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Reaction chemistry of tricarbonyl-η^5-pentadienylmanganese: Straightforward synthesis of stable manganese carbonyl terminal thiolates and a dinuclear bis (ethylenediaminyl) complex

Karla Patricia Salas-Martin, Marisol Reyes-Lezama, Noé Zúñiga-Villarreal*

Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, 04510 México, D.F., México

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ABSTRACT

Tricarbonyl-η^5-pentadienylmanganese reacts with mercaptans RSH, R = Ph, C_6F_5, *m*-$NH_2C_6H_4$, *p*-$NH_2C_6H_4$, and $HSCH_2CH_2$ in the presence of ECH_2CH_2E, E = $-PPh_2$ or $-NH_2$ to give novel stable terminal thiolate mononuclear complexes *fac*-$Mn(CO)_3(SR)(Ph_2PCH_2CH_2PPh_2$-$\kappa^2$-*P,P'*) for R = Ph, C_6F_5, *m*-$NH_2C_6H_4$, *p*-$NH_2C_6H_4$, and $HSCH_2CH_2$ and *fac*-$Mn(CO)_3(SR)(H_2NCH_2CH_2NH_2$-$\kappa^2$-*N,N'*) for R = Ph and C_6F_5. Upon reaction of tricarbonyl-η^5-pentadienylmanganese with ethylenediamine a dinuclear complex [*fac*-$Mn(CO)_3(\mu$-$H_2NCH_2CH_2NH$-κ^2-*N,N'*)]$_2$ was formed wherein the diaminyl ligand functions in the capacity of chelating and bridging ligand.

1. Introduction

Transition metal pentadienyl complexes have been thoroughly studied [1]. As far as their reaction chemistry is concerned nucleophilic attack on pentadienyl complexes has been extensively explored [2]. Several years ago we reported on the reaction chemistry of tricarbonyl-η^5-pentadienylmanganese towards mercaptans [2d,3a]. We found that in the resulting products the pentadienyl ligand was not present (Scheme 1a). Such ligand loss is not uncommon in the chemistry of polyenyl metal carbonyls [4]; however, one remarkable aspect of this process is that the vacant sites available after enyl elimination can be potentially occupied by virtually any ligand present in the reaction medium provided that the polyenyl adds a hydrogen atom to form the corresponding polyene in order to leave the metal center coordination sphere.

In the light of such assumptions we decided to undertake a study of the synthetic possibilities that the pentadienyl ligand offers when extruded from the metal's coordination sphere. We have found that binuclear complexes with two thiolate bridges and one bridging carbonyl were obtained upon reaction of $Mn(\eta^5$-$C_5H_7)(CO)_3$ with mercaptans in the presence of tertiary phosphines (Scheme 1b) [3b]. Selenium analogs of the above mentioned sulfur complexes were prepared by one pot syntheses; in addition, a selenium heterocubane and a terminal phenylselenolate complex could be obtained (Scheme 1a and c) [3c].

Terminal thiolates of mononuclear manganese carbonyls are often unstable to CO loss to form thiolate-bridged dinuclear species [5]. Stabilization of mononuclear terminal thiolate carbonyls can be accomplished either by introducing electron-withdrawing substituents in the mercaptan backbone in order to lower the basicity of the sulfhydryl sulfur atom or by coordination of electron rich ligands to the metal center to prevent CO substitution. As an example of the first case it was possible to isolate and characterize the mononuclear pentacarbonyl complex $Mn(CO)_5SC_6F_5$ [6]. To date and to the best of our knowledge no examples of the second case have been reported; this can be ascribed to the synthetic difficulty posed by the introduction of a thiolate ligand to an electron rich metal center. With a view of extending the application of the pentadienyl-extrusion synthetic approach and encouraged by the realization of a terminal selenolate complex we set out to explore the influence of 1,2-bis (diphenylphosphino)ethane (dppe) and ethylenediamine on the reaction of mercaptans with $Mn(\eta^5$-$C_5H_7)(CO)_3$.

* Corresponding author. Tel.: +52 5622 44 31; fax: +52 56 16 22 03.
E-mail address: zuniga@unam.mx (N. Zúñiga-Villarreal).

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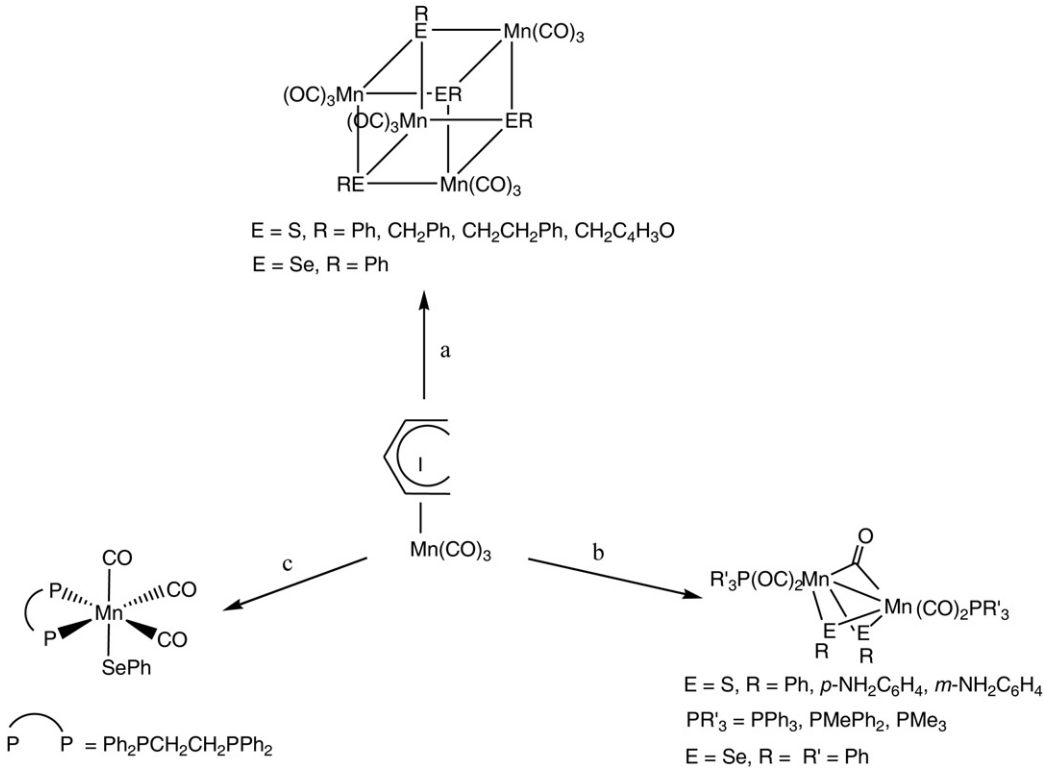


Scheme 1.

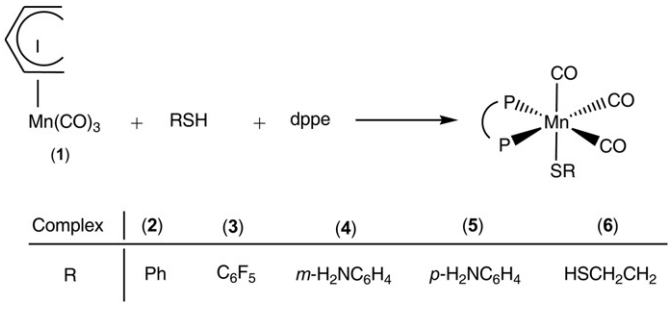
2. Results and discussion

2.1. Complexes fac-Mn(CO)$_3$(SR)(Ph$_2$PCH$_2$CH$_2$PPh$_2$-κ^2-P,P′), R = Ph, (**2**), C$_6$F$_5$, (**3**) m-NH$_2$C$_6$H$_4$ (**4**), p-NH$_2$C$_6$H$_4$, (**5**); HSCH$_2$CH$_2$, (**6**)

Reaction of pentadienyl complex (**1**) with mercaptans RSH, R = Ph, C$_6$F$_5$, *m*-NH$_2$C$_6$H$_4$, *p*-NH$_2$C$_6$H$_4$, and HSCH$_2$CH$_2$ in the presence of dppe afforded complexes (**2**)–(**6**) as shown in Scheme 2.

The reactions were conducted under cyclohexane reflux with equimolar ratios of (**1**) and the corresponding mercaptan. Reaction times were from 1 to 2 h (see experimental for further details). Yields fell within the range 85.0–96.0%. Complexes (**2**) and (**3**) are light yellow solids whereas (**4**)–(**6**) are greenish-brown solids; all complexes were stable for several weeks in the solid state in air and in solution they stood from 1 to 2 days without decomposing (at low temperature they can be stored under nitrogen for an indefinite period).

Addition order of reagents was instrumental in the formation of (**2**) and (**6**); since, when phenyl mercaptan was added before dppe the reaction gave a mixture of heterocubane [Mn(μ$_3$-SPh)(CO)$_3$]$_4$ [3a] and (**2**). Addition of 1,2-ethanedithiol to a solution of Mn(η^5-C$_5$H$_7$)(CO)$_3$ without dppe in the reaction medium afforded a trinuclear complex [7] instead of complex (**6**). Addition order for preparing (**3**)–(**5**) posed no problems; since, neither C$_6$F$_5$SH, *m*-NH$_2$C$_6$H$_4$SH nor *p*-NH$_2$C$_6$H$_4$SH reacts with Mn(η^5-C$_5$H$_7$)(CO)$_3$ at cyclohexane boiling temperature. Due to low solubility of (**4**) and (**5**) in cyclohexane their reaction times were determined by monitoring the disappearance of the IR ν(CO) bands of Mn(η^5-C$_5$H$_7$)(CO)$_3$; for all other complexes the reaction times were established by monitoring the final products' IR ν(CO) bands.



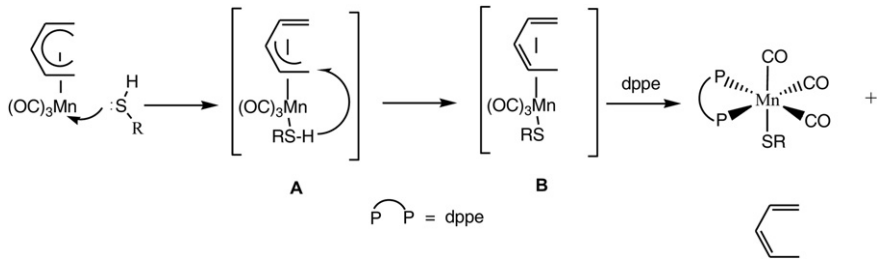
Complex	(2)	(3)	(4)	(5)	(6)
R	Ph	C_6F_5	*m*-$H_2NC_6H_4$	*p*-$H_2NC_6H_4$	$HSCH_2CH_2$

Scheme 2.

Complexes (**2**)–(**6**) are octahedral and possess a C$_s$ point group that gives rise to three carbonyl stretching modes (2A′ + A″) in their IR spectra [8]. It can be concluded from IR data of complexes (**2**)–(**6**) (see Experimental) that there is no distinct general correlation between the electronic or steric properties of the thiolates and their ν(CO) bands.

Formation of mononuclear dppe complexes can be divided into two categories depending on the relative dppe's nucleophilicity against the mercaptans'. The first category takes in the formation of complexes (**2**) and (**6**) since phenyl mercaptan and 1,2-ethanedithiol are stronger nucleophiles than dppe towards [Mn(η^5-C$_5$H$_7$)(CO)$_3$]: (i) initial coordination of the mercaptan to the metal center of Mn(η^5-C$_5$H$_7$)(CO)$_3$ would generate an η^3 intermediate **A** (Scheme 3).

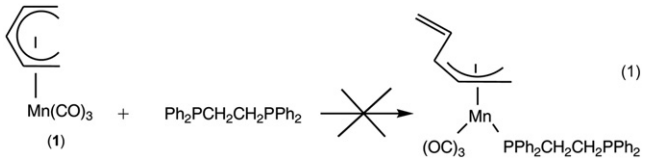
This reaction step would involve an η^3-species. These species are well known as intermediates in carbonyl substitution reactions of (**1**) by tertiary phosphines and phosphites [9]. (ii) Hydrogen migration from the sulfur atom of the coordinated mercaptan to the η^3-pentadienyl ligand of **A** would afford intermediate **B**. It is apparent from IR and ^{1}H-NMR monitoring of the reactions that mercaptan coordination as well as intramolecular hydrogen migration are relative fast processes that preclude detection of intermediates **A** and **B**. The formation of *cis*-pyperilene detected by



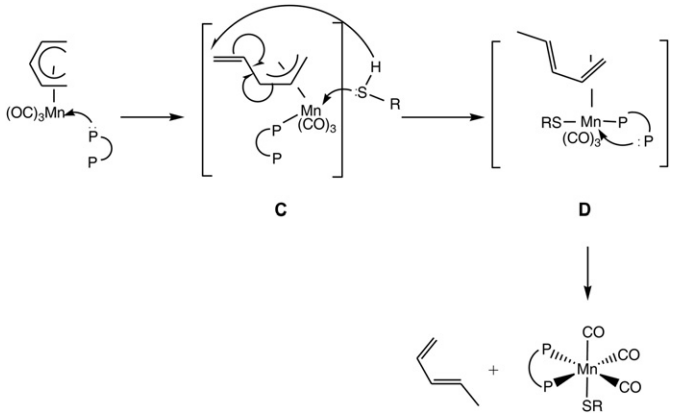
Scheme 3.

^{1}H-NMR in the reaction medium as in the closely related process where phenyl mercaptan attacks Mn(η^5-C_5H_7)$(CO)_3$ to give dinuclear carbonyl complexes [3b] suggests the presence of **B**. (iii) Substitution of *cis*-pyperilene by dppe gives a mononuclear complex with a terminal thiolate. It is known that conjugate diene carbon–metal bonds to transition metals are more stable than isolated olefins [10]; notwithstanding, in the present case step (iii) *cis*-pyperilene yields its coordination sites to dppe which stabilizes the terminal thiolate complex. Thus, dppe chelation is preferred over diene chelation. We propose step (iii) for the transformation of **B** to the final product; although, we are aware that several steps could be involved. The second category covers the mercaptans that are less nucleophilic than dppe. Mercaptans C_6F_5SH, *m*-$NH_2C_6H_4SH$, and *p*-$NH_2C_6H_4SH$ do not react towards Mn(η^5-C_5H_7)$(CO)_3$ in boiling cyclohexane; so, formation of complexes (**3**), (**4**), and (**5**) must take place by initial attack by dppe. We propose in this case the mechanism shown in Scheme 4.

Step (i) consists in the formation of η^3-complex **C** by dppe monocoordination. We tried to obtain this intermediate by reaction of (**1**) with dppe according to Eq. (1). The reaction resulted in a mixture of products that could not be characterized [11].



Monitoring of the reaction by ^{1}H-NMR for preparation of (**3**) in an NMR tube showed the occurrence of *trans*-pyperilene in 60 min at 45 °C. This suggests that hydrogen migration occurs to an S-η^3-pentadienyl ligand (see Scheme 4, intermediate **C**). This conformation has been reported for the η^3-pentadienyl ligand in the complex Mn(η^3-C_5H_7)$(CO)_3(PMe_3)$ [9]. Coordination by the other dppe phosphorus atom with concomitant elimination of *trans*-pyperilene afford the final product.



Scheme 4.

Mononuclear manganese carbonyl complexes with chelating dppe have been extensively reported [12]; however, terminal manganese carbonyl thiolates with dppe are scarce [13].

The structures obtained by single crystal X-ray diffraction of (**2**)–(**5**) are shown from Figs. 1–4. In all cases the complexes' structures are similar and exhibit a distorted octahedral geometry around the manganese atom with a *fac* arrangement of the carbonyl groups. The Mn–S distances are all comparable within experimental error. The geometry around the sulfur atom is angular with two lone pairs (sp^3 hybridization).

2.2. Complexes *fac*-Mn(CO)$_3$(SR)($H_2NCH_2CH_2NH_2$-κ^2-*N*,*N*′), R = Ph (**7**) and C_6F_5 (**8**)

Reaction of pentadienyl complex (**1**) with mercaptans RSH, R = Ph and C_6F_5, in the presence of ethylenediamine gave (**7**) and (**8**) as shown in Scheme 5.

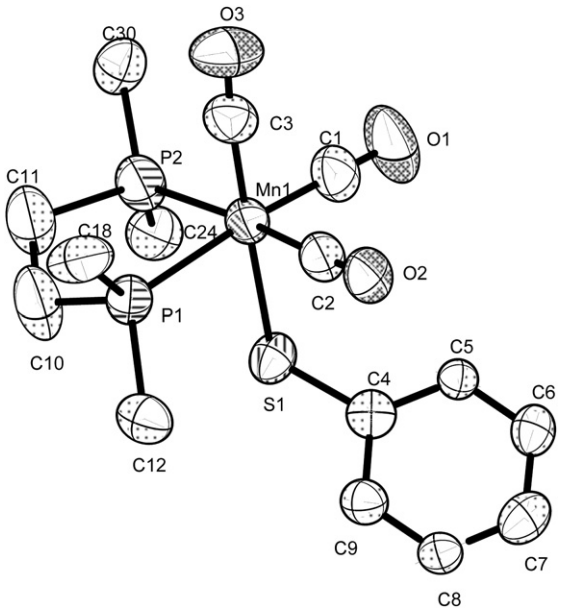


Fig. 1. Molecular structure of (**2**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Only phenyl *ipso* carbon atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)–C(1) 1.799(4); Mn(1)–C(3) 1.774(4); Mn(1)–S(1) 2.411(1); Mn(1)–P(1) 2.326(1). S(1)–Mn(1)–C(3) 178.4(1), C(1)–Mn(1)–P(1) 169.8(1), C(2)–Mn(1)–P(2) 174.7(1), C(4)–S(1)–Mn(1) 110.9(1), P(1)–Mn(1)–P(2) 84.41(4).

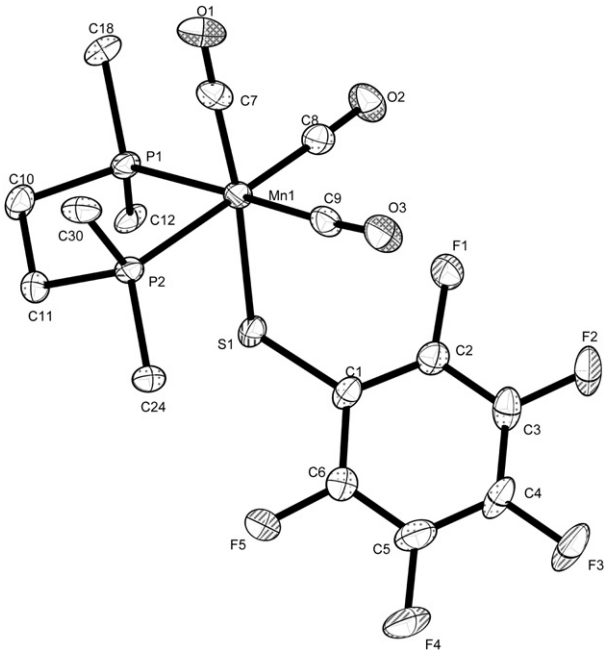


Fig. 2. Molecular structure of (**3**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles [°]: Mn(1)–C(7) 1.797(3); Mn(1)–C(8) 1.834(3); Mn(1)–S(1) 2.4154(7); Mn(1)–P(1) 2.3095(7). S(1)–Mn(1)–C(7) 173.90(8), C(9)–Mn(1)–P(1) 178.55(8), C(8)–Mn(1)–P(2) 174.18(8), C(1)–S(1)–Mn(1) 113.02(9), P(1)–Mn(1)–P(2) 85.02(2).

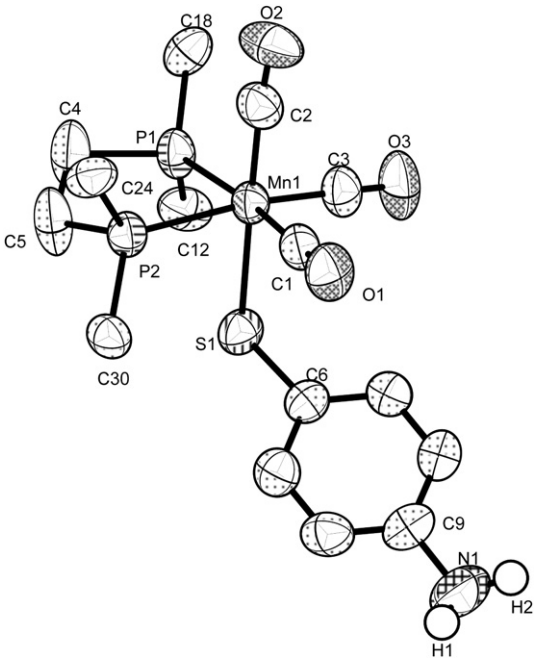


Fig. 4. Molecular structure of (**5**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Only phenyl *ipso* carbon atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)–C(1) 1.813(3); Mn(1)–C(2) 1.790(3); Mn(1)–S(1) 2.4098(9); Mn(1)–P(1) 2.3194(8). S(1)–Mn(1)–C(2) 177.97(10), C(1)–Mn(1)–P(1) 174.10(9), C(3)–Mn(1)–P(2) 169.59(10), C(6)–S(1)–Mn(1) 110.93(9), P(1)–Mn(1)–P(2) 84.52(3).

The reactions were carried out under cyclohexane reflux with equimolar ratio; the reaction yields were around 70% for both complexes. Complexes (**7**) and (**8**) are light yellow solids insoluble in hydrocarbons; (**7**) is partially soluble in alkyl chlorides, while (**8**) is soluble. Both complexes were stable for several weeks in the solid state in air; in solution they decomposed within two weeks (at low temperature they can be stored under nitrogen for an indefinite period).

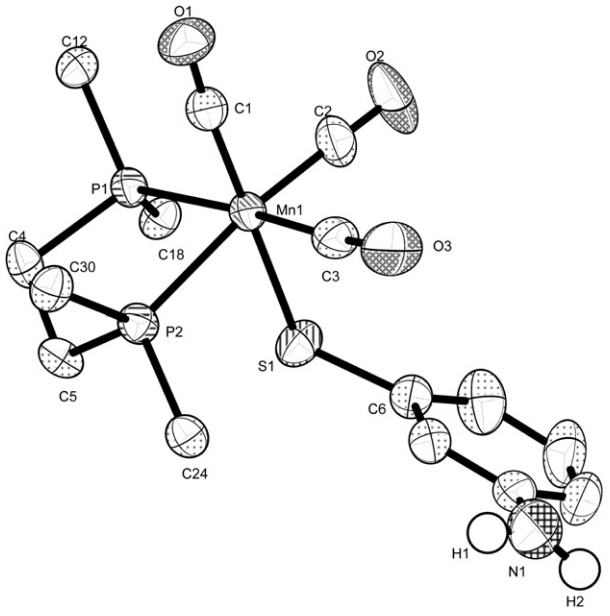
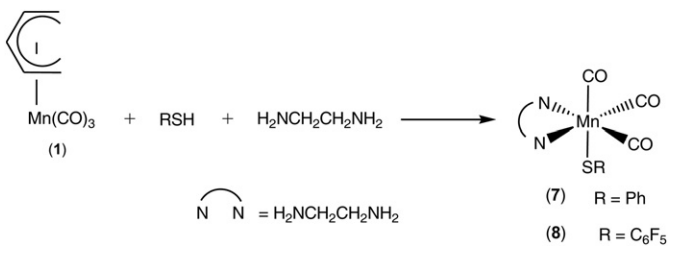


Fig. 3. Molecular structure of (**4**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles [°]: Mn(1)–C(1) 1.786(4); Mn(1)–C(2) 1.805(4); Mn(1)–S(1) 2.406(1); Mn(1)–P(1) 2.334(1). S(1)–Mn(1)–C(1) 175.34(12), C(3)–Mn(1)–P(1) 176.24(12), C(2)–Mn(1)–P(2) 169.19(13), C(6)–S(1)–Mn(1) 115.5(1), P(1)–Mn(1)–P(2) 84.02(3).

The infrared spectra of (**7**) and (**8**) present ν(CO) bands (2015, 1919, 1897 and 2022, 1926, 1906 cm^{-1} all strong, in CH_2Cl_2 for (**7**) and (**8**) resp.) with similar shape and wave numbers to those of (**2**)–(**6**) (see Table 1); notwithstanding, one perceptible difference is observed in the wave number of the band assigned to the A″ stretching mode (1919 and 1926 cm^{-1}, for (**7**) and (**8**), resp.). It has been proposed that this band stems from the out-of-phase vibration (antisymmetric with respect to the mirror plane of the molecule) of equatorial carbonyls [8] that in (**7**) and (**8**) are *trans* to the ethylenediamine $-NH_2$ groups. This fact suggests that ethylenediamine donates more electron density to the manganese than it can receive, if at all, rendering the A″ mode ν(CO) band to appear at lower wave number than in (**2**)–(**6**).

The relative nucleophilicities of ethylenediamine vs. PhSH and C_6F_5SH are apparent from the reaction times. It has already been pointed out that C_6F_5SH does not react with (**1**) at cyclohexane reflux temperature. So, formation of (**7**) takes place in 2 h by



Scheme 5.

Table 1
Crystal data for (**2**)–(**5**), (**7**)–(**9**).

	(**2**)	(**3**)	(**4**)	(**5**)
Empirical formula	$C_{35}H_{29}MnO_3P_2S$	$C_{35}H_{24}F_5MnO_3P_2S$ with toluene	$C_{35}H_{30}MnNO_3P_2S$ with ½ of CH_2Cl_2	$C_{35}H_{30}MnNO_3P_2S$
M	646.52	828.62	704.00	661.54
Temperature (K)	293(2)	100(2)	298(2)	298(2)
Crystal size (mm)	0.24 × 0.22 × 0.12	0.42 × 0.34 × 0.29	0.30 × 0.22 × 0.18	0.38 × 0.32 × 0.30
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P_{-1}	$P2_1/c$	$P2_1/c$
a (Å)	11.846(1)	11.1234(7)	8.8228(4)	11.9575(9)
b (Å)	18.253(1)	13.0909(8)	33.2242(15)	17.7232(13)
c (Å)	14.498(1)	14.3952(9)	11.9256(5)	15.0621(11)
α (°)	90	90	90	90
β (°)	96.992(1)	108.5560(10)	108.1140(10)	96.264(2)
γ (°)	90	95.2980(10)	90	90
V (Å^3)	3111.3(3)	1880.1(2)	3322.5(3)	3173.0(4)
Z	4	2	4	4
θ Range for data collection (°)	1.73–25.02	1.57–25.00	1.23–25.00	1.71–25.00
Reflections collected	25,279	10,695	27,208	25,530
Independent reflections	5484 ($R_{int} = 0.0635$)	6558 ($R_{int} = 0.0211$)	5853 ($R_{int} = 0.0638$)	5577 ($R_{int} = 0.0388$)
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0540$, $wR_2 = 0.0696$	$R_1 = 0.0403$, $wR_2 = 0.1020$	$R_1 = 0.0594$, $wR_2 = 0.1137$	$R_1 = 0.0453$, $wR_2 = 0.1072$
R indices (all data)	$R_1 = 0.0884$, $wR_2 = 0.0735$	$R_1 = 0.0442$, $wR_2 = 0.1048$	$R_1 = 0.0780$, $wR_2 = 0.1214$	$R_1 = 0.0608$, $wR_2 = 0.1127$

	(**7**)	(**8**)	(**9**)
Empirical formula	$C_{11}H_{13}MnN_2O_3S$	$C_{11}H_8F_5MnN_2O_3S$	$C_{10}H_{14}Mn_2N_4O_6$
M	308.23	398.19	396.13
Temperature (K)	298(2)	298(2)	298(2)
Crystal size (mm)	0.40 × 0.28 × 0.24	0.28 × 0.24 × 0.06	0.33 × 0.14 × 0.08
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	P_{-1}
a (Å)	14.5032(10	10.1409(8	6.7643(10)
b (Å)	10.6241(7)	14.7688(12)	8.0924(11)
c (Å)	17.4978(12)	10.2144(8)	8.1427(12)
α (°)	90	90	62.566(2)
β (°)	90	108.9600(10)	88.754(2)
γ (°)	90	90	70.872(2)
V (Å^3)	2696.1(3)	1446.8(2)	369.29(9)
Z	8	4	1
θ Range for data collection (°)	2.33–25.00	2.46–25.37	2.85–25.00
Reflections collected	20,245	11,823	2973
Independent reflections	2379 ($R_{int} = 0.0421$)	2656 ($R_{int} = 0.0381$)	1299 ($R_{int} = 0.0309$)
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0308$, $wR_2 = 0.0674$	$R_1 = 0.0330$, $wR_2 = 0.0712$	$R_1 = 0.0304$, $wR_2 = 0.0720$
R indices (all data)	$R_1 = 0.0394$, $wR_2 = 0.0700$	$R_1 = 0.0422$, $wR_2 = 0.0739$	$R_1 = 0.0339$, $wR_2 = 0.0733$

initial attack of PhSH, whereas initial attack by ethylenediamine leads to complex (**8**) in 13 h. Both complexes possess free $-NH_2$ groups. This speaks of the stability of the pentadienyl ligand to N–H addition of ethylenediamine; since, it is known that primary and secondary amines react with (**1**), at cyclohexane reflux temperature, with N–H bond scission and N–C(pentadienyl) bond formation to afford aminopentenyl complexes [2f]. The reciprocal effect between the $-NH_2$ groups and the presence of C_6F_5SH in the present case prevent ethylenediamine attack to (**1**) in any other way than coordination through the diamine lone pairs: ethylenediamine in (**7**) and (**8**) is ligated in a chelate fashion.

As in the case of (**2**)–(**6**) two mechanisms of formation can be envisioned for achieving (**7**) and (**8**). The first would be analogous to the one shown in Scheme 3, where phenyl mercaptan attacks (**1**) to give an η^3-species. The second proposed mechanism would resemble that in Scheme 4 with ethylenediamine initially attacking complex (**1**).

A large number of manganese carbonyl complexes exist that contain Mn–N bonds; in most of them the nitrogen atom is that of an imine, imide or part of an aromatic system [14], however, primary diamine chelators with carbonyl manganese thiolates are virtually unknown [13]. Complexes (**7**)–(**9**) leave open the possibility for further reaction chemistry at the NH_2 groups.

The X-ray structures of (**7**) and (**8**) are shown in Figs. 5 and 6, respectively.

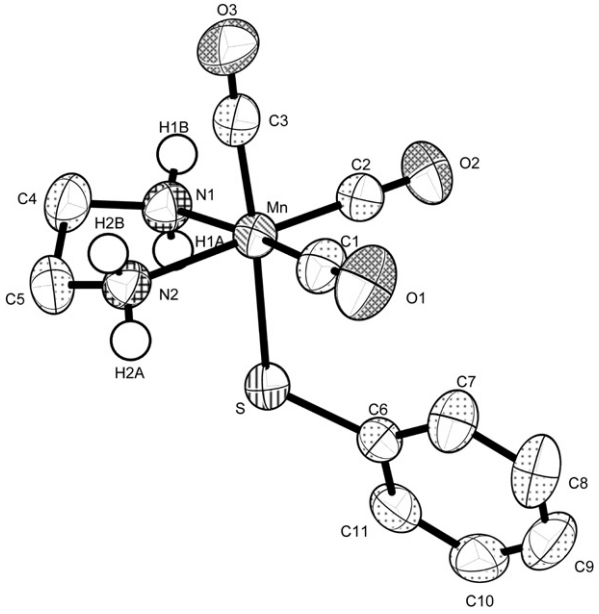


Fig. 5. Molecular structure of (**7**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Mn–C(1) 1.786(2); Mn–C(3) 1.800(3); Mn–S 2.3916(6); Mn–N(1) 2.083(2). S–Mn–C (3) 174.73(8), C(1)–Mn–N(1) 174.62(9), C(2)–Mn–N(2) 173.57(9), C(6)–S–Mn 117.69 (7), N(1)–Mn–N(2) 80.19(8).

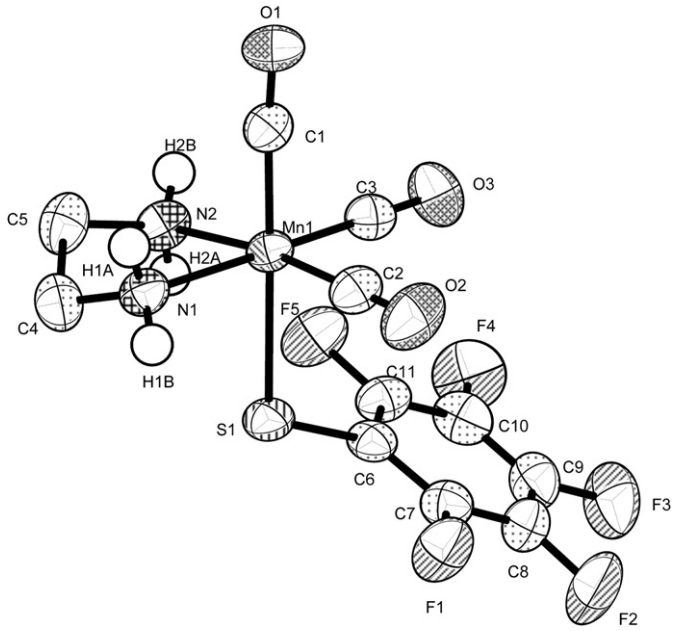


Fig. 6. Molecular structure of (**8**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Mn(1)–C(1) 1.795(3); Mn(1)–C(2) 1.803(3); Mn(1)–S(1) 2.4212(7); Mn(1)–N(1) 2.096(2). S(1)–Mn(1)–C(1) 178.05(8), C(3)–Mn(1)–N(1) 175.04(10), C(2)–Mn(1)–N(2) 172.27(10), C(6)–S(1)–Mn(1) 109.70(8), N(1)–Mn(1)–N(2) 80.46(8).

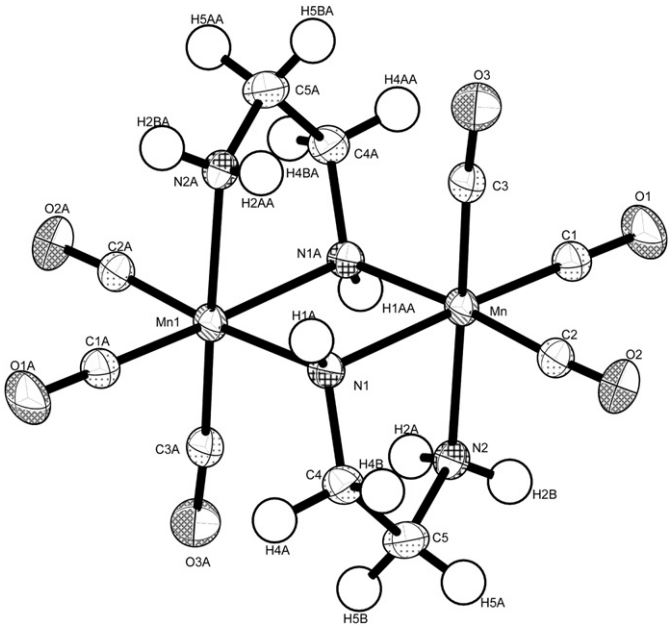
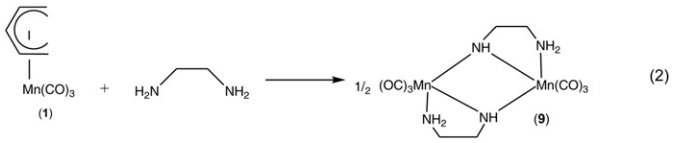


Fig. 7. Molecular structure of (**9**) including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Mn–C(1) 1.803(3); Mn–C(3) 1.790(3); Mn–N(1) 2.049(2); Mn–N(2) 2.089(2). C(1)–Mn–N(1) 170.10(10), C(2)–Mn–N(1A) 175.37(9), C(3)–Mn–N(2) 174.18(11), Mn–N(1)–Mn(1) 100.97(8).

Both present an octahedral geometry around the metal center with the carbonyls in a *fac* disposition. In comparison with the structures of (**2**)–(**5**) the distortion from an octahedral geometry in (**7**) and (**8**) is slightly greater due to the smaller size of the nitrogen atom compared with the phosphorus atom; this is reflected in the N–Mn–N angles (around 80°) vs. P–Mn–P angles (ca 84°). The Mn–S distances in all mononuclear complexes here reported fall in the range 2.3916(6)°–2.4212(7)°. The manganese–carbon atom distances of the carbonyl groups are all similar within each complex: no *trans* effect is noticeable whatsoever.

2.3. Complex [fac-Mn(CO)$_3$(μ-H$_2$NCH$_2$CH$_2$NH-κ^2-N,N′)]$_2$, (**9**)

Reaction of (**1**) with ethylenediamine (molar ratio 8:1, amine:(**1**)) at cyclohexane reflux temperature for 12 h afforded complex (**9**) as a yellow solid with low yield (21%) according to Eq. (2).



(2)

(**9**) is insoluble in hydrocarbons but readily dissolves in chlorinated hydrocarbons. The stability of (**9**) is remarkable: after one month in air it did not decompose. Unreacted (**1**) could be recovered by extraction with hexane from the reaction mixture. The IR spectrum of (**9**) shows five ν(CO) bands for terminal carbonyls.

Diamine concentration (8:1 molar ratio) and reaction time (12 h) point out the difficulty for this process to occur and suggest that ethylenediamine coordination to manganese is necessary so that N–H bond cleavage and H migration to the pentadienyl ligand may take place. In the absence of any suitable hydrogen atom (like that of a mercaptan's sulfhydryl group) ethylenediamine NH hydrogens saturate the pentadienyl ligand to *trans*-pyperilene; so, ethylenediamine in (**9**) acts as chelating and bridging ligand to realize an 18 electron configuration at each manganese center. The structure of (**9**), determined by an X-ray analysis, is shown in Fig. 7.

Both manganese atoms present a distorted octahedral geometry due to the amine–amide bridges. There are two Mn–N distances: for Mn–NH and Mn–NH$_2$ bonds being the former shorter (2.049(2), 2.089(2) Å, resp.). The geometry around nitrogen atoms speaks of an sp^3 hybridization. The Mn–CO bond distances are all equal within experimental error.

3. Conclusions

Terminal new carbonyl manganese thiolates could easily be obtained by means of a straightforward reaction involving bifunctional phosphorus and nitrogen ligands. In both cases the ligands acted as chelators; forcing reaction conditions rendered ethylenediamine reactive towards tricarbonyl(η^5-pentadienyl) manganese to achieve a dinuclear complex with two ethylenediaminyl moieties bridging two Mn(CO)$_3$ fragments via two (μ–NH) interactions while the other two –NH$_2$ groups bind each a metal center through their lone electron pairs. Bridging and/or chelating capacities of ethylenediamine towards manganese depend on the presence of hydrogen atoms attached to nitrogen: Chelation is achieved when NH$_2$ groups remain intact; while N–H scission led to obtaining bridging ethylenediaminyl. Our studies have shown that tricarbonyl-η^5-pentadienylmanganese is an adequate starting material to prepare diverse manganese carbonyls with ligands of the group 15 and 16 bonded to the same coordination sphere. We anticipate that the synthetic method here reported has great potential; further work is underway.

4. Experimental

General considerations. All reactions were conducted under nitrogen atmosphere using standard vacuum line and Schlenk techniques. The reactions were monitored by IR spectroscopy in the ν(CO) region and the reaction times reported correspond to the time when no further changes were observed in the CO groups' patterns. Complex (**1**) [15] was prepared according to literature procedures. 1,2-Bis(diphenylphosphino)ethane, ethylenediamine, 1,2-ethanedithiol, phenyl mercaptan, pentafluorophenyl mercaptan, *m*-, and *p*-aminothiophenols were acquired from Aldrich Chemical Co. and used as received. IR spectra were obtained in solution (4000–580 cm^{-1}) using a Nicolet FT-IR 55X spectrometer and in KBr disk (4000–200 cm^{-1}) in a Perkin Elmer 283B spectrometer. NMR spectra were obtained at room temperature on Varian Unity 300, Perkin Elmer 283B, and Jeol GX300 spectrometers. ^{1}H-NMR spectra were referenced to residual solvent peaks with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were externally referenced to 85% H_3PO_4. FAB(+) mass spectra were recorded on a JEOL SX-102A instrument. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN. USA. Melting points were determined on a Fisher–Johns apparatus and are uncorrected.

4.1. General method for the synthesis of complexes (**2**)–(**6**)

Equimolar amounts of Mn(η^5-C_5H_7)(CO)$_3$, (**1**) and dppe were mixed in 100 mL of cyclohexane in a 250 mL round bottom flask charged with a magnetic stirrer and previously purged with nitrogen, the solution turned turbid yellow; since dppe is insoluble in cyclohexane at room temperature. An equimolar amount of mercaptan (RSH, R = Ph, C_6F_5, *m*-$NH_2C_6H_4$, *p*-$NH_2C_6H_4$, $HSCH_2CH_2$ see below for amounts, reaction times and yields) was then added and the mixture was set at reflux temperature. Samples were collected every 10 min for monitoring purposes (ν(CO) IR pattern). After 1–2 h the reaction was completed. The reaction was left to reach room temperature. The solvent was eliminated under reduced pressure remaining light yellow solids (complexes (**2**) and (**3**)) or greenish-brown solids (complexes (**4**), (**5**), and (**6**)). The dry residue was washed with hexane (3 × 10 mL) to eliminate unreacted (**1**). The remaining material was dissolved in dichloromethane (ca. 20 mL) and filtered via cannula to a Schlenk flask. Evaporation of dichloromethane under reduced pressured afforded complexes (**2**)–(**6**) as fine powders. Crystallization in a dichloromethane–MeOH solution of (**2**), or in a toluene solution of (**3**) at −4 °C afforded crystals suitable to conduct X-ray diffraction analyses. Crystallization from dichloromethane at −4 °C afforded crystals suitable of (**4**) and (**5**) to conduct X-ray diffraction analyses.

Complex *fac*-Mn(CO)$_3$(SPh)($Ph_2PCH_2CH_2PPh_2$-κ^2-*P*,*P*′) (**2**). Phenyl mercaptan, 2.2 mmol, 247 mg; (**1**) 2.2 mmol, 462 mg; dppe 2.2 mmol, 894 mg. Reaction time: 1 h. Anal. found (calcd.): C 65.32 (65.02); H 4.86 (4.52) Yield 94.0%, m.p. 158 °C dec. IR (KBr): ν(CO) 1999 s, 1942 s, 1893 s cm^{-1}. IR ($CHCl_3$): ν(CO) 2011 s, 1945 s 1910 s cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.55 [d, 2H, H_o, −SPh, J_{H-P} = 18.3 Hz]; 7.34 [S, broad, 20H, PPh_2]: 6.77 [t, 2H, H_m, −SPh, J_{H-H} = 9.09 Hz]; 6.69 [d, 2H, H_p, −SPh, J_{H-H} = 9.03 Hz]; 3.26 [d, 2H, $Ph_2PCH_2CH_2PPh_2$, J_{H-P} = 7.68 Hz]; 2.60 [d, 2H, $Ph_2PCH_2CH_2PPh_2$, J_{H-P} = 8.04 Hz], $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 79.0 s. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 145.85 [t, C_i, $Ph_2P(CH_2)_2PPh_2$, J_{Ci-P} = 5.77 Hz]; 135.55 [t, C_i, −SPh, J_{Ci-P} = 17.80 Hz]; 134.78 [s, C_o, −SPh] 132.13 [d, C_o, $Ph_2P(CH_2)_2PPh_2$, J_{Co-P} = 43.2 Hz]; 130.07 [d, C_m, SPh, J_{C-P} = 35.60 Hz]; 128.57 [d, C_m, $Ph_2P(CH_2)_2PPh_2$, J_{C-P} = 43.2 Hz]; 127.11 [s, C_p, $Ph_2P(CH_2)_2PPh_2$], 123.37 [s, C_p, −SPh]; 25.09 [t C_{CH_2}, $Ph_2P(CH_2)_2PPh_2$, J_{C-P} = 21.62 Hz]. FAB+ MS (*m*/*e*): 562 $[M-3CO]^+$; 537 $[M-SPh]^+$; 453 [M − 3CO − SPh].

Complex *fac*-Mn(CO)$_3$(SC_6F_5)($Ph_2PCH_2CH_2PPh_2$-κ^2-*P*,*P*′) (**3**). Pentafluorophenyl mercaptan, 2.43 mmol, 485 mg; (**1**) 2.43 mmol, 500 mg; dppe 2.43 mmol, 967 mg. Reaction time: 1 h 40 min. Anal. found (calcd.) (3)·toluene: C 61.3 (60.9); H 3.59 (3.89). Yield 92.0%. M.p. 146 °C dec. IR (KBr): ν(CO) 2012 s, 1946 s, 1920 s, cm^{-1}. IR ($CHCl_3$): ν(CO) 2018 s, 1952 s, 1920 s, cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.22–7.78 [m, 20H, $(H_5C_6)_2P(CH_2)_2P(C_6H_5)_2$]; 3.13 [s, 2H, $(H_5C_6)_2PCH_2CH_2P(C_6H_5)_2$]; 2.71 [s, 2H, $(H_5C_6)_2PCH_2CH_2P(C_6H_5)_2$]. ^{31}P-NMR$\{^1H\}$ ($CDCl_3$, 121.7 MHz): δ/ppm: 72.0 s. ^{19}F-NMR$\{^1H\}$ ($CDCl_3$, 282 MHz): δ/ppm: −127.95 [d, F_o, $-S(C_6F_5)$, J_{Fo-Fm} = 24.5 Hz], −161.93 [t, F_p, $-S(C_6F_5)$, J_{Fp-Fm} = 20.88 Hz], −164.78 [t, F_m, $-S(C_6F_5)$, $J_{Fm-Fo,\ Fp}$ = 22 Hz], $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 134.87 [t, C_i, $Ph_2P(CH_2)_2PPh_2$, J_{Ci-P} = 18.82 Hz]; 131.57 [d, C_o, $Ph_2P(CH_2)_2PPh_2$, J_{Co-P} = 24.33 Hz]; 130.28 [d, C_m, $Ph_2P(CH_2)_2PPh_2$, J_{Cm-P} = 21.00 Hz]; 128.61 [d, C_p, $Ph_2P(CH_2)_2PPh_2$, J_{Cp-P} = 48.74 Hz]; 24.62 [t, C_{CH_2}, $Ph_2P(CH_2)_2PPh_2$, J_{CH_2-P} = 21.00 Hz]. FAB+ MS (*m*/*e*): 652 $[M-3CO]^+$, 537 $[M-S(C_6F_5)]^+$, 453 $[M-3CO-S(C_6F_5)]^+$.

Complex *fac*-Mn(CO)$_3$(SC_6H_4-*m*-NH_2)($Ph_2PCH_2CH_2PPh_2$-κ^2-*P*,*P*′) (**4**). *m*-Aminothiophenol 2.43 mmol, 304 mg; (**1**) 2.43 mmol, 500 mg; dppe 2.43 mmol, 967 mg. Reaction time: 2 h. Anal. found (calcd.): C 63.15 (63.55); H 4.85 (4.57). Yield 95.0%. M. p. 121–124 °C. IR (KBr): ν(CO) 1999 s, 1946 s, 1894 s, cm^{-1}. IR($CHCl_3$): ν(CO) 2007 s, 1943 s, 1909 s, cm^{-1}. ^{1}H-NMR ($CDCl_3$ + D_2O, 300 MHz): δ/ppm: 7.64–7.25 [m, 20H, $(H_5C_6)_2P(CH_2)_2P(C_6H_5)_2$]; 6.64 [t, 1H, H_m, $-S(C_6H_4-m-NH_2)$, J_{H-H} = 7.68 Hz]; 6.35 [d, 1H, H_o, $-S(C_6H_4-m-NH_2)$, J_{Ho-Hm} = 7.14 Hz]; 6.22 [d, 1H, H_p, $-S(C_6H_4-m-NH_2)$, J_{Hm-Ho} = 7.68 Hz]; 5.82 [s, 1H, $H_{o'}$, $-S(C_6H_4-m-NH_2)$]; 3.73 [s, 2H, H_{NH_2}, $-S(C_6H_4-m-NH_2)$]; 3.03 [t, 2H, H_{CH_2}, $Ph_2P-CH_2-CH_2-PPh_2$, J_{C-P} = 5.55 Hz]; 2.59 [t, 2H, H_{CH_2}, $Ph_2P-CH_2-CH_2-PPh_2$, J_{C-P} = 6.03 Hz]; ^{31}P-NMR$\{^1H\}$ ($CDCl_3$, 121.7 MHz): δ/ppm: 72.97 s. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 167.84 [s, C_i(N), $-S(C_6H_4-m-NH_2)$]; 132.54 [s C_i(S),-(SC_6H_4-m-NH_2)]; 131.88 [s, C_o, $Ph_2P(CH_2)_2PPh_2$, J_{Co-P} = 4.84 Hz] 130.96 [s, C_m, $Ph_2P(CH_2)_2PPh_2$]; 130.32 [s, C_m(S), $S(C_6H_4-m-NH_2)$]; 129.87 [s, C_o(S), $-SC_6H_4-m-NH_2$]; 128.88 [s, C_p, $Ph_2P(CH_2)_2PPh_2$], 128.36 [s, $C_{o'}$, $-S(C_6H_4-m-NH_2)$]; 23.90 [d C_{CH_2}, $Ph_2P(CH_2)_2PPh_2$, J_{CH_2-P} = 57.43 Hz]. FAB+ MS (*m*/*e*): 661 $[M]^+$, 577 $[M-3CO]^+$, 453 $[M-3CO-SC_6H_4-m-NH_2]^+$.

Complex *fac*-Mn(CO)$_3$((SC_6H_4-p-NH_2))($Ph_2PCH_2CH_2PPh_2$-κ^2-*P*) (**5**). *p*-Aminothiophenol 2.43 mmol, 304 mg; (**1**) 2.43 mmol, 500 mg; dppe 2.43 mmol, 967 mg. Reaction time: 2 h. Anal. found (calcd.): C 63.17 (63.55); H 4.15 (4.57). Yield 96.0%. M. p. 82–86 °C. IR (KBr): ν(CO) 2002 s, 1934 s, 1899 s, cm^{-1}. IR($CHCl_3$): ν(CO) 2009 s, 1944 s, 1907 s, cm^{-1}. ^{1}H-NMR ($CDCl_3$ + D_2O, 300 MHz): δ/ppm: 7.65–7.37 [m, 20H, $(H_5C_6)_2P(CH_2)_2P(C_6H_5)_2$]; 7.25 [d, 2H, H_o(S), $-S(C_6H_4-p-NH_2)$, J_{Ho-Hm} = 6.87 Hz]; 6.57 [d, 2H, H_m(S), $-S(C_6H_4-p-NH_2)$, J_{Hm-Ho} = 7.7 Hz]; 3.33 [s, 2H, H_{NH_2}, $-S(C_6H_4-p-NH_2)$]; 3.00 [d, 2H, $Ph_2P-CH_2-CH_2-PPh_2$, J_{H-P} = 6.4 Hz]; 2.53 [d, 2H, $Ph_2P-CH_2-CH_2-PPh_2$, J_{H-P} = 5.5 Hz]; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 73.52 s. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 221.47 [s broad, *C*O]; 147.02 [s, C_i(N), $-S(C_6H_4-p-NH_2)$]; 135.62 [t C_i(P), $Ph_2P(CH_2)_2PPh_2$, J_{Ci-P} = 23.0 Hz]; 133.86 [s, C_o(S), $SC_6H_4-p-NH_2$]; 132.06 [d, C_o(P), $Ph_2P(CH_2)_2$–PPh_2, J_{Co-P} = 34.3 Hz]; 129.89 [d, C_m(P), $Ph_2P-CH_2-CH_2-PPh_2$, J_{Cm-P} = 40.5 Hz]; 128.41 [d, C_p(P), $Ph_2P(CH_2)_2PPh_2$, J_{Cp-P} = 44.8 Hz]; 125.63 [s, C_i(S), $-S(C_6H_4-p-NH_2)$]; 115.30 [s, C_m(S), $-S(C_6H_4-p-H_2N)$], 114.79 [s, $C_{m'}$(S), $-S(C_6H_4-p-H_2N)$]; 24.92 [t, C_{CH_2}, $PPh_2(CH_2)_2PPh_2$; J_{C-P} = 21.5 Hz]. FAB+ MS (*m*/*e*): 577 $[M-3CO]^+$, 453 $[M-3CO-(SC_6H_4-p-H_2N)]^+$.

Complex *fac*-Mn(CO)$_3$(SCH_2CH_2SH)($Ph_2PCH_2CH_2PPh_2$-κ^2-*P*,*P*′) (**6**). 1,2-ethanedithiol 1.21 mmol, 114 mg; (**1**) 1.21 mmol, 250 mg; dppe 1.21 mmol, 483 mg. Reaction time: 1 h 15 min. Anal. found (calcd.): C 58.92 (59.05); H 4.65 (4.64). Yield 85.0%. M. p. 125 °C dec. IR (KBr): ν(CO) 2001 s, 1934 s 1897 s; cm^{-1}, IR($CHCl_3$): ν(CO) 2010 s, 1944 s, 1907 s, cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.83–7.97 [m, 20H, $(H_5C_6)_2P(CH_2)_2P(C_6H_5)_2$]; 3.75 [s broad, $2H_{CH_2}$, $-SCH_2CH_2SH$]; 3.16 [s broad, 2H, $Ph_2PCH_2CH_2Ph_2$]; 2.75 [s broad, 2H, $Ph_2PCH_2CH_2Ph_2$]; 2.16

[s broad, H_{SH}, SCH_2CH_2SH]; 1.85 [s broad, $2H_{CH_2}$, SCH_2—CH_2SH]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 73.11 s. ^{13}C-NMR$\{^1H\}$ ($CDCl_3$, 75.6 MHz): δ/ppm: 219.88 [s broad, CO]; 129.73 [broad, C_{Ph}, $(H_5C_6)P(CH_2)_2(C_6H_5)_2$]; 37.53 [broad, C_{CH_2}, $-SCH_2CH_2SH$]; 25.19 [broad, C_{CH_2}, $-Ph_2P(CH_2CH_2)PPh_2$]. FAB+ MS (m/e): 537 $[M - SCH_2CH_2SH]^+$.

4.2. General method for the synthesis of complexes (**7**) and (**8**)

Complex (**1**) (1.0 mmol, 206.0 mg) was dissolved in 100 mL of cyclohexane in a 250 mL round bottom flask with a magnetic stirrer previously purged with nitrogen. Ethylenediamine was added in an equimolar amount (1.0 mmol, 67 μL). The corresponding mercaptan was added (PhSH 1.0 mmol, 102 μL; C_6F_5SH 1.0 mmol, 133 μL) and the solution turned turbid. The temperature was raised to reflux until the IR spectrum in the ν(CO) region remained unchanged (see below for reaction times and yields). As the reaction progressed an insoluble yellow material appeared. Reaction monitoring was conducted taking aliquots and then eliminating the cyclohexane and dissolving the sample in dichloromethane to run the IR spectrum in the ν(CO) region. At the reaction end the reaction was allowed to reach room temperature and the solvent was eliminated under reduced pressure. The yellow material obtained after solvent evaporation was washed with hexane to remove unreacted (**1**). The resulting material was dissolved in dichloromethane (20 mL), filtered through a cannula and the solvent evaporated under reduced pressure remaining complexes (**7**) and (**8**) as light yellow materials. Crystallization by diffusion of a dichloromethane solution of (**7**) or (**8**) in hexane at −4 °C afforded crystals suitable to conduct X-ray diffraction analyses.

Complex *fac*-$Mn(CO)_3(SPh)(H_2NCH_2CH_2NH_2$-$\kappa^2$-*N*,*N*′) (**7**) Reaction time: 2 h. Anal. found (calcd.): C 42.53 (42.86); H 4.37 (4.25); N 8.71 (9.08). Yield 70.0%. M. p. 147–152 °C. IR (KBr): ν(CO) 2006 s, 1885 s cm^{-1}. IR (CH_2Cl_2): ν(CO) 2015 s, 1919 s, 1897 s cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ/ppm: 7.38 [s broad, H_o, −SPh], 7.00 [s broad, H_m, −SPh], 6.88 [s(a), H_p, −SPh], 4.69 [s broad, $NH_2(CH_2)_2NH_2$], 2.75 [s broad, $NH_2(CH_2)_2NH_2$], 2.42 [s broad, H, H*, $NH_2(CH_2)_2NH_2$]. ^{13}C-NMR (DMSO-d_6, 75 MHz): δ/ppm: 223.54 [s broad, CO], 147.29 [s, C_i, −SPh]; 133.42 [s, C_o, −SPh], 127.52 [s, C_m, −SPh]; 122.20 [s, C_p, −SPh]. FAB+ MS (m/e): 308, $[M]^+$; 224 $[M - 3CO]^+$.

Complex *fac*-$Mn(CO)_3(SC_6F_5)(H_2NCH_2CH_2NH_2$-$\kappa^2$-*N*,*N*′) (**8**) Reaction time: 13 h. Anal. found (calcd.): C 33.52 (33.18); H 2.46 (2.03). Yield 69.0%. m.p. 160 °C dec. IR (KBr): ν(CO) 2024 s, 1929 s, 1884 s cm^{-1}. IR (CH_2Cl_2): ν(CO) 2022 s, 1926 s, 1906 s cm^{-1}. NMR-^{1}H (CD_2Cl_2, 300 MHz): δ/ppm: 3.23 [s broad, $NH_2(CH_2)_2NH_2$], 2.88 [s broad, $NH_2(CH_2)_2NH_2$], 2.76 [s(a), H, H*, $NH_2H_3(CH_2)_2NH_2H_3$]. ^{13}C-NMR (CD_2Cl_2, 75 MHz): δ/ppm: 120.57 [s broad, C_i, $-S(C_6F_5)$]; 149.49 [d, C_o, $J_{C4-F1} = 228.3$ Hz, $-S(C_6F_5)$], 138.17 [d, C_m, $J_{C5-F2} = 255.0$ Hz, $-S(C_6F_5)$], 130.23 [d, C_p, $J_{C6-F3} = 160.2$ Hz, $-S(C_6F_5)$]. ^{19}F-NMR (CD_2Cl_2, 282 MHz): δ/ppm: −132.48 [d, F_o, $^3J_{F1-F2} = 21.9$ Hz, $-S(C_6F_5)$]; −161.67 [t, F_m, $^3J_{F1-F2-F3} = 20.7$ Hz, $-S(C_6F_5)$]; −164.33 [t, F_p, $^3J_{F3-F2} = 4.9$ Hz, $^4J_{F3-F1} = 23.2$ Hz, $-S(C_6F_5)$]. FAB+ MS (m/e): 398, $[M]^+$; 314 $[M - 3CO]^+$.

4.3. Synthesis of complex [fac-$Mn(CO)_3(\mu$-$H_2NCH_2CH_2NH$-κ^2-*N*,*N*′)]$_2$ (**9**)

Complex (**1**) (1.0 mmol, 206.0 mg) was dissolved in 100 mL of cyclohexane in a 250 mL round bottom flask with a magnetic stirrer previously purged with nitrogen. Ethylenediamine was added (8.0 mmol, 536 μL). The reaction mixture was heated to cyclohexane reflux and maintained for 12 h. Samples were taken every 30 min for monitoring purposes. There was a change in color from light yellow to amber and at the end of the reaction to dark red. The reaction mixture was allowed to cool to room temperature after which a brown precipitate was formed. After filtering off the precipitate (dark brown material) the solvent was eliminated under reduced pressure. The resulting product was washed with hexane and crystallized from dichloromethane giving a yellow solid in 21.0%. Crystallization by diffusion of a dichloromethane solution of (**9**) and hexane at −4 °C afforded suitable crystals to accomplish an X-ray diffraction analysis.

Complex $[Mn_2(CO)_6(\mu$-$NH(CH_2)_2NH_2$-κ^2-*N*,*N*′$)_2]$ (**9**) M. p. 142 °C dec. Anal. found (calcd.): C 29.92 (30.32); H 3.86 (3.56). IR (KBr): ν(CO) 2024 w, 1986 s, 1864 s cm^{-1}. IR (CH_2Cl_2): ν(CO) 2024 m, 1989 s, 1921 s, 1895 s, 1877 s cm^{-1}. ^{1}H-NMR (THF-d_8, 300 MHz): δ/ppm: 5.27 [s(a), Mn(μ-N*H*)Mn,], 3.83[s broad, H4, μ-NH(CH_2—CH_2)NH_2], 3.58 [s broad, H, μ-NH(CH_2—CH_2)NH_2], 2.98 [s broad, μ-NH(CH_2—CH_2)NH_2], 2.81 [s broad, μ-NH(CH_2—CH_2)NH_2]. ^{13}C-NMR (THF-d_8, 75 MHz): δ/ppm: 229.78 - 217.57 [s broad, CO]; 57.72 [s, μ-NH(CH_2—CH_2)NH_2]; 44.22 [s broad, μ-NH_2(CH_2—CH_2)NH_2].

4.4. ^{1}H-NMR monitoring experiments

Formation of complex (**3**) was monitored by proton NMR. 15.4 mg (0.075 mmol) of (**1**) and 29.0 mg (0.075 mmol) of dppe were dissolved in cyclohexane-d_{12}, previously degassed in an NMR tube saturated with nitrogen; 10 μL (0.075 mmol) of C_6F_5SH were added, heated to 75 °C and recording a spectrum every 15 min.

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Appendix A. Supplementary material

CCDC 778682–778688 contain supplementary crystallographic data for (**7**), (**8**), (**9**), (**2**), (**3**), (**4**), and (**5**) resp. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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