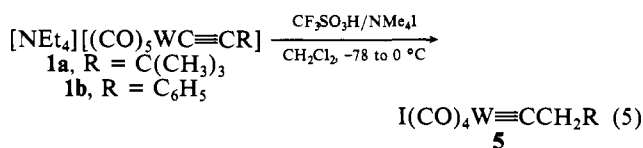


as trans halide tetracarbonyl tungsten carbyne complexes.<sup>2</sup>

Protonation of the vinylidene complexes **2** seems to be a facile process as indicated by the immediate disappearance of the deep green color during the addition of the acid at  $-70\text{ }^\circ\text{C}$ . The first product of this protonation reaction is presumably the cationic carbyne complex  $[(\text{CO})_5\text{W}=\text{CCH}(\text{CMe}_3)\text{R}]^+[\text{CF}_3\text{SO}_3]^-$ .<sup>16</sup> We have studied the protonation of **2a** by  $^{13}\text{C}$  NMR in an attempt to observe this cationic intermediate. However, the  $^{13}\text{C}$  NMR spectrum of the reaction mixture between  $(\text{CO})_5\text{W}=\text{C}=\text{C}(\text{CMe}_3)(\text{Me})$  (**2a**) and  $\text{CF}_3\text{SO}_3\text{H}$  (1:1,  $\text{CD}_2\text{Cl}_2$ ) at  $-80\text{ }^\circ\text{C}$  (in the absence of iodide) shows any signals that can be assigned either to the vinylidene complex **2a** or to *trans*- $\text{CF}_3\text{SO}_3(\text{CO})_4\text{W}=\text{CCH}(\text{CMe}_3)(\text{Me})$  (**4**).<sup>17</sup> At  $-20\text{ }^\circ\text{C}$ , only the signals of the neutral carbyne complex **4** are observed.<sup>17</sup> Loss of carbonyl from the cationic intermediate seems to be a fast process. Since the solubility of  $\text{NMe}_4\text{I}$ , which is used as the source of iodide ions, is very low in  $\text{CH}_2\text{Cl}_2$ , it is likely that formation of the iodo-substituted complexes **3** proceeds via *trans*-(trifluoromethanesulfonato)tetracarbonyl tungsten carbyne species such as complex **4**.

Transformation of acetylide complexes into carbyne complexes is also possible in a single synthesis step. Protonation of  $[\text{NEt}_4][(\text{CO})_5\text{WC}=\text{CR}]$ , (**1a**,  $\text{R} = \text{C}(\text{CH}_3)_3$ ; **1b**,  $\text{R} = \text{C}_6\text{H}_5$ ) with excess  $\text{CF}_3\text{SO}_3\text{H}$  in the presence of  $\text{NMe}_4\text{I}$  affords the carbyne complexes *trans*- $\text{I}(\text{CO})_4\text{W}=\text{CCH}_2\text{R}$  (**5**) (eq 5). The reaction



conditions and the workup procedure are the same as those used in the preparation of the carbyne complexes **3**. The products are isolated in 50–60% yield and easily characterized.<sup>18</sup>

In this protonation reaction, formation of the presumed intermediates of mono and double protonation, the neutral vinylidene complexes  $(\text{CO})_5\text{W}=\text{C}=\text{CHR}$  and the cationic complexes  $[(\text{CO})_5\text{W}=\text{C}-\text{CH}_2\text{R}]^+$ , respectively, is indicated by the appearance of a green color after addition (at  $-78\text{ }^\circ\text{C}$ ) of only 1 equiv of acid and the formation of an almost colorless solution after addition of more than 2 equiv of acid.

Double  $\beta$ -addition of electrophiles to acetylide ligands provides a simple access to metal carbyne complexes. Since the addition of electrophiles to  $\beta$ -atoms is generally more facile in electron-rich metal complexes,<sup>4,9</sup> this method should work particularly well for low-valent, electron-rich acetylide complexes. This work shows how it can be applied as an efficient synthesis of complexes of the type *trans*- $\text{I}(\text{CO})_4\text{W}=\text{CCHRR}'$  which is fundamentally different from the well-established alkoxide abstraction with  $\text{BX}_3$  from pentacarbonyl tungsten alkoxy carbene complexes.<sup>2</sup>

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**Registry No.** **1a**, 88780-71-6; **1b**, 88780-79-4; **2a**, 88780-72-7; **2b**, 88780-73-8; **3a**, 88780-74-9; **3b**, 88780-75-0; **4**, 88780-76-1; **5a**, 88780-77-2; **5b**, 88780-78-3.

(16) This cationic carbyne complex may be in equilibrium with the neutral carbene complex  $(\text{CO})_5\text{W}=\text{C}(\text{X})\text{CH}(\text{CMe}_3)\text{R}'$  ( $\text{X} = \text{CF}_3\text{SO}_3$  or  $\text{I}$ ). Addition of  $\text{HX}$  molecules to give carbene ligands is a common reaction for vinylidene ligands, e.g., a cationic chlorocarbene complex,  $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeC}(\text{Cl})\text{CH}_3][\text{BF}_4]$ , was synthesized by reaction of the corresponding vinylidene complex with  $\text{HCl}$ : Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635–639.

(17)  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_2$ ) **4**: 323 ( $\text{C}_a$ ), 195 ( $\text{CO}$ ).

(18) **5a**: MS ( $m/e$ ,  $^{184}\text{W}$ ) 506; IR ( $\text{cm}^{-1}$ , pentane)  $\nu_{\text{CO}}$  2118 (w), 2034 (s);  $^{13}\text{C}$  NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 291 ( $\text{C}_a$ ), 190 ( $\text{CO}$ ). **5b**: MS ( $m/e$ ,  $^{184}\text{W}$ ) 526; IR ( $\text{cm}^{-1}$ , cyclohexane)  $\nu_{\text{CO}}$  2120 (w), 2038 (s);  $^{13}\text{C}$  NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 283 ( $\text{C}_a$ ), 190 ( $\text{CO}$ ).

#### [4.4.4]Propella-2,4,7,9,12-pentaene. Synthesis and Remarkable Thermal Stability

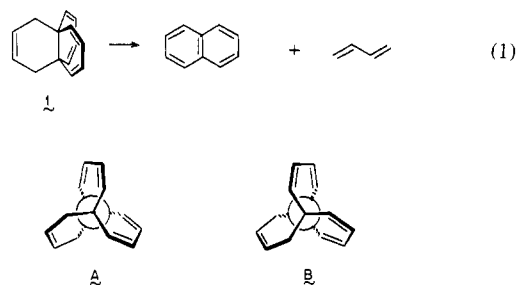
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The apparent paradox that surrounds many symmetry-allowed cycloaddition reactions that pass through an aromatic transition state yet have large activation barriers has recently been analyzed.<sup>1</sup> The conclusion was reached that considerable energy is required to distort the reactants away from their closed-shell geometries in order to facilitate stabilizing HOMO–LUMO interaction. Trivial as it may first appear, the converse of this conclusion must also be true. For example, molecules possessing structural features highly conducive to fragmentation but held rigidly in an unsuitable conformation should prove relatively stable. Concerted bond cleavage cannot occur until the distortion is first redressed—an energy-demanding state of affairs.

A particularly relevant case in point is [4.4.4]propella-2,4,7,9,12-pentaene (**1**), the most highly unsaturated propellane known to date. Inference has earlier been made on the basis of limited experimental data that **1** is particularly prone to retrograde Diels–Alder fragmentation,<sup>2</sup> presumably to naphthalene and butadiene. However, Dreiding models of **1** clearly indicate the



molecule to exist in one or the other enantiomerically related conformation A or B, in line with X-ray crystal data for lesser unsaturated analogues.<sup>3</sup> Not only are the double bonds in its cyclohexadiene rings not mutually coplanar, but the C(1)–C(11) and C(6)–C(14) single bonds of the cyclohexene subunit are pronouncedly tilted in opposite directions. Unambiguous is the fact that substantial topological realignment must precede fragmentation. Less obvious is the magnitude of the energy impediment that these features introduce. For these reasons, we have undertaken to synthesize **1** and the related tetraene **4** and to assess their thermal stability.<sup>4</sup>

It must be emphasized that the structural features embodied in **1** and **4** make these molecules ideally suited to this investigation. Although both *cis*-<sup>5</sup> and *trans*-1,4,4a,8a-tetrahydronaphthalenes<sup>6</sup> are known, heating of these hydrocarbons can be expected to induce kinetically preferred electrocyclization rather than retrograde [4 + 2] fragmentation.<sup>7</sup> The presence of a third six-membered ring safeguards against disrotatory ring opening and introduces well-defined ground-state conformational characteristics.

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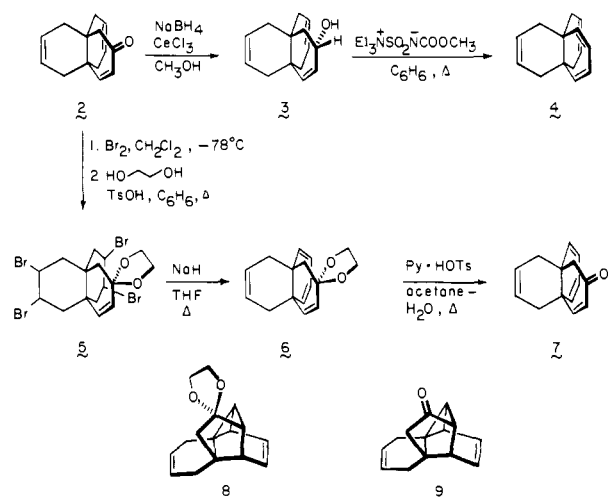
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To secure **4**, the previously described trienone **2**<sup>8</sup> was reduced to allylic alcohol **3** with cerium(III) chloride doped sodium borohydride.<sup>9</sup> Heating **3** with a slight excess of the Burgess reagent<sup>10</sup> in benzene solution (50 °C, 1 h) delivered **4** efficiently (92%). The C<sub>2v</sub> symmetry of this colorless oily hydrocarbon was evidenced most clearly in its five-line <sup>13</sup>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<sub>2</sub>Cl<sub>2</sub> 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<sup>11</sup> 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%).<sup>12</sup> Subsequent re-



duction as in the previous series with NaBH<sub>4</sub>/CeCl<sub>3</sub> in methanol gave a 3:1 mixture of diastereomeric tetraenols (93%),<sup>13</sup> heating of which with Burgess reagent (C<sub>6</sub>H<sub>6</sub>, 50 °C, 16 h) resulted in transformation to **1** (26%):<sup>14</sup> λ<sub>max</sub> cyclohexane 250 nm (ε 10010); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 5.91 (dd, J<sub>2,3</sub> = J<sub>4,5</sub> = J<sub>7,8</sub> = J<sub>9,10</sub> = 7.5 Hz, J<sub>2,4</sub> = J<sub>3,5</sub> = J<sub>7,9</sub> = J<sub>8,10</sub> = 2.9 Hz, H<sub>2,5,7,10</sub>), 5.84 (t, J<sub>11,12</sub> = J<sub>13,14</sub> = 1.4 Hz, H<sub>12,13</sub>), 5.48 (dd, J<sub>2,3</sub> = J<sub>4,5</sub> = J<sub>7,8</sub> = J<sub>9,10</sub> = 7.5 Hz, J<sub>2,4</sub> = J<sub>3,5</sub> = J<sub>7,9</sub> = J<sub>8,10</sub> = 2.9 Hz, H<sub>3,4,8,9</sub>), 2.09 (d, J<sub>11,12</sub> = J<sub>13,14</sub> = 1.4 Hz, H<sub>11,14</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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*<sub>5</sub> 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.<sup>15</sup> Since as little as 3% reaction could easily have

been detected, the rate constant for this unobserved reaction must be less than 1 × 10<sup>-7</sup> s<sup>-1</sup>. 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 × 10<sup>-4</sup> s<sup>-1</sup>.

If bond scission is concerted, the observed kinetic inequality likely reflects the extent to which the widely divergent C<sub>10</sub>H<sub>8</sub>/C<sub>6</sub>H<sub>6</sub> 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.<sup>16</sup> Extrapolation of his data at 95 °C gives a first-order rate constant of 2.9 × 10<sup>-25</sup> s<sup>-1</sup>! 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<sup>-5</sup> s<sup>-1</sup> at 278 °C.<sup>17</sup> 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<sup>18,19</sup> may well protect **1** from spontaneous disintegration at room temperature.<sup>20</sup>

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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,<sup>1,2</sup> 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<sub>2</sub> without fragmentation<sup>2</sup> while others have been used as catalysts or catalyst precursors.<sup>3</sup> Bridging phosphido ligands have generally been assumed to be relatively inert and strongly binding. However, we<sup>4,5</sup> and others<sup>1a,6</sup> have provided evidence that in some cases phosphido bridges are not sufficient to maintain complex integrity. Herein, we describe

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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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