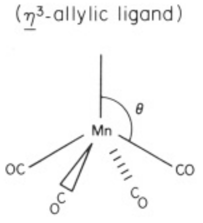
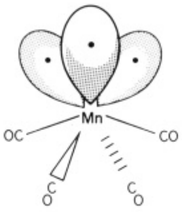
complexes so facilely. We would like to suggest that similar analogies might be useful in explaining otherwise unique or esoteric reactions of organometallic compounds. By using this formalism, one can predict several related reactions of various classes of metalla-β-diketonate complexes or other types of complexes which contain some degree of metal–carbon multiple bonding to adjacent ligands. A general *formal* representation of η^n ligands in an all-σ description rather than as a π-delocalized description may lead to a better understanding of how such ligands are formed, particularly when 18-electron metal moieties are involved.

Another interesting observation is evident from the molecular structure of anion **5**, where M is *cis*-$(OC)_4Mn$.[2] The $Mn(CO)_4$ moiety now has a slight square-pyramidal distortion where the axial OC–Mn–CO angle of 168° is now bent *away from* the η^3-allylic ligand. This gives a θ angle[7] and 96°, as shown in **8**. Although this angle does not have the preferred θ value of ca. 105°,[7] the distortion is in the correct direction for the $Mn(CO)_4$ moiety to attain a threefold set of three acceptor fragment orbitals.[7] As shown in **9**, this neutral, d^7 $Mn(CO)_4$ moiety is then quite analogous to a neutral sp^3-methine radical.



8



9

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Registry No. 1, 73426-86-5; **2**, 82621-98-5.

Grignard-Type Carbonyl Addition of Allyl Unit with $MnCl_2$–$LiAlH_4$ Reagent

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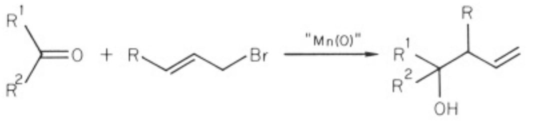
Summary: The manganese reagent derived from equimolar amounts of $MnCl_2$ and $LiAlH_4$ is found to attain carbonyl addition of allylic bromides with characteristic stereoselectivities.

Manganese is one of most promising marine metallic resources for the future.[1] Because of the salient features of manganese species of high oxidation state,[2] the metal has been widely used for oxidation of organic compounds. The lower valent manganese species, on the other hand, remained unutilized possibly due to the instability of Mn(I) species[3] and inactivity of metallic Mn.[4] Herewith we report that manganese(II) chloride is readily reduced with lithium aluminum hydride and the resulting manganese reagent is capable of Grignard-type reaction (eq 1).

$$MnCl_2 + LiAlH_4 \xrightarrow[\text{THF}]{0\ °C} \text{“Mn(0)”} + H_2 \qquad (1)$$

Anhydrous manganese(II) chloride[5] suspended in tetrahydrofuran (THF) was reduced with an equimolar amount of lithium aluminum hydride at 0 °C. The initial pink color of the reaction mixture turned black. Although details of the resulting species are not at hand, a brief note by Rice,[6] who records that the manganese(II) ion is reduced to Mn(0) by aluminum hydride or lithium aluminum hydride, is informative. Thus, we call it "Mn(0)" reagent.[7] When the reagent was treated with allyl bromide and then with aldehydes or ketones, the allyl unit was effectively added to the carbonyl groups of these compounds (eq 2). Our results are summarized in Table I.



(2)

Characteristic features of the allyl addition by the "Mn(0)" reagent are as follows. (1) Both aldehydes and ketones give corresponding adducts in good yields. (2) α,β-Unsaturated aldehydes and ketones undergo 1,2 addition (runs 10, 11, 12, and 17). (3) With crotyl bromide carbonyl addition takes place at the γ-position exclusively, and the aldehyde adducts are in general erythro–threo mixture (runs 13, 14, 15, 16, and 17).[8] (4) α-Erythro induction[9,11] (run 7) was moderate. (5) Addition to 4-*tert*-butylcyclohexanone occurs predominantly from the equatorial direction. Particularly remarkably high selectivity is observed for crotyl addition, and hereby the axial alcohol[12] is produced almost exclusively in sharp contrast to the corresponding Grignard reagent.[12,13] (6) Reaction of prenyl bromide was less effective than allyl or crotyl

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[1] Cronan, D. S. "Underwater Minerals"; Academic Press: London, 1980; p 362. Mizuno, A. *Kagaku-no-Ryoiki*, **1982**, *36*, 110–118 and references cited therein.

[2] House, H. O. "Modern Synthetic Reactions"; Benjamin, W. A.: Menlo Park, CA, 1972; pp 257–291.

[3] Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. Some Mn(–I) complexes stabilized by carbonyls have found synthetic applications recently. For example: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. See also: Marsi, M.; Gladysz, J. A. *Tetrahedron Lett.* **1982**, *23*, 631 and references cited therein.

[4] Reduction by means of manganese powder: Battaglia, L. P.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Organomet. Chem.* **1981**, *209*, C7–C9. Synthetic application of reactive manganese metal: Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *Tetrahedron Lett.* **1981**, *21*, 3861–3865.

[5] Dehydration of commercially available manganese(II) chloride–water (1/4) was effected with thionyl chloride (cf. Pray, A. R. *Inorg. Synth.* **1954**, *5*, 153–156).

[6] Rice, M. J. *Nucl. Sci. Abstr.* **1956**, *10*, No. 1641. Gmelin, L. "Handbuch der anorganischen Chemie, Mn, Teil C5, Halogenverbindungen"; Verlag Chemie: Weinheim, 1978; p29.

[7] The reagent generated from 1:1 mixture of $MnCl_2$ and $LiAlH_4$ gave the best results in the reaction. When smaller or larger amounts of $LiAlH_4$ were used, the yields of the adducts were lower. For example, the reagent generated from $MnCl_2$–$LiAlH_4$ (2:1) gave the adduct of run 1 (Table I) in 75% yield. When the reagent from $MnCl_2$–$LiAlH_4$ (4:1) was used for the same reaciton, 1,2-diphenylethane-1,2-diol was produced in 35% yield. In the case of $MnCl_2$–$LiAlH_4$ (1:2), benzyl alcohol was the major product.

[8] The results surprisingly contrast with those of chromium (threo selective)[9] and tin (erythro selective).[10]

[9] Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *21*, 1037–1040. Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561–568. See also: Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1981**, *22*, 2895–2899. Sato, F.; Iida, K.; Iijima, S.; Moriya, H.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1140–1141.

[10] Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548–4550.

[11] Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett.* **1978**, 1685–1689.

[12] Cherest, M. *Tetrahedron* **1980**, *36*, 1593–1598. Selective equatorial attack is realized by alternative methods. See: ref 9 and Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919–923.

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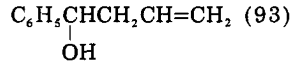
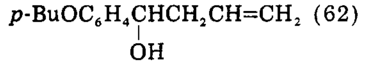
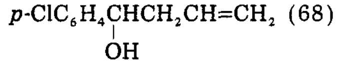
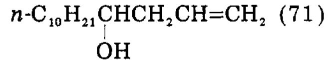
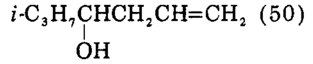
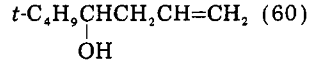
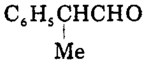
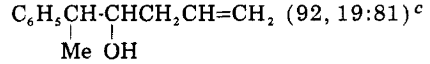
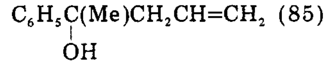
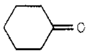
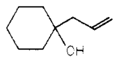
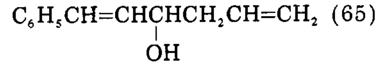
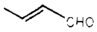
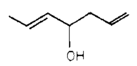
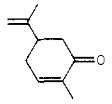
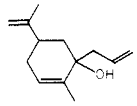
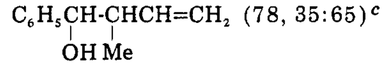
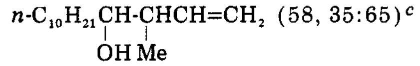
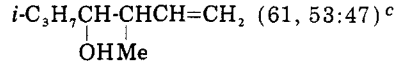
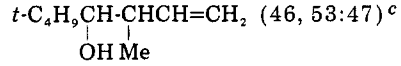
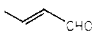
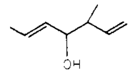
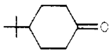
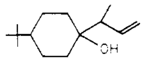
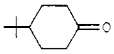
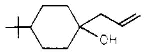
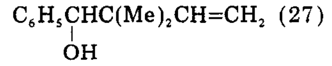
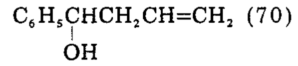
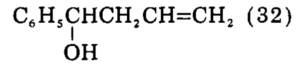
Table I. Carbonyl Addition of the Allylic Unit by "Mn(0)" Reagent

run	aldehyde or ketone	allylic halide[a]	product (% yield,[b] ratio)
1	C_6H_5CHO	AB	 $C_6H_5\underset{OH}{C}HCH_2CH=CH_2$ (93)
2	p-$BuOC_6H_4CHO$	AB	 p-$BuOC_6H_4\underset{OH}{C}HCH_2CH=CH_2$ (62)
3	p-ClC_6H_4CHO	AB	 p-$ClC_6H_4\underset{OH}{C}HCH_2CH=CH_2$ (68)
4	n-$C_{10}H_{21}CHO$	AB	 n-$C_{10}H_{21}\underset{OH}{C}HCH_2CH=CH_2$ (71)
5	i-C_3H_7CHO	AB	 i-$C_3H_7\underset{OH}{C}HCH_2CH=CH_2$ (50)
6	t-C_4H_9CHO	AB	 t-$C_4H_9\underset{OH}{C}HCH_2CH=CH_2$ (60)
7	 $C_6H_5\underset{Me}{C}HCHO$	AB	 $C_6H_5\underset{Me}{C}H\text{-}\underset{OH}{C}HCH_2CH=CH_2$ (92, 19:81)[c]
8	C_6H_5COMe	AB	 $C_6H_5\underset{OH}{C}(Me)CH_2CH=CH_2$ (85)
9		AB	 (81)
10	$C_6H_5CH=CHCHO$	AB	 $C_6H_5CH=CH\underset{OH}{C}HCH_2CH=CH_2$ (65)
11		AB	 (58)
12		AB	 (49)
13	C_6H_5CHO	CB	 $C_6H_5\underset{OH}{C}H\text{-}\underset{Me}{C}HCH=CH_2$ (78, 35:65)[c]
14	n-$C_{10}H_{21}CHO$	CB	 n-$C_{10}H_{21}\underset{OH}{C}H\text{-}\underset{Me}{C}HCH=CH_2$ (58, 35:65)[c]
15	i-C_3H_7CHO	CB	 i-$C_3H_7\underset{OH}{C}H\text{-}\underset{Me}{C}HCH=CH_2$ (61, 53:47)[c]
16	t-C_4H_9CHO	CB	 t-$C_4H_9\underset{OH}{C}H\text{-}\underset{Me}{C}HCH=CH_2$ (46, 53:47)[c]
17		CB	 (56, 30:70)[c]
18		CB	 (100, >99:1)[d]
19		AB	 (82, 69:31)[d]
20	C_6H_5CHO	PB	 $C_6H_5\underset{OH}{C}HC(Me)_2CH=CH_2$ (27)
21	C_6H_5CHO	AP	 $C_6H_5\underset{OH}{C}HCH_2CH=CH_2$ (70)
22	C_6H_5CHO	AC	 $C_6H_5\underset{OH}{C}HCH_2CH=CH_2$ (32)

[a] AB = allyl bromide, CB = crotyl bromide, PB = prenyl bromide, AP = allyl diethyl phosphate, and AC = allyl chloride. [b] Isolated yield after purification by column chromatography. [c] The ratio of threo:erythro. Cf. ref 9. [d] The ratio of axial alcohol:equatorial alcohol. See ref 9.

bromide (run 20). (7) Allyl phosphate and chloride can be used in place of the bromide (runs 21 and 22).[14] Butyl or methyl iodide did not give the corresponding adduct.

(8) Since details of the "Mn(0)" reagent are unclear, the reagent usually employed was twice the molar amount of allyl halides. Although the stoichiometric amount of the

reagent and allyl halides should be sufficient for the reaction, a little excess amount of halides is used for the sake of effective addition.

A typical experimental procedure is as follows. Lithium aluminum hydride (0.152 g, 4.0 mmol)[15] was added portionwise to a THF (10 mL) suspension of anhydrous manganese(II) chloride (0.50 g, 4.0 mmol) at 0 °C under an argon atmosphere. Spontaneous hydrogen evolution was observed, and a black fine suspension was produced. After the mixture was stirred at 0 °C for 30 min and at room temperature for 1 h, allyl bromide (0.174 mL, 2.0 mmol) dissolved in THF (5 mL) was added at room temperature, and the reaction mixture was stirred for 1.5 h. Benzaldehyde (0.143 mL, 1.41 mmol) in THF (5 mL) was then added to the reaction mixture, and the whole was stirred for 1.5 h at room temperature. Water (ca. 20 mL) was added, and the organic layer was extracted with ether. The ethereal layer was dried over anhydrous magnesium sulfate and concentrated. Chromatography of the residue on silica gel gave 1-phenyl-3-buten-1-ol (0.194 g, 93% yield).

Since chemoselective carbonyl addition is also observed for alkylmanganese iodides which are generated by metal exchange of alkyllithium with manganese(II) iodide,[16] C–C bond formation with manganese reagents will find expanding application. Synthetic studies dealing with low-valent manganese reagents are currently in progress in our laboratories.

Registry No. C_6H_5CHO, 75-07-0; *p*-$BuOC_6H_4CHO$, 5736-88-9; *p*-ClC_6H_4CHO, 104-88-1; *n*-$C_{10}H_{21}CHO$, 112-44-7; *i*-C_3H_7CHO, 78-84-2; *t*-C_4H_9CHO, 630-19-3; $C_6H_5CH(Me)CHO$, 93-53-8; C_6H_5COMe, 98-86-2; $C_6H_5CH{=}CHCHO$, 104-55-2; (*E*)-$CH_3CH{=}CHCHO$, 123-73-9; $C_6H_5CH(OH)CH_2CH{=}CH_2$, 936-58-3; *p*-$BuOC_6H_4CH(OH)CH_2CH{=}CH_2$, 82431-49-0; *p*-$ClC_6H_4CH(OH)CH_2CH{=}CH_2$, 14506-33-3; *n*-$C_{10}H_{21}CH(OH)CH_2CH{=}CH_2$, 26496-21-9; *i*-$C_3H_7CH(OH)CH_2CH{=}CH_2$, 32815-70-6; *t*-$C_4H_9CH(OH)CH_2CH{=}CH_2$, 19550-89-1; $C_6H_5CH(Me)CH(OH)CH_2CH{=}CH_2$ Isomer I, 80410-52-2; $C_6H_5CH(Me)CH(OH)CH_2CH{=}CH_2$ Isomer II, 80401-09-8; $C_6H_5C(OH)(Me)CH_2CH{=}CH_2$, 4743-74-2; $C_6H_5CH{=}CHCH(OH)CH_2CH{=}CH_2$, 13891-95-7; (*E*)-$CH_3CH{=}CH{-}CH(OH)CH_2CH{=}CH_2$, 24581-03-1; $C_6H_5CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 52922-19-7; $C_6H_5CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 52922-10-8; *n*-$C_{10}H_{21}CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 82431-51-4; *n*-$C_{10}H_{21}CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 82431-52-5; *i*-$C_3H_7CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 1502-90-5; *i*-$C_3H_7CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 1502-91-6; *t*-$C_4H_9CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 1502-89-2; *t*-$C_4H_9CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 1502-88-1; $CH_3CH{=}CHCH(OH)CH(Me)CH{=}CH_2$ (*E*) Isomer I, 82468-21-1; $CH_3CH{=}CHCH(OH)CH(Me)CH{=}CH_2$ (*E*)-Isomer II, 82468-22-2; $C_6H_5CH(OH)C(Me)_2CH{=}CH_2$, 27644-02-6; $C_6H_5CH(OH)CH_2CH{=}CH_2$, 936-58-3; cyclohexanone, 108-94-1; 5-isopropenyl-2-methyl-2-cyclohexenone, 99-49-0; *p-tert*-butylcyclohexanone, 98-53-3; 1-(2-propenyl)cyclohexanol, 1123-34-8; 5-isopropenyl-2-methyl-1-(2-propenyl)-2-cyclohexenol, 82431-50-3; *cis-p-tert*-butyl-1-(1-methyl-2-propenyl)cyclohexanol, 75735-19-5; *trans-p-tert*-butyl-1-(1-methyl-2-propenyl)cyclohexanol), 75735-06-7; *cis-p-tert*-butyl-1-(2-propenyl)cyclohexanol, 42437-24-1; *trans-p-tert*-butyl-1-(2-propenyl)cyclohexanol, 42437-23-0; allyl bromide, 106-95-6; crotyl bromide, 4784-77-4; prenyl bromide, 870-63-3; allyl diethyl phosphate, 3066-75-9; allyl chloride, 107-05-1; manganese(II) chloride, 7773-01-5; manganese, 7439-96-5.

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(13) The stereochemistry in the nucleophilic addition to cyclohexanones has been discussed by Cieplak recently. According to his theory, the crotyl anion is softer than the allyl anion, and therefore equatorial attack is preferred in the crotyl addition. Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552. See also: Gaudemar, M. *Tetrahedron* **1976**, *32*, 1689–1691.

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(15) Purchased from A. G. Metalgeselschaft West Germany.

(16) Cahiez, G.; Normant, J. F. *Tetrahedron Lett.* **1977**, 3383–3384; *Bull. Soc. Chim. Fr.* **1977**, 570. Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* **1977**, 130–133. Cahiez, G. *Tetrahedron Lett.* **1981**, *22*, 1239.

Catalysis by Solvated Transition-Metal Cations. 3.[1] Novel Catalytic Transformations of Alkenes by Cationic Compounds of Molybdenum and Tungsten

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Summary: The compounds $[M(NO)_2(CH_3CN)_4](BF_4)_2$; (**2**, M = Mo; **3**, M = W) were synthesized through reactions of the corresponding metal hexacarbonyls with 2 equiv of $NOBF_4$ in acetonitrile. These compounds catalyze the polymerization, oligomerization, and rearrangement of olefins.

In previous communications,[1] we had demonstrated, using $[Pd(CH_3CN)_4](BF_4)_2$, **1**, as an example, that incipient carbonium ions may be generated by the interaction of olefins with electrophilic transition-metal centers and that such species may play an important role in transition-metal-catalyzed oligomerization, polymerization, and rearrangement of olefins. We now show, using cationic compounds of molybdenum and tungsten as examples, that the above-mentioned process is indeed quite general and with small variations is also observed for "early" transitional elements.

The compounds *cis*-$[Mo(NO)_2(CH_3CN)_4](BF_4)_2$,[2a] **2**, and *cis*-$[W(NO)_2(CH_3CN)_4](BF_4)_2$,[2b] **3**, were synthesized through the reactions of the corresponding metal hexacarbonyls with 2 equiv of $NOBF_4$ in acetonitrile (eq 1).

$$\mathrm{M(CO)_6 + 2NOBF_4 \xrightarrow[25\ ^{\circ}C]{CH_3CN} [M(NO)_2(CH_3CN)_4](BF_4)_2 + 6\ CO} \qquad (1)$$

2, M = Mo
3, M = W

Following precipitation by diethyl ether, dark green hygroscopic solids were isolated. The ^1H NMR spectra (in CD_3NO_2) of both **2** and **3** exhibited two absorptions of equal intensity at 2.65 and 2.55 ppm, respectively, which is an indication of cis configuration of NO groups around the metals. In CD_3CN, for freshly prepared solutions of both **2** and **3**, only one peak at 2.55 ppm is visible together with a peak at 1.95 ppm corresponding to uncomplexed CH_3CN, perhaps indicating the greater lability of two of the four bound CH_3CN molecules. Furthermore, when the solutions were left standing for several hours at room temperature, the peak at 2.55 ppm for both **2** and **3** disappears completely together with an increase in intensity of the peak at 1.95 ppm. Thus all four CH_3CN molecules in **2** and **3** are labile and exchange with free CH_3CN molecules (eq 2).

$$\mathrm{M(NO)_2(CH_3CN)_4{}^{2+} + 4CD_3CN \xrightarrow[25\ ^{\circ}C]{} M(NO)_2(CD_3CN)_4{}^{2+} + 4CH_3CN} \qquad (2)$$

2, M = Mo
3, M = W

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(1) For previous parts in this series, see: (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) *Organometallics* **1982**, *1*, 415.

(2) (a) $[Mo(NO)_2(CH_3CN)_4](BF_4)_2$, **2**: IR (Nujol) $\bar{\nu}(C{\equiv}N)$ 2360, 2310 cm^{-1}, $\bar{\nu}(NO)$ 1860, 1760, 1730 cm^{-1}, $\bar{\nu}(BF_4^-)$ 1200–1000 cm^{-1}. Anal. Calcd for $MoC_8H_{12}N_6O_2B_2F_8$: C, 19.5; H, 2.5. Found: C, 19.0; H, 2.4. (b) $[W(NO)_2(CH_3CN)_4](BF_4)_2$, **3**: IR (Nujol) $\bar{\nu}(C{\equiv}N)$ 2330, 2300 cm^{-1}; $\bar{\nu}(NO)$ 1860, 1820, 1770, 1730 cm^{-1}; $\bar{\nu}(BF_4^-)$ 1200–1000 cm^{-1}; conductivity (CH_3CN) slope ($\Lambda_o - \Lambda_e$ vs. $C^{1/2}$) = 355. Anal. Calcd for $WC_8H_{12}N_6O_2B_2F_8$: C, 16.4; H, 2.1. Found: C, 16.7; H, 2.1.

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