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Transformations of Group 7 Carbonyl Complexes: Possible Intermediates in a Homogeneous Syngas Conversion Scheme

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A variety of C−H and C−C bond forming reactions of group 7 carbonyl complexes have been studied as potential steps in a homogeneously catalyzed conversion of syngas to C_{2+} compounds. The metal formyl complexes $M(CO)_3(PPh_3)_2(CHO)$ (M = Mn, Re) are substantially stabilized by coordination of boranes BX_3 (X = F, C_6F_5) in the form of novel boroxycarbene complexes $M(CO)_3(PPh_3)_2(CHOBX_3)$, but these boron-stabilized carbenes do not react with hydride sources to undergo further reduction to metal alkyls. The related manganese methoxycarbene cations $[Mn(CO)_{5-x}(PPh_3)_x(CHOMe)]^+$ ($x = 1$ or 2), obtained by methylation of the formyls, do react with hydrides to form methoxymethyl complexes, which undergo further migratory insertion under an atmosphere of CO. The resulting acyls, *cis*- and *trans*-$Mn(PPh_3)(CO)_4(C(O)CH_2OMe)$, can be alkylated to form the cationic carbene complex $[Mn(PPh_3)(CO)_4(C(OR)CH_2OMe)]^+$, which undergoes a 1,2 hydride shift to form 1,2-dialkoxyethylene, which is displaced from the metal, releasing triflate or diethyl ether adducts of $[Mn(PPh_3)(CO)_4]^+$. The acyl can also be protonated with HOTf to form a hydroxycarbene complex, which rearranges to $Mn(PPh_3)(CO)_4(CH_2COOMe)$ and is protonolyzed to yield methyl acetate and $[Mn(PPh_3)(CO)_4]^+$; addition of L (L = PPh_3, CO) to the manganese cation regenerates $[Mn(PPh_3)(CO)_4(L)]^+$. Since the original formyl complex can be obtained by the reaction of $[Mn(PPh_3)(CO)_5]^+$ with $[PtH(dmpe)_2]^+$, which in turn can be generated from H_2, this set of transformations amounts to a stoichiometric cycle for selectively converting H_2 and CO into a C_2 compound under mild conditions.

Introduction

With anticipated decreases in the availability of petroleum, there is great interest in new methods for utilizing coal and natural gas as alternative feedstocks for production of valuable chemicals. Many such approaches involve conversion of synthesis gas (syngas), a mixture of CO and H_2 readily obtained from either resource. Syngas conversion is dominated by the Fischer−Tropsch process and methanol synthesis, both heterogeneously catalyzed reactions. During the oil crisis of the 1970s and 1980s, a good deal of attention turned to homogeneous catalytic hydrogenation of CO as a possible route to selective synthesis of more complex products, resulting in considerable progress toward the identification and preparation of potential intermediates in syngas transformations.[1−3] The recent volatility of oil supply and prices has sparked renewed interest in this field.

Both C−H and C−C bond forming steps will obviously be crucial components of catalytic transformation of syngas to any C_{2+} product, and both have been shown to be difficult in the context of organometallic chemistry.[2,4−6] Coordination of a Lewis acid to the oxygen of CO or an intermediate derived therefrom has been found to facilitate one or both of these processes in a number of cases;[2,5,7−13] we recently reported a rhenium carbonyl complex incorporating a pendant Lewis acid that achieves both transfer of hydrogen (from $[(dmpe)_2PtH]^+$, a species obtainable directly from H_2) to CO and C−C bond formation.[14] Generation of useful products from syngas might be effected by a sequence of reactions starting with those shown in Scheme 1.

Group 7 carbonyl complexes are attractive candidates for exploring this approach; in particular, the cationic species $[M(CO)_4(PPh_3)_2]^+$ (M = Mn, **1a**; M = Re, **1b**) and $[Mn(CO)_5(PPh_3)]^+$ (**12**) are easily synthesized and have been

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(1) Henrici-Olivé, G.; Olivé, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag: New York, 1984.
(2) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.
(3) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325.
(4) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.
(5) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1986**, *13*, 121.
(6) Crawford, E. J.; Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6202.
(7) Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Stimson, R. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 5864.
(8) Labinger, J. A.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6856.
(9) Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6858.
(10) Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733.
(11) Wayland, B.; Fu, X. *Science* **2006**, *311*, 790.
(12) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90.
(13) Okazaki, M.; Ohtani, T.; Inomata, S.; Tagaki, N.; Ogino, H. *J. Am. Chem. Soc.* **1998**, *120*, 9135.
(14) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 11874.

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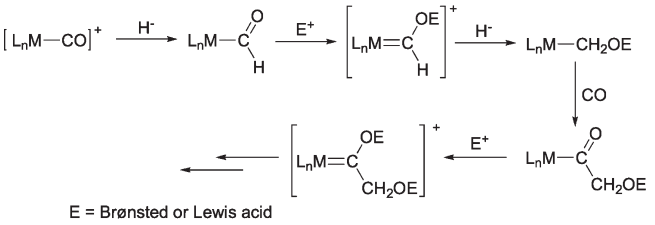
Scheme 1



shown to react with strong hydride sources, such as LiHBEt$_3$, to form neutral formyl complexes.[15−17] We report here on the stabilization of such formyl complexes by coordination to electron-deficient boranes, the insertion of CO into manganese(methoxymethyl) bonds, and the reactions of resulting acyl complexes with alkylating agents or Brønsted acids to ultimately yield *trans*-dialkoxyethylenes or methyl acetate, respectively. In addition, we have integrated individual steps to produce a stoichiometric cycle for conversion of CO to methyl acetate by reaction with $[(dmpe)_2PtH]^+$, methanol, and acid.

Results and Discussion

Boroxycarbene Complexes. Reaction of the formyl complexes M(PPh$_3$)$_2$(CO)$_3$(CHO) (**2**)[17] with methyl triflate has been previously reported to afford the cationic Fischer methoxycarbenes $[M(CO)_3(PPh_3)_2(CHOCH_3)]^+[OTf]^-$ (**3**);[18] we anticipated that an analogous siloxycarbene might be more reactive toward further transformation. Surprisingly, addition of a CH_2Cl_2 solution of $SiMe_3OTf$ (OTf = CF_3SO_3) to **2b** (prepared *in situ* from $[Re(PPh_3)_2(CO)_4][BF_4]$ and LiHBEt$_3$) led to the neutral borane-stabilized rhenium formyl Re(PPh$_3$)$_2$(CO)$_3$(CHOBF$_3$) (**4b**) in good yield. The unexpected product probably results from abstraction of a fluoride from $[BF_4]^-$ by $SiMe_3OTf$, releasing triflate and BF_3, which coordinates to the formyl oxygen. The direct reaction of **2b** with $BF_3\cdot OEt_2$ gives **4b** nearly quantitatively; in the same way, **2b** reacts with B(C$_6$F$_5$)$_3$ to form Re(PPh$_3$)$_2$(CO)$_3$(CHOB(C$_6$F$_5$)$_3$) (**5b**). The Mn analogues **4a** and **4b** were obtained similarly from **2a** (Scheme 2).

The crystal structure of **4b** is shown in Figure 1; the Re−C4 (2.096(3) Å) and C4−O4 (1.270(4) Å) bond lengths may be compared to those of the isoelectronic cationic methoxycarbene complex $[Re(CO)_3(PPh_3)_2(CHOCH_3)][OTf]$ (**3b**) (2.064(3) and 1.290(4) Å, respectively),[19] as well as the neutral formyl complex Re(C$_5$Me$_5$)(NO)(PPh$_3$)(CHO)

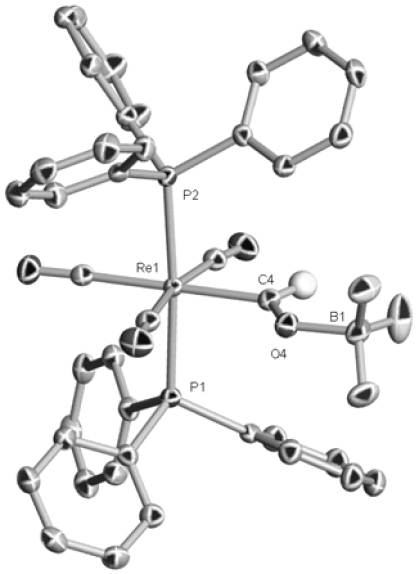
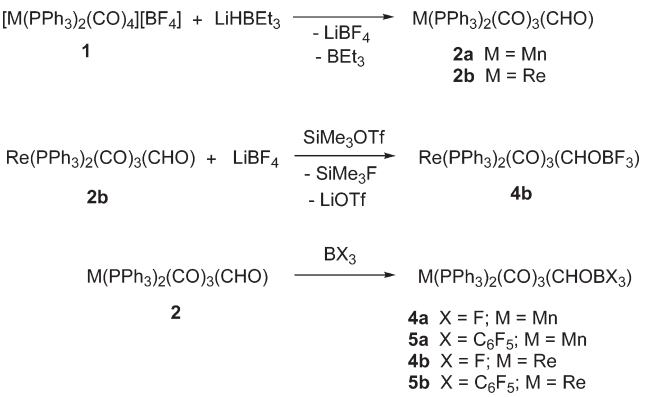
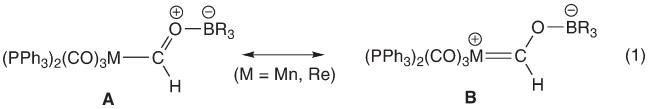


Figure 1. Structural drawing of **4b** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Re−C4, 2.096(3); Re-CO (av), 1.980; C4−O4, 1.270(4); O4−B, 1.544(4); Re−C4−O4, 125.8(2); C4−O4−B, 124.6(3).

Scheme 2



(2.055 and 1.221 Å, respectively).[20] Typical Re−C single bond lengths fall in the range 2.24−2.32 Å.[21−24]



(1)

These values indicate that complex **4b** can be best described as somewhere between a borane-stabilized formyl (**A**) and a boroxycarbene complex (**B**) (eq 1); the C−O distances in particular suggest a somewhat greater contribution of the latter form.

Structures of **5a** and **5b** were also determined (Figure 2) and are completely analogous. The only such complex previously crystallographically characterized (to the best of our knowledge) is the example with tethered boranes cited above;[14] a number of borane complexes of transition metal acyls have been reported.[25−27]

(15) Weiler, G.; Huttner, G.; Zsolnai, L.; Berke, H. *Z. Naturforsch., B. Anorg. Chem., Org. Chem.* **1987**, *42B*, 203.
(16) Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624.
(17) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.
(18) Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1990**, *9*, 1936.
(19) See Supporting Information for structure.
(20) Wong, W. K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.
(21) Bleeke, J. R.; Rausher, D. J.; Moore, D. A. *Organometallics* **1987**, *6*, 2614.
(22) Bleeke, J. R.; Earl, P. L. *Organometallics* **1989**, *8*, 2735.
(23) Brown, D. A.; Mandal, S. K.; Ho, D. M.; Becker, T. M. *J. Organomet. Chem.* **1999**, *592*, 61.
(24) Bodner, G. S.; Patton, A. T.; Smith, D. E.; Georgiou, S.; Tam, W.; Wong, W. K.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1987**, *6*, 1954.
(25) Anderson, G. D. W.; Boys, O. J.; Cowley, A. R.; Green, J. C.; Green, M. L. H.; Llewellyn, S. A.; von Beckh, C. M.; Pascu, S. I.; Vei, I. C. *J. Organomet. Chem.* **2004**, *689*, 4407.
(26) Llewellyn, S. A.; Green, M. L. H.; Cowley, A. R. *Dalton Trans.* **2006**, 1776.
(27) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.

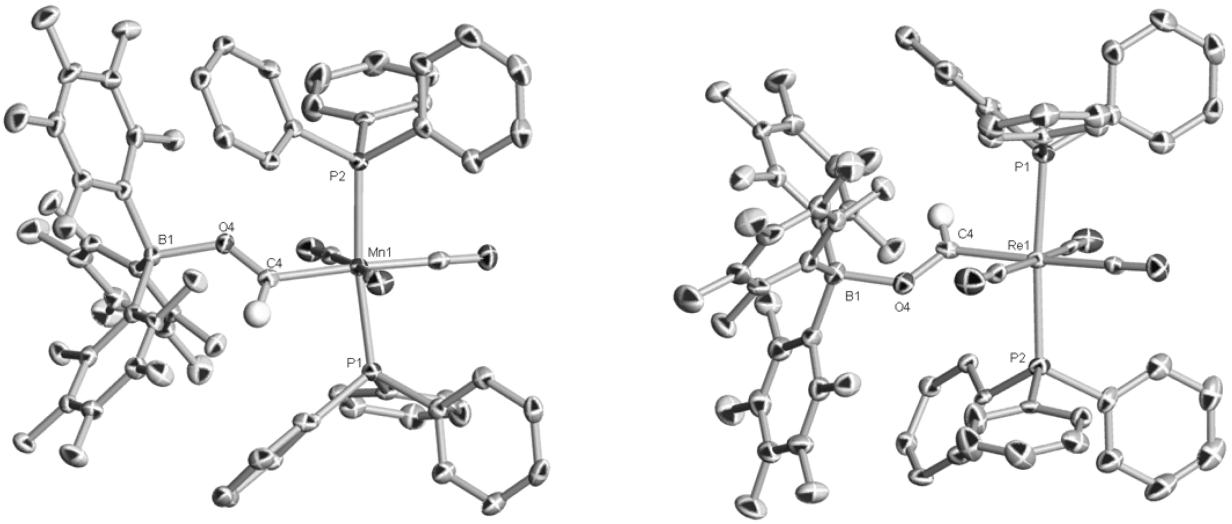
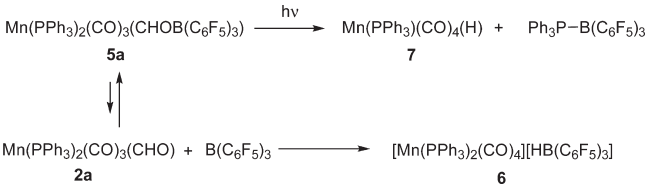


Figure 2. Structural drawings of **5a** and **5b** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **5a**: Mn−C4, 1.994(2); Mn−CO (av), 1.839; C4−O4, 1.275(2); O4−B, 1.593(3); Mn−C4−O4, 127.40(16); C4−O4−B, 129.96(17). Selected bond lengths (Å) and angles (deg) for **5b**: Re−C4, 2.125(5); Re−CO (av), 1.980; C4−O4, 1.282(5); O4−B, 1.575(6); Mn−C4−O4, 126.9(3); C4−O4−B, 130.6(4).

Scheme 3



Formyl complexes are typically quite labile in solution, often decomposing irreversibly to the corresponding carbonyl hydride species with concomitant loss of a ligand;[1,28] in the case of **2**, preferential loss of a phosphine over a CO ligand is observed.[17] Surprisingly, both **4a** and **4b** are quite stable, both in solution and in the solid state. Virtually no reaction (less than 1% of free PPh_3 was detected) of **4b** could be observed after several days, even on treatment with PMe_3 at 40 °C or exposure to 1−10 atm CO, in attempts to induce C−C bond formation. **5b** is likewise stable, showing no sign of decomposition in solution at room temperature after 24 h, but **5a** decomposes at room temperature to the borohydride salt of the parent cationic carbonyl, $[Mn(CO)_4(PPh_3)_2][(C_6F_5)_3BH]$, **6** (Scheme 3). Apparently the manganese formyl is effectively a stronger hydride donor than $[(C_6F_5)_3B-H]^-$. In the absence of light, the conversion of **5a** to **6** (followed by ^1H NMR) exhibits clean first-order kinetics. It seems reasonable to suggest that **5a** reversibly dissociates to **2a** (although no evidence for this "naked" formyl was observed) plus $B(C_6F_5)_3$ followed by hydride transfer (Scheme 3). In contrast, on exposure to light, **5a** is converted to manganese hydride **7** and the phosphine-borane adduct $Ph_3P-B(C_6F_5)_3$. **7** does not appear to arise via **6**, since the latter is stable to irradiation: exposing a 4:1 mixture of **6** and **5a** to light results in a 4:1 mixture of **6** and **7**. The requirement of light to induce formation of **7** suggests possible involvement of radical pathways, as has been shown for related systems.[29,30]

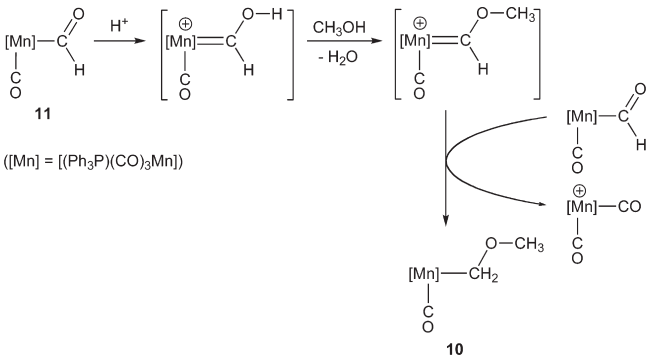
(28) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.
(29) Ruszczyk, R. J.; Huang, B.-L.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *299*, 205.
(30) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087.

In view of our recent findings that an intramolecularly stabilized rhenium formyl can accept a second hydride to yield a boroxymethyl species, which then undergoes CO insertion to form a C−C bond,[14] we treated **4a** and **4b** with $LiHBEt_3$ or $NaHBEt_3$. However, these reactions led only to the partial re-formation of the parent formyls (**2a** and **2b**, respectively) and $[HBF_3]^-$; no further reduction of the borane-stabilized formyl to a boroxyalkyl species was observed. It appears that the BX_3 species used here exhibit greater hydride affinity than the borane-stabilized formyls, a trend also manifested in the decomposition of **5a**.

Conversion of **4a** to a traditional Fischer carbene by reaction with CH_3OTf proceeds slowly (15 h: 10%; 36 h: 17%) to give $[Re(CO)_3(PPh_3)_2(CHOMe)][OTf]$ (**3b**); the reaction is only slightly accelerated when an excess of Et_2O is added to promote the formation of the $BF_3\cdot OEt_2$ adduct. The analogous reactions of **5a** and **5b** with CH_3OTf gave slow conversion to CH_4 and $[M(CO)_4(PPh_3)_2][OTf]$ as well as minor unidentified products; it is not clear at what stage CH_4 is formed. The siloxycarbene complex $[Re(PPh_3)_2(CO)_3(CHOSiMe_3)][BPh_4]$ (**8**), the initial target of this part of the project, can be obtained by generating $Re(PPh_3)_2(CO)_3(CHO)$ *in situ* from $[Re(PPh_3)_2(CO)_4][B(C_6H_5)_4]$ and $[BHEt_3]^-$, followed by treatment with $SiMe_3OTf$; use of the $B(C_6H_5)_4^-$ counteranion eliminates the problems caused by reactive fluoride. However, somewhat surprisingly (considering the expected strong Si−O bond), **8** decomposes rapidly at room temperature to the cationic tetracarbonyl precursor **2a** and trimethylsilane. This instability precluded isolation of **8** in high purity; it was characterized by ^1H and ^{31}P NMR only, with the former displaying a diagnostic signal at δ 11.3.

Formation and Carbonylation of Manganese Methoxymethyl Complexes. Because of the resistance of the above boroxycarbene complexes toward further reduction, we turned to manganese methoxycarbene complexes, which are known to accept a hydride to form manganese methoxymethyl compounds.[18] $Mn(PPh_3)_2(CO)_3(CH_2OCH_3)$ (**9**) can be synthesized via initial reduction of $[Mn(PPh_3)_2(CO)_4][BF_4]$ (**1a**) to the manganese formyl (**2a**) by reaction with a

Scheme 4



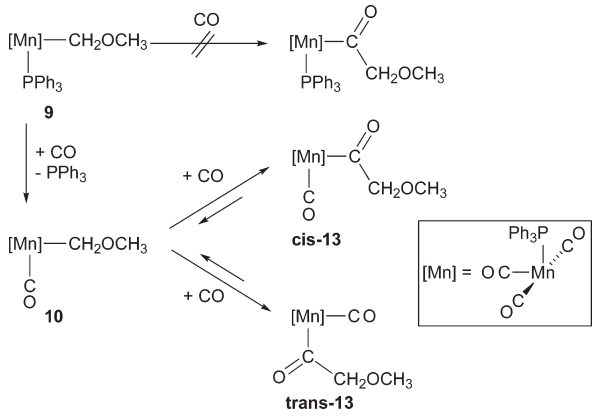
hydride source, such as $LiHBEt_3$,[17] followed by treatment with methyl triflate to give methoxycarbene complex **3a**, which in turn is reduced with another equivalent of hydride to the desired complex **9**. All of these steps have been demonstrated previously, and **9** has been characterized crystallographically.[31]

A similar synthesis of monophosphine analog $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (**10**) was thwarted by the instability of intermediate $Mn(PPh_3)(CO)_4(CHO)$ (**11**), which quickly decomposes to *cis*-$Mn(PPh_3)(CO)_4H$. (The multiple decomposition pathways of manganese and rhenium formyl complexes have been studied previously.[32,33]) Attempts to slow the decomposition by performing the reduction with $LiHBEt_3$ in the dark at low temperature were only partially successful. The best yield of the formyl was obtained using $[PtH(dmpe)_2][PF_6]$ as reductant, with $< 10\%$ of the hydride observed after 10 min at room temperature, but a stable carbene complex could not be obtained under these conditions.

However, **10** can be synthesized following a procedure discovered by Gibson, which avoids isolation of an intermediate carbene complex: protonation of $Mn(PPh_3)(CO)_4(CHO)$ (**11**) in methanol results in formation of half an equivalent each of **10** and $[Mn(PPh_3)(CO)_5]^+$ (**12**), presumably via initial formation of a hydroxycarbene, exchange with methanol, and hydride transfer (Scheme 4).[34] Indeed, we find that addition of methanol to a flask containing $[(dmpe)_2PtH][PF_6]$ and $[Mn(PPh_3)(CO)_5][BF_4]$ (**12**) followed by the addition of *p*-toluenesulfonic acid after 3 min at room temperature affords $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (**10**) and $[Mn(PPh_3)(CO)_5]^+$ (**12**) in good yields. **10** can also be prepared via reaction of $Na[Mn(PPh_3)(CO)_5]$ with $ClCH_2OCH_3$ in THF.[35]

Bisphosphine complex $Mn(PPh_3)_2(CO)_3(CH_2OCH_3)$ (**9**) reacts slowly in C_6D_6 solution under 1 atm of CO at room temperature to generate three new products as determined by ^1H NMR. One minor product was identified as monophosphine complex **10** by comparison to an authentic sample. Signals attributable to the $Mn(CH_2OMe)$ protons for both the major and the other minor product show no coupling to phosphorus ($Mn(CO)_5(CH_2OCH_3)$ was ruled out by comparison to an authentic sample),[36] suggesting the possible formation of acyls. The products were definitively identified as the isomers *cis*-$Mn(CO)_4(PPh_3)(COCH_2OCH_3)$ (***cis*-13**) and *trans*-$Mn(CO)_4(PPh_3)(COCH_2OCH_3)$ (***trans*-13**), respectively, formed in a 6:1 ratio (Scheme 5), by comparison to literature data as well as independent synthesis from $Na[Mn(CO)_4(PPh_3)]$ and $ClC(O)CH_2OCH_3$. A peak corresponding to free PPh_3 was observed in the ^{31}P NMR spectrum, consistent with phosphine loss from **9**. Independent synthesis of the acyl species yields an equilibrium mixture of ***cis*-13**, ***trans*-13**, and $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (**10**), as previously reported.[37,38] Addition of 2 equiv of free PPh_3 does not significantly change either the product distribution or the reaction rate. The reaction is accelerated in coordinating solvents such as THF and even more so in methanol (12 h for complete reaction, vs 7 days in benzene), as has been observed in analogous migratory insertion reactions.[37]

Scheme 5

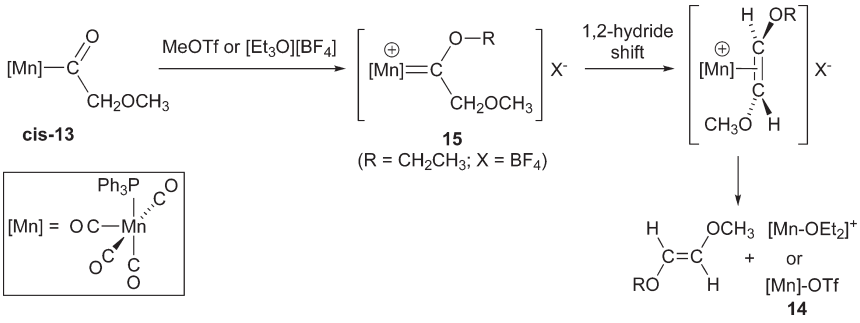


Carbonylation of **10** under the same conditions leads, after several days, to an identical product distribution by ^1H NMR; the ^{13}C NMR spectrum shows the growth of the diagnostic acyl peaks corresponding to ***cis*-13** (272.8 ppm) and ***trans*-13** (263.4 ppm).[39] The presence of $Mn(CO)_5(COCH_2OCH_3)$ can be ruled out, as its high-frequency IR stretching band (2130 cm^1)[36] is absent from the spectrum of the product mixture; moreover, **10** does not disproportionate in solution to give **9** and $Mn(CO)_5(CH_2OCH_3)$. These results suggest that **9** does not undergo direct carbonylation to an acyl, but rather phosphine displacement by CO to give **10**, which subsequently undergoes migratory insertion (Scheme 5).

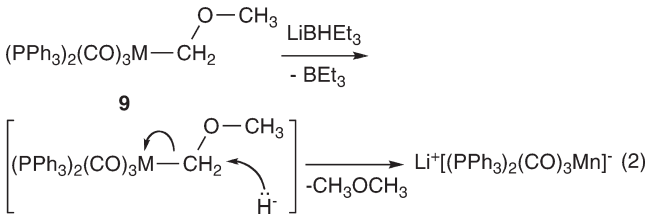
We also observed that **9** reacts with $LiHBEt_3$ to give dimethyl ether in moderate yield (ca. 60−75%, depending on the conditions) along with minor unidentified products. Presumably this transformation involves nucleophilic attack of hydride at the methylene carbon (eq 2);[40] the byproduct $[Mn(PPh_3)_2(CO)_3]^-$ likely undergoes further reaction with reactive impurities or borane present in solution. The rhenium analogue $Re(PPh_3)_2(CO)_3(CH_2OCH_3)$ showed no

(31) See Supporting Information for structural data.
(32) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.
(33) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802.
(34) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1991**, *10*, 1203.
(35) Hevia, E.; D., M.; Perez, , J.; Riera, V. *Organometallics* **2006**, *25*, 4909.
(36) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.
(37) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806.
(38) Noack, K.; Ruch, M.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 345.
(39) Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 739.
(40) Alternate pathways such as initial hydride transfer to CO or to Mn followed by reductive elimination cannot be ruled out.

Scheme 6



such reactivity, possibly reflecting the stronger M−C bond.

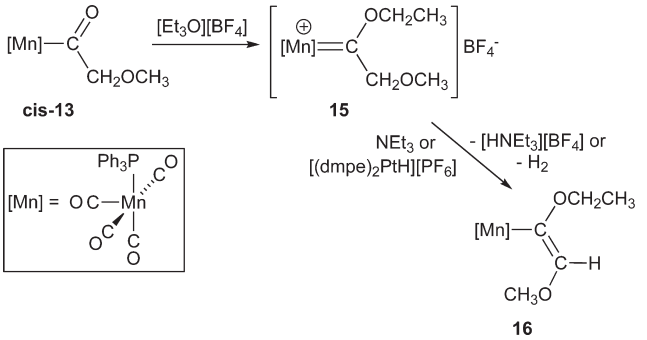


Liberation of C_2 Species. The previous section demonstrated formation of the C−C coupled species $Mn(CO)_4(PPh_3)(COCH_2OCH_3)$ (**13**), whose organic group is derivable entirely (in principle) from CO and H_2. An attractive approach to further progress would be addition of an electrophile to the acyl oxygen of **13** to form a new carbene complex, which might add hydride to form an alkyl and grow the chain via another CO insertion or could undergo protonolysis of the Mn−C bond to give a C_2 organic product. Addition of MeOTf to acyl complex **13** gives no immediately detectable reaction, but over a period of 24 h the MeOTf ^{1}H NMR signal disappears and a new product grows in, whose ^{1}H NMR spectrum corresponds to *trans*-1,2-dimethoxyethene,[41] accompanied by growth of a ^{31}P NMR signal at 42 ppm, identified as belonging to $Mn(PPh_3)(CO)_4(OTf)$ (**14**).[42] The yield of this reaction is greater than 80% by ^{1}H NMR.

If EtOTf is used as the alkylating agent, the reaction proceeds similarly to give the asymmetrically substituted olefin *trans*-1-ethoxy-2-methoxyethene, whose ^{1}H NMR spectrum matches literature data.[41] With triethyloxonium tetrafluoroborate, in contrast, alkylation of the acyl oxygen occurs over a period of several hours, forming the originally expected cationic carbene complex $[Mn(PPh_3)(CO)_4(=C(OEt)CH_2OMe)][BF_4]$ (**15**), identified by its ^{1}H NMR signals (ethyl triplet and quartet at δ 4.28 and 1.36, respectively; methylene singlet at δ 4.12; methoxy singlet at δ 3.68). **15** decomposes over time to liberate *trans*-1-ethoxy-2-methoxyethene.

The dialkoxyolefins probably arise via alkylation of the acyl oxygen followed by a 1,2 hydride shift. The coordinated olefin is then displaced by triflate anion, or diethyl ether in the case of Et_3O^+ (Scheme 6). The latter is apparently a (kinetically) more effective alkylating agent, allowing the intermediate carbene complex **15** to be observed. Similar transformations have been reported for $CpFe(CO)_2(C(=O)CH_2OMe)$[4,6,43] as well as unstabilized iron and rhenium carbenes.[44−48] Apparently hydride migration is stereoselective, as only *trans* olefins are produced, even though the *cis* isomers are thermodynamically preferred; if trace acid is present, some isomerization to the more stable *cis* species is observed.[41,49]

Scheme 7



Attempted reduction of the manganese carbene intermediate **15** with $[(dpme)_2PtH][PF_6]$ resulted instead in deprotonation to form the vinyl complex $Mn(PPh_3)(CO)_4(C(OEt)=C(H)(OMe))$ (**16**); this transformation is also effected by triethylamine (Scheme 7). Like the above hydride migration, deprotonation is stereoselective, leading to the vinyl isomer in which the alkoxy groups are *trans* to one another. Deprotonation of cationic rhenium carbenes has previously been found to lead to rhenium vinyl complexes.[46−48] In contrast, Cutler found that the analogous iron carbene will accept a hydride from $LiHBEt_3$.[4,50] Placing a methanol solution of **16** under 1000 psi of CO does not lead to observable carbonylation products.

Protonation gives a quite different outcome from alkylation: addition of HOTf to **13** results in rapid formation of the hydroxycarbene $[Mn(PPh_3)(CO)_4(=C(OH)CH_2OMe)][OTf]$ (**17**), whose ^{1}H NMR spectrum displays signals for the hydroxy proton (broad singlet at δ 14.76), the methylene group (singlet at δ 4.01), and the methoxy group (singlet at δ 3.38). **17** decomposes over time to yield manganese triflate **14**. Other strong acids may be used as well; the stability of the product depends on the nature of the counterion. Behavior

(41) Taskinen, E. *Magn. Reson. Chem.* **1998**, *36*, 573.
(42) Schwieger, M.; Beck, W. *Z. Anorg. Allg. Chem.* **1991**, *595*, 203.
(43) Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130.
(44) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(45) Dazinger, G.; Kirchner, K. *Organometallics* **2004**, *23*, 6281.
(46) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.
(47) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.
(48) Peng, T.-S.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2884.
(49) Taskinen, E.; Bjorkqvist, H. *Struct. Chem.* **1994**, *5*, 321.
(50) Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2471.

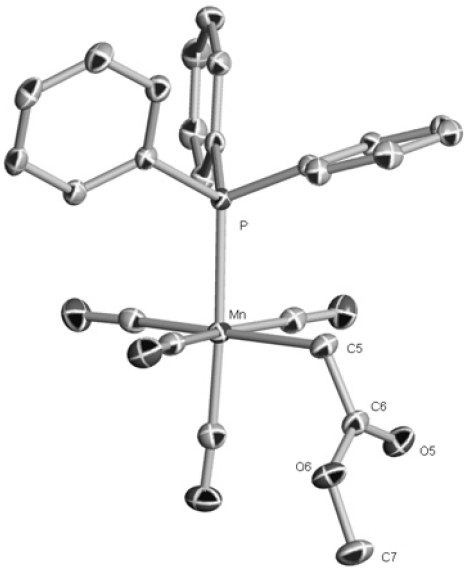
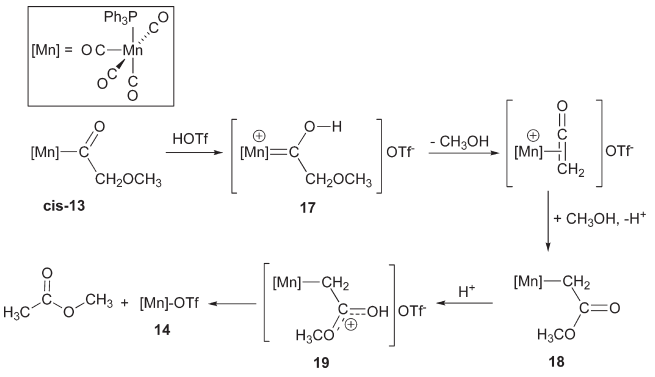


Figure 3. X-ray crystal structure of $(PPh_3)Mn(CO)_4(CH_2CO_2Me)$ (**18**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **18**: Mn−C5, 2.1948(11); C5−C6, 1.4775(14); C6−O5, 1.2231(12); C6−O6, 1.3555(13); Mn−C5−C6, 108.98(6); O5−C6−O6, 121.39(10).

Scheme 8



analogous to the above alkylation reactions would be expected to yield methoxyacetaldehyde by hydride migration followed by tautomerization. We see none of this product; rather methyl acetate is formed.[51] Most probably this is the result of protonolysis of the methoxy group to yield a ketene intermediate, which undergoes rapid nucleophilic attack at the central carbon to form carbomethoxymethyl complex **18**, followed by protonolysis (Scheme 8).[6]

Complex **18** was independently synthesized in good yield by addition of $TsOCH_2C(O)OCH_3$ to a solution of [Na]-$[(PPh_3)Mn(CO)_4]$ in THF; the spectroscopic data match those for the previously reported synthesis (in 0.2% yield),[52] and the structure was further characterized by X-ray crystallography (Figure 3). The ^1H NMR spectrum of **18** in CD_2Cl_2 displays a doublet at δ 0.91 ppm ($J_{PH} = 7$ Hz) for the methylene and a singlet at δ 3.51 for the methyl group; addition of triflic acid causes downfield shifts to δ 1.42 and 4.00 ppm, assigned to cation **19**. The latter peaks are observed at intermediate stages during NMR monitoring of the protonation of **13**, supporting the proposed mechanism via **19**. The analogous acid-catalyzed isomerization of $CpFe(CO)_2(C(=O)CH_2OMe)$ to $CpFe(CO)_2(CH_2C(=O)OMe)$, as well as formation of methyl acetate with a stoichiometric amount of acid, has been previously reported.[4,6,43] Placing a methanol solution of **18** under 1000 psi of CO does not lead to products resulting from migratory insertion.

Prospects and Conclusions

Reactions of the sort shown in Scheme 1 have long been studied as models for potential steps in promising homogeneous catalytic approaches to syngas conversion. The more recent discovery of late transition metal complexes that activate dihydrogen to generate metal hydrides sufficiently nucleophilic to attack coordinated CO may provide a way to realize that potential. However, a number of hurdles still need to be surmounted; in particular, the nature of the reagents and reaction conditions required to effect each of the various steps will generally differ strongly. For example, a Lewis acid added to facilitate hydride transfer or CO insertion may interfere with generation of the metal hydride reagent or the hydride transfer step, or it may bind so strongly to an intermediate or product as to preclude catalysis, as is the case with our earlier linked rhenium−boron complex.[14] More detailed understanding of the individual steps and the range of reagents/conditions under which they can be carried out is needed to determine whether and how they can be assembled into a practical catalytic system.

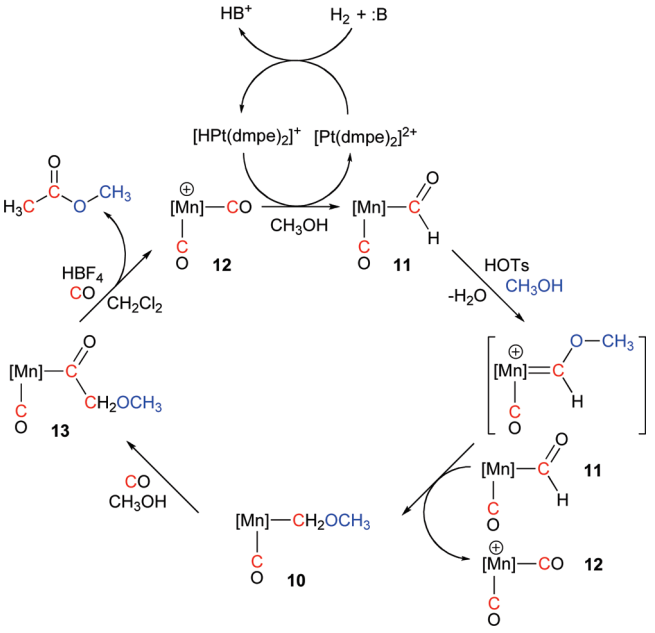
In the present work we first attempted to overcome the instability of group 7 formyls with the use of Lewis acidic boranes. While this approach was successful in that it allowed isolation and structural characterization of these potential intermediates, coordination of boranes does *not* facilitate further reduction or C−C coupling; indeed, in several cases C−H bond formation was eventually reversed by transfer of hydride to boron. We next turned to bis(phosphine)manganese complex $[Mn(CO)_4(PPh_3)_2]^+$ (**1a**), which Gibson has previously used as a model system, wherein it is possible to isolate all of the intermediates in the reduction (using borohydrides) of CO to a methoxymethyl group.[34] Methoxymethyl complex $Mn(PPh_3)_2(CO)_3(CH_2OCH_3)$ (**9**) undergoes CO migratory insertion under very mild conditions (RT, 1 atm CO), a result that seems surprising considering the strength of the Mn−CO bonds (as indicated by the low average CO stretching frequency of 1938 cm^{-1}). In fact, the reaction almost certainly begins with displacement of one phosphine by CO, since carbonylation of the monophosphine complex $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (**10**) gives the same product distribution.

Unlike **1a**, $[Mn(PPh_3)(CO)_5]^+$ (**12**) reacts with the transition metal hydride donor $[(dmpe)_2PtH]^+$. This represents important progress toward a catalytic system, as Dubois has shown that this hydride can be formed by cleavage of H_2 with $[(dmpe)_2Pt]^{2+}$ and base, potentially delivering H^- and H^+ from H_2. By adding $[(dmpe)_2PtH][PF_6]$ followed by *p*-toluenesulfonic acid to **12** in methanol, we can carry out the overall conversion to **10** (previously reported as a sequence of separate steps) in a one-pot reaction. Since methanol solutions of **10** undergo facile migratory insertion with CO, this amounts to conversion of two CO molecules to the C_2 species $Mn(PPh_3)(CO)_4(C(=O)CH_2OCH_3)$ (**13**), using an

(51) This ^1H NMR data matches that available for methyl acetate in the Spectral Database for Organic Compounds. Vacuum transfer of the volatiles from a completed NMR-scale reaction contained methyl acetate, further confirming its release during the reaction.

(52) Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* **1981**, *204*, 79.

Scheme 9



H_2-derived hydride reagent, in a one-pot reaction, in a relatively short amount of time.

Alkylation of the acyl oxygen of **13** with alkyl triflates or oxonium reagents is fairly slow. The alkoxycarbene intermediate (not observed with triflates) undergoes hydride migration to give free *trans*-dialkoxyethylene; no manganese coordinated olefin is observed. The inability of this metal center to support a bound olefin stands in contrast to the $[CpFe(CO)_2]^+$ system, for which the olefin remains bound after hydride migration; it is also interesting that while hydride migration is stereoselective for both systems, they give the opposite stereochemistry: *cis* olefin for Fe,[4,6] *trans* for Mn.

On the other hand, **13** reacts rapidly with HOTf, a strong Brønsted acid; the initially formed hydroxycarbene $[Mn(PPh_3)(CO)_4(=C(OH)CH_2OMe)][OTf]$ (**17**) rearranges via coordinated ketene and ultimately yields free methyl acetate. (Similar transformations have been reported by Cutler for the release of C_2 products from $CpFe(CO)_2(C(=O)CH_2OR)$,[4,6,43] but a key difference between the two systems is that the iron methoxymethyl does *not* undergo migratory insertion under CO, instead requiring phosphine addition.) This completes (on paper) a cycle for the synthesis of C_2 organics from CO, starting with recyclable $[Mn(PPh_3)(CO)_5]^+$ (**12**), as shown in Scheme 9.

Of course, as written, this cycle cannot be carried out catalytically, since (as noted above) several steps require reagents and conditions that are not mutually compatible. To cite just one example, the protonolytic release of methyl acetate was achieved in CH_2Cl_2; it does not occur in methanol, the solvent in which **13** is generated, probably because of the leveling of the acid strength. Nonetheless, it suggests intriguing possibilities, as can be seen if the reactions of Scheme 9, along with the formation of the Pt hydride reagent, are rewritten substituting a generic acid BH^+ for the various acids actually involved (Scheme 10). With the addition of one more step, hydrolysis of methyl acetate, the overall reaction amounts to direct catalytic conversion of syngas to acetic acid, a process that currently is carried out indirectly via methanol synthesis and carbonylation. This approach to homogeneous syngas conversion, if a set of compatible reagents and conditions *can* be found, appears quite promising.

Scheme 10

$$2\,Pt^{2+} + 2\,H_2 + 2\,B \longrightarrow 2\,PtH^+ + 2\,BH^+$$
$$2\,PtH^+ + 2\,Mn(CO)^+ \longrightarrow 2\,Mn(CHO) + 2\,Pt^{2+}$$
$$Mn(CHO) + BH^+ + MeOH \longrightarrow Mn{=}CHOMe^+ + B + H_2O$$
$$Mn{=}CHOMe^+ + Mn(CHO) \longrightarrow Mn(CH_2OMe) + Mn(CO)^+$$
$$Mn(CH_2OMe) + CO \longrightarrow Mn(C(O)CH_2OMe)$$
$$Mn(C(O)CH_2OMe) + BH^+ \longrightarrow CH_3CO_2Me + B + Mn^+$$
$$Mn^+ + CO \longrightarrow Mn(CO)^+$$
$$CH_3CO_2Me + H_2O \longrightarrow CH_3CO_2H + MeOH$$
$$2\,CO + 2\,H_2 \longrightarrow CH_3CO_2H$$

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or calcium hydride or by passage through activated alumina columns.[53] Benzene-d_6 was purchased from Cambridge Isotopes and dried over sodium benzophenone ketyl. Dichloromethane-d_2 was purchased from Cambridge Isotopes and distilled from calcium hydride. THF-d_8 was purchased from Cambridge Isotopes and dried either over sodium benzophenone ketyl or by passage through a column of activated alumina. Other materials were used as received. $Re(CO)_5Br$ and $Mn(CO)_5Br$ were obtained from Strem, while $ClCH_2OCH_3$ and $ClC(O)CH_2OCH_3$ were purchased from Aldrich. Preparations of $Re(CO)_3(PPh_3)_2Br$,[54] $[Re(CO)_4(PPh_3)_2][BF_4]$,[17] $Mn(CO)_4(PPh_3)Br$,[55] $[Mn(CO)_5(PPh_3)][BF_4]$,[17] $Mn(CO)_3(PPh_3)_2Br$,[54] $[Mn(CO)_4(PPh_3)_2][BF_4]$,[17] $[Pt(dmpe)_2][PF_6]_2$,[56] $[Pt(dmpe)_2H][PF_6]$,[56] $[Re(CO)_3(PPh_3)_2(CHOMe)][BPh_4]$,[18] $[Mn(CO)_3(PPh_3)_2(CHOCH_3)][OTf]$,[18] and *cis*-$Mn(CO)_4(PPh_3)(CH_2OCH_3)$[35] were carried out using literature procedures.

Instrumentation. ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 299.868 and 121.389 MHz, respectively, at room temperature. ^{13}C NMR spectra were recorded on a Varian INOVA-500 spectrometer at 125.903 MHz at room temperature. All ^1H NMR chemical shifts are reported relative to TMS, and ^1H (residual) chemical shifts of the solvent are used as secondary standard. ^{13}C NMR chemical shifts are reported relative to the internal solvent. ^{31}P NMR chemical shifts are reported relative to an external H_3PO_4 (85%) standard. ^{19}F NMR chemical shifts are reported relative to an external CCl_3F standard. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. X-ray crystallography was carried out by Dr. Michael W. Day and Lawrence M. Henling using an Enraf-Nonius CAD-4 diffractometer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. High-pressure NMR experiments were carried out using similar equipment and procedures to those described previously.[57]

(53) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(54) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978**, *17*, 2842.
(55) Angelici, R. J.; Basolo, F. *J. Am. Chem. Soc.* **1962**, *84*, 2495.
(56) Miedaner, A.; DuBois, D. L.; Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1993**, *12*, 299.
(57) Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2006**, *128*, 2005.

NMR-Scale Preparation of $Re(CO)_3(PPh_3)_2(CHO)$ (2b). $[Re(CO)_4(PPh_3)_2][BF_4]$ (**1b**) (19 mg, 0.022 mmol) was placed in a J-Young NMR tube and suspended in THF-d_8 (0.7 mL). $LiHBEt_3$ (1 M in THF, 22 μL, 1 equiv) was syringed into the tube. The sealed tube was shaken vigorously to give a yellow solution. ^{1}H NMR (RT, 300 MHz, THF-d_8): δ 7.32−7.43 (18H, m, ArH), 7.45−7.56 (12H, m, ArH), 13.86 (1H, s, CHO). ^{31}P NMR (RT, 121 MHz, THF-d_8): 13.2 ppm (s).

NMR-Scale Reduction of $[Mn(CO)_5(PPh_3)][BF_4]$ (12). In the glovebox, $[Mn(CO)_5(PPh_3)][BF_4]$ (**12**) (11 mg, 0.019 mmol) was placed in a J-Young NMR tube and suspended in THF-d_8 (0.4 mL). The suspension was frozen in the cold well. Fresh THF-d_8 was added to the top of the layer and frozen. Finally, $LiHBEt_3$ (1 M in THF, 20 μL, 1 equiv) was syringed into the tube and frozen as well. Outside the glovebox, the tube was placed in a −78 °C bath until ready to collect data. The tube was thawed and shaken vigorously immediately before placing it into the NMR probe, giving a yellow solution that contained *cis*- and *trans*-$Mn(CO)_4(PPh_3)(CHO)$ (**11**) and $Mn(CO)_4(PPh_3)H$ in a 10.5:1:3 ratio, respectively. ^{1}H NMR (RT, 300 MHz, THF-d_8): δ −7.26 (d, $^2J_{H-P}$ = 33.6 Hz, Mn−H), 7.23−7.74 (m, ArH), 13.59 (d, $^3J_{H-P}$ = 2.3 Hz, *cis*-CHO), 14.37 (d, $^3J_{H-P}$ = 9.0 Hz, *trans*-CHO). ^{31}P NMR (RT, 121 MHz, THF-d_8): 57.2 (s, br).

When a tube containing a similar mixture was filled with 1 atm of CO on the Schlenk line before warming to room temperature, the resulting yellow solution contained *cis*- and *trans*-$Mn(CO)_4(PPh_3)(CHO)$ and $Mn(CO)_4(PPh_3)H$ in a 14:1:7 ratio, respectively. When the reagents were mixed at room temperature, only *cis*-$Mn(CO)_4(PPh_3)(CHO)$ and $Mn(CO)_4(PPh_3)H$ were observed, in a 3:7 ratio.

NMR-Scale Reduction of $[Mn(CO)_5(PPh_3)][BF_4]$ (12) Using $[Pt(dmpe)_2H][PF_6]$ at Room Temperature. $[Mn(CO)_5(PPh_3)][BF_4]$ (**12**) (13 mg, 0.024 mmol) and $[Pt(dmpe)_2H][PF_6]$ (15 mg, 0.024 mmol) were placed in a J-Young NMR tube and suspended in THF-d_8 (0.7 mL). The tube was sealed and shaken vigorously to give a yellow solution containing *cis*-$Mn(CO)_4(PPh_3)(CHO)$ (**11**), *trans*-$Mn(CO)_4(PPh_3)(CHO)$ (**11**), and $Mn(CO)_4(PPh_3)H$ in a 11:1.5:1 ratio, respectively, as well as other unidentified decomposition products. After 2.5 h, the ^{1}H NMR spectrum shows the same products in 7:1:3.5 ratio, demonstrating that the formyl decomposes to the hydride via loss of CO.

NMR-Scale Preparation of $Mn(CO)_3(PPh_3)_2(CHO)$ (2a). $[Mn(CO)_4(PPh_3)_2][BF_4]$ (**1a**) (5 mg, 0.006 mmol) was placed in a J-Young NMR tube and suspended in THF-d_8 (0.7 mL). $LiHBEt_3$ (1 M in THF, 6 μL, 1 equiv) was syringed into the tube. The sealed tube was shaken vigorously to give a yellow solution. ^{1}H NMR (RT, 300 MHz, THF-d_8): δ 7.17−7.68 (30H, m, ArH), 13.55 (1H, t, $^3J_{H-P}$ = 2.0 Hz, CHO).

$Re(CO)_3(PPh_3)_2(CHOBF_3)$ (4b). Method A. In the glovebox, a suspension of $[Re(CO)_4(PPh_3)_2][BF_4]$ (**1b**) (125 mg, 0.142 mmol) in THF (3 mL) was stirred in a vial. $LiHBEt_3$ (1 M in THF, 142 μL, 1 equiv) was syringed in to give a yellow solution after filtration. THF was evaporated to give the crude formyl species and $LiBF_4$ byproduct as a yellow residue. TMSOTf (21 μL, ca. 1 equiv) was dissolved in CH_2Cl_2 (5 mL) and added to the residue, stirring for 5 min, after which the solvent was evaporated. Colorless crystals of the product were obtained upon recrystallization with CH_2Cl_2/petroleum ether. Yield: 72 mg (0.085 mmol, 60%). ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.32−7.64 (30H, m, ArH), 13.38 (1H, s, $CHOBF_3$). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2): 129.3 (t, J_{C-P} = 5.1 Hz, Ar), 131.3 (s, Ar), 133.4 (t, J_{C-P} = 5.7 Hz, Ar), 134.8 (t, J_{C-P} = 25.5 Hz, Ar), 192.9 (t, J_{C-P} = 8.3 Hz, *cis* CO's), 196.1 (t, J_{C-P} = 8.1 Hz, *trans* CO), 300.7 (s, $CHOBF_3$). ^{31}P NMR (RT, 121 MHz, CD_2Cl_2): 12.6 ppm (s). ^{19}F NMR (RT, 471 MHz, CD_2Cl_2): −156.5 ppm (s). IR: ν_{CO} (cm^{-1}, CH_2Cl_2) 2063, 2003, 1964. HRMS (FAB+) *m*/*z* calcd for $C_{40}H_{31}BF_2O_4P_2Re$ (M − F) 873.1317, found 873.1331; for $C_{40}H_{30}O_4P_2Re$ (M − BF_3 − H) 823.1177, found 823.1055.

Method B. In the glovebox, a suspension of $[Re(CO)_4(PPh_3)_2][BF_4]$ (**1b**) (333 mg, 0.378 mmol) in THF (3 mL) was stirred in a vial. $LiHBEt_3$ (1 M in THF, 378 μL, 1 equiv) was syringed in to give a yellow solution after filtration. THF was evaporated to give the crude formyl species and $LiBF_4$ byproduct as a yellow residue. $BF_3\cdot OEt_2$ (62 μL, 1.3 equiv) was dissolved in CH_2Cl_2 (5 mL) and added to the residue, and the solution was stirred for 5 min, after which the solvent was evaporated. The solid was recrystallized from CH_2Cl_2/petroleum ether to give 292 mg (0.340 mmol, 90%) of a white crystalline solid.

$Mn(CO)_3(PPh_3)_2(CHOBF_3)$ (4a). In the glovebox, a suspension of $[Mn(CO)_4(PPh_3)_2][BF_4]$ (**1a**) (331 mg, 0.425 mmol) in THF (3 mL) was stirred in a vial. $LiHBEt_3$ (1 M in THF, 425 μL, 1 equiv) was syringed in to give a yellow solution after filtration. $BF_3\cdot OEt_2$ (70 μL, 0.56 mmol, 1.3 equiv) was syringed into the THF solution and stirred for 5 min, after which the solvent was evaporated. The solid was recrystallized from THF/petroleum ether to give 204 mg (0.268 mmol, 63%) of a yellow crystalline solid. Anal. Calcd for $C_{40}H_{31}BF_3MnO_4P_2$: C, 62.93; H, 4.49. Found: C, 62.86; H, 4.22. ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.38−7.58 (30H, m, ArH), 12.80 (1H, s, $CHOBF_3$). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2) partial: 129.4 (t, J_{C-P} = 5.0 Hz, Ar), 131.2 (s, Ar), 133.4 (t, J_{C-P} = 5.2 Hz, Ar), 134.5 (d, J_{C-P} = 44.5 Hz, Ar), 218.2 (t, J_{C-P} = 18.2 Hz, *cis* CO's), 220.9 (t, J_{C-P} = 16.5 Hz, *trans* CO); a signal for the carbene carbon could not be observed. ^{31}P NMR (RT, 121 MHz, CD_2Cl_2): 63.2 ppm (s). ^{19}F NMR (RT, 471 MHz, CD_2Cl_2): −156.3 ppm (s).

$Mn(CO)_3(PPh_3)_2(CHOB(C_6F_5)_3)$ (5a). In the glovebox, a suspension of $[Mn(CO)_4(PPh_3)_2][BF_4]$ (**1a**) (95 mg, 0.122 mmol) in toluene (3 mL) was stirred in a vial. $NaHBEt_3$ (1 M in toluene, 122 μL, 1 equiv) was syringed in to give a yellow solution after filtration. $B(C_6F_5)_3$ (62 mg, 0.122 mmol) was dissolved in toluene (5 mL) and added to the reaction mixture, which was stirred for 5 min before evaporating the solvent. The solid was recrystallized from CH_2Cl_2/petroleum ether and dried *in vacuo* to give 95 mg (0.079 mmol, 65%) of a yellow crystalline solid. Anal. Calcd for $C_{58}H_{31}BF_{15}MnO_4P_2$: C, 57.83; H, 2.59. Found: C, 57.79; H, 3.04. ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.29−7.48 (30H, m, ArH), 13.22 (1H, s, $CHOB(C_6F_5)_3$). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2) partial: 130.2 (t, J_{C-P} = 5.3 Hz, Ar), 132.8 (s, Ar), 133.1 (t, J_{C-P} = 5.3 Hz, Ar), 134.1 (Ar), 137.1 (m, $B(C_6F_5)$), 148.6 (m, $B(C_6F_5)$), 212.4 (m, *cis* CO's); a signal for the carbene carbon could not be observed. ^{31}P NMR (RT, 121 MHz, CD_2Cl_2): 64.8 ppm (s). ^{19}F NMR (RT, 471 MHz, CD_2Cl_2): −132.2, −159.2, −165.2 ppm.

$Re(CO)_3(PPh_3)_2(CHOB(C_6F_5)_3)$ (5b). In the glovebox, a suspension of $[Re(CO)_4(PPh_3)_2][BF_4]$ (**1b**) (187 mg, 0.212 mmol) in THF (3 mL) was stirred in a vial. $LiHBEt_3$ (1 M in THF, 212 μL, 1 equiv) was syringed in to give a yellow solution after filtration. THF was evaporated to give the crude formyl species and $LiBF_4$ byproduct as a yellow residue. $B(C_6F_5)_3$ (109 mg, 0.213 mmol) was dissolved in CH_2Cl_2 (5 mL) and added to the residue; after stirring for 5 min the solvent was evaporated. The solid was recrystallized from THF/petroleum ether and dried *in vacuo* to give 125 mg (0.0954 mmol, 45%) of a white crystalline solid. Anal. Calcd for $C_{58}H_{31}BF_{15}O_4P_2Re$: C, 52.15; H, 2.34. Found: C, 52.85; H, 2.34. ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.30−7.47 (30H, m, ArH), 13.84 (1H, s, $CHOB(C_6F_5)_3$). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2): 118.2 (m, $B(C_6F_5)$), 129.0 (t, J_{C-P} = 5.0 Hz, Ar), 131.2 (s, Ar), 133.4 (t, J_{C-P} = 5.5 Hz, Ar), 134.6 (t, J_{C-P} = 24.4 Hz, Ar), 137.3 (dm, J_{C-F} = 250 Hz, $B(C_6F_5)$), 140.2 (dm, J_{C-F} = 252 Hz, $B(C_6F_5)$), 148.4 (dm, J_{C-F} = 242 Hz, $B(C_6F_5)$), 192.9 (t, J_{C-F} = 8.9 Hz, *cis* CO's), 195.0 (t, J_{C-F} = 7.2 Hz, *trans* CO), 298.9 (s, CHOB). ^{31}P NMR (RT, 121 MHz, CD_2Cl_2): 12.6 ppm (s). ^{19}F NMR (RT, 471 MHz, CD_2Cl_2): −132.1 (6F, m, *ortho*-C_6F_5), −159.4 (3F, m, *para*-C_6F_5), −165.2 (6F, m, *meta*-C_6F_5). HRMS (FAB+): *m*/*z* calcd for $C_{52}H_{31}BF_{10}O_4P_2Re$ (M − C_6F_5) 1169.119, found 1169.121; for $C_{40}H_{30}O_4P_2Re$ (M− $B(C_6F_5)_3$ − H) 823.1177, found 823.1798.

NMR-Scale Preparation of $[Re(CO)_3(PPh_3)_2(CHOSiMe_3)][BPh_4]$ (8). In the glovebox, a suspension of $[Re(CO)_4(PPh_3)_2][BPh_4]$ (**1b**) (11 mg, 0.010 mmol) in THF (3 mL) was stirred in a

vial. $LiHBEt_3$ (1 M in THF, 10 μL, 1 equiv) was syringed in to give a yellow solution. Solvent was evaporated to give the crude formyl species and $LiBPh_4$ byproduct as a yellow residue. The residue was dissolved in CD_2Cl_2 (0.4 mL) and transferred to a J-Young NMR tube, and the solution frozen in the cold well. $SiMe_3OTf$ (2 μL, 0.01 mmol, 1 equiv) was dissolved in CD_2Cl_2 (0.3 mL) and the resulting solution added to the J-Young tube and frozen in the cold well. The contents of the tube were kept at LN_2 temperature until ready to be placed into the NMR probe, where it was thawed and shaken vigorously to give a yellow solution. ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ −0.09 (9H, s, $OSi(CH_3)_3$), 6.83−6.90 (4H, m, $B(C_6H_5)_4$), 6.98−7.07 (8H, m, $B(C_6H_5)_4$), 7.27−7.36 (8H, m, $B(C_6H_5)_4$), 7.37−7.47 (12H, m, Ar−H), 7.48−7.56 (18H, m, ArH), 13.91 (1H, s, $CHOSiMe_3$). ^{31}P NMR (RT, 121 MHz, CD_2Cl_2): 11.3 ppm (s).

$Mn(CO)_3(PPh_3)_2(CH_2OCH_3)$ (9). In a vial, $[Mn(CO)_3(PPh_3)_2(CHOMe)][OTf]$ (40 mg, 0.047 mmol) was suspended in THF (2 mL). $LiHBEt_3$ (1 M in THF, 47 μL, 1 equiv) was syringed into the vial. After 2 min of mixing followed by filtration, the resulting yellow solution was placed into a small vial, which was in turn placed in a larger vial containing petroleum ether (5 mL) for crystallization by diffusion. After 15 h the resulting long yellow needles were decanted, washed with petroleum ether, and dried under vacuum to give 25 mg (0.036 mmol, 76% yield) of **9**. Anal. Calcd for $C_{41}H_{35}MnO_4P_2$: C, 69.20; H, 5.38. Found: C, 68.96; H, 5.17. ^{1}H NMR (RT, 300 MHz, C_6D_6): δ 2.73 (3H, s, OCH3), 3.60 (2H, t, $^3J_{H-P}$ = 7.6 Hz, CH_2), 6.93−7.01 (6H, m, Ar−H), 7.02−7.11 (12H, m, Ar−H), 7.87−7.97 (12H, m, Ar−H). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2): 63.8 (s, OCH_3), 75.3 (t, J_{C-P} = 12.9 Hz, CH_2OMe), 128.6 (t, J_{C-P} = 4.6 Hz, Ar), 129.9 (s, Ar), 133.9 (t, J_{C-P} = 5.1 Hz, Ar) 136.7 (m, Ar), 222.8 (t, J_{C-P} = 17.8 Hz, *trans* CO), 224.4 (t, J_{C-P} = 21.3 Hz, *cis* CO's). ^{31}P NMR (RT, 121 MHz, C_6D_6): 76.6 ppm (s). ^{19}F NMR (RT, 471 MHz, C_6D_6): no signal, confirming the absence of OTf^-. IR: ν_{CO} (cm^{-1}, CH_2Cl_2) 2009, 1921, 1885.

***cis*-$Mn(CO)_4(PPh_3)(CH_2OCH_3)$ (10).** In the glovebox, Na/Hg (0.5 wt %, 4 equiv) was prepared in a flask. A THF (20 mL) solution of $Mn(PPh_3)(CO)_4Br$ (388 mg, 0.762 mmol) was slowly added onto the amalgam. The mixture was allowed to stir in the absence of light for 2 h. In another flask, $ClCH_2OCH_3$ (58 μL, 1 equiv) was dissolved in THF (10 mL) and placed in a Schlenk tube. On the Schlenk line, the manganese solution was decanted into the $ClCH_2OCH_3$ solution using a filter-tipped cannula. The mixture was allowed to stir in the absence of light for 2 h, after which all volatiles were removed. The residue was dissolved in THF, filtered, recrystallized from THF/petroleum ether, and dried under vacuum to give 319 mg (0.670 mmol, 88%) of **10** as a yellow crystalline solid. ^{1}H NMR (RT, 300 MHz, C_6D_6): δ 3.11 (3H, s, OCH_3), 3.90 (2H, d, $^3J_{H-P}$ = 7.0 Hz, CH_2), 6.93−7.02 (9H, m, Ar−H), 7.50−7.59 (6H, m, Ar−H). ^{13}C NMR (RT, 126 MHz, CD_2Cl_2): 63.4 (s, OCH_3), 71.1 (t, J_{C-P} = 11.7 Hz, CH_2OMe), 128.8 (d, J_{C-P} = 9.5 Hz, Ar), 130.6 (s, Ar), 133.4 (d, J_{C-P} = 10.4 Hz, Ar) 133.8 (d, J_{C-P} = 40.3 Hz, Ar), 215.7 (CO), 218.4 (d, J_{C-P} = 21.8 Hz, CO), 218.8 (CO). ^{31}P NMR (RT, 121 MHz, C_6D_6): 61.2 ppm (s). HRMS (FAB+): *m*/*z* calcd for $C_{24}H_{23}MnO_5P$ (M + H − H_2) 473.0351, found 473.0373.

Carbonylation of $Mn(CO)_3(PPh_3)_2(CH_2OCH_3)$ (10) to Form 13. To a flask was added $Mn(CO)_3(PPh_3)_2(CH_2OCH_3)$ (150 mg, 0.212 mmol) followed by C_6H_6 (20 mL). The flask was degassed on the Schlenk line and then filled with CO (1 atm). The flask was sealed and allowed to stir for 7 days protected from light. After removing all volatiles, the resulting yellow oil was triturated several times with hexanes and dried *in vacuo* to give 140 mg (0.197 mmol, 93%) of a yellow solid. The composition of the solid is a mixture containing *cis*-$Mn(PPh_3)(CO)_4(C(O)CH_2OCH_3)$ (***cis*-13**) (80%), *trans*-$Mn(PPh_3)(CO)_4(C(O)CH_2OCH_3)$ (***trans*-13**) (13%), and $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (**10**) (7%). If the same procedure is followed but CH_3OH is used instead of C_6H_6, the reaction is complete overnight. *cis*-$Mn(PPh_3)(CO)_4(C(O)CH_2OCH_3)$ (***cis*-13**): ^{1}H NMR (RT, 300 MHz, C_6D_6): δ 3.17 (3H, s, OCH_3), 3.60 (2H, s, CH_2), 6.98−7.07 (m, ArH), 7.35−7.44 (m, ArH), 7.59−7.67 (m, ArH). ^{13}C NMR (RT, 126 MHz, C_6D_6): 58.9 (s, OCH_3), 90.5 (d, J_{C-P} = 3.0 Hz, CH_2), 128.6, 130.8, 134.0, 135.1, 215.0 (CO), 215.6 (CO), 217.7 (CO), 272.3 (dt, J_{C-P} = 16.2 Hz, J_{C-C} = 3.5 Hz, $C(O)CH_2OCH_3$). ^{31}P NMR (RT, 121 MHz, C_6D_6): 53.5 ppm (s, br). IR CO (cm^{-1}, CH_2Cl_2): 2070, 1994, 1962, 1920, 1624. HRMS (FAB+): *m*/*z* for $C_{25}H_{21}MnO_6P$ (M + H) 503.0456, found 503.0465. *trans*-$Mn(PPh_3)(CO)_4(C(O)CH_2OCH_3)$ (***trans*-13**): ^{1}H NMR (RT, 300 MHz, C_6D_6): 3.27 (3H, s, OCH_3), 3.94 (2H, s, CH_2), 6.98−7.07 (m, ArH), 7.71−7.80 (m, ArH), 7.80−7.88 (m, ArH). ^{13}C NMR (RT, 126 MHz, C_6D_6): 59.1 (s, OCH_3), 91.6 (d, J_{C-P} = 4.6 Hz, CH_2), 128.8, 132.7, 135.6, 263.4 (br, $C(O)CH_2OCH_3$), The carbonyl ligand signals could not be assigned, as they overlap with other peaks. IR ν_{CO} (cm^{-1}, CH_2Cl_2): 1636, other stretches could not be assigned due to overlap.

General Procedure for NMR-Scale Addition of Electrophiles to $Mn(PPh_3)(CO)_4(COCH_2OCH_3)$ (13). In the drybox 15 mg (0.030 mmol) of $Mn(PPh_3)(CO)_4(COCH_2OCH_3)$ (**13**) was added to a vial. To the vial was added 0.6 mL of CD_2Cl_2 followed by 0.030 mmol of the desired electrophile. The solution was pipetted into a J-Young NMR tube, and disappearance of ***cis*-13** and appearance of products monitored by ^{1}H and ^{31}P NMR.

Methylation of 13 with MeOTf. MeOTf (3.4 uL, 4.9 mg, 0.030 mmol) was added, leading to formation of **14** and *trans*-1,2-dimethoxyethene over time.

Ethylation of 13 with EtOTf. EtOTf (3.9 uL, 5.3 mg, 0.030 mmol) was added, leading to formation of **14** and *trans*-1-ethoxy-2-methoxyethene over time.

Ethylation of 13 with $[Et_3O][BF_4]$. $[Et_3O][BF_4]$ (5.7 mg 0.030 mmol) was added, leading to formation of **15** and ultimately *trans*-1-ethoxy-2-methoxyethene over time. Spectroscopic data for $[Mn(PPh_3)(CO)_4(C(OEt)CH_2OCH_3)$ (**15**): ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.5 (15H, m, Ph); 4.28 (2H, q, $^3J_{H-H}$ = 7 Hz, OCH_2CH_3); 4.12 (2H, s, CH_2OCH_3); 3.68 (3H, s, OCH_3); 1.36 (3H, t, $^3J_{H-H}$ = 7 Hz, OCH_2CH_3). ^{31}P NMR (RT, 121 MHz, C_6D_6): 52.2 (s, br).

Protonation of 13 with HOTf. HOTf (2.7 uL, 4.5 mg, 0.030 mmol) was added, leading to formation of **18** and ultimately **14** and methyl acetate over time.

Formation of $Mn(PPh_3)(CO)_4(C(OEt)=CHOCH_3)$ (16). In the drybox 30 mg (0.060 mmol) of **13** and 11.4 mg (0.0600 mmol) of $[Et_3O][BF_4]$ were added to a vial. To the vial was added 0.6 mL of CD_2Cl_2. The solution was shaken, then pipetted into a J-Young NMR tube, and the reaction was monitored by ^{1}H and ^{31}P NMR. When the alkoxycarbene **15** was at its maximum concentration (~ 6 h), triethylamine (11 uL, 7.9 mg, 7.8 mmol, 1.3 equiv) was added to the solution. ^{1}H NMR (RT, 300 MHz, CD_2Cl_2): δ 7.5 (15H, m, Ph); 6.35 (1H, d, $^4J_{P-H}$ = 2.7 Hz, C=C*H*); 3.49 (3H, s, OMe); 3.17 (2H, q, $^3J_{H-H}$ = 7 Hz, OCH_2CH_3); 0.75 (3H, t, $^3J_{H-H}$ = 7 Hz, OCH_2CH_3). ^{31}P NMR (RT, 121 MHz, C_6D_6): 54.3 (s, br).

Synthesis of $Mn(PPh_3)(CO)_4(CH_2COOCH_3)$ (18). In the drybox 500 mg (0.982 mmol) of $Mn(PPh_3)(CO)_4Br$ was added to a vial and dissolved in THF. This solution was pipetted into a flask containing a Na/Hg amalgam (0.5%, 4 equiv), and the mixture was stirred for 2 h. In a separate flask 287.5 mg (1.178 mmol, 1.2 equiv) of methyl 2-(tosyloxy)acetate was dissolved in THF. The solution of $[Na][Mn(PPh_3)(CO)_4]$ was filtered through Celite into the flask containing methyl 2-(tosyloxy)acetate. The mixture was stirred overnight before being filtered through Celite, dried *in vacuo*, and triturated with pentane to yield 420 mg (0.837 mmol, 85%) of **18**. X-ray quality crystals were obtained by layering a toluene solution of **18** with pentane and placing in a −35 °C freezer overnight. ^{1}H NMR (RT, 300 MHz, C_6D_6): δ 7.47 (6H, m, Ph); 6.93 (9H, m, Ph); 3.63 (3H, s, OMe); 1.36 (2H, d, $^3J_{P-H}$ = 7.2 Hz, CH_2). ^{31}P NMR (RT, 121 MHz, C_6D_6): 57.9 (s, br).

Table 1. Crystal Data and Structure Refinement for 4b, 5a, 5b, and 18

	4b	5a	5b	17
empirical formula	$C_{41}H_{33}BCl_2F_3O_4P_2Re$	$C_{58}H_{31}BF_{15}O_4P_2Mn \cdot 1.37(CH_2Cl_2)$[58]	$C_{58}H_{31}BF_{15}O_4P_2Re \cdot 0.51(CH_2Cl_2),0.49(C_5H_{12})$[59]	$C_{25}H_{20}O_6PMn$
mol wt	976.52	1320.44	1414.34	502.32
temperature, K	100(2)	100(2)	100(2)	100(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	12.165(2)	12.514(1)	12.6862(8)	9.9363(4)
b, Å	12.4987(2)	29.923(1)	29.8277(19)	14.5616(5)
c, Å	14.550(3)	14.991(1)	15.0080(9)	15.7421(6)
α, deg	95.935(2)	90	90	90.000
β, deg	97.794(2)	101.670(4)	102.822(4)	92.966(2)
γ, deg	113.704(2)	90	90	90.000
vol, Å^3	1976.2(6)	5497.4(6)	5537.4(6)	2274.65(15)
Z	2	4	4	4
density (calcd), Mg/m^3	1.641	1.595	1.697	1.467
μ, mm^{-1}	3.346	0.531	2.401	0.690
F(000)	964	2653	2792	1032
cryst size, mm^3	0.30 × 0.20 × 0.06	0.31 × 0.24 × 0.14	0.18 × 0.13 × 0.05	0.26 × 0.23 × 0.22
2θ range, deg	1.81 to 28.23	2.37 to 29.67	2.34 to 24.00	1.91 to 38.37
index ranges	$-15 \le h \le 15$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-17 \le h \le 16$ $-41 \le k \le 41$ $-19 \le l \le 20$	$-19 \le h \le 19$ $-45 \le k \le 45$ $-23 \le l \le 23$	$-15 \le h \le 16$ $-20 \le k \le 25$ $-25 \le l \le 25$
reflns collected	16 967	103 862	177 247	57 123
indep reflns	8763 [R(int) = 0.0197]	15 189 [R(int) = 0.0536]	21 028 [R(int) = 0.1340]	10 030 [R(int) = 0.1014]
data/restraints/params	8763/0/487	15 189/8/795	21 028/16/778	10 030/0/378
goodness-of-fit on F^2	1.067	2.805	1.739	1.540
final R indices [$I > 2\sigma(I)$]	R1 = 0.0259 wR2 = 0.0647	R1 = 0.0525 wR2 = 0.0843	R1 = 0.0639 wR2 = 0.0939	R1 = 0.0326 wR2 = 0.0774
R indices (all data)	R1 = 0.0275 wR2 = 0.0654	R1 = 0.0766 wR2 = 0.0855	R1 = 0.1212 wR2 = 0.0975	R1 = 0.0460 wR2 = 0.0793
largest diff peak and hole, e Å^{-3}	2.021 and −1.306	1.962 and −1.484	7.047 and −4.595	0.679 and −0.702

Formation of $Mn(PPh_3)(CO)_4(CH_2OCH_3)$ (10) from $[Mn(PPh_3)(CO)_5][BF_4]$ (12) with $[(dmpe)_2PtH][PF_6]$ and HOTs. To a Schlenk flask in the drybox was added $[Mn(PPh_3)(CO)_5][BF_4]$ (**12**) (100 mg, 0.184 mmol) and $[(dmpe)_2PtH][PF_6]$ (141.5 mg, 0.220 mmol, 1.2 equiv). The flask was removed from the box, put on a Schlenk line, and cooled to −78 °C. Methanol was cannulated into the flask and the mixture stirred for 15 min. A solution of HOTs (77 mg, 0.41 mmol, 2.2 equiv) in methanol was cannulated into the flask. The solution was allowed to warm to RT and stirred for 1 h at RT. Solvent was removed *in vacuo* and the residue dissolved in benzene, filtered through Celite, evaporated to dryness, and triturated with pentane to yield 35 mg (0.74 mmol, 40% yield) of **10**.

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Supporting Information Available: The crystal structures of **3b** and **9** are reported. The .cif files for all of the structures are available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 685551 (**3b**), 686292 (**5a**), 685990 (**5b**), 644905 (**9**), and 742899 (**17**).