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# 2-Diphenylphosphinoazacyclopentadienylmanganese tricarbonyl as a new bridging ligand

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## Abstract

Treatment of [$Mn_2(CO)_{10}$] with diphenyl(2-pyrrolyl)phosphine ($Ph_2P$-2-$C_4H_3NH$) leads to simple substitution products, the product of P–C bond cleavage [$Mn_2(\mu$-H)($\mu$-$PPh_2$)$(CO)_8$], but the most interesting product (21%) is the trinuclear compound [$Mn_3$($\mu_3$-*P*,*N*,$\eta^5$-$Ph_2PC_4H_3N$)$(CO)_{11}$], the X-ray structure of which shows it to contain the bidentate ligand, 2-diphenylphosphinoazacyclopentadienylmanganese tricarbonyl, Mn($\eta^5$-$Ph_2PC_4H_3N$)$(CO)_3$, which bridges across a $Mn_2(CO)_8$ unit as a novel four-electron donating chiral *N*,*P*-ligand. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Manganese; Pyrrolylphosphine; Azacyclopentadienyl; Clusters

## 1. Introduction

The ligand 2-$Ph_2PC_4H_3NH$ [1] preferentially coordinates as a simple tertiary phosphine through the phosphorus atom, but in doing so, the pyrrole ring may subsequently become bonded to an adjacent metal atom if one is present. For example, we have shown that the ligand reacts with [$Ru_3(CO)_{12}$] to give the product [$Ru_3(\mu$-H)($\mu_3$-2-$Ph_2PC_4H_2NH$)$(CO)_9$] in which the phosphorus atom is coordinated and the pyrrole has been orthometallated at a second metal atom [2]. Treatment of this product with more [$Ru_3(CO)_{12}$] leads to P–C cleavage and the products [$Ru_4$($\mu_4$-PPh)($\mu_4$-2-$C_4H_2NH$)$(CO)_{11}$] with a *C*,*C*-bonded pyrrolyne ligand and its *C*,*N*-bonded isomer [2]. However, this type of chemistry, dominated by orthometallation and C–H bond cleavage, does not occur so readily with [$Mn_2(CO)_{10}$] or [$Re_2(CO)_{10}$]. For example, in our work we have shown that diphenyl(2-thienyl)phosphine undergoes C–H cleavage with [$Ru_3(CO)_{12}$] [3] or [$Os_3(CO)_{12}$] [4] to give $\mu_3$-2-$Ph_2PC_4H_2S$ systems whereas [$Mn_2(CO)_{10}$] or [$Re_2(CO)_{10}$] react with the same ligand leading to a P–C bond cleavage to give the $\mu$-thienyl complexes [$Mn_2$($\mu$-$PPh_2$)($\mu$-$\eta^1$,$\eta^5$-$C_4H_3S$)$(CO)_6$] and [$Re_2$($\mu$-$PPh_2$)($\mu$-*C*,*S*-$C_4H_3S$)$(CO)_8$], respectively [5]. Because of these major differences, we wished to establish whether the ligand $Ph_2P$-2-$C_4H_3NH$ would behave like the analogous thienyl phosphine and undergo P–C bond cleavage to give $\mu$-pyrrolyl complexes with Mn and Re carbonyls. An alternative mode of reaction of the pyrrole ring, not possible for thiophene, is deprotonation at nitrogen which could lead to $\eta^5$-coordination of an azacyclopentadienyl ring. The azacyclopentadienyl complex [Mn($\eta^5$-$C_4H_4N$)$(CO)_3$] has been long known [6]. Our results show that combinations of these possibilities occur. P–C cleavage and deprotonation to give an azacyclopentadienyl ligand system but the chemistry is generally quite unlike that of diphenyl(2-thienyl)phosphine.

## 2. Results and discussion

The progress of the reaction of [$Mn_2(CO)_{10}$] with diphenyl(2-pyrrolyl)phosphine in refluxing toluene was followed by recording the IR spectrum of the solution periodically. After 1 h the solution contained considerable amounts of the simple axially-substituted product [$Mn_2$($Ph_2P$-2-$C_4H_3NH$)$(CO)_9$]. IR signals for this species decreased to a low level after 7 h by which time there was a little more change in the IR spectrum. The

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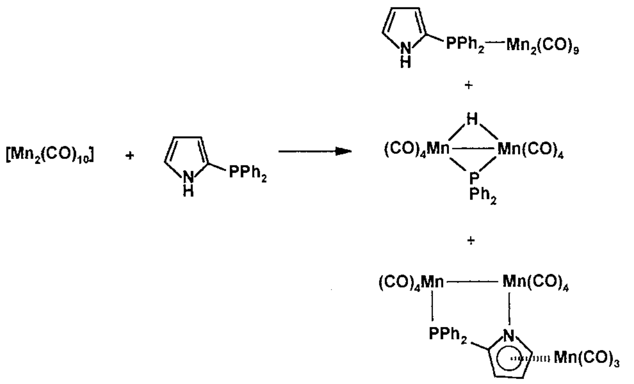
reaction mixture was worked-up by TLC separation on silica. Some unreacted $[Mn_2(CO)_{10}]$ and a little of the substitution product $[Mn_2(Ph_2P\text{-}2\text{-}C_4H_3NH)(CO)_9]$ (7%) were isolated. The latter was characterised spectroscopically by comparison with related complexes of type *axial*-$[Mn_2(L)(CO)_9]$ [7]. The $^1H$-NMR spectrum showed the expected four pyrrolyl ring protons at $\delta$ 7.88, 6.98, 6.94 and 6.38, quite similar shifts to those of the signals for the free ligand at $\delta$ 8.10, 6.95, 6.51 and 6.31. Therefore coordination is through the phosphorus atom while the pyrrole ring is hanging free and not attached directly to the metal atoms. In addition, a low yield of the known complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ [8] (4%) was obtained by P–C bond cleavage but the main and most interesting product was $[Mn_3(\mu_3\text{-}P,N,\eta^5\text{-}Ph_2PC_4H_3N)(CO)_{11}]$, isolated as a red microcystalline solid (21%). This complex gave ten IR absorptions assigned to $\nu$(CO), consistent with its polynuclear nature, and a peak at $m/z = 723$ was obtained as the highest mass ion in the FABMS consistent with this formula. Unfortunately the $^1H$- and $^{13}C\{^1H\}$-NMR spectra were very broad and of little use in establishing its structure. The compound is not paramagnetic but possibly paramagnetic impurities are present. Its formulation is therefore based largely on its single-crystal structure determination (Scheme 1).



Scheme 1.

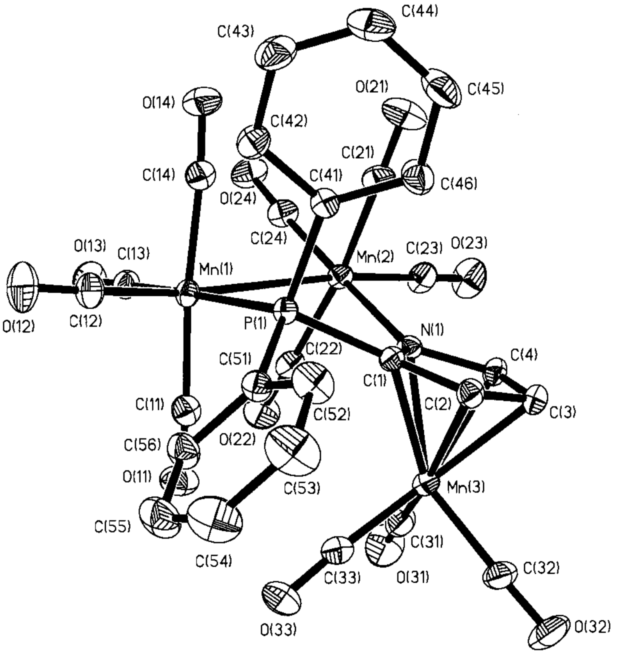


Fig. 1. Molecular structure of the cluster $[Mn_3(\mu_3\text{-}P,N,\eta^5\text{-}Ph_2PC_4H_3N)(CO)_{11}]$.

Table 1
Selected bond lengths (Å) and angles (°) for the compound $[Mn_3(\mu_3\text{-}P,N,\eta^5\text{-}Ph_2PC_4H_3N)(CO)_{11}]$

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Mn(1)–Mn(2) | 2.913(1) | Mn(3)–C(2) | 2.167(4) |
| Mn(1)–P(1) | 2.287(1) | Mn(3)–C(3) | 2.147(4) |
| Mn(1)–C(11) | 1.835(5) | Mn(3)–C(4) | 2.122(4) |
| Mn(1)–C(12) | 1.804(5) | Mn(3)–C(31) | 1.804(5) |
| Mn(1)–C(13) | 1.825(5) | Mn(3)–C(32) | 1.793(5) |
| Mn(1)–C(14) | 1.831(5) | Mn(3)–C(33) | 1.797(5) |
| Mn(2)–N(1) | 2.096(3) | P(1)–C(1) | 1.831(4) |
| Mn(2)–C(21) | 1.851(5) | N(1)–C(1) | 1.381(6) |
| Mn(2)–C(22) | 1.849(4) | N(1)–C(4) | 1.397(5) |
| Mn(2)–C(23) | 1.808(5) | C(1)–C(2) | 1.423(5) |
| Mn(2)–C(24) | 1.789(5) | C(2)–C(3) | 1.409(6) |
| Mn(3)–N(1) | 2.156(3) | C(3)–C(4) | 1.393(7) |
| Mn(3)–C(1) | 2.165(4) | | |
| *Bond angles* | | | |
| Mn(1)–Mn(2)–N(1) | 88.7(1) | Mn(1)–P(1)–C(51) | 120.6(1) |
| Mn(2)–Mn(1)–P(1) | 83.1(1) | Mn(2)–N(1)–C(1) | 126.3(2) |
| Mn(1)–P(1)–C(1) | 113.2(1) | P(1)–C(1)–N(1) | 117.8(3) |
| Mn(1)–P(1)–C(41) | 116.0(1) | | |

The molecular structure of $[Mn_3(\mu_3\text{-}P,N,\eta^5\text{-}Ph_2PC_4H_3N)(CO)_{11}]$ is shown in Fig. 1 and selected bond lengths and angles are in Table 1. The three manganese atoms, Mn(1)–Mn(3) in the trinuclear compound, are coordinated to 4, 4 and 3 CO ligands, respectively. One way to consider the cluster is that it contains a 2-diphenylphosphino-substituted azacyclopentadienyl manganese tricabonyl unit which acts as a four-electron donor bridge across a $Mn_2(CO)_8$ subunit. The organic ligand itself has been deprotonated at the nitrogen atom, allowing the formation of the Mn(2)–N(1) bond and $\eta^5$ coordination of the azacyclopentadienyl ring to Mn(3). This is contrast to the reaction of this ligand with $[Ru_3(CO)_{12}]$ in which the ligand undergoes C–H cleavage *ortho* to the $PPh_2$ substituent rather than N–H bond cleavage as in this case [2]. The dimanganese unit Mn(1)Mn(2) adopts a conformation approximately half way between eclipsed and staggered with a P(1)Mn(1)Mn(2)N(1) torsional angle of 24.8°. It is possible to compare the coordination of the tertiary phosphine and the azacyclopentadienyl groups in this structure. The Mn–CO distance *trans* to nitrogen is the shortest in the molecule [Mn(2)–C(24) 1.789(5) Å], shorter than that *trans* to phosphorus [Mn(1)–C(13) 1.825(5) Å] and the average of the other

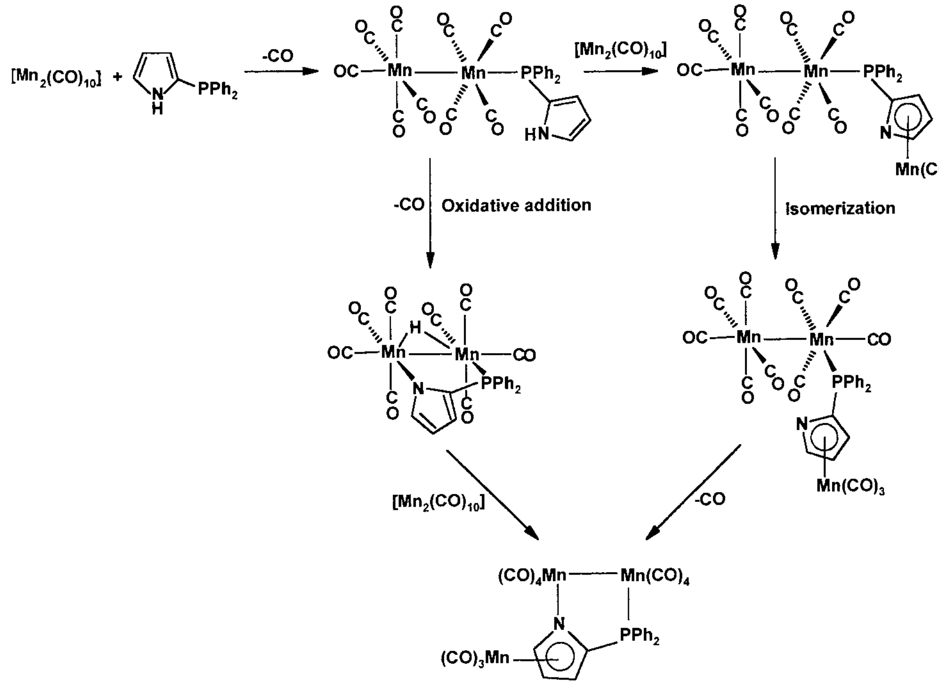
Mn–CO bond lengths at Mn(2) [also 1.825 Å]. Therefore, we believe that the azacyclopentadienyl ring coordinated through nitrogen has a weak *trans* influence, less that those of CO or tertiary phosphine. The substituents Mn(2) and P(1) at the $\eta^5$-pyrrolyl ring are bent out of the plane of the ring by 0.491 and 0.350 Å, respectively away from the $Mn(3)(CO)_3$ group. Bending back of substituents is commonly associated with the bonding of unsaturated rings to metal atoms but, in this case this may be enhanced by interactions of CO ligands at Mn(3) with those at Mn(1) and Mn(2). The shortest C–C contacts between CO ligands are C(22)...C(31) [3.284(6) Å] and C(33)–C(11) [3.358(6) Å]. If the substituents, Mn(2) and P(1), at the $\eta^5$-pyrrolyl ring were in the plane of the ring, these distances would be unfavourably short.

The probable route to this $Mn_3$ compound (Scheme 2) is the reaction of $[Mn_2(CO)_{10}]$ with the unattached pyrrole ring of $[Mn_2(Ph_2P\text{-}2\text{-}C_4H_3NH)(CO)_9]$, a compound which we have shown to be formed in the early stages of the reaction. This would generate a dangling azacyclopentadienyl manganese tricarbonyl group which then could displace CO from the adjacent Mn atom to form the bridged system isolated. An alternative is that $[Mn_2(Ph_2P\text{-}2\text{-}C_4H_3NH)(CO)_9]$ decarbonylates and undergoes oxidative addition with N–H bond cleavage to give $[Mn_2(\mu\text{-}H)(\mu\text{-}Ph_2P\text{-}2\text{-}C_4H_3N)(CO)_8]$, which reacts with further $[Mn_2(CO)_{10}]$ to give the observed product. Other examples of compounds involving coordination of the nitrogen atom of azacyclopentadienyl manganese tricarbonyl, $[Mn(C_4H_4N)(CO)_3]$ are $[M(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}\eta^1,\eta^5\text{-}C_4H_4N)Mn(CO)_3]$ (M = Mn or Re) [9] and $[Os_3(\mu\text{-}H)\{\mu\text{-}2\text{-}C_4H_3NMn(CO)_3\}(CO)_{10}]$ [10,11].

The room temperature reaction of $[Mn_2(CO)_{10}]$ with diphenyl-2-pyrrolylphosphine in toluene under UV photolysis gave no indication of the formation of $[Mn_3(\mu_3\text{-}P,N,\eta^5\text{-}Ph_2P\text{-}2\text{-}C_4H_3N)(CO)_{11}]$ but instead two P–C cleavage products were obtained in reasonable yield: $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (52%) and a derivative of this $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)\{Ph_2P\text{-}2\text{-}C_4H_3NH\}(CO)_7]$ (20%). Also the thermal treatment of $[Mn_2(CO)_{10}]$ with diphenyl-3-pyrrolylphosphine gave $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ and the substitution complex $[Mn_2(Ph_2P\text{-}3\text{-}C_4H_3NH)(CO)_9]$ which was also formed photochemically. Thermal treatment of $[Re_2(CO)_{10}]$ with diphenyl-2-pyrrolylphosphine at 190°C gave the compound $[Re_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (37%) as the only isolable product. Thus none of these reactions which occur by P–C cleavage resulted in the formation of μ-pyrrolyl complexes as in the formation of μ-thienyl dimanganese and dirhenium complexes from diphenyl-2-thienylphosphine [5].

## 3. Experimental

Following the method described for diphenyl-2-pyrrolylphosphine [1], we were able to separate the mixed isomeric product by column or TLC chromatography ($SiO_2$) to give diphenyl-2-pyrrolylphosphine as a white solid (45%) and diphenyl-3-pyrrolylphosphine as a colourless oil (40%). $[Mn_2(CO)_{10}]$ or $[Re_2(CO)_{10}]$ were used as supplied by Strem.



Scheme 2.

### 3.1. Treatment of [$Mn_2(CO)_{10}$] with diphenyl-2-pyrrolylphosphine in refluxing toluene

A solution of [$Mn_2(CO)_{10}$] (0.197 g) and $Ph_2P$-2-$C_4H_3NH$ (0.136 g, 1 mol per mol of $Mn_2$) in toluene (40 $cm^3$) was heated under reflux under nitrogen for 8 h. By monitoring the IR spectrum of the reacting solution [$Mn_2(Ph_2P$-2-$C_4H_3NH)(CO)_9$] was shown to be formed as a major product after 1.5 h but this gave very weak signals at the later stages of the reaction. Solvent was removed under reduced pressure and TLC work-up of the orange–brown residue [$SiO_2$; eluent, hexane–dichloromethane (5:3 v/v)] produced four bands yielding unreacted [$Mn_2(CO)_{10}$] (0.053 g) and [$Mn_2(\mu$-H)($\mu$-$PPh_2)(CO)_8$] as a yellow solid (0.010 g, 4%) which was characterized by comparison of its spectra with those reported [8]; Anal. Calc. for $C_{20}H_{11}O_8PMn_2$: C, 46.2; H, 2.1; P, 5.95. Found: C, 45.8; H, 2.5; P, 6.4%; $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2093w, 2063m, 2010vs, 2000m, 1965s; parent molecular ion observed in FABMS (MNBA medium); $^1$H-NMR ($CDCl_3$, 298 K): $\delta$ 7.85, 7.35 (Ph multiplets), $-16.12$ (d, $J_{PH} = 35.5$ Hz, hydride). The third band gave [$Mn_2(Ph_2P$-2-$C_4H_3NH)(CO)_9$] as an orange solid (0.021 g, 7%); $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2091w, 2012m, 1995vs, 1973m, 1962vw, 1942m, weak parent molecular ion in FABMS (MNBA medium); $^1$H-NMR ($CDCl_3$, 298 K): $\delta$ 7.88 (br s, NH), 7.40 (m, Ph), 6.96 (m, $H^2/H^5$, pyrrolyl), 6.38 (m, $H^4$, pyrrolyl). The final band gave [$Mn_3(\mu_3$-$P,N,\eta^5$-$Ph_2P$-2-$C_4H_3N)(CO)_{11}$] as a red microcystalline solid (0.077 g, 21%), $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2067w, 2049m, 2000s, 1991w, 1980m, 1967s, 1955w, 1942vw, 1926sh, 1899m; parent molecular ion in FABMS (MNBA medium); $^1$H- and $^{13}$C-NMR data are not reported because these were both very broad and ill-defined.

### 3.2. Treatment of [$Mn_2(CO)_{10}$] with diphenyl-3-pyrrolylphosphine in toluene

A solution of [$Mn_2(CO)_{10}$] (0.105 g, 0.270 mmol) and diphenyl-3-pyrrolylphosphine (0.069 g, 1 mol per mol $Mn_2$) in refluxing toluene (40 $cm^3$) gave a red–orange suspension after 8 h which gave a dark orange solid on removal of solvent. TLC work-up [$SiO_2$; eluent, hexane–dichloromethane (1:1 v/v)] gave three bands which gave unreacted [$Mn_2(CO)_{10}$] (0.012 g) and [$Mn_2(\mu$-H)($\mu$-$PPh_2)(CO)_8$] as a yellow solid (0.013 g, 9%). The third band gave [$Mn_2(Ph_2P$-3-$C_4H_3NH)(CO)_9$] as an orange solid (0.031 g, 19%) by evaporation of a dichloromethane solution; Anal. Calc. for $C_{25}H_{14}O_9NPMn_2$: C, 49.0; H, 2.3; N, 2.3; P, 5.05. Found: C, 50.0; H, 2.8; N, 2.4; P, 5.5%; $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2089m, 2010s, 1993vs, 1970s, 1959vw, 1937s, weak parent molecular ion in FABMS (MNBA medium). Photochemical treatment of a solution of [$Mn_2(CO)_{10}$] (0.198 g) and diphenyl-3-pyrrolylphosphine (0.507 mmol) in toluene (100 $cm^3$) gave unreacted [$Mn_2(CO)_{10}$] (0.007 g) and [$Mn_2(Ph_2P$-3-$C_4H_3NH)(CO)_9$] as an orange solid (0.077 g, 25%).

### 3.3. Photochemical treatment of [$Mn_2(CO)_{10}$] with diphenyl-2-pyrrolylphosphine

A solution of [$Mn_2(CO)_{10}$] (0.240 g) and $Ph_2P$-2-$C_4H_3NH$ (0.161 g) in toluene (100 $cm^3$) was treated with UV irradiation for 20 h. The solvent was removed from the orange solution under reduced pressure and TLC or the residual orange solid [$SiO_2$; eluent, hexane–dichloromethane, 5:3 v/v] gave two bands, the first of which was characterized as [$Mn_2(\mu$-H)($\mu$-$PPh_2)(CO)_8$] as a yellow solid (0.168 g, 52%) (see above). The second band gave [$Mn_2(\mu$-H)($\mu$-$PPh_2)\{Ph_2P$-2-$C_4H_3NH\}(CO)_7$] as orange crystals (0.091 g, 20%) by evaporation of a dichloromethane solution; Anal. Calc. for $C_{35}H_{25}O_7NPMn_2$: C, 56.55; H, 3.4; N, 1.9; P, 8.30. Found: C, 55.9; H, 3.5; N, 1.8; P, 8.6%; $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2089m, 2011s, 1993vs, 1970s, 1959vw, 1937s; a weak parent molecular ion was observed in the FABMS (MNBA medium); NMR spectra are very broad and data are not reported here.

### 3.4. Treatment of [$Re_2(CO)_{10}$] with diphenyl-2-pyrrolylphosphine at 190°C

A 20 $cm^3$ Carius tube was charged with [$Re_2(CO)_{10}$] (0.199 g, 0.305 mmol) and diphenyl-2-pyrrolylphosphine (0.077 g, 1 mol per mol $Re_2$) in decane (5 $cm^3$). The mixture was degassed by three freeze-pump-thaw cycles, sealed under vacuum and heated at 190°C for 24 h. The colourless suspension had become orange and TLC work-up [$SiO_2$; eluent, hexane–dichloromethane, 5:3 v/v] gave only one tractible product: [$Re_2(\mu$-H)($\mu$-$PPh_2)(CO)_8$] as a very pale yellow solid (0.088 g, 37%) by evaporation of a dichloromethane solution; $\nu$(CO) ($cm^{-1}$) (cyclohexane): 2108m, 2084s, 2076sh, 2014vs, 1998vs, 1983vw; parent molecular ion was observed in the FABMS (MNBA medium); $^1$H-NMR ($CDCl_3$, 298°C): $\delta$ 7.82 (ddd, $J = 1.5$, 7.3, 11.5 Hz, 4H, *ortho*), 7.80–7.28 (m, 6H, *meta*/*para*), $-15.02$ (d, $J = 4.6$ Hz, ReHRe); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 298°C): $\delta$ 185.1 (d, $J = 28.0$ Hz, 2CO *trans* to $PPh_2$), 183.7 (d, $J = 3.1$ Hz, 2CO), 182.3 (d, $J = 6.7$ Hz, 4CO), 138.8 (d, $J = 40.3$ Hz, *ipso*), 134.5 (d, $J = 11.7$ Hz, *ortho*), 129.8 (s, *para*), 128.8 (d, $J = 10.6$ Hz, *meta*); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298°C): $\delta$ 42.9 (s).

### 3.5. Crystal structure determination of [$Mn_3(\mu_3$-$P,N,\eta^5$-$Ph_2PC_4H_3N)(CO)_{11}$]

A suitable orange–red crystal (size: 0.22 × 0.28 × 0.30 mm) was selected from a batch of crystals obtained by slow evaporation of a mixed hexane–dichloromethane solution. The structure was determined with a Nicolet R3V/m diffractometer using graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell was determined from the setting angles of 30 orientation reflections in the $2\theta$ range 16–28°. Intensity data collected at 291(1) K were corrected for crystal decay based on the 8% intensity loss of three check reflections, for Lorentz and polarization effects, and for absorption (empirical absorption correction based on $\Psi$-scans). The structure was solved by direct methods (SHELXTL-PLUS [12]) and refined (SHELXL 93 [13]) by full-matrix least-squares cycles and difference Fourier synthesis with all non-hydrogen atoms anisotropic. All 13 hydrogen atoms were detected and these were included using a riding model. The largest peak in the final difference Fourier map was 0.334 e Å$^{-3}$.

Crystal data for $C_{27}H_{13}Mn_3NO_{11}P$. $M_f = 723.20$, monoclinic, space group $P2_1/c$, $a = 12.520(4)$ Å, $b = 14.837(3)$ Å, $c = 15.800(3)$ Å, $\beta = 101.86(2)°$, $V = 2872.5(11)$ Å$^3$, $Z = 4$, $D_{calc.} = 1.67$ g cm$^{-3}$, $\lambda$(Mo–$K_\alpha$) = 0.71073 Å, $\mu = 14.16$ cm$^{-1}$, $F(000) = 1440$. 5506 independent reflections were measured in the $\theta$ range 2.5–26° and 5498 data were used in refining 308 parameters to give $R_1 = 0.0669$ and $wR_2 = 0.1144$ (all data) and $R_1 = 0.0429$ and $wR_2 = 0.0938$. [data with $I_0 \geq 2(I_0)$].

## 4. Supplementary material

Fractional atomic coordinates for the complex together with additional material comprising thermal parameters and full tables of bond lengths and angles are available from the Cambridge Crystallographic Data Centre, CCDC number 133929.

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