close to that observed for 17. The longer Pd-C(2) distance computed for 16 is a direct result of the slightly smaller ring puckering angle,  $\theta$ .

The carbonyl bond in 5 displays a characteristic "tipping" motion toward the Pt atom. The angle of inclination between the C(2)-O axis and the C(1)-C(2)-C(3) plane,  $\tau$ , was 16.9°. Previous studies of platinum and palladium oxodimethylenemethane complexes have displayed values of  $\tau$  from 6.46° to 13.0°.<sup>1-5</sup> This tipping motion is reproduced in the geometry optimization of 16 with  $\tau$  being 11.2°. At both the *ab initio* and extended Hückel levels we see no sign of incipient bonding between Pd and O. Rather, the bending motion serves to decrease antibonding, primarily between  $b_2$  and  $\pi_2$  (see Figure 2), thus reinforcing Pd-C(2) bonding. This is precisely what occurs (and for the same reason) with substituents at the central carbon atom in  $\pi$ -allyl complexes. For example, the methyl group in  $[(\eta^3\text{-2-methylallyl})\text{PdCl}]_2$  is inclined by 10.9° out of the allyl plane, toward Pd.<sup>18</sup> The hydrogen on the central carbon in  $[(\eta^3\text{-allyl})\text{PdCl}]_2$ <sup>32</sup> and  $(\eta^3\text{-allyl})_2\text{Ni}$ <sup>33</sup> are tipped by 13.7° and 15.8°, respectively, as determined by neutron diffraction in both cases.

Notice from Table III that the hydrogens on the methylene carbons in 16 are predicted to lie appreciably out of the C(1)-C(2)-C(3) plane in 16. The anti hydrogens, H(1) in 16, are twisted by 64.7° out of the C(1)-C(2)-C(3) plane in a direction away from Pd. The syn hydrogens, H(2) in 16, are twisted by 20.3° toward Pd. Thus, each methylene

group is calculated to be slightly pyramidalized and rotated toward Pd. The uncertainty associated with locating the hydrogen atoms in the X-ray structures of 5 and 17 are large. Nevertheless, the same distortions are experimentally observed. Furthermore, in 17 the syn and anti carbonyl carbons make dihedral angles with respect to C(1)-C(2)-C(3) of 168.3° and 60.0°, respectively. These are quite close to the values reported for H(2) and H(1) in Table III. An identical distortion is observed for the methylene groups in the neutron structures of  $(\pi\text{-allyl})_2\text{Ni}$ <sup>33</sup> and  $[(\pi\text{-allyl})\text{PdCl}]_2$ ,<sup>32</sup> although to a lesser degree, particularly for the anti hydrogens (the corresponding average dihedral angle was 29.0° for the former compound and 31° for the latter). Twisting and pyramidalization of the methylene groups strengthens the metal-carbon bonds.<sup>33,34</sup> In the context of oxodimethylenemethane complexes, rotation of the methylene groups in the observed sense serves to reorient the p atomic orbitals in  $\pi_3$  (see Figure 2) toward the metal atom, and pyramidalization will hybridize the atomic orbitals in  $\pi_3$ <sup>24</sup> toward the metal. Both factors then create, in particular, a larger overlap between  $\pi_3$  and the  $b_1$  fragment orbital on  $\text{ML}_2$ . We feel, however, that there is another important factor at work for oxodimethylenemethane- $\text{ML}_2$ .

The optimization of 16 revealed an extremely flat potential surface around the minimum. In particular, sizable reductions in the optimized value of the ring puckering angle,  $\theta$ , require little energy. The ring puckering internal coordinate is furthermore strongly coupled to the H(2)-C(1)-C(2)-C(3) and H(1)C(1)-C(2)-C(3) dihedral angles. As  $\theta$  decreases, H(2)-C(1)-C(2)-C(3) decreases while H(1)-C(1)-C(2)-C(3) increases. The ultimate structure formed as  $\theta$  decreases to 0° is metallacycle 18. The geo-



metrical parameters for 18 optimized at the *ab initio* level within a  $C_{2v}$  symmetry constraint are also given in Table III. The conversion of 16 and 18 is symmetry-allowed. The construction of a Walsh diagram for the conversion of 16 to 17 is not informative. There are only very small changes of the orbital energies as a function of  $\theta$ . This is consistent with our findings at the *ab initio* level that ring puckering is a low-frequency motion. Referring back to Figure 2, rotation and pyramidalization of the methylene groups causes both  $\pi_2$  and  $\pi_3$  to be destabilized. They become the symmetric ( $n_s$ ) and antisymmetric ( $n_a$ ) lone-pair combinations at the methylene groups. The pyramidalization of the methylene hydrogens again serves to hybridize the p atomic orbitals in  $\pi_2$  and  $\pi_3$  in a direction toward the metal atom. Furthermore, there is an intermixing between  $\pi_1$ ,  $\pi_2$ , and  $\pi_4$  so that  $\pi_2$  ( $n_s$  at geometry 18) as well as  $\pi_3$  ( $n_a$  at geometry 18) of course become localized on the methylene carbons. The  $n_s$  fragment orbital interacts with  $3a_1$  on the  $\text{ML}_2$  unit and  $n_a$  with  $b_1$  to form the two Pd-C  $\sigma$  bonds. The  $\pi_1$  fragment orbital becomes a CO  $\pi$  orbital while  $\pi_4$  evolves into CO  $\pi^*$ . These later two orbitals along with  $a_2$ ,  $b_2$ ,  $1a_1$ , and  $2a_1$  on  $\text{ML}_2$  remain basically non-bonding. Since the energies of  $\pi_2$  and  $\pi_3$  are raised when the methylene groups rotate, one might think that the energy of 18 will be much higher than 16. This is not the case because the overlaps between  $n_s$  and  $3a_1$  along with

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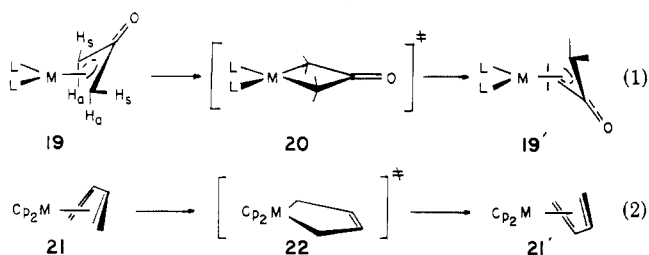
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Scheme III



that between  $n_a$  and  $b_1$  are larger in 18 than the corresponding overlaps in 16.

Experimentally, the conversion of 16 and 18 will exchange the syn and anti hydrogens on the methylene groups, as shown by reaction 1 in Scheme III. The  $^1\text{H}$  NMR spectrum of 5 measured at  $-105^\circ\text{C}$  in  $\text{THF}-d_3$  showed the expected features for the static structure with two resonances due to the syn and anti protons at 2.01 and 2.25 ppm, respectively. The assignment of the higher field resonances to the anti protons is consistent with the  $^1\text{H}$  NMR data for other monosubstituted oxodimethylenemethane complexes.<sup>21,35,36</sup> The magnitudes of the  $^1\text{H}-^1\text{H}$ ,  $^1\text{H}-^{31}\text{P}$ , and  $^1\text{H}-^{195}\text{Pt}$  couplings could not be determined due to poor resolution at the low temperature. Upon warming, the resonances for the methylene protons collapse to a single multiplet with the protons appearing as the A part of an  $A_4XX'$  spin system ( $X = ^{31}\text{P}$ ) along with the expected  $^{195}\text{Pt}$  satellites. This dynamic process is consistent with inversion of the oxodimethylenemethane ligand through a planar,  $C_{2v}$ , transition state illustrated by 20 in Scheme III. The activation energy,  $\Delta G^\ddagger$ , for the ring inversion was calculated to be 9.2 kcal/mol from the coalescence temperature ( $-78^\circ\text{C}$ ) by using the Gutowsky-Holm equation.<sup>37</sup> This is slightly larger than  $\Delta G^\ddagger$  for 1,3-disubstituted oxodimethylenemethane platinum complexes which lie in the range of 8.4–8.9 kcal/mol,<sup>3,5</sup> although it is smaller than  $\Delta G^\ddagger$  for the corresponding palladium complexes which are 9.6–12.2 kcal/mol.<sup>4</sup> Our ab initio calculations at the Hartree-Fock level yield an energy difference between 16 and 18 of 6.4 kcal/mol. Some allowance for electron correlation was made by carrying out calculations at the MP2 level. The barrier was raised to 7.9 kcal/mol in moderately good agreement with the experimental value for 5. The ring inversion process we have demonstrated here had been discounted some time ago for syn-anti isomerization in  $\pi$ -allyl- $\text{ML}_2$  complexes in favor of an  $\eta^3-\eta^1-\eta^3$  mechanism.<sup>38</sup> However, a directly analogous process, shown by reaction 2 in Scheme III, has been observed for  $\text{Cp}_2\text{M}$ (butadiene) complexes ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ).<sup>39-41</sup> In fact, a potential energy surface has been constructed<sup>42</sup> which relates the solid-state structures for

these complexes along the reaction path for ring inversion. Substitution of more electronegative oxygen atoms for the methylene groups in  $\text{Cp}_2\text{M}$ (butadiene) causes the planar metallacycle 22 to be the ground state.<sup>43</sup> The same occurs for oxodimethylenemethane complexes; for example, carbonate-metal complexes are planar.<sup>44</sup> Our calculations reveal that the primary internal coordinate along the reaction path from 19 to 20 is the ring puckering angle  $\theta$ . The same has been experimentally established<sup>42</sup> for the 21 and 22 conversion where a quantitative relationship could be established between  $\Delta G^\ddagger$  for reaction 2 and  $\theta$ . At least a qualitative relationship exists for oxodimethylenemethane- $\text{ML}_2$  complexes. For example, 16 is the most puckered compound observed to date and its room-temperature NMR spectrum is consistent with a static, ground-state structure. Let us now return to our initial thesis concerning the metallacyclobutane, 1, versus  $\pi$ -allyl, 2, bonding descriptions. These are rather crude, heuristic models that immediately invoke structural implications. Our delocalized construction of the bonding in oxodimethylenemethane- $\text{ML}_2$  complexes does not provide a bias toward 1 or 2, and, indeed, there are many similarities. The critical difference is the presence or absence of metal to central carbon ( $\text{C}_2$  in 16 or 18) bonding. In platinacyclobutanes, for example, this bonding interaction is absent. Consequently, as mentioned previously,  $\theta$  is quite small. For trimethylenemethane- $\text{ML}_2$  complexes the  $\text{M}-\text{C}_2$  interaction is presumably quite strong,<sup>25-28</sup> and, therefore,  $\theta$  is predicted to be quite close to  $90^\circ$ . Oxodimethylenemethane- $\text{ML}_2$  compounds represent an intermediate situation. The interplay between the stabilization from  $\pi_2$  and  $\pi_4$  to especially  $b_2$  (see Figure 2), which favors large values of  $\theta$ , and the increased overlap of  $n_s$  to  $3a_1$  and  $b_1$ , which favor small values of  $\theta$ , is finely balanced in this instance. A deliberate perturbation of these competing factors by structural/electronic modifications should produce a sizable variation of  $\theta$ . We shall explore a quantitative reaction path mapping in the future.

## Experimental Section

**General Information.** Melting points were recorded in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 580 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz or on a Bruker Spectrospin WH 400 spectrometer at 400.13 MHz, with  $\text{SiMe}_4$  (0.0 ppm) as internal reference, positive values being to high frequency (low field).  $^{13}\text{C}$ ,  $^1\text{H}$  decoupled NMR spectra were recorded on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz, with  $\text{SiMe}_4$  (0.0 ppm) as internal reference, in  $\text{CDCl}_3$ .  $^{31}\text{P}$ ,  $^1\text{H}$  decoupled NMR spectra were recorded on a JEOL JNM-FX 60 spectrometer at 24.15 MHz with  $[\text{P}(\text{OH})_4]^+$  in  $\text{D}_2\text{O}$  (0.0 ppm) as external reference. Elemental analyses were carried out by C. H. N. Analysis Ltd., Leicester, United Kingdom. Experiments were carried out under a dry, oxygen-free nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use from the following drying agents: THF, diethyl ether (Na/benzophenone), petroleum ether, bp  $40-60^\circ\text{C}$  (Na), dichloromethane ( $\text{CaH}_2$ ). The compounds 3-chloro-1-(trimethylsilyl)propan-2-one,<sup>8</sup>  $[\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2]$ ,<sup>45</sup> and  $\text{cis-}[\text{PtCl}(\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{Cl})(\text{PPh}_3)_2]$ <sup>46</sup> were prepared by literature

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**Table IV. Data for X-ray Diffraction Analysis of [Pt( $\eta^3$ -CH<sub>2</sub>C(O)CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (5 • CH<sub>2</sub>Cl<sub>2</sub>)**

A. Crystal Data	
cryst system	monoclinic
space group	P2 <sub>1</sub> /c
a, Å	13.835 (4)
b, Å	17.560 (9)
c, Å	15.42 (3)
$\beta$ , deg	109.7 (1)
V, Å <sup>3</sup>	3526.9
fw, amu	860.67
d(calcd), g cm <sup>-3</sup>	1.62
Z	4
$\mu$ , cm <sup>-1</sup>	40.62
$\lambda$ (Mo K $\alpha$ ), Å	0.7107
B. Data Collection and Analysis Summary	
cryst dimens, mm	0.34 × 0.28 × 0.17
reflectns sampled	$\pm h, k, l$
2 $\theta$ range for centered reflectns	7 ≤ 2 $\theta$ ≤ 50°
total no. of measd reflectns	6081
no. of unique data used	4361
max. transmissn factor	0.561
min. transmissn factor	0.300
R	0.0526
R'	0.0532
F(000)	1704

procedures.

**Preparation of [Pt( $\eta^3$ -CH<sub>2</sub>C(O)CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (5).** [Pt(*trans*-stilbene)(PPh<sub>3</sub>)<sub>2</sub>] (0.3 g, 0.3 mmol) and 3-chloro-1-(trimethylsilyl)propan-2-one (0.33 g, 2.0 mmol) in diethyl ether (15 cm<sup>3</sup>) were stirred for 2 h at room temperature. The slightly cloudy solution was filtered and petroleum ether (10 cm<sup>3</sup>) added. A white solid precipitated that was washed with petroleum ether and dried

in vacuo to give the title complex **5** (0.14 g, 60%): mp 190 °C dec; IR  $\nu$ (CO) 1550 cm<sup>-1</sup>. NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H (400 MHz)  $\delta$  2.25 [br m, 4 H, CH<sub>2</sub>C(O)CH<sub>2</sub>, J(PtH) = 48.4 Hz] and 7.3 ppm (m, 30 H, Ph); <sup>13</sup>C-<sup>1</sup>H (100 MHz)  $\delta$  49.6 [dd, CH<sub>2</sub>C(O)CH<sub>2</sub>, AX' spin system, J = 56.5, 5.0 Hz, J(PtC) = 251.5 Hz], 125–140 (m, Ph), and 183.8 ppm [s, CH<sub>2</sub>C(O)CH<sub>2</sub>]; <sup>31</sup>P-<sup>1</sup>H (24 MHz)  $\delta$  23.19 ppm [s, J(PtP) = 2978 Hz]; <sup>1</sup>H (400 MHz, THF-d<sub>6</sub>, -105 °C)  $\delta$  2.01 (br, 2 H), 2.25 (br, 2 H), 7.5 ppm (m, 30 H, Ph). Anal. Calcd for C<sub>39</sub>H<sub>34</sub>OP<sub>2</sub>Pt: C, 60.4; H, 4.4. Found: C, 60.0; H, 4.4.

**Alternative Preparation of 5.** A solution of the complex *cis*-[PtCl(CH<sub>2</sub>C(O)CH<sub>2</sub>Cl)(PPh<sub>3</sub>)<sub>2</sub>] (0.19 g, 0.225 mmol) in THF (30 cm<sup>3</sup>) was added to a sodium amalgam prepared from 2 cm<sup>3</sup> of mercury and 0.2 g of sodium. The mixture was swirled for 15 min, whereupon the colorless solution turned deep yellow. The solution was decanted from the amalgam, filtered, and evaporated to dryness under reduced pressure to afford a brownish oil. Dissolution of the oil in dichloromethane (2 cm<sup>3</sup>) followed by addition of light petroleum (50 cm<sup>3</sup>) gave pale yellow microcrystals of the title complex (0.152 g, 87%).

**X-ray Data Collection and Structure Analysis of 5-CH<sub>2</sub>Cl<sub>2</sub>.** Crystals of 5-CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray crystallography were grown slowly from dichloromethane-petroleum ether. A colorless crystal was mounted on a glass fiber in air. The unit-cell dimensions of the crystal were determined from an oscillation photograph for the rotation axis *c* and from the refined data of zero and layer reflections for axes *a* and *b*, on a Weissenberg diffractometer. The intensities of 6081 unique reflections (7 ≤ 2 $\theta$  ≤ 50°,  $\pm h, k, l$ ) were measured on a Stoe STADI-2 Weissenberg diffractometer with graphite-monochromated Mo K $\alpha$  radiation using an  $\omega$ -scan technique. The 4361 reflections having  $I \geq 3\sigma(I)$  were corrected for Lorentz and polarization effects. Further details regarding the refined lattice parameters are summarized in Table IV. Computations were carried out by using the computer program SHELX.<sup>47</sup> The structure was solved by Patterson and Fourier

**Table V. Fractional Atomic Coordinates for (Ph<sub>3</sub>P)<sub>2</sub>PtCH<sub>2</sub>C(O)CH<sub>2</sub>**

atom	x	y	z	atom	x	y	z
Pt	0.18130 (3)	-0.00481 (2)	0.15964 (2)	C(35)	0.3434 (5)	-0.0300 (4)	-0.1077 (3)
P(1)	0.27578 (19)	-0.09661 (14)	0.11892 (17)	C(36)	0.3475 (5)	-0.0409 (4)	-0.0169 (3)
P(2)	0.17953 (19)	-0.04463 (13)	0.30093 (16)	H(32)	0.1426 (5)	-0.1586 (4)	0.0554 (3)
C(1)	0.0784 (8)	0.0893 (6)	0.1522 (8)	H(33)	0.1355 (5)	-0.1394 (4)	-0.2165 (3)
H(1)	0.081 (7)	0.116 (5)	0.191 (6)	H(34)	0.2639 (5)	-0.0572 (4)	-0.2499 (3)
H(2)	0.008 (8)	0.081 (5)	0.122 (6)	H(35)	0.3995 (5)	0.0058 (4)	-0.1223 (3)
C(2)	0.1335 (9)	0.1207 (7)	0.0940 (8)	H(36)	0.4066 (5)	-0.0134 (4)	0.0387 (3)
C(3)	0.1512 (11)	0.0577 (7)	0.0358 (10)	C(41)	0.0668 (4)	-0.1016 (3)	0.2940 (4)
H(3)	0.081 (8)	0.032 (6)	0.002 (7)	C(42)	-0.0243 (4)	-0.0847 (3)	0.2229 (4)
H(4)	0.207 (8)	0.078 (5)	0.016 (6)	C(43)	-0.1127 (4)	-0.1270 (3)	0.2129 (4)
O(1)	0.1848 (9)	0.1812 (5)	0.1112 (8)	C(44)	-0.1101 (4)	-0.1863 (3)	0.2738 (4)
Cl(1)	0.4061 (5)	0.34817 (29)	0.5413 (5)	C(45)	-0.0190 (4)	-0.2032 (3)	0.3449 (4)
Cl(2)	0.4668 (6)	0.3553 (4)	0.7403 (6)	C(46)	0.0695 (4)	-0.1609 (3)	0.3550 (4)
C(7)	0.3994 (16)	0.3039 (10)	0.6425 (12)	H(42)	-0.0263 (4)	-0.0388 (3)	0.1757 (4)
C(11)	0.2210 (5)	-0.1908 (3)	0.1165 (5)	H(43)	-0.1832 (4)	-0.1139 (3)	0.1579 (4)
C(12)	0.2758 (5)	-0.2576 (3)	0.1172 (5)	H(44)	-0.1785 (4)	-0.2190 (3)	0.2661 (4)
C(13)	0.2274 (5)	-0.3282 (3)	0.1107 (5)	H(45)	-0.0169 (4)	-0.2491 (3)	0.3921 (4)
C(14)	0.1242 (5)	-0.3319 (3)	0.1035 (5)	H(46)	0.1400 (4)	-0.1740 (3)	0.4100 (4)
C(15)	0.0695 (5)	-0.2650 (3)	0.1028 (5)	C(51)	0.2867 (4)	-0.1005 (3)	0.3744 (4)
C(16)	0.1179 (5)	-0.1945 (3)	0.1094 (5)	C(52)	0.2972 (4)	-0.1767 (3)	0.3534 (4)
H(12)	0.3556 (5)	-0.2548 (3)	0.1228 (5)	C(53)	0.3823 (4)	-0.2184 (3)	0.4068 (4)
H(13)	0.2698 (5)	-0.3799 (3)	0.1112 (5)	C(54)	0.4568 (4)	-0.1839 (3)	0.4811 (4)
H(14)	0.0868 (5)	-0.3864 (3)	0.0984 (5)	C(55)	0.4463 (4)	-0.1078 (3)	0.5021 (4)
H(15)	-0.0104 (5)	-0.2679 (3)	0.0972 (5)	C(56)	0.3612 (4)	-0.0661 (3)	0.4487 (4)
H(16)	0.0755 (5)	-0.1428 (3)	0.1088 (5)	H(52)	0.2395 (4)	-0.2033 (3)	0.2959 (4)
C(21)	0.4138 (4)	-0.1034 (4)	0.1820 (5)	H(53)	0.3904 (4)	-0.2773 (3)	0.3906 (4)
C(22)	0.4774 (4)	-0.1479 (4)	0.1491 (5)	H(54)	0.5227 (4)	-0.2162 (3)	0.5224 (4)
C(23)	0.5827 (4)	-0.1510 (4)	0.1976 (5)	H(55)	0.5040 (4)	-0.0811 (3)	0.5596 (4)
C(24)	0.6242 (4)	-0.1096 (4)	0.2789 (5)	H(56)	0.3531 (4)	-0.0071 (3)	0.4649 (4)
C(25)	0.5605 (4)	-0.0650 (4)	0.3118 (5)	C(61)	0.1764 (5)	0.0335 (3)	0.3773 (4)
C(26)	0.4553 (4)	-0.0619 (4)	0.2633 (5)	C(62)	0.1310 (5)	0.0248 (3)	0.4449 (4)
H(22)	0.4453 (4)	-0.1800 (4)	0.0862 (5)	C(63)	0.1340 (5)	0.0843 (3)	0.5056 (4)
H(23)	0.6320 (4)	-0.1855 (4)	0.1721 (5)	C(64)	0.1824 (5)	0.1526 (3)	0.4987 (4)
H(24)	0.7056 (4)	-0.1120 (4)	0.3164 (5)	C(65)	0.2278 (5)	0.1613 (3)	0.4311 (4)
H(25)	0.5927 (4)	-0.0329 (4)	0.3747 (5)	C(66)	0.2248 (5)	0.1018 (3)	0.3704 (4)
H(26)	0.4060 (4)	-0.0275 (4)	0.2888 (5)	H(62)	0.0936 (5)	-0.0281 (3)	0.4503 (4)
C(31)	0.2751 (5)	-0.0872 (4)	0.0019 (3)	H(63)	0.0989 (5)	0.0776 (3)	0.5579 (4)
C(32)	0.1987 (5)	-0.1227 (4)	-0.0700 (3)	H(64)	0.1847 (5)	0.1988 (3)	0.5457 (4)
C(33)	0.1946 (5)	-0.1119 (4)	-0.1608 (3)	H(65)	0.2652 (5)	0.2142 (3)	0.4257 (4)
C(34)	0.2670 (5)	-0.0656 (4)	-0.1796 (3)	H(66)	0.2599 (5)	0.1085 (3)	0.3181 (4)

techniques. Scattering factors for the atoms were taken from ref 48. An absorption correction was applied to the data. The hydrogen atoms of the phenyl rings were treated as rigid groups with C-H fixed at 1.08 Å, and the thermal parameters of these atoms were refined with two related values for each group. The hydrogen atoms of the oxodimethylenemethane ligand were located from a difference Fourier, for which the contribution of low-angle reflections was enhanced, and the positional and isotropic thermal parameters were refined independently. All other atoms were refined anisotropically. For final cycles, a weighting parameter,  $g(0.00044)\omega \propto [1/(\sigma^2 F + gF^2)]$ , was employed and gave the final residual indices  $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.0526$  and  $R' = [\sum\omega(|F_o| - |F_c|)^2]^{1/2} = 0.0532$ . The highest residual peak in the final difference Fourier map was  $\sim 1.5e$  at 1 Å from Pt. An analysis of the weighting scheme over  $|F_o|$  and  $(\sin \theta)/\lambda$  was satisfactory.

The values for the refined positional parameters for all of the atoms are provided in Table V. A full table of the interatomic distances and bond angles and their estimated standard deviations are given in the supplementary material. Tables of the refined temperature factors and the observed and calculated structure factors for the structure are also available as supplementary material.

**Computational Details.** The parameters used in the extended Hückel calculations<sup>49</sup> were taken from the literature.<sup>50</sup> The geometry used for 16 was taken from the experimental values for 17<sup>4</sup> and that for 18 from the optimized ab initio values except that the Pd-P distance was fixed at 2.33 Å. The ab initio SCF calculations used the GAUSSIAN 82 program.<sup>51</sup> A relativistic effective core potential was used for the core electrons in Pd<sup>52</sup> (up to 4s) and P<sup>53</sup> (up to 3s). The basis sets used were double- $\zeta$

for the valence region and of the form (341,431,31) for Pd<sup>52</sup> and (21,21) for P.<sup>53</sup> The 3-21G basis<sup>54</sup> was used for the oxodimethylenemethane ligand and STO-3G<sup>55</sup> for the hydrogens on the PH<sub>3</sub> groups. A full geometry optimization was carried out on 16 under a C<sub>s</sub> symmetry constraint and for 18 under C<sub>2v</sub> symmetry except that in each case the P-H distances were held constant at 1.42 Å and the Pd-P-H angles at 123.1°. The total energies computed for optimized 16 and 18 were -331.573 72 and -331.563 62 hartrees, respectively. Single-point calculations were carried out by using frozen core second-order Møller-Plesset (MP2) perturbation theory<sup>56</sup> at the optimum geometries. The total energies were -332.271 77 and -332.259 14 hartrees for 16 and 18, respectively.

**Acknowledgment.** T.A.A. thanks the Robert A. Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for a generous allocation of computer time at the Pittsburgh Supercomputing Center. R.D.W.K. acknowledges the SERC for funding and provision of high-field NMR facilities, Dr. O. W. Howarth (University of Warwick) and Miss M. Robinson (University of Leicester) for high-field NMR measurements, and Johnson Matthey plc for the generous loan of platinum metal salts.

**Registry No.** 5, 105302-65-6; 5-CH<sub>2</sub>Cl<sub>2</sub>, 121443-75-2; 16, 18, 121443-76-3; [Pt(*trans*-stilbene)(PPh<sub>3</sub>)<sub>2</sub>], 39697-14-8; *cis*-[PtCl(CH<sub>2</sub>C(O)CH<sub>2</sub>Cl)(PPh<sub>3</sub>)<sub>2</sub>], 121443-74-1; 3-chloro-1-(trimethylsilyl)propan-2-one, 71482-65-0.

**Supplementary Material Available:** Full tables of bond lengths and angles (Tables S1 and S2) and atomic thermal parameters (Table S3) for 5-CH<sub>2</sub>Cl<sub>2</sub> (5 pages); a listing of structure factors (Table S4) for 5-CH<sub>2</sub>Cl<sub>2</sub> (17 pages). Ordering information is given on any current masthead page.

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## Alkoxytelluration of Olefins for the Preparation of Bis( $\beta$ -alkoxyalkyl) Ditellurides and ( $\beta$ -Alkoxyalkyl)tellurium Trichlorides

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Received January 17, 1989

Bis( $\beta$ -alkoxyalkyl) ditellurides (1) were obtained when terminal olefins were heated with tellurium dioxide in alcoholic aqueous hydrochloric acid and the products, without isolation, were reduced with sodium disulfite. Only Markovnikov addition to the double bond was observed. Olefins containing a suitably positioned hydroxy group afforded cyclic ethers formed via an intramolecular oxytelluration reaction. By treatment with sulfuryl chloride the ditellurides were converted in high yields to ( $\beta$ -alkoxyalkyl)tellurium trichlorides.

### Introduction

In 1968 a patent procedure described a process for the manufacture of ethylene chlorohydrin from ethylene by using tellurium dioxide, TeO<sub>2</sub>, as the catalytic oxidant in

aqueous hydrochloric acid (eq 1).<sup>1</sup> Since this transformation seems to be closely related to the well-known

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