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Preparation, characterization, and reactivity studies of chelated substituted cyclopentadienylmanganesedicarbonyl complexes

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Abstract

Chelates of the parent compounds $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ (1), $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_3$ (2), $(\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_3$ (3), $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_3$ (4), and $(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)Mn(CO)_3$ (5) were prepared by photolysis. Only the chelates $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ (2chelate) and $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_2$ (3chelate) were stable enough to be isolated. The X-ray structure of 2chelate was determined and demonstrated ring strain in the chelate ring. Derivatives of the chelates were obtained by thermal substitution of the chelated group. Substitution of the chelated groups in $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_2$ (1chelate), $(\eta^1:\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_2$ (4chelate), and $(\eta^1:\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)Mn(CO)_2$ (5chelate) occurred within a few minutes, whereas 2chelate and 3chelate required refluxing for several hours to convert them to the substituted products. The substituted products have the general formula $(\eta^5\text{-}C_5H_4R)Mn(CO)_2L$ (where R is the substituent of either 1-5 and L is either a phosphine, phosphite, or tetrahydrothiophene). The weaker Mn-O bond was suggested for the differences in the reactivities of the chelated complexes.

Keywords: Manganese; Chelates; Cyclopentadienyl derivatives; X-ray diffraction; Photochemistry; Phosphine

1. Introduction

In recent years, several types of aromatic ligand with substituents that could form chelates were reported [1-4]. The aromatic ligands included cyclopentadienyl (Cp) and benzene. The chelatable groups included alkenes [2,3], phosphorus [4], thiol ether [1], ether [1], and esters [1]. Although the complexes of the chelated and unchelated forms were reported, little was reported about the reactivity of these types of compound. We have been interested in studying these compounds, since they could be useful in catalytic technologies. Our initial work reported the synthetic methods for the preparation of several Cp ligands with different chelatable substituents [1]. In this paper, we report the preparation and the reactivity studies of five new chelate compounds. Only two of the chelates could be isolated and are completely characterized.

2. Experimental

NMR spectra were recorded on a Varian VXR-300 NMR or Jeol 270 NMR spectrometer and referenced to appropriate solvent resonances. IR spectra were recorded on a Matt on Galaxy 2020 FTIR with a resolution of $2 \, cm^{-1}$. UV-visible spectra were recorded on an HP diode array model 8452a. All column chromatography used silica gel grade 643 (Aldrich). The solvents for chromatography were used as-received. All photolyses were performed using a Rayonet photochemical reactor with the 350 nm light source. Elemental analyses were carried out by either Desert Analytics, Tucson, AZ, or Galbraith Laboratories, Inc., Knoxville, TN.

All solvents were obtained from Fisher. The solvents were dried and distilled under argon before use in synthetic procedures. $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ (1), $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_3$ (2), $(\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_3$ (3), $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_3$ (4), and $(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)Mn(CO)_3$ (5) were synthesized as described previously [1]. The phosphines and phosphites were

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obtained from Strem. The triphenylphosphine was re-crystallized from ethanol before being used. The tributylphosphine and triethylphosphite were distilled under argon before being used. The tri-p-tolylphosphine and triphenylphosphite were used as-received. Tetrahydrothiophene (THT) was used as-received from Aldrich.

2.1. Synthesis of $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn$ $(CO)_2(chelate)$ (2chelate)

$(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_3$ (1.0 g) was dissolved in 250 ml of cyclohexane in a photochemical reactor. The reactor was then irradiated with the Rayonet system while evolving CO bubbled through an oil bubbler. After 2 h of irradiation the ν_{C-O} at 2033 and 1960 cm^{-1} disappeared and two new peaks appeared at 1956 and 1898 cm^{-1}. The solvent was removed under vacuum and the red residue was chromatographed using an ethyl acetate–benzene solution (1/7 ratio) as the eluant. The red band contained the product and it was characterized. The yield was 73.7%. (Found: C, 45.41; H, 3.60; Mn, 19.24. Calc.: C, 45.47; H, 3.43; Mn, 20.80%.) Spectroscopic data are given in Table 1. Red-brown crystals of $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ suitable for X-ray crystallography were grown by slow evaporation (3 months) of a cyclohexane solution in a dry box.

2.2. Synthesis of $(\eta^1:\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn$ $(CO)_2$ (chelate) (3chelate)

$(\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_3$ (0.99 g) was dissolved in 250 ml of cyclohexane in a photochemical

reactor and photolyzed for about 2 h. The IR spectrum of the reaction solution only contained ν_{C-O} for a new compound. The solvent was removed under vacuum and the residue was chromatographed as described for the previous chelate. The red solid product was isolated in 46.1% yield. (Found: C, 48.04; H, 3.99; Mn, 17.72; S, 10.57. Calc.: C, 47.49; H, 3.98; Mn, 19.75; S, 11.52%.) Spectroscopic data are given in Table 1.

2.2.1. Crystal data

$C_{10}H_9MnO_3S$, $M = 264.17$, crystal dimensions $0.20\times0.17\times0.17$ mm^3, monoclinic, space group $P2_1/n$, $a = 7.637(2)$, $b = 7.976(2)$, $c = 17.405(5)$ Å, $\beta = 91.08(2)°$, $U = 1060.00$ Å^3, $Z = 4$, $F(000) = 536.00$, $D_c = 1.655$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) = 1.37 mm^{-1}.

2.2.2. Data collection and processing

X-ray diffraction studies were carried out on a Syntex P2$_1$ diffractometer with graphite-monochromated Mo Kα radiation. The ω scan mode was employed; $2\theta_{max} = 60.0°$. Cell dimensions were obtained from 15 reflections with 2θ angle in the range 12.82–24.17°. No significant variations were observed in three check reflections that were collected after every 100 reflections. The final least squares cycle was calculated with 24 atoms, 136 parameters and 1380 ($I > 2.5\sigma(I)$) out of 3098 unique reflections. No absorption correction was necessary.

2.2.3. Structure analysis and refinement

Direct methods were employed, and calculations were performed with the NRCVAX crystal structure pro-

Compound	^{1}H NMR (δ)	^{13}C NMR [a] (δ)	IR [b] (cm^{-1})
2Chelate	4.92 (m, 1 H, C(2))	231.2 (CO)	1956(s)
	4.51 (m, 1 H, C(5))	193.5 (–C(O)–)	1898(s)
	3.97 (m, 1 H, C(4))	107.8 (Cp)	1713(m)
	3.18 (m, 1 H, C(3))	84.5 (Cp, $J_{CH} = 169$ Hz)	
	2.64 (d, 1 H, –CH$_2$–)	82.3 (Cp, $J_{CH} = 174$ Hz)	
	1.93 (d, 1 H, –CH$_2$–)	77.3 (Cp, $J_{CH} = 173$ Hz)	
	1.36 (s, 3 H, –SCH$_3$)	75.5 (Cp, $J_{CH} = 172$ Hz)	
		49.7 (–CH$_2$–, $J_{CH} = 144$ Hz)	
		26.7 (–CH$_3$, $J_{CH} = 139$ Hz)	
3Chelate	4.83 (br, 1 H, H(2))	230.4 (CO)	1952(s)
	4.49 (br, 1 H, H(5))	199.8 (–C(O)–)	1904(s)
	4.12 (br, 1 H, H(4))	106.4 (Cp)	1676(m)
	3.62 (br, 1 H, H(3))	91.3 (Cp, $J_{CH} = 174$ Hz)	
	2.53 (br d, 1 H, CCH$_2$)	84.8 (Cp, $J_{CH} = 177$ Hz)	
	1.88 (br d, 2 H, CH$_2$S)	83.2 (Cp, $J_{CH} = 176$ Hz)	
	1.41 (br, 3 H, –SCH$_3$)	78.8 (Cp, $J_{CH} = 177$ Hz)	
		54.9 (–CCH$_2$–, $J_{CH} = 139$ Hz)	
		38.3 (–CH$_2$S–, $J_{CH} = 130$ Hz)	
		26.6 (–SCH$_3$, $J_{CH} = 140$ Hz)	

[a] C_6D_6 was the solvent and chemical shifts are assigned relative to residual proton of the solvent. [b] Cyclohexane was used as the solvent.

grams (National Resource Council, Ottowa, Canada). Weights based on counting statistics were used. In the final difference map, the deepest hole and the highest peak were $-0.390 e \text{Å}^{-3}$ and $0.460 e \text{Å}^{-3}$ respectively; the maximum Δ/σ ratio was 0.000. Final R (0.051) and R' (0.049) values were calculated from the relationships: $R = \Sigma(F_o - F_c)/\Sigma F_o$ and $R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$. Atomic coordinates and a summary of principal bond lengths and angles are presented in Tables 2 and 3 respectively.

Additional materials are available from the Cambridge Crystallographic Data Centre.

2.3. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn$ $(CO)_2 P(C_6H_5)_3$ $(2PPh_3)$

All the phosphine or phosphite adducts were synthesized using a similar procedure as described here for the triphenylphosphine adduct. Thus, $(\eta^1:\eta^5\text{-}C_5H_4C(O) CH_2SCH_3)Mn(CO)_3$ (0.20 g) was placed in a 100 ml three-neck round-bottom flask with 50 ml of benzene and 2.50 g of PPh₃. The mixture was boiled under reflux for 21 h. The benzene was removed under vacuum and the residue was purified by column chromatography using benzene as the eluant. The yellow band was collected and the solvent removed to give a yellow-brown solid. The yield was 36.1%. (Found: C,

Table 2
Atomic coordinates and B_{iso} for $(\eta^1:\eta^5\text{-}C_5H_4C(O)$ $CH_3SCH_3)Mn(CO)_3$ with standard deviations in the last digit in parentheses

Atom	x	y	z	B_{iso} (Å)²
Mn	0.43906(16)	0.22524(15)	0.13844(8)	2.86(5)
S	0.1832(3)	0.1190(3)	0.08826(15)	3.84(11)
O1	0.0112(8)	0.5270(8)	0.1298(4)	4.9(3)
O2	0.6394(11)	0.2092(10)	−0.0027(4)	6.5(4)
O3	0.5743(9)	−0.1029(8)	0.1835(4)	5.0(3)
C1	0.2746(11)	0.4147(10)	0.1828(5)	3.1(4)
C2	0.4114(11)	0.4940(10)	0.1441(5)	3.7(4)
C3	0.5695(12)	0.4446(12)	0.1810(6)	4.1(5)
C4	0.5305(11)	0.3393(11)	0.2424(6)	3.8(4)
C5	0.3459(11)	0.3187(10)	0.2441(5)	3.1(4)
C6	0.0906(11)	0.4058(11)	0.1528(5)	3.4(4)
C7	0.0242(10)	0.2294(12)	0.1459(5)	3.8(4)
C8	0.1398(14)	0.2145(15)	−0.0028(6)	5.8(6)
C9	0.5561(12)	0.2157(12)	0.0517(6)	3.9(4)
C10	0.5185(11)	0.0258(12)	0.1657(5)	3.3(4)
H21	0.418	0.583	0.102	3.9
H31	0.689	0.483	0.164	3.9
H41	0.872	0.782	0.223	3.9
H51	0.233	0.756	0.216	3.9
H71	0.921	0.227	0.118	5.5
H71	0.012	0.173	0.202	5.5
H81	0.771	0.781	0.035	6.3
H82	0.191	0.350	−0.004	6.3
H83	0.980	0.775	0.015	6.3

ᵃ B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 3
Principal bond lengths (Å) and bond angles (deg) with standard deviations in the last digit in parentheses

Mn–S	2.288(3)	Mn–C1	2.119(8)
Mn–C2	2.156(8)	Mn–C3	2.139(9)
Mn–C4	2.130(9)	Mn–C5	2.120(8)
Mn–C9	1.770(10)	Mn–C10	1.764(10)
S–C7	1.817(9)	S–C8	1.784(11)
O1–C6	1.205(11)	O2–C9	1.151(13)
O3–C10	1.205(11)	C1–C2	1.404(12)
C1 –C5	1.415(12)	C1–C6	1.491(12)
C2–C3	1.412(13)	C3–C4	1.396(15)
C4–C5	1.420(12)	C6–C7	1.500(13)
S–Mn–C1	83.99(23)	S–Mn–C9	95.7(3)
S–Mn–C10	93.2(3)	C9–Mn–C10	90.8(4)
Mn–S–C7	100.6(3)	Mn–S–C8	108.9(4)
C7–S–C8	99.7(5)	C2–C1–C6	124.0(8)
O1–C6–C1	122.9(8)	O1–C6–C7	123.9(8)
C1–C6–C7	112.8(7)	O1–C6–C7	105.7(6)

64.53; H, 4.83; Mn, 10.61. Calc.: C, 63.88; H, 4.60; Mn, 10.44%.) Spectroscopic data are given in Table 4.

2.4. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ $P(n\text{-}Bu)_3$ $(2PBu_3)$

This adduct was synthesized by refluxing 10 h. The yield was 76.2%. (Found: C, 56.94; H, 7.87; Mn, 11.59. Calc.: C, 56.64; H, 7.78; Mn, 11.78%.) Spectroscopic data are given in Table 4.

2.5. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ $P(OCH_2CH_3)_3$ $(2P(OEt)_3)$

The reaction mixture was refluxed only 10 h. The yield was 70.6%. (Found: C, 44.92; H, 5.72; Mn, 13.35; S, 7.39. Calc.: C, 44.66; H, 5.62; Mn, 12.77; S, 7.45%.) Spectroscopic data are given in Table 4.

2.6. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ $P(OC_6H_5)_3$ $(2P(OPh)_3)$

The yield was 74.9%. (Found: C, 58.66; H, 4.13; Mn, 9.11. Calc.: C, 58.54; H, 4.21; Mn, 9.56%.) Spectroscopic data are given in Table 4.

2.7. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2$ $P(p\text{-}tolyl)_3$ $(2P(tol)_3)$

The yield was 76.2%. (Found: C, 66.64; H, 5.37; P, 5.83; S, 5.16. Calc.: C, 65.49; H, 5.32; P, 5.45; S, 5.64%.) Spectroscopic data are given in Table 4.

2.8. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)$ $Mn(CO)_2P(Ph)_3$ $(3PPh_3)$

The yield was 45.3%. (Found: C, 62.93; H, 4.70; P, 5.97; S, 4.65. Calc.: C, 64.44; H, 4.85; P, 5.73; S, 5.93%.) Spectroscopic data are given in Table 5.

Table 4
^{1}H, ^{13}C NMR and IR data for the derivatives with the formulas $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_2L$

Compound	^{1}H NMR [a] (δ)	^{13}C NMR [a] (δ)	IR [b] (cm^{-1})
2PPh$_3$	7.37 (m, 15 H, Ph)	230.5 (d,CO, J_{PH} = 28 Hz)	1946(s)
	5.19 (t, 2 H, Cp)	193.3 (s, –C(O)–)	1887(s)
	4.06 (t, 2 H, Cp)	137.1 (d, Ph, J_{pc} = 47 Hz)	1670(m)
	3.35 (s, 2 H, CH$_2$)	132.8 (d, Ph, J_{pc} = 11 Hz)	
	2.13 (s, –SCH$_3$)	129.1 (d, Ph, J_{pc} = 2 Hz)	
		128.3 (d, Ph, J_{pc} = 11 Hz)	
		87.7 (Cp1)	
		86.4 (Cp)	
		85.8 (Cp)	
		39.7 (s, –CH$_2$–)	
		15.9 (s, –SCH$_3$)	
2PBu$_3$	4.89 (m, 2 H, Cp) [c]	231.6 (d,CO, J_{PH} = 26 Hz) [c]	1935(s)
	4.13 (m, 2 H, Cp)	192.5 (s, –C(O)–)	1875(s)
	3.31 (s, 2 H, CH$_2$)	88.7 (Cp1)	1659(m)
	1.88 (s, 3 H, CH$_3$)	86.0 (Cp)	
	1.52–1.39 (m)	82.1 (Cp)	
	1.33–1.19 (m)	40.0 (s, –CH$_2$–)	
	0.88–0.83 (m)	28.8 (d, C of phosphine)	
		25.9 (d, C of phosphine)	
		24.5 (d, C of phosphine)	
		15.8 (s, –SCH$_3$)	
		13.9 (s, C of phosphine)	
2P(OEt)$_3$	5.07 (t, 2 H, Cp)	229.1 (d,CO, J_{PH} = 36 Hz)	1956(s)
	4.17 (m, 2 H, Cp)	191.9 (s, –C(O)–)	1894(s)
	3.73 (q, 6 H, PCH$_2$)	89.8 (Cp1)	1672(m)
	3.29 (s, 2 H, CH$_2$)	85.7 (Cp)	
	1.90 (s, 3 H, –CH$_3$)	82.8 (Cp)	
	1.02 (t, 9 H, PCH$_3$)	60.8 (m, C of phosphine)	
		39.8 (s, –CH$_2$–)	
		16.1 (d, C of phosphine)	
		15.6 (s, –SCH$_3$)	
2P(OPh)$_3$	7.28 (m, 15 H, Ph) [d]	227.4 (d,CO, J_{PH} = 35 Hz) [d]	1959(s)
	4.96 (m, 2 H, Cp)	192.1 (s, –C(O)–)	1910(s)
	4.07 (m, 2 H, Cp)	152.7 (d, OPh)	1672(m)
	3.28 (s, 2 H, CH$_2$)	130.5 (OPh)	
	2.02 (s, –SCH$_3$)	125.7 (OPh)	
		122.4 (d, OPh)	
		91.0 (Cp1)	
		85.5 (Cp)	
		83.6 (Cp)	
		39.9 (s, –CH$_2$–)	
		15.7 (s, –SCH$_3$)	
2P(Tol)$_3$	7.22 (m, 12 H, Ph)	230.7 (d,CO, J_{PH} = 26 Hz)	1944(s)
	5.17 (t, 2 H, Cp)	193.5 (s, –C(O)–)	1885(s)
	4.04 (t, 2 H, Cp)	139.8 (d, Ph, J_{pc} = 2 Hz)	1667(m)
	3.35 (s, 2 H, CH$_2$)	134.1 (d, Ph, J_{pc} = 44 Hz)	
	2.34, (s, PhCH$_3$)	132.7 (d, Ph, J_{pc} = 10 Hz)	
	2.13 (s, –SCH$_3$)	129.0 (d, Ph, J_{pc} = 10 Hz)	
		87.6 (Cp1)	
		86.6 (Cp)	
		85.2 (Cp)	
		39.7 (s, –CH$_2$–)	
		21.3 (s, PhCH$_3$)	
		16.0 (s, –SCH$_3$)	

[a] CDCl$_3$ was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent. [b] Toluene was used as the solvent. [c] C$_6$D$_6$ was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent. [d] THF-d_8 was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent (the H with the larger chemical shift).

2.9. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_2$ SC_4H_8 (1THT)

$(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ (0.10 g, 0.36 mmol) and 0.60 g of THT were put into a photolysis apparatus with 250 ml of cyclohexane. The apparatus was photolyzed for 46 min until the IR peak at 2033 cm^{-1} was reduced to ca. 3% of its initial value. The solution was filtered with aid of Celite to remove a precipitate. The solvent from the orange colored solution was removed under vacuum. The reddish-orange residue was chromatographed with 8% ethyl acetate–benzene eluant. A dark red solid (0.12 g) was obtained upon evaporation of the solvent. Yield 99%. (Found: C, 49.98; H, 5.21; Mn, 16.32; S, 9.46. $C_{14}H_{17}MnO_4S$. Calc.: C, 50.00; H, 5.10; Mn, 16.34; S, 9.53%.) Spectroscopic data are given in Table 5.

2.10. Synthesis of $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn$ $(CO)[P(OC_2H_5)_3]_2$ $(4(P(OEt)_3)_2)$

$(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_3$ (0.59 g, 2.1 mmol) and $P(OC_2H_5)_3$ (4.29 g, 28.0 mmol) were placed in a photolysis apparatus with 200 ml of cyclohexane. The mixture was photolyzed for 1 h until the peak at 2025 cm^{-1} disappeared. The solvent was removed under vacuum. The residue was chromatographed using pure benzene to separate the excess $P(OC_2H_5)_3$, and 7% ethyl acetate–benzene solution to elute the product. The yellow band was collected and afforded 0.95 g of a yellow liquid. Yield 80%. (Found: C, 45.27; H 7.16; Mn, 9.64; P, 11.25. $C_{21}H_{40}MnO_9P_2$. Calc.: C, 45.66; H, 7.12; Mn, 9.94; P, 11.21%.) Spectroscopic data are given in Table 5.

2.11. Synthesis of $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_2$ $P(OC_2H_5)_3$ $(4P(OEt)_3)$

$(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)[P(OC_2H_5)_3]_2$ was dissolved in cyclohexane in the photolysis apparatus. A slow flow of CO was bubbled through the solution during the photolysis. The reaction was monitored by following the disappearance of the 1869 cm^{-1} peak. After this peak became small, the solvent was removed under vacuum, and the residue was chromatographed with pure benzene. The benzene was evaporated, and the product was extracted with pentane at acetone–dry-ice temperature to remove trace impurities. This method yielded an analytically pure light-yellow liquid. A yield was not calculated since the starting manganese compound was not pure. (Found: C, 46.50; H, 5.78; Mn, 13.18; P, 7.26. $C_{16}H_{24}MnO_7P$. Calc.: C, 46.39; H, 5.84; Mn, 13.26; P, 7.48%.) Spectroscopic data are given in Table 5.

2.12. Synthesis of $(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)$ $Mn(CO)[P(OC_2H_5)_3]_2$ $(5(P(OEt)_3)_2)$

$(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)Mn(CO)_3$ (0.71 g, 2.45 mmol) and $P(OC_2H_5)_3$ (6.10 g, 36.7 mmol) were put into a photolysis apparatus filled with 220 ml cyclohexane. The solution was photolyzed as described for $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)_3$ until the peak at 2023 cm^{-1} disappeared. The solvent was evaporated and the residue chromatographed as described for the purification of $(\eta^5\text{-}C_5H_4CH_2COOCH_3)Mn(CO)$ $[P(OC_2H_5)_3]_2$. The product was a yellow liquid. Not all of the product was purified, therefore no yield was calculated. (Found: C, 47.05; H, 7.25; Mn, 9.64; P, 10.93. $C_{22}H_{41}MnO_9P_2$. Calc.: C, 46.65; H, 7.30; Mn, 9.70; P 10.94%.) Spectroscopic data are given in Table 5.

2.13. Synthesis of $(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)$ $Mn(CO)_2P(OC_2H_5)_3$ $(5P(OEt)_3)$

$(\eta^5\text{-}C_5H_4CH_2CH_2COOCH_3)Mn(CO)[P(OC_2H_5)_3]_2$ (0.11 g, 0.30 mmol) and $P(OC_2H_5)_3$ (0.14 ml, 0.80 mmol) were placed in a photolysis apparatus filled with 220 ml of cyclohexane and the mixture was photolyzed until peaks grew in at 1885 and 1867 cm^{-1}. A slow flow of CO was bubbled through the solution during the photolysis. The photolysis was stopped before the 1867 cm^{-1} peak became larger than the 1885 cm^{-1} peak. The solvent was removed and the residue was chromatographed as described for the similar derivatives. The product was a light-yellow liquid. A yield was not determined. (Found: C, 48.23; H, 6.17; Mn, 11.53; P, 7.52. $C_{17}H_{26}MnO_7P$. Calc.: C, 47.67; H, 6.12; Mn, 12.83; P, 7.23%.) Spectroscopic data are given in Table 5.

3. Results and discussion

$(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ (1), $(\eta^5\text{-}C_5H_4$ $C(O)CH_2SCH_3)Mn(CO)_3$ (2), $(\eta^5\text{-}C_5H_4$ $C(O)CH_2CH_2SCH_3)Mn(CO)_3$ (3), $(\eta^5\text{-}C_5H_4CH_2$ $COOCH_3)Mn(CO)_3$ (4), and $(\eta^5\text{-}C_5H_4CH_2$ $CH_2COOCH_3)Mn(CO)_3$ (5) lose a carbonyl ligand upon UV irradiation in nonpolar solvents like heptane or cyclohexane. A red color and a metal–carbonyl stretching frequency near 1890 cm^{-1} indicates the formation of a chelated compound (see Fig. 1).

All attempts to form the chelate complexes by thermal substitution were unsuccessful. Only the chelates of 2 and 3 (2chelate and 3chelate respectively) could be isolated (see Table 1 for spectroscopic data). The chelates of 1, 4, and 5 undergo decomposition reactions upon attempts to isolate them. Presumably the weak

Table 5
^{1}H, ^{13}C NMR and IR data for the derivatives with the formulas (η^5-C$_5$H$_4$C(O)CH$_2$OCH$_3$)Mn(CO)$_2$L, (η^5-C$_5$H$_4$C(O)CH$_2$CH$_2$SCH$_3$)Mn(CO)$_2$L (η^5-C$_5$H$_4$CH$_2$COOCH$_3$)Mn(CO)$_{3-n}$L$_n$ (where $n = 1$ or 2), and (η^5-C$_5$H$_4$CH$_2$CH$_2$COOCH$_3$)Mn(CO)$_{3-n}$L$_n$ (where $n = 1$ or 2)

| Compound	^{1}H NMR ^{a} (δ)	^{13}C NMR ^{a} (δ)	IR ^{b} (cm^{-1})
1THT	5.08 (t, 2 H, Cp)	231.3 (–CO)	1946 (vs) ^{c}
	4.56 (t, 2 H, Cp)	194.6 (–C(O)–)	1884 (vs)
	4.34 (s, 2 H, –CH$_2$–)	87.4 (Cp, J_{CH} = 178 Hz)	1686 (m)
	3.46 (s, 3 H, –OCH$_3$)	86.4 (Cp1)	1660 (m)
	2.73 (br, 4 H, THT)	81.1 (Cp, J_{CH} = 179 Hz)	
	1.96 (br, 4 H, THT)	75.4 (–OCH$_3$, J_{CH} = 146 Hz)	
		59.4 (–CH$_2$–, J_{CH} = 142 Hz)	
		43.6 (THT, J_{CH} = 146 Hz)	
		30.0 (THT, J_{CH} = 1660 Hz)	
3PPh$_3$	7.4 (b, Ph)	230.4 (CO)	1946(s)
	5.15 (t, 2 H, Cp)	197.7 (–C(O)–)	1885(s)
	4.06 (t, 2 H, Cp)	137.1 (d, Ph, J_{pc} = 42 Hz)	1678(m)
	2.80 (m, –CH$_2$–)	132.8 (d, Ph, J_{pc} = 11 Hz)	
	2.12 (s, 3 H, –SCH$_3$)	129.8 (d, Ph, J_{pc} = 2 Hz)	
		128.3 (d, Ph, J_{pc} = 10 Hz)	
		89.4 (Cp1)	
		86.4 (Cp)	
		84.6 (Cp)	
		39.0 (–C(O)CH$_2$–)	
		28.5 (–CH$_2$S–)	
		15.8 (–SCH$_3$)	
4(P(OEt)$_3$)$_2$	4.24 (m, 2 H, Cp)	233.8 (–CO)	1869(vs) ^{d}
	4.17 (m, 2 H, Cp)	172.4 (–COO–)	1750(s)
	3.90 (m, 12 H, CH$_2$(OEt))	90.6 (Cp 1)	
	3.65 (s, 3 H, –OCH$_3$)	80.7 (Cp, J_{CH} = 175 Hz)	
	3.27 (s, 2 H, –CH$_2$–)	79.4 (Cp, J_{CH} = 177 Hz)	
	1.21 (t, 18 H, CH$_3$(OEt))	59.5 (CH$_2$(OEt), J_{CH} = 127 Hz)	
		51.9 (–CH$_2$–, J_{CH} = 147 Hz)	
		34.4 (OCH$_3$, J_{CH} = 130 Hz)	
		16.4 (CH$_3$(OEt), J_{CH} = 145 Hz)	
4P(OEt)$_3$	4.57 (m, 2 H, Cp)	230.0 (–CO)	1950(vs) ^{d}
	4.40 (m, 2 H, Cp)	171.3 (–COO–)	1888(vs)
	3.90 (m, 6 H, CH$_2$(OEt))	94.0 (Cp1)	1752 (m)
	3.68 (s, 3 H, –OCH$_3$)	82.7 (Cp, J_{CH} = 170 Hz)	
	3.27 (s, 2 H, –CH$_2$–)	81.1 (Cp, J_{CH} = 178 Hz)	
	1.26 (t, 9 H, CH$_3$(OEt))	60.3 (CH$_2$(OEt), J_{CH} = 144 Hz)	
		51.9 (–CH$_2$–, J_{CH} = 147 Hz)	
		34.4 (OCH$_3$, J_{CH} = 130 Hz)	
		16.4 (CH$_3$(OEt), J_{CH} = 134 Hz)	
5(P(OEt)$_3$)$_2$	4.12(t, 2 H, Cp)	234.0 (–CO)	1867 (vs)
	4.06 (t, 2 H, Cp)	173.5 (–COO–)	1748(s)
	3.90 (m, 12 H, CH$_2$(OEt))	98.4 (Cp1)	
	3.64 (s, 3 H, –OCH$_3$)	79.5 (Cp, J_{CH} = 175 Hz)	
	2.56 (m, 4 H, –CH$_2$CH$_2$–)	78.7 (Cp, J_{CH} = 174 Hz)	
	1.21 (t, 18 H, CH$_3$(OEt))	59.4 (CH$_2$(OEt), J_{CH} = 144 Hz)	
		51.5 (OCH$_3$, J_{CH} = 147 Hz)	
		36.0 (–CH$_2$COO–, J_{CH} = 131 Hz)	
		24.0 (CpCH$_2$–, J_{CH} = 130 Hz)	
5P(OEt)$_3$	4.40 (t, 2 H, Cp)	230.2 (–CO)	1948 (vs)
	4.34 (t, 2 H, Cp)	173.1 (–COO–)	1887 (vs)
	3.89 (m, 6 H, CH$_2$(OEt))	101.8 (Cp1)	1750(s)
	3.66 (s, 3 H, –OCH$_3$)	81.1 (Cp, J_{CH} = 178 Hz)	
	2.56 (m, 4 H, –CH$_2$CH$_2$–)	80.8 (Cp, J_{CH} = 177 Hz)	
	1.25 (t,9 H, CH$_3$(OEt))	60.2 (CH$_2$(OEt), J_{CH} = 146 Hz)	
		51.6 (OCH$_3$, J_{CH} = 147 Hz)	
		35.3 (–CH$_2$COO–, J_{CH} = 130 Hz)	
		23.6 (CpCH$_2$–, J_{CH} = 131 Hz)	
		16.2 (CH$_3$(OEt), J_{CH} = 130 Hz)	
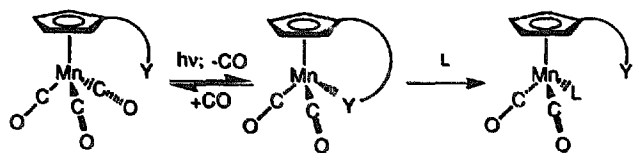
Fig. 1. Photochemical reaction scheme where Y is a group with a two electron donor atom and L is ligand with a two electron donor atom.

Mn–O chelate bond is easily broken and the compounds then undergo decomposition. This is different from the pronounced chelate effect observed for $(\eta^5:\eta^2$-$C_5(CH_3)_4CH_2CH_2CH=CH_2)Co(L)$ (where $L = CO$, $P(OCH_3)_3$, or alkene) [2]. The yield of **2chelate** was almost twice that of **3chelate**. The difference is probably related to the larger absorbance of **3chelate** ($\varepsilon_{337} =$ 1370 Abs cm^{-1} M^{-1} in heptane) than **2chelate** ($\varepsilon_{337} =$ 491 Abs cm^{-1} M^{-1} in heptane). **3chelate** may undergo secondary photolysis reactions that lead to decomposition, since it absorbs more light at the same concentration of **2chelate**.

The crystal structure of **2chelate** reveals one molecule per asymmetric unit (Fig. 2). The manganese metal has a geometry similar to other reported CpMnL$_3$ compounds [5,6]. All five ring carbons are an average of 2.133 Å from the metal (see Table 3), which is similar to other C_{cp}–Mn bond distances [5,6]. The five carbons of the ring are planar as expected. The carbonyl carbon–manganese bond length is an average of 1.767 Å and the C–O bond length is average of 1.152 Å. These are within experimental error of the bond lengths reported for other compounds [5,6].

The ketone carbonyl has a dihedral angle of 48° relative to the plane of the Cp carbons (Fig. 2). This carbonyl has lost most of its conjugation with the cyclopentadienyl ring because its stretching frequency is similar to that for free ketones [7]. The C1–C6–C7 bond angle is only 112.8°, which is less than the ideal for an sp^2 hybridized carbon atom as in $(\eta^5$-$C_5H_4C(O)CH_3)Mn(CO)_3$ [8]. The strain in the chelate ring forces the ketone carbonyl out of the Cp plane and causes the smaller C1–C6–C7 bond angle. The ring strain limits the Mn–S bond strength and hence the amount of electron density donated by S to the metal center. **3chelate** has metal–carbonyl stretching frequencies at lower wavenumbers than **2chelate** (see Table 1, both bands shifted by 4 cm^{-1}) indicating a more electron-rich metal center. The ^{13}C NMR data also support this conclusion [9]. The chelate ring in **3chelate** contains one more carbon atom, and therefore should have
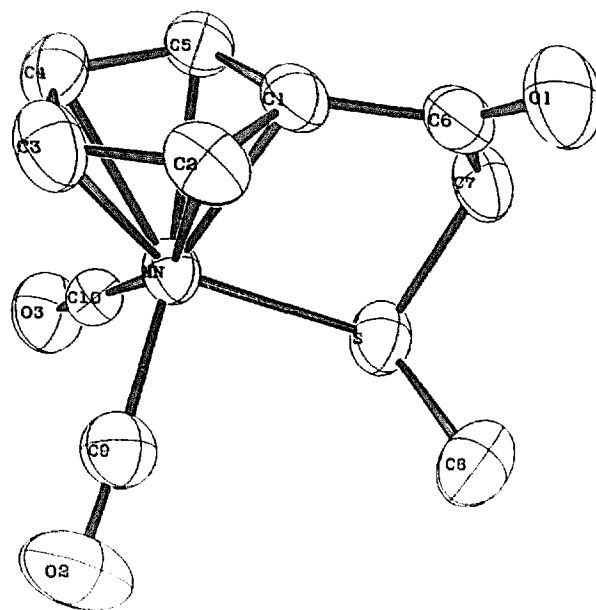

Fig. 2. ORTEP view of **2chelate**. Ellipsoids are drawn at 50% probability.

less ring strain, which allows more electron donation from S.

The ketone carbonyl stretching frequencies for **2chelate** and **3chelate** indicate that the carbonyl in **3chelate** is conjugated with the ring. The X-ray crystal structure of **2chelate** indicates that the ketone carbonyl is not conjugated with the Cp ring and its stretching frequency shifts +31 cm^{-1} from that in **2** [1]. The stretching frequency for the ketone in **3chelate** must have conjugation with the ring to have a shift to lower wavenumbers (-37 cm^{-1} compared with the ketone in **2chelate**) [10]. Furthermore, the ketone in **3chelate** shifts -18 cm^{-1} from the ketone in **3** [1]. This indicates greater conjugation between the ring and the ketone group in the chelated structure and a smaller dihedral angle between the ketone and the Cp in **3chelate** than that in **2chelate**.

In the COSY spectrum of **2chelate**, the two methylene protons (H6 and H7) are split into two doublets (see Table 1) with a J value of 13 Hz, which is a typical coupling constant for geminal protons [9]. The doublet at lower field is assigned to H6, which is on the same side as the lone pair of the S atom and lying in the cone whose axis is along the ketone carbonyl bond. Therefore, H6 is deshielded by the anisotropic effect of the ketone carbonyl [9]. The NMR data indicate that the five-membered chelate ring is 'frozen' by the 'rigid'

Notes to Table 5:
[a] CDCl$_3$ was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent. [b] Toluene was used as the solvent.
[c] Cyclohexane was used as the solvent. [d] Heptane was used as the solvent.

structure of Mn–C_5H_4R and the high inversion barrier of the sulfur atom. The ketone carbonyl can oscillate about its equilibrium position, which is about 48° dihedral angle to the Cp ring plane, but will not pass 90° unless the ring flips. If the ketone carbonyl was to undergo a larger range of flipping movement, the four Cp ring protons would probably show two pseudo-triplets like its parent compound (2), and the two methylene protons would have a smaller difference in their chemical shifts.

As stated earlier, the chelates of 1, 4, and 5 are not stable and decompose within a few minutes. These chelates will react with other ligands, like phosphines or phosphites, to form stable complexes. The derivatives 1THT, 4(P(OEt)₃)₂, 4P(OEt)₃, 5(P(OEt)₃)₂, and 5P(OEt)₃ were synthesized by this approach (see Fig. 1 and for spectroscopic data Table 5). The disubstituted products were probably obtained from a two photon process, since two ligand loss with a single photon has not been reported for any organometallic compound in solution to the best of our knowledge. We could not synthesize the trisphosphite by photolysis. The reaction never went beyond the diphosphite. Clearly, another method is required to prepare them, and at least one is reported in the literature [11].

The phosphine or phosphite derivatives of **2chelate** and **3chelate** could not be obtained from simply photolyzing **2** and **3** in the presence of the desired ligand. Evidently, the formation of the chelate is much faster than the addition of the ligand to the coordinatively unsaturated intermediate. The phosphine or phosphite derivatives were synthesized by thermal substitution of chelate compounds with the desired ligands (see Tables 4 and 5 for spectroscopic data and Fig. 1). These reaction were slow and required several hours. Kinetic studies of these substitutions will be reported later.

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