# Reaction of Electrophiles with Manganese(I) and Rhenium(I) Alkoxide Complexes: Reversible Absorption of **Atmospheric Carbon Dioxide**

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The transition metal alkoxides fac-(CO)<sub>3</sub>(P-P)MOR [where M is Mn or Re, P-P is either 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp), and R is either  $CH_3$ ,  $C_2H_5$ , or  $CF_3CH_2$  react readily at room temperature with  $CO_2$ ,  $CS_2$ , and PhNCO by insertion of these electrophiles into the metal-oxygen bond. The reactions with  $CO_2$  leading to the corresponding carbonato complexes fac-(CO)<sub>3</sub>(P-P)MOC(O)OR are of special interest; benzene solutions of the alkoxides can even absorb  $CO_2$  from the atmosphere. All the carbonato complexes release  $CO_2$  when argon is bubbled through solutions of them, regenerating the alkoxides. These equilibrium reactions make it possible to exchange the  $CO_2$  of the carbonato complexes by treatment of them with  $CS_2$  or PhNCO. Only the  $CO_2$  reaction is reversible under mild conditions. When a solution of fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub> is treated with CH<sub>3</sub>NH<sub>2</sub> followed by  $CO_2$  the metalloure than complex  $(CO)_3(dppe)MnOC(O)NHCH_3$  is formed. The X-ray crystal structure of fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub> is presented.

### Introduction

Transition metal alkoxides,  $L_nM$ -OR, are of particular interest because they undergo insertion of small molecules such as CO, CO<sub>2</sub>, CS<sub>2</sub>, and RNCO into the metal-oxygen bond:<sup>1</sup> such insertions are believed to be an early step in several catalytic reactions.<sup>2</sup> Recently, we reported<sup>3</sup> a rather simple synthesis, as well as the properties, of some octahedral manganese (and rhenium) alkoxide complexes. fac-(CO)<sub>3</sub>(dppe)MnOR, and found that CO may be inserted to give the alkoxycarbonyl complexes fac-(CO)<sub>3</sub>-

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(dppe)MnC(O)OR. Now we report the reversible insertion of  $CO_2$  and the insertion of the electronically similar molecules CS<sub>2</sub> and PhNCO into these and similar alkoxides. Insertion of  $CO_2$  into the Mn methoxide gives the carbonato complex fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub> whose crystal structure we also report here. Our reaction of the alkoxides with carbon dioxide is of particular interest because we believe it be the first reported example of reversible absorption of  $CO_2$  from the atmosphere (concentration 0.03%) by simple alkoxides of neutral mononuclear low valent transition metal carbonyl complexes.

#### **Experimental Section**

General Information. All manipulations were conducted under an argon atmosphere. Solvents were dried by distillation from appropriate reagents and were deoxygenated prior to use. All reagents were commercially available and were used without further purification unless otherwise indicated. Phenyl isocyanate was distilled under reduced pressure just before use. fac-(CO)<sub>3</sub>(dppe)MnOTs,<sup>3</sup> fac-(CO)<sub>3</sub>(dppe)ReOTs,<sup>3</sup> fac-(CO)<sub>3</sub>(dppe)-MnOCH<sub>3</sub>,<sup>3</sup> fac-(CO)<sub>3</sub>(dppe)MnOC<sub>2</sub>H<sub>5</sub>,<sup>4</sup> fac-(CO)<sub>3</sub>(dppe)ReOCH<sub>3</sub>,<sup>3</sup> and  $fac-(CO)_3(dppe)ReOC_2H_5^3$  were prepared by published procedures.

The IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR instrument. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 250.133 and 62.869 MHz, respectively, on a Brucker AC-250 FT spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation of fac-(CO)<sub>3</sub>(dppp)MnH (1).<sup>4</sup> A mixture of 1.0 g (2.564 mmol) of Mn<sub>2</sub>(CO)<sub>10</sub>, 2.115 g of dppp (5.128 mmol), and 100 mL of 1-propanol was refluxed for 6 h. After the solution was cooled, the solvent was removed on a rotary evaporator and the residue was extracted with 50 mL of benzene. Hexane was added to the solution which was then cooled. The almost white precipitate which separated was collected by filtration, washed

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with hexane, and dried under vacuum to give 2.719 g (4.922 mmol, 96%) of 1, mp 195–197 °C. IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>):  $\nu$ (C=O) 1999 (s), 1928 (s), 1902 (s). Anal. Calcd for C<sub>30</sub>H<sub>27</sub>MnO<sub>3</sub>P<sub>2</sub>: C, 65.2; H, 4.9. Found: C, 65.2; H, 4.9.

**Preparation of** fac-(CO)<sub>3</sub>(**dppp**)**MnOTs** (2).<sup>3</sup> To 0.50 g of 1 (0.905 mmol) in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> was added a slight excess of *p*-toluenesulfonic acid. After hydrogen evolution ceased, the excess acid was removed by extraction with water. The CH<sub>2</sub>Cl<sub>2</sub> was concentrated, hexane was added, and the solution was cooled. The orange microcrystals which precipitated were collected by filtration, washed with hexane, and dried under vacuum to give 2 (0.595 g, 0.823 mmol, 91%), mp 180–183 °C dec. IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=O) 2036 (s), 1969 (s), 1911 (s). Anal. Calcd for C<sub>37</sub>H<sub>33</sub>MnO<sub>6</sub>P<sub>2</sub>S: C, 61.5; H, 4.6. Found: C, 61.2; H, 4.8.

**Preparation of fac-(CO)<sub>3</sub>(dppp)MnOCH<sub>3</sub> (3).<sup>3</sup>** To 0.50 g (0.691 mmol) of the tosylate 2 suspended in 100 mL of methanol was added 1.61 mL of a 0.43 M solution of NaOCH<sub>3</sub> (0.691 mmol, 0.0373 g) freshly prepared from the reaction of Na with methanol. The solution was stirred at room temperature, and the progress of the reaction was monitored by IR spectroscopy and was complete in 6 h. The solution was evaporated to dryness, and the residue was extracted with 15 mL of benzene. The benzene solution was diluted with 30 mL of hexane and cooled. The resulting yellow microcrystals were collected by filtration, washed with hexane, and dried under vacuum to give 3 (0.342 g, 0.587 mmol, 85%), mp 112–115 °C dec. IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>):  $\nu$ (C=O) 2010 (s), 1937 (s), 1890 (s). Anal. Calcd for C<sub>31</sub>H<sub>29</sub>MnO<sub>2</sub>P<sub>2</sub>·O.5CH<sub>3</sub>-OH: C, 63.3; H, 5.3.

**Preparation of** fac-(CO)<sub>3</sub>(dppp)MnOC<sub>2</sub>H<sub>5</sub> (4). A 1.0-g (1.72-mmol) quantity of 3 was slurried with 25 mL of dry ethanol. The mixture was stirred while a slow stream of argon was bubbled through it. After 2 h the yellow solid was filtered out and washed with 5 mL of cold hexane. The filtrate was evaporated to dryness. The combined weight of 4 was 0.985 g (1.65 mmol, 96%). mp 126–129 °C dec. IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>):  $\nu$ (C=O) 2010 (s), 1936 (s), 1890 (s). Anal. Calcd for C<sub>32</sub>H<sub>31</sub>MnO<sub>4</sub>P<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH: C, 63.5; H, 5.8. Found: C, 63.4; H, 5.5.

Preparation of fac-(CO)<sub>3</sub>(dppe)MOCH<sub>2</sub>CF<sub>3</sub> (5, M = Mn; 6, M = Re). Approximately 2.5 mmol of fac-(CO)<sub>3</sub>(dppe)MOTs was slurried with 30 mL of CF<sub>3</sub>CH<sub>2</sub>OH, and the mixture was stirred at room temperature with 1 molar equiv of CF<sub>3</sub>CH<sub>2</sub>ONa (freshly prepared from the reaction of Na with  $CF_3CH_2OH$ ) for 4 h at which time the reaction was complete. The solvent was removed under vacuum, and the residue was extracted with 15 mL of benzene. On dilution of the benzene with 30 mL of hexane and cooling, the yellow manganese complex 5 and the white rhenium complex 6 crystallized. The crystals were filtered out, washed with 5 mL of cold hexane, and dried in vacuum to give 5 (77%) and 6 (71%). Data for 5: mp 130-133 °C; IR (cm<sup>-1</sup>;  $C_6H_6$ )  $\nu$ (C=O) 2014 (s), 1940 (s), 1902 (s). Anal. Calcd for C31H26F3MnO4P2: 58.5; H, 4.1. Found: C, 58.4; H, 4.2. Data for 6: mp 142-145 °C; IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>)  $\nu$ (C=O) 2018 (s), 2034 (s), 1892 (s). Anal. Calcd for C<sub>31</sub>H<sub>26</sub>F<sub>3</sub>ReO<sub>4</sub>P<sub>2</sub>: C, 48.6; H, 3.4. Found: C, 48.5; H, 3.6.

Carbon Dioxide Insertion Reactions: (a) Preparation of Alkyl Carbonato Complexes fac-(CO)<sub>3</sub>(P-P)MOC(O)OR (7, M = Mn, P-P = dppe,  $R = CH_3$ ; 8, M = Mn, P-P = dppe, R =  $C_2H_5$ ; 9, M = Mn, P-P = dppp, R =  $CH_3$ ; 10, M = Mn, P-P = dppp, R = C<sub>2</sub>H<sub>5</sub>; 11, M = Re, P-P = dppe, R = CH<sub>3</sub>; 12, M = Re, P-P = dppe,  $R = C_2H_5$ ). A stream of pure CO<sub>2</sub> was bubbled through a 0.15 M benzene solution of the alkoxides. Rapid reaction occurred, and the corresponding carbonato complexes precipitated after about 5 min. Filtration afforded about 95% of 7-12, and the remaining 5% was recovered by evaporation of the filtrate. The solids were recrystallized from  $CH_2Cl_2/C_6H_6/$ hexane (1:5:2). Data for 7: mp 157-160 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C=O) 2027 (s), 1957 (s), 1912 (s), and  $\nu$ (C=O) 1651 (m). Anal. Calcd for C<sub>31</sub>H<sub>27</sub>MnO<sub>6</sub>P<sub>2</sub>·0.75C<sub>6</sub>H<sub>6</sub>: C, 63.5; H, 4.7. Found: C, 63.8; H, 4.8. Data for 8: mp 120-123 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) v-(C=O) 2026 (s), 1956 (s), 1911 (s) and  $\nu$ (C=O) 1651 (m). Anal.

Calcd for  $C_{32}H_{29}MnO_6P_2$ ·C<sub>6</sub>H<sub>6</sub>: C, 64.7; H, 5.0. Found: C, 64.4; H, 5.2. Data for 9: mp 161–164 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C==O) 2030 (s), 1961 (s), 1906 (s) and  $\nu$ (C==O) 1666 (m). Anal. Calcd for  $C_{32}H_{29}MnO_6P_2$ : C, 61.3; H, 4.7. Found: C, 61.2; H, 4.7. Data for 10: mp 147–150 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C==O) 2029 (s), 1961 (s), 1905 (s) and  $\nu$ (C==O) 1666 (m). Anal. Calcd for  $C_{33}H_{31}$ -MnO<sub>6</sub>P<sub>2</sub>: C, 61.9; H, 4.9. Found: C, 61.8; H, 5.0. Data for 11: mp 124–126 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C==O) 2032 (s), 1952 (s) 1903 (s) and  $\nu$ (C==O) 1666 (m). Anal. Calcd for  $C_{31}H_{27}ReO_6P_2$ ·0.75C<sub>6</sub>H<sub>6</sub>: C, 53.1; H, 3.9. Found: C, 53.0; H, 3.9. Data for 12: mp 151–154 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C==O) 2032 (s), 1952 (s), 1903 (s) and  $\nu$ (C==O) 1657 (m). Anal. Calcd for  $C_{32}H_{29}ReO_6P_2$ ·0.25CH<sub>2</sub>Cl<sub>2</sub>: C, 49.7; H, 3.8. Found: C, 49.9; H, 3.8.

(b) Absorption of Pure CO<sub>2</sub> without Bubbling. In an unsuccessful attempt to obtain qualitative rate data for CO<sub>2</sub> absorption by alkoxides, solutions of them were exposed to a buret filled with CO<sub>2</sub> at room temperature using the following procedure. About 1.5 mmol of fac-(CO)<sub>3</sub>(P-P)MOR was dissolved in 5 mL of benzene and the solution placed in a 50-mL flask containing 5 mL of benzene saturated with CO<sub>2</sub>. The flask was immediately connected to a 50-mL buret filled with CO<sub>2</sub>, and stirring with a magnetic stirrer commenced. Under these conditions the absorption of CO<sub>2</sub> was so rapid that significant rate distinctions could not be made between the various alkoxides, although the Re alkoxides seemed to react marginally slower.

(c) Absorption of  $CO_2$  from Air. About 250 mL of a 0.05 M solution of the alkoxide in toluene was placed with stirring in a 300-mL crystallizing dish and the solution exposed to air with stirring. After about 5 h the manganese alkoxides were completely converted to the corresponding carbonato complexes (IR spectra) accompanied by a small amount of decomposition. Under similar conditions only a small quantity of the rhenium alkoxides were converted.

(d) Absorption of  $CO_2$  from Air by Crystalline Mn Alkoxides, fac-(CO)<sub>3</sub>(P-P)MnOR. About 0.05 g of the alkoxide was placed on a watch glass and exposed to the air for a few days. IR and NMR spectra showed the presence of some carbonato complexes.

(e) Preparation of fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>2</sub>CF<sub>3</sub>. A 0.5-g sample of the alkoxide 5 was dissolved in 50 mL of benzene, and CO<sub>2</sub> was bubbled through the solution with periodic monitoring by IR. In contrast to the non-fluorine containing Mn alkoxides, the reaction was very slow; only about 10% of the alkoxide was converted to the carbonato complex in 5 h and complete conversion required 2 days. The reversion to starting material by CO<sub>2</sub> extrusion was so rapid that in the time required to remove the solvent and examine the residue, substantial alkoxide was present. Accordingly, the carbonato complex could not be isolated or further characterized.

(f) Preparation of fac- $(CO)_3(dppe)ReOC(O)OCH_2CF_3$ . A benzene solution of the trifluoroethyl alkoxide 6 was treated with  $CO_2$  as above. The reaction was even slower than with the Mn analog (IR) and only 5% of the alkoxide was converted to the carbonato complex after 2 days. It was not further characterized.

Release of CO<sub>2</sub> from the Carbonato Complexes fac-(CO)<sub>3</sub>-(P-P)MOC(O)OR, 7-12. About 0.25 g of each of the complexes was dissolved in 100 mL of benzene, and argon was bubbled through the solution at room temperature with stirring. The course of the reaction was monitored by periodic examination by IR. The complexes were slowly converted to the corresponding alkoxides; complete conversion of the Re compounds 11 and 12 required about 2 h but complete conversion of the Mn analogs 7-10 required about 24 h.

CS<sub>2</sub> Insertion: Preparation of fac-(CO)<sub>3</sub>(dppe)MSC(S)-OR (13, M = Mn, R = CH<sub>3</sub>; 14, M = Re, R = C<sub>2</sub>H<sub>5</sub>). Carbon disulfide (25mL) was added to 0.8 mmol of fac-(CO)<sub>3</sub>(dppe)-MnOCH<sub>3</sub> and fac-(CO)<sub>3</sub>(dppe)MnOC<sub>2</sub>H<sub>5</sub> each dissolved in 15 mL of benzene. After stirring for 5 h, the solvents were removed on a rotary evaporator. The residue was recrystallized from CH<sub>2</sub>-Cl<sub>2</sub>/C<sub>6</sub>H<sub>6</sub>/hexane to yield red crystalline 13 and 14 in 81-86% yield. Data for 13: mp 130-133 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=O) 2018 (s), 1952 (s), 1909 (s) and  $\nu$ (C=S) 1435 (m). Anal. Calcd for C<sub>31</sub>H<sub>27</sub>MnO<sub>4</sub>P<sub>2</sub>S<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>: C, 61.5; H, 4.6. Found: C, 61.6; H, 4.5. Data for 14: mp 186–189 °C; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C=O) 2029 (s), 1955 (s), 1916 (s) and  $\nu$ (C=O) 1436 (m). Anal. Calcd for C<sub>31</sub>H<sub>27</sub>ReO<sub>6</sub>P<sub>2</sub>: C, 48.6; H, 3.7. Found: C, 48.2; H, 3.8.

PhNCO Insertion: Preparation of fac-(CO)<sub>3</sub>(dppe)MN-(C<sub>6</sub>H<sub>5</sub>)C(O)OCH<sub>3</sub> (15, M = Mn; 16, M = Re). To 0.8 mmol of the alkoxide in 25 mL of benzene there was added 0.8 mmol of PhNCO, and the solution was stirred for 0.5 h. The solvent was removed under vacuum, and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>6</sub>/hexane to give 15 and 16 in 88–91% yield. Data for 15: mp 122–124 °C; IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>)  $\nu$ (C=O) 2017 (s), 1944 (s), 1912 (s) and  $\nu$ (C=O) 1630 (m). Anal. Calcd for C<sub>37</sub>H<sub>32</sub>MnNO<sub>5</sub>P<sub>2</sub>·0.5C<sub>6</sub>H<sub>6</sub>: C, 66.1; H, 4.9. Found: C, 66.0; H, 4.9. Data for 16: mp 213–215 °C; IR (cm<sup>-1</sup>, C<sub>6</sub>H<sub>6</sub>)  $\nu$ (C=O) 2022 (s), 1939 (s), 1906 (s) and  $\nu$ (C=O) 1634 (m). Anal. Calcd for C<sub>37</sub>H<sub>32</sub>NO<sub>5</sub>P<sub>2</sub>Re·0.5C<sub>6</sub>H<sub>6</sub>: C, 56.0; H, 4.2. Found: C, 56.1; H, 4.5.

**Exchange Reactions of the Carbonato Complexes 7 and** 11. (a) With CS<sub>2</sub>. About 0.3 mmol of 7 and 11 was stirred with 25 mL of CS<sub>2</sub> at room temperature for 5 h. The solvent was removed, and the residue was recrystallized from  $CH_2Cl_2/C_6H_6/$ hexane to give 13 and 14 in almost quantitative yield.

(b) With PhNCO. About 0.3 mmol of PhNCO was added to 0.3 mmol of the alkoxides 7 and 11 in 25 mL of benzene and the solution stirred for 0.5 h. The solvent was removed in vacuum, and the residue was recrystallized from  $CH_2Cl_2/C_6H_6$ /hexane to give 15 and 16 in almost quantitative yield.

**Reaction with CH<sub>3</sub>NH<sub>2</sub> Followed by CO<sub>2</sub>.** Methylamine was bubbled into a benzene solution of the alkoxide fac-(CO)<sub>3</sub>-(dppe)MnOCH<sub>3</sub> (0.05 M). The solution turned brown, and after about 5 min, CO<sub>2</sub> was bubbled through the solution with cooling. The excess amine reacted with excess CO<sub>2</sub> to precipitate a white salt which was formed in the highly exothermic reaction. The solution was filtered, and the filtrate evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the mixture was filtered, and the filtrate was concentrated and then diluted with hexane and cooled. The yellow crystalline complex was collected to give a 71% yield of fac-(CO)<sub>3</sub>(dppe)MnOC(O)NHCH<sub>3</sub> (17), mp 167– 170 °C. IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C $\equiv$ O) 2023 (s), 1954 (s), 1906 (s), and  $\nu$ (C $\equiv$ O) 1609 (m). Anal. Calcd for C<sub>31</sub>H<sub>28</sub>MnNO<sub>5</sub>-P<sub>2</sub>-0.75C<sub>6</sub>H<sub>6</sub>: C, 63.6; H, 4.9. Found: C, 63.5; H, 5.0.

Single Crystal X-ray Diffraction Study of fac-(CO)<sub>3</sub>-(dppe)MnOC(O)OCH<sub>3</sub> (7). A pale-yellow platelike crystal of 7 was mounted on a glass fiber with epoxy cement and transferred to a Siemens R3m/V four-circle diffractometer for characterization and data collection.

Unit cell parameters were determined from the angular settings of 25 well-centered reflections  $(25^{\circ} < 2\theta < 36^{\circ})$  and were as follows: a = 11.262(1) Å, b = 15.792(2) Å, c = 19.460(2) Å,  $\beta =$ 103.606(8)°, and V = 3363 Å<sup>3</sup>. Axial photographs and a limited search through the octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group  $P2_1/c$ .

One quadrant of data  $(\pm h, +k, +l)$  was collected in the  $2\theta$ - $\theta$  scan mode with  $2\theta$  ranging from 4.0 to 55.0°. Scan speeds were varied from 4.0 to 8.0/min. A total of 8278 reflections were measured and corrected for Lorentz and polarization effects, but not for absorption. The minimum and maximum drift corrections (based on a set of 3 standards measured for every 37 reflections) were 0.9961 and 1.0238, respectively. Data processing yielded 7762 unique reflections of which 4715 had  $F > 3\sigma(F)$  with R(int) = 0.0237 for the averaging of equivalent reflections.

The structure was successfully solved by heavy-atom methods (XS:PATT, SHELXTL-PLUS Program package<sup>5</sup>) in the monoclinic space group  $P2_1/c$  (No. 14) and refined by full-matrix least squares. The non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were al-

Table I. Crystallographic Data for fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub>·C<sub>6</sub>H<sub>6</sub> (7)

$C_{37}H_{33}MnO_6P_2$	fw = 690.58
cryst syst: monoclinic	space group: $P2_1/c$ (No. 14)
a = 11.262(1) Å	T = 294 K
b = 15.792(2) Å	radiation ( $\lambda$ ): Mo K $\alpha$ (0.710 73 Å)
c = 19.460(2) Å	$\rho_{calcd} = 1.36$ g cm <sup>-3</sup>
$\beta = 103.606(8)^{\circ}$	$\mu = 5.13$ cm <sup>-1</sup>
$\beta = 103.006(8)^{-3}$	$\mu = 5.13 \text{ cm}^{-1}$
$V = 3363.7(6) \text{ Å}^{3}$	P(F) = 0.0677
Z = 4	$R_{\rm w}(F) = 0.0601$

lowed to ride on their respective carbons (C-H = 0.96 Å, U(H) = 0.08), an extinction correction was made, and a weighting scheme based on  $\sigma(F)$  was employed. The benzene solvent molecule in the lattice was refined as a rigid regular hexagon with H atoms at calculated positions. The final residuals were R(F) = 0.0677 and  $R_w(F) = 0.0601$  where  $R(F) = \sum (|F_o| - |F_c|)/\sum |F_o|$  and  $R(F) = [\sum (w||F_o| - |F_c||^2)/\sum (w|F_o|^2]^{1/2}$ . The goodness-of-fit was 1.24. In the refinement the quantity minimized was  $\sum w(F_o - F_o)^2$ . The weighting scheme used in the final refinement was  $w = [\sigma^2(F) + |g|F^2]^{-1}$ , where g = 0.000399. Crystal data are given in Table I, and atomic coordinates and equivalent isotropic displacement parameters are given in Table II. Selected bond distances and bond angles are presented in Table III.

#### **Results and Discussion**

Alkyl Carbonato Complexes. These complexes may be prepared by bubbling  $CO_2$  through benzene solutions of the manganese and rhenium alkoxide complexes, eq 1. Absorption is rapid  $(1-2 \min)$  at room temperature to give the alkyl carbonato complexes fac-(CO)<sub>3</sub>(P-P)MOC(O)-OR (7-12). The IR spectra of these complexes in  $CH_2Cl_2$ all exhibit three strong  $\nu$ (C=O)'s characteristic of facial geometry. The  $\nu$ (C=O)'s are observed in the 1666-1665-cm<sup>-1</sup> range. The <sup>13</sup>C NMR resonances of the terminal carbonyls of the manganese complexes are broad. However, each of the two rhenium complexes show a lower field doublet of doublets centered at  $\delta$  194.0 ( $J_{P-C} = 62$ Hz, 10 Hz) due to the two CO's cis to OC(O)OR and a low field triplet at  $\delta$  193.0 ( $J_{P-C} = 5$  Hz) due to the CO trans to OC(O)OR. Similar <sup>13</sup>C resonances were also observed in the corresponding alkoxide complexes fac-(CO)<sub>3</sub>(dppe)-ReOR.<sup>3</sup> The carbonato carbon resonances are observed at about  $\delta$  160.0 similar to those observed in other carbonato complexes.<sup>1h-l</sup>

**Reversible Insertion of Carbon Dioxide.** After complete conversion of the alkoxide complexes to their corresponding carbonato complexes, argon is bubbled through the benzene solution and the carbonato complexes are slowly decarboxylated (2 h for rhenium and 24 h for manganese complexes). Apparently, the equilibrium (1) lies on the right side of eq 1; the carbonato complexes appear to be much more stable than the corresponding alkoxides.

$$CO_2 + fac (CO)_3 (P-P) MOR \rightleftharpoons fac (CO)_3 (P-P) MOC (O) OR$$
(1)

Somewhat analogous Re alkoxide complexes fac-(CO)<sub>3</sub>(L<sub>2</sub>)ReOC(O)OR where L<sub>2</sub> was either trimethylphosphine or o-phenylenebis(dimethylarsine) (diars) have been shown to undergo extremely rapid CO<sub>2</sub> absorption in contrast to the corresponding phenoxides which were inert.<sup>1k</sup> There is general agreement that the insertion involves direct electrophilic attack of the CO<sub>2</sub> on the oxygen atom of the alkoxide without prior M-CO<sub>2</sub> coordination.<sup>1h,k</sup>

<sup>(5)</sup> SHELXTL-PLUS 3.43 for R3/V and R3m/V Crystallographic Systems. G. M. Sheldrick, University of Goettingen, Germany, and Siemans/Nicolet Analytical X-Ray Instruments, Inc., Madison, WI, 1988.

Table II. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\dot{A}^2 \times 10^3$ ) for fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub>-C<sub>6</sub>H<sub>6</sub> (7)

atom	x	У	Z	$U(eq)^a$
Mn	1244(1)	1781(1)	2326(1)	34(1)
P(1)	-656(1)	2082(1)	1569(1)	34(1)
P(2)	1943(1)	2904(1)	1753(1)	33(1)
<b>O</b> (1)	3697(3)	1526(3)	3261(2)	80(2)
O(2)	197(4)	349(2)	2980(2)	80(2)
O(3)	1952(4)	528(2)	1388(2)	76(2)
O(4)	775(3)	2745(2)	2899(2)	39(1)
O(5)	-2(3)	3453(2)	3635(2)	57(1)
O(6)	144(3)	2037(2)	3746(2)	64(2)
CÌÌ	2743(5)	1648(3)	2913(3)	47(2)
$\hat{C}(2)$	572(5)	932(3)	2752(3)	48(2)
CG	1649(4)	1031(3)	1746(3)	47(2)
$\tilde{C}(4)$	309(4)	2672(3)	3430(3)	41(2)
cú	-620(5)	3459(4)	4199(3)	79(3)
Cíci	-462(4)	2963(3)	984(2)	41(2)
C(7)	600(4)	3532(3)	1339(2)	39(2)
C(8)	-1504(4)	1302(3)	950(2)	39(2)
C	-1283(5)	444(3)	1016(3)	52(2)
CUD	-1972(5)	-115(3)	537(3)	64(2)
	-2866(5)	171(4)	-9(3)	61(2)
C(12)	-3114(5)	1016(4)	-82(3)	59(2)
C(13)	-2446(4)	1588(3)	397(3)	47(2)
C(14)	-1813(4)	2444(3)	2015(2)	37(2)
C(15)	-2477(4)	1859(3)	2292(2)	49(2)
C(16)	-3353(5)	2115(4)	2645(3)	61(2)
C(17)	-3563(5)	2953(4)	2731(3)	67(2)
C(18)	-2902(5)	3540(4)	2468(4)	80(3)
C(10)	-2022(5)	3299(3)	2109(3)	61(2)
C(20)	2022(3)	3699(3)	2236(3)	39(2)
C(20)	3150(4)	3808(3)	2250(5)	49(2)
C(21)	3046(5)	4423(3)	3311(3)	$\frac{4}{61(2)}$
C(22)	4573(5)	4929(3)	2048(3)	63(2)
C(23)	4403(5)	4837(3)	2278(3)	61(2)
C(25)	3628(5)	4225(3)	1874(3)	52(2)
C(25)	2600(4)	$\frac{7223(3)}{2610(3)}$	1057(2)	32(2) 35(2)
C(20)	2077(+) 3824(4)	2010(3)	1256(3)	49(2)
C(28)	4480(5)	1001(3)	763(3)	61(2)
C(20)	4400(5)	2168(4)	61(3)	62(2)
C(29)	2885(5)	2100(4)	-145(3)	63(2)
C(30)	2005(5)	2300(-) 2784(3)	-1+5(3) 345(2)	49(2)
C(1n)	3805(6)	270 + (3) 0173(7)	4908(6)	$\frac{1}{166(7)}$
C(1s)	3452	9173(7)	5447	130(5)
C(23)	7250	8075	5627	125(3)
C(3s)	1614	0569	5269	123(3) 141(5)
C(43)	1014	10014	4730	153(7)
C(6s)	3061	9816	4550	169(7)
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<sup>*a*</sup> Equivalent isotropic U defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

In the case of the rhenium complexes the 7-coordinate transition state was described as



This transition state is consistent with our qualitative observations, e.g., the lack of ligand dissociation. The absorption of  $CO_2$  by the alkoxides is so rapid that even without bubbling the gas through solutions,  $CO_2$  is rapidly absorbed from a buret containing it. Crude attempts to measure the rate of absorption at room temperature in order to differentiate between alkoxides as a function of ligand and as a function of metal were unsuccessful. More detailed methodologies than we initially used will be required for such a study, and it was not undertaken at this time.

Toluene solutions of the Mn alkoxides on exposure to the atmosphere where the concentration of  $CO_2$  is approximately 0.03% resulted in the slow (about 5 h) but

Table III. Selected Bond Distances and Angles for fac-(CO)<sub>3</sub>(dppe)MnOC(O)OCH<sub>3</sub>·C<sub>6</sub>H<sub>6</sub> (7)

	/J(-FF-/		,
	Bond Dis	tances (Å)	
Mn-P(1)	2.343(1)	P(2) - C(20)	1.824(4)
Mn-P(2)	2.329(1)	P(2) - C(26)	1.822(5)
Mn-O(4)	2.029(3)	O(1) - C(1)	1.144(6)
Mn-C(1)	1.814(5)	O(2) - C(2)	1.145(7)
Mn-C(2)	1.829(5)	O(3)–C(3)	1.158(7)
Mn-C(3)	1.769(5)	O(4)–C(4)	1.271(6)
P(1) - C(6)	1.843(5)	O(5)-C(4)	1.368(6)
P(1)-C(8)	1.827(4)	O(5) - C(5)	1.431(7)
P(1) - C(14)	1.819(5)	O(6)-C(4)	1.213(6)
P(2)-C(7)	1.829(4)	C(6)–C(7)	1.525(6)
	Bond An	gles (deg)	
P(1)-Mn-P(2)	84.6(1)	P(1)-C(14)-C(15)	119.5(4)
P(1) - Mn - O(4)	82.9(1)	P(1)-C(14)-C(19)	122.0(4)
P(2) - Mn - O(4)	81.5(1)	P(2) - C(20) - C(21)	121.5(4)
P(1) - Mn - C(1)	174.9(2)	P(2) - C(20) - C(25)	119.8(4)
P(2) - Mn - C(1)	91.2(2)	P(2) - C(26) - C(27)	117.7(3)
O(4) - Mn - C(1)	93.7(2)	P(2) - C(26) - C(31)	123.7(3)
P(1)-Mn-C(2)	91.1(1)	C(7)-P(2)-C(20)	102.8(2)
P(2)-Mn-C(2)	175.4(2)	P(1)-C(14)-C(19)	122.0(4)
O(4)-Mn-C(2)	96.5(2)	Mn - P(2) - C(26)	115.6(1)
C(1)-Mn-C(2)	93.0(2)	C(7)-P(2)-C(26)	107.1(2)
P(1) - Mn - C(3)	94.0(1)	C(20)-P(2)-C(26)	101.6(2)
P(2)-Mn-C(3)	92.1(2)	Mn - O(4) - C(4)	126.1(3)
O(4)-Mn-C(3)	173.1(2)	C(4) - O(5) - C(5)	115.7(4)
C(1)-Mn-C(3)	89.0(2)	Mn-C(1)-O(1)	176.2(5)
C(2)-Mn-C(3)	89.7(2)	Mn-C(2)-O(2)	173.5(5)
Mn-P(1)-C(6)	108.6(1)	Mn-C(3)-O(3)	177.2(4)
Mn - P(1) - C(8)	122.4(1)	O(4) - C(4) - O(5)	109.8(4)
C(6) - P(1) - C(8)	102.8(2)	O(4) - C(4) - O(6)	129.1(5)
Mn - P(1) - C(14)	114.5(1)	O(5)-C(4)-O(6)	121.2(5)
C(6) - P(1) - C(14)	105.1(2)	P(1)-C(6)-C(7)	111.0(3)
C(8) - P(1) - C(14)	101.8(2)	P(2)-C(7)-C(6)	111.0(3)
Mn - P(2) - C(7)	106.7(2)	P(1)-C(8)-C(9)	123.1(3)
Mn-P(2)-C(20)	121.8(2)	P(1)-C(8)-C(13)	118.4(4)

complete conversion to carbonato complexes. Under the same conditions, the Re alkoxides gave only very small quantities of carbonato complexes. The solid Mn alkoxides on exposure to air slowly absorb  $CO_2$ ; about 5 days was required to see substantial conversion.

As noted elsewhere,<sup>1k</sup> fluorinated alkyl groups retard the rate of  $CO_2$  absorption by alkoxides. The electronwithdrawing character of the fluorine atoms reduces the nucleophilicity of the alkyl oxygen which is the site of attack by the electrophilic carbon of carbon dioxide. Thus our fluoroalkyl alkoxides 5 and 6 only very slowly absorb  $CO_2$ , unlike anionic fluoroalkyl complexes<sup>1i</sup> which are much more nucleophilic owing to their negative charge.

**Insertion of Other Electrophiles.** Insertions of carbon disulfide and alkyl and aryl isocyanates into the metal-oxygen bond of alkoxide complexes have been reported previously.<sup>1j</sup> We have observed analogous insertion into our *fac*-(CO)<sub>3</sub>(dppe)MOR to give the corresponding xanthates and carbamates, respectively (see the Experimental Section).

As we anticipated, when the carbonato complexes 7 and 11 are treated with  $CS_2$  and PhNCO, the xanthates 13 and 14 and urethanes 15 and 16, identical with those obtained by direct treatment of the alkoxides with the same electrophiles, are immediately formed. Clearly, these exchange products result from the intermediate formation of the alkoxides which are present as the result of the rapid equilibrium expressed by eq 1.

When the alkoxide fac-(CO)<sub>3</sub>(dppe)MnOCH<sub>3</sub> is treated with methylamine followed by carbon dioxide, the metallourethane complex, fac-(CO)<sub>3</sub>(dppe)MnOC(O)NHCH<sub>3</sub> is formed, almost certainly via an intermediate amido

Table IV. <sup>1</sup> H and <sup>13</sup> C NMR Data for Compounds in	Text*
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	'Η ΝΜR (δ)		<sup>13</sup> C NMR $(\delta)^{b}$			
compd	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub>	other	CO	CH <sub>2</sub>	other
(CO) <sub>3</sub> (dppp)MnH (1)	7.50 (m, 20 H)	1.75 (m, 6 H)	-6.5 (t, J 42 Hz, H)	223.4 (t, J 7 Hz), 221.9 (t, J 12 Hz)	30.1 (t, J 15 Hz), 19.4 (s)	
(CO) <sub>3</sub> (dppp)MnOTs (2)	7.25 (m, 24 H)	1.85 (m, 6 H)	2.25 (s, 3 H, CH <sub>3</sub> )	222.1 (t, J 19 Hz), 215.6 (s)	25.1 (t, J 11 Hz), 18.9 (s)	21.5 (s, CH <sub>3</sub> )
(CO) <sub>3</sub> (dppp)MnOCH <sub>3</sub> . 0.5CH <sub>3</sub> OH (3)	7.49 (m, 20 H)	2.10 (m, 6 H)	4.05 (s, 3 H, CH <sub>3</sub> ), 3.25 (s, CH <sub>3</sub> OH)	218.5 (s, br)	23.8 (t, J 13 Hz), 18.5 (s)	65.1 (t, J 5 Hz, CH <sub>3</sub> ), 50.3 (s, CH <sub>3</sub> OH)
(CO) <sub>3</sub> (dppp)MnOC <sub>2</sub> H <sub>5</sub> . C <sub>2</sub> H <sub>5</sub> OH (4)	7.26 (m, 20 H)	4.31 (q, 2 H), 2.81 (m, 6 H)	1.27 (t, 3 H, CH <sub>3</sub> )	218.8 (s, br)	71.8 (s, br), 24.1 (t, J 14 Hz)	18.5 (s, CH <sub>3</sub> )
(CO) <sub>3</sub> (dppe)Mn- OCH <sub>2</sub> CF <sub>3</sub> (5)	7.15 (m, 20 H)	3.33 (q, 2 H), 2.31 (m, 4 H)		218.6 (s, br)	73.2 (qd, J 29 Hz, 5 Hz), 25.7 (t, J 21 Hz)	125.1 (q, J 284 Hz, CF <sub>3</sub> )
$(CO)_3(dppe)Re-OCH_2CF_3 (6)$	7.50 (m, 20 H)	3.93 (q, 2 H), 2.45 (m, 4 H)		195.1 (dd, J 58 Hz, 6 Hz), 192.6 (t, J 5 Hz)	76.0 (qd, J 34 Hz, 6 Hz), 26.3 (m)	125.2 (q, J 285 Hz, CF <sub>3</sub> )
(CO) <sub>3</sub> (dppe)MnOC(O)- OCH <sub>3</sub> ·0.75C <sub>6</sub> H <sub>6</sub> (7)	7.50 (m, 24 H)	2.88 (m, 4 H)	3.00 (s, 3 H, CH <sub>3</sub> )	219.4 (m)	26.0 (t, J 19 Hz)	159.5 (C=O), 53.3 (s, CH <sub>3</sub> )
$(CO)_3(dppe)MnOC(O)-OC_2H_5 C_6H_6 (8)$	7.57 (m, 26 H)	3.50 (q, 2 H), 2.85 (m, 4 H)	0.95 (t, CH <sub>3</sub> )	219.4 (m)	61.6 (s), 26.0 (t, J 19 Hz)	159.1 (s, C=O), 15.1 (s, CH <sub>3</sub> )
(CO) <sub>3</sub> (dppp)MnOC(O)- OCH <sub>3</sub> (9)	7.50 (m, 20 H)	2.30 (m, 6 H)	3.62 (s, CH <sub>3</sub> )	216.9 (s, br)	24.8 (t, J 13 Hz), 19.1 (s)	160.2 (s, C=O), 54.7 (s, CH <sub>3</sub> )
(CO) <sub>3</sub> (dppp)MnOC(O)- OC <sub>2</sub> H <sub>5</sub> (10)	7.48 (m, 20 H)	4.06 (q, 2 H)	1.29 (t, 3 H, CH <sub>3</sub> ), 2.36 (m, 6 H)	221.6 (s, br), 216.7 (s, br)	62.0 (s), 24.7 (t, J 13 Hz)	159.5 (t, J 6 Hz, C=O), 15.5 (s, CH <sub>3</sub> ), 19.0 (s, br)
(CO) <sub>3</sub> (dppe)ReOC(O)- OCH <sub>3</sub> •0.75C <sub>6</sub> H <sub>6</sub> (11)	7.47 (m, 24 H)	2.86 (m, 2 H)	3.06 (s, CH <sub>3</sub> )	194.0 (dd, J 62 Hz, 10 Hz), 193.0 (t, J 5 Hz)	27.0 (m)	159.1 (s, C=O), 53.6 (s, CH <sub>2</sub> )
(CO) <sub>3</sub> (dppe)ReOC(O)- OC <sub>2</sub> H <sub>5</sub> •0.25CH <sub>2</sub> Cl <sub>2</sub> (12)	7.57 (m, 20 H)	3.41 (q, 2 H), 2.71 (m, 4 H)	0.90 (t, 3 H, CH <sub>3</sub> )	194.0 (dd, J 62 Hz, 10 Hz), 193.0 (t, J 5 Hz)	61.9 (s), 27.0 (m)	158.7 (s, C=O), 15.0 (s, CH <sub>3</sub> )
$(CO)_3(dppe)MnSC(S)-OCH_3 \cdot C_6H_6$ (13)	7.54 (m, 4 H)	2.82 (m, 4 H)	2.95 (s, 3 H, CH <sub>3</sub> )	218.7 (s, br)	26.1 (t, J 20 Hz)	221.7 (s, br, C=S), 54.2 (s, CH <sub>3</sub> )
$(CO)_{3}(dppe)ReSC(S)-OC_{2}H_{5}$ (14)	7.57 (m, 20 H)	4.33 (q, 2 H), 2.82 (m, 4 H)	1.35 (t, 3 H)	193.5 (dd, J 56 Hz, 8 Hz), 191.1 (t, J 6 Hz)	70.0 (s), 26.7 (m)	221.5 (t, J 5 Hz, C=S), 13.9 (s, CH <sub>3</sub> )
$(CO)_{3}(dppe)MnN(C_{6}H_{6})-C(O)OCH_{3}0.5C_{6}H_{6}$ (15)	7.51 (m, 23 H)	3.20 (m, 4 H)	2.51 (s, 3 H, CH <sub>3</sub> )	216.1 (s, br)	29.8 (t, J 21 Hz)	157.8 (s, C=O), 52.1 (s, CH <sub>3</sub> )
$(CO)_{3}(dppe)ReN(C_{6}H_{6})-C(O)OCH_{3}.0.5C_{6}H_{6}$ (16)	7.54 (m, 23 H)	3.32 (m, 4 H)	2.45 (s, 3 H, CH <sub>3</sub> )	194.0 (dd, J 56 Hz, 8 Hz), 191.6 (t, J 8 Hz)	29.8 (m)	158.2 (s, C=O), 52.3 (s, CH <sub>3</sub> )
(CO) <sub>3</sub> (dppe)MnOC(O)- NHCH <sub>3</sub> -0.75C <sub>6</sub> H <sub>6</sub> (17)	7.52 (m, 24 H)	2.82 (m, 4 H)	2.30 (s, br, 3 H, CH <sub>3</sub> )	218 (s, br)	25.9 (t, J 21 Hz)	163.2 (s, C=O), 75.4 (s, br, CH <sub>3</sub> )

<sup>a</sup> Recorded in C<sub>6</sub>H<sub>6</sub> for 1 and 3-6, in CD<sub>2</sub>Cl<sub>2</sub> for 2 and 7-16, and in CDCl<sub>3</sub> for 17. <sup>b</sup> Phenyl resonances are observed as multiplets at  $\delta$  140.0-123.0. For 15 and 16 resonances at  $\delta$  156.9 (s) and 156.0 (s) due to ipso NPh are observed. <sup>c</sup> The manganese complex resonances due to terminal CO's are not well resolved and are observed as broad singlets except in 1 and 2. However for rhenium complexes terminal CO's are well resolved and the lowest fields are observed as doublets of doublets and the next lowest field is a triplet; the intensity ratio of the lowest signal to the next lowest is 2:1.

complex which we could not isolate.<sup>6</sup> The IR and NMR spectra are consistent with the above structure, and we are certain of the linkage sequence because of the X-ray structure which we will publish elsewhere.

Solid State Structure of (CO)<sub>3</sub>(dppe)MnOC(O)- $OCH_3$  (7). Crystals of 7 were grown from a concentrated  $CH_2Cl_2/C_6H_6$ /hexane solution saturated with  $CO_2$ . The complex crystallized in the space group  $P2_1/c$ . A thermal ellipsoid drawing of 7 is shown in Figure 1. The coordination sphere of the manganese is roughly octahedral and consists of two phosphorus atoms from a chelating dppe ligand, an oxygen atom of a methyl carbonate ligand, and three carbon atoms from a facial arrangement of three terminally bound carbon monoxides. The average of Mn-P and Mn-CO(eq) distances are 2.34(1) and 1.82(1)Å, respectively. The Mn-CO(ax) distance is 1.769(5) Å, and the P-Mn-P bite angle is 84.1(1)°. The C-O bond of the axial carbonyl is 1.158(7) Å and is slightly longer than the values of 1.144(6) and 1.145(7) Å observed for the equatorial carbonyls. All of these structural features are comparable to those previously observed<sup>7</sup> in  $(CO)_3$ -(dppe)MnL complexes.<sup>8</sup>



Figure 1. Perspective drawing of molecule 7, fac- $Mn(CO)_3(dppe)OC(O)OCH_3$ .

The Mn-O(4) bond to the methyl carbonate ligand is 2.029(3) Å. To the best of our knowledge, Mn-O(alkyl carbonate) linkages have not been previously characterized

<sup>(6)</sup> The Re amido complex was prepared from the reaction of the Re alkoxide with aniline: Simpson, R. D.; Bergman, R. G. Organometallics 1992, 11, 3980.

<sup>(7) (</sup>a) Allen, F. H.; Kennard, O.; Taylor, R. Acc. Chem. Res. 1983, 16, 146. (b) The Cambridge Database [Version 4.6, January 1992] lists five  $Mn(CO)_{::}(dppe)$  fragments. The following average values were obtained for these fragments: Mn-P = 2.32(1) Å,  $P-Mn-P = 84(1)^{\circ}$ , Mn-CO(eq) = 1.82(1) Å, Mn-CO(ex) = 1.80(2) Å, CO(eq) = 1.14(1) Å<sup>2</sup>, and CO(ax) = 1.16(2) Å<sup>2</sup>.

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## Electrophile Reaction with Mn(I) and Re(I) Alkoxides

by X-ray diffraction, so a comparison to known examples is not possible. The Mn–O(methyl carbonate) bond is, however, well within the range of bond distances (2.020– 2.042 Å) observed for Mn–O(carboxylate) found trans to carbonyl ligands.<sup>9,10</sup> The Mn atom is bound to the methyl carbonate in a syn conformation and is 0.18° out of the plane defined by the carbonate atoms. The methyl group is also slightly displaced (0.10°) out of and to the same side of the carbonate plane as the Mn atom. The methyl carbonate and one of the equatorial carbonyls are eclipsed due to crystal packing forces, which results in the C(2)– Mn–O(4)–C(4) torsion angle being only 7.8°. The features of the methyl carbonate ligand itself are normal. The O(4)–C(4)–O(5) angle is acute at 109.8(4)° but is not surprising since the O–C(O)–OR angles in alkyl carbonates are known to occur over a wide range of values, and angles smaller than 109.8° have been previously reported.<sup>11-13</sup>

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Supplementary Material Available: For compound 7, tables of anisotropic displacement parameters, H atom coordinates, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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