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Synthetic studies on the preparation of $[Mn(CO)_3{P(OR)_3}{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2}]$, R = Ph, Et^{\Rightarrow}



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ABSTRACT

Complexes [Mn(CO)₃P(OR)₃{ κ^2 -S,S'-Ph₂P(S)NP(S)Ph₂}], R = Ph, Et were prepared using four reaction routes. P(OPh)₃ presented similar electronic properties to CO in substitution reactions. Triorganylphosphites turned out to be finer electronic tuners than triorganylphosphines in related carbonyl complexes. The best route for preparation of each complex was dependent on the nature of the phosphite. Characterizations were achieved by IR, mass, NMR (¹H, ¹³C, ³¹P) spectroscopies, and by singlecrystal X-ray diffraction.

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1. Introduction

The complexes containing tetraphenylimidodichalcogenodiphosphinate ligands ($[N(EPPh_2)_2]^- E = O, S, Se, and Te$) have attracted wide attention in several areas of chemistry such as bioinorganic chemistry [1], homogeneous catalysis [2], material sciences [3] to mention but a few. The coordination modes of these ligands are accountable for the structure and reactivity that their metal complexes exhibit [4] and; in this respect, we have been investigating the chemistry of Mn and Re bromocarbonyls towards the $[N(EPR_2)_2]^-(E = O, S, Se; R = Me, Ph)$ anions and the reactivity of the resulting carbonyl complexes with phosphines which possess the ability to tune electron density at the metal center [5]. Phosphites are less sensitive to oxidation than phosphines displaying a comparable capacity to tune electron density at the metal center [6]; and their applications are not unknown, for example, in catalytic processes: Hydroformylation of olefins with a rhodium triphenyl phosphite complex is documented since the end of the 60's [7]; and more recently, it was reported the intermolecular hydroamination of olefins by a triphenyl phosphite gold complex [8]. It

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goes without saying that synthetic coordination and organometallic chemistry will benefit from further studies on the coordination capabilities of the phosphites. In the present study we turned our attention to assessing the coordination behavior of phosphites $P(OR)_3$, R = Et, Ph vs $[N(EPR_2)_2]^-$ towards $[MnBr(CO)_5]$.

2. Experimental

All preparative work was conducted in an atmosphere of dry oxygen free nitrogen using conventional Schlenk techniques. Toluene and cyclohexane were carefully dried and deoxygenated by distillation from sodium benzophenone ketyl. Dichloromethane was dried by distillation from phosphorus pentoxide. [MnBr(CO)₅], chlorodiphenylphosphine, hexamethyldisilazane, and potassium tert-butoxide were acquired from Strem Chemicals, Co. and used with further purification except for the no chlorodiphenylphosphine which was distilled under vacuum (102 °C, 1 mmHg). Triphenyl and triethyl phosphite were acquired from Sigma-Aldrich. Triethyl phosphite was distilled under vacuum. Sulfur was from Fisher Reagents Scientific Company. K[N(SPPh₂)₂] [9] and $[Mn(CO)_4{Ph_2P(S)NP(S)Ph_2-\kappa^2S}]$ (**a**) [10] were prepared according to literature procedures. IR spectra were obtained in solution (4000–580 cm⁻¹) and in KBr disk (4000-200 cm⁻¹) using a Bruker Alpha FT-IR spectrometer. ¹H(300 MHz), ¹³C(75.6 MHz), and ³¹P(121.7 MHz) NMR spectra were recorded in chloroform-d,



^{*} In memory of Professor Erika Martin Arrieta.

dichloromethane-d₂ and bezene-d₆ solutions at room temperature using a Bruker Advance 300 instrument, unless otherwise stated. Chemical shifts are reported in ppm relative to TMS (for ¹H and ¹³C) and H₃PO₄ (85% aqueous solution for ³¹P). FAB(+) mass spectra were recorded using a JEOL-SX 102A instrument with *m*-nitrobenzyl alcohol as matrix. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Reaction times were determined by IR spectroscopy (monitoring of the ν (CO) bands) and established as the time when no further changes occurred in the spectra.

2.1. Procedures

2.1.1. Route A

Synthesis of $[Mn(CO)_3{P(OR)_3}{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2}]$, R = Ph (1) and Et (2).

 $[Mn(CO)_4[\kappa^2-S,S'-Ph_2(S)NP(S)Ph_2]]$ (a) (0.043 g, 0.07 mmol) was added to a 250-mL round-bottom flask with stirring containing 100 mL of dry toluene. The temperature was set at 50 °C. An equimolar amount of the corresponding phosphite was added (triphenyl phosphite 0.022 g, 19 µL; triethyl phosphite 0.012 g, 13 µL) and after some time (30 min for triphenyl phosphite and 10 min for triethyl phosphite) the reaction finished and the heating was withdrawn. The solvent was eliminated under reduced pressure leaving an oily yellow product. A solid material was obtained when cold dry hexane (15 mL) was added. Crystallization was effected in a toluene/dichloromethane mixture at 4 °C for several days giving crystalline vellow powder.

Complex (1): Yield: 0.038 g (61%); m.p. 114–116 °C (dec.). $\nu_{max}(-ATR)/cm^{-1} 2020s$, 1948s, 1915s (CO); 1212s $\nu_{as}(P_2N)$; 569vs $\nu_{as}(PS)$; 515s $\nu_s(PS)$. $\nu_{max}(CH_2Cl_2)/cm^{-1} 2031s$, 1962s, 1928s (CO). ¹H NMR (CD₂Cl₂, 300 MHz): δ /ppm: 8.1–7.9 [m, H_o and H_o'(PNP)], 7.5–7.2 [m, aromatic protons: PNP and P(OPh₃)]. ¹³C{¹H} NMR (CD₂Cl₂, 75.6 MHz): δ /ppm: 151.72 [d, C_i, {P(OPh)₃}, ²J_{Ci-P[P(OPh)₃] = 12 Hz], 138.63 [d, C_i', (PNP), J_{Ci}-P(PNP) = 106 Hz], 137.48 [dd, C_i, (PNP), J_{Ci}-P(PNP) = 114 Hz, ⁴J_{Ci}-P[P(OPh)₃] = 8 Hz], 131.15–130.47 [m, C_m and C_m' (PNP)], 129.63 [s, broad, C_p and C_p' (PNP)], 129.58 [s, C_m {P(OPh)₃}], 128.30–127.72 [m, C_o and C_o' (PNP)], 124.87 [s, C_p {P(OPh)₃}], 121.22 [d, C_o {P(OPh)₃}, ³J_{Co}-[P(OPh)₃] = 4 Hz]. ³¹P{¹H} NMR (CD₂Cl₂, 121.7 MHz): δ /ppm: 173.7 [m, broad, {P(OPh)₃}], 40.8 [d, (PNP)³]_PNP-P(OPh)₃ = 24 Hz]. MS (m/e): 897 [M]⁺, 813 [M-3CO]⁺, 503 [M-3(CO) {P(OPh)₃}]⁺. Anal. Calcd for C₄₅H₃₅NO₆P₃S₂Mn: C, 60.20; H, 3.9; N, 1.56; S, 7.13%. Found: C, 58.31; H, 4.02; N, 1.56; S, 6.89%.}

Complex (**2**): Yield: 0.012 g (22%); m.p. 99–100 °C (dec.). $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2024s, 1950s, 1917s (CO). ¹H NMR (C₆D₅CD₃, 300 MHz): δ /ppm: 8.15–7.92 [m, H_o and H_o'(PNP)], 7.62–7.22 [m, aromatic protons, PNP], 4.25 [6H, quintet, $-OC\underline{H_2}CH_3$, ³J_{H-H} = 6 Hz, ³J_{H-P[P(OEt)3]} = 6 Hz], 1.16 [9H, t, $-OCH_2C\underline{H_3}$, ³J_{H-H} = 6 Hz]. ¹³C{¹H} NMR (C₆D₅CD₃, 75.6 MHz): δ /ppm: 219.68 [d, C_{eq}, (CO), ²J_{C-P} = 35 Hz], 214.91 [d, C_{ax}, (CO), ²J_{C-P} = 63 Hz], 140.46 [d, C_i (PNP), J_{Ci-P(PNP)} = 106 Hz], 139.39 [dd, C_i', (PNP), J_{Ci-P(PNP)} = 108 Hz, ⁴J_{Ci-P[P(OEt)3]} = 5 Hz], 131.89 [d, C_m (PNP), J_{Ci-P(PNP)} = 11 Hz], 131.62[s, C_p (PNP)], 131.05 [d, C_m' (PNP), J_{Ci-P(PNP)} = 11 Hz], 131.04 [s, C_p' (PNP)], 130.68–128.1 [m, C_o and C_o' (PNP)]], 62.52 [d, $-OC\underline{H_2CH_3}^2 J_{C-P[P(OEt)3]} = 6$ Hz], 16.65 [d $-OCH_2\underline{CH_3}$, ³J_{C-P[P(OEt)3]} = 5 Hz], ³¹P{¹H} NMR (C₆D₅CD₃, 121.7 MHz): δ /ppm: 153.42 [m, broad, {P(OEt)₃]], 36.45 [d, ³J_{PNP-P[P(OEt)3]} = 27 Hz]. MS (m/e): 753 [M]⁺, 669 [M-3CO]⁺, 503 [M-3(CO){P(OEt)₃]⁺. Anal. Calcd. for C₃₃H₃₅NO₆P₃S₂Mn: C, 52.59; H, 4.68; N, 1.86; S, 8.38%. Found: C, 52.86; H, 4.85; N, 1.74; S, 8.05%.

When the reaction for complex (**2**) was carried out in dichloromethane for 10 min at room temperature using equimolar amounts of the starting materials and an isolation procedure identical to the one above mentioned, the yield was 72%.

2.1.2. Route B

 $[MnBr(CO)_4{P(OR)_3}], R = Ph (b) and Et (c).$

[MnBr(CO)₅] (0.298 g, 1.08 mmol) was added to a round-bottom flask, equipped with a stirring bar, containing 200 mL of cyclohexane and heated to 50 °C; an equimolar amount of the corresponding phosphite (triphenyl phosphite 0.3 mL and triethyl phosphite, 0.2 mL) was added. The reaction was left for 90 min and after reaching room temperature, evaporation under vacuum afforded an oily yellow material, complex (**b**), that was washed with cold hexane (10 mL). The hexane was removed under reduced pressure leaving behind complex (**b**) as an orange solid material. In the case of complex (**c**), no isolation was effected due to decomposition of the product and, as soon as complex (**c**) was detected as the main product, the reaction was left at room temperature and stored at 0 °C; and the yield was calculated based on the amount of complex (**2**) obtained in a further step (see below).

Complex (**b**): Yield: 0.559 g (93%); m.p. 74–76 °C. $v_{max}(C_6H_{14})/cm^{-1}$ 2100 m, 2034s, 2021vs, 1976s (CO). ¹H NMR (CDCl₃, 300 MHz): δ /ppm: 7.3–7.2 [m, H_m], 7.2–7.1 [m, H_o and H_p]. ¹³C{¹H} NMR (CDCl₃, 75.6 MHz): δ /ppm: 150.91 [d, C_i, ²J_{Ci-P} = 11 Hz], 129.97 [s, C_m], 125.84 [s, C_p], 121.22 [d, C_o, ²J_{Co-P} = 5 Hz]. ³¹P{¹H} NMR (CDCl₃, 121.7 MHz): δ /ppm: 147.0 [s, broad]. MS (m/e): 556 [M]⁺, 477 [M – Br]⁺, 449 [M-Br(CO)]⁺, 444 [M-4(CO)]⁺, 365 [M-Br4(CO)]⁺. Anal. Calcd for C₂₂H₁₅O₇PBrMn: C, 47.44; H, 2.70%. Found: C, 47.29; H, 2.91%.

Complex (c): Yield: 0.11 g (25%); $\nu_{max}(C_6H_{14})/cm^{-1}$ 2094 m, 2030s, 2007vs, 1975s (CO). ³¹P{¹H} NMR (CDCl₃, 121.7 MHz): δ / ppm: 155.42 [s,{P(OEt)₃}].

2.1.2.1. $[Mn(CO)_3\{P(OPh)_3\}\{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2\}]$ (1) from (**b**). (0.1 g, 0.18 mmol) of $[MnBr(CO)_4P(OPh)_3]$ (**b**) and an equimolar amount of K[N(SPPh_2)_2] (0.088 g) were added to a round-bottom flask containing 150 mL of dry toluene. The reaction mixture was set at reflux temperature for 70 min; the heating was withdrawn and the reaction mixture was left to reach room temperature and passed through a sintered glass funnel containing CeliteTM. The solvent was eliminated under reduced pressure giving an oily yellow material. 5 mL of cold hexane was added obtaining a yellow powder. The solid was washed with ice cold hexane (3 × 5 mL) to afford complex (1). Yield: 0.077 g (48%).

2.1.2.2. $[Mn(CO)_3\{P(OEt)_3\}\{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2\}]$ (2) from (c). Complex (c) $[MnBr(CO)_4\{P(OEt)_3\}]$, dissolved in 180 mL of cyclohexane previously stored at 0 °C, was allowed to reach room temperature in a 250-mL round-bottom flask with a magnetic stirring bar and $K[N(SPPh_2)_2]$ (0.283 g, 0.58 mmol) was added and maintained under cyclohexane reflux for 3 h. The solution was left to reach room temperature and passed through a sintered glass funnel containing CeliteTM. The solvent was removed under reduced pressure giving an oily yellow material. 15 mL of ice cold hexane was added obtaining a yellow solid after evaporation under reduced pressure. The compound was purified using a silica gel column under an inert atmosphere. Complex (**2**) was obtained in 47% yield (0.2 g) based on K[N(SPPh_2)_2].

2.1.3. Route C

2.1.3.1. mer,trans-[MnBr(CO)₃{P(OPh)₃}₂] (**d**). Into a 200-mL roundbottom flask, furnished with a stirring bar and 150 mL of dry cyclohexane, were added 1.1 mmol (0.3 g) of [MnBr(CO)₅] and 2.2 mmol (0.6 mL) of triphenyl phosphite. The reaction mixture was set at reflux temperature and left for 90 min. The IR spectrum showed bands at 2067w, 2050s, 1994s and 1949s cm⁻¹ indicating the presence of both isomers *fac/mer,trans* in a rate roughly estimated as 40/1, resp. The solvent was eliminated under reduced pressure obtaining a yellow powder, which was washed with 10 mL of cold hexane. After complex (**d**) was crystalized from a 1:1 mixture of CH₂Cl₂/hexane at 4 °C for several days isomerization had occurred to isomer *mer,trans* showing IR ν (CO) bands in hexane at 2067w, 1994s and 1949s cm⁻¹. Yield: 0.75 g (82%), m.p. 161–163 °C. ν_{max} (CH₂Cl₂)/cm⁻¹ 2070w, 2000s, 1949s (CO). ¹H NMR (CDCl₃, 300 MHz): δ /ppm: 7.22–7.17 [m, H_m], 7.09–7.04 [m, H_o and H_p]. ¹³C {¹H} NMR (CDCl₃, 75.6 MHz): δ /ppm: 151.50 [d, C_i . ²J_{Ci-P[P(OPh)3]} + ⁴J Ci-P[P(OPh)3'] = 11 Hz], 129.63 [s, C_m], 125.10 [s, C_p], 121.3 [s, C_o]. ³¹P {¹H} NMR (CDCl₃, 121.7 MHz): δ /ppm: 155.60 [s, broad]. MS (m/e): 840 [M]²⁺, 838 [M]⁺, 759 [M - Br]⁺, 675 [M-3(CO)Br]⁺, 365 [M-3(CO)Br{P(OPh)₃]⁺. Anal. Calcd for C₃₉H₃₀O₉P₂BrMn: C, 55.81; H, 3.58%. Found: C, 55.40; H, 3.69%.

2.1.3.2. fac-[MnBr(CO)₃{ $P(OEt)_3$ }₂] (e). To a 250-mL round-bottom flask with 80 mL of dry cyclohexane were added 0.58 mmol (0.160 g) of [MnBr(CO)₅] and 1.166 mmol (0.2 mL) of triethyl phosphite. The reaction mixture was heated to 55 °C and stirred for 90 min. The solvent was eliminated under reduced pressure, obtaining a yellow powder, which was dissolved in hexane and purified using a silica gel column. Crystallization was effected in a mixture of hexane/dichloromethane at 4 °C for several days yielding crystalline orange powder.

Complex (**e**): Yield 0.26 g (79%), m.p. 98–99 °C. $\nu_{max}(C_6H_{12})/cm^{-1}$ 2043s, 1968vs, 1935s (CO). ¹H NMR (CDCl₃, 300 MHz): δ /ppm: 4.20 [12H, m, $-OC\underline{H}_2CH_3$], 1.36 [18H, t, $-OCH_2C\underline{H}_3$, ³J_{H-H} = 6 Hz]. ¹³C {¹H} NMR (CDCl₃, 75.6 MHz): δ /ppm: 219.01 [s, C_{eq} , (CO)], 214.48 [m, C_{ax} , (CO)], 61.85 [s, $-OC\underline{H}_2CH_3$], 16.02 [s, $-OCH_2C\underline{H}_3$]. ³¹P{¹H} NMR (CDCl₃, 121.7 MHz): δ /ppm: 164.35 [s,{P(OEt)_3}]. MS (m/e): 552 [M]⁺, 466 [M-3CO]⁺, 387 [M-Br3(CO)]⁺, 300 [M-{P(OEt)_33(CO)}, 221 [M-Br{P(OEt)_33(CO)}^+Anal. Calcd for C₁₅H₃₀O₉P₂BrMn: C, 32.69; H, 5.49%. Found: C, 32.56; H, 5.41%.

2.1.3.3. $[Mn(CO)_3{P(OR)_3}{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2}]R = Ph, (1) from (d) and <math>R = Et$, (2) from (e). fac-[MnBr(CO)_3{P(OR)_3}_2], R = Ph 0.12 mmol, 0.1 g, 85 µL; R = Et, 0.12 mmol, 0.07 g, 72 µL was dissolved in 150 mL of dry toluene. An equimolar amount (0.058 g) of K[N(SPPh_2)_2] was added. The reaction mixture was set to reflux temperature for 95 min and the heat was withdrawn to allow the mixture to reach room temperature. Then it was passed through a sintered glass funnel which contained CeliteTM. The solvent was eliminated under reduced pressure giving an oily-yellow material which was dissolved in 5 mL of cold hexane and stirred for 30 min, noticing the formation of a yellow solid. The solid was filtered and washed with ice cold hexane (3 × 5 mL) and dried under vacuum. Complex (1): Yield 0.066 g (61%). In the case of P(OEt)_3 the reaction

Table 1Crystal data of (1) and (2).

	(1)	(2)	
Molecular formula	$C_{45}H_{35}MnNO_6P_3S_2$	C ₃₃ H ₃₅ MnNO ₆ P ₃ S ₂	
M	897.71	753.59	
Temperature	100(2)K	298(2)K	
Crystal size (mm)	$0.48 \times 0.42 \text{ x } 0.35$	$0.41 \times 0.37 \ x \ 0.22$	
Crystal system	Monoclinic	Triclinic	
Space group	P2 ₁ /c	P-1	
a (Å)	20.749(3)	9.38080(10)	
b (Å)	10.1326(16)	12.02600(10)	
<i>c</i> (Å)	19.751(3)	17.2940(2)	
α (°)	90	94.1020(10)	
β(°)	95.818(3)	92.0340(10)	
γ (°)	90	110.6820(10)	
V (Å ³)	4131.1(11)	1816.73(3)	
Z	4	2	
θ Range for data collection (°)	1.97-25.00	1.817-25.348	
Reflections collected	38902	17822	
Independent reflections	7280 ($R_{int} = 0.0457$)	$6631 (R_{int} = 0.0224)$	
Goodness-of-fit on F ²	1.144	1.052	
Data/restraints/parameters	7280/0/523	6631/0/418	
Final R indices $[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0382$, w $R_2 = 0.0909$	$R_1 = 0.0341$, $wR_2 = 0.0885$	
R indices (all data)	$R_1 = 0.0399, wR_2 = 0.0920$	$R_1 = 0.0404, wR_2 = 0.0938$	

(1)

was left under toluene reflux for 4 h during which the IR ν (CO) pattern did not change.

2.1.4. Route D 'one-pot'

2.1.4.1. Synthesis of $[Mn(CO)_3\{P(OR)_3\}\{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2\}]$, R = Ph (**1**) and Et (**2**). In a 200 mL round bottom flask with 150 mL of dry toluene were added $[MnBr(CO)_5]$ (0.106 g, 0.38 mmol), an equimolar amount of phosphite (P(OPh)_3, 0.1 mL, $\rho = 1.184$ g/mL and P(OEt)_3, 0.065 mL, $\rho = 0.969$ g/mL) and 0.186 g of K[N(SPPh_2)_2]. The reaction mixture was stirred and set at reflux temperature and after some time (40 min for triphenyl phosphite and 30 min for triethyl phosphite) the reaction finished and the heating was withdrawn. The reaction was left to reach room temperature and filtered using a sintered glass funnel containing CeliteTM. The solvent was eliminated under reduced pressure leaving an oily yellowish product. 5 mL of ice cold hexane was added and after stirring for 20 min a yellow powder formed. Finally, the solid material was filtered off and dried under vacuum. Complex (**1**): Yield: 0.14 g (40%); Complex (**2**): Yield 0.046 g (16%).

2.2. Crystal data

X-ray diffraction data were collected on Bruker Smart Apex CCD diffractometer Mo K α ($\lambda = 0.7103$ Å) [11] at 100 K. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix last-squares procedures on F^2 and corrected for absorption with SADABS (SAINT-NT) [12]. Structure solution refinement and data output were carried out with the SHELXL-97 program package [13]. Non-hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in geometrically calculated positions using the riding model.

Suitable crystals of (1), (2), (d), and (e) were obtained from a $CH_2Cl_2/hexane 1:1$ solution and (b) from hexane; all of them at 4 °C for several days. Data were collected on a Bruker Smart Apex CCD diffractometer. The X-ray analysis of the poor-quality crystals, in the case of complex (e), served only to establish atom connectivity.

See Table 1 for Crystal data of complexes (1) and (2) and Tables SM1 and SM2 of the Supplementary Material for (b) and (d), respectively.

2.2.1.
$$[Mn(CO)_3 \{P(OR)_3\} \{\kappa^2 - S, S' - Ph_2P(S)NP(S)Ph_2\}], R = Ph(1), Et(2)$$

 (\mathbf{n})

3. Results and discussion

3.1. Syntheses

3.1.1. Route A

The preparation of precursor (**a**), $[Mn(CO)_4[\kappa^2-S,S'-Ph_2P(S)NP(S) Ph_2]]$, was effected according to the literature [10].

3.1.1.1. Step ii. The relative nucleophilicity of the triorganophosphites was reflected in the reaction times determined by IR spectroscopy (10 min vs 30 min for triethyl vs triphenyl phosphite in toluene at 55 °C, resp.). Since it is well known that most carbonyl compounds react by a dissociative mechanism [14], it is noteworthy that complex (a) does not. Such behavior is a result of the presence of $[N(SPPh_2)_2]$ in (**a**)'s coordination sphere and has been found in substitution reactions with trialkyl- and triarylphosphines [5(a)]. When the reaction was carried out in boiling cyclohexane the reaction time was 1.5 h, however, the yield was not determined due to extensive decomposition of complex (2). The low yield of (2) both in toluene and boiling cyclohexane, therefore, may have stemmed from its thermal instability. In both cases the reaction mixture reached a yellow color which eventually faded to afford a dark brown precipitate, presumably MnO₂. On the other hand, when the reaction was effected in dichloromethane it took 10 min to completion at room temperature with a 72% yield. It is apparent that solvent polarity plays a key role in this type of reaction and solvent change brings about a change in reaction mechanism. The carbonyl substitution regioselectivity was a result of a mutually CO's *trans* effect to afford the corresponding *fac* manganacycle carbonyls (1) and (2).

3.1.2. Route B

3.1.2.1. Step iii. Our aim to prepare products (**b**) and (**c**) was to assess their reactivity towards $K[[N(SPPh_2)_2]]$. A couple of syntheses of (**b**) have been previously reported: One consisted in the reaction of $[Mn_2(CO)_8\{P(OPh)_3\}_2]$ and Br_2 [15]; and the other, in the reaction of $[MnBr(CO)_5]$ with $P(OPh)_3$ [16]; neither report informed about the procedure details and characterization was accomplished solely by IR spectroscopy. We chose to synthesize (**b**) according to the latter procedure due to commercial availability of the starting materials. Equimolar amounts of $[MnBr(CO)_5]$ and $P(OPh)_3$ were reacted in cyclohexane at 50 °C for 90 min giving (**b**) in 93% (see **Experimental**). IR monitoring of the reaction showed that diphosphite complex (**d**) was present in small amounts even when an excess of the manganese carbonyl precursor was used at lower reaction temperatures. No separation of (**d**) was effected due to its similar physical properties to (**b**).

In the case of the triethyl phosphite analog, complex (**c**), the same procedure as (**b**), i.e., starting from [MnBr(CO)₅] and P(OEt)₃, was followed. At the end of the reaction (**c**) was the major product (characterization of (**c**) by spectroscopies other than ${}^{31}P{}^{1}H{}-NMR$ and IR was not successful due to is instability); attempts at isolating (**c**) were unsuccessful though. No reaction intermediates were observed by IR reaction monitoring of *v*(CO) bands (Supplementary Material SM3).

3.1.2.2. Step iv. The IR monitoring of formation of complex (1) starting from (**b**), step (iv) of Scheme 1, is shown in Fig. 1.



 $\label{eq:scheme 1. Reaction routes for the synthesis of [Mn(CO)_3{P(OR)_3}{$c^-S,S'-Ph_2P(S)NP(S)Ph_2]}, R = Ph (1) and Et (2).$

(1). Route A: i, 1:1, r.t., THF, 6 h, 74%; ii, 1:1, 50 °C, toluene, 30 min, 61%. Route B: iii, 1:1, 50 °C, cyclohexane 90 min, 93%; iv, 1:1, toluene reflux, 70 min, 48%. Route C: v, 2:1 (P(OPh)₃:MnBr(CO)₅), cyclohexane reflux, 90 min, 82% (*fac/mer,trans*, 40/1, resp.); vi, 1:1, toluene reflux, 95 min, 61%. Route D: vii, 1:1:1, toluene reflux, 40 min, 40%. (2). Route A: ii, 1:1, r.t., dichloromethane, 10 min, 72% (50 °C, toluene, 10 min, 22%). Route B: iii, 1:1, 50 °C, cyclohexane 90 min, 90%; iv, 1:1, cyclohexane reflux, 3 h, 47%. Route C: v, 2:1 P(OEt)₃:MnBr(CO)₅, 55 °C, cyclohexane, 90 min, 79%. vi, 1:1, toluene reflux, 4 h, no reaction. Route D: vii, 1:1:1, toluene reflux, 30 min, 16%.

The tetracarbonyl complex $[Mn(CO)_4[\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2]]$ (2088, 2017, 1994, 1953 cm⁻¹) (**a**) appears at 30 min and is present till the end of the reaction as a minor product; its presence may be justified by formation of complex (**f**) (not detected in the ir monitoring), depicted in Fig. 2, resulting from attack by $K[N(SPPh_2)_2]$ to $[MnBr(CO)_4[P(OPh)_3]]$ (**b**): Once complex (**f**) is formed coordination of the other sulfur atom of the $[N(SPPh_2)_2]^-$ ligand gives rise, upon extrusion of triphenyl phosphite, to chelate complex (**a**) on the one hand; and, on the other to complex (**1**) upon extrusion of a carbonyl group. At the end of the reaction the main product was (**1**) due to recoordination of $P(OPh)_3$ and CO release.

When the reaction was carried out with complex (**c**) no complex (**a**), $[Mn(CO)_4[\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2]]$, was detected. Such behavior underlines the difference in steric (Tolman cone angle P(OR)₃, R = Ph, 128°, R = Et, 109°) and electronic (pKa P(OR)₃, R = Ph, -2.0, R = Et, 3.31) properties of the phosphites used in the present work [17], being triphenyl phosphite closely related to a CO group in its coordination behavior; while the



Fig. 2. Reactions of complex (f).



Fig. 1. Reaction monitoring of formation of complex (1).

triethyl phosphite binds stronger the metal center and thus preventing the formation of the tetracarbonyl complex [Mn(CO)₄{ κ^2 -S,S'-Ph₂P(S)NP(S)Ph₂}] (a).

3.1.3. Route C

3.1.3.1. Step v. The similarity of the coordinating ability of $P(OPh)_3$ and CO encouraged us to prepare diphosphite complexes (**d**) and (**e**) and explore their reactivity towards $K[N(SPPh_2)_2]$ to achieve (**1**) and (**2**), for comparison purposes.

Triphenyl phosphite and $[MnBr(CO)_5]$ were reacted in a 2:1 M ratio, resp. under cyclohexane reflux for 90 min to give (**d**) in 85% yield as a mixture of isomers *fac/mer,trans* being the latter in small amounts (40:1 resp. as roughly determined by IR). Both isomers have been reported and characterized by elemental analysis and IR spectroscopy and proposed that the *fac/mer,trans* isomerization takes place by way of a five coordinate intermediate [18]. The *fac* isomer was reported to form at 37 °C for 12 h; while, the *mer,trans* isomer formed at 55–60 °C for 16 h; both in chloroform and with a molar ratio 5:1 Triphenyl phosphite/[MnBr(CO)₅] resp.; in our hands, isomer *fac* was the main reaction product and when it was set at low temperature for several days it crystalized as the *mer,trans* isomer as determined by a single crystal X-ray analysis and IR spectroscopy. Such solid-state isomerization has been observed in [MnBr(CO)₄PPh₃] when rearranging from *cis* to *trans* isomer [15].

Complex *fac*-(**e**) was formed upon reaction of a 2:1 M ratio, $P(OEt)_3/[MnBr(CO)_5]$ resp., in cyclohexane at 55 °C for 90 min and isolated as a yellow material in 79% yield. IR monitoring showed that after 90 min the *fac* isomer started to isomerize to the *mer*,*trans* isomer and at 2.5 h isomerization reaches an equilibrium where the *fac* isomer is still the major isomer. IR spectra of both *fac* and *mer*,*trans* isomers of complex (**e**) have been reported and our data match well [19].

3.1.3.2. Step vi. When complex (**d**), freshly prepared, and K [N(SPPh₂)₂] were set to react under toluene reflux for 95 min complex (**1**) was achieved in 61% yield. The reaction monitoring by IR and ³¹P-{¹H} NMR showed no extrusion of carbonyl group to realize the bis(triphenyl phosphite) complex [Mn(CO)₂{-P(OPh)₃}₂{ κ^2 -S,S'-Ph₂P(S)NP(S)Ph₂}], but straightforward formation, upon triphenyl phosphite elimination, of final product [Mn(CO)₃{P(OPh)₃}{ κ^2 -S,S'-Ph₂P(S)NP(S)Ph₂}] (**1**). No apparent isomerization of *fac* to *mer,trans* isomer was detected by IR monitoring of the ν (CO) bands (Supplementary Material SM4).

IR monitoring of reaction of complex (\mathbf{e}) with $K[N(SPPh_2)_2]$

Table 2			
Summary of Routes A – D for complexes	(1)) and	(2)

under the reaction conditions employed for preparation of complex (**1**) showed no formation of complex (**2**) whatsoever, the spectrum remaining unchanged for 4 h (not even *fac* to *mer,trans* transformation was detected). Such lack of reactivity could be caused by the higher electron density at the metal center of (**e**) (2043, 1968, and 1935 cm⁻¹ in cyclohexane) compared to (**d**) (2050 1994, and 1949 cm⁻¹ in hexane) as inferred from their *fac* isomers' IR *v*(CO) bands.

3.1.4. Route D

The equimolar reaction of [MnBr(CO)₅], K[N(SPPh₂)₂], and the corresponding phosphite constituted one pot Route D. Both reactions were carried out in toluene at reflux temperature. In the case of P(OPh)₃, the reaction took 60 min to reach completion giving complex (1), $[Mn(CO)_3{P(OPh)_3}{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2}]$, in 40% yield. IR reaction monitoring (Supplementary Material SM5) showed that at 20 min monophosphine complex (b) started to appear along with the tetracarbonyl complex (**a**). This shows that both $P(OPh)_3$ and $K[N(SPPh_2)_2]$ are competing for $[MnBr(CO)_5]$. At 35 min of heating, complex (1) was present along with complex (a). It is apparent then that complex (1) is firstly form from reaction of (**b**) and K[N(SPPh₂)₂]. At 45 min both complexes, (**a**) and (**1**), reached an equilibrium where the latter was the major product. The comparative nucleophilic power of K[N(SPPh₂)₂] and P(OPh)₃ rendered Route D's yield low. Under same reaction conditions [MnBr(CO)₅], K[N(SPPh₂)₂], and triethyl phosphite formed complex (2), $[Mn(CO)_3{P(OEt)_3}{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2}]$, in 16% yield within 30 min at toluene reflux temperature; IR monitoring of the reaction showed no further changes upon longer heating. Such poor yield may be accounted for by formation of complex (**e**) within 30 min at toluene reflux temperature which, as above mentioned, was reluctant to further react with K[N(SPPh₂)₂].

The yields of the reaction Routes A - B are shown in Table 2 for comparative purposes.

3.2. Infrared spectroscopy

The IR spectra of (1) and (2) are similar and show three bands in CH_2Cl_2 solution in the $\nu(CO)$ carbonyl region corresponding to the 2A' + A" vibrational modes [20] arising from the carbonyl groups' local symmetry with a C_s point group assigned to mononuclear complexes with *fac* disposition involving both sulfur atoms [21]. The higher energy wavenumber corresponding to an A' vibrational mode (2031 and 2024 cm⁻¹ for complexes (1) and (2), resp.) reflects

Route	Complex	Step	Molar Ratio	Reaction conditions	Reaction time	Partial Yield (%)	Total Yield (%)
Α	(1)	i	1:1	THF, r. t.	6 h	74.0	45.1
		ii	1:1	Toluene, 50 °C	30 min	61.0	
	(2)	i	1:1	THF, r. t.	6 h	74.0	53.3
		ii	1:1	CH_2Cl_2 , r. t.	10 min	72.0	
В	(1)	iii	1:1	Cyclohexane reflux	90 min	93.0	44.6
		iv	1:1	Toluene reflux	70 min	48.0	
	(2)	iii	1:1	Cyclohexane reflux	90 min	90.0	42.3
		iv	1:1	Cyclohexane reflux	3 h	47.0	
С	(1)	v	2:1 P(OPh) ₃ /MnBr(CO) ₅	Cyclohexane reflux	90 min	85.0	51.9
		vi	1:1	Toluene reflux	95 min	61.0	
	(2)	v	2:1	Cyclohexane 55C	90 min	79.0	_
			P(OEt) ₃ /MnBr(CO) ₅	-			
		vi	1:1	Toluene reflux	4 h	_	
D	(1)	vii	1:1:1	Toluene reflux	40 min	_	40.0
	(2)	vii	1:1:1	Toluene reflux	30 min	_	16.0

a stronger interaction of triethyl phosphite with the metal center compared with triphenyl phosphite.

In a previous work by us, the syntheses of complexes $[Re(CO)_3(PR_3)\{\kappa^2-S,S'-Ph_2P(S)NP(S)Ph_2\}]$, R = Ph, Me; among others, were reported [5a]; their $\nu(CO)$ wave numbers together with those of complexes (1) and (2) are shown in Table 3.

The difference in wave number values between the phosphine complexes is small (ca. 5 cm⁻¹) compared to the phosphite complexes (7–12 cm⁻¹); such behavior points to a finer electronic tuning at the metal center by the phosphites in the manganese complexes; further studies are needed to find out if this holds true for phosphites in the respective rhenium complexes or, for that matter, in the respective phosphine complexes of manganese.

The IR spectra of complexes (**b**) [15], (**d**) [18], and (**e**) [19] have been reported elsewhere and agree with ours. The IR spectrum of (**c**) presents four bands in the ν (CO) region in cyclohexane: 2094 m, 2030s, 2007vs, 1975s cm⁻¹ pointing to a C_{2v} local symmetry arising from the 2A₁ + B₁ + B₂ vibrational modes [22].

3.3. NMR spectroscopy

The ³¹P{¹H} NMR spectra of complexes (1) and (2) show symmetrical coordination of the inorganic ligand $[N(SPPh_2)_2]^-$ as evidenced by the appearance of a doublet at 40.8 ppm for (1) with a coupling constant of 24 Hz and 36.45 ppm for (2) with a couple constant of 27 Hz. Both phosphine complexes $[Re(CO)_3(PR_3)]\kappa^2$ - $S,S'-Ph_2P(S)NP(S)Ph_2$], R = Ph, Me [5a] presented an [N(SPPh_2)_2] ³¹P{¹H} NMR signal around 40 ppm (with coupling constants of 18 and 22 Hz, resp.). The ${}^{31}P{}^{1}H{}$ NMR chemical shifts of complexes (1) and (2) concur with the observation made in the IR spectroscopy section 3.2. that, in complexes (1) and (2), the phosphites make finer electronic tuners than phosphines in their respective complexes. The coordinated phosphites appear as a broad signal at 173.7 ppm for complex (1) and at 153.42 ppm for complex (2) (free $P(OPh)_3$ appears at 127.9 ppm and free $P(OEt)_3$ at 133 ppm). ¹³C{¹H} NMR spectra of complexes (1) and (2) (Supplementary Material SM6 and SM7, resp.) show two ipso carbon atoms Ci: 138.63 and 137.48 ppm for complex (1) and 140.46 and 139.39 ppm for complex (2), resp. (see **Experimental**), indicating two inequivalent phenyl rests on each phosphinoyl group, $P=S(Ph_2)(Ph)_2P=S$, of the $[N(SPPh_2)_2]^-$ ligand. In complex (1) one Ci appears as a doublet with a coupling constant of 106 Hz, while the other appears as a double of doublets with two coupling constants, 114 and 8 Hz. Such couplings arise from the spatial disposition of the phenyl groups of the $[N(SPPh_2)_2]^-$ ligand with respect to the coordinated phosphite: One Ci couples to the phosphorus nucleus attached to it and to the phosphorus nucleus of the phosphite located in a cisoid position (W coupling), Fig. 3, while the other Ci couples only to the phosphorus nucleus adjacent to it. The same situation presents in complex (2), wherein the corresponding coupling constants amount to 106 Hz for one C_i and 108 and 5 Hz for the other.

The ${}^{13}C{}^{1}H$ NMR spectrum of diphosphite complex (**d**) shows the *mer,trans* configuration found in the solid state (see *Structrual studies*): the *Ci* of the triphenyl phosphite appears as a 'virtual

Table 3

IR v(CO) bands of complexes (1), (2) and [Re(CO)₃(PR₃){ κ^2 -S,S'-Ph₂P(S)NP(S)Ph₂}], R = Ph, Me.

Complex	ν (CO)/cm ⁻¹ bands in CH ₂ Cl ₂ ^a
(1)	2031 1962 1928
(2)	2024 1950 1917
[Re(CO) ₃ (PPh ₃){ κ^2 -S,S'-Ph ₂ P(S)NP(S)Ph ₂ }]	2023 1933 1899
[Re(CO) ₃ (PMe ₃){ κ^2 -S,S'-Ph ₂ P(S)NP(S)Ph ₂ }]	2020 1928 1894

^a All bands' intensities are strong.



Fig. 3. Magnetic inequivalence of the Ph groups in (1), R = Ph and (2), R = Et.

triplet' with an apparent coupling constant of 6 Hz (Supplementary Material SM9), although it might be expected to appear as a doublet due to coupling to the adjacent phosphorus nucleus. Being a second order spin system, the coupling constant can be broken down as ²J $_{Ci-P[P(OPh)3]} + {}^{4}J_{Ci-P[P(OPh)3']} = 11$ Hz, where coupling is realized to both *trans* positioned phosphite phosphorus nuclei [23]. As a comparison, the ${}^{13}C{}^{1}H{}$ NMR spectrum of the monophosphite complex (**b**) depicts at 150.91 ppm a doublet with a coupling constant of 11 Hz assigned to the phenyl phosphite C_i (Supplementary Material SM8).

3.4. Structural studies

The molecular structures of complexes (1) and (2) including their atom numbering scheme are shown in Figs. 4 and 5, resp. together with some selected bond distances and angles.

The molecular structures of complexes (**b**) and (**d**), their atom numbering scheme, and some selected bond distances and angles appear in the Supplementary Material (SM10 and SM11, resp.). Structure similarity between complexes (**1**) and (**2**) warrants a general discussion of their structural details. The dithioimidodiphosphinate effects a virtually symmetrical ligation to the manganese center through both sulfur atoms (within experimental error) rendering a six-membered ring manganacycle; the Mn-S bond lengths are equivalent within experimental error indicating covalent interactions (Σ_{cov} (Mn,S) = 2.44 Å) [24]. The phosphorussulfur and phosphorus-nitrogen bond distances in the SPNPS backbone are equivalent. They are longer and shorter, respectively, than the corresponding bonds in free (S=PPh₂)₂NH (cf. P-S (double bond) 1.936(1), 1.950(1), P-N (single bond) av. 1.678(2) Å [25]. Their magnitude is intermediate between single and double phosphorus-



Fig. 4. Molecular structure of (1) with atom numbering scheme (ORTEP drawing with 50% probability ellipsoids, only *ipso* carbons shown on phosphorus triphenyl phosphite's and PNP's for clarity). Selected bond lengths [Å] and angles [°]; Mn(1)-S(1) 2.4108(7), Mn(1)-S(2) 2.4176(7), Mn(1)-C(1) 1.895(6), Mn(1)-C(2) 1.799(2), Mn(1)-C(3) 1.790(2), Mn(1)-P(3) 2.2599(7), S(1)-P(1) 2.0130(8), P(1)-N(1) 1.588(2), P(2)-N(1) 1.588(2); P(1)-N(1)-P(2)135.23(13), S(1)-Mn(1)-S(2) 91.94(2), S(1)-Mn(1)-S(2) 91.94(2), P(3)-Mn(1)-C(1) 174.95(7), C(3)-Mn(1)-S(1) 175.87(8), C(2)-Mn(1)-S(2) 170.69(7).



Fig. 5. Molecular structure of (2) with atom numbering scheme (ORTEP drawing with 50% probability ellipsoids only ipso carbons shown on phosphorus PNP's for clarity). Selected bond lengths [Å] and angles [°]; Mn(1)-S(1) 2.4258(6), Mn(1)-S(2) 2.4200(6), Mn(1)-C(1) 1.841(2), Mn(1)-C(2) 1.790(2), Mn(1)-C(3) 1.785(3), Mn(1)-P(3) 2.2878(6), S(1)-P(1) 2.0131(7), P(1)-N(1) 1.590(2), P(2)-N(1) 1.588(2); P(1)-N(1)-P(2) 133.11(12), S(1)-Mn(1)-S(2) 92.61(2), P(3)-Mn(1)-C(1) 176.46(7), C(3)-Mn(1)-S(1) 173.14(7), C(2)-Mn(1)-S(2) 177.64(7).

sulfur (cf. 2.139(1) and 1.930(1) Å in Ph₂P(=S)-S-S-P(=S)-Ph₂ [26]) and single and double phosphorus-nitrogen bond distances (cf. 1.662(2) and 1.529(2) Å in $[(Me_3Si)_2N-P(=NBu^t)S]_2[27])$, this points to electron delocalization over the inorganic MnS₂P₂N ring in complexes. The MnS₂P₂N ring is not planar and a chair conformation is displayed. The coordination geometry around the manganese centers is distorted octahedral. The Mn-C(O) distances are equal within experimental error. No clear-cut trans influence is observed arising whether from the sulfur or phosphorus ligands trans to carbonyls.

4. Conclusions

Routes A – D for formation of complexes $[Mn(CO)_3{P(OR_3)}]{\kappa^2}$ - $S,S'-Ph_2P(S)NP(S)Ph_2$ R = Ph (1), Et (2) were explored. It has been found that for complex (1) the best route, based on yields, turned out to be Route C; while for (2), Route A proved to be more adequate. The intermediacy of monophosphate complex (b) to realize (1) showed that the coordination ability of phenyl phosphite and carbonyl group are comparable. Infrared data showed that electronic tuning at the metal center can be better detected for phosphite complexes herein reported than for rhenium phosphine analogs elsewhere reported. Further studies are needed to find out if this holds true for phosphites in the respective rhenium complexes or, for that matter, in the respective phosphine complexes of manganese.

5. Supplementary material

Crystal data of complexes (b) and (d), IR monitoring of formation of (c), of complex (1) starting from (d), and of formation of (1) by Route D. ${}^{13}C{}^{1}H$ -NMR spectra of (1), (2), (b) and (d) and molecular structures of (**b**) and (**d**). Crystallographic data have been deposited for compounds (**d**), (**b**), (**2**) and (**1**) with the Cambridge Crystallographic Database, CCDC nos. 1519034, 1519035, 1519036, and 1528187, respectively, in CIF format. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2017.05.017.

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