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THE SYNTHESIS OF ALKOXYCARBONYL, CARBAMOYL AND ISOCYANATO COMPLEXES, *fac*-$M(CO)_3(P\text{-}P)Z$ [M = Mn, Re; P-P = dppe, dppp; Z = C(O)OMe, C(O)OEt, C(O)NHPr^n, NCO]. THE SINGLE CRYSTAL STRUCTURES OF *fac*-$Mn(CO)_3(dppp)C(O)OEt$ AND *fac*-$Mn(CO)_3(dppe)NCO$[1]

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Abstract—The title compounds were prepared by the reaction of the cationic complex $[M(CO)_4(P\text{-}P)]^+[BF_4]^-$ with the appropriate nucleophiles leading to *fac*-$M(CO)_3(P\text{-}P)Z$ [M = Mn, Re; P-P = dppe, dppp; Z = C(O)OMe, C(O)OEt, C(O)NHPr^n, NCO] complexes. The X-ray structures of *fac*-$Mn(CO)_3(dppp)C(O)OEt$ and *fac*-$Mn(CO)_3(dppe)NCO$ are also reported.

Nucleophilic attack on carbon monoxide coordinated to transition metals leads to functional groups sigma-bonded to the metal. The resulting compounds are similar in some respects to species that are postulated intermediates in the catalytic reactions of carbon monoxide.[2] Such reactions with manganese and rhenium carbonyls are particularly useful because many of the resulting complexes are unreactive and accordingly relatively easy to characterize and study. Thus, the formyl complexes $M_2(CO)_9(CHO)^-$ and $M(CO)_2[P(OPh)_3]_3CHO$ (M = Mn, Re) were obtained from the neutral[3] and cationic[4] complexes $M_2(CO)_{10}$ and $[M(CO)_3\{P(OPh)_3\}_3]^+$, respectively, when these were treated with borohydride. Similarly, reactions of $[Re(CO)_6]^+$ with sodium azide, $[Mn(CO)_5(PPh_3)]^+$ with ammonia and *trans*-$[M(CO)_4(PPh_3)_2]^+$ with sodium alkoxides gave $M(CO)_5NCO$,[5] *cis*-$Mn(CO)_4(PPh_3)C(O)NH_2$[6] and *mer,trans*-$M(CO)_3(PPh_3)_2C(O)OR$,[7] respectively. However, reactions of nucleophiles with manganese and rhenium carbonyl cationic complexes, $[M(CO)_4(P\text{-}P)][BF_4]$, where P-P are chelated phosphines, have not been studied extensively[8] and such reactions constitute the basis of the present study.

RESULTS AND DISCUSSION

Equation (1) shows the general reaction used to prepare the compounds of interest:

$$\underset{\mathbf{1}}{[M(CO)_4(P\text{-}P)][BF_4]} + Nu^- \longrightarrow \underset{\mathbf{2}}{fac\text{-}M(CO)_3(P\text{-}P)Z} \quad (1)$$

1	M	P-P	Nu^-	**2**	Z
a	Mn	dppe	OEt	**a**	C(O)OEt
b	Mn	dppp	OEt	**b**	C(O)OEt
c	Re	dppe	OEt	**c**	C(O)OEt
d	Re	dppp	OMe	**d**	C(O)OMe
b	Mn	dppp	(H_2NPr^n)	**e**	C(O)NHPr^n
a	Mn	dppe	N_3	**f**	NCO
b	Mn	dppp	N_3	**g**	NCO
c	Re	dppe	N_3	**h**	NCO

[P-P is $Ph_2P(CH_2)_nPPh_2$:
$n = 2$ for dppe; $n = 3$ for dppp).

In these reactions attack of the nucleophile occurs regioselectively on one of the two equivalent COs *cis* to the chelated bis(diphenylphosphino)alkane ligand, leading exclusively to facial isomers.

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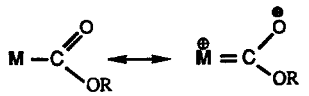
Alkoxycarbonyl complexes

When the nucleophile in eq. (1) is sodium alkoxide, the corresponding alkoxycarbonyl complexes **2a–d** are formed in 85–96% yield. The IR spectra of **2a–d** exhibit three strong $\nu(C\equiv O)$ vibrations characteristic of facial geometry.[9] These complexes show one $\nu(C{=}O)$ as a medium intensity band in the region 1606–1598 cm^{-1}. The $\nu(C{=}O)$ vibrations in most simple organic aldehydes, acids and esters are observed at much higher frequencies.[10] The carboxylate carbonyl resonances in the ^{13}C NMR spectra of **2a–d** are observed at relatively low fields (δ 218–197) compared to organic carbonyl compounds. The low $\nu(C{=}O)$ vibrations in the IR spectra and lower field chemical shifts in the ^{13}C NMR spectra of **2a–d** may be attributed to significant contributions from their carbene resonance forms:



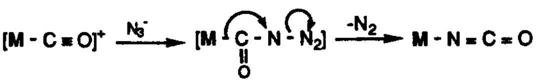
Alkoxycarbonyl complexes containing the phosphorus atoms in five-membered rings (**1a** and **2c**) decompose in benzene solution and are less reactive than the alkoxycarbonyl complexes containing the phosphorus atoms in six-membered rings (**1b** and **1d**). The identity of the decomposition product of **1a** is not known; however, **1c** cleanly converts to a bridging carbonato dimer, $[Re(CO)_3(dppe)]_2(\mu\text{-}O_3C)$, whose full characterization will be reported elsewhere. All the alkoxycarbonyl complexes slowly ionize in CH_2Cl_2 to give the corresponding cationic complexes.

Carbamoyl complex

Treatment of the cationic complex **1b** with n-$C_3H_7NH_2$ [eq. (1)] readily affords the carbamoyl complex *fac*-$Mn(CO)_3(dppp)C(O)NHC_3H_7$ (**2e**) in 87% yield. The IR spectrum shows three strong $\nu(C\equiv O)$ vibrations characteristic of facial geometry and a medium intensity $\nu(C{=}O)$ at 1549 cm^{-1}. The NH proton in the ^1H NMR spectrum is observed as a triplet. The carbamoyl carbon resonance in the ^{13}C NMR spectrum is observed as a triplet at δ 213.3 in the same region as those of **2a-d**. Rather surprisingly, the amide linkage in **2e** ionizes in CH_2Cl_2 to the corresponding cation. Analogous ionization has been observed for a related complex, $Re(\eta^5\text{-}C_5H_5)(CO)(N_2)C(O)NH_2$.[11]

Isocyanato complexes

Reactions of the cationic complexes **1a–c** with sodium azide give the isocyanato complexes **2f–h** in 89–90% yield. The reactions may proceed through the following sequence:[12]



Unlike a similar reaction of the molybdenum complex $[Mo(\eta^5\text{-}C_5Me_5)(CO)_3(PPh_3)][BF_4]$,[13] no azido complexes, M—N_3, are formed. The IR spectra of **2f–h** exhibit the three strong $\nu(C\equiv O)$ vibrations associated with facial geometry as well as one strong $\nu(NCO)$ in the expected range 2242–2233 cm^{-1}.[13,14] The isocyanato carbon resonances in the ^{13}C NMR spectra of **2f** and **2h** occur at δ 128.6 and 127.7, respectively, consistent with the N—C—O linkage rather than the possible alternate O—N—C linkage.[14] The complex **2f** reacts with HBr, HOTs and formic acid affording the bromo, tosylate and formate complexes, respectively [eq. (2)].

$$\underset{\mathbf{2f}}{Mn(CO)_3(dppe)NCO} + HX \longrightarrow \underset{\mathbf{3}}{Mn(CO)_3(dppe)X} \quad (2)$$

3a X = Br
3b X = OTs
3c X = OC(O)H

These results are consistent with those reported for the reaction of the nitrosyl cationic rhenium isocyanato complex, $[Re(L)(NO)(CO)(NCO)]^+$ (L = 1,4,7-triazacyclononane), with HBr, HOTf and formic acid which also gave the bromo, triflate and formate complexes, respectively.[15] The complexes **3a**[16] and **3b**[17] synthesized by alternate routes have been characterized previously. The IR spectrum of **3c** exhibits three strong $\nu(C\equiv O)$ vibrations characteristic for facial geometry and one strong $\nu(C{=}O)$ at 1613 cm^{-1}. The ^1H and ^{13}C NMR spectra show the formate proton resonance at δ 8.35 and carbon resonance at δ 167.6, respectively.

X-ray structure of fac-$Mn(CO)_3(dppp)C(O)OEt$ (**2b**)

A thermal ellipsoid plot of **2b** is shown in Fig. 1. The atoms connected to the manganese atom define a distorted octahedral geometry. The equatorial plane of the octahedron is occupied by two carbon monoxide ligands and the two phosphorus atoms of the chelating dppp ligand. One of the axial sites is filled by a third carbon monoxide ligand. The ethoxy-carbonyl group —C(O)OEt has been built into the remaining axial position. Some selected bond distances and angles of **2b** have been compiled in Table 1. The Mn—P distances of 2.346(1) and

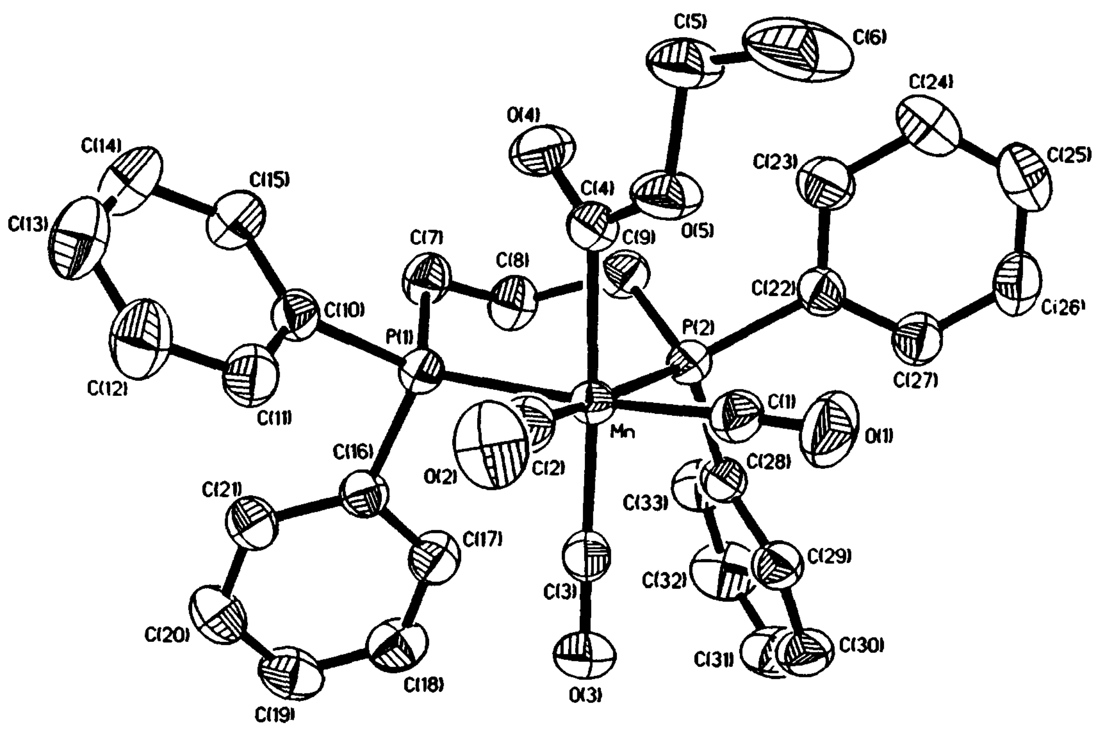


Fig. 1. Perspective drawing of the molecule *fac*-$Mn(CO)_3(dppp)C(O)OEt$ (**2b**).

2.340(1) Å are nearly equivalent. The corresponding *trans* Mn—CO distances of 1.808(2) and 1.805(3) Å in the equatorial plane are nearly equal, but the axial Mn—CO distance of 1.814(2) Å is slightly longer. For comparison, the corresponding Mn—P, *trans* Mn—CO and axial Mn—CO distances in the related *fac*-$[Mn(CO)_3(dppp)C(OH)CH_3][OTf]$ are 2.356(1), 2.357(1), 1.796(5), 1.805(6) and 1.852(4) Å, respectively.[18] The longer Mn—P and axial Mn—CO bonds in the cationic hydroxycarbene are attributed in part to a decrease in π-back-bonding to the diphosphine and to the axial CO as a result of the cationic nature of the complex and the strong π-acceptor ability of the hydroxycarbene (vs ethoxycarbonyl) ligand. The Mn—C (carboxylate) distance of 2.059(2) Å in **2b** and Mn—C (carbene) distance of 1.968(4) Å in the hydroxycarbene are consistent and reflective of the inability of the ethoxycarbonyl ligand to compete effectively for metal $d\pi$-electron density. The Mn—C (carboxylate) bond in **2b** exhibits essentially minimal multiple-bond character, and compares favourably with the single bond distances of 2.05(1) and 2.06(1) Å in *cis*-$Mn(CO)_4(Ph_3)C(O)OMe$[19] and 2.062(7) Å in $Mn(CO)_2[P(OPh)_3]C(O)CH_3$.[4a] The bond distances and angles in the ethoxycarbonyl ligand are unexceptional and the ethoxycarbonyl is in the expected conformation, i.e. with the sterically more demanding ethoxy group oriented over the $Mn(CO)_2$ equatorial plane rather than over the Mn(dppp) unit.

X-ray structure of fac-$Mn(CO)_3(dppe)NCO$ (**2f**)

The molecular structure of **2f** is shown in Fig. 2 and like **2b**, also possesses a *facial* octahedral coordination geometry about the metal atom. The dppe is in the equatorial plane and one of the axial sites is occupied by the isocyanato ligand. To our knowledge, this is the first example of a complete crystallographic analysis of a low-valent manganese(I) isocyanato complex. Some selected bond distances and angles of **2f** are shown in Table 2. The Mn(CO) and Mn(dppe) distances and angles are normal. The most interesting feature of **2f** is the bound isocyanato ligand. The Mn—N, N—C and C—O distances are 1.993(6), 1.129(9) and 1.217(10) Å, respectively. These distances may be compared to 2.051(5), 1.157(8) and 1.203(8) Å in the manganese(II) compound $[Mn_2(tren)_2(NCO)_2][BPh_4]_2$,[20] and 1.934(3), 1.171(5), 1.193(5)/1.918(3), 1.164(5) and 1.223(5) Å observed in the manganese(IV) complex $Mn(TPP)(NCO)_2$.[21] The NCO ligands in all three of these compounds are linear with N—C—O angles of 178.9(8), 178.8(7) and 176.5(4)/176.3(5)° for **2f**, $[Mn_2(tren)_2(NCO)_2][BPh_4]$ and $Mn(TPP)(NCO)_2$, respectively. It is interesting to

Table 1. Selected bond distances (Å) and angles (°) for *fac*-$Mn(CO)_3$(dppp)C(O)OEt (**2b**)

Bond distances			
Mn—P(1)	2.346(1)	P(2)—C(28)	1.830(2)
Mn—P(2)	2.340(1)	O(1)—C(1)	1.131(3)
Mn—C(1)	1.808(2)	O(2)—C(2)	1.145(3)
Mn—C(2)	1.805(3)	O(3)—C(3)	1.152(3)
Mn—C(3)	1.814(2)	O(4)—C(4)	1.212(3)
Mn—C(4)	2.059(2)	O(5)—C(4)	1.371(3)
P(1)—C(7)	1.844(2)	O(5)—C(5)	1.449(3)
P(1)—C(10)	1.836(2)	C(5)—C(6)	1.492(5)
P(1)—C(16)	1.840(2)	C(7)—C(8)	1.531(3)
P(2)—C(9)	1.838(2)	C(8)—C(9)	1.530(4)
P(2)—C(22)	1.844(2)		
Bond angles			
P(1)—Mn—P(2)	91.4(1)	C(7)—P(1)—C(16)	101.3(1)
P(1)—Mn—C(1)	175.5(1)	C(10)—P(1)—C(16)	102.1(1)
P(2)—Mn—C(1)	86.1(1)	Mn—P(2)—C(9)	117.4(1)
P(1)—Mn—C(2)	94.9(1)	Mn—P(2)—C(22)	115.5(1)
P(2)—Mn—C(2)	171.9(1)	C(9)—P(2)—C(22)	99.6(1)
C(1)—Mn—C(2)	87.3(1)	Mn—P(2)—C(28)	114.1(1)
P(1)—Mn—C(3)	93.5(1)	C(9)—P(2)—C(28)	105.5(1)
P(2)—Mn—C(3)	96.4(1)	C(22)—P(2)—C(28)	102.8(1)
C(1)—Mn—C(3)	90.5(1)	C(4)—O(5)—C(5)	118.3(2)
C(2)—Mn—C(3)	88.4(1)	Mn—C(1)—O(1)	177.5(2)
P(1)—Mn—C(4)	86.6(1)	Mn—C(2)—O(2)	173.4(2)
P(2)—Mn—C(4)	88.4(1)	Mn—C(3)—O(3)	173.0(2)
C(1)—Mn—C(4)	89.6(1)	Mn—C(4)—O(4)	130.5(2)
C(2)—Mn—C(4)	86.7(1)	Mn—C(4)—O(5)	111.2(1)
C(3)—Mn—C(4)	175.1(1)	O(4)—C(4)—O(5)	118.4(2)
Mn—P(1)—C(7)	118.0(1)	O(5)—C(5)—C(6)	106.2(2)
Mn—P(1)—C(10)	116.7(1)	P(1)—C(7)—C(8)	115.5(1)
C(7)—P(1)—C(10)	101.9(1)	C(7)—C(8)—C(9)	113.5(2)
Mn—P(1)—C(16)	114.4(1)	P(2)—C(9)—C(8)	116.0(2)

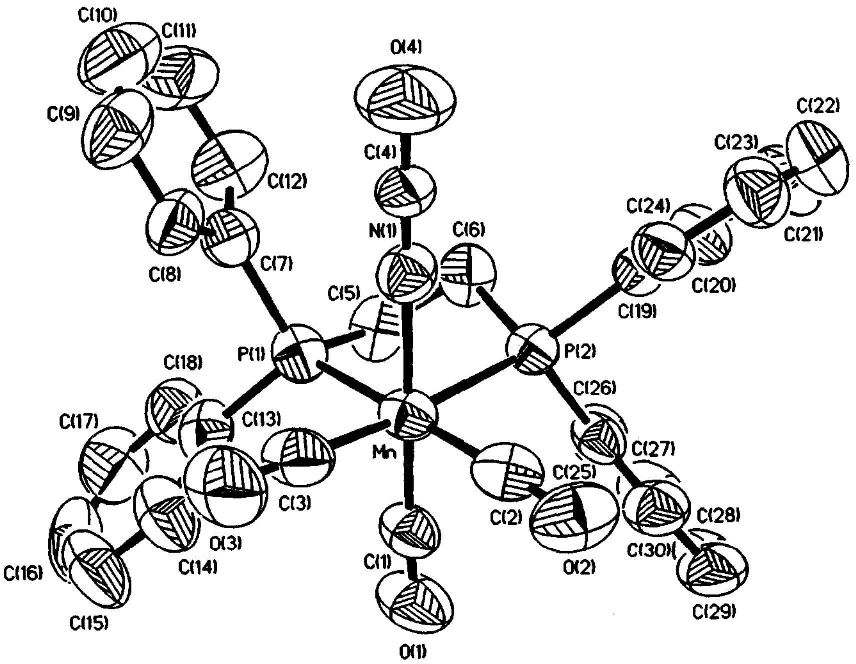


Fig. 2. Perspective drawing of the molecule *fac*-$Mn(CO)_3$(dppe)NCO (**2f**).

Table 2. Selected bond distances (Å) and angles (°) for *fac*-$Mn(CO)_3(dppe)NCO$ (**2f**)

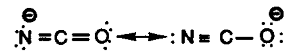
Bond distances

Mn—P(1)	2.341(2)	P(2)—C(6)	1.847(7)
Mn—P(2)	2.329(2)	P(2)—C(19)	1.823(7)
Mn—N(1)	1.993(6)	P(2)—C(25)	1.829(7)
Mn—C(1)	1.797(7)	O(1)—C(1)	1.150(9)
Mn—C(2)	1.802(8)	O(2)—C(2)	1.152(10)
Mn—C(3)	1.808(7)	O(3)—C(3)	1.147(9)
P(1)—C(5)	1.816(7)	O(4)—C(4)	1.217(10)
P(1)—C(7)	1.840(8)	N(1)—C(4)	1.129(9)
P(1)—C(13)	1.822(8)	C(5)—C(6)	1.535(10)

Bond angles

P(1)—Mn—P(2)	84.4(1)	C(5)—P(1)—C(7)	105.4(4)
P(1)—Mn—N(1)	89.5(2)	Mn—P(1)—C(13)	119.6(3)
P(2)—Mn—N(1)	86.3(2)	C(5)—P(1)—C(13)	103.6(3)
P(1)—Mn—C(1)	87.7(3)	C(7)—P(1)—C(13)	103.4(4)
P(2)—Mn—C(1)	91.0(2)	Mn—P(2)—C(6)	106.9(2)
N(1)—Mn—C(1)	176.3(3)	Mn—P(2)—C(19)	121.4(2)
P(1)—Mn—C(2)	174.6(2)	C(6)—P(2)—C(19)	105.0(3)
P(2)—Mn—C(2)	91.8(2)	Mn—P(2)—C(25)	115.8(2)
N(1)—Mn—C(2)	94.1(3)	C(6)—P(2)—C(25)	106.1(3)
C(1)—Mn—C(2)	88.5(3)	C(19)—P(2)—C(25)	100.3(5)
P(1)—Mn—C(3)	93.5(3)	Mn—N(1)—C(4)	175.5(6)
P(2)—Mn—C(3)	174.5(2)	Mn—C(1)—O(1)	176.8(7)
N(1)—Mn—C(3)	88.6(3)	Mn—C(2)—O(2)	176.0(6)
C(1)—Mn—C(3)	94.0(3)	Mn—C(3)—O(3)	177.2(7)
C(2)—Mn—C(3)	90.6(4)	O(4)—C(4)—N(1)	178.9(8)
Mn—P(1)—C(5)	106.2(3)	P(1)—C(5)—C(6)	108.9(5)
Mn—P(1)—C(7)	117.0(2)	P(2)—C(6)—C(5)	107.3(5)

note that the NCO ligand in **2f** is linearly bound rather than markedly bent as in the latter two compounds, e.g. the Mn—N—C angle in **2f** is 175.5(6)° vs 158.3(5) and 136.5(3)/133.1(3) for the latter two complexes. All of these structural features of the Mn—NCO unit in **2f** suggest that there is a significant contribution of the resonance form **B** to the observed bonding of the isocyanato ligand:



$$\overset{\ominus}{N}=C=O \longleftrightarrow :N\equiv C-\overset{\ominus}{O}:$$

A **B**

Although it is difficult to distinguish NCO from OCN ligation by X-ray only, the fact that the N—C distance is much shorter than the C—O distance, as well as the ^{13}C NMR data mentioned earlier, are consistent with the NCO sequence. This problem has been addressed previously.[14]

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of argon. Solvents were purified by standard methods. The IR spectra were recorded on a Perkin–Elmer 1600 Series FT-IR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^1H; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel–Temp apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc.

Starting materials

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) were purchased from commercial sources (either Pressure or Strem Chemical Co.). HBr (48% aqueous solution), *p*-toluenesulphonic acid monohydrate and NaN_3 were purchased from Aldrich. *Fac*-$Mn(CO)_3(P\text{-}P)Br$[16] and *fac*-$Re(CO)_3(dppe)Br$[22] were prepared according to literature procedures.

Preparation of fac-$Re(CO)_3(dppp)Br$

$Re(CO)_5Br$[23] (1.0 g, 2.462 mmol) and dppp (1.015 g, 2.460 mmol) were mixed with benzene (100 cm^3) and refluxed for *ca* 16 h. The solvent was removed using a rotary evaporator to yield a white solid residue (1.782 g, 2.337 mmol, 95%). Recrystallization from CH_2Cl_2/hexane afforded white microcrystalline *fac*-Re(CO)$_3$(dppp)Br. Data: m.p. > 260°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2035s, 1957s, 1902s. ^{1}H NMR (δ, $CDCl_3$): 7.32 (m, 20H), 2.81 (m, 4H), 1.61 (qn, $J = 5$ Hz, 2H). Found: C, 47.2; H, 3.5. Calc. for $C_{30}H_{26}BrO_3P_2Re$: C, 47.2; H, 3.4%.

General procedure for the preparation of [M(CO)$_4$(P-P)][BF$_4$] (**1a–d**)[24]

To a solution of *fac*-M(CO)$_3$(P-P)Br (approx. 3 mmol) in refluxing CH_2Cl_2 (100 cm^3) was added a slight excess of $AgBF_4$ while bubbling a stream of CO through the solution. After *ca* 16 h the solution was cooled and filtered through a pad of celite. The filtrate was concentrated and a small quantity of ether was added to precipitate the salt [M(CO)$_4$(P-P)][BF$_4$]. Finally, vacuum drying afforded almost-white **1a–d** in 89–93% yield. Data for **1a**: m.p. 230–232°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2094s, 2026s,sh, 2012vs, 1998s,sh. ^{1}H NMR (δ, $CDCl_3$): 7.56 (m, 20H), 3.36 (m, 4H). Found: C, 54.6; H, 3.8. Calc. for $C_{30}H_{24}BF_4MnO_4P_2$: C, 55.2; H. 3.7%. Data for **1b**: m.p. 180–182°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2092s, 2030s, 2003vs. ^{1}H NMR (δ, $CDCl_3$): 7.51 (m, 20H), 2.56 (m, 6H). Found: C, 55.6; H, 3.9. Calc. for $C_{31}H_{26}BF_4MnO_4P_2$: C, 55.8; H, 3.9%. Data for **1c**: m.p. 275–276°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2110s, 2029s,sh, 2017vs, 1999s,sh. ^{1}H NMR (δ, $CDCl_3$): 7.51 (m, 20H), 3.31 (m, 4H). Found: C, 45.9; H, 3.2. Calc. for $C_{30}H_{24}BF_4O_4P_2Re$: C, 45.9; H, 3.1%. Data for **1d**: m.p. 210–211°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2109s, 2033s, 2007vs. ^{1}H NMR (δ, $CDCl_3$): 7.41 (m, 20H), 2.64 (m, 6H). Found: C, 46.3; H, 3.2. Calc. for $C_{31}H_{26}BF_4O_4P_2Re$: C, 46.6; H, 3.2%.

General procedure for the preparation of fac-M(CO)$_3$(P-P)C(O)OR (**2a–d**)

A solution of [M(CO)$_4$(P-P)][BF$_4$] (**1a–d**) (*ca* 1 mmol) in ROH (approx. 75 cm^3) was treated with an equimolar solution of NaOR in ROH at 0°C. After brief stirring, the solutions were evaporated to dryness and the solid residues were extracted with approximately 50 cm^3 of benzene. The benzene solutions were concentrated and hexane was added to give white precipitates. Vacuum drying gave **2a–d** in 85–96% yield. Recrystallization of **2b** from benzene/hexane afforded light-yellow crystals suitable for single crystal X-ray crystallographic studies. Data for **2a**: m.p. 70–73°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2009s, 1936s, 1920s and $\nu(C{=}O)$ 1606m. ^{1}H NMR (δ, C_6D_6): 7.50 (m, 20H, C_6H_5), 4.11 (q, OCH_2CH_3, 2H), 2.75 (m, CH_2, 4H), 0.85 (t, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 223.4 (s, br, $2C\equiv O$), 217.5 (t, $J = 15$ Hz, $C\equiv O$), 214.9 (t, $J = 25$ Hz, $C{=}O$), 137.2–128.3 (m, C_6H_5), 57.3 (s, CH_2), 26.9 (t, $J = 21$ Hz, H_2CCH_2), 14.7 (s, CH_3). Found: C, 62.9; H, 5.0. Calc. for $C_{32}H_{29}MnO_5P_2$: C, 62.9; H, 4.8%. Data for **2b**: m.p. 167–168°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2013s, 1946s, 1915s and $\nu(C{=}O)$ 1598m. ^{1}H NMR (δ, C_6D_6): 7.35 (m, 20H, C_6H_5), 4.29 (q, 2H, OCH_2CH_3), 2.50 (m, CH_2, 6H), 1.25 (t, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 220.5 (s, br, $2C\equiv O$), 219.0 (t, $J = 15$ Hz, $C\equiv O$), 218.2 (t, $J = 22$ Hz, $C{=}O$), 138.3–127.6 (m, C_6H_5), 57.6 (s, OCH_2CH_3), 25.1 (t, $J = 12$ Hz, $H_2CCH_2CH_2$), 19.8 (s, $H_2CCH_2CH_2$), 15.3 (s, CH_3). Found: C, 63.7; H, 5.0. Calc. for $C_{33}H_{31}MnO_5P_2$: C, 63.4; H, 5.0%. Data for **2c**: m.p. 151–153°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2021s, 1941s, 1921s and $\nu(C{=}O)$ 1603m. ^{1}H NMR (δ, C_6D_6): 7.41 (m, 20H, C_6H_5), 3.65 (q, 2H, H_2CHH_3), 2.61 (m, 4H), 0.85 (t, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 197.2 (t, $J = 13$ Hz, $C{=}O$), 195.1 (dd, $J = 52$ Hz, 10 Hz, $2C\equiv O$), 193.6 (t, $J = 6$ Hz, $C\equiv O$), 136.6–127.6 (m, C_6H_5), 56.1 (s, H_2CCH_3), 26.5 (m, CH_2), 14.8 (s, CH_3). Found: C, 52.0; H, 4.3. Calc. for $C_{32}H_{29}O_5P_2Re$: C, 51.8; H, 4.0%. Data for **2d**: m.p. 209–210°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2026s, 1950s, 1916s and $\nu(C{=}O)$ 1610m. ^{1}H NMR (δ, C_6D_6): 7.32 (m, 23H, C_6H_5), 3.62 (s, 3H, CH_3), 2.42 (m, 6H). ^{13}C NMR (δ, C_6D_6): 200.9 (t, $J = 13$ Hz, $C{=}O$), 195.3 (t, $J = 8$ Hz, $2C\equiv O$), 192.3 (t, $J = 19$ Hz, $C\equiv O$), 137.5–127.5 (m, C_6H_5), 48.8 (s, CH_3), 24.5 (t, $J = 13$ Hz, $H_2CCH_2CH_2$), 19.9 (s, $H_2CCH_2CH_2$). Found: C, 53.7; H, 3.9. Calc. for $C_{32}H_{29}O_5P_2Re \cdot 0.5C_6H_6$: C, 53.8; H, 4.1%.

Kinetic stability of **2a–d** *in organic solvents*

Compounds **2a–d** (*ca* 0.05 mmol) were dissolved in C_6H_6 (50 cm^3) and kept at room temperature under an argon atmosphere over a period of time. In *ca* 1 day **2a** decomposed fully to as yet unidentified compounds and **2c** converted cleanly to a bridging carbonato dimer, [Re(CO)$_3$(dppe)$_2$](μ-O$_3$C). However, **2b** and **2d** were stable under similar conditions. When **2a–d** were dissolved in CH_2Cl_2 or CH_3OH, they ionized fully to the corresponding cations as evidenced by their characteristic $C\equiv O$ bands in the IR spectra.

Preparation of fac-Mn(CO)$_3$(dppp)C(O)NHPr^n (**2e**)

To **1b** (0.5 g, 0.75 mmol) was added n-propylamine (15 cm^3) and the solution was stirred for

1 day. The solvent was removed *in vacuo* and the resulting solid was recrystallized from benzene/hexane. The yellow crystals were isolated by filtration, washed with hexane and vacuum dried to give **2e** in 87% yield. Data for **2e**: m.p. 176–177°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 1998s, 1919s, 1906s and $\nu(C{=}O)$ 1549m. ^1H NMR (δ, C_6D_6): 7.32 (m, 20H, C_6H_5), 5.74 (t, $J = 5$ Hz, NH), 3.22 (q, 2H, NCH_2), 2.75 (m, 6H, $H_2CCH_2CH_2$), 1.40 (sext, 2H, $CH_2CH_2CH_3$), 0.81 (t, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 222.7 (t, $J = 5$ Hz, $2C\equiv O$), 218.1 (t, $J = 14$ Hz, $C\equiv O$), 213.3 (t, $J = 21$ Hz, $C{=}O$), 138.3–128.5 (m, C_6H_5), 42.2 (s, NCH_2), 24.7 (t, $J = 11$ Hz, $H_2CCH_2CH_2$), 23.7 (s, $CH_2CH_2CH_3$), 20.0 (s, $H_2CCH_2CH_2$), 11.8 (s, CH_3). Found: C, 63.9; H, 5.3. Calc. for $C_{34}H_{34}MnNO_4P_2$: C, 64.0; H, 5.3%.

Ionization of **2e** *in* CH_2Cl_2

Compound **2e** (*ca* 0.039 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and the IR spectra, recorded periodically, showed that **2e** slowly ionized.

General procedure for the preparation of fac-$M(CO)_3(P\text{-}P)NCO$ (**2f–h**)

To $[M(CO)_4(P\text{-}P)][BF_4]$ (**1a–c**) (0.6–0.8 mmol) dissolved in CH_3OH (approx. 100 cm^3) was added an equimolar solution of NaN_3 in CH_3OH. The reaction mixtures were allowed to stir for 1 day. The solvent was removed *in vacuo* and the resulting solid was extracted with benzene. The benzene solutions were evaporated to dryness to give the white to pale yellow solids **2f–h** in 86–90% yield. Recrystallization of **2f** from benzene/hexane afforded pale yellow crystals of diffraction grade quality. Data for **2f**: m.p. 184–185°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2027s, 1957s, 1917s and $\nu(NCO)$ 2236s. ^1H NMR (δ, C_6D_6): 7.41 (m, 20H, C_6H_5), 2.31 (m, 4H, CH_2). ^{13}C NMR (δ, C_6D_6); 219.8 (s, br, $C\equiv O$), 134.8–127.8 (m, C_6H_5), 128.6 (s, NCO), 26.3 (t, $J = 10$ Hz, CH_2). Found: C, 62.1; H, 4.3. Calc. for $C_{30}H_{24}MnNO_4P_2$: C, 62.1; H, 4.2%. Data for **2g**: m.p. 175–177°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2030s, 1965s, 1911s and $\nu(NCO)$ 2233s. ^1H NMR (δ, C_6D_6): 7.36 (m, 23H, C_6H_5), 2.25 (m, 6H, CH_2). ^{13}C NMR (δ, C_6D_6): 220.5 (s, br, $C\equiv O$), 137.9–128.5 (m, C_6H_5), 25.2 (t, $J = 12$ Hz, $H_2CCH_2CH_2$), 18.8 (s, $H_2CCH_2CH_2$). Found: C, 64.1; H, 4.7. Calc. for $C_{31}H_{26}MnNO_4P_2 \cdot 0.5C_6H_6$: C, 64.5; H, 4.6%. Data for **2h**: m.p. 228–229°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2029s, 1952s, 1908s and $\nu(NCO)$ 2242s. ^1H NMR (δ, C_6D_6): 7.65 (m, 20H, C_6H_5), 2.83 (m, 4H). ^{13}C NMR (δ, C_6D_6): 192.2 (s, br, $C\equiv O$), 190.9 (s, br, $C\equiv O$), 133.3–127.7 (m, C_6H_5), 27.1 (m, CH_2), 127.7 (s, NCO). Found: C, 50.7; H, 3.5. Calc. for $C_{30}H_{24}NO_4P_2Re$: C, 50.7; H, 3.4%.

General reaction of fac-$Mn(CO)_3(dppe)NCO$ (**2f**) *with* HX (X = Br, OTs, OC(O)H)

To **2f** (0.5 mmol) dissolved in CH_3OH (150 cm^3) was added about a 10-fold excess of HX and the solution was stirred for 5 h. The solvent was removed using a rotary evaporator and the solid residue was dissolved in CH_2Cl_2 (25 cm^3). Excess acid was removed by extracting with water. The volume of CH_2Cl_2 was reduced to approximately 5 cm^3 and then hexane (25 cm^3) was added to precipitate $Mn(CO)_3(dppe)X$. Vacuum-drying gave **3a–c** in 83–87% yield. Yellow microcrystalline **3c** was obtained after recrystallization from benzene/hexane. Data for **3c**: m.p. 155–156°C. IR (cm^{-1}, C_6H_5): $\nu(C\equiv O)$ 2024s, 1955s, 1911s and $\nu(C{=}O)$ 1613s. ^1H NMR (δ, C_6D_6): 8.35 [s, 1H, OC(O)H], 7.35 (m, 21H, C_6H_5), 2.45 (m, 4H, CH_2). ^{13}C NMR (δ, CD_2Cl_2): 219.9 (s, br, $C{=}O$), 167.6 (s, $C{=}O$), 134.1–128.8 (m, C_6H_5), 128.6 (s, C_6H_6), 26.1 (t, $J = 20$ Hz, CH_2). Found: C, 62.8; H, 4.5. Calc. for $C_{30}H_{25}MnO_5P_2 \cdot 0.25C_6H_6$: C, 62.8; H, 4.4%.

X-ray structure determinations

Crystallographic data for **2b** and **2f** are summarized in Table 3. For each compound, unit cell parameters were determined from the angular settings of 25 centred reflections having 2θ values greater than 20°, intensity data were collected on a Siemens R3m/V diffractometer to $2\theta = 55°$, 2θ–θ scans were employed and three standards were measured for every 37 reflections. The SHELXTL PLUS programs[25] were used throughout for data reduction, structure solution and refinement. All structures were refined by full-matrix least-squares. Non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were idealized with C—H = 0.96 Å and were assigned fixed isotropic temperature parameters, $U(H) = 0.08$ Å^2. Selected details specific to each determination are given below.

2b. A fragment measuring $0.25 \times 0.25 \times 0.32$ mm was cut from a pale yellow prism and sealed in a glass capillary. Corrections were made for Lorentz–polarization, absorption and extinction effects. The structure was solved by direct methods. The minimum and maximum excursions in the final difference map were -0.26 and 0.28 e Å^{-3}, respectively.

2f. A thin pale yellow plate $0.08 \times 0.032 \times 0.50$ mm in size was mounted on a glass fibre with epoxy cement. Corrections were made for Lorentz–

Table 3. Crystallographic data for *fac*-$Mn(CO)_3$(dppp)C(O)OEt (**2b**) and *fac*-$Mn(CO)_3$(dppe)NCO (**2f**)

Compound	**2b**	**2f**
Formula	$C_{33}H_{31}MnO_5P_2$	$C_{30}H_{24}MnNO_4P_2$
fw	624.52	579.43
Space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a (Å)	9.974(1)	21.921(3)
b (Å)	11.215(1)	16.756(3)
c (Å)	14.171(2)	15.056(2)
α (°)	80.258(9)	
β (°)	81.041(9)	
τ (°)	77.532(8)	
V (Å^3)	1513.6(3)	5530(1)
Z	2	8
$d_{\text{calc.}}$ (g cm^{-3})	1.37	1.39
μ (cm^{-1})	5.60	6.06
Temperature (K)	294	294
Radiation (λ, Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
hkl limits	± 12, ± 14, ± 18	$+28$, $+21$, $+19$
Refls collected	7264	7016
Independent refls	6981	6371
R_{int}	0.0271	—
Data/parm	13.6	8.8
R	0.0332	0.0879
R_w	0.0468	0.0719

polarization effects but not for absorption or extinction. The structure was solved by heavy-atom methods. The minimum and maximum features on the final difference map were -0.45 and 0.53 e Å^{-3}, respectively.

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