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One pot synthesis of dimanganese carbonyl complexes containing sulfur and phosphorus donor ligands using tricarbonylpentadienylmanganese

Marisol Reyes-Lezama [a], Herbert Höpfl [b], Noé Zúñiga-Villarreal [a,*]

[a] Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, 04510 México DF, México
[b] Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62210 Cuernavaca Morelos, México

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Abstract

The reaction of tricarbonylpentadienylmanganese with aryl mercaptans in the presence of phosphines or phosphites afforded dinuclear complexes, $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$; R = Ph for $PR'_3 = PPh_3$, PMe_3, $P(OMe)_3$, $P(OEt)_3$, $PMePh_2$ and R = *m*-, *p*-$NH_2C_6H_4S$–, for $PR'_3 = PPh_3$ in one pot synthesis. Two reaction routes were proposed for the formation of the dinuclear complexes depending on the relative basicity of the sulfur vs. phosphine ligands. Characterization of the complexes was effected in solution and, for $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PPh_3)_2]$, $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(P(OEt)_3)_2]$, and $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PMe_3)_2]$, by X-ray crystallographic analysis.

Keywords: Manganese carbonyls; Pentadienyl ligand; Phosphites; Tertiary phosphines; Thiols

1. Introduction

Transition metal pentadienyl complexes have drawn attention over the last two decades [1]. The bonding capabilities of the pentadienyl ligand are held responsible for the rich structural, synthetic, and reaction chemistry of the complexes containing it. As far as the reaction chemistry is concerned nucleophilic attack on pentadienyl complexes has been extensively explored. The range of tested pentadienyl complexes and nucleophiles is wide and includes both neutral and charged species in either the pentadienyl complex or the nucleophile, for obvious reasons reaction chemistry studies between neutral species have received least attention. Studies on the reactivity of the neutral complex η^5-tricarbonylpentadienylmanganese, $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ (**1**), (see Scheme 1) towards tertiary phosphines show that phosphine substitution for a carbonyl group takes place via an associative mechanism [2]. Interestingly, preparation of amino-, and -phosphinopentenyl ligands coordinated in an η^3-N and η^3-P fashion by reaction of **1** with amines, both secondary [3a] and primary [3c], and secondary phosphines [3b] involves formation of carbon–nitrogen and carbon–phosphorus bonds, respectively, with concomitant saturation of the pentadienyl ligand. When mercaptans react with **1** the pentadienyl ligand eliminates and the sulfur ligands coordinate to afford thiolate heterocubane species [4]. The potential synthetic advantages of the extrusion of the pentadienyl ligand by mercaptans has attracted our interest. Herein we describe the details of the reaction chemistry of **1** concerning the synthesis of dinuclear manganese complexes wherein the incorporation of the sulfur and phosphine ligands was effected in one pot syntheses.

2. Experimental

General considerations. All reactions were conducted under dry nitrogen atmosphere using standard vacuum line

* Corresponding author. Tel.: +52 5622 4431; fax: +52 56 16 22 03.
E-mail address: zuniga@servidor.unam.mx (N. Zúñiga-Villarreal).

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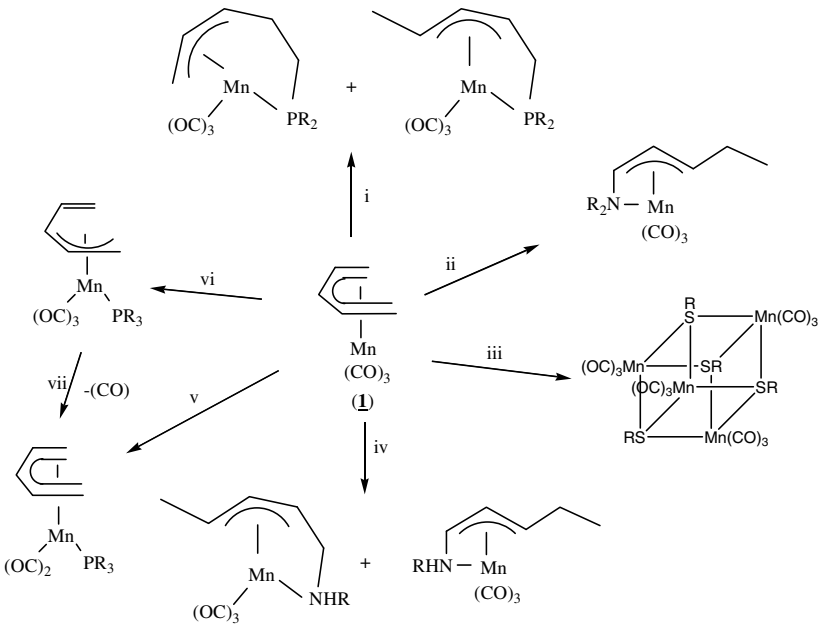


i, $PHPh_2$, rt, 41%; ii, R_2NH, Δ, 19.4-53.5%; iii, RSH, Δ, 21-24%; iv, $C_6H_{11}NH_2$, Δ, 29.2%; v, PR_3 and $P(OR)_3$, Δ, 10-51%; vi, PR_3, rt, 31-66%; vii, Δ.

Scheme 1.

and Schlenk techniques. Cyclohexane proved to be an adequate reaction solvent for the preparation of complexes **2**–**8** due to its relative high boiling point and low polarity. In all cases the products were insoluble in cyclohexane and product isolation was easily achieved (see below). 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 *ν*(CO) groups patterns. The starting materials in the cases of complexes **6** and **7** were insoluble in cold cyclohexane; however, heating of the reaction medium at cyclohexane reflux temperature afforded the products. The reaction times for these last two cases were determined by monitoring the consumption of **1** by IR spectra. 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. ^1H 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. Complex **1** [5] and $[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PMe_3)]$ [2] were prepared according to literature procedures. Phenyl mercaptan, phosphites, phosphines, *o*-, *m*-, and *p*-aminothiophenols were acquired from Aldrich and used as received. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. USA. Melting points were determined on a Fisher–Johns apparatus and are uncorrected.

2.1. General procedure for the synthesis of complexes 2–5

Equimolar amounts of $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ (**1**), (0.49 mmol, 100 mg) and the phosphine compound were mixed in 60 mL of fresh distilled cyclohexane in a 100 mL round bottom flask previously purged with nitrogen. Phenyl mercaptan (0.97 mmol, 107 mg) was then added and the mixture was set at reflux temperature. Samples were collected every 10 min for monitoring purposes (*ν*(CO) infrared pattern). After 40 min the reaction was completed. The solvent was eliminated under reduced pressure leaving behind deep purple products. The dry residue was treated with hexane (3 × 10 mL) to wash off unreacted starting materials. The remaining fraction was dissolved in dichloromethane (ca. 20 mL) and transferred via cannula to a Schlenk tube. Evaporation of dichloromethane under reduced pressured afforded complexes **2**–**5** as fine powders. Suitable crystals to conduct X-ray diffraction analyses were obtained from chloroform at 5 °C for a period of five days for **2** and from a mixture of dichloromethane/ethanol (4:1 resp.) at 5 °C for 6 weeks for **5**. Best results were obtained for **2** and in the case of **5** the atoms' connectivity could only be established due to a disorder in the ethoxy group of the coordinated phosphite.

Compound **2**: 74% yield, m.p. 154–157 °C. ^1H NMR ($CDCl_3$, 300 MHz): *δ*/ppm: 7.12 [m, SPh and PPh_3]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): *δ*/ppm: 66.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): *δ*/ppm: 138.0 [s, C_i, SPh]; 134.42 [s, C_o, SPh]; 127.11 [s, C_m, SPh]; 126.4 [s, C_p, SPh]; 133.41 [d, C_o, $^2J_{PC} = 10.6$ Hz, PPh_3]; 128.57 [d, C_m, $^3J_{PC} = 12.0$ Hz, PPh_3]; 129.0 [s, C_p, PPh_3]. MS (*m*/*e*): 992 $[M]^+$.

Compound **3**: 83% yield, m.p. 112–115 °C. Anal. Calc. for $C_{43}H_{36}O_5P_2S_2Mn_2$: C, 59.45; H, 4.71. Found: C, 58.69; H, 4.48%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.27 [m, SPh, PPh_2]; 2.17 [s br, PMe]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 49.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 138.14 [s, C_i, SPh]; 134.05 [s, C_o, SPh]; 127.58 [s, C_m, SPh]; 126.62 [s, C_p, SPh]; 136.56 [d, C_i, $^1J_{PC} = 40.5$ Hz, PPh_2]; 131.94 [d, C_m, $^2J_{PC} = 9.0$ Hz, PPh_2]; 129.47 [s, C_p, PPh_3]; 18.53 [d, $^1J_{PC} = 30.0$ Hz, Me]. MS (*m*/*e*): 868 $[M]^+$.

Compound **4**: 82% yield, m.p. 115–120 °C. Anal. Calc. for $C_{23}H_{28}O_{11}P_2S_2Mn_2$: C, 38.55; H, 3.91. Found: C, 37.86; H, 4.06%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.4 [m, 4H, H_o, SPh]; 7.1 [m, 6H, H_mH_p, SPh]; 3.63 [br s, 18H, $P(OMe)_3$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 181.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 138.34 [s, C_i, SPh]; 133.60 [s, C_o, SPh]; 127.99 [s, C_m, SPh]; 126.89 [s, C_p, SPh]; 52.82 [s br, $P(OMe)_3$]. MS (*m*/*e*): 716 $[M]^+$.

Compound **5**: 80% yield, m.p. 115–118 °C. Anal. Calc. for $C_{29}H_{40}O_{11}P_2S_2Mn_2$: C, 41.75; H, 5.15. Found: C, 41.89; H, 5.01%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.4 [m, 4H, H_o, SPh]; 7.1 [m, 6H, H_mH_p, SPh]; 3.98 [q, 12H, $^3J_{HH} = 7.5$ Hz, $P(OCH_2CH_3)_3$]; 1.23 [t, 18H, $^3J_{HH} = 7.5$ Hz, $P(OCH_2CH_3)_3$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 175.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 138.77 [s, C_i, SPh]; 133.62 [s, C_o, SPh]; 127.73 [s, C_m, SPh]; 126.6 [s, C_p, SPh]; 61.56 [s br, $P(OCH_2CH_3)_3$]; 16.1 [s br, $P(OCH_2CH_3)_3$]. MS (*m*/*e*): 800 $[M]^+$.

2.1.1. Detection of cis-1,4-pentadiene by ^{1}H NMR

Complex **1** and PPh_3 (1:1 molar ratio) were dissolved in degassed dry cyclohexane-d_{12} in an NMR tube purged with dry nitrogen. Two equivalents of PhSH were added. The reaction mixture was heated to 60 °C and monitored by ^{1}H NMR in the region 5.5–7 ppm (internal hydrogens of *cis*-piperylene) and the signals of 0.52 and 2.56 ppm corresponding to H_{anti} and H_{syn} of **1**, respectively. Complete disappearance of the latter and formation of *cis*-piperylene occurred within 30 min of reaction.

2.1.2. General procedure for the synthesis of complexes 6 and 7

Equimolar amounts of $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ (1.5 mmol, 300 mg for **6** and 1.2 mmol, 250 mg for **7**) and triphenylphosphine (1.5 mmol, 381 mg and 1.2 mmol, 318 mg, resp.) were mixed in 150 mL of fresh distilled cyclohexane in a 250 mL round bottom flask previously purged with nitrogen. Two equivalents of aminothiophenol (2.9 mmol, 364 mg of *m*- and 2.4 mmol, 303 mg of *p*-aminothiophenol) were then added and the mixture was set at reflux temperature. Samples were collected every 15 min for monitoring purposes. After 2 h for *m*-aminothiophenol and 2.5 h for *p*-aminothiophenol the reaction was completed. The reaction mixture was passed through a filter to separate the cyclohexane soluble **1** which did not react. The residue was dissolved in 20 mL of dichloromethane and filtered. The solvent was eliminated under reduced pressure leaving behind **6** and **7** as purple powders.

Compound **6**: 62% yield, m.p. 97–101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.39 [m, 30H, PPh_3]; 6.79 [s, 2H, H_m, *m*-$H_2NC_6H_4S$–]; 6.46 [s, 2H, H_o, *m*-$H_2NC_6H_4$-S–]; 6.15 [s, 2H, $H_{o'}$, *m*-$H_2NC_6H_4S$–]; 6.00 [s, 2H, H_p, *m*-$H_2NC_6H_4S$–]; 3.66, 3.43 [s, 4H, $-NH_2$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 66.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 249.14 [s, (μ-*C*O)]; 222.15 [d, *C*O, $^2J_{C-P} = 23.6$ Hz]; 145.36 [s, C_i(N), *m*-$H_2NC_6H_4S$–]; 138.97 [s, C_i(S), *m*-$H_2NC_6H_4S$–]; 137.24 [d, C_i, PPh_3, $J_{Ci-P} = 10.9$ Hz]; 133.90 [d, C_o, PPh_3, $^2J_{Co-P} = 8.6$ Hz]; 130.78 [s, C_o, *m*-$H_2NC_6H_4S$–]; 129.48 [s, C_p, PPh_3]; 128.88 [d, C_m, PPh_3, $^3J_{Cm-P} = 8.6$ Hz]; 124.75 [s, C_p, *m*-$H_2NC_6H_4S$–]; 121.06 [s, $C_{o'}$, *m*-$H_2NC_6H_4S$–]; 113.6 [s, C_m, *m*-$H_2NC_6H_4S$–]. MS (*m*/*e*): 967 $[M-2CO]^+$.

Compound **7**: 63% yield, m.p. 112–115 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.39 [m, 30H, PPh_3]; 6.55 [d, 4H, H_m, $^3J_{H_oHm} = 9.1$ Hz, *p*-$H_2NC_6H_4S$–]; 6.33 [d, 4H, H_o, $^3J_{H_mHo} = 9.1$ Hz, *p*-$H_2NC_6H_4S$–]; 3.6 [s, 4H, $-NH_2$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 67.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 250.11 [s, (μ-*C*O)]; 222.15 [d, *C*O, $^2J_{C-P} = 12.9$ Hz]; 145.26 [s, C_i(N), *p*-$H_2NC_6H_4S$–]; 136.79 [s, C_i(S), *p*-$H_2NC_6H_4S$–]; 135.41 [d, C_i, PPh_3, $J_{Ci-P} = 3.2$ Hz]; 133.80 [d, C_o, PPh_3, $^2J_{Co-P} = 9.8$ Hz]; 132.10 [s, C_o, *p*-$H_2NC_6H_4S$–]; 129.36 [s, C_p, PPh_3]; 127.84 [d, C_m, PPh_3, $^3J_{Cm-P} = 7.6$ Hz]; 115.42 [s, C_m, *p*-$H_2NC_6H_4S$–]. MS (*m*/*e*): 1023 $[M]^+$.

2.1.3. Preparation of 8

Equimolar amounts of $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ (**1**), (0.73 mmol, 150 mg) and trimethylphosphine (0.73 mmol, 55 mg) were mixed in 150 mL of fresh distilled cyclohexane in a 250 mL round bottom flask previously purged with nitrogen. Phenyl mercaptan (1.46 mmol, 160 mg) was then added and the mixture was set at reflux temperature. Samples were collected every 15 min for monitoring purposes (ν(CO) infrared pattern). After 1.5 h the reaction was completed. The solvent was eliminated under reduced pressure leaving behind a dark purple powder. The powder was washed with hexane (3 × 10 mL). Elimination of the solvent under reduced pressure afforded **8**; 87% yield. Suitable crystals for an X-ray analysis were obtained by diffusion of a dichloromethane solution of **8** in hexane at 5 °C for 2 weeks.

2.1.4. Alternative preparation of 8

Phenyl mercaptan (0.89 mmol, 98 mg) and $[\eta^3\text{-}(C_5H_7)Mn(PMe_3)(CO)_3]$ (0.45 mmol, 126 mg) were dissolved in 150 mL of cyclohexane in a 250 mL round bottom flask. The reaction mixture was refluxed for 1 h (until no further changes in the ν(CO) region of the IR spectrum were detected). The purple powder formed was separated by filtration, washed with hexane (ca. 20 mL) and dried under vacuum.

Compound **8**: 96% yield, m.p. 119–121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.33 [s, 2H, H_p, SPh]; 7.24 [s,

4H, H_o, SPh]; 7.13 [s, 4H, H_m, SPh]; 1.54 [d, 18H, PMe_3, $^2J = 8.5$ Hz]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 28.0 s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 246.61 [s, (μ-*C*O)]; 221.57 [br, *C*O]; 138.65 [s, C_i(S), SPh]; 133.58 [s, C_o, PMe_3]; 128.07 [s, C_m, SPh]; 19.17 [d, PMe_3, $J_{C-P} = 28.3$ Hz]. MS (*m*/*e*): 620 $[M]^+$.

2.2. Crystal data

See Table 1.

2.3. Crystal structure determinations

Data for complexes **2** and **8** were collected on a Bruker Smart Apex CCD diffractometer and used in the full matrix least squares refinement. The structures were solved by direct methods from final difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The residual electron densities were in the ranges of 0.911, −0.438 for **2** and 0.638, −0.241 e Å^{-3} for **8**. In the case of **8** a methyl group, C20, is distorted and was refined isotropically in two major contributors with site occupational factors of 0.51/0.49 for each atom. Suitable crystals of **2** were obtained from concentrated solutions in chloroform after several days at −4 °C, while crystals for **8** were obtained by slow vapor phase diffusion between its methylene chloride solution and hexane at 5 °C.

3. Results and discussion

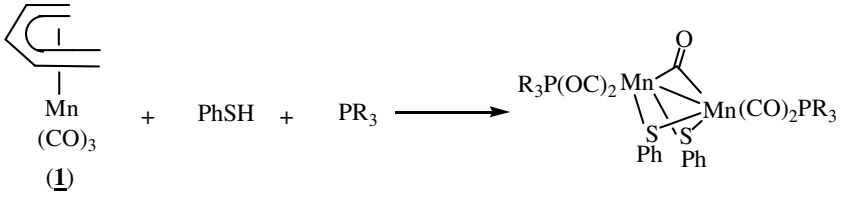
3.1. Synthesis of the dinuclear complexes $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PR_3)_2]$, $PR_3 = PPh_3$ (**2**), $PMePh_2$ (**3**), $P(OMe)_3$ (**4**), $P(OEt)_3$ (**5**), $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PPh_3)_2]$, $R = m\text{-}NH_2C_6H_4$ (**6**), $p\text{-}NH_2C_6H_4$ (**7**), and $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PMe_3)_2]$ (**8**)

3.1.1. Complexes **2**–**5**

Reaction of the pentadienyl complex **1** with sulfur and phosphine ligands afforded the dinuclear complexes shown in Scheme 2.

Table 1
Crystal data for **2**, **5**, and **8**

	2	**5**	**8**
Empirical formula	$C_{53}H_{45}Mn_2O_5P_2S_2$	$C_{29}H_{40}Mn_2O_{11}P_2S_2$	$C_{23}H_{28}Mn_2O_5P_2S_2$
M	992.8	800.55	620.39
Temperature (K)	100(2)	293(2)	293(2)
Crystal size (mm)	0.43 × 0.26 × 0.24	0.40 × 0.36 × 0.14	0.34 × 0.26 × 0.26
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pbca*
a (Å)	19.9882(11)	18.079(2)	18.5590(14)
b (Å)	22.1262(12)	21.510(3)	13.5015(10)
c (Å)	10.2251(5)	9.912(1)	22.9164(17)
α (°)	90	90	90
V (Å^3)	4522.2(4)	4522.2(4)	5742.3(7)
Z	4	4	8
θ Range for data collection (°)	2.04–25.00	1.50–25.00	1.78–25.00
Reflections collected	35940	3257	44551
Independent reflections	4087 [$R_{int} = 0.0577$]	3257	5052 [R_{int}=0.0531]
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0617$, $wR_2 = 0.1280$	$R_1 = 0.0896$, $wR_2 = 0.1914$	$R_1 = 0.0369$, $wR_2 = 0.0889$
R indices (all data)	$R_1 = 0.0658$, $wR_2 = 0.1299$	$R_1 = 0.2040$, $wR_2 = 0.2503$	$R_1 = 0.0520$, $wR_2 = 0.0935$



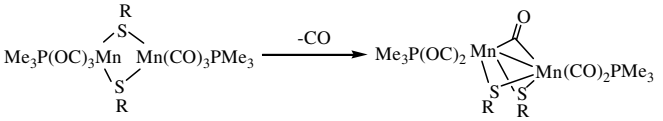
Complex	(**2**)	(**3**)	(**4**)	(**5**)
PR_3	PPh_3	$PMePh_2$	$P(OMe)_3$	$P(OEt)_3$

Scheme 2.

Preparation of **2**–**5** was achieved in one pot syntheses and best yields were obtained with the stoichiometric ratio 1:2:1 (**1**, mercaptan, phosphine, resp.) and 40 min under cyclohexane reflux. Reactions' yields varied in the range 74–83%. When phenyl mercaptan was used in an equimolar amount longer reaction times and lower yields were obtained. The products **2**–**5** are dark purple solids which decompose in solution at room temperature. In the solid state **2**–**5** are stable for long periods of time.

The formation of dinuclear complexes can be explained by the presence of the phosphine or phosphite in the reaction medium, since when no phosphine ligands are present phenyl mercaptan and **1** afford at room temperature the stable heterocubane tetramer $[Mn(SPh)(CO)_3]_4$ which is inert toward tertiary phosphines and phosphites at cyclohexane reflux temperature [4]; for this reason, the sequence of addition of the reagents must be controlled: the phenyl mercaptan should be added to a solution of **1** and the phosphine ligand. Monitoring of the reactions by IR in the *ν*(CO) region shows that **1** gradually disappears to yield dinuclear complexes **2**–**5**. As *cis*-1,3-pentadiene is a by-product of the reaction (see Section 2) we presume that the S–H bond of the sulfhydryl group undergoes fission to oxidatively add to the metal center to produce the $[Mn(H)(SPh)(\eta^3\text{-}C_5H_7)(CO)_3]$ species and by migration of H from the metal center to the pentadienyl ligand weakly coordinated *cis*-1,3-pentadiene is formed. At this stage we propose that the phosphine ligand displaces *cis*-1,3-pentadiene to afford the 16-electron species $[Mn(SPh)(PPh_3)(CO)_3]$ which dimerizes to $[Mn(\mu\text{-}SPh)(PPh_3)(CO)_3]_2$ in order to reach the more stable 18-electron configuration. Finally, loss of one CO renders complexes **2**–**5**, $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PR_3)_2]$. The reaction was monitored at room temperature for 48 h. No reaction intermediates were detected. We suggest that the transience of the proposed intermediates prevented their detection by IR spectroscopy.

Dinuclear complexes $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PPh_3)_2]$, R = Me, *p*-$MeC_6H_5$, are known since the late 1960s [6] and on the basis of IR spectroscopy their structure was proposed to be *trans*-$[Mn(\mu\text{-}SR)(PPh_3)(CO)_3]_2$. Over a decade later the methyl analog $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SMe)_2(PMe_3)_2]$ was reported [7] and the structure assigned by IR spectroscopy in solution corresponded to the structure determined by X-ray analysis 10 years later when the electrochemical behavior of a number of $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ complexes was reported [8]. Table 2 shows several methods for the preparation of $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ complexes. The introduction of phosphines or mercaptans in methods **A**–**E** is accomplished by steps; the yields in every case were those of the last reaction step. Method **F** consists in the formation of $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PMe_3)_2]$ by loss of a CO from the corresponding complexes *cis*-$[Mn(\mu\text{-}SR)(PMe_3)(CO)_3]_2$ by heating in benzene at 40 °C for 4 h [7] or heating at acetone, MeCN, or THF reflux temperature for 2 h [9] as shown in Eq. (1). Although it has been reported that the loss of a carbonyl group from *cis*-$[Mn(\mu\text{-}SMe)(PMe_3)(CO)_3]_2$ to yield $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SMe)_2(PMe_3)_2]$ takes place even at room temperature [7]

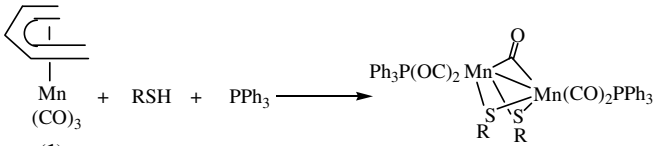


(1)

Method **G** (this work) has the advantage of incorporating mercaptans and phosphines in one step in one pot syntheses thus increasing the variety of ligands available for this reaction type (and the yield of the overall reaction as well), not leaving aside the potentiality of the present approach to pentadienyl compounds of other metals. It is worth mentioning that the nuclearity of the products obtained by reaction of **1** with mercaptans can be controlled by introduction of the phosphine ligand; thus, when no phosphine ligand is present in the reaction medium a nuclearity of four (heterocubane) is obtained. On the other hand, the presence of phospine ligands in the reaction medium of **1** with mercaptans leads to dinuclear complexes (the present case). In this respect it is important to mention that a related nuclearity control has been observed in the formation of carbonyl manganese disulfido or monosulfido clusters of arsines or phosphines of nuclearity 2, 4, and 6 prepared from $(Mn_2(CO)_9L)$, L = MeCN, PMe_2Ph and thiirane by sequential addition of the pnictogen ligands [10].

3.1.2. Complexes 6 and 7

In order to gain further insight into the formation path of the dinuclear complexes $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ we decided to utilize functionalized aryl mercaptans. The *o*-, *m*-, and *p*-aminothiophenols were made to react with a cyclohexane solution of **1** and PPh_3 under reflux. Complexes **6** and **7** (*m*, and *p*-aminothiophenol, resp.) were obtained with yields of ca. 60% according to the following equation:



Complex (**6**) R = *m*-$NH_2C_6H_4$-

(**7**) R = *p*-$NH_2C_6H_4$-

(2)

As in the case of complexes **2**–**5** in complexes **6** and **7** the 1:2:1 molar ratio (**1**, mercaptan, PPh_3, resp.) gave best yields. Products **6** and **7** are dark purple solids which decompose in solution at room temperature and in the solid state are stable for months. They are insoluble in non-polar organic solvents and soluble in dichloromethane and chloroform. Reaction times of 2 h for the formation of **6** and 2.5 h for **7** indicate that the amino $-NH_2$ group plays a part in diminishing the nucleophilicity of the *m*- and

Table 2
Preparation methods for $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ complexes

Synthetic method[a]	$[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ PR'_3/SR	Molar ratio	Reaction conditions	Reaction time	Yield (%)	Reference
A	PPh_3/SMe	$MnBr(PPh_3)(CO)_4$/	1,2-Dimethoxyethane reflux	1 h	75.0	[6]
	PPh_3/S-*p*-MeC_6H_4	Me_3SnSR 1:1.1			63.0	
B	PPh_3/SMe	$MnCl(PPh_3)_2(C\ O)_3$/		3 h	42.0	
		Me_3SnSMe 1:1.1				
C	PPh_3/SMe	$MnBr(PPh_3)_2(CO)_3$/	THF reflux	3 h	51.0	[8]
	PPh_3/SPh	nBu_3SnSR 1:1.5			46.0	
D	PMe_3/SMe	$Mn_2(\mu\text{-}SR)_2(CO)_8$/	THF reflux	2 h	82.0	
	PMe_3/SPh	$PMe_3$1:2.9			85.0	
	PMe_3/S-Bu^t			4 h	68.0	
	PMe_3/SMe	$Mn_2(\mu\text{-}SR)_2(CO)_8$/	Benzene 40 °C	4 h	22.0	[7]
		PMe_3 1:4.2				
E	PMe_3/SPh	$Et_4N[Mn_2(\mu\text{-}SR)_3\ (CO)_6]$/	Dichloromethane 25 °C	50 min	28.0	[9]
	PMe_3/S-Bu^t	$[Me_3O]BF_4/PMe_3$ 1:1.1:2			36.0	
	PMe_3/SMe				82.0	
F	PMe_3/SPh	*cis*-$[Mn_2(\mu\text{-}SR)_2(CO)_6$	Acetone, MeCN or THF reflux	2 h	85.0	
	PMe_3/S-Bu^t	$(PMe_3)]$			59.0	
	PMe_3/SMe	(see text)			Not reported	
G	PPh_3/SPh	η^5-$C_5H_7Mn(CO)_3$/	Cyclohexane reflux	40 min	73.9	This work
	PMe_3/SPh	PR'_3/RSH 1:1:2		1.5 h	87.0	
	PPh_3/S-*p*-$H_2NC_6H_4$			2 h	63.0	

[a] Methods: **A**: $MnBr(PPh_3)(CO)_4/Me_3SnSR$. **B**: $MnCl(PPh_3)_2(CO)_3/Me_3SnSMe$. **C**: $MnBr(PPh_3)_2(CO)_3/nBu_3SnSR$. **D**: $Mn_2(\mu\text{-}SR)_2(CO)_8/PMe_3$. **E**: $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]/[Me_3O]BF_4/PMe_3$. **F**: *cis*-$[Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)]$. **G**: η^5-$C_5H_7Mn(CO)_3/PR'_3/RSH$.

p-aminothiophenols: reaction times are longer than with phenyl mercaptan (40 min) for the same process under the same conditions. In the latter case introduction of phosphites $P(OR)_3$ has no consequences in the reaction time as it depends on the nucleophilicity of phenyl mercaptan. When the *o*-, *m*-, and *p*-aminothiophenols were reacted with **1** under cyclohexane reflux no reaction was detected due to the low solubility of the aminothiols in cyclohexane. Addition of the triphenylphosphine produced complexes **6** and **7**. Reaction of *o*-aminothiophenol with **1** and PPh_3 resulted in a deep purple compound in very low yields (less than 10%) insoluble in most organic solvents. IR spectroscopy in KBr pellet shows a ν(CO) pattern not corresponding with a dinuclear species $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}o\text{-}NH_2C_6H_4S\text{–})_2(PPh_3)_2]$ and in the ^{31}P NMR spectrum free $Ph_3P{=}O$ appears (presumably oxidized by adventitious oxygen). We believe that the amino group in the ortho position prevents coordination to the metal center for steric reasons. A related complex, Fig. 1, was obtained via a 16-electron carbonylmanganate [11]. In the present case such complex could be obtained by displacement of the phosphines; however, solubility data and ν(CO) indicate that we have a different species.

3.1.3. Complex 8

Phenyl mercaptan was added to a cyclohexane solution of **1** and PMe_3 and set at reflux temperature for 1.5 h. Complex **8**, $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PMe_3)_2]$, was obtained with 87% yield. The stoichiometry of the reaction was 1:2:1; **1**, phenyl mercaptan, trimethylphosphine, respectively. An increase in the amount of trimethylphosphine resulted in lower yields due to formation of $Me_3P{=}O$

Fig. 1. Molecular structure of a dinuclear carbonyl manganese complex with *o*-aminothiophenol.

(due to adventitious oxygen). Longer reactions times and lower yields were obtained when an equimolar ratio was employed. Complex **8** presents similar properties as **2**–**7**: deep purple color, stable for months in the solid state, unstable in solution of halogenorganic solvents, and not soluble in nonpolar organic solvents. The reaction time for the preparation of **8** seems to be controlled by the nucleophilicity of the PMe_3. Addition of phenyl mercaptan

Table 3
Infrared data for complexes **3**–**7**

Complex	ν(CO) cm^{-1}	
	Chloroform	KBr
3	1986 vs, 1950 s, 1908 m, 1807 wbr	1978 vs, 1944 s, 1908 m, 1786 wbr
4	2001 vs, 1965 s, 1924 m, 1831 wbr	1994 vs, 1962 s, 1912 m, 1808 wbr
5	1999 vs, 1962 s, 1921 m, 1824 wbr	1996 vs, 1964 s, 1914 m, 1808 wbr
6	1986 vs, 1951 s, 1909 m, 1799 wbr	1982 vs, 1946 s, 1901 m, 1792 wbr
7	1985 vs, 1948 s 1905 m, 1798 wbr	1980 vs, 1844 s, 1896 m, 1793 wbr

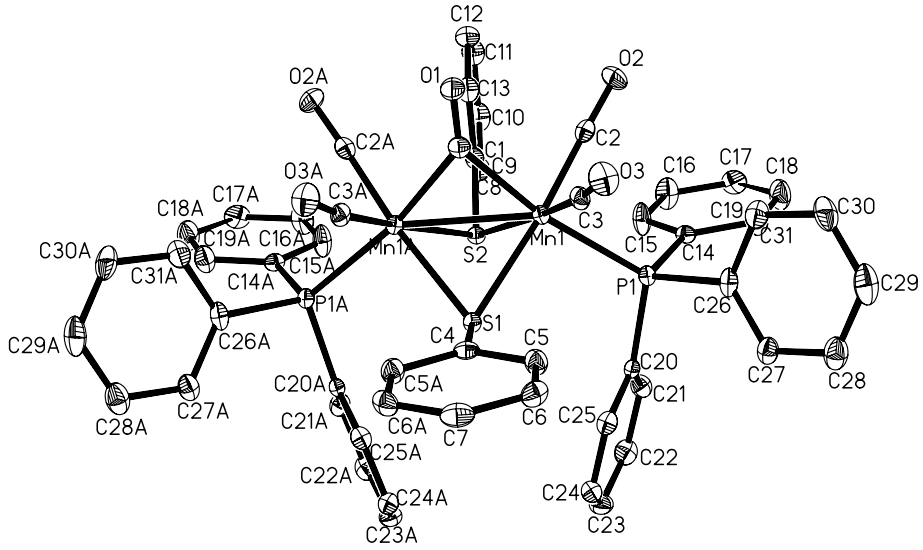
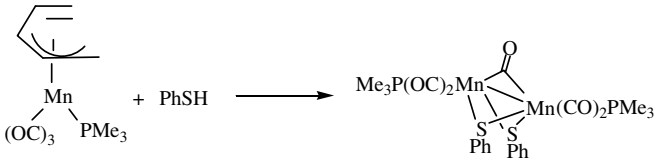


Fig. 2. Molecular structure of **2** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Mn(1)–Mn(1A) 2.648(1), Mn(1)–C(1) 2.008(4), Mn(1)–P(1) 2.347(1), Mn(1)–S(1) 2.323(1), C(1)–O(1) 1.168(6); Mn(1)–S(1)–Mn(1A) 69.49(4), Mn(1)–C(1)–Mn(1A) 82.5(2), C(3)–Mn(1)–P(1) 93.18(12), P(1)–Mn(1)–C(1) 170.2(1), C(2)–Mn(1)–S(1) 173.5(1), C(3)–Mn(1)–S(2) 170.1(1).

should be done once that **1** and PMe_3 are in solution; otherwise, formation of the stable heterocubane species $[Mn(SPh)(CO)_3]_4$ prevents the formation of **8**. Monitoring of the reaction by IR spectroscopy in the ν(CO) region showed that **1** gradually disappears to give place to an intermediate and then the reaction goes on to give **8**. It is known that **1** reacts with PMe_3 at room temperature to give $[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PMe_3)]$ [2] (see Scheme 1 entry vi of Section 1). Reaction of $[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PMe_3)]$ with phenyl mercaptan in a 1:2 molar ratio ($[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PMe_3)]$, phenyl mercaptan, resp.) under cyclohexane reflux for 1 h afforded complex **8** with 96% yield according to Eq. (3). Both reaction time and yield suggest the intermediacy of $[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PMe_3)]$ to **8**. It is worth noting that in the cases of complexes **2**–**7** the analogous complexes $[\eta^3\text{-}(C_5H_7)Mn(CO)_3(PR_3)]$ are not known.



(8) (3)

3.2. Infrared spectroscopy

Complexes **2**–**8** show, in solution and in the solid state, four characteristic bands within the ν(CO) carbonyl region: one very strong, one strong, one medium, and one weak in intensity. The first three bands correspond to terminal carbonyls and the weak one to the bridging CO.

In Table 3 are listed the IR ν(CO) frequencies of the new complexes reported in this work. IR spectroscopy was fundamental in the discovery of complexes $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$. When $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SMe)_2(PPh_3)_2]$ was first prepared, it was actually formulated as *trans*-$[Mn(\mu\text{-}SMe)(PPh_3)(CO)_3]_2$ on the basis of ν(CO) bands at 1979 s, 1946 s, and 1904 s cm^{-1} arising from terminal carbonyl groups [6]. No bridging carbonyl was reported. The first complex in which the bridging carbonyl group was assigned was $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SMe)_2(PMe_3)_2]$ [7]. Interestingly, this complex also provided the

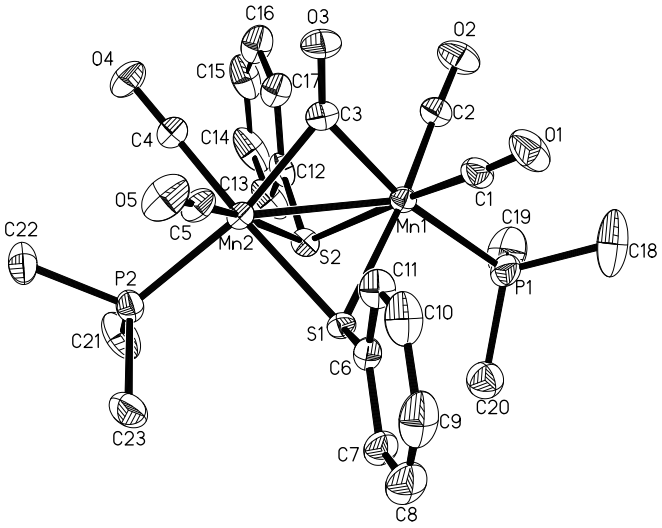


Fig. 3. Molecular structure of **8** including atom numbering scheme (ORTEP drawing with 25% probability ellipsoids). Selected bond lengths (Å) and angles (°): Mn(1)–Mn(2) 2.6002(6), Mn(1)–C(3) 2.011(3), Mn(1)–P(1) 2.2770(9), Mn(1)–S(1) 2.3462(8), C(3)–O(3) 1.165(3), Mn(2)–C(3) 2.028(3), Mn(2)–P(2) 2.2698(9), Mn(2)–S(1) 2.3342(8); Mn(1)–S(1)–Mn(2) 67.50(2), Mn(1)–C(3)–Mn(2) 80.16(11), C(3)–Mn(1)–P(1) 169.92(9), C(2)–Mn(1)–S(1) 170.81(10), C(1)–Mn(1)–S(2) 172.24(10), C(3)–Mn(2)–P(2) 168.14(9), C(4)–Mn(2)–S(1) 173.09(9), C(5)–Mn(2)–S(2) 170.68(9).

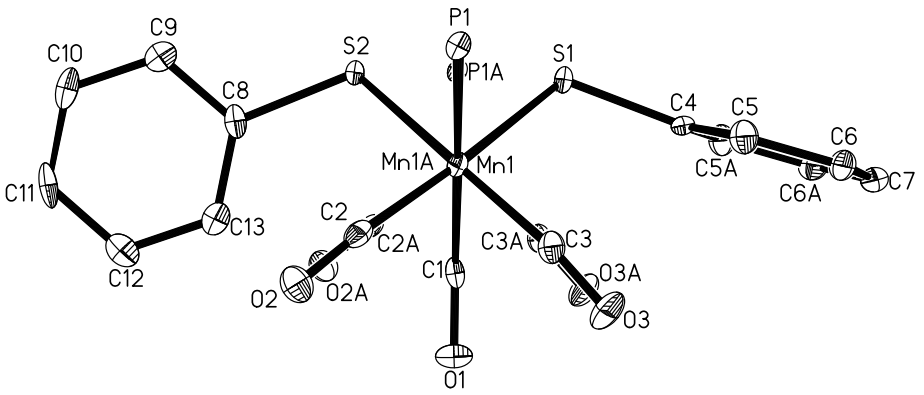


Fig. 4. View along the Mn(1)–Mn(1A) axis of complex **2**.

first and, to our knowledge, only structural data of the dinuclear complexes of the type $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ (see below) [8].

3.3. Structural studies

Suitable crystals for an X-ray analysis in the solid state were obtained for complexes **2**, **5**, and **8**. A disorder in the ethoxy groups of **5** prevented an adequate structure refining; as a result, only the atoms' connectivity could be established. In Figs. 2 and 3 are shown the structures of complex **2** and **8**, including their atom numbering schemes, respectively.

An X-ray analysis has been reported for the complex $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SMe)_2(PMe_3)_2]$ [8]. The structural characteristics for the complexes so far reported can be summarized as follows: the geometry around the manganese center is distorted octahedral. The distances of the Mn–Mn bonds lie within the range 2.581(1)–2.648(1) Å. The bulkier the substituent on the phosphorus or sulfur atoms the longer the Mn–Mn distances. The bridging thiolates and the bridging carbonyls are symmetrical. The carbon atom of the bridging carbonyl lies trans to the phosphine ligands, while the sulfur atoms of the thiolate ligands are trans to carbonyl groups. The substituents on the sulfur atoms present an *exo–syn* conformation and in complex **2** and **5** the phenyl rings orient themselves perpendicularly to each other, see Fig. 4, while in complex **8** the phenyl rings are parallel, Fig. 3.

4. Conclusions

Simple, one pot syntheses were devised for the preparation of dinuclear complexes of the type $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SR)_2(PR'_3)_2]$ using $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ and the corresponding phosphines and mercaptans. The relative nucleophilicity of both the mercaptan and the phosphine determines the reaction times. Shortest reaction times were observed for phenyl mercaptan. The incorporation of both phosphine and sulfur ligands in one reaction step is possible due to the occupancy of the vacant sites that the pentadienyl ligand leaves behind after its elimination. In this respect the complex $[\eta^5\text{-}(C_5H_7)Mn(CO)_3]$ can be regarded as an $-Mn(CO)_3$ transfer agent. We are currently further exploring the scope of this reaction for other nucleophiles.

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Appendix A. Supplementary material

CCDC 664666, 664667 and 664668 contain the supplementary crystallographic data for **2**, **5** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.015.

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