To secure **4**, the previously described trienone **2**[8] was reduced to allylic alcohol **3** with cerium(III) chloride doped sodium borohydride.[9] Heating **3** with a slight excess of the Burgess reagent[10] in benzene solution (50 °C, 1 h) delivered **4** efficiently (92%). The C_{2v} symmetry of this colorless oily hydrocarbon was evidenced most clearly in its five-line ^{13}C NMR spectrum.

The route to **1** was less straightforward. Advantage was first taken of the low reactivity of the enone double bond in **2** toward electrophilic reagents. Treatment with 2 equiv of bromine in CH_2Cl_2 at −78 °C proceeded with full chemoselectivity to give the tetrabromo ketone (95%). Direct ketalization under standard conditions ensued to furnish **5** as a colorless solid, mp 183–185 °C, in quantitative yield. When **5** was allowed to react with excess sodium hydride in refluxing tetrahydrofuran[11] and the product mixture was subjected to silica gel chromatography, the desired **6** (45%) was isolated alongside **8** (8%). The latter ketal is recognized to be the intramolecular [4 + 2] cycloadduct of **6**. This conversion, which is duly accelerated on heating, appears to be irreversible.

The greater proclivity of tetraenone **7** for cyclization to **9** necessitated that **6** be deketalized under controlled conditions (py·HOTs, wet acetone, 0 °C, 15 h, 100%).[12] Subsequent reduction as in the previous series with $NaBH_4/CeCl_3$ in methanol gave a 3:1 mixture of diastereomeric tetraenols (93%),[13] heating of which with Burgess reagent (C_6H_6, 50 °C, 16 h) resulted in transformation to **1** (26%):[14] λ_{max} cyclohexane 250 nm (ϵ 10010); ^1H NMR ($CDCl_3$, 200 MHz) δ 5.91 (dd, $J_{2,3} = J_{4,5} = J_{7,8} = J_{9,10}$ = 7.5 Hz, $J_{2,4} = J_{3,5} = J_{7,9} = J_{8,10}$ = 2.9 Hz, $H_{2,5,7,10}$), 5.84 (t, $J_{11,12} = J_{13,14}$ = 1.4 Hz, $H_{12,13}$), 5.48 (dd, $J_{2,3} = J_{4,5} = J_{7,8} = J_{9,10}$ = 7.5 Hz, $J_{2,4} = J_{3,5} = J_{7,9} = J_{8,10}$ = 2.9 Hz, $H_{3,4,8,9}$), 2.09 (d, $J_{11,12} = J_{13,14}$ = 1.4 Hz, $H_{11,14}$); ^{13}C NMR ($CDCl_3$) ppm 134.56, 128.66, 123.96, 38.07, 35.61. This colorless oil proved to be indefinitely stable at room temperature.

The task of determining the thermal stabilities of **1** and **4** was addressed by sealing dilute degassed chlorobenzene-d_5 solutions of the hydrocarbons into evacuated NMR tubes. Heating of **4** at 160 °C for 90 h gave no evidence for retrograde Diels–Alder fragmentation.[15] Since as little as 3% reaction could easily have been detected, the rate constant for this unobserved reaction must be less than 1×10^{-7} s^{-1}. On the other hand, **1** was found to fragment smoothly at 95 °C according to eq 1 with good first-order kinetics: $k = 1.67 \times 10^{-4}$ s^{-1}.

If bond scission is concerted, the observed kinetic inequality likely reflects the extent to which the widely divergent $C_{10}H_8/C_6H_6$ resonance energies (61 vs. 36 kcal/mol) are evident in the respective transition states. Direct comparisons with other systems prove troublesome because the end products are necessarily divergent. For example, Tsang employed shock tube conditions at 900–1150 K to achieve the conversion of cyclohexene to butadiene and ethylene.[16] Extrapolation of his data at 95 °C gives a first-order rate constant of 2.9×10^{-25} s^{-1}! In another context, 9,10-dihydro-9,10-ethanoanthracene, a molecular in which relevant torsion angles approach zero, reverts to anthracene with a rate constant of 7.11×10^{-5} s^{-1} at 278 °C.[17] Although **1** is clearly more reactive than either of these substrates, it should no longer be viewed as a highly fragile molecule. An anticipated barrier to enantiomerization on the order of 16 kcal/mol[18,19] may well protect **1** from spontaneous disintegration at room temperature.[20]

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(12) In contrast, deketalization of **6** at 50 °C provided **9** in 91% yield after purification.
(13) The major component is that in which the hydroxyl group is positioned syn to the diene moiety.
(14) The low yield arises because of incomplete dehydration. With present recognition of the thermal stability of **1**, longer reaction times and/or a higher reaction temperature should suffice to improve efficiency significantly.
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Coupling of Bridging Phosphido Ligands with Alkyl, Hydride, and Carbene Ligands To Give Bridge Elimination Reactions

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Bridging phosphido ligands have been suggested to be useful for retarding fragmentation reactions of polynuclear complexes,[1,2] a feature that should facilitate the search for bimetallic reactivity effects. For example, several such complexes sustain moderate pressures (≥100 atm) of CO and H_2 without fragmentation[2] while others have been used as catalysts or catalyst precursors.[3] Bridging phosphido ligands have generally been assumed to be relatively inert and strongly binding. However, we[4,5] and others[1a,6] have provided evidence that in some cases phosphido bridges are not sufficient to maintain complex integrity. Herein, we describe

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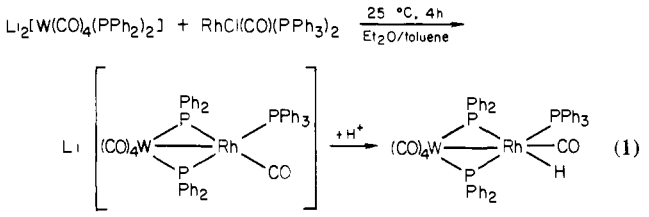
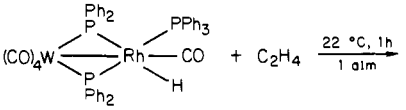
some definitive examples of the degradation of phosphido bridges via their coupling with alkyl, hydride, and carbene ligands.

The new bisphosphido-bridged WRh complex **1** was prepared by the reaction shown in eq 1.[7] Complex **1** has been spectro-



1 (49%)

scopically characterized[8,9] and appears isostructural to $(CO)_4W(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)$ (**2**), which was earlier characterized by a crystal structure determination.[2b] However, unlike **2**, the WRh complex **1** reacts with ethylene to quantitatively yield the monophosphido-bridged complex **3**[10] (eq 2). While the mecha-



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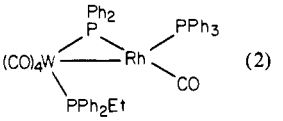
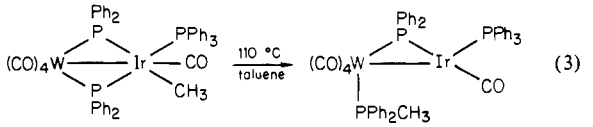


3

nism of this reaction is unknown, it most likely involves initial formation of an ethyl ligand on Rh, via ethylene insertion into the Rh–H bond, followed by reductive coupling of the ethyl and μ-PPh_2 ligands.

Support for this suggested mechanism comes from a similar transformation of the methyl complex $(CO)_4W(\mu\text{-}PPh_2)_2Ir(CH_3)(CO)(PPh_3)$ (**4**). Complex **4** was prepared by a reaction sequence analogous to that of eq 1 using *trans*-$IrCl(CO)(PPh_3)_2$ and adding $CH_3SO_3CF_3$ to the anionic intermediate. Spectroscopic data[11] imply a structure analogous to that of **1** and **2** with CH_3 having replaced the hydride ligand in **2**. Although complex **4** is stable at 22 °C, when heated to 110 °C, it undergoes coupling of the methyl and phosphido ligands to give the *mono*-phosphido-bridged complex **5**[12] (eq 3).



4 5

Coupling of *carbene* and μ-PPh_2 ligands has also been observed on a related WOs compound. The starting point for this transformation is the bis(phosphido)-bridged complex **6**[13] prepared by

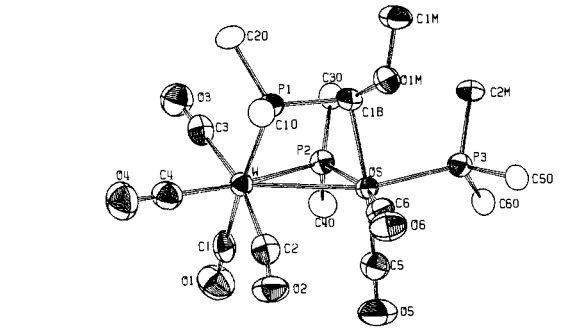
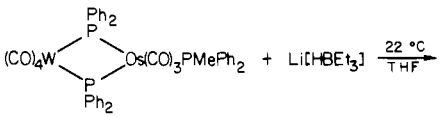
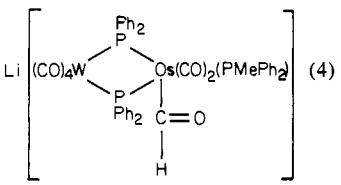


Figure 1. ORTEP drawing of **8**. Only the phenyl carbons attached to the phosphorus atoms are drawn for clarity. Relevant bond distances (Å) and angles (deg): Os–W, 3.022 (1); Os–P(2), 2.357 (7); W–P(1), 2.521 (3); W–P(2), 2.538 (3); Os–C(1B), 2.24 (1); P(1)–C(1B), 1.85 (1); P(2)–Os–C(1B), 87.9 (3); Os–C(1B)–P(1), 100.5 (5); W–P(1)–C(1B), 103.3 (3); P(1)–W–P(2), 90.17 (9); Os–P(2)–W, 76.14 (8).

the reaction of $Li_2[W(CO)_4(PPh_2)_2]$ with $Os(CO)_4Br_2$ followed by addition of $PMePh_2$. Complex **6** reacts with $Li[HBEt_3]$ to give the binuclear WOs formyl complex **7**[14] (eq 4). This formyl

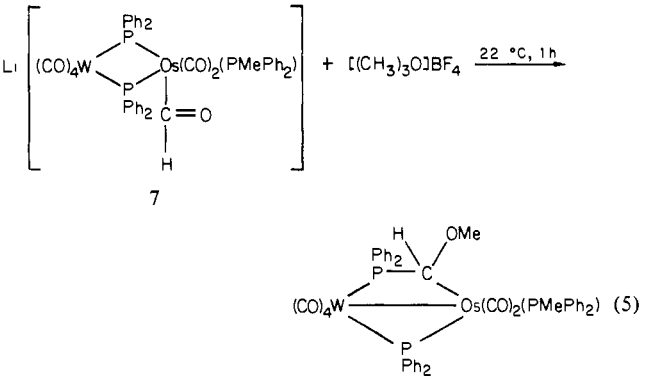


6



7 (~90%)

complex is remarkably stable, decomposing at 110 °C to give a 25:75 mixture of $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMePh_2)]$ and $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_3]$, along with free $PMePh_2$. In an attempt to prepare a binuclear carbene complex from **7**, the latter was treated with $[(CH_3)_3O]BF_4$. However, the product of this reaction (eq 5) was not a carbene complex but rather



7

8 (66%)

compound **8**,[15] in which the W and Os atoms are bridged by μ-PPh_2 and μ-$PPh_2C(OMe)H$ ligands. An ORTEP drawing of **8** is shown in Figure 1.[16] The μ-$PPh_2C(OMe)H$ ligand presumably

(7) $Li_2[W(CO)_4(PPh_2)_2]$ was generated in situ by addition of MeLi to $W(CO)_4(PPh_2H)_2$.[2b]

(8) IR, mass spectral, and analytical data for the new complexes described herein are given as supplementary material.

(9) ^1H NMR δ −12.5 (br t, J = 14.1 Hz); $^{31}P\{^1H\}$ NMR δ 166.7 (dd, μ-PPh_2, J_{PP} = 33.7, J_{PRh} = 107.5 Hz), 54.0 (dt, PPh_3, J_{PRh} = 163.6 Hz).

(10) ^1H NMR δ 2.17 (m, $PPh_2CH_2CH_3$), 0.64 (dt, $PPh_2CH_2CH_3$); $^{31}P\{^1H\}$ NMR δ 89.2 (ddd, μ-PPh_2), 30.2 (dd, Rh-PPh_3), 8.3 (d, $WPPh_2Et$).

(11) ^1H NMR δ −0.57 (dt, CH_3); $^{31}P\{^1H\}$ NMR δ 136.6 (d, μ-PPh_2), 25.6 (t, PPh_3).

(12) ^1H NMR δ 1.84 (d, PPh_2CH_3, J_{HP} = 7.2 Hz); $^{31}P\{^1H\}$ NMR δ 71.9 (dd, μ-PPh_2), 30.9 (d, $IrPPh_3$), −9.0 (d, $WPPh_2CH_3$). The rate of decomposition of **4** and the yields of **5** are variable, depending upon solvent and reaction conditions, suggesting that the **4** → **5** transformation may not be a simple reductive-coupling process.

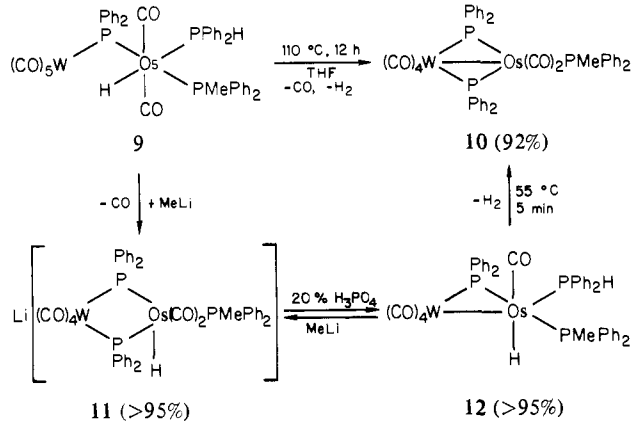
(13) $^{31}P\{^1H\}$ NMR δ −122.9 (dd, μ-PPh_2), −130.6 (dd, μ-PPh_2), −25.0 (dd, $OsPPh_2Me$).

(14) ^1H NMR δ 15.1 (dd, CHO); $^{31}P\{^1H\}$ NMR δ −110.5 (dd, μ-PPh_2), −134.6 (dd, μ-PPh_2), −20.0 (dd, $OsPPh_2Me$); ν_{CO}(CHO) 1525 cm^{-1}.

(15) ^1H NMR δ 4.4 (ddd, $C(H)OCH_3$), 2.8 (s, OCH_3), 2.1 (d, PPh_2CH_3); $^{31}P\{^1H\}$ NMR δ 79.1 (d, μ-PPh_2), −7.0 (d, PPh_2Me), 1.9 (dd, μ-$PPh_2C(H)OCH_3$).

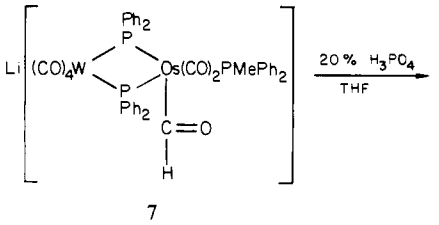
(16) Complete crystallographic data for compound **8** are given in the supplementary material.

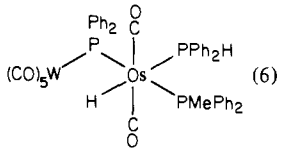
Scheme I



derives by coupling of a μ-PPh_2 ligand with a C(OMe)H carbene ligand generated by methylation of the formyl oxygen. A few other compounds have been prepared containing bridging μ-PR_2CRR' ligands[17] but none by a route such as this.

A phosphido bridge is also eliminated from **7** by protonation with 20% H_3PO_4 to give complex **9**[18] with a terminal PPh_2H ligand (eq 6). Reaction of **7**, labeled with deuterium at the formyl





(6)

position, with 20% H_3PO_4 gives **9** with a deuterium label at the hydride position, showing that the PPh_2H hydrogen derives from the added acid. While this product could form via reductive coupling of μ-PPh_2 and hydride ligands, we cannot exclude direct protonation at the phosphorus ligand. The phosphido bridge can be regenerated from **9** by heating to expel H_2 and CO to yield **10** (Scheme I). Alternatively, complex **10** can be obtained by the series of bridge cleavage/formation reactions illustrated in Scheme I, proceeding through complexes **11**[19] and **12**,[20] which can be individually isolated.

The experiments described herein clearly demonstrate that phosphido bridges are not inert and that they can participate in complex reactions. Such bridge elimination reactions may limit the utility of phosphido-bridged complexes in homogeneous catalysis[5,6] and must be considered in the exploration of the chemistry of this class of compounds.

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Supplementary Material Available: Spectroscopic data for complexes **1-12** and crystallographic data for **8** (3 pages). Ordering information is given on any current masthead page.

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(18) ^1H NMR δ 6.6 (dddd, PPh_2H), -6.2 (dddd, OsH); $^{31}P\{^1H\}$ NMR δ -64.9 (dd, μ-PPh_2), -20.5 (dd, PPh_2Me), -11.2 (dd, PPh_2H).

(19) ^1H NMR δ -3.7 (ddd, OsH); $^{31}P\{^1H\}$ NMR δ -119.4 (dd, μ-PPh_2), -128.7 (dd, μ-PPh_2), -3.5 (dd, PPh_2Me).

(20) ^1H NMR δ -12.8 (t, OsH); $^{31}P\{^1H\}$ NMR δ 53.3 (d, μ-PPh_2), -35.0 (dd, PPh_2Me), -13.9 (d, PPh_2H).

Stereoelectronic Effects in the Hydrolysis of Methyl Ethylene Phosphate

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On the basis of a series of molecular orbital calculations, we had predicted that a significant fraction of the 10^6-10^8 rate acceleration of five-membered ring cyclic phosphate esters relative to their acyclic analogues was attributable to a stereoelectronic effect.[1-4] Westheimer and co-workers[5-10] had clearly demonstrated that release of ring strain in forming a trigonal-bipyramidal pentacovalent phosphorane transition state/intermediate was responsible for at most 4-6 kcal/mol of the 10-11 kcal/mol difference in activation energies between the base-catalyzed hydrolysis of methyl ethylene phosphate (**1**) and that of trimethyl phosphate (similar differences exist between ethylene phosphate and dimethyl phosphate).[6,10] As pointed out by Gerlt et al.,[10] ring strain arguments could not be used to explain why the five-membered ring cyclic transition states were still nearly 6 kcal/mol lower in energy than the equally strain-free acyclic pentacovalent transition states.

In the cyclic transition state, **2**, however, the two lone pairs on the basal ring oxygen (assumed sp^3 hybridized)[4] are oriented partially antiperiplanar (app) to the axial ring ester bond leaving group (Figure 1). The MO calculations suggested that this app lone pair orientation could significantly facilitate P-O ester bond cleavage and that proper orbital overlap (stereoelectronic effect) could be responsible for as much as 11 kcal/mol lowering of transition-state energies.[1-3]

However, a major difficulty with the stereoelectronic effect explanation for the remaining 10^3-10^5 rate acceleration (4-6 kcal/mol difference in activation energies) was the observation of significant exocyclic cleavage in the reaction.[8,9] In dilute acid

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