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ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS XXIII*. SOME INDENYL AND FLUORENYL DERIVATIVES OF MANGANESE CARBONYL

R. B. KING** AND A. EFRATY***
Department of Chemistry, University of Georgia, Athens, Georgia (U.S.A.)

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SUMMARY

Reaction between sodium fluorenide and $Mn(CO)_5Br$ in tetrahydrofuran solution gives yellow-orange crystalline h^5-fluorenyltricarbonylmanganese, $C_{13}H_9Mn(CO)_3$, the first unequivocal example of an h^5-fluorenyl derivative. The corresponding h^5-indenyl derivative, yellow-orange $C_9H_7Mn(CO)_3$, was prepared from sodium indenide and $Mn(CO)_5Br$. Photochemical reactions of $C_{13}H_9Mn(CO)_3$ with triphenylphosphine and of $C_9H_7Mn(CO)_3$ with the triphenyl derivatives $(C_6H_5)_3E$ (E = P, As, or Sb) gave the monosubstituted derivatives $C_{13}H_9Mn(CO)_2P(C_6H_5)_3$ and $C_9H_7Mn(CO)_2E(C_6H_5)_3$ (E = P, As, or Sb), respectively. The infrared and proton NMR spectra of the new compounds are discussed.

INTRODUCTION

Numerous transition metal complexes with *pentahapto*-cyclopentadienyl and indenyl ring systems have been prepared. However, corresponding h^5-fluorenyl derivatives of transition metals are almost unknown. Fluorenyltricarbonylmanganese, $C_{13}H_9Mn(CO)_3$ (I: L = CO), is cited as an example in several patents[3] but has never been fully characterized. A fluorenyl derivative of zirconium $(C_{13}H_9)_2ZrCl_2$ has also been reported[4], but no definite evidence such as proton NMR or X-ray crystallography for the presence of the h^5-fluorenyl ligand in this compound has been given. Unsuccessful attempts of previous workers to prepare h^5-fluorenyl derivatives of iron such as $C_5H_5FeC_{13}H_9$[5] and $(C_{13}H_9)_2Fe$[6] had created some doubt as to whether h^5-fluorenyl derivatives could exist; it appeared entirely possible that involvement of four of the five π-electrons of the central five-membered ring of the fluorenyl system in the aromatic sextets of both outer six-membered benzenoid rings could make these five π-electrons unavailable for donation to a single metal atom in a manner similar to the *pentahapto*-cyclopentadienyl and indenyl derivatives.

This paper describes in detail the preparation and properties of fluorenyltri-

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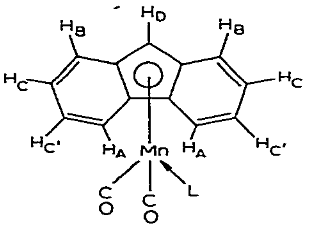
[*] For Part XXII see ref. 1.
[**] Fellow of the Alfred P. Sloan Foundation, 1967–1969.
[***] Post-doctoral research associate, 1968–1970.

carbonylmanganese, $C_{13}H_9Mn(CO)_3$ (I: L=CO) thereby providing the first unequivocal evidence that a *pentahapto*-fluorenyl ligand can indeed bond to a transition metal. The preparation and properties of the closely related indenyltricarbonylmanganese (benzocymantrene), $C_9H_7Mn(CO)_3$ (II: L=CO), are also described; this compound has been previously mentioned in several patents[3] but has not been described in detail anywhere. Previously described indenylmetal carbonyl derivatives are limited to compounds of molybdenum[7], rhenium[8], and iron[7,9].



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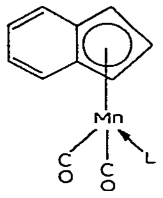

(II)

EXPERIMENTAL

A nitrogen atmosphere was routinely provided for the following operations: (*a*) Carrying out reactions; (*b*) Admitting to evacuated vessels; and (*c*) Handling filtered solutions of organometallic derivatives. Tetrahydrofuran was purified by distillation over lithium aluminum hydride. Decacarbonyldimanganese[10] was prepared by carbonylation of $CH_3C_5H_4Mn(CO)_3$. Reaction of $Mn_2(CO)_{10}$ with bromine in CH_2Cl_2 or CCl_4 was used to prepare $Mn(CO)_5Br$[11].

TABLE 1

SOME π-INDENYL AND π-FLUORENYL DERIVATIVES OF MANGANESE CARBONYL

Compound	Color	M.p. (°C)	Yield (%)	Analyses[a], found (calcd.) (%)		
				C	H	O
(A). π-Indenyl derivatives						
$C_9H_7Mn(CO)_3$	Yellow-orange	50–51	56	56.9	2.7	20.0
				(56.7)	(2.7)	(19.7)
$C_9H_7Mn(CO)_2P(C_6H_5)_3$	Orange	168–169	60	70.5	4.7	6.2
				(71.3)	(4.5)	(6.6)
$C_9H_7Mn(CO)_2As(C_6H_5)_3$	Orange	156–157	19	65.2	4.1	6.0
				(65.4)	(4.0)	(6.0)
$C_9H_7Mn(CO)_2Sb(C_6H_5)_3$	Orange	120–121	45	60.0	3.6	5.0
				(60.0)	(3.5)	(5.5)
(B). π-Fluorenyl derivatives						
$C_{13}H_9Mn(CO)_3$[b]	Yellow-orange	118–119	11	63.6	3.0	16.0
				(63.3)	(2.8)	(15.8)
$C_{13}H_9Mn(CO)_2P(C_6H_5)_3$	Orange	196–197	50	73.4	4.5	5.8
				(73.7)	(4.5)	(6.0)

[a] These microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.
[b] Manganese analysis: found 18.1%, calcd. 18.0%.

Preparation of fluorenyltricarbonylmanganese

A mixture of 2.9 g (18 mmoles) of fluorene, 1.5 g (32.5 mg-atom of sodium) of 50% sodium dispersion in mineral oil, and 50 ml of redistilled tetrahydrofuran was boiled under reflux for 12 h. The resulting sodium fluorenide solution was filtered under nitrogen. The filtrate was added dropwise to a solution of 5.0 g (18.2 mmoles) of $Mn(CO)_5Br$ in 100 ml of redistilled tetrahydrofuran. After addition of the sodium fluorenide solution was complete, the reaction mixture was stirred at room temperature for 5 h and then boiled under reflux for an additional $1\frac{1}{2}$ h. During the reflux period the color of the reaction mixture changed from yellow-orange to deep red. After allowing the reaction mixture to cool to room temperature, the tetrahydrofuran was removed at 25°/35 mm. The residue was dissolved in dichloromethane/cyclohexane 1/10 and chromatographed on a 3 x 60 cm alumina column. The orange band of product was eluted with dichloromethane/hexane 3/20. The eluate was evaporated at 25°/35 mm and the crude product purified by recrystallization from pentane and sublimation at 70°/0.25 mm to give 0.62 g (11% yield) of yellow-orange fluorenyltricarbonylmanganese, m.p. 118–119°. Infrared spectrum (KBr pellet): ν(CH) frequencies too weak to be unequivocally observed; ν(CO) frequencies at 2009 (s) and 1926 (vs) cm^{-1}; other bands at 1621 (vw), 1474 (w), 1448 (w), 1443 (w), 1404 (w), 1397 (w), 1335 (w), 1318 (w), 1285 (vw), 1215 (vw), 1194 (m), 1163 (w), 1124 (vw), 1105 (w), 995 (vw), 976 (w), 952 (vw), 875 (m), 866 (vw),844 (w), 840 (vw), 813 (m), 803 (vw), 752 (s), 742 (m), 724 (m), 717 (w), 676 (w), 663 (m), and 643 (m) cm^{-1}.

Preparation of indenyltricarbonylmanganese

A mixture of 5 g (48.5 mmoles) of indene, 1.37 g (29.5 mg-atom of sodium) of 50% sodium dispersion in mineral oil, and 30 ml of redistilled tetrahydrofuran was boiled under reflux for several hours until all of the sodium dissolved. The resulting solution of sodium indenide was added dropwise to a solution of 6.0 g (21.8 mmoles) of $Mn(CO)_5Br$ in 100 ml of tetrahydrofuran. The reaction mixture was boiled under reflux for 15 h. Solvent was then removed at 25°/30 mm. The product was extracted from the residue with hot pentane and the pentane solution chromatographed on a 3 x 50 cm alumina column. Development of the column with a 1/8 mixture of dichloromethane and pentane gave a small yellow band followed by a much larger yellow

TABLE 2

A COMPARISON OF ν(CO) FREQUENCIES OF π-INDENYL- AND π-FLUORENYLMANGANESE CARBONYL DERIVATIVES

These spectra were run in the indicated media on Perkin–Elmer Model 257 and 621 spectrometers with grating optics.

Compound	Medium	ν(CO) (cm^{-1})
$C_9H_7Mn(CO)_3$	Cyclohexane	2030(s), 1949(s), 1940(s)
$C_{13}H_9Mn(CO)_3$	Cyclohexane	2027(s), 1944(vs)
$C_9H_7Mn(CO)_2P(C_6H_5)_3$	Nujol mull	1931(s), 1863(s)
$C_{13}H_9Mn(CO)_2P(C_6H_5)_3$	Nujol mull	1916(s), 1855(s)
$C_9H_7Mn(CO)_2As(C_6H_5)_3$	Nujol mull	1932(s), 1864(s)
$C_9H_7Mn(CO)_2Sb(C_6H_5)_3$	Nujol mull	1924(s), 1915(s), 1860(s), 1853(s)
$C_9H_7Mn(CO)_2Sb(C_6H_5)_3$	Dichloromethane	1931(s), 1864(s)

band. Both bands were eluted with the same solvent mixture and the filtered eluates evaporated at 25°/30 mm. The first small yellow band gave 0.2 g of $Mn_2(CO)_{10}$ (4.7% yield). The residue from evaporation of the eluate from the second band was purified by crystallization from pentane followed by sublimation at 45–50°/0.3 mm to give 3.1 g. (56% yield) of yellow-orange indenyltricarbonylmanganese, m.p. 50–51° (reported in patents[3]: m.p. 50–51°). Infrared spectrum (KBr pellet): ν(CH) frequencies too weak to be unequivocally observed; ν(CO) frequencies at 2023 (s), 1950 (s), and 1930 (s) cm^{-1}; other bands at 1478 (w), 1450 (w), 1407 (w), 1398 (w), 1346 (w), 1338 (w), 1210 (w), 1202 (vw), 1190 (vw), 1156 (w), 1122 (w), 1040 (w), 996 (w), 986 (w), 936 (vw), 870 (m), 847 (w), 840 (w), 837 (w), 760 (s), 748 (s), 736 (w), 668 (s), 640 (s), and 629 (s) cm^{-1}.

Reactions of indenyltricarbonylmanganese and fluorenyltricarbonylmanganese with the triphenyl derivatives $(C_6H_5)_3E$ *(E = P, As,* or *Sb)*

A mixture of 1.1 to 1.4 mmoles of $C_9H_7Mn(CO)_3$ or $C_{13}H_9Mn(CO)_3$, excess (1.6 to 2.3 mmoles) of the $(C_6H_5)_3E$ (E = P, As, or Sb) derivative, and 60–80 ml of cyclohexane was exposed for 1½ to 2 h to the ultraviolet irradiation from a ~125 watt mercury lamp placed 5 cm from the reaction vessel. Solvent was removed from the reaction mixture at 25°/30 mm. A solution of the residue in chloroform/hexane 1/9 or dichloromethane/hexane 1/9 was chromatographed on a 2 × 30 cm alumina column. The orange band of the product was eluted with a mixture of dichloromethane and hexane and the crude product purified by recrystallization from dichloromethane/hexane.

Attempts to prepare the triphenylstibine derivative $C_9H_7Mn(CO)_2Sb(C_6H_5)_3$ by this procedure resulted in complete decomposition during the chromatography step. Therefore this triphenylstibine complex was purified by washing several times with 10% aqueous hydrochloric acid followed by recrystallization from hot pentane.

DISCUSSION

The proton NMR spectrum of the yellow-orange product $C_{13}H_9Mn(CO)_3$ obtained from sodium fluorenide and $Mn(CO)_5Br$ clearly indicates it to be the h^5-fluorenyl derivative (I: L = CO). Three sets of resonances are observed of approximate relative intensities 2/2/4 in the expected region for protons on an uncomplexed six-membered benzenoid ring. The two of these resonances of relative intensities 2 correspond to the two pairs of protons on carbon atoms of the benzenoid rings which are bonded to carbon atoms of the central five-membered ring [H_A and H_B in (I)]. The benzenoid proton resonance of relative intensity four can then correspond to overlapping resonances from the remaining two pairs of benzenoid protons H_C and $H_{C'}$. All of the resonances consist of at least three unsymmetrical peaks in accord with the non-equivalence of all four protons of each benzenoid ring and the possibilities for spin–spin coupling.

The single proton attached to the five-membered ring in the h^5-fluorenyl derivative $C_{13}H_9Mn(CO)_3$ (I: L = CO) appears as the expected singlet of relative intensity 1. The chemical shift of τ 4.44 for this proton falls in the range expected for a proton on a five-membered ring bonded to a transition metal through all five carbon atoms. Replacement of one of the strongly π-accepting carbonyl groups in $C_{13}H_9$-

TABLE 3

PROTON NMR SPECTRA OF INDENYL AND FLUORENYL DERIVATIVES OF MANGANESE CARBONYL[a]

Compound	NMR chemical shifts, τ					
	Six-membered ring protons			Five-membered ring protons		
	H_A	H_B	$(C_6H_5)_3E$	H_C	H_D	J_{CD}
(A). π-Indenyl derivatives						
$C_9H_7Mn(CO)_3$	2.81	3.04		4.96	5.18	[b]
$C_9H_7Mn(CO)_2P(C_6H_5)$	[c]	3.13	2.86	5.50	5.50	
$C_9H_7Mn(CO)_2As(C_6H_5)_3$	[c]	~3.2	2.89	~5.4[d]	~5.4[d]	
$C_9H_7Mn(CO)_2Sb(C_6H_5)_3$	2.88[e]	3.28[e]	2.70	5.01	5.16	2
	Six-membered ring protons[f]			Five-membered ring proton[g]		
(B). π-Fluorenyl derivatives						
$C_{13}H_9Mn(CO)_3$	~2.0 (2)	~2.6 (2)	~2.8 (4)	4.44 s		
$C_{13}H_9Mn(CO)_2P(C_6H_5)_3$	~2.6 (2)	~2.9 (15)	~3.15 (6)	5.17 d		

[a] These spectra were run in $CDCl_3$ solution on either a Perkin–Elmer Hitachi R-20 spectrometer at 60 Mc or a Varian HA-100 spectrometer at 100 Mc. [b] The fine structure in the H_C and H_D resonances could not be resolved. [c] This resonance was hidden under the resonance arising from the fifteen protons of the ligand. [d] Some evidence of fine structure was observed. [e] These resonances were both double doublets with J_1 7 Hz and J_2 2 Hz. [f] These resonances were all complex unsymmetrical combinations of peaks. Relative intensities are given in parentheses. [g] These resonances had relative intensities of 1; s = singlet, d = doublet.

$Mn(CO)_3$ with the much more weakly π-accepting triphenylphosphine to give $C_{13}H_9Mn(CO)_2P(C_6H_5)_3$ [I: L = $(C_6H_5)_3P$] raises the chemical shift of the five-membered ring proton to τ 5.17. A similar increase in the chemical shifts of π-cyclopentadienyl NMR resonances in cyclopentadienylmetal carbonyl derivatives upon replacing strongly π-accepting carbonyl groups with weaker π-acceptors has been observed[12]. The five-membered ring fluorenyl proton resonance in $C_{13}H_9Mn(CO)_2$-$P(C_6H_5)_3$ is a doublet ($J = 2$ Hz) owing to coupling of this proton with the phosphorus atom ($I = \frac{1}{2}$) of the triphenylphosphine ligand; similar couplings are observed in the π-cyclopentadienyl resonances in the proton NMR spectra of many phosphine-substituted cyclopentadienyl derivatives.

The infrared spectrum of the π-cyclopentadienyl derivative $C_5H_5Mn(CO)_3$ under optimum conditions (cyclohexane solution, grating optics[13]) exhibits the two ν(CO) frequencies ($A_1 + E$) expected for C_{3v} symmetry[14]. In the infrared spectrum of the π-pyrrolyl derivative $C_4H_4NMn(CO)_3$ under comparable conditions the E mode is split[15,16] owing to sufficient assymmetry of the π-pyrrolyl-manganese bond to cause significant deviation from cylindrical symmetry. The infrared spectrum of the π-indenyl derivative $C_9H_7Mn(CO)_3$ (II: L = CO) under comparable conditions also exhibits a similar splitting of the E mode indicating that the single fused benzene ring of the h^5-indenyl ligand like the nitrogen atom of the π-pyrrolyl ligand can cause a significant deviation of the ring–metal bond from cylindrical symmetry. However, the infrared spectrum of the h^5-fluorenyl derivative $C_{13}H_9Mn(CO)_3$ (I: L = CO) under comparable conditions exhibits no detectable splitting of the E mode apparently because the effects of two fused benzene rings at opposite sides of the π-cyclopentadienyl ring cancel each other enough so that the deviation from cylindrical symmetry of the ring–metal bond no longer is sufficient to give a detectable splitting of the E ν(CO) frequency in the infrared spectrum.

Ultraviolet irradiation of the h^5-indenyl derivative $C_9H_7Mn(CO)_3$ (II : L = CO) with the ligands $(C_6H_5)_3E$ (E = P, As, or Sb) results in the facile replacement of one carbonyl group giving the substituted derivatives $C_9H_7Mn(CO)_2E(C_6H_5)_3$ [II: L = $(C_6H_5)_3E$; E = P, As, or Sb]. The stability of these substituted indenylmanganese carbonyl derivatives decreases in the expected sequence $(C_6H_5)_3P$ (most stable) > $(C_6H_5)_3As$ > $(C_6H_5)_3Sb$ (least stable) and is particularly evident from their behavior upon chromatography on alumina. Thus the triphenylphosphine derivative can be chromatographed on alumina with little apparent decomposition; the triphenylarsine derivative decomposes extensively but not completely upon attempted chromatography on alumina; and the triphenylstibine derivative decomposes completely upon attempted chromatography on alumina. A similar stability sequence appears to occur in the substituted h^5-fluorenyl derivatives $C_{13}H_9Mn(CO)_2E(C_6H_5)_3$ since despite visual indications that a substitution had taken place the triphenylarsine derivative could not be isolated from a preparation carried out analogously to the preparation of the corresponding triphenylphosphine derivative $C_{13}H_9Mn(CO)_2$-$P(C_6H_5)_3$. Preparation of the triphenylstibine derivative $C_{13}H_9Mn(CO)_2Sb(C_6H_5)_3$ was not attempted owing to the inability to obtain the triphenylarsine derivative and the relatively small available amounts of fluorenyltricarbonylmanganese.

All of the infrared spectra of the $C_9H_7Mn(CO)_2E(C_6H_5)_3$ (E = P, As, and Sb) and $C_{13}H_9Mn(CO)_2P(C_6H_5)_3$ derivatives exhibited the expected two ν(CO) frequencies when taken in Nujol mulls except for the triphenylstibine derivative $C_9H_7Mn(CO)_2Sb(C_6H_5)_3$ which exhibited an 8 ± 1 cm^{-1} splitting of both frequencies. That this was a solid state effect possibly arising from two different orientations of the molecules in the crystal structure was shown by the disappearance of this splitting in spectra obtained in dichloromethane solution under high resolution conditions.

In an attempt to evaluate differences in forward (σ and π) bonding and retrodative (δ) bonding upon fusion of benzene rings to the π-cyclopentadienyl ligand to form successively the h^5-indenyl and h^5-fluorenyl ligands, the Cotton–Kraihanzel approximate force constants were calculated for the $QMn(CO)_3$ derivatives (Table 4); the secular equations derived for the *cis*-$L_3M(CO)_3$ derivatives are clearly applicable here. These calculations support the previous assertion[15] that

TABLE 4

COTTON–KRAIHANZEL APPROXIMATE FORCE CONSTANTS FOR $QMn(CO)_3$ DERIVATIVES

These approximate force constants are given in dynes/cm. The calculation procedure and symbols are similar to those used by Cotton and Kraihanzel[14]. In cases of derivatives with split E modes the mean frequency of the two E modes was used for the calculation. The ν(CO) frequencies used for these calculations were all determined in cyclohexane solution.

Compound	K	K_c
$C_5H_5Mn(CO)_3$	15.75	0.35
$C_9H_7Mn(CO)_3$	15.73	0.46
$C_{13}H_9Mn(CO)_3$	15.70	0.44
$C_4H_4NMn(CO)_3$	16.00	0.34

the negative charge on the metal atom is less in the π-pyrrolyl derivative than in the corresponding π-cyclopentadienyl derivative. However, the stretching force constants showed no significant change upon going from the cyclopentadienyl derivative to the corresponding indenyl and fluorenyl derivatives indicating that nearly the same changes in the forward and the backward donation occur upon fusion of benzene rings to a π-cyclopentadienyl ring in such a manner as to nearly cancel each other leaving the negative charge on the metal atom essentially the same. The lower stability of indenyl and fluorenyl derivatives relative to cyclopentadienyl derivatives[6] suggests a weakening of the forward metal–ring bond upon fusion of benzene rings. In order to preserve a similar total negative charge on the metal atom the backward metal–ring δ bonding must also be correspondingly weaker. We thus infer that both the donor (σ and π) and acceptor (δ) characteristics of the cyclopentadienyl ligand decrease synergistically upon successive fusion of benzene rings in the following sequence: cyclopentadienyl (greatest) > indenyl > fluorenyl (least).

Although fusion of benzene rings to the π-cyclopentadienyl ligand has little effect on the carbon–oxygen stretching force constants in $QMn(CO)_3$ derivatives, such fusion of benzene rings increases markedly the carbon–oxygen *interaction* force constants k_c (as measured crudely by the separation of the A_1 and E modes). Furthermore, the interaction force constants k_c of $C_5H_5Mn(CO)_3$ and $C_4H_4NMn(CO)_3$, neither of which has a fused benzene ring, are essentially identical.

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