Table II. Competition Studies of 1a with Alkene Pairs

entry	alkenes	product ratios	yields, combined
1	CH_2=CHPh CH_2=$CHCO_2Me$	3a + 4a = 100 4b = 36	86%
2	CH_2=CHPh CH_2=CHOEt	3a + 4a = 100 3c = 23	
3	CH_2=$CHCO_2Me$ CH_2=CHOEt	4b = 100 3a = 70	73%

similar to those involved in the reactions of **1** with alkenes and found no evidence of rearrangement. For example, neither treatment of **7** with $Fe_2(CO)_9$ in THF at 60 °C for 1 h under argon nor at 50 °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.

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(14) Ethyl 2-ethoxy-2-phenylcyclopropanecarboxylate was prepared by the reaction of ethyl diazoacetate with α-ethoxystyrene at 60 °C in the presence of a catalytic amount of anhydrous cuprous sulfate. See: Doyle, M. P.; van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787–789.

Hydrido, Alkyl, and Ethylene 1,2-Bis(dimethylphosphino)ethane Complexes of Manganese and the Crystal Structures of $MnBr_2(dmpe)_2$, $[Mn(AlH_4)(dmpe)_2]_2$, and $MnMe_2(dmpe)_2$

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While many BH_4^- derivatives of the transition elements have been prepared and characterized,[1] few AlH_4^- transition-metal complexes have even been claimed, and none are structurally well understood.[2] We now report some 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of manganese and the first X-ray crystal structure of a tetrahydridoaluminate transition-metal complex.

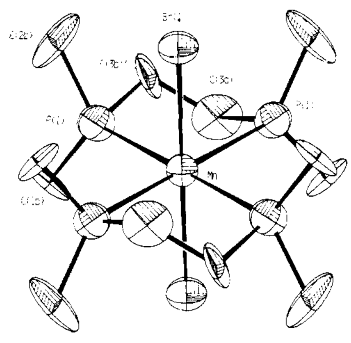

Figure 1. Structure of $MnBr_2(dmpe)_2$. Only one of the two dmpe conformations is shown, and the thermal ellipsoids of the CH_2 and CH_3 carbons clearly show the motion involved in moving from one conformation to the other, which corresponds to a twist about the equatorial 2-fold axis along the vector jointly the midpoints of the CH_2-CH_2 bond and the metal atom. Important bond lengths (Å) and angles (°): Mn-Br 2.666 (5), Mn-P 2.655 (6); Br-Mn-P 90.7 (2), P-Mn-P 78.7 (2).

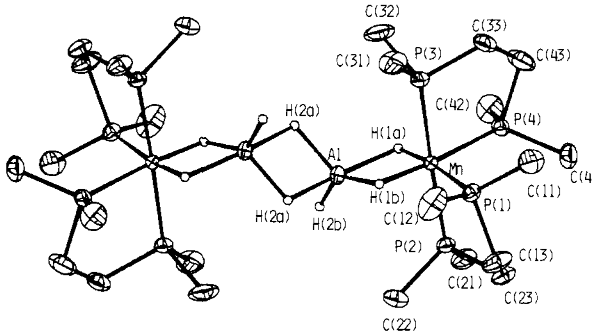

Figure 2. Structure of the centrosymmetric dimer $[(dmpe)_2MnH_2AlH_2]_2$. Important bond lengths (Å) and angles (°): Mn–P(1) 2.206(3), Mn–P(2) 2.218 (3), Mn–P(3) 2.218 (3), Mn–P(4) 2.215 (3), Mn–H(1a) 1.61 (3), Mn–H(1b) 1.63 (3), Al–H(1a) 1.81 (3), Al–H(1b) 1.81 (3). Al–H(2a) 1.80 (3), Al–H(2b) 1.51 (3), Al–H(2a) 1.64 (3); H(1b)–Mn–H(1a) 98 (1), P(1)–Mn–P(2) 84.0 (2), P(3)–Mn–P(4) 83.1 (2), H(1a)–Al–H(1b) 85(1), H(1a)–Al–H(2b) 96 (1), H(1a)–Al–H(2a) 108 (1), H(1b)–Al–H(2b) 138 (1), H(1b)–Al–H(2a) 112 (1), H(2a)–Al–H(2a*) 75 (1), H(1b)–Al–H(2a*) 111.6 (12).

Only one monomeric phosphine adduct of a manganese(II) halide has been reported previously.[3] We find that $MnBr_2$ and MnI_2 react readily with dmpe in dichloromethane to give the colorless octahedral complexes *trans*-$MnX_2(dmpe)_2$, X = Br and I. Both compounds are high-spin d^5 in toluene solution at 30 °C (μ = 5.9 μ_B) and give X-band EPR spectra in toluene at -196 °C characteristic of $^6S_{5/2}$ ground states with near-axial symmetry.[4] X-ray crystal structure[5] of $MnBr_2(dmpe)_2$ confirms the trans

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(5) Tetragonal crystals from toluene, space group $P4_2/ncm$, with a = 14.014 (2) Å, c = 12.220 (7) Å, V = 2400.2 Å^3, Z = 4; R = 0.072 for 720/1134 observed data [$F_o > 3\sigma(F_o)$] measured on a diffractometer (CAD4, MoKα radiation, λ = 0.71069 Å, $\omega/2$ scan mode). The molecule lies on a position of symmetry $2/m$. The dmpe ligands are disordered over two conformations that leave the phosporus atoms unmoved, but the methyl and methylene carbon atoms equally occupying two sets of positions (see Figure 1).

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stereochemistry (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 $MnCl_2(LL)_2$, LL = *o*-phenylenebis(dimethylphosphine).[3a]

The reaction of $MnBr_2(dmpe)_2$ with excess $LiAlH_4$ in toluene gives a yellow diamagnetic Mn^I complex of stoichiometry $Mn(AlH_4)(dmpe)_2$. Infrared stretches at 1740, 1610, and 970 cm^{-1} may be assigned to various Al–H and Mn–H–Al modes.[6] In the ^1H NMR spectrum, a Mn*H*Al 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 dmpe ^1H and $^{13}C\{^1H\}$ NMR resonances indicate a cis-octahedral arrangement about manganese, while the $^{31}P\{^1H\}$ NMR spectrum is uninformative, again due to quadrupolar effects.

In view of the rarity of transitional-metal AlH_4 complexes, we have determined the X-ray crystal structure of $Mn(AlH_4)(dmpe)_2$ (Figure 2).[7] In the solid state the compound exists as a centrosymmetric dimer, $[Mn(AlH_4)(dmpe)_2]_2$, due to the formation of a $Mn(\mu\text{-}H_2)AlH(\mu\text{-}H)_2AlH_2(\mu\text{-}H)_2Mn$ 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 $Al(\mu\text{-}H)_2Al$ 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 $Mn(\mu\text{-}H)_2Al$ 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 AlH_4^- complex to be structurally determined, other complexes containing M–H–Al bridges have been examined crystallographically.[8] The structure of $[Ta(AlH_2(OCH_2CH_2OMe)_2)(dmpe)_2]_2$[8d] is similar to the manganese molecule described here, but as is often the case,[8b–e] the hydrogen atoms were not located.

Alkylation of $MnBr_2(dmpe)_2$ with $MgMe_2$ in diethyl ether gives red *trans*-$MnMe_2(dmpe)_2$. This complex is low spin ($\mu = 2.4\ \mu_B$); evidently, the stronger ligand field strength of alkyls relative to halides is sufficient to effect spin pairing. This is substantiated by the X-ray crystal structure,[9] which shows that the Mn–P distances are ca 0.4 Å shorter than in *trans*-$MnBr_2(dmpe)_2$.

Alkylation of $MnBr_2(dmpe)_2$ with $MgEt_2$ in diethyl ether gives the yellow diamagnetic Mn^I complex *trans*-$MnH(CH_2{=}CH_2)(dmpe)_2$ presumably by β-hydride transfer in an intermediate ethyl compound. The NMR parameters are consistent with a trans-octahedral structure, 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.[10]

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Registry No. *trans*-$MnBr_2(dmpe)_2$, 87450-48-4; *trans*-$MnI_2(dmpe)_2$, 87450-51-9; $[Mn(AlH_4)(dmpe)_2]_2$, 87450-49-5; *trans*-$MnMe_2(dmpe)_2$, 87450-50-8; *trans*-$MnH(CH_2{=}CH_2)(dmpe)_2$, 87450-52-0.

Supplementary Material Available: Atom coordinates, anisotropic temperature factors, bond lengths, and bond angles for $MnBr_2(dmpe)_2$ and $[Mn(AlH_4)(dmpe)_2]_2$ (5 pages). Ordering information is given on any current masthead page.

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[9] Monoclinic, crystals from light petroleum, space group $P2_1/n$, with a = 9.576 Å, (2) Å, b = 12.642 Å, (3) Å, c = 8.953 (2) Å, β = 90.13 (2)°, V = 1083.8 Å^3, Z = 2, R = 0.12 for 1234/1907 observed data. Refinement has been hindered due to severe disorder of the dmpe ligands, and the results must be considered preliminary. In spite of the problems, the centrosymmetric trans structure is well-defined, and we consider the Mn–P and Mn–C distances of 2.241 (5)–2.251 (4) and 2.20 (2) Å to be reliable.

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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,[1,2] 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,[2] 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.

(1)

Vinylcyclopropanols are readily available from saturated ketones by a straightforward process. Reacting the ketones with cyclopropyldiphenylsulfonium fluoroborate and powdered potassium hydroxide in Me_2SO at room temperature produces oxaspiropentanes in virtually quantitative yield.[3] Extraction of the Me_2SO solution with pentane followed by exposure of the oxaspiropentane solution to lithium diethylamide generates the vinylcyclopropanol in 70–90% isolated yield as shown in Scheme I for cyclopentanone.[3,4] Chemoselective addition of an electrophile to the double bond of **1** should initiate ring expansion to the cyclobutanone.[5–7] Since secosulfenylation[8] and secobromination[9] (a

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