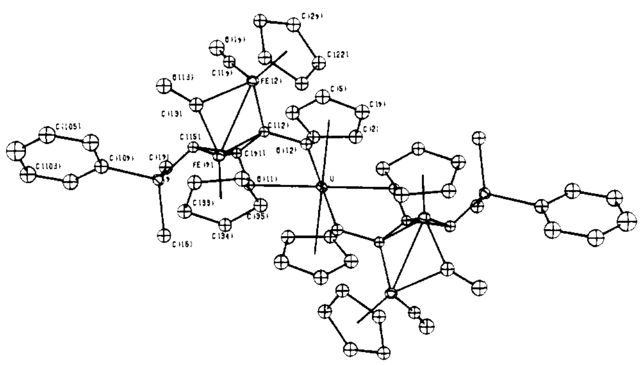
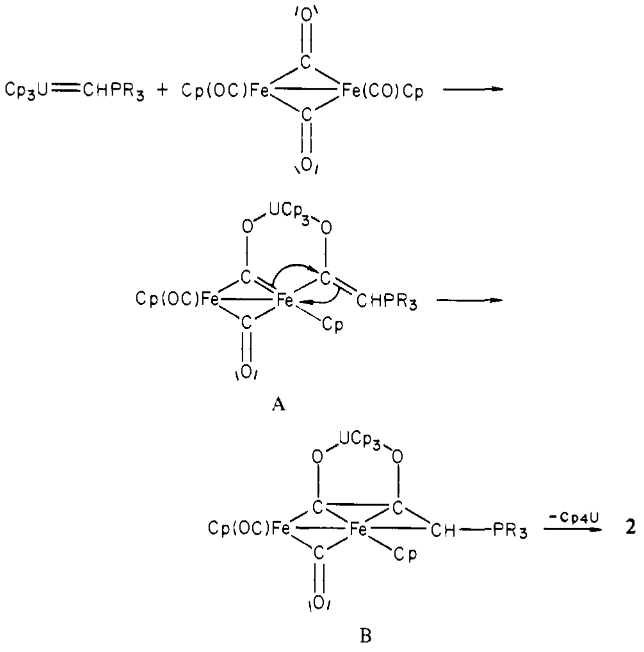
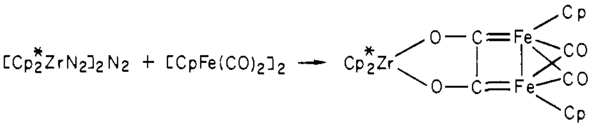


Figure 1. Labeled, perspective ORTEP view of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$.

Scheme I



Carbon monoxide coupling in early transition metal carbonyls is unusual. The single other well-documented example is the recently reported reaction (eq 3),[21] which also involves carbonyl coupling in $[CpFe(CO)_2]_2$; however, important differences exist between **2** and **4**. Formation of **2** (eq 1) involves the formation of two new C–C multiple bonds to produce an $\eta^1{:}\eta^3$-allyl. Uranium(IV) is present at the beginning and end of the reaction. In contrast, in **4** one new C–C single bond has formed, Zr(II) has been oxidized to Zr(IV), and **4** is a Fischer type dicarbene complex. The fact that CO coupling can produce two dissimilar products from the same metal carbonyl indicates that direct CO coupling is a versatile reaction pathway.

 (3)

4

$Cp^* = (CH_3)_5C_5^-$

Acknowledgment. The support of this work by the National Science Foundation, Grant CHE-8210244 to J.W.G. and R.E.C., is gratefully acknowledged.

Supplementary Material Available: Table I, nuclear magnetic resonance data; Table II, infrared spectral data; Table III, summary of crystal data; Table IVa, interatomic distances of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table IVb, interatomic distances of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table Va, bond angles of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table Vb, bond angles of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table VIa, positional and thermal parameters for $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table VIb, positional and thermal parameters for $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table VIIa, listing of $10|F_o|$ vs. $10|F_c|$ of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table VIIb, listing of $10|F_o|$ vs. $10|F_c|$ of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$ (37 pages). Ordering information is given on any current masthead page.

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[20] Lukehart, C. M.; Srinivasan, K. *Organometallics* **1982**, *1*, 1247–1249.

[21] Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715.

Coupling of Alkenes with Fischer-Type Alkylidene Complexes of Iron

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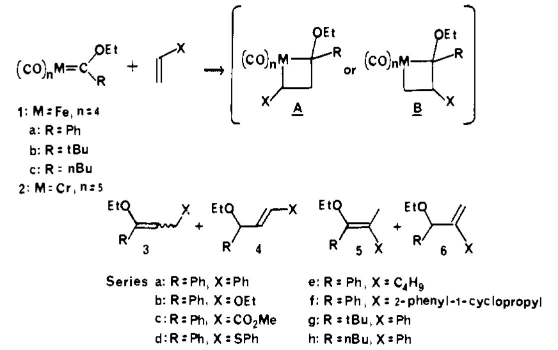
Received June 27, 1983

A general method of preparation of (ethoxyalkylidene)tetracarbonyliron(0) complexes[1,2] (**1**) makes possible the first inquiry into their chemical reactivity.[5] In this paper, we report the generality of a new carbon–carbon coupling reaction of functionalized alkenes with **1a–c**. The reaction proceeds with high regioselectivity, and we report preliminary experiments that probe the nature of the intermediates. It was demonstrated that the chromium analogues (**2**) react with polarized alkenes (acrylates, vinyl ethers) to generate cyclopropanes and alkene metathesis products, processes that can be written via metallacyclobutanes (A and B).[6] Rearrangement to coupling products **3** and **4** (from **A**) and **5** and **6** (from **B**) can also be written, but has hitherto not been observed with Fischer-type alkylidene complexes.[7]



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[1] Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099–4101.

[2] Complexes of type **1** have been characterized in special cases;[3,4] we are unaware of examples of their chemical reactivity.

[3] (a) Fischer, E. O.; Beck, H.-J.; Krieter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162–172. (b) Fischer, E. O.; Beck, H.-J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72–74.

[4] Condor, H. L.; Darensbourg, M. Y. *Inorg. Chem.* **1974**, *13*, 506–511.

[5] A recent paper has predicted structural and reactivity parameters for **1** (and for the better-studied chromium analogues of **1**) through calculations: Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426–434.

[6] For reviews, see: (a) Fischer, E. O.; Kiener, V. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (b) Cardin, D. J.; Cetinkaya, B.; Doyle, M. T.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545–574. (c) Brown, F. J. *Prog. Inorg. Chem.* **1981**, *27*, 1–122. (d) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651.

[7] No *functionalized* alkene has been reported to give products such as **3–6** with alkylidene–metal complexes of any sort. However, a few isolated examples have been noted with simple alkenes. The coupling of alkylidene–tantalum and –niobium complexes with styrene and *tert*-butylethylene to produce homologous alkenes has been observed: McLain, S. M.; Wood, C. D.; Shrock, R. R. *J. Am. Chem. Soc.* **1977**, *95*, 3519–3520. The alkylidene complexes of niobium and tantalum complexes show polarization of the alkylidene carbon opposite of that of the Fischer-type alkylidene complexes, and the pathways may be quite different. Shrock et al. postulate an intermediate metallacyclobutane and rearrangement to the alkene, with regioselectivity controlled by the polarization in the alkylidene complex.

Table I. Reaction of Complexes 1 with Alkenes

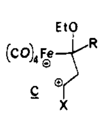
entry	complex	alkene	product ratio 3/4 (yield)[a]
1	1a	CH_2=CHPh	0:100 (60%)[b] [53:47 (62%)][c]
2	1a	CH_2=CHOEt	100:0 (76%)[b] (68%)[c] (76%)[d,e]
3	1a	CH_2=CHCO$_2$Me	0:100 (61%)[b] (65%)[c]
4	1a	CH_2=CHSPh	57:43 (75%)[c]
5	1a	CH_2=CHC$_4$H$_9$	100:0 (56%)[e]
6	1b	CH_2=CHPh	0:100 (43%)[e]
7	1c	CH_2=CHPh	0:100 (29%)[b]
8	1a	CH_2=CHCH(CHPh)CH_2	100:0 (61%)[b]

[a] The yields are based on the weight of the mixture 3 + 4 after flash chromatography or short-path distillation. [b] The complex (typically 1 mmol) was heated at 50 °C for 1 h with 3-5 mL of alkene at 55 psi of CO. [c] The complex (1 mmol), THF (1 mL), and the alkene (0.5 mL) were heated together at 50 °C for 1-2 h under argon. [d] Conditions as in *b* except at 650 psi CO. [e] Conditions as in *b* except a reaction time of 4 h. [f] The starting alkene and the product (3f) are mixtures of cis and trans isomers about the cyclopropyl ring.

Table I displays the results with **1a** and six alkenes as well as **1b** and **1c** with styrene.[8] Without exception, the primary products (**3** and **4**) arise from coupling of the unsubstituted end of the alkene with the alkylidene carbon. Careful analysis by GLPC and NMR failed to detect isomers **5**, **6** or **7** in any case. Preliminary tests of changes in the medium, concentration of alkene, and CO pressure show small effects on rate of conversion of **1**, the yields of **3** + **4**, and the ratio **3**/**4**. Exceptions are **1a** with styrene, where the ratio **3a**/**4a** changed with the reaction conditions (entry 1) and with 1-hexene, where only decomposition products of **1a** were obtained in the absence of CO (compare entry 5). Even at 650 psi of CO, reaction is complete within 4 h at 50 °C (entry 2). Careful variation of CO pressure in partial reaction of CH_2=CHCO$_2$Et with **1a** (42 °C, 1.0 h) showed ca. 25% decrease in overall rate over the range 10–50 psi (72% conversion at 10 psi; 68% at 30 psi; 57% at 50 psi).

The approximate relative reactivity of the alkenes was determined by three competition experiments, where 1 mmol of **1a** was allowed to react with pairs of alkenes in excess (10 mmol each) in THF at 50 °C. After complete conversion of **1a**, the ratios of coupled products (**3** and **4**) were determined by GLPC and ^{1}H NMR analysis (Table II). The data make clear that the order of reactivity is CH_2=CHPh > CH_2=CHCO$_2$Me > CH_2=CHOEt and that the electronic effect of the substitutents on rates is not large (factor of 4 comparing phenyl and ethoxy substituents).

The mechanism of this reaction bears further study, but at this stage several potential intermediates appear unlikely. Formation of the critical C–C bond by a polar mechanism through an intermediate (or transition state) such as C is inconsistent with the regioselectivity of the coupling (methyl acrylate would be expected to react with orientation the reverse of ethyl vinyl ether) and the relative rates (CH_2=CHOEt is expected to be fast). By parallel arguments, an intermediate with opposite polarization (D) is not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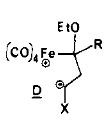
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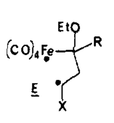
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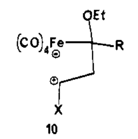
reasonable (styrene faster than methyl acrylate); such an intermediate would also imply an unexpected polarization for **1a** (however, see ref 5). A diradical pathway fits the relative rate data[9] but is less attractive in view of the coupling of a vinylcyclopropane *without* rearrangement (entry 8).[10] We favor the metallacyclobutane **8** as the product-determining intermediate,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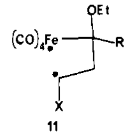
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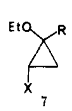
although it is not yet required by the data. The regioselectivity might then depend primarily on steric effects, leading to **8** with the less hindered end of the alkene forming the shorter bond to the alkylidene carbon.[11] β-Hydride elimination (to give **9**, **10**,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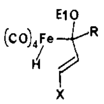
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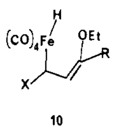
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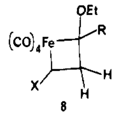
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or the η^3-allyl analogue) and reductive elimination would produce structures **3** and **4**.[12]

An alternative possibility is equilibration of regioisomeric metallacyclobutanes via reductive elimination (e.g., of **8**) to give cyclopropanes such as **7**, followed by ring opening (back to **8** or a regioisomer).[13] We prepared[14] **7** and subjected it to conditions

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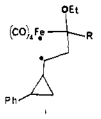
[8] Experiments were conducted under argon in THF solution with 3-5 mol equiv of alkene or under 55 psi of CO with 30–50 mol equiv of alkene and no other solvent. For the reactions under argon, the mixture of **1** (typically 1.0 mmol), alkene (0.5 mL), and THF (1.0 mL) was heated at 50 °C until TLC analysis of an aliquot indicated complete conversion of **1**. The solution was then cooled to 25 °C and concentrated by careful rotary evaporation. The residue was purified by chromatography on silica gel, with mixtures of ether in hexane, or by short path distillation. For reactions under CO pressure, a heavy-walled glass tube with a cap fitted with a pressure gauge and CO inlet was employed ("Griffen-Worden" vessel, Kontes No. K-767100, borosilicate). A solution of **1** (1.0 mmol) in the alkene (3–5 mL) was transferred to the pressure vessel, which was previously flushed with CO. The vessel was pressurized with CO and then heated at 50 °C. The reaction was run several times for each example, interrupting it at various times to establish minimal reaction times for complete conversion. After the reaction was complete, the vessel was cooled, the CO was vented, and the products were isolated as before.

[9] The substituent effects on relative rates in free radical polymerization of monosubstituted alkenes are roughly parallel with the effects observed here. See: (a) Starks, C. M. "Free Radical Telomerization"; Academic Press: New York, 1974; pp 35–42. (b) Mayo, F. R.; Walling, C. *Chem. Rev.* **1950**, *46*, 191.

[10] Following a process involving radical intermediates such as E, a vinylcyclopropane would produce a cyclopropylcarbinyl radical (i). Fast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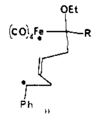
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rearrangement to an allylcarbinyl radical (ii) is expected, and ring-opened products should result. The rearrangement for the parent cyclopropylcarbinyl radical shows a rate constant $k = 1.3 \times 10^8\ s^{-1}$; see: Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

[11] In the reactions of substituted alkynes with the chromium complex **2**, the regioselectivity is again apparently independent of the electronic effect of the substituents and appears to be dominated by steric factors. See: (a) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1981**, *209*, C4. (b) Dötz, K. H.; Pruskil, I.; Mühlemeier, J. *Chem. Ber.* **1982**, *115*, 1278. (c) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (d) Wulff, W. D.; Tang, T. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, **103**, 7677–7678. (e) Dötz, K. H.; Dietz, R.; von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033–2038. (f) Dötz, K. H.; Dietz, R. *Ibid.* **1977**, *110*, 1555–1563. (g) Dötz, K. H.; Mühlemeir, J.; Schuber, U.; Orama, I. *J. Organomet. Chem.* **1983**, *247*, 187–201.

[12] A similar fragmentation of a nickelacyclobutane is attributed to R. Grubbs in: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organo-transition Metal Chemistry"; University Science Books: Mill Valley, CA, 1981; p 517. The formation of propenylbenzenes during thermolysis of a 2-phenyl-1-platinacyclobutane has also been observed: Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *Chem. Commun.* **1976**, 626–627. Reaction of an (η^3-allyl)bis(η^5-cyclopentadienyl)molybdenum cation complex with sodium borohydride produces a metallacyclobutane by addition of hydride at C-2 of the allyl ligand. While it is implied that the reaction proceeds by direct nucleophilic addition to the allyl ligand, the process can also be written as an example of the reverse (**9** → **8**) of the process reported here, through initial addition of hydride to the metal. See: Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131.

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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(13) Metallacycles have been isolated by insertion of a metal into a three-membered ring: (a) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233–4236. (b) Rajaram, J.; Ibers, J. A. *Ibid.* **1978**, *100*, 829–838. (c) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, **152**, C42–C44. (d) Al-Essa, R. J. Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *Ibid.* **1978**, *150*, 295–307. (e) Brown, D. B.; Viens, V. A. *Ibid.* **1977**, **142**, 110–121. (f) Johnson, B. F. G.; Lewis, J.; Tam, S. W. *Ibid.* **1976**, *101*, 4201–4211. Direct rearrangement of 2-carbomethoxy-1-methoxy-2-phenylcyclopropane to 4 (R = Ph, X = CO_2Me) catalyzed by Pt(II) and Ru(II) has been observed: Doyle, M. P.; Leusen, D. V. *J. Am. Chem. Soc.* **1981**, *103*, 5917–5919.

(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.

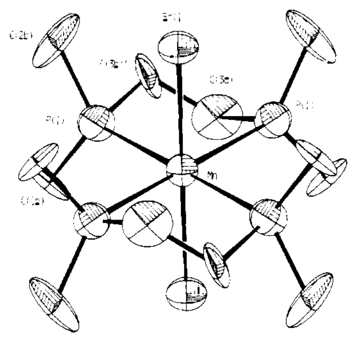

Figure 1. Structure of $MnBr_2(dmpe)_2$. Only one of the two dmpe conformations is shown, and the thermal ellipsoids of the CH_2 and CH_3 carbons clearly show the motion involved in moving from one conformation to the other, which corresponds to a twist about the equatorial 2-fold axis along the vector 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).

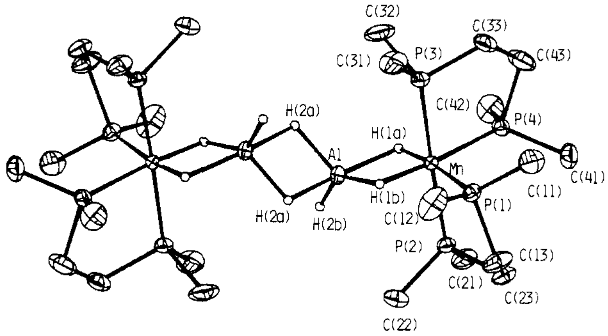

Figure 2. Structure of the centrosymmetric dimer $[(dmpe)_2MnH_2AlH_2]_2$. Important bond lengths (Å) and angles (°): Mn–P(1) 2.206(3), Mn–P(2) 2.218 (3), Mn–P(3) 2.218 (3), Mn–P(4) 2.215 (3), Mn–H(1a) 1.61 (3), Mn–H(1b) 1.63 (3), Al–H(1a) 1.81 (3), Al–H(1b) 1.81 (3). Al–H(2a) 1.80 (3), Al–H(2b) 1.51 (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 ($\mu = 5.9\ \mu_B$) 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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(1) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293.

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(3) (a) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126–3140. However, see: (b) McAuliffe, C. A. *J. Organomet. Chem.* **1982**, *228*, 255–264 and references therein.

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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, ω/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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