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Synthesis and Electrochemistry of $C_5H_5Mn(CNR)_3$ Compounds

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The complexes $Mn(C_5H_5)(CNR)_3$ (R = CH_3, C_6H_5, p-ClC_6H_4, C_6Cl_5) are formed from $Mn(C_5H_5)(CO)_3$ and excess isocyanide using ultraviolet irradiation. Cyclic voltammetry shows that these complexes undergo two sequential one-electron oxidations.

Introduction

Cyclopentadienylmanganese tricarbonyl shows a great reluctance to undergo substitution reactions. Forcing conditions are generally required to effect substitution of various ligands for carbon monoxide; ordinarily ultraviolet photolyses of the reactants is the synthetic technique used [1]. Monosubstitution is fairly common; disubstitution is less well known, being so far limited to a few common phosphines and arsines [2, 3]. Trisubstitution has been accomplished directly with PF_3 [4]. The trisubstituted thiocarbonyl complex $Mn(C_5H_5)(CS)_3$, has been prepared indirectly, in a three step sequence, each step involving substitution of a carbonyl by an olefin followed by reaction with triphenylphosphine and carbon disulfide [5]. The complex $Mn(C_5H_5)(CNC_6H_5)_3$ has also been reported being formed from $[Mn(CNC_6H_5)_6]^+$ and $Na[C_5H_5]$ [6].

The direct reaction of $Mn(C_5H_5)(CO)_3$ and excess isocyanide had not been attempted prior to this work yet this reaction to give $Mn(C_5H_5)(CNR)_3$ complexes appears to have a high probability for success considering the characteristics of isocyanides as ligands. If prepared by this route, these compounds are likely to be of further interest since they would appear to be excellent candidates for a project on electrochemical and chemical oxidative studies ongoing in our group [7–9]. Hence we were led into this study; we report the results below.

Experimental

All reactions were carried out under nitrogen. Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-10 spectrometer using CH_2Cl_2 solution. Nuclear magnetic resonance spectra were taken on a Varian A-60 60 MHz or JEOL MN-100 100 MHz instrument, $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Electrochemical measurements were made at 25 °C using a three electrode configuration, with a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (aq. KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research electrochemistry system, Model 170, with compensation for internal resistive potential drop. Substrate concentrations in CH_2Cl_2 were approximately 5×10^{-3} *M*. Tetrabutylammonium perchlorate, 0.1*M*, was employed as a base electrolyte. Sweep rates were varied from 50–200 mV/sec to optimize peak shapes. Data are given in Table I.

Cyclopentadienylmanganese tricarbonyl was prepared by the method of Cordes and Neubauer [10]. Phenyl isocyanide, *p*-chlorophenyl isocyanide, pentachlorophenyl isocyanide [11] and methyl isocyanide [12] were prepared by the cited literature methods.

Preparation of $Mn(C_5H_5)(C_6H_5NC)_3$

To a solution of $Mn(C_5H_5)(CO)_3$ (2.0 g, 10 mmol) in 100 ml THF in a 250 ml three-necked Pyrex flask fitted with condenser was added C_6H_5NC (4.5 g, 44 mmol). The solution was irradiated with a 100-watt General Electric mercury lamp for 48 h. The solvent was evaporated and the residue washed with several 100 ml portions of hexane. The hexane was removed and 3.0 g of orange cubes were crystallized from deaerated acetone–hexane (70% yield). Mp. 100 °C. *Anal.* Found: C, 72.63; H, 4.66; N, 9.83. $C_{26}H_{20}N_3Mn$: Calcd: C, 72.72; H, 4.70; N, 9.79%. Infrared: ν(CN) 2070m, 1955s,br. Pmr: τ3.00 (int. 15), τ5.50 (int. 5).

The following compounds were prepared by the same route.

TABLE I. Voltammetric Data.

Compound	$1/2\ [E_{p,c} + E_{p,a}]^a$	$\vert E_{p,c} - E_{p,a}\vert$	Process
$Mn(C_5H_5)(C_6H_5NC)_3$	0.13 1.12^b	180mV	$+0 \rightarrow +1$ $+1 \rightarrow +2$
$Mn(C_5H_5)(p\text{-}ClC_6H_4NC)_3$	0.22 1.05	220mV	$+0 \rightarrow +1$ $+1 \rightarrow +2$
$Mn(C_5H_5)(C_6Cl_5NC)_3$	0.65	100mV	$+0 \rightarrow +1$
$Mn(C_5H_5)(CH_3NC)_3$	−0.30 0.72^b 1.80^b	210mV	$+0 \rightarrow +1$ $+1 \rightarrow +2$ $+2 \rightarrow +3$
$Mn(C_5H_5)(CO)_3$	1.41	300mV	$+0 \rightarrow +1$
$Mn(C_5H_5)(CO)_2(CH_3NC)$	0.74	260mV	$+0 \rightarrow +1$

[a] Cathodic and anodic peak potentials in volts *vs.* SCE (aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3} *M*) with Bu_4NClO_4 (0.1 *M*) as supporting electrolyte . All processes are 1e oxidations; none meet the defined criterion for electrochemical reversibility, *i.e.*, $\vert E_{p,c} - E_{p,a}\vert < 0.059$ V. Generally reduction currents were slightly less than oxidation currents, indicative of chemical irreversibility. [b] The oxidation peak, $E_{p,a}$, is given; no reduction peak is seen.

$Mn(C_5H_5)(p\text{-}ClC_6H_4NC)_3$

After 96 h irradiation time, solvent was evaporated and the residue sublimed at 50 °C to remove unreacted ligand. The product was obtained as bright yellow needles on crystallization from acetone–diethyl ether (75% yield). Mp. 132 °C. *Anal.* Found: C, 58.33; H, 3.09; N, 7.79, $C_{26}H_{17}N_3Cl_3Mn$: Calcd: C, 58.62; H, 322; N, 7.89%. Infrared: ν(CN) 2070m, 1955s, br, Pmr: τ3.00m (int. 12), τ5.43s (int. 5).

$Mn(C_5H_5)(C_6Cl_5NC)_3$

The solution was irradiated for 27 h, the solvent removed, and the residue washed with acetone leaving red–orange crystals. The product was recrystallized as red cubes from toluene–chloroform (34% yield). Mp. 270 °C. *Anal.* Found: C, 32,98; H, 0.41; N, 4.38. $C_{26}H_5N_3Cl_{15}$: Calcd: C, 33.00; H, 0.53; N, 4.44%. Infrared: ν(CN) 2060m, 1915s,br.

$Mn(C_5H_5)(CH_3NC)_3$

Irradiation for 29 h was used. The product was obtained as yellow air-sensitive crystals from tetrahydrofuran–heptane (46% yield). Mp. 148–150 °C (sealed capillary). The poor analyses probably reflect the thermal and oxidative instability of this compound. *Anal.* Found: C, 55.24; H, 5.32; N, 16.09. $C_{11}H_{14}N_3Mn$: Calcd: C, 54.33; H, 5.80; N, 17.28%. Infrared: ν(CN) 2100m, 2030s, 1950m,br. Pmr: τ5.96 (int. 5), τ6.80 (int. 9).

Preparation of $Mn(C_5H_5)(CO)_2(CH_3NC)$

A mixture of 2.0 g (20 mmol) $Mn(C_5H_5)(CO)_3$ and 0.41 g (20 mmol) CH_3NC in 100 ml tetrahydrofuran was irradiated for 18 h. The solvent was evaporated and the residue was chromatographed on alumina. The major yellow band was collected, solvent evaporated, and the residue crystallized from petroleum ether solvent at −78 °C to give yellow crystals of the product (1.8 g, 90% yield). Mp. 92–93 °C. *Anal.* Found: C, 50.02; H, 3.51; N, 6.38; MW. 217. $C_9H_8NO_2Mn$: Calcd: C, 49.80; H, 3.69; N, 6.46%; MW. 217 (mass spect). Infrared: ν(CN) 2150m, ν(CO) 1950s, 1890s. Pmr. τ5.60(5), τ6.67(3).

Attempts to Prepare $Mn(C_5H_5)(CO)(CH_3NC)_2$

(i) To a solution of $Mn(C_5H_5)(CO)_3$ (4.0 g, 20 mmol) in 100 ml tetrahydrofuran was added CH_3NC (1.8 g, 44 mmol). The solution was irradiated for 18 h and the solvent evaporated. The residue was found to be air-sensitive so all crystallization attempts were performed under nitrogen in deaerated solvents. In spite of these precautions, periodic sampling for infrared spectra revealed changing patterns. The residue was finally sublimed to yield the only isolable product, 1.0 g $Mn(C_5H_5)(CO)_2(CH_3NC)$, identified by comparison of infrared and nmr spectra, and mp. (ii) To a solution of $Mn(CO)CH_3NC)_4Br$ (1.5 g, 4.6 mmol) in 100 ml tetrahydrofuran was added $Tl(C_5H_5)$ (1.5 g, 5.6 mmol). The solution was refluxed for 12h, the precipitate was removed by filtration and discarded, and the remaining red solution was evaporated to dryness. The residue was sublimed in vacuum at ~50 °C for 12 h yielding 0.20 g of yellow crystals which had the same infrared and nmr spectra and mp as the previously mentioned $Mn(C_5H_5)(CO)_2(CH_3NC)$.

Attempted Chemical Oxidation of $Mn(C_5H_5)L_3$ Compounds

Reactions of $AgPF_6$ with three $Mn(C_5H_5)L_3$ compounds (L = ClC_6H_4NC, C_6H_5NC, CH_3NC) were attempted. In each case encouraging color changes and infrared spectral changes occurred, and silver metal precipitated. Various workups of the reaction mixtures failed to yield any organometallic product however.

Results and Discussion

Only a few isocyanide derivatives of cyclopentadienylmanganese tricarbonyl were known prior to this work. The monosubstituted complexes, $Mn(C_5H_4Me)(CO)_2CNEt$ and $Mn(C_5H_5)(CO)_2CNH$, were prepared by alkylation and protonation of the respective cyano complexes. The trisubstituted complex, $Mn(C_5H_5)(CNPh)_3$, has been reported as the product of NaC_5H_5 and $[Mn(CNPh)_6]^+$. Some time ago one complex, $Mn(C_5H_5)(CO)_2(CN_6H_{11})$, was prepared by ligand substitution using either $Mn(C_5H_5)(CO)_3$ [14] or $Mn(C_5H_5)(CO)_2(py)$ [15] as a precursor. In part, the lack of study of this direct ligand substitution reaction prompted this work. It seemed likely that these reactions are the easiest route to the complexes $Mn(C_5H_5)(CO)_{3-n}(CNR)_n$.

Prolonged irradiation of $Mn(C_5H_5)(CO)_3$ and excess isocyanide was found here to lead to complete substitution; *viz.*:

$$Mn(C_5H_5)_3(CO)_3 + 3\ CNR \xrightarrow{h\nu} Mn(C_5H_5)(CNR)_3 + 3\ CO$$

$$(R = C_6H_5, C_6H_4Cl, C_6Cl_5, Me)$$

Reactions were run in tetrahydrofuran usually for about 20 hr; the extent of the reaction was monitored using infrared spectroscopy, periodic sampling the reaction mixture, and watching the disappearance of ν(CO) peaks of the partially substituted species. Generally monosubstitution was complete in an hour or so. Then the reaction progressed slowly to the fully substituted product. The reaction could be stopped at an early stage and the monosubstituted product isolated. Generally though, it was easier to obtain the monosubstituted products by using stoichiometric amounts of the reactants.

While monitoring the reaction of $Mn(C_5H_5)(CO)_3$ and CH_3NC no evidence was obtained for a disubstituted species. Only infrared absorptions associated with the mono- and tris- substituted species were observed; a lower frequency ν(CO) absorption expected for $Mn(C_5H_5)(CO)(CH_3NC)_2$ (probably to be found around 1820 cm^{-1}, the value found in $Mn(C_5H_5)(CO)(phos)_2$ compounds [3]) was not observed. Regardless, two attempts at synthesis were made. The first was a direct reaction of the reactants using the appropriate stoichiometry. The second, using milder conditions was via $Mn(CO)(CNMe)_4Cl$ [7] and TlC_5H_5. Both reactions yielded only the monosubstituted derivatives $Mn(C_5H_5)(CO)_2(CH_3NC)$. From the latter experiment, particularly, it appears that the disubstituted complex is unstable, either to disproportionation or because of facile $CNCH_3$ substitution.

The trisubstituted complexes, $Mn(C_5H_5)(CNR)_3$, (R = aryl) are yellow crystalline species. They are thermally stable and unreactive toward oxygen. However the alkyl isocyanide complex of this stoichiometry $Mn(C_5H_5)(CH_3NC)_3$, decomposes rapidly in air and required care in handling. Pmr spectra were recorded for each species, relative intensities defining their stoichiometry. Infrared spectra (in CH_2Cl_2 solutions and Nujol mulls) of these complexes revealed the expected ν(CN) absorptions. The same type of broad absorption is seen in $Cr(CNR)_6$ complexes [9]. The positions of the ν(CN) absorptions, well below the frequencies of the free ligand are indicative of high electron density at the metal resulting in extensive backbonding to these ligands.

It appeared likely that the complexes prepared here would undergo electron transfer reactions. Earlier we had studied the $[Mn(C_5H_5)(CO)diphos]^{0,1+}$ system using cyclic voltammetry, and had isolated stable 17e oxidized species [8]. The presence of good donor ligands such as phosphines and isocyanides is expected to lead to relatively facile oxidative reactions. Moreover the general inertness of the $Mn(C_5H_5)L_3$ species suggested that isolation of the oxidized species here might also be a possibility. Hence we investigated the oxidation chemistry of these compounds.

All of the trisubstituted complexes, $Mn(C_5H_5)(CNR)_3$, showed two oxidation waves on the cyclic voltammetry current–voltage scans, which corresponded to sequential one-electron oxidations. The first oxidations were at quite low voltages, −0.30v for the CH_3NC complex, +0.13v and 0.22v for the C_6H_5NC and p-ClC_6H_4NC complexes respectively. The pentachlorophenyl isocyanide complex was oxidized at a somewhat higher value, +0.65v reflecting the higher electron withdrawing effect of the C_6Cl_5 group. Interestingly, the systems did not appear to be chemically reversible since $i_{p,c} < i_{p,a}$. The difference was small, but indicative that difficulty might be encountered in attempts at synthesis of the 17e species. Indeed this proved to be the case. Oxidative reactions using $AgPF_6$ appeared to proceed as expected, giving Ag metal, and an increase of ν(CN); however isolation of the 17e complexes was never achieved though substantial effort was directed to this goal. Probably, the 17e species $[Mn(C_5H_5)(RNC)_3]^+$ are unstable with respect to ligand dissociation. The same observation had been made with the complex $Mn(C_5H_5)(CO)(PPh_3)_2$, which decomposed on oxidation [8].

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