similar to those involved in the reactions of 1 with alkenes and found no evidence of rearrangement. For example, neither treatment of 7 with Fe₂(CO)₉ in THF at 60 °C for 1 h under 60 psi of CO produced any change in 7 (92–95% recovery of 7).

These results delineate a new reaction of Fischer-type carbene complexes with functionalized alkenes and demonstrate remarkable regioselectivity and generality. While dipolar and long-lived diradical intermediates appear to be unlikely in the key carbon-carbon coupling step, the basis for regioselectivity is not yet apparent.

Acknowledgment.

We acknowledge financial support from the National Science Foundation (Grant CHE 82-04339).

Supplementary Material Available: More experimental details including spectral data on new compounds (6 pages). Ordering information is given on any current masthead page.

Table II. Competition Studies of 1a with Alkene Pairs

<table>
<thead>
<tr>
<th>entry</th>
<th>alkenes</th>
<th>product ratios</th>
<th>yields, combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂=CHPh</td>
<td>3a + 4a = 100</td>
<td>86%</td>
</tr>
<tr>
<td>2</td>
<td>CH₂=CHCO₂Me</td>
<td>4b = 36</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CH₂=CHOEt</td>
<td>3a + 4a = 100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CH₂=CHMe</td>
<td>3c = 23</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CH₂=CHCO₂Me</td>
<td>4b = 100</td>
<td>73%</td>
</tr>
<tr>
<td>6</td>
<td>CH₂=CHOEt</td>
<td>3a = 70</td>
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Hydrido, Alkyl, and Ethylene

| 1,2-Bis(dimethylphosphino)ethane Complexes of Manganese and the Crystal Structures of MnBr₂(dmpe)₂, [Mn(AlH₄)]₂(dmpe)₂, and MnMe₂(dmpe)₂ |

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While many BH₄⁻ derivatives of the transition elements have been prepared and characterized,¹ few AlH₄⁻ transition-metal complexes have even been claimed, and none are structurally well understood.² We now report some 1,2-bis(dimethyl-
stereochimistry (Figure 1), and the derived bond lengths agree with the high-spin electronic configuration. The Mn–P distance compares favorably with that found (2.625 Å) in MnCl2(LL)2, LL = α-phenylethenedimethylphosphine. The reaction of MnBr2(dmpe)2 with excess LiAlH4 in toluene gives yellow diamagnetic Mn¹ complex of stoichiometry Mn(AlH4(dmpe)2). Infrared stretches at 1740, 1610, and 970 cm⁻¹ may be assigned to various Al–H and Mn–H–Al modes. In the $^1H$ NMR spectrum, a Mn/HAl hydride resonance occurs at δ = −15.02 broadened due to the quadrupole moments of manganese and aluminum. A terminal AlH signal at δ = +5.05 is similarly broadened, although to a lesser extent; the ratio of bridging to terminal hydrides is 1:1 by integration. The $^1H$ and $^13C$($^1H$) NMR resonances indicate a cis-octahedral arrangement about manganese, while the $^{11}P$($^1H$) NMR spectrum is uninformative, again due to quadrupolar effects.

In view of the rarity of transitional-metal AlH complexes, we have determined the X-ray crystal structure of Mn(AlH4)(dmpe)2 (Figure 2). In the solid state the compound exists as a centrosymmetric dimer, [Mn(AlH4)(dmpe)2]2, due to the formation of a Mn(μ-H)Al(μ-H)Al(μ-H)Mn bridge. The aluminum atoms have trigonal-bipyramidal geometries. The dihydride bridges are all formed from one axial and one equatorial hydrogen atom on each aluminum. The central Al(μ-H)2Al unit is asymmetric, with the long and short Al–H distances differing by ca. 0.2 Å. Thus, the molecule can be thought of as a loosely bound dimer, and this is compatible with the monomeric structure implied by the solution NMR data. In the Mn(μ-H)Al units, the Mn–H distances are equal and shorter than the two Al–H distances by 0.2 Å, indicating a strong affinity of the hydrides for the manganese atom. The geometries about Mn are cis octahedral, with the Mn–P distances trans to the hydrides being slightly shorter than the Mn–P distances trans to each other.

Although this is the first example of a transition-metal AlH2 complex to be structurally determined, other complexes containing M–H–Al bridges have been examined crystallographically. The structure of [Ta(AlH4(OCH2CH2OMe)2)(dmpe)2]2 is similar to the manganese molecule described here, but as is often the case, the hydrogen atoms were not located.

Alkylation of MnBr2(dmpe)2 with MgEt2 in diethyl ether gives red trans-MnMe2(dmpe)2. This complex is low spin (μ = 2 μB); evidently, the stronger ligand field strength of alkyls relative to the ethylene makes Mn2(dmpe)2 a terminal AlH4 complex, with rotation of the ethylene being fast on the NMR time scale. Only two other ethylene complexes of manganese are known, both being carbonyl species.

Acknowledgment. We thank C. G. Howard for helpful discussions, the SERC for support of the X-ray work, and the National Science Foundation for a NATO Postdoctoral Fellowship (G.S.C.). Supplementary Material Available: Atom coordinates, anisotropic temperature factors, bond lengths, and bond angles for Mn(AlH4)(dmpe)2 and Mn2(dmpe)2 (5 pages). Ordering information is given on any current masthead page.

α-Substitution–Spiroannulation of Saturated Ketones

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The elaboration of molecular architecture around a carbonyl group constitutes the most important approach for the synthesis of complex molecules. Substitution at the α-position and replacing the C–O bonds by C–C bonds, normally only one but occasionally both C–O bonds, forms the heart of this approach. Improving the efficiency and selectivity of this strategy represents an important goal. Based upon the concept of small strained rings as pseudofunctional groups and their ease of introduction at a carbonyl group, we envisioned a stereocontrolled approach for the replacement of both C–O bonds of the carbonyl group (i.e., a geminal alkylation) and simultaneous introduction of substituents at the position α to a carbonyl group as shown in eq 1.

Vinycyclopropanols are readily available from saturated ketones by a straightforward process. Reacting the ketones with cyclopropyldiethylsulfonium fluoroborate and powdered potassium hydroxide in Me2SO at room temperature produces oxaspiropentanes in virtually quantitative yield. Extraction of the Me2SO solution with pentane followed by exposure of the oxaspiropentane solution to lithium diethylamide generates the vinycyclopropanol in 70–90% isolated yield as shown in Scheme 1 for cyclopentane. Chemoselective addition of an electrophile to the double bond of I should initiate ring expansion to the cyclobutane. Since secosulfenylation and secocarbomethylation