# A Comparative Study of the Reactivity of $Mn(NO)_2L_2H$ and $Mn(CO)_3L_2H$ Complexes (L = Phosphorus Donor)☆

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$Mn(NO)_2L_2H$ complexes [L = $PMe_3$ **1a**, $PEt_3$ **1b**, $P(OMe)_3$ **1c**, $P(OEt)_3$ **1d**, $P(OiPr)_3$ **1e**] have been prepared by the reaction of the corresponding $Mn(NO)_2L_2Br$ compounds with $NaBH_4$ in ethanol. The reactivity of **1a** and **1b** is compared to that of $Mn(CO)_3L_2H$ species (L = $PMe_3$ **2a**, L = $PEt_3$ **2b**). Compound **1b** reacts with weak acids like PhOH, $(CF_3)_2CHOH$ and $CH_3COOH$ to yield $Mn(NO)_2(PEt_3)_2X$ complexes [X = OPh **3a**, $OCH(CF_3)_2$ **3b**, $OC(O)CH_3$ **3c**] and $H_2$. Compound **2b** does not undergo reaction with these acids. At room temperature in toluene **1a**, **b** undergo facile $CO_2$ insertion processes, while **2a**, **b** do not show this reactivity even under more rigorous reaction conditions. From **1a**, **b** and $CO_2$ formato complexes $Mn(NO)_2L_2[OC(O)H]$ (L = $PMe_3$ **4a**, L = $PEt_3$ **4c**) are obtained. The reaction of **1b** with salicylaldehyde in toluene proceeds with the formation of a [2-(hydroxymethyl)-phenoxy]dinitrosylbis(triethylphosphane)manganese complex **5b**, which exchanges the phenoxy ligand in the presence of excess of salicylaldehyde to give (2-formylphenoxy)-dinitrosylbis(triethylphosphane)manganese (**6b**) and α,2-dihydroxytoluene. *p*-Hydroxybenzaldehyde, vanilline, and 4-hydroxy-3,5-dimethoxybenzaldehyde and **1b** also afford phenoxy derivatives $Mn(NO)_2(PEt_3)_2(OAr)$ [Ar = *p*-$OC_6H_4$-CHO **7a**; $OC_6H_3$-2-$OCH_3$-4-CHO **7b**; $OC_6H_2$-2,6-$(OCH_3)_2$-4-CHO **7c**] and $H_2$. Compounds **2a**, **b** do not react with any of these hydroxybenzaldehydes. Compounds **1a**, **b** have been converted into $Mn(NO)_2L_2[(Z)$-C(COOR')=C(R)H] species (L = $PMe_3$, R = H, R' = Me **8a**; L = $PEt_3$, R = H, R' = Me **8b**; L = $PMe_3$ R, R' = Me **9a**; L = $PMe_3$, R = Ph, R' = Et **10a**; L = $PMe_3$, R = COOMe, R' = Me **11a**; L = $PEt_3$, R = COOMe, R' = Me **11b**) in the presence of alkyl propiolates RC≡CCOOR' (R = H, Me, Ph, COOMe; R' = Me, Et). Similarly, but under more rigorous conditions, insertion of RC≡CCOOMe (R = H, COOMe) into **2a**, **b** occurs and α metalation products $Mn(CO)_3(PMe_3)_2[(Z)$-C(COOMe)=CHR] (L = $PMe_3$, R = H **12a**; L = $PEt_3$, R = H **12b**; L = $PMe_3$, R = COOMe **13a**; L = $PEt_3$, R = COOMe **13b**) are formed. In the case of the methyl propiolate insertion into **2a**, 10% of an additional β-metalation compound $Mn(CO)_3(PMe_3)_2[(Z)$-CH=CH(COOMe)] (**12c**) have been detected spectroscopically. Compounds **11b** and **13a**, **b** have been transformed into manganacyclic complexes $\overline{Mn[C(COOMe)=CH(COOMe)]}$-$(NO)_2(PEt_3)_2$ (**14b**) and $\overline{Mn[C(COOMe)=CH(COOMe)]}$-$(CO)_2L_2$ (L = $PMe_3$ **15a**; L = $PEt_3$, CO **15b**; L = $PEt_3$ **15c**). Compound **15c** has been identified spectroscopically, and **1a**, **8a**, and **9a** have been characterized by X-ray structure determinations.

Recently, our research interest has focussed on the preparation and reactivity of nitrosyl hydride complexes[1]. The nitrosyl ligand[2] is supposed to activate the metal-hydrogen bond inducing a hydridic polarization[3] and also weakening of it, thus providing more facile access to insertion reactions with especially polar unsaturated molecules. In earlier papers of our group this subject has been addressed to with studies of the physical properties and the reactivity of chromium, tungsten[4], and rhenium nitrosyl hydride compounds[5]. In this paper we describe some reactions of $Mn(NO)_2L_2H$ complexes (L = phosphorus donor) and compare them to those of $Mn(CO)_3L_2H$ compounds. Both types of species differ by the isoelectronic replacement of three 2-electron CO by two 3-electron NO donors. The aim of those reactivity studies is to establish a "nitrosyl effect" with reference to the ligand CO.

## Results and Discussion

The $Mn(NO)_2(PPh_3)_2H$ complex was already prepared by Hieber and coworkers more than thirty years ago[6a]. Beck et al. have improved this synthesis by slight modifications[6b]. A quite general preparative route to a variety of phosphorus donor-substituted compounds $Mn(NO)_2L_2H$ [L = $PMe_3$ **1a**, $PEt_3$ **1b**, $P(OMe)_3$ **1c**, $P(OEt)_3$ **1d**, $P(OiPr)_3$ **1e**] has now been developed and affords yields between 75 and 89% by utilizing the reaction of $Mn(NO)_2L_2Br$ complexes with $NaBH_4$ in ethanol (eq. 1). The required bromo compounds are synthesized with some changes according to the original procedure of Hieber et al.[6a], which starts from the corresponding $Mn(CO)_3L_2Br$ complexes and NO.

Complexes **1** have a trigonal-bipyramidal structure with the phosphorus ligands arranged axially and the nitrosyl and H substituents in the equatorial plane. This geometry is derived from an exemplary X-ray investigation of **1a**. The same structure is assigned to the other complexes **1b–e** based on the resemblance of their spectroscopic properties. The IR spectra of **1** exhibit two ν(NO) bands with the approximate intensity ratio of 1:2 and a difference in wavelength of 35–45 $cm^{-1}$. These $\nu_s$ or $\nu_{as}$ absorptions lie at 1637–1667 and 1683–1712 $cm^{-1}$, respectively, and show a very good correlation with Tolman's electronic parameters χ[7] for the phosphorus substituents ($r$ = 0.996). The ν(NO)

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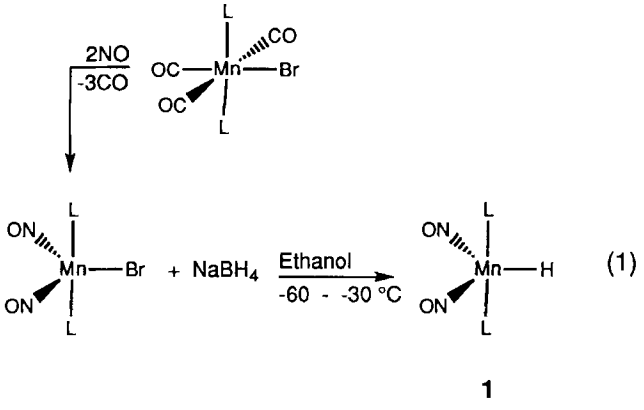
vibration is deemed an appropriate indicator of the electronic properties of such molecules.




(1)

**1**

L = $PMe_3$ **a**; $PEt_3$ **b**; $P(OMe)_3$ **c**; $P(OEt)_3$ **d**; $P(OiPr)_3$ **e**

Even upon application of very concentrated solutions of **1a–e**, no additional IR band (range between 2100 and 1500 $cm^{-1}$) which might be attributed to a ν(MnH) vibration has been found. Note, that it is a relatively common phenomenon in transition metal hydride chemistry that ν(MH) absorptions cannot be detected due to their very low intensity. In polar solvents like methanol the IR spectra of **1a** and **1b** are characterized by three intense bands (Table 1). For a proper assignment of these bands the $^2H$ isotopomer of **1b** $Mn(NO)_2(PEt_3)_2D$ (**1b$^D$**) was prepared. In ethanol compound **1b$^D$** also shows three bands in nearly the same positions, thus indicating that none of them can be assigned to a ν(MnH) vibration. This splitting phenomenon of the ν(NO) bands in polar solvents can at present not be explained. Compared with the IR spectrum of **1b**, the $\nu_s$(NO) absorption of **1b$^D$** in ether is shifted to higher wavelengths by about 6 $cm^{-1}$ suggesting a very weak coupling with ν(MnH). This low coupling value can be interpreted in terms of an ON–Mn–H angle considerably smaller than 180°, and since $\nu_{as}$(NO) moves to higher wavelengths for **1b$^D$**, we assume, that ν(MnH) is presumably located above 1670 $cm^{-1}$.

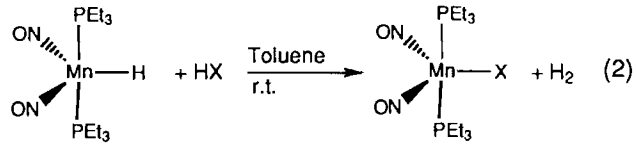
The $^1H$-NMR spectra of **1** show resonances typical of the organo substituents of the *trans*-located phosphorus ligands, which leads for most compounds to higher-order $J_{PH}$ coupling patterns. The hydride ligands appear as triplets with $^2J_{PH}$ between 95 and 108 Hz and are in a relatively narrow chemical shift range (δ between −0.6 and 0.1).

Complexes **1b** and **1e** are yellow and **1a**, **1d**, and **1c** orange solids. Compound **1c** is an oil at room temperature. The phosphane-substituted derivatives **1a** and **1b** are air-stable for minutes even in solution, while the phosphite derivatives **1c–e** very rapidly decompose under this condition. This result is in accord with the observation of Tilset and Parker[8]. They have shown that the kinetic stability of transition metal hydrides toward air oxidation increases with the stronger electron-donating power of an ancillary phosphorus substituent.

From temperature-dependent $^2H$-NMR measurements[9] of the quadrupole coupling constant of **1b$^D$** and of the complex $Mn(CO)_3(PEt_3)_2D$ (**2b$^D$**) the bond ionicities have been calculated to be 75 and 71%, respectively. The higher value for **1b$^D$** may be indicative of an enhanced propensity of complexes **1** to undergo reactions with polar substrates. For the intended comparative studies it was necessary to prepare $Mn(CO)_3L_2H$ complexes (L = $PMe_3$, **2a**; $PEt_3$, **2b**). These are obtained by the reduction of the corresponding bromides with sodium amalgam in THF and subsequent acidification of the resulting metalate anions with MeCOOH[10].

| $Mn(CO)_3L_2H$ | $Mn(CO)_3(PEt_3)_2D$ |
|---|---|
| $PMe_3$ **2a** | **2b$^D$** |
| $PEt_3$ **2b** | |

In an examplary way **1b** and **2b** are allowed to react with phenol ($pK_a$ = 9.9), hexafluoro-2-propanol ($pK_a$ = 9.3), and acetic acid ($pK_a$ = 4.8). Evolution of $H_2$ is observed with all three reagents in the case of **1b** (eq. 2), but no conversion at all occurs for **2b** with any of these acids. From the reactions of **1b** the aniono derivatives **3a–c** are isolated as orange solids in good to excellent yields (**3a** 98, **3b** 71, **3c**, 67%). These complexes give correct elemental analyses.




(2)

**1b** **3**

X = OPh **3a**; $OCH(CF_3)_3$ **3b**; $OC(O)CH_3$ **3c**

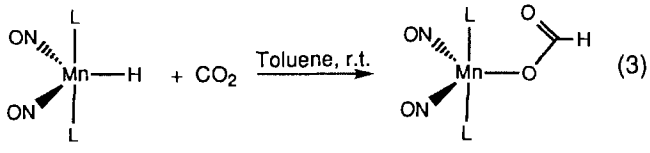
The transformations to **3a** and **3b** take about 8 h, while the formation of **3c** is complete within 20 min. On a qualitative scale, the reaction rates apparently decrease with the $pK_a$ of the applied acid, and since weak acids have been used one might conclude that the hydride **1b** indeed bears a great deal of hydridic character on the manganese-bound H atom. The difference in reactivity of **1b** and **2b** is quite striking, since they bear the same phosphorus donor ligands. Hence, this observation may be taken as a hint that the Mn–H bond in **2b** is indeed less hydridic.

The structures of complexes **3a–c** are assigned by IR and NMR spectroscopy. The IR spectra resemble those of the hydride compounds **1**. They display two ν(NO) bands between 1704 and 1640 $cm^{-1}$. The $^1H$-NMR spectra exhibit quintet resonances for the organo residues of the phosphorus donor and the following characteristic signals for the X groups. For X = OPh (**3a**), two multiplets for the Ph protons are observed at δ = 7.18–7.08 and 6.93–6.64, respectively. The $H_{methyne}$ nucleus of **3b** appears as a septet at δ = 4.49 ($^3J_{FH}$ = 6.4 Hz) and X = acetate of **3c** is characterized by a singlet at δ = 1.90. In the $^{13}C$-NMR spectrum of **3a** four resonances for the phenyl ring are found, while the $C_{methyne}$ nucleus of **3b** is recognized as a triplet of a septet at δ = 80.3 ($^3J_{PC}$ = 5.7, $^2J_{FC}$ = 29.4 Hz).

It should be mentioned that in the reaction of **1b** and **2b** with $CD_3OD$ ($pK_a$ 15.5) at room temperature no H/D

exchange is observed. While this observation is expected for **2b**, H/D exchange is anticipated to occur in the case of **1b**, since other "hydridic" hydrides[4g], showing a comparable acid/base behaviour (eq. 2), have been found to exhibit this reaction feature. Even though this chemical property of **1b** must be left unexplained, a pronounced hydridic character seems to be well-established presumably for all compounds **1**.

The exploration of the reactivity of nitrosyl- and carbonyl-substituted hydrides was then continued with the investigations of insertion reactions of $CO_2$[11,4b] and of organic carbonyl compounds. When **1a**, **b** are treated with carbon dioxide in toluene (room temperature, 1 bar) reactions start immediately and are complete within two hours (eq. 3).



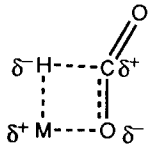

(3)

**1a,b**

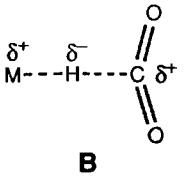
L = $PMe_3$, **4a**
L = $PEt_3$, **4b**

Orange $\eta^1$-formato compounds **4a** and **4b** are formed, which are isolated in 94 and 98% yield, respectively. These insertions are irreversible even at 110°C. Compounds **2a** and **2b** do not react with $CO_2$ under comparable or even more drastic conditions (80°C) or when polar solvents, like acetonitrile or DMF, are applied. Note that $CO_2$ insertions are expected to be accelerated in polar solvents[12]. The spectroscopic data of **4a** and **4b** are consistent with their trigonal-bipyramidal structure with the two NO groups and the formato ligand in equatorial and the $PMe_3$ or the $PEt_3$ substituents in axial positions. In the IR spectra two ν(NO) bands and characteristic $\nu(CH)_{formato}$ and $\nu(CO_2)$ absorptions are identified. The $^1$H-NMR spectra of **4a** and **4b** display resonances at δ = 8.88 (**4a**) and 8.83 (**4b**), respectively, which are attributed to the $H_{formato}$ nucleus in either case. In the $^1$H-coupled $^{13}$C-NMR spectra the corresponding resonances for the $C_{formato}$ atom are found as doublets at $\delta \approx 166$.

As stated by others, insertions of $CO_2$ are thought to require a rather polar $\overset{\delta+}{M}-\overset{\delta-}{H}$ bond and are expected to pass through polar transition states **A** or **B**[12].




**A**



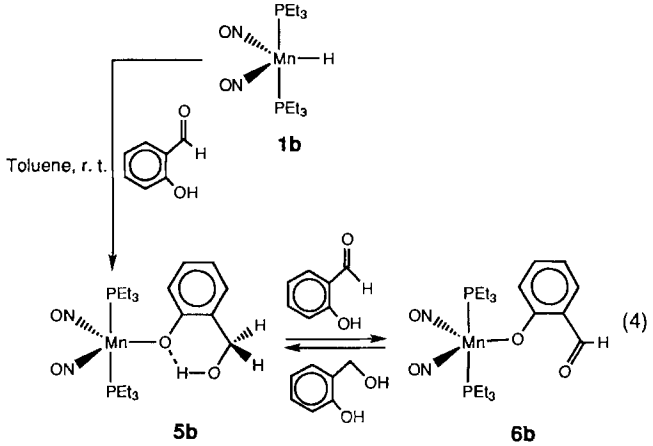

**B**

Darensbourg and coworker[13] have indeed found a correlation between the rates of insertion of $CO_2$ into $M(CO)_4LH^-$ complexes (M = Cr, Mo, W; L = CO, $PR_3$) and the nucleophilicity of these species, which depends on the donating ability of the ligand L. Apparently, the nitrosyl-substituted complexes **1a**, **b** have attained sufficient nucleophilicity for reactions with $CO_2$, while the carbonyl derivatives **2a**, **b** have not. It is noteworthy that the observation that the reactions to **4a**, **b** cannot be reversed even at temperatures above 100°C may imply that the Mn−H bonds of these compounds are weak. The thermodynamics of $CO_2$ insertions into $L_nM-H$ bonds should be dependent on the relative $L_nM-H/L_nM-O_{formate}$ bond strengths. $L_nM-H$ species which display a strong driving force for this kind of reactivity should either have a strong $L_nM-O$ or a weak $L_nM-H$ bond. Based on the HSBA principle the $L_nM-O$ bond is anticipated to be relatively weak for manganese(−I) centers. Hence, one has to assume that the Mn−H bond in compounds **1** is weak.

The $CO_2$ insertion chemistry indicates that the nitrosyl-substituted compounds show a greater propensity to undergo this type of transformation than their CO congeners. Therefore, we wanted to further investigate this difference in reactivity and attempted conversions of **1** with organic carbonyl derivatives. Compared with $CO_2$ these substrates are considered to be of similar electrophilicity.

However, neither **1b** nor **2b** react with aldehydes like propanal, pivaldehyde, or benzaldehyde. It should be mentioned that nitrosyl complexes $W(NO)(CO)_2L_2H$ [L = $PMe_3$, $P(OiPr)_3$] undergo reactions with aldehydes[4b,d,e]. Compound **1b** reacts with the electron-deficient pyridine-2-carbaldehyde, *p*-nitro- and *p*-cyanobenzaldehyde. It is however not possible to properly isolate and characterize the reaction products.

In earlier investigations we have found that aldehyde insertions into the W−H bond can greatly be accelerated in the presence of weak acids[4b,c]. Convenient reagents for such reactions are compounds with built-in acidic functions like salicylaldehyde. In fact, **1b** is converted in the presence of 3 equivalents of salicylaldehyde into (hydroxymethyl)-phenoxy complex **5b** within a few hours. In a subsequent step release of α,2-dihydroxytoluene and formation of a dinitrosyl(salicylato)bis(triethylphosphane)manganese species **6b** occur (eq. 4).




(4)

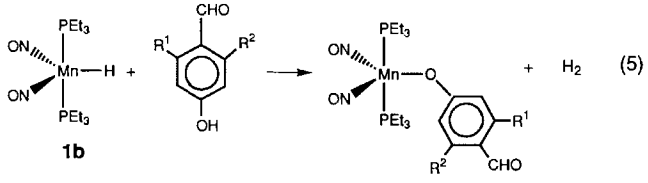
**5b** **6b**

This reaction is expected to proceed via primary formation of an alkoxide compound, which we have not been able to detect IR- or NMR-spectroscopically. The first species to

be observed and isolated is the *o*-(hydroxymethyl)phenoxide complex **5b**, which is presumably generated by prototropic rearrangement of the initial benzyloxy compound. Such a species and a complex comparable to **5b** has been identified in the analogous transformation of $W(CO)_2(NO)(PMe_3)_2H$ with salicylaldehyde[4c].

$^1$H-NMR spectroscopic pursuit ($C_6D_6$) of the substitution of salicylaldehyde for α,2-dihydroxytoluene in **5b** yielding the (salicylato)manganese complex **6b** reveals that this reaction is an equilibrium reaction. When 2 equivalents of salicylaldehyde per equivalent of **5b** are used, **5b** and **6b** are present at room temperature in an approximate 1:1 ratio. α,2-Dihydroxytoluene is also identified in these experiments. Compound **5b** precipitates from a quite concentrated toluene mixture, while **6b** is isolated by workup of the remaining solution. The structures of **5b** and **6b** have been unambiguously assigned on the basis of their spectroscopic data preferably in comparison with those of the related complex **3a**. Their IR spectra show two ν(NO) bands, which are located very close to those of the phenoxy compounds **3a**. In addition, the single $^{31}$P resonances of **3a**, **5b**, and **6b** appear in a narrow chemical shift range of 4 ppm indicating their chemical relationship. Characteristic $^1$H-NMR resonances are observed for the methylene protons of **5b** at δ = 4.33 and for the CHO group of **6b** at δ = 10.42.

In contrast to the reaction of **1b** with salicylaldehyde, the attempted analogous transformation with *p*-hydroxybenzaldehyde does not lead to an insertion product. Instead, the phenoxy complex **7a** is formed in an acid/base reaction with liberation of $H_2$ (eq. 5). This reaction behaviour contrasts again with the results of the conversion of $W(CO)_2NO(PMe_3)_2H$ with *p*-hydroxybenzaldehyde, in which case insertion of the carbonyl function into the W−H bond indeed takes place[4c]. The basic behaviour of **1a** toward *p*-hydroxybenzaldehyde cannot be turned into nucleophilic reactivity at the carbonyl groups of the aldehydes, even when less acidic methoxy-substituted hydroxybenzaldehydes are employed. Acid/base reactions are also observed in these cases generating **7b** and **7c** (eq. 5).



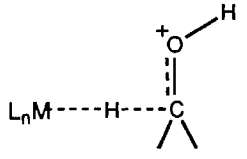

(5)

| | $R^1$ | $R^2$ |
|---|---|---|
| **7a** | H | H |
| **7b** | MeO | H |
| **7c** | MeO | MeO |

The obtained dinitrosylbis(triethylphosphane)(phenoxy)-manganese derivatives **7a**–**c** are isolated in 94–98% yield.

The proposed structures of complexes **7** are closely related to those of **3a** and **6b**. The phenolic residues of **7** are identified by specific IR and $^1$H-NMR absorptions. The $^1$H- and $^{31}$P-NMR properties of their identical $Mn(NO)_2(PEt_3)_2O$ moieties show distinct IR spectroscopic resemblance, thus leading to the structural assignment given in eq. (5).

The reaction pattern of compound **1b** reveals a chemical character different from that of the $W(CO)_2(NO)(PMe_3)_2H$ species. $W(CO)_2(NO)(PMe_3)_2H$ may be considered more nucleophilic, while the reactivity of **1b** can be attributed to a higher basicity of the hydride center. The reason for this difference is not clear. The mechanisms of these insertion processes are not established yet. We and others have proposed earlier that such proton-assisted reactions might involve a primary protonation of the $O_{aldehyde}$[4c,14,15] followed by hydride transfer from the metal center to the activated substrate.



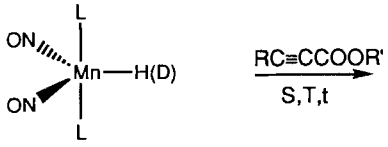

The proton-$O_{aldehyde}$ contact is indeed expected to be kinetically more effective for salicylaldehyde, since intramolecular hydrogen bonding between the phenolic proton and the $O_{aldehyde}$ atom is well-known. The hydrogen bonding can be envisaged as a preliminary stage of a complete proton transfer to the carbonyl group and hence accelerate the reactions. By this activation mechanism salicylaldehyde seems to be perfectly prepared for an insertion process. Apparently, it is therefore the only electronically unactivated carbonyl substrate of our series to react with the $Mn(NO)_2(PEt_3)_2H$ complex in this manner.

The selectivity of the metal fragment toward reductions or acid/base reactions may not only be determined by different basicities of the metal-bound hydrides but also by the $H^-$ transferability. The latter should go along with the stabilization of the unsaturated $[L_nM]^+$ cation formally left behind after reaction of the $H^-$ ligand. A high energetic position of its LUMO and a reasonable HOMO/LUMO gap of it is required[1,3]. The former condition is probably satisfied by both the $[Mn(NO)_2L_2]^+$ and the $[W(CO)_2(NO)L_2]^+$ cation (L = phosphorus donor) leading to strong hydridicity and also basicity of these hydrides, while the other electronic property, which mainly influences the $H^-$ transfer capability, is apparently only displayed by $[W(CO)_2(NO)L_2]^+$.

In further investigations the insertion potential of type **1** and **2** hydrides towards activated acetylenes (i.e., bearing electron-withdrawing ester groups) was explored. According to eqs. (6a) and (6b) methyl propiolate insertions into the Mn−H bond of **1a**, **b** and **2a**, **b** occur forming the α-metalated vinyl compounds **8a**, **b** and **12a**, **b**, respectively.

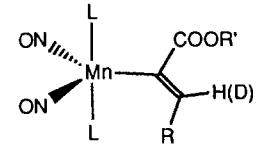
A detailed $^1$H- and $^{13}$C-NMR study of the insertion reaction of **2a** with HC≡CCOOMe in $C_6D_6$ at room temperature shows that for this specific case also 10% of β-metalation with *trans* addition has occurred. Complex **12c** is additionally formed, which however cannot be isolated from reaction mixtures on a preparative scale.

The assignment of the *Z* configuration to the olefinic residue of **12c** (*trans* insertion chemistry of **2a**) is based on

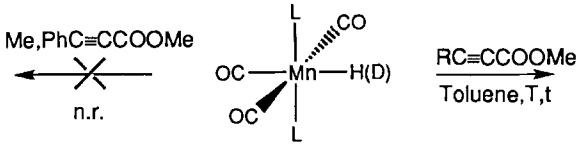



**1a,1b,1b$^D$**

L = $PMe_3$ **a**, $PEt_3$ **b** (6a)

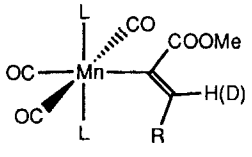



| | S | T | t |
|---|---|---|---|
| R = H, R' = Me **8a,8b,8b$^D$** | Toluene | 0 °C | sec |
| R,R' = Me **9a** | MeOH | r.t. | 3d |
| R = Ph, R' = Et **10a** | Toluene | r.t. | 2d |
| R = COOMe,R' = Me **11a,b** | Toluene | -60 °C | sec |

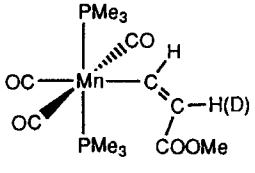



**2a,2a$^D$,2b**

(6b)




| | T | t |
|---|---|---|
| R = H **12a,12a$^D$,12b** | r.t., 40 °C | 6h, 30 min |
| R = COOMe **13a,b** | r.t., 0 °C | sec, min |




**12c, 12c$^D$**

the presence of a vicinal $^3J_{HH}$ coupling of 14 Hz for the $H_{vinyl}$ nuclei.

In the HC≡CCOOMe insertion processes according to eqs. (6a) and (6b) a high regioselectivity is combined with a *trans* addition stereospecificity. This has additionally been confirmed for the reactions of **1b** and **2a** in deuterium-labeling $^1$H-NMR studies. Products **8b$^D$**, **12a$^D$**, and **12c$^D$** are obtained by starting from **1b$^D$** or **2a$^D$** *E* (D, $L_nMn$).

It is important to note that the nitrosyl-substituted hydrides **1a**, **b** react smoothly with HC≡CCOOMe at 0°C within seconds, while the reaction of **2a** requires 6 h at room temperature, and the transformation of **2b** to the vinyl compounds is completed within 30 min at 40°C. Hence, there is a remarkable difference in the activity of the NO- and CO-substituted complexes, being higher for the NO cases.

The reactions of **1a**, **b** and **2a**, **b** with methyl 2-butynoate and ethyl phenylpropiolate reveal also differences in the reaction behaviour of both types of hydride complexes (eq. 6a). The sterically less hindered nitrosyl hydride compound **1a** is converted to (*E*)-(methyl, phenyl)(alkoxycarbonyl)-vinyl complexes **9a** or **10a** (eq. 6a), again generating an α-metalation regiochemistry. The *E* configuration at the double bond of **9a** and **10a** demonstrates *trans* addition stereochemistry, which has also been found for the reactions of **1a**, **b** with HC≡CCOOMe.

Presumably for steric reasons **1b** does not react with the methyl- or phenyl-substituted acetylenes at ambient temperature; at higher temperature decomposition of the reaction mixture occurs. The carbonyl derivatives **2a**, **b** undergo no reactions with these substituted acetylenic substrates under the same conditions described for the transformations of **1a**. Compound **2a** does not even react at 80°C in toluene or in $CH_3OH$ at 50°C.

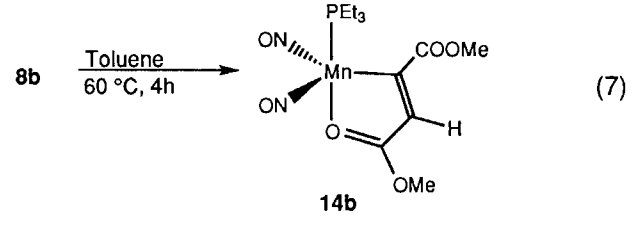
From reactions of the quite electron-deficient acetylenedicarboxylate MeOOCC≡CCOOMe with **1a**, **b** and **2a**, **b** the *trans* insertion products **11a**, **b** and **13a**, **b** are obtained. However, milder reaction conditions are required for the NO complexes, e.g. **11a**, **b** need −60°C and a few seconds to react, while **13a**, **b** are formed at room temperature or 0°C within seconds or some minutes, respectively. This again establishes a considerably higher reactivity of the Mn−H bonds in NO-substituted complexes.

The $^1$H-NMR spectra of **8a**, **b** and **12a**, **b** exhibit resonances for the two types of vinyl protons at δ = 6.8−6.3 and 5.8−5.2, which are geminally coupled with $^2J_{HH}$ values in the range of 3.6 and 4.4 Hz. The low-field resonances are assigned to the *E*-configurated protons. These show a stronger $^4J_{PH}$ coupling than the *Z*-configurated $H_Z$ nuclei. The $^1$H-coupled $^{13}$C-NMR spectra consist among others of $C_{vinyl}$ signals in the range of δ = 168−176 and 126−131. The latter are attributed to the $C_\beta$ atoms, since they appear as triplets with $^1J_{CH}$ of 155 Hz. The $C_\alpha$ and $C_\beta$ nuclei in **9a** and **10a** have similar chemical shifts and coupling values. The unambiguous assignment of the configuration at the C=C bond of such systems is difficult, if it is merely based on spectroscopic data. Still a suitable indicator for the vinyl stereochemistry is the $^3J_{CH}$ coupling of the $H_{vinyl}$ to the $C_{ester}$ atom, which has been used by Herberich et al.[16] for the determination of the relative positions of these groups in rhenocene and molybdenocene vinyl compounds. For **9a** and **10a** couplings of 9.6 and 10.3 Hz have been found, which are typical of a *Z* arrangement. Finally, the stereochemistry of the vinyl groups of compounds **9a** and **10a** has been elucidated by their X-ray structure determinations.

Compounds **9a** and **10a** are supposedly kinetic products, since they face great steric repulsion between the *Z*-arranged $Mn(NO)_2(PMe_3)_2$ fragment and the Me or the Ph group, respectively. An attempt to isomerize **10a** into the *E*

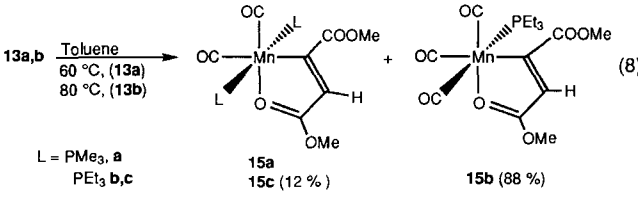
compound by heating it in toluene at 80°C has failed. It should be noted that thermal *Z/E* isomerization has been observed for the stereochemically related $W(CO)_2(NO)(PMe_3)_2$[*Z*-C(COOMe)=C(Ph)H] complex[4f].

The assignment of *E* positions for the $Mn(NO)_2L_2$ and the H substituent at the olefinic moiety of **11a, b** is essentially based on the $^4J_{HP}$ couplings between 7 and 9 Hz of $H_E$, which compare well with the analogous ones measured for **8a, b**. Furthermore, upon heating there is a subsequent reaction of **8b** forming a five-membered manganacycle **14b** with elimination of a $PEt_3$ ligand. Since the reaction according to eq. (7) cannot easily be anticipated for a hypothetical *cis* addition isomer of **8b**, this observation provides further evidence for the given stereochemical assignment. The same process has been attempted for **8a**. However, upon heating to 60°C it decomposes to non-identifiable products.



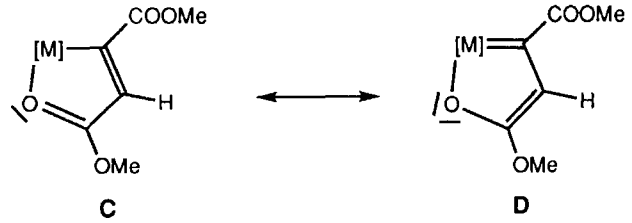

(7)

Compounds **13a, b** have smaller $^4J_{HP}$ couplings of 4–5 Hz for the vinylic protons than **11a, b**, which makes it impossible to specify their position with respect to the manganese center. The room temperature $^{13}$C-NMR spectra of **13a, b** reveal slow rotation of the vinyl groups around the Mn–C bond relative to the NMR time scale. This is indicated by the appearance of three $^{13}$CO signals for **13b** and two very broad ones for **13a**. Heating to 80°C produces spectra with two $^{13}$CO resonances in both cases. Upon heating to 60 or 80°C in toluene these complexes are also transformed into the five-membered metallacyclic systems **15a** and **15b, c** with loss of a CO group or a phosphorus donor (eq. 8). This observation again confirms the assignment of *E* positions of the $Mn(CO)_3L_2$ and the H substituents in **13a, b**. We have not succeeded in isolating **15c**; it has however been characterized spectroscopically in solution.



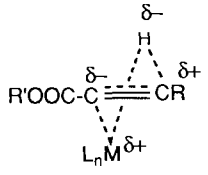

(8)

The structural assignment of **14b**, **15a** and **15b, c** is based on specific spectroscopic features. The IR spectra of these complexes exhibit two ν(C=O) bands for the ester residues, and **15a, c** in addition display two ν(C≡O) absorptions, which are typical of a *cis* $(OC)_2M$ moiety. The $Mn(CO)_3$ unit in **15b** is characterized by three intense ν(CO) absorptions. In the $^{13}$C-NMR spectra, the α $C_{vinyl}$ atoms of **14b** and **15a, b, c** experience a remarkable low-field shift, indicative of the formation of electron-delocalized metallacycles[17]. Their electronic description is based on the resonance structures **C** and **D**.




The α $C_{vinyl}$ signals are doublets for **14b** and **15b** and triplets for **15a, c** demonstrating the coupling to one or two phosphorus nuclei.

The mechanisms of the acetylene insertion reactions are still a matter of discussion. A pathway which involves opening of a coordination site by bending of a NO ligand and precoordination of the acetylenic moiety can presumably be ruled out. This would necessarily be accompanied by *cis* addition of the $L_nM-H$ unit to the a bond, which has not been observed. In addition it has been suggested that antara addition of the metal fragment and the H ligand across an acetylenic triple bond can take place[4f].

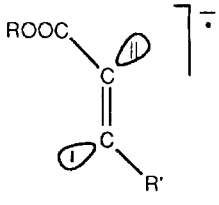



This model can explain the regiospecificity of the insertions with the given polarization of the reacting partners $L_nM^{\delta+}-H^{\delta-}$ and $R'C^{\delta+}\equiv C^{\delta-}-COOR$. The *trans* addition transition state can, however, not be rationalized on the basis of this arrangement.

Another reaction squence for a R'C≡CCOOR insertion has been suggested by Clark et al.[18]. For *trans*-$PtH_2(PR_3)_2$ compounds a cage-trapped radical pathway with an initial single-electron transfer has been claimed, which could presumably be applied to the reactions of **1a, b** and **2a, b** as well.

$$L_nMH + R'C{\equiv}CCOOR \rightarrow [L_nMH^{+\bullet}, R'C{\equiv}CCOOR^{-\bullet}]$$
$$H^+ + L_nM^\bullet \leftarrow L_nMH^{+\bullet} \rightarrow L_nM^+ + H^\bullet$$

The character of the $[L_nMH]^{+\bullet}$ species representing an $H^\bullet$ or an $H^+$ transfer agent (hydridic parent hydrides should lead to an $H^\bullet$, less hydridic hydrides to an $H^+$ source) determines the regiochemistry of the addition, since $H^\bullet$ or $H^+$ will combine with the radical or the anionic centers of the acetylene radical anion. They are arranged in an *E* fashion at the R'- or ester-substituted carbon atoms, respectively. This would also explain the *trans* addition mode.



Assuming such a mechanism, **8**–**13** are formed by α-metalation from an $H^\bullet$ source, except for the generation of **11c** which requires an $H^+$ donator. The latter observation may be interpreted in terms of a reduced hydridic character of **2b** causing an ambiphilic character of the $[L_nMH]^{+\bullet}$ species. A higher propensity to form $H^+$ from $[L_nMH]^{+\bullet}$ may be anticipated for all higher CO-substituted hydride compounds. In this context it should be mentioned that Re, $Mn(CO)_5H$[19], $cp_2ReH$[16], $[Os(C_6H_6)(PiPr_3)_2H]^+$[17b], and $RuCl(CO)(PPh_3)_3H$(3,5-dimethylpyrazole)[20] are supposedly all $H^+$ sources as radical cations and less hydridic metal hydrides in their parent states, since they all generate β-metalation products upon addition of activated 1-alkynes like HC≡CCOOMe, $HC{\equiv}CCF_3$ and HC≡CCN.

### Structure Determinations of 1a, 9a, and 10a

The complexes of type **1** have been demonstrated to show activated reaction behaviour. We therefore wanted to check, whether this is reflected in the ground-state properties of these molecules displaying significant structural deformations. Complex **1a** is characterized by an X-ray structure determination. A pseudo trigonal-bipyramidal coordination geometry has been found with the $PMe_3$ donors in axial position and the two NO groups and the H ligand in equatorial positions (see Figure 1).

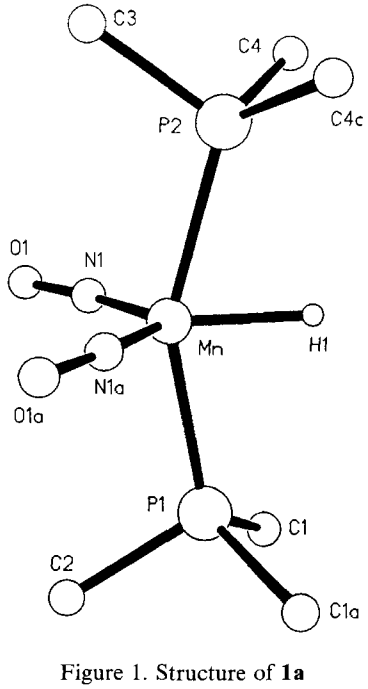



Figure 1. Structure of **1a**

Table 1. Selected bond lengths and angles for **1a**

| |
|---|
| Bond lengths [pm]: Mn-P1 224.9(1), Mn-P2 225.8(1), Mn-N1 166.1(2), Mn-H1 158.8(29), N1-O1 119.4(2); Bond angles [°]: P1-Mn-P2 154.7(1), P1-Mn-N1 95.1(1), P2-Mn-N1 97.1(1), P1-Mn-H1 81.2(10), P2-Mn-H1 73.6(10), N1-Mn-H1 119.1(10), N1-Mn-N1a 121.7(1), Mn-N1-O1 173.0(1). |

The phosphorus substituents strongly "lean over" toward the H ligand, which is quite commonly observed in transition metal hydrides[21]. A similar but much less pronounced distortion of the P–Mn–P angle (166.5°) has been found in the structure of $MnCl(NO)_2[P(OMe)_2Ph]_2$[22]. The ON–Mn–NO angle of **1a** is close to the ideal 120° of a trigonal-bipyramidal arrangement (Table 1). The observed angle is identical with the observed ON–Fe–CO angle in the isoelectronic $Fe(CO)(NO)(PMe_3)_2H$ complex[23]. The nitrosyl groups are practically linear (Mn–N–O angle 173°), which justifies a three-electron count for them in this series of molecules.

The Mn–P distances are shorter than in other trigonal-bipyramidal or octahedral Mn(I) complexes[24], which presently cannot be explained. The Mn–H distance of 1.59 Å, although having a high standard deviation, is in good agreement with the spectroscopically determined value of 1.59 ± 0.02 Å[25] for **1b** and fits well to the neutron diffraction value of 1.601(16) Å in $Mn(CO)_5H$[26].

The structures of **9a** and **10a** have been determined by single-crystal X-ray diffraction in support of the NMR spectroscopic assignment of the double bond stereochemistry of these compounds. Both complexes have a pseudo trigonal-bipyramidal coordination geometry with the phosphorus donors in axial positions and the NO groups and the vinyl ligand in equatorial positions. The crystal structure of **9a** reveals two independent molecules, which have essentially identical parameters within the standard deviations. Therefore, we will refer to the bonding parameters of the structure of **9a** shown in Figure 2 which are compiled in Table 2.

The phosphorus substituents of **9a** and **10a** are slightly "leaning over" towards the vinyl groups (P–Mn–P angles of 167.6 and 170.5°, respectively), and the ON–Mn–NO angles are for both molecules marginally closer than 120°. In either case this deviation is presumably due to steric crowding in the equatorial plane.

The vinyl geometries of both molecules **9a** and **10a** confirm the α-metalation regiochemistry and the *trans* addition stereochemistry of the insertion reactions of **1a** with the corresponding acetylenes. There are significant distortions of the angles around the metal-bound C1 atom (Table 2 and 3). While the C2–C1–Mn angles are widened to 127.1 and 137.7°, respectively, the $Mn–C1–C_{ester}$ angles are smaller than 120°.

The C2–C1–Mn angle of 137.7° represents an extreme case of structural distortion, presumably indicating strong steric repulsions between the phenyl group and one of the NO ligands. In this regard it is also quite surprising that the Ph residue is arranged coplanarly with respect to the vinyl plane. This may be taken as an indication of a strong conjugational interaction between both moieties. The ester group of **10a** is oriented orthogonally to the vinyl plane in contrast to **9a**, where these substituents are in the same plane. Apparently, there is a competition between the Ph and the ester groups for π interaction with the C=C double bond in **10a**, which is "won" by the Ph substituent.

Financial support from the *Swiss National Science Foundation* is gratefully acknowledged.

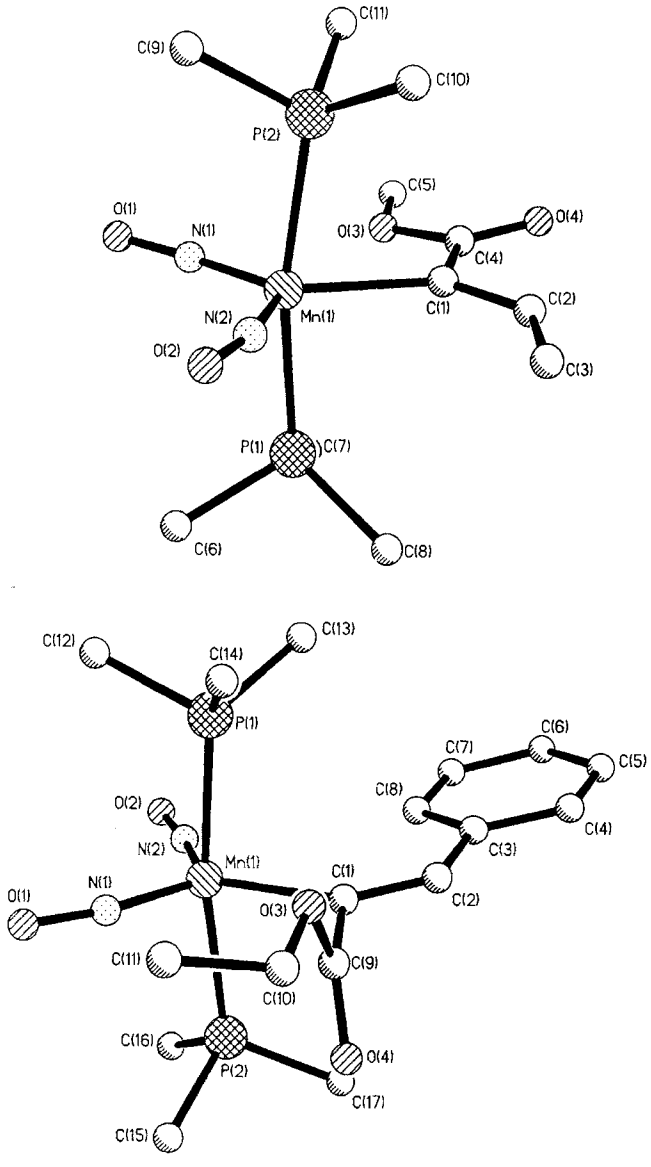



Figure 2. Structures of **9a** (above) and **10a** (below)

## Experimental

All preparations and manipulations were carried out under dry nitrogen by conventional Schlenk techniques. Solvents were dried and freshly distilled before use. Acetylene compounds were purchased from commercial suppliers. $MnBr(CO)_3L_2$ complexes [L = $PMe_3$, $PEt_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OiPr)_3$] were prepared according to published procedures[27]. – IR: Biorad FTS-45. – MS: Finnigan MAT-8230. FAB spectra were taken in a matrix of 3-nitrobenzyl alcohol. – NMR: Gemini 300 BB, $^1H$ at 300.08 MHz, $^{13}C$ at 75.46 MHz, and $^{31}P$ at 121.47 MHz. All spectra were recorded at room temperature. $^1H$- and $^{13}C$-NMR chemical shifts are related to TMS and $^{31}P$ NMR shifts related to $H_3PO_4$. *J* values in Hz. – Column chromatography: Kieselgel 60 (Merck).

*Preparation of $MnBr(NO)_2L_2$ Complexes with L = $PMe_3$, $PEt_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OiPr)_3$:* 5.0 g of the corresponding $MnBr(CO)_3L_2$ compound was dissolved in toluene. Nitric oxide, purified by passing it through 3 traps (conc. $H_2SO_4$, 50% KOH, $CaCl_2$ at −80°C) was bubbled through the refluxing solution. The progress of the reaction was monitored by IR spectroscopy, and after completion of the reaction (4–6 h) the solution was filtered through Celite. Removal of the solvent in vacuo was followed by treatment of the redish residues with hexane (3 × 250 ml). Orange crystalline products remained. Additional material was obtained from the hexane extracts, which were reduced in volume and left for crystallization at −30°C.

Table 2. Selected bond lengths and angles for **9a**

Bond lengths [pm]: Mn1-P1 230.3(2), Mn1-P2 229.0(2), Mn1-N1 163.2(6), Mn1-N2 166.6(5) Mn1-C1 213.4(9), N1-O1 119.5(10), N2-O2 118.5(7), C1-C2 133.0(11), C1-C4 144.8(12), C2-C3 146.3(11), C4-O3 132.3(11), C4-O4 122.5(13), O3-C5 142.0(9); Bond angles [°]: P1-Mn1-P2 167.6(1), P1-Mn1-N1 91.8(2), P1-Mn1-N2 95.5(2), P2-Mn1-N1 93.1(2), P2-Mn1-N2 92.5(2), P1-Mn1-C1 84.5(2), P2-Mn1-C1 83.4(2), N1-Mn1-N2 116.9(3), N1-Mn1-C1 125.7(3), N2-Mn1-C1 117.4(3), Mn1-N1-O1 172.1(6), Mn1-N2-O2 169.3(6), Mn1-C1-C2 127.1(6), Mn1-C1-C4 116.9(6), C2-C1-C4 116.0(9), C1-C2-C3 131.1(9), C1-C4-O3 117.3(8), C1-C4-O4 126.8(9).

Table 3. Selected bond lengths and angles for **10a**

Bond lengths [pm]: Mn1-P1 229.8(3), Mn1-P2 232.8(3), Mn1-N1 167.5(7), Mn1-N2 165.8(8) Mn1-C1 209.6(8), N1-O1 118.1(10), N2-O2 119.8(11), C1-C2 134.2(11), C1-C9 148.2(15), C2-C3 148.0(14), C9-O3 130.9(14), C9-O4 118.5(16), O3-C10 144.6(19); Bond angles [°]:P1-Mn1-P2 170.5(1), P1-Mn1-N1 92.4(3), P1-Mn1-N2 90.8(3), P2-Mn1-N1 94.1(3), P2-Mn1-N2 92.2(3), P1-Mn1-C1 85.8(3), P2-Mn1-C1 85.2(3), N1-Mn1-N2 118.4(4), N1-Mn1-C1 113.9(4), N2-Mn1-C1 127.4(4), Mn1-N1-O1 169.3(7), Mn1-N2-O2 173.0(7), Mn1-C1-C2 137.7(8), Mn1-C1-C9 108.4(6) C2-C1-C9 113.8(8), C1-C2-C3 131.2(9), C1-C9-O3 114.1(10), C1-C9-O4 124.6(11).

*$MnBr(NO)_2(PMe_3)_2$:* Yield 4.2 g (89%). – IR (EtOH): ν(NO) = 1707 m, 1662 st $cm^{-1}$. – $C_6H_{18}BrMnN_2O_2P_2$ (347.0): calcd. C 20.77, H 5.23, N 8.07; found C 20.49, H 5.40, N 8.39.

*$MnBr(NO)_2(PEt_3)_2$:* Yield 4.4 g (93%). – IR (EtOH): ν(NO) = 1703 m, 1658 st $cm^{-1}$. – $C_{12}H_{30}BrMnN_2O_2P_2$ (431.2): calcd. C 33.43, H 7.01, N 6.50; found C 33.71, H 6.89, N 6.27.

*$MnBr(NO)_2[P(OMe)_3]_2$:* Yield 3.5 g (73%). – IR (EtOH): ν(NO) = 1740 m, 1691 st $cm^{-1}$. – $C_6H_{18}BrMnN_2O_8P_2$ (443.0): calcd. C 16.27, H 4.10, N 6.32; found C 16.14, H 4.41, N 6.17.

*$MnBr(NO)_2[P(OEt)_3]_2$:* Yield 3.7 g (78%). – IR (EtOH): ν(NO) = 1737 m, 1686 st $cm^{-1}$. – $C_{12}H_{30}BrMnN_2O_8P_2$ (527.2): calcd. C 27.34, H 5.74, N 5.31; found C 27.16, H 5.60, N 5.12.

*$MnBr(NO)_2[P(OiPr)_3]_2$:* Yield 4.6 g (95%). – IR (EtOH): ν(NO) = 1728 m, 1675 st $cm^{-1}$. – $C_{18}H_{42}BrMnN_2O_8P_2$ (611.3): calcd. C 35.37, H 6.92, N 4.58; found C 35.11, H 6.78, N 4.32.

*trans-$MnH(NO)_2(PMe_3)_2$* (**1a**): 0.12 g (3.2 mmol) of $NaBH_4$ was added to 1.0 g (2.88 mmol) of $MnBr(NO)_2(PMe_3)_2$ in ethanol at room temp. The reaction was monitored by IR spectroscopy. After 1 h the solvent was removed in vacuo followed by two recrystallizations from toluene/hexane (2:1) at −30°C. Compound **1a** was obtained as orange air-sensitive crystals. Yield 0.66 g (86%). – IR (ether): ν(NO) = 1683 m, 1637 st $cm^{-1}$. – IR (ethanol): ν(NO) = 1663 st, 1634 st, 1611 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 1.20 (t, $J_{PH}$ 9.0, $CH_3$); 0.10 (t, $J_{PH}$ 107.5, MnH). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 19.7 (t, $J_{PH}$ 31.6). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 30.9 (s). – MS (EI), *m/z*: 268 (30) [$M^+$], 238 (42) [$M^+$ − NO], 237 (18) [$M^+$ − NO − H], 208 (23) [$M^+$ − 2 NO], 207 (5) [$M^+$ − 2 NO − H], 162 (168) [$M^+$ − NO − $PMe_3$], 161 (39) [$M^+$ − NO − $PMe_3$ − H], 132 (100) [$M^+$ − 2 NO − $PMe_3$], 131 (44) [$M^+$ − 2 NO − $PMe_3$ − H]. – $C_6H_{19}MnN_2O_2P_2$ (268.1): calcd. C 26.88, H 7.14, N 10.45; found C 26.60, H 6.82, N 10.63.

*trans-MnH(NO)$_2$(PEt$_3$)$_2$* (**1b**): 0.05 (1.3 mmol) of $NaBH_4$ was added to a solution of 0.50 g (1.29 mmol) of $MnBr(NO)_2(PEt_3)_2$ in 70 ml of ethanol at −30°C. After warming to room temp. and subsequent stirring for 2 h the solvent was removed in vacuo. The residual reaction mixture was extracted with hexane. Column chromatography of the extract on silica gel at −20°C and elution with hexane/ether (2:1) afforded **1b** as a lemon-coloured fraction (a green front band was discarded). Removal of the solvent in vacuo gave **2b** as yellow crystals. Yield 0.40 g (89%). − IR (ether): ν(NO) = 1669 m, 1634 st $cm^{-1}$. − IR (ethanol): ν(NO) = 1665 st, 1631 st, 1608 st $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 1.55 (quint, $J_{HH}$ 7.7, $J_{PH}$ 7.7, $CH_2$); 1.01 (quint, $J_{HH}$ 7.7, $J_{PH}$ 16.3, $CH_3$); −0.49 (t, $J_{PH}$ 101.1, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 22.1 (t, $J_{PC}$ 27.6, $CH_2$); 7.9 (s, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 66.8 (s). − MS (EI), *m/z*: 352 (22) [$M^+$], 322 (50) [$M^+$ − NO], 292 (23) [$M^+$ − 2 NO], 204 (79) [$M^+$ − NO − $PEt_3$], 174 (100) [$M^+$ − 2 NO − $PEt_3$]. − $C_{12}H_{31}MnN_2O_2P_2$ (352.3): calcd. C 40.91, H 8.87, N 7.95; found C 40.72, H 8.92, N 7.66.

*trans-MnD(NO)$_2$(PEt$_3$)$_2$* (**1b$^D$**) was prepared analogously by starting from $MnBr(NO)_2(PEt_3)_2$ and $NaBD_4$. − IR (ether): ν(NO) = 1675 m, 1633 st $cm^{-1}$.

*trans-MnH(NO)$_2$[P(OMe)$_3$]$_2$* (**1c**): 0.09 g (2.4 mmol) of $NaBH_4$ was added within 10 min to a solution of 1.0 g (1.26 mmol) of $MnBr(NO)_2[P(OMe)_3]_2$ in 80 ml of ethanol at −60°C. When the reaction was complete (IR monitoring), the solvent was removed in vacuo with the exclusion of light at −30°C. The residue was extracted with pentane. Removal of pentane from the extract yielded 0.62 g of yellow crystals of **1c** (75%). − IR (ether): ν(NO) = 1712 m, 1667 st $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 3.44 (t, $J_{PH}$ 12.8, $OCH_3$); −0.60 (t, $J_{PH}$ 95.7, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): 52.1 (s). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 187.1 (s). − MS (EI), *m/z*: 364 (75) [$M^+$], 334 (18) [$M^+$ − NO], 333 (14) [$M^+$ − NO − H], 304 (4) [$M^+$ − 2 NO], 303 (4) [$M^+$ − 2 NO − H], 179 (100) [$M^+$ − 2 NO − H − $P(OCH_3)_3$]. − $C_6H_{19}MnN_2O_8P_2$ (364.1): calcd. C 19.79, H 5.26, N 7.69; found C 19.68, H 5.39, N 7.64.

*trans-MnH(NO)$_2$[P(OEt)$_3$]$_2$* (**1d**): A procedure analogous to the preparation of **1c** was used. 1.0 g (1.89 mmol) of $MnBr(NO)_2[P(OEt)_3]_2$. Two recrystallizations from hexane at −80°C afforded orange crystals. Yield 0.67 g (79%). − IR (ether): ν(NO) = 1706 m, 1661 st $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 4.09 (m, $J_{HH}$ 7.0, $J_{PH}$ 12.2, $OCH_2$); 1.14 (t, $J_{HH}$ 7.0, $CH_3$); 0.23 (t, 96.4, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): 61.7 (s, $CH_2$); 16.0 (s, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 180.6 (s). − MS (EI), *m/z*: 448 (11) [$M^+$], 418 (46) [$M^+$ − NO], 417 (13) [$M^+$ − NO − H], 388 (7) [$M^+$ − 2 NO], 252 (100) [$M^+$ − NO − $P(OEt)_3$ − H], 222 (88) [$M^+$ − 2 NO − $P(OEt)_3$], 221 (31) [$M^+$ − 2 NO − $P(OEt)_3$ − H]. − $C_{12}H_{31}MnN_2O_8P_2$ (448.3): calcd. C 32.15, H 6.97, N 6.25; found C 32.02, H 6.78, N 6.02.

*trans-MnH(NO)$_2$[P(OiPr)$_3$]$_2$* (**1e**): A procedure analogous to the preparation of **1b** was applied. 0.60 g (1.10 mmol) of $MnBr(NO)_2[P(OiPr)_3]_2$ in 70 ml of ethanol. Two recrystallizations from hexane at −80°C. Yellow oil at room temp. Yield 0.50 g (85%). − IR (ether): ν(NO) = 1699 m, 1655 st $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 4.85 (m, $J_{HH}$ 6.2, $J_{PH}$ 12.6, OCH); 1.27 (d, $J_{HH}$ 6.2, $CH_3$); −0.13 (t, $J_{PH}$ 95.6, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 70.0 (s, CH); 23.8 (s, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 176.1 (s). − MS (EI), *m/z*: 532 (24) [$M^+$], 502 (86) [$M^+$ − NO], 501 (27) [$M^+$ − NO − H], 472 (50) [$M^+$ − $C_3H_8O$], 442 (16) [$M^+$ − $C_3H_8O$ − NO], 294 (100) [$M^+$ − $P(OiPr)_3$], 264 (29) [$M^+$ − $C_3H_8O$ − $P(OiPr)_3$]. − $C_{18}H_{43}MnN_2O_8P_2$ (532.4): calcd. C 40.61, H 8.14, N 5.26; found C 40.72, H 8.00, N 5.41.

*Preparation of Complexes Mn(CO)$_3$HL$_2$* (L = $PMe_3$ **2a**; L = $PEt_3$ **2b**): The $MnBr(CO)_3L_2$ complex was dissolved in THF and the solution was stirred with an excess of sodium amalgam for 4 h at room temp. The orange solution was filtered over Celite and cooled to −80°C. Over a period of 30 min 1 equiv. of MeCOOH in 20 ml of THF was added. After warming to room temp. the reaction mixture was stirred for 1 h, and the solvent was completely evaporated in vacuo. The residue was extracted with hexane and the extract filtered over Celite. The volume of the filtrate was reduced. Crystallization at −30°C afforded **2a** or **2b**.

*mer,trans-Mn(CO)$_3$H(PMe$_3$)$_2$* (**2a**): 1.0 g (2.70 mmol) of $MnBr(CO)_3(PMe_3)_2$, 0.6 g of Na in 4.7 ml of Hg, 150 ml of THF, and 152 µl of MeCOOH in 20 ml of THF. Yield 0.63 g (87%). − IR (hexane): ν(CO) = 1908 $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 1.14 (t, $J_{PH}$ 8.0, $CH_3$); −8.46 (t, $J_{PH}$ 34.5, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): 228.1 (t, $J_{PC}$ 14.4, $(CO)_{trH}$); 225.0 (t, $J_{PC}$ 18.6, $(CO)_{cisH}$); 21.9 (m, $J_{PC}$ 29.7, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 30.0 (s). − MS (EI), *m/z*: 292 (100) [$M^+$], 291 (11) [$M^+$ − H], 263 (15) [$M^+$ − H − CO], 235 (6) [$M^+$ − H − 2 CO], 208 (47) [$M^+$ − 3 CO], 207 (18) [$M^+$ − H − 3 CO], 132 (58) [$M^+$ − 3 CO − $PMe_3$], 131 (40) [$M^+$ − H − 3 CO − $PMe_3$]. − $C_9H_{19}MnO_3P_2$ (292.1): calcd. C 37.01, H 6.56; found C 36.82, H 6.49.

For the preparation of *mer,trans*-$Mn(CO)_3D(PMe_3)_2$ (**2a$^D$**) the same procedure as for **2a** was used with MeCOOD instead of MeCOOH.

*mer,trans-Mn(CO)$_3$H(PEt$_3$)$_2$* (**2b**): 0.50 g (1.10 mmol) of $MnBr(CO)_3(PEt_3)_2$, 0.25 g of Na in 1.9 ml Hg, 80 ml of THF, and 62 µl of MeCOOH in 20 ml of THF. Yield 0.33 g (91%). − IR (hexane): ν(CO) = 1900 $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 1.52 (quint, $J_{HH}$ 7.6, $J_{PH}$ 7.6, $CH_2$); 1.01 (quint, $J_{HH}$ 7.6, $J_{PH}$ 15.0, $CH_3$); −8.50 (t, $J_{PH}$ 31.3, MnH). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 225.6 (t, $J_{PC}$ 15.1, $(CO)_{trH}$); 225.2 (t, $J_{PC}$ 20.6, $(CO)_{cisH}$); 22.8 (m, $J_{PC}$ 25.2 $CH_2$); 8.1 (s, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 62.6 (s). − MS (EI), *m/z*: 376 (100) [$M^+$], 375 (34) [$M^+$ − H], 347 (5) [$M^+$ − H − CO], 319 (12) [$M^+$ − H − 2 CO], 292 (49) [$M^+$ − 3 CO], 291 (15) [$M^+$ − H − 3 CO], 174 (26) [$M^+$ − 3 CO − $PEt_3$], 173 (10) [$M^+$ − H − 3 CO − $PEt_3$]. − $C_{15}H_{31}MnO_3P_2$ (376.3): calcd. C 47.88, H 8.30; found C 47.61, H 8.07.

*trans-Mn(OPh)(NO)$_2$(PEt$_3$)$_2$* (**3a**): 0.05 g (0.57 mmol) of phenol was added to a solution of 0.20 g (0.57 mmol) of **1b** in 10 ml of toluene. $H_2$ evolution was observed for about 2 h. After 8 h the solution was filtered over Celite, and the solvent was removed from the filtrate in vacuo leaving **3a** as an orange solid. Yield 0.25 g (98%). − IR (hexane): ν(NO) = 1694 m, 1640 st $cm^{-1}$. − $^1H$ NMR ($C_6D_6$): δ = 7.18−7.08 (m, Ph); 6.93−6.64 (m, Ph); 1.56 (quint, $J_{HH}$ 7.5, $J_{PH}$ 7.5, $CH_2$); 0.93 (quint, $J_{HH}$ 7.5, $J_{PH}$ 16.1, $CH_3$). − $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 167.5, 129.5, 120.5, 115.0 (s, Ph); 16.2 (t, $J_{PC}$ 26.8, $CH_2$); 7.5 (s, $CH_3$). − $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 48.0 (s). − MS (EI), *m/z*: 444 (6) [$M^+$], 414 (8) [$M^+$ − NO], 384 (14) [$M^+$ − 2 NO], 352 (31) [$M^+$ − $C_6H_4O$], 322 (74) [$M^+$ − $C_6H_4O$ − NO], 292 (36) [$M^+$ − $C_6H_4O$ − NO], 266 (10) [$M^+$ − 2 NO − $PEt_3$], 204 (96) [$M^+$ − $C_6H_4O$ − NO − $PEt_3$], 174 (100) [$M^+$ − $C_6H_4O$ − 2 NO − $PEt_3$]. − $C_{18}H_{35}MnN_2O_3P_2$ (444.4): calcd. C 48.65, H 7.94, N 6.30; found C 48.41, H 7.70, N 6.68.

*trans-Mn[OCH(CF$_3$)$_2$](NO)$_2$(PEt$_3$)$_2$* (**3b**): 0.30 g (0.85 mmol) of **1b** and 0.18 ml (1.70 mmol) of hexafluoro-2-propanol were dissolved in toluene, and the obtained solution was stirred at room temp. for 8 h. During the first hour a weak evolution of $H_2$ was observable. The reaction mixture was filtered over Celite. The solvent was then removed from the filtrate in vacuo, and the oily residue was recrystallized from toluene/hexane (1:1) at −80°C. Orange crystals of **3b**. Yield 0.31 g (71%). − IR (toluene): ν(NO) = 1691

m, 1644 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 4.49 (sept, $J_{FH}$ 6.4, CH); 1.61 (m, $CH_2$); 0.78 (quint, $J_{HH}$ 7.8, $J_{FH}$ 15.6, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 125.4 (q, $J_{FC}$ 292.3, $CF_3$): 80.3 (tsept, $J_{PC}$ 5.7, $J_{FC}$ 29.4, CH); 16.1 (t, $J_{PC}$ 21.3, $CH_2$); 7.5 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 48.0 (s). – MS (FAB), *m/z*: 351 [$M^+$], 321 (100) [$M^+$ – NO]. – No satisfactory elemental analysis could be obtained.

*Mn(OOCMe)(NO)$_2$(PEt$_3$)$_2$* (**3c**): 81 µl (1.42 mmol) of MeCOOH was added to a solution of 0.50 g (1.42 mmol) of **1b** in 20 ml of ether at 0°C. A vigorous evolution of $H_2$ was observed. After 20 min the reaction mixture was filtered over Celite, and the filtrate was evaporated to dryness in vacuo. Recrystallization of the residue from hexane afforded orange crystals of **3c**. Yield 0.39 g (67%). – IR (ether): ν(NO) = 1704 m, 1658 st $cm^{-1}$, ν($CO_2$) = 1633 w. – $^1H$ NMR ($C_6D_6$): δ = 1.90 (s, $O_2CCH_3$); 1.58 (quint, $J_{HH}$ 7.9, $J_{PH}$ 7.9, $CH_2$); 0.97 (quint, $J_{HH}$ 7.9, $J_{PH}$ 15.6, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 49.2 (s). – MS (EI), *m/z*: 410 (6) [$M^+$], 380 (11) [$M^+$ – NO], 350 (62) [$M^+$ – 2 NO], 232 (100) [$M^+$ – 2 NO – $PEt_3$]. – $C_{14}H_{33}MnN_2O_4P_2$ (410.3): calcd. C 40.98, H 8.11, N 6.83; found C 40.81, H 8.06, N 6.59.

*trans-Mn(OOCH)(NO)$_2$(PMe$_3$)$_2$* (**4a**): 0.20 g (0.75 mmol) of **1a** was dissolved in 30 ml of toluene, and the solution was stirred for 2 h under $CO_2$. It was then filtered over Celite, and the solvent was removed from the filtrate in vacuo. Recrystallization of the residue from ethanol at −30°C afforded dark red crystals of **4a**. Yield 0.23 g (94%). – IR (hexane): $\nu(CH)_{formate}$ = 2834 w $cm^{-1}$, ν($CO_2$) = 1658 m, ν(NO) = 1695 m, 1649 st. – $^1H$-NMR ($C_6D_6$): δ = 8.88 (br., s, $HCO_2$); 1.13 (t, $J_{PH}$ 8.6, $CH_3$). – $^{13}C$ NMR ($C_6D_6$): δ = 166.3 (d, $^1J_{CH}$ 189, $CO_2$); 13.4 (t, $J_{PC}$ 25.6, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 21.2 (s). – MS (EI), *m/z*: 268 (46) [$M^+$ – $CO_2$ – NO], 238 (33) [$M^+$ – $CO_2$ – NO], 208 (100) [$M^+$ – $CO_2$ – 2 NO], 162 (68) [$M^+$ – $CO_2$ – NO – $PMe_3$], 132 [$M^+$ – $CO_2$ – 2 NO – $PMe_3$]. – $C_7H_{19}MnN_2O_4P_2$ (312.1): calcd. C 26.94, H 6.14, N 8.98; found C 26.68, H 6.00, N 9.36.

*trans-Mn(OOCH)(NO)$_2$(PEt$_3$)$_2$* (**4b**): A procedure analogous to the preparation of **4a** was applied. 0.20 g (0.57 mmol) of **1b**, 30 ml toluene. Yield 0.22 g (98%). – IR (hexane): $\nu(CH)_{formate}$ = 2834 w $cm^{-1}$, ν($CO_2$) = 1657 m, ν(NO) = 1658 m, 1640 st. – $^1H$-NMR ($C_6D_6$): δ = 8.83 (t, $J_{PH}$ 3.5, $HCO_2$); 1.57 (q, $J_{HH}$ 7.7, $J_{PH}$ 7.7, $CH_2$); 0.95 (q, $J_{HH}$ 7.7, $J_{PH}$ 15.8, $CH_3$). – $^{13}C$ NMR ($C_6D_6$): δ = 166.2 (d, $^1J_{HC}$ 187, $CO_2$); 16.1 (t, $J_{PC}$ 22.8, $CH_2$); 7.3 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 49.6 (s). – MS (EI), *m/z*: 352 (62) [$M^+$ – $CO_2$], 322 (94) [$M^+$ – $CO_2$ – NO], 292 (50) [$M^+$ – $CO_2$ – 2 NO], 204 (81) [$M^+$ – $CO_2$ – NO – $PEt_3$], 174 (100) [$M^+$ – $CO_2$ – 2 NO – $PEt_3$]. – $C_{13}H_{31}MnN_2O_4P_2$ (396.3): calcd. C 39.42, H 7.88, N 7.07; found C 39.35, H 7.91, N 7.19.

*Mn(OC$_6$H$_4$-o-CH$_2$OH)(NO)$_2$(PEt$_3$)$_2$* (**5b**) *and Mn(OC$_6$H$_4$-o-CHO)(NO)$_2$(PEt$_3$)$_2$* (**6b**): 0.26 g (0.74 mmol) of **1b** and 0.23 ml (2.2 mmol) of salicylaldehyde were dissolved in 30 ml of hexane, and the resulting solution was stirred for 18 h at room temp. The precipitate of **5b** was collected by filtration, washed with cold hexane, and recrystallized from toluene. The filtrate was filtered over a small amount of silica gel, and the volume of the filtrate was reduced to 10 ml in vacuo. **6b** crystallized from this solution at −80°C.

**5b**: Yield 0.21 g (67%). – IR (hexane): ν(NO) = 1691 m, 1649 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 6.92, 6.87, 6.60, 6.32 (m, $C_6H_4$); 4.33 (s, $OCH_2$); 1.50 (quint, $J_{HH}$ 7.7, $J_{PH}$ 7.7, $CH_2$); 0.98 (quint, $J_{HH}$ 7.7, $J_{PH}$ 15.2, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 166.0, 131.8, 128.9, 126.9, 118.6, 114.7 (s, $C_6H_4$); 66.4 (s, $OCH_2$); 15.9 (t, $J_{PC}$ 25.4, $CH_2$); 7.2 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 51.3 (s). – MS (EI), *m/z*: 474 (4) [$M^+$], 321 (68) [$M^+$ – $C_7H_7O_2$ – NO], 291 (19) [$M^+$ – $C_7H_7O_2$ – 2 NO], 203 (80) [$M^+$ – $C_7H_7O_2$ – NO – $PEt_3$], 173 (100) [$M^+$ – $C_7H_7O_2$ – 2 NO – $PEt_3$]. – $C_{19}H_{37}MnN_2O_4P_2$ (474.4): calcd. C 48.11, H 7.89, N 5.90; found C 48.45, H 7.59, N 6.23.

**6b**: Yield 0.08 g (22%). – IR (hexane): ν(NO) = 1693 m, 1647 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 10.42 (s, CHO); 7.04, 6.98, 6.50, 6.45 (m, $C_6H_4$); 1.51 (quint, $J_{HH}$ 7.7, $J_{PH}$ 7.7, $CH_2$); 0.98 (quint, $J_{HH}$ 7.7, $J_{PH}$ 15.0, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 191.0 (s, CHO); 172.7, 135.6, 126.7, 125.9, 121.7, 114.1 (s, $C_6H_4$); 16.0 (t, $J_{PC}$ 25.6, $CH_2$); 7.1 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 51.6 (s). – MS (EI), *m/z*: 472 (3) [$M^+$], 351 (24) [$M^+$ – $C_7H_5O_2$], 321 (61) [$M^+$ – $C_7H_5O_2$ – NO]), 291 (55) [$M^+$ – $C_7H_5O_2$ – 2 NO]), 203 (82) [$M^+$ – $C_7H_5O_2$ – NO – $PEt_3$], 173 (100) [$M^+$ – $C_7H_5O_2$ – 2 NO – $PEt_3$]. – $C_{19}H_{35}MnN_2O_4P_2$ (472.4): calcd. C 48.31, H 7.47, N 5.93; found C 48.19, H 7.25, N 5.70.

*Preparation of Mn(OAr)(NO)$_2$(PEt$_3$)$_2$ Complexes* **7a–c**: The aromatic aldehyde ArCHO was added to a solution of **1b** at room temp. in toluene or hexane. The reaction was monitored by IR spectroscopy. After completion of the reaction the mixture was filtered through Celite and the filtrate evaporated to dryness. Complexes **7** were recrystallized from ether or toluene at −30°C.

*Mn(OC$_6$H$_4$-p-CHO)(NO)$_2$(PEt$_3$)$_2$* (**7a**): 0.38 g (1.08 mmol) of **1b**, 0.13 g (1.08 mmol) of *p*-hydroxybenzaldehyde. Recrystallization from ether. Yield 0.48 g (95%). – IR (toluene): ν(NO) = 1695 m, 1644 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 9.82 (s, CHO); 7.78, 6.63 (m, Ph); 1.37 (quint, $J_{HH}$ 8.1, $J_{PH}$ 8.1, $CH_2$); 0.84 (quint, $J_{HH}$ 8.1, $J_{PH}$ 15.8, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 190.9 (s, CHO); 117.1, 133.4, 121.3, 125.1 (s, Ph); 17.3 (t, $J_{PC}$ 22.0, $CH_2$); 8.0 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 48.8 (s). – MS (EI), *m/z*: 472 (4) [$M^+$], 351 (24) [$M^+$ – $C_7H_5O_2$], 321 (78) [$M^+$ – $C_7H_5O_2$ – NO], 291 (42) [$M^+$ – $C_7H_5O_2$ – 2 NO], 203 (88) [$M^+$ – $C_7H_5O_2$ – O – $Et_3$], 173 (100), [$M^+$ – $C_7H_5O_2$ – 2 NO – $PEt_3$]. – $C_{19}H_{35}MnN_2O_4P_2$ (472.4): calcd. C 48.31, H 7.47, N 5.93; found C 48.15, H 7.24, N 5.62.

*Mn(OC$_6$H$_3$-2-OCH$_3$-4-CHO)(NO)$_2$(PEt$_3$)$_2$* (**7b**): 0.35 g (0.99 mmol) of **1b**, 0.15 g (0.99 mmol) of vanilline. Recrystallization from ether. Yield 0.49 g (98%). – IR (hexane): ν(NO) = 1699 m, 1640 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 9.84 (s, CHO); 7.50–7.42, 7.26–7.22, 6.46–6.42 (m, Ph); 3.44 (s, $OCH_3$); 1.44 (quint, $J_{HH}$ 7.7, $J_{PH}$ 7.7, $CH_2$), 0.92 (quint, $J_{HH}$, 7.7, $J_{PH}$ 15.3, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 188.8 (s, CHO); 166.3, 153.5, 128.8, 124.4, 119.5, 109.3 (s, Ph); 55.2 (s, $OCH_3$); 16.3 (t, $J_{PC}$ 24.8, $CH_2$); 7.5 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): 49.5 (s). – MS (EI), *m/z*: 502 (7) [$M^+$], 351 (23) [$M^+$ – $C_8H_7O_3$], 442 (11), [$M^+$ – 2 NO], 321 (69) [$M^+$ – $C_8H_7O_3$ – NO], 291 (39) [$M^+$ – $C_8H_7O_3$ – 2 NO], 203 (92) [$M^+$ – $C_8H_7O_3$ – NO – $PEt_3$], 173 (100) [$M^+$ – $C_8H_7O_3$ – 2 NO – $PEt_3$]. – $C_{20}H_{37}MnN_2O_5P_2$ (502.4): calcd. C 48.11, H 7.42, N 5.58; found C 48.02, H 7.37, N 5.51.

*Mn[OC$_6$H$_2$-2,6-(OCH$_3$)$_2$-4-CHO](NO)$_2$(PEt$_3$)$_2$* (**7c**): 0.30 g (0.85 mmol) of **1b**, 0.16 g (0.85 mmol) of 4-hydroxy-3,5-dimethoxybenzaldehyde. Recrystallization from toluene. Yield 0.43 g (94%). – IR (toluene): ν(NO) = 1692 m, 1641 st $cm^{-1}$. – $^1H$ NMR ($C_6D_6$): δ = 9.85 (s, CHO); 7.26 (s, Ph); 3.61 (s, $OCH_3$); 1.43 (quint, $J_{HH}$ 7.8, $J_{PH}$ 7.8, $CH_2$); 0.88 (quint, $J_{HH}$ 7.8, $J_{PH}$ 15.6, $CH_3$). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 184.2 (s, CHO); 157.5, 151.5, 121.3, 107.8 (s, Ph); 54.8 (s, $OCH_3$); 15.4 (t, $J_{PC}$ 25.6, $CH_2$); 7.1 (s, $CH_3$). – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 49.0 (s). – MS (EI), *m/z*: 508 (2) [$M^+$], 351 (25) [$M^+$ – $C_9H_9O_4$], 321 (63) [$M^+$ – $C_6H_9O_4$ – NO], 291 (38) [$M^+$ – $C_9H_9O_4$ – 2 NO], 203 (94) [$M^+$ – $C_9H_9O_4$ – NO – $PEt_3$], 173 (100) [$M^+$ – $C_9H_9O_4$ – NO – $PEt_3$]. – $C_{21}H_{39}MnN_2O_6P_2$ (532.4): calcd. C 44.89, H 7.73, N 5.51; found C 44.61, H 7.56, N 5.25.

*Preparation of Mn[Z-C(COOMe)=CHR](NO)$_2$L$_2$ Complexes* **9–11**: The substituted methyl propiolate RC≡CCOOMe (R = H, Me, Ph, COOMe) was added to a toluene solution of **1a** or **1b** at a temp. depending on the acetylene. After completion of the reaction (IR monitoring) the reaction mixture was filtered through Celite and the filtrate evaporated to dryness in vacuo. Further purification of the complexes **8a**, **8b**, **9a**, **11a**, and **11b** was achieved either by column chromatography or recrystallization.

*Mn[C(CO$_2$Me)=CH$_2$](NO)$_2$(PMe$_3$)$_2$* (**8a**): 0.15 g (1.86 mmol) of **1a**, 0.16 ml (2.0 mmol) of HC≡CCOOMe in 50 ml of toluene at 0°C. Recrystallization from hexane at −30°C. Yield 0.59 g (90%). – IR (hexane): ν(C=O) = 1701 w cm$^{-1}$; ν(NO) = 1689 m, 1651 st. – $^1$H NMR ($C_6D_6$): δ = 6.51 [dt, $J_{HH}$ 4.2, $J_{PH}$ 7.9, (=CH)$_E$]; 5.20 [dt, $J_{HH}$ 4.2, $J_{PH}$ 4.6, (=CH)$_Z$]; 3.40 (s, $OCH_3$); 1.22 (t, $J_{PH}$ 9.6, $CH_3$). – $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 177.0 (s, $CO_2CH_3$); 175.3 (t, $J_{PC}$ 43.4, MnC); 128.1 (t, 9.0, $CH_2$); 50.5 (s, $OCH_3$); 14.6 (t, $J_{PC}$ 27.4, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 22.7 (s). – MS (EI), *m/z*: 352 (22) [M$^+$], 322 (18) [M$^+$ − NO], 292 (100) [M$^+$ − 2 NO], 216 (57) [M$^+$ 2 NO − $PMe_3$]. – $C_{10}H_{23}MnN_2O_4P_2$ (352.2): calcd. C 34.10, H 6.58, N 7.95; found C 34.02, H 6.54, N 8.02.

*Mn[C(CO$_2$Me)=CH$_2$](NO)$_2$(PEt$_3$)$_2$* (**8b**): 0.50 g (1.14 mmol) of **1b**, 0.17 ml (1.2 mmol) of HC≡$CCO_2Me$ in 50 ml of toluene, 0°C. Column chromatography (silica gel), elution with hexane/ether (2:1). Orange crystals. Yield 0.37 g (75%). – IR (ether): ν(C=O) = 1700 w cm$^{-1}$, ν(NO) = 1680 m, 1642 st. – $^1$H-NMR ($C_6D_6$): δ = 6.74 [dt, $J_{HH}$ 4.4, $J_{PH}$ 7.3, (=CH)$_E$]; 5.41 [dt, $J_{HH}$ 4.4, $J_{PH}$ 5.7, (=CH)$_Z$]; 3.46 (s, $OCH_3$); 1.75 (quint, $J_{HH}$ 7.8, $J_{PH}$ 7.8, $CH_2$); 0.96 (quint, $J_{HH}$ 7.8, $J_{PH}$ 15.4, $CH_3$). – $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 178.0 (s, $CO_2CH_3$); 173.6 (t, $J_{PC}$ 41.9, MnC); 130.5 (t, $J_{PC}$ 8.5, $=CH_2$); 50.7 (s, $OCH_3$); 16.4 (t, $J_{PC}$ 24.2, $CH_2$); 7.2 (s, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 49.1 (s). – MS (EI), *m/z*: 436 (4) [M$^+$], 406 (30) [M$^+$ − NO], 376 (32) [M$^+$ − 2 NO], 322 (28) [M$^+$ − NO − $C_4H_4O_2$], 288 (33) [M$^+$ − NO − Et$_3$], 258 (100) [M$^+$ − 2 NO − $PEt_3$]. – $C_{16}H_{35}MnN_2O_4P_2$ (436.1): calcd. C 44.04, H 8.08, N 6.42; found C 43.73, H 8.00, N 6.27.

The same procedure was applied to the preparation of **8b$^D$** by starting from **1b$^D$**.

*Mn[Z-C(CO$_2$Me)=CH(Me)](NO)$_2$(PMe$_3$)$_2$* (**9a**): 0.23 g (0.86 mmol) of **1a**, 0.26 ml (2.6 mmol) of MeC≡$CCO_2Me$ in 20 ml of MeOH, room temp., after 3 d. Column chromatography (silica gel). Elution with $CH_2Cl_2$. Yield 0.26 g (83%). – IR ($CH_2Cl_2$): ν(C=O) = 1695 w cm$^{-1}$; ν(NO) = 1685 m, 1649 st. – $^1$H NMR ($C_6D_6$): δ = 7.20 (qt, $J_{HH}$ 6.7, $J_{PH}$ 8.4, =CH); 3.45 (s, $OCH_3$); 1.61 (dt, $J_{HH}$ 6.7, $J_{PH}$ 3.9, $CHCH_3$); 1.14 (t, $J_{PH}$ 9.5, $CH_3$). – $^{13}$C NMR ($C_6D_6$): δ = 176.9 (dt, $J_{PC}$ 1.7, $^3J_{CH}$ 9.6, $CO_2CH_3$); 164.3 (t, $J_{PC}$ 44.8, MnC); 137.6 (t, $J_{PC}$ 8.8, $CHCH_3$); 50.5 (s, $OCH_3$); 22.3 (t, $J_{PC}$ 3.4, $=CHCH_3$); 15.0 (t, $J_{PC}$ 26.4, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 25.0 (s). – MS (EI), *m/z*: 366 (6) [M$^+$], 336 (50) [M$^+$ − NO], 306 (26) [M$^+$ − 2 NO], 260 (12) [M$^+$ − NO − $PMe_3$], 238 (27) [M$^+$ − NO − $C_5H_6O_2$], 230 (80) [M$^+$ − 2 NO − $PMe_3$], 162 (100) [M$^+$ − NO − $PMe_3$ − $C_5H_6O_2$], 132 (39) [M$^+$ − 2 NO − $PMe_3$ − $C_5H_6O_2$], 131 (17) [M$^+$ − 2 NO − $PMe_3$ − $C_5H_7O_2$]. – $C_{11}H_{25}MnN_2O_4P_2$ (366.2): calcd. C 36.8, H 6.88, N 7.65; found C 36.23, H 6.71, N 7.41.

*Mn[Z-C(CO$_2$Et)=CH(Ph)](NO)$_2$(PEt$_3$)$_2$* (**10a**): 0.50 g (1.5 mmol) of **1b**, 0.74 ml (4.5 mmol) of PhC≡$CCO_2Et$ in 30 ml of toluene, room temp., 2 d. Evaporation of the solvent in vacuo. Yield 0.54 g (87%). ν(C=O) = 1690 w cm$^{-1}$; ν(NO) = 1686 m, 1650 st. – $^1$H NMR ($C_6D_6$): δ = 7.70 (t, $J_{PH}$ 8.2, =CH); 7.42, 7.26, 7.14 (m, Ph); 4.08 (q, $J_{HH}$ 7.1, $OCH_2$); 1.43 (t, $J_{PH}$ 9.7, $CH_3$); 1.24 (t, $J_{PH}$ 7.1, $CH_2CH_3$). – $^{13}$C NMR ($C_6D_6$): δ = 180.6 (d, $^3J_{CH}$ 10.3, $CO_2CH_2$); 171.5 (t, $J_{PC}$ 42.9, MnC); 142.6, 129.4, 129.3, 128.0 (s, Ph); 141.6 (t, $J_{PC}$ 8.4,H); 60.9 (s, $OCH_2$); 15.8 (t, $J_{PC}$ 27.6, $CH_3$); 15.2 (s, $CH_2CH_3$). – $^{31}$P{$^1$H} NMR ($CD_3NO_2$): δ = −12.3 (s). – MS (EI), *m/z*: 442 (7) [M$^+$], 412 (79) [M$^+$ − NO], 382 (54) [M$^+$ − 2 NO], 336 (18) [M$^+$ − NO − $PMe_3$], 306 (100) [M$^+$ − 2 NO − $PMe_3$]. – $C_{17}H_{29}MnN_2O_4P_2$ (442.3): calcd. C 46.16, H 6.61, N 6.33; found C 46.01, H 6.38, N 6.72.

*Mn[Z-C(CO$_2$Me)=CH(CO$_2$Me)](NO)$_2$(PMe$_3$)$_2$* (**11a**): 0.5 g (1.86 mmol) of **1a**, 0.25 ml (2.05 mmol) of $MeO_2CC{\equiv}CCO_2Me$ in 50 ml of toluene, −60°C. Column chromatography at 0°C (silica). Elution with $CH_2Cl_2$ and removal of the solvent in vacuo. Yield 0.66 g (87%). – IR (hexane): ν(C=O) 1705 w cm$^{-1}$, ν(NO) = 1694 m, 1657 st. – $^1$H-NMR ($C_6D_6$): δ = 6.94 (t, $J_{PH}$ 7.6, =CH); 3.45, 3.37 (s, $OCH_3$); 1.20 (t, $J_{PH}$ 10.6, $CH_3$). – $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 198.6 (t, $J_{PC}$ 38.4, MnC); 179.0 (t, $J_{PC}$ 1.9, $CO_2CH_3$); 169.1 (t, $J_{PC}$ 3.5, $CO_2CH_3$); 126.2 (t, $J_{PC}$ 3.5, =CH); 50.6, 50.5 (s, $OCH_3$); 14.9 (t, $J_{PC}$ 27.4, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 19.4 (s). – MS (EI), *m/z*: 410 (2) [M$^+$], 380 (26) [M$^+$ − NO], 350 (31) [M$^+$ − 2 NO], 274 (100) [M$^+$ − 2 NO − $PMe_3$], 244 (37), 198 (10) [M$^+$ − 2 NO − 2 $PMe_3$], 162 (19) [M$^+$ − NO − $PMe_3$ − $C_6H_6O_4$], 132 (25) [M$^+$ − 2 NO − $PMe_3$ − $C_6H_6O_4$], 131 (6) [M$^+$ − NO − $PMe_3$ − $C_6H_7O_4$]. – $C_{12}H_{25}MnN_2O_6P_2$ (410.2): calcd. C 35.14, H 6.14, N 6.83; found C 35.32, H 6.37, N 6.46.

*Mn[Z-C(CO$_2$Me)=CH(CO$_2$Me)](NO)$_2$(PEt$_3$)$_2$* (**11b**): 0.80 g (2.27 mmol) of **1b**, 0.35 ml (2.85 mmol) of $MeO_2CC{\equiv}CCO_2Me$ in 100 ml of toluene, −60°C. Column chromatography (silica gel). Elution with $CH_2Cl_2$. Yield 0.91 g (81%). – IR (ether): ν(C=O) = 1703 w cm$^{-1}$, ν(NO) = 1688 m, 1649 st. – $^1$H NMR ($C_6D_6$): δ = 6.69 (t, $J_{PH}$ 7.0, =CH); 3.63, 3.61 (s, $OCH_3$); 1.94 (quint, $J_{HH}$ 7.6, $J_{PH}$ 7.6, $CH_2$); 1.1 (quint, $J_{HH}$ 7.6, $J_{PH}$ 15.4, $CH_3$). – $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 200.1 (t, $J_{PC}$ 36.4, MnC); 181.0 (s, $CO_2CH_3$); 170.8 (t, $J_{PC}$ 3.3, $CO_2CH_3$); 130.7 (t, $J_{PC}$ 7.3, =CH); 51.8, 51.5 (s, $OCH_3$); 17.6 (t, $J_{PC}$ 23.8, $CH_2$); 7.9 (s, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 46.3 (s). – MS (EI), *m/z*: 494 (8) [M$^+$], 464 (19) [M$^+$ − NO], 434 (27) [M$^+$ − 2 NO], 402 (94) [M$^+$ − 2 NO − $CH_4O$], 316 (100) [M$^+$ − 2 NO − $PEt_3$], 261 (58), 174 (40) [M$^+$ − 2 NO − $PEt_3$ − $C_6H_6O_4$]. – $C_{18}H_{37}MnN_2O_6P_2$ (494.4): calcd. C 43.73, H 7.54, N 5.67; found C 43.58, H 7.42, N 5.90.

*Preparation of Mn(CO)$_3$[Z-(CCO$_2$Me)=CHR]L$_2$ Complexes* **12a**, **b** and **13a**, **b**: *mer,trans*-$Mn(CO)_3HL_2$ **2a** or **2b** was dissolved in toluene, and 4 equiv. of the acetylene $MeO_2CC{\equiv}CR$ (R = H, COOMe) was added to the solution. When the reaction was complete (IR monitoring) the orange solution was filtered over Celite and the solvent was removed from the filtrate in vacuo. The residue was subjected to column chromatography on silica gel. After elution of an orange band the solvent was evaporated in vacuo. If not indicated otherwise further purification was accomplished by recrystallization from hexane.

*Mn(CO)$_3$[C(CO$_2$Me)=CH$_2$](PMe$_3$)$_2$* (**12a**): 0.50 g (1.33 mmol) of **2a**, 0.76 ml (5.32 mmol) of HC≡$CCO_2Me$, in 50 ml of toluene, room temp., 6 h. Yield 0.42 g (84%). – IR (hexane): ν(CO) = 2015 w, 1927 st, 1907 m cm$^{-1}$; ν(C=O) = 1695 w. – $^1$H NMR ($C_6D_6$): δ = 6.22 [dt, $J_{HH}$ 3.6, $J_{PH}$ 5.3, (=CH)$_E$]; 5.55 [dt, $J_{HH}$ 3.6, $J_{PH}$ 3.9, (=CH)$_Z$]; 3.51 (s, $OCH_3$); 1.19 (t, $J_{PH}$ 8.1, $CH_3$). – $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 221.4 (br, CO); 220.3 (br, CO); 180.7 (s, $CO_2CH_3$); 168.5 (t, $J_{PC}$ 23.2, MnC); 126.1 (t, $J_{PC}$ 5.0, $=CH_2$); 50.1 (s, $OCH_3$); 18.9 (m, $J_{PC}$ 27.8, $CH_3$). – $^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 20.0 (s). – MS (CI), *m/z*: 376 (52) [M$^+$], 348 (77) [M$^+$ − CO], 292 (51) [M$^+$ − 3 CO or M$^+$ − $C_4H_4O_2$], 291 (100) [M$^+$ − $C_4H_5O_2$]. – $C_{13}H_{23}MnO_5P_2$ (376.2): calcd. C 41.50, H 6.16; found C 41.36, H 5.98.

*Mn(CO)$_3$[C(COOMe)=CHD](PMe$_3$)$_2$* (**12a$^D$**) was prepared in the same way as described for **12a** by using **2a$^D$**.

*Mn(CO)$_3$[C(CO$_2$Me)=CH$_2$](PEt$_3$)$_2$* (**12b**): 0.41 g (1.09 mmol) of **2b**, 0.62 ml (4.34 mmol) of HC≡CCO$_2$Me in 40 ml of toluene, 40°C, 30 min. Removal of the solvent in vacuo. Yield 0.46 g (91%). – IR (hexane): ν(CO) = 2010 w, 1922 st, 1898 m cm$^{-1}$. – $^1$H NMR (C$_6$D$_6$): δ = 6.33 [dt, $J_{HH}$ 3.6, $J_{PH}$ 4.8, (=CH)$_E$]; 5.71 [q, $J_{HH}$ 3.6, $J_{PH}$ 3.6, (=CH)$_Z$]; 3.53 (s, OCH$_3$); 1.77 (quint, $J_{HH}$ 7.6, $J_{PH}$ 7.6, CH$_2$); 1.13 (quint, $J_{HH}$ 7.6, $J_{PH}$ 14.5, CH$_3$). – $^{13}$C{$^1$H} NMR (CD$_3$NO$_2$): δ = 224.4 (br, CO); 182.1 (s, *C*O$_2$CH$_3$); 168.5 (t, $J_{PC}$ 20.3, MnC); 128.8 (t, $J_{PC}$ 4.4, =CH$_2$); 51.0 (s, OCH$_3$); 20.4 (m, $J_{PC}$ 23.4, CH$_2$); 8.1 (s, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 45.9 (s). – MS (CI), *m/z*: 460 (79) [M$^+$], 432 (10) [M$^+$ – CO], 376 (37) [M$^+$ – 3 CO or M$^+$ – C$_4$H$_4$O$_2$], 375 (43) [M$^+$ – C$_4$H$_5$O$_2$], 253 (100). – C$_{19}$H$_{35}$MnO$_5$P$_2$ (460.4): calcd. C 49.57, H 7.66; found C 49.44, H 7.50.

*Mn(CO)$_3$[Z-CH=CH,D(COOMe)](PMe$_3$)$_2$* (**12c** and **12c$^D$**): Compound **12c** or **12c$^D$** (10%) was detected NMR-spectroscopically in reactions of **1a** or **1a$^D$** with HC≡CCOOMe in C$_6$D$_6$ solution at room temp. **12a** or **12a$^D$** was the major product (90%). – **12c**: $^1$H NMR (C$_6$D$_6$): δ = 8.64 (dt, $J_{HH}$ 14.0, $J_{PH}$ 5.3, MnCH); 7.38 (dt, $J_{HH}$ 14.0, $J_{PH}$ 4.9, =CH); 3.56 (s, OCH$_3$); 1.33 (m, $J_{PH}$ 8.1, CH$_3$). – $^{13}$C{$^1$H} NMR (D$_6$D$_6$): δ = 220.9 (br, CO); 220.5 (Br, CO); 180.6 (s, OCH$_3$); 170.3 (t, $J_{PC}$ 22.9, MnC); 132.5 (t, $J_{PC}$ 4.6, =CH); 50.4 (s, OCH$_3$); 23.5 (m, $J_{PC}$ 27.4, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 21.6 (s).

*Mn(CO)$_3$[Z-C(CO$_2$Me)=CH(CO$_2$Me)](PMe$_3$)$_2$* (**13a**): 0.30 g (1.03 mmol) of **2a**, 0.5 ml (4.12 mmol) of MeO$_2$CC≡CCO$_2$Me in 20 ml of toluene, 0°C, s. Yield 0.44 g (95%). – IR (toluene): ν(CO) = 2017 w, 1928 st, 1900 m cm$^{-1}$; ν(C=O) = 1710 w, 1694 w. – $^1$H NMR (C$_6$D$_6$): δ = 6.86 (t, $J_{PH}$ 4.9, =CH); 3.45 (s, OCH$_3$, 6H); 1.28 (t, $J_{PH}$ 8.5, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 220.2 [br, (CO)$_2$]; 217.4 (br, CO); 193.8 (t, $J_{PC}$ 21.9, MnC); 181.7, 170.4 (s, *C*O$_2$CH$_3$); 126.3 (t, $J_{PC}$ 4.2, =CH); 50.3, 49.8 (s, OCH$_3$); 18.9 (m, $J_{PC}$ 27.9, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 18.9 (s). – MS (EI), *m/z*: 434 (2) [M$^+$], 350 (8) [M$^+$ – 3 CO], 358 (8) [M$^+$ – PMe$_3$], 274 (100) [M$^+$ – 3 CO – PMe$_3$], 132 (63) [M$^+$ – 3 CO – PMe$_3$ – C$_6$H$_6$O$_4$], 131 (45) [M$^+$ – 3 CO – PMe$_3$ – C$_6$H$_7$O$_4$]. – C$_{15}$H$_{25}$MnO$_7$P$_2$ (434.2): calcd. C 41.49, H 5.80; found C 41.56, H 5.69.

*Mn(CO)$_3$[Z-C(CO$_2$Me)=CH(CO$_2$Me)](PEt$_3$)$_2$* (**13b**): 0.30 g (0.80 mmol) of **2b**, 0.39 ml (3.2 mmol) of MeO$_2$CC≡CCO$_2$Me in 20 ml of toluene, 0°C, a few min. Recrystallization from toluene/hexane (3:2) at −80°C. Yield 0.41 g (98%). – IR (hexane): ν(CO) = 2017 w, 1930 st, 1902 m cm$^{-1}$; ν(C=O) = 1717 w, 1698 w. – $^1$H NMR (C$_6$D$_6$): δ = 7.10 (t, $J_{PH}$ 4.3, =CH); 3.51 (s, OCH$_3$, 6H); 1.95 (m, $J_{HH}$ 7.6, $J_{PH}$ 7.6, CH$_2$, 6H); 1.88 (m, $J_{HH}$ 7.6, $J_{PH}$ 7.6, CH$_2$, 6H); 0.95 (quint, $J_{HH}$ 7.6, $J_{PH}$ 14.5, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 222.4 (br, CO); 221.9 (br, CO); 219.3 (t, $J_{PC}$ 20.3, CO); 195.4 (t, $J_{PC}$ 18.6, MnC); 181.8, 170.3 (s, *C*O$_2$CH$_3$); 129.7 (t, $J_{PC}$ 3.8, =CH); 50.3, 49.9 (s, OCH$_3$); 19.1 (m, $J_{PC}$ 23.8, CH$_2$); 7.2 (s, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 44.1 (s). – MS (EI), *m/z*: 518 (4) [M$^+$], 462 (3) [M$^+$ – 2 CO], 434 (12) [M$^+$ – 3 CO], 400 (2) [M$^+$ – PEt$_3$]), 372 (2) [M$^+$ – CO – PEt$_3$], 344 (5) [M$^+$ – 2 CO – PEt$_3$]), 316 (100) [M$^+$ – 3 CO – PEt$_3$], 174 (58) [M$^+$ – 3 CO – PEt$_3$ – C$_6$H$_6$O$_4$], 173 (12) [M$^+$ – 3 CO – PEt$_3$ – C$_6$H$_7$O$_4$]. – C$_{21}$H$_{37}$MnO$_7$P$_2$ (518.4): calcd. C 48.66, H 7.19; found C 48.51, H 6.97.

*Mn{C(CO$_2$Me)=CH[C(O)OMe]}(NO)$_2$PEt$_3$* (**14b**): 0.20 g (0.41 mmol) of **11b** was heated in toluene to 60°C. After 10 h the dark-red solution was filtered over Celite, and the solvent was removed from the filtrate in vacuo. Yield 0.10 g (58%). – IR (toluene): ν(C=O) = 1704 w, 1598 w cm$^{-1}$; ν(NO) = 1728 m, 1644 st. – $^1$H NMR (C$_6$D$_6$): δ = 6.8 (d, $J_{PH}$ 3.6, =CH); 3.63, 3.06 (s, CO$_2$CH$_3$); 1.38 (quint, $J_{HH}$ 7.9, $J_{PH}$ 7.9, CH$_2$); 0.83 td, $J_{HH}$ 7.9, $J_{PH}$ 15.8, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 225.7 (d, $J_{PC}$ 34.2, MnC); 176.5, 173.6 (d, $J_{PC}$ 11.8, *C*O$_2$CH$_3$); 133.4 (d, $J_{PC}$ 6.5, =CH); 52.9, 51.3 (s, CO$_2$CH$_3$); 16.5 (d, $J_{PC}$ 21.1, CH$_2$); 7.5 (s, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 43.8 (s). – No satisfactory elemental analysis could be obtained.

*Mn{C(CO$_2$Me)=CH[C(O)OMe]}(CO)$_2$(PMe$_3$)* (**15a**): A solution of 0.20 g (0.46 mmol) of **13a** in 20 ml of toluene was heated to 60°C for 12 h. After filtration over Celite the solvent was removed from the filtrate in vacuo. The dark-red product was recrystallized from toluene/hexane (2:1) at −30°C. Yield 0.18 g (95%). – IR (hexane): ν(CO) = 1922 st, 1844 m cm$^{-1}$; ν(C=O) = 1699 w, 1582 w. – $^1$H NMR (C$_6$D$_6$): δ = 6.66 (t, $J_{PH}$ 4.1, =CH); 3.65, 3.23 (s, OCH$_3$); 1.11 (t, $J_{PH}$ 7.7, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 249.7 (t, $J_{PC}$ 18.1, MnC); 231.5 (t, $J_{PC}$ 22.6, CO); 225.8 (t, $J_{PC}$ 17.8, CO); 178.7, 178.6 (s, *C*O$_2$CH$_3$); 117.5 (t, $J_{PC}$ 3.5, =CH); 52.5, 50.5 (s, CO$_2$CH$_3$); 16.3 (t, $J_{PC}$ 22.6, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 21.8 (s). – C$_{14}$H$_{25}$MnO$_6$P$_2$ (406.2): calcd. C 41.39, H 6.20; found C 41.02, H 6.08.

*Mn{C(CO$_2$Me)=CH[C(O)OCH$_3$]}(CO)$_3$(PEt$_3$)* (**15b**): A solution of 0.25 g (0.48 mmol) of **13b** in 10 ml of toluene was stirred for 6 d at 80°C. The reaction mixture was filtered over Celite, and the solvent was evaporated from the filtrate in vacuo. Recrystallization of the residue from toluene/hexane (1:1) at −30°C afforded **15b** as dark-red crystals. Yield 0.19 g (98%). – IR (hexane): ν(CO) = 2018 st, 1939 st, 1904 st cm$^{-1}$; ν(C=O) = 1703 w, 1586 w. – $^1$H NMR (C$_6$D$_6$): δ = 6.66 (d, $J_{PH}$ 3.9, =CH); 3.63, 3.10 (s, OCH$_3$); 1.45 (m, $J_{HH}$ 7.4, $J_{PH}$ 7.4, CH$_2$, 3H); 1.26 (m, $J_{HH}$ 7.4, $J_{PH}$ 7.4, CH$_2$, 3H); 0.78 (quint, $J_{HH}$ 7.4, $J_{PH}$ 14.8, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 232.1 (d, $J_{PC}$ 18.6, MnC); 220.5 [br, (CO)$_2$]; 215.9 (br, CO); 180.6, 176.7 (s, *C*O$_2$CH$_3$); 122.3 (d, $J_{PC}$ 3.8, =CH); 54.0, 51.4 (s, CO$_2$CH$_3$); 17.2 (d, $J_{PC}$ 21.4, CH$_2$); 7.7 (s, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 37.3 (s). – C$_{15}$H$_{22}$MnO$_7$P (400.3): calcd. C 45.01, H 5.54; found C 44.75, H 5.31.

*Spectroscopic Detection of Mn{Z-C(CO$_2$Me)=CH[C(O)OMe]}(CO)$_2$(PEt$_3$)$_2$* (**15c**): In an NMR experiment **13b** was heated in C$_6$D$_6$ to 50°C. After 6 d the reaction was complete furnishing 67% of **15c** and 33% of **15b**. Attempts to separate **15c** from a preparative-scale reaction failed. Evaporation of the solvent and dissolution of the residue in hexane allowed the IR-spectroscopic investigation of the reaction mixture. – IR (hexane): ν(CO) = 1917 st, 1841 st cm$^{-1}$; ν(C=O) = 1696 w, 1582 w. – $^1$H NMR (C$_6$D$_6$): δ = 6.79 (t, $J_{PH}$ 3.8, =CH); 3.67, 3.30 (s, OCH$_3$); 1.67 (m, $J_{HH}$ 7.5, $J_{PH}$ 7.5, CH$_2$, 6H); 1.45 (m, $J_{HH}$ 7.5, $J_{PH}$ 7.5, CH$_2$, 6H); 0.96 (quint, $J_{HH}$ 7.5, $J_{PH}$ 14.0, CH$_3$). – $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 249.4 (t, $J_{PC}$ 17.9, MnC); 226.8, 226.4 (br, CO): 178.2, 178.1 (s, *C*O$_2$CH$_3$); 120.6 (t, $J_{PC}$ 3.2, =CH); 53.2, 50.9 (s, OCH$_3$); 18.1 (t, $J_{PC}$ 18.8, CH$_2$); 8.0 (s, CH$_3$). – $^{31}$P{$^1$H} NMR (C$_6$D$_6$): δ = 46.1 (s).

*Crystal Structure Determinations of* **1a**, **9a**, *and* **10a**: The crystals of the compounds were mounted on glass fibers by using 5-min epoxy resin. The unit cells were determined and refined from 24 equivalent reflections with 2Θ ≥ 24–30° obtained with a Siemens R3m/v four-circle diffractometer (Mo-$K_\alpha$, λ = 0.71073 Å). An empirical absorption correction[28] was performed for **9a** (min./max. transmission 0.1292/0.1748). Backgrounds were scanned for 25% of the peak widths on each end of the scans. Three reflections were monitored periodically for each compound as a check for crystal decomposition or movement.

All structures were solved by direct methods to locate the Mn and P atoms. The other atoms were found in subsequent difference Fourier maps. Anisotropic refinement was applied to all non-hydro-

Table 4. Data collection and processing parameters for complexes **1a**, **9a**, and **10a**

| | 1a | 9a | 10a |
|---|---|---|---|
| Formula | $C_6H_{19}MnN_2O_2P_2$ | $C_{11}H_{25}MnN_2O_4P_2$ | $C_{17}H_{29}MnN_2O_4P_2$ |
| Cryst. system | orthorhombic | triclinic | triclinic |
| Space group | Pnma | $P\bar{1}$ | $P\bar{1}$ |
| a[Å] | 9.464(3) | 9.760(3) | 8.703(2) |
| b[Å] | 11.278(3) | 14.819(4) | 9.927(3) |
| c[Å] | 12.385(4) | 14.971(4) | 13.365(5) |
| α[°] | | 67.75(2) | 100.34(3) |
| β[°] | | 88.20(2) | 93.16(3) |
| γ[°] | | 70.97(2) | 98.18(2) |
| V[Å3] | 1322.0(7) | 1884.0(8) | 1120.5(6) |
| Z | 4 | 4 | 2 |
| ρcalcd [g/cm3] | 1.347 | 1.291 | 1.311 |
| Abs coeff [cm-1] | 11.77 | 8.51 | 13.11 |
| F000 | 560 | 768 | 464 |
| T [°C] | -40 | 25 | 25 |
| Scan type | 2θ–θ | ω | Wyckoff |
| Scan speed [°/min] | 2.00-14.65 | 3.97-14.65 | 2.00-14.65 |
| 2θ range | 4.0-58.0 | 5.0-50.0 | 4.0-55.0 |
| No of unique data | 1852 | 6677 | 5135 |
| No of refl obsd ($F \geq n\sigma(F)$) | 1592(n=6) | 3646(n=6) | 2602(n=8) |
| No of variables | 72 | 362 | 236 |
| weighting scheme | unit weights | $w^{-1}=\sigma^2(F)+0.000F^2$ | $w^{-1}=\sigma^2(F)+0.000F^2$ |
| R | 0.025 | 0.053 | 0.075 |
| $R_w$ | 0.027 | 0.044 | 0.077 |
| residual extrema in final diff map[e Å-3] | 0.28 to -0.22 | 0.47 to -0.39 | 0.59 to -0.64 |

gen atoms. The hydride atom in **1a** was extracted from a difference Fourier map and refined isotropically. The other H atoms in **1a**, **9a**, and **10a** were generated geometrically (C–H bond fixed at 0.96 Å). Computations were performed by using the SHELXTL PLUS program package[29] on a VAX station 3100. For details of crystal parameters, data collection and structure refinement see Table 4. Tables of structure determination summaries, lists of anisotropic displacement parameters, lists of atom coordinates, and full lists of bond lengths and angles were deposited[30].


☆ Dedicated to Prof. *E. Lindner*, Universität Tübingen, on the occasion of his 60th birthday.

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[30] Further details of the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. Requests should contain the deposition number CSD-58398, names of authors, and citation of this article.


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