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COMPETITIVE METALATION OF η^5-INDENYL- AND η^5-CYCLOPENTADIENYLTRICARBONYL COMPLEXES OF MANGANESE AND RHENIUM

I.A. LOBANOVA, V.I. ZDANOVICH, P.V. PETROVSKII and N.E. KOLOBOVA *

A.N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, Vavilov St. 28, Moscow 117813 (U.S.S.R.)

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Summary

Competitive metalation of the η^5-indenyl- and η^5-cyclopentadienyl-tricarbonyl complexes of manganese and rhenium by n-butyllithium in THF has been carried out and subsequent treatment of the lithium derivatives with trimethylchlorosilane has been performed. The following mixtures of compounds have been investigated: η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_3$, η^5-$C_9H_7Re(CO)_3$ and η^5-$C_5H_5Re(CO)_3$, η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_9H_7Re(CO)_3$, η^5-$C_5H_5Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$. It was shown that η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_3$ do not undergo metalation in the presence of the corresponding complexes of rhenium. On metalation η^5-indenyl and η^5-cyclopentadienyl ligands coordinated to the same metal differ slightly in reactivity. The trimethylsilyl derivatives of the η^5-indenyltricarbonyl complexes of manganese and rhenium were isolated as a mixture of two isomers in approximately equal amounts.

Introduction

Although indenyl π-complexes of transition metals are analogous to π-cyclopentadienyl species, they nevertheless exhibit some specific properties. In an indenyl ligand, a benzene ring fused with a 5-membered ring takes part in distribution of π-electron density. According to ref. 1, a weakening of both forward and backward metal-ring bonding occurs in η^5-indenyl complexes, which lowers their stability as compared with η^5-cyclopentadienyl species.

The comparative reactivity of the η^5-indenyl and η^5-cyclopentadienyl complexes of the transition metals was previously studied only for the exchange reactions of the coordinated CO for other n-donor ligands [2,3,4]. In this study we investigated the reactivity of the η^5-indenyl ligand, as compared with η^5-cyclopentadienyl species, in the hydrogen substitution reaction. With this in mind, we have studied metalation of

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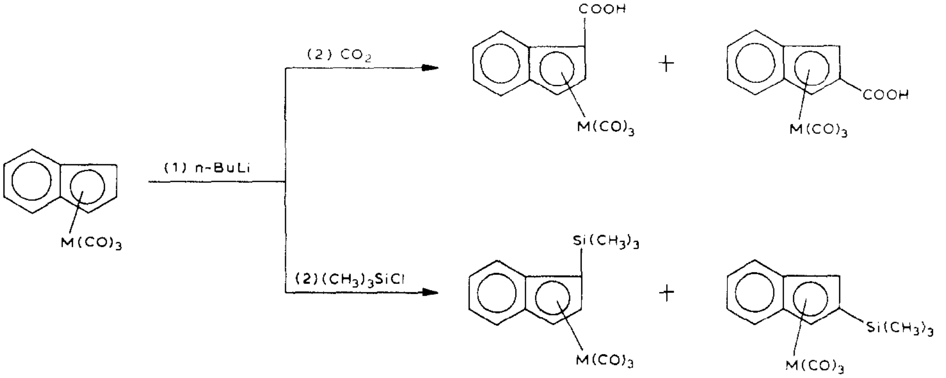
η^5-indenyltricarbonyl complexes of manganese and rhenium, η^5-$C_9H_7M(CO)_3$ (M = Mn, Re), by n-butyllithium in THF at −40 to −50°C with subsequent treatment of the lithium derivatives with solid CO_2 [5] or $(CH_3)_3SiCl$.

Results and discussion

We have found that the indenyltricarbonyl complexes of the Group VII metals undergo metalation only along the five-membered ring of the η^5-indenyl ligand to yield a mixture of 1- and 2-isomers. It is noteworthy that under these conditions benzene did not undergo metalation [6].



The yield and ratio of the isomers are dependent on the reaction conditions. For example, on metalation by one equivalent of n-butyllithium, the yield of a mixture of isomeric carboxylic acids is as large as 22%, while the ratio of the isomers, $(1\text{-}HOOC)C_9H_6M(CO)_3$ to $(2\text{-}HOOC)C_9H_6M(CO)_3$ is 1.7/1.0 for manganese complexes, and 1.2/1.0 for rhenium compounds [5]. It is known [7] that on metalation of the η^5-cyclopentadienyltricarbonyls of manganese and rhenium by one equivalent of n-butyllithium in THF followed by treatment with solid CO_2, carboxylic acids are produced in quantitative yields. The foregoing might suggest that η^5-cyclopentadienyl complexes possess greater reactivity than η^5-indenyl compounds. This study has shown that metalation of the η^5-indenyltricarbonyl complexes of manganese and rhenium by a twofold excess of n-butyllithium raises the yields of carboxylic acids to 67–70%, the ratio of isomers being 2.3/1.0 for manganese, and 2.6/1.0 for rhenium. To make a quantitative estimation of the comparative reactivity of the complexes involved, we have carried out competitive metalation of the mixtures η^5-$C_9H_7M(CO)_3$ and η^5-$C_5H_5M(CO)_3$ (M = Mn, Re) by n-butyllithium for the following pairs of compounds: (1) η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_3$, (2) η^5-$C_9H_7Re(CO)_3$ and η^5-$C_5H_5Re(CO)_3$, (3) η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_9H_7Re(CO)_3$; (4) η^5-C_5H_5-$Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$. Metalation was performed using one equivalent of n-butyllithium and one equivalent of each complex in THF at −40 to −50°C. Upon treatment of the reaction mixture with trimethylchlorosilane, the solvent was evaporated and the residue was chromatographed to isolate a fraction containing both the starting materials and reaction products. Decomposition in the course of the reaction and during treatment was negligible. The mixture obtained was analyzed by ^1H NMR spectroscopy. The ratio of the reaction products as well as that of the unreacted starting compounds were calculated from the integrated signal intensity of

TABLE 1

THE RESULTS OF COMPETITIVE METALATION OF $C_9H_7M(CO)_3$ AND $C_5H_5M(CO)_3$ (M = Mn, Re)

Reagents	Mixture	Products (%)	Yield [a]	Molar ratio of unreacted complexes in mixture [b]	Molar ratio of reaction products in mixture [b]		Molar ratio of isomers $\frac{1\text{-}(CH_3)_3SiC_9H_6M(CO)_3}{2\text{-}(CH_3)_3SiC_9H_6M(CO)_3}$	
					1 [c]/	2 [d]/	1 [c]/	2 [d]
$C_5H_5Re(CO)_3$	4	$(CH_3)_3SiC_5H_4Re(CO)_3$	60	2.0				
$C_5H_5\overset{+}{Mn}(CO)_3$		–	–					
$C_9H_7Re(CO)_3$	3	$(CH_3)_3SiC_9H_6Re(CO)_3$	39	1.7			1.4	1.1
$C_9H_7\overset{+}{Mn}(CO)_3$								
$C_5H_5Mn(CO)_3$	1	$(CH_3)_3SiC_5H_4Mn(CO)_3$	33	1.2	1.2	1.3		
$C_9H_7\overset{+}{Mn}(CO)_3$		$(CH_3)_3SiC_9H_6Mn(CO)_3$	33				1.3	0.9
$C_5H_5Re(CO)_3$	2	$(CH_3)_3SiC_5H_4Re(CO)_3$	11	0.8	1.6	1.4		
$C_9H_7\overset{+}{Re}(CO)_3$		$(CH_3)_3SiC_9H_6Re(CO)_3$	20				1.5	1.3

[a] Yields were determined with the amounts of molar fractions of the starting complexes and products in the mixture being assumed to be 100%. [b] The ratio is given for C_9H_7/C_5H_5 complexes and Mn/Re complexes. [c] Determination from the overall integrated ^1H NMR signal intensity of a five-membered ring. [d] Determination from the integrated ^1H NMR signal intensity of CH_3 groups.

protons of $(CH_3)_3Si$ groups and the overall signal intensity of protons of the five-membered ring. Similarly, the two methods were used to calculate the ratio of 1- and 2-isomeric trimethylsilyl derivatives. The results obtained are summarized in Table 1 which shows that rhenium compounds exhibit a much greater tendency for protophilic substitution reactions than do similar manganese complexes. So in the presence of rhenium complexes, the cyclopentadienyl and indenyl derivatives of manganese will not undergo metalation at all. This is in accordance with the conclusion that the $Re(CO)_3$ group has a larger electron-acceptor effect than $Mn(CO)_3$ [8]. It was earlier reported [9] that the rate of protophilic isotope hydrogen exchange of $C_5H_5Re(CO)_3$ with C_2H_5OD in the presence of bases is 26 times as high as that for $C_5H_5Mn(CO)_3$. Table 1 also indicates that the η^5-indenyl complexes are somewhat more reactive than the corresponding η^5-cyclopentadienyl compounds, although they differ only slightly. It has also been found that the 1- and 2-positions of the five-membered ring of the η^5-indenyl ligand of the manganese and rhenium complexes show essentially similar reactivity in the metalation reaction. It is noteworthy that under the conditions of competitive metalation the yields of trimethylsilyl derivatives range from 20 to 30%. Higher yields (up to 80%) were obtained using a twofold excess of n-butyllithium. In this case the ratio of the 1- and 2-isomers would remain unchanged at about unity.

Experimental

Experiments were run in an inert gas atmosphere. ^1H NMR spectra were obtained on a Bruker WP-200-SY spectrometer (200, 13 MHz, TMS as an internal standard), IR spectra on a UR-20 and Specord 71IR, and mass spectra on a MS-30 at 70 eV. Use was made of solvents distilled in Ar, the sorbent being SiO_2 L 100/200 μ.

Competitive metalation

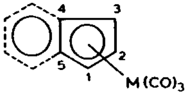
A 1.0 N solution of $n\text{-}C_4H_9Li$ (1 mmol) in hexane was added to a mixture of 1 mmol of both complexes of the mixtures 1–4 in THF and stirred at -50 to -55°C. After stirring at -40 to -45°C for 30 min, 3–6 mmol of $(CH_3)_3SiCl$ was added to the reaction mixture. This was slowly heated to 20°C, the solvent was evaporated and the residue was chromatographed on the column. Pentane was used to elute a wide band containing a mixure of starting materials and products. Upon removal of the solvent in vacuum, the mixture was analyzed by ^1H NMR spectroscopy (Table 2).

Trimethylsilylindenyltricarbonylmanganese

3.35 ml of a 1.01 N solution of $n\text{-}C_4H_9Li$ (3.39 mmol) in hexane was added to a solution of 0.43 g (1.7 mmol) of $\eta^5\text{-}C_9H_7Mn(CO)_3$ [10] in 21 ml of THF and stirred at -55°C. After stirring at -40 to -50°C for one hour, 2 ml (15.72 mmol) of $(CH_3)_3SiCl$ was added to the reaction mixture, and slowly heated to 20°C. The solvent was then evaporated, and the residue was chromatographed on the column. Petroleum ether was used to elute a wide band which, upon repeated chromatography, yielded 0.04 g (9.3%) of $C_9H_7Mn(CO)_3$ (identified by TLC, mass and IR spectra) and 0.36 g (66%) of a mixture of $1\text{-}(CH_3)_3SiC_9H_6Mn(CO)_3$ and $2\text{-}(CH_3)_3SiC_9H_6Mn(CO)_3$ (eluent petroleum ether/CH_2Cl_2, 50/1). IR spectrum (CH_2Cl_2) $\nu(CO)$: 2021, 1940 cm^{-1}. Anal. Found: C, 55.23; H, 4.69; Si, 8.46. $C_{15}H_{15}MnO_3Si$ calcd.: C, 55.21; H, 4.63; Si, 8.61%.

TABLE 2

PARAMETERS OF THE ^1H NMR SPECTRA OF $XC_9H_6M(CO)_3$ AND $XC_5H_4M(CO)_3$ (X = H, $Si(CH_3)_3$; M = Mn, Re (acetone-d_6))

Starting compounds	Chemical shifts of protons of 5-membered ring δ, ppm		Reaction products	Chemical shifts of protons, δ, ppm					
				CH_3	five-membered ring				
	H^1 and H^3	H^2			H^1	H^2	H^3	H^4	H^5
$C_5H_5Mn(CO)_3$	4.86 s		$(CH_3)_3SiC_5H_4Mn(CO)_3$	0.22	–	4.93	5.00	5.00	4.93
$C_5H_5Re(CO)_3$	5.56 s		$(CH_3)_3SiC_5H_4Re(CO)_3$	0.23	–	5.63	5.66	5.66	5.63
$C_9H_7Mn(CO)_3$	5.36 d	5.11t	1-$(CH_3)_3SiC_9H_6Mn(CO)_3$	0.43	–	5.15 d	5.60 d		
			2-$(CH_3)_3SiC_9H_6Mn(CO)_3$	0.25	5.49s	–	5.49s		
$C_9H_7Re(CO)_3$	5.95d	5.82t	1-$(CH_3)_3SiC_9H_6Re(CO)_3$	0.42	–	5.83d	6.17d	(J(2,3) 3,0; J(3,4) 0,7 Hz)	
			2-$(CH_3)_3SiC_9H_6(CO)_3$	0.26	6.04s	–	6.04s		

Trimethylsilylindenyltricarbonylrhenium

To a stirred solution of 0.23 g (0.6 mmol) of η^5-$C_9H_7Re(CO)_3$ [10] in 15 ml of THF at −55°C was added 1.3 ml of 1.02 *N* solution of n-C_4H_9Li (1.33 mmol) in hexane. After stirring at −40 to −50°C for 105 min, 1 ml (7.86 mmol) of $(CH_3)_3SiCl$ was added, the reaction mixture was allowed to warm to 20°C, and the solvent was evaporated. The residue was chromatographed on the column. A mixture of petroleum ether and ether (10/1) was used to elute a pale-yellow band, which, on repeated chromatography, yielded 0.22 g (80.5%) of the mixture of 1-$(CH_3)_3SiC_9H_6Re(CO)_3$ and 2-$(CH_3)_3SiC_9H_6Re(CO)_3$ (petroleum ether eluent). IR spectrum (CH_2Cl_2) ν(CO): 2020, 1926 cm^{-1}. Anal Found: C, 39.90; H, 3.44; Re, 40.91; Si, 5.94 $C_{15}H_{15}ReO_3Si$ calcd.: C, 39.37; H, 3.30; Re, 40.69; Si, 6.14%.

Preparation of η^5-$C_9H_6(COOH)Mn(CO)_3$

To a stirred solution of 0.41 g (1.62 mmol) of η^5-$C_9H_7Mn(CO)_3$ in 20 ml of THF at −50°C was added dropwise 4.05 ml of 0.8 *N* solution of n-C_4H_9Li (3.24 mmol) in hexane. After stirring at −40 to −50°C for one hour, the reaction mixture was treated with solid CO_2. Upon volatilization of CO_2, the solution was evaporated, and the residue was extracted by pentane to yield 0.08 g (19.5%) of $C_9H_7Mn(CO)_3$. The resulting solid was dissolved in aqueous $NaHCO_3$, filtered, and HCl was added to the filtrate up to pH 1. The yellow precipitate was filtered, washed with water, and dried in vacuo at 56°C to yield 0.34 g (70.5%) of $(HOOC)C_9H_6Mn(CO)_3$ (the mixture of 1 and 2-isomers) IR spectrum (KBr): 1685, 1690 (ν(C=O)), 1942, 1955, 2025 (ν(C≡O)), 2500–3100 (OH) cm^{-1}. Mass spectrum, *m/z*: 298 $(M)^+$, 270 $(M-CO)^+$, 242 $(M-2CO)^+$, 214 $(M-3CO)^+$. Anal. Found: C, 52.40; H, 2.76; Mn, 18.50. $C_{13}H_7MnO_5$ calcd.: C, 52.37; H, 2.37; Mn, 18.43%.

Preparation of η^5-$C_9H_6(COOH)Re(CO)_3$

To a stirred solution of 0.32 g (0.84 mmol) of η^5-$C_9H_7Re(CO)_3$ in 15 ml of THF at −45°C was added 2 ml of 0.9 *N* solution of n-C_4H_9Li (1.8 mmol) in hexane. After stirring at −40 to −50°C for 1.5 h, the reaction mixture was treated with solid CO_2. On volatilization of CO_2, the solution was evaporated and the residue was extracted by pentane to yield 0.07 g (22%) of $C_9H_7Re(CO)_3$ identified by TLC, IR and mass spectra. Following pentane extraction, the residue was dissolved in aqueous $NaHCO_3$, filtered, and the filtrate was acidified by HCl up to pH 1. A white precipitate was filtered, washed with water, and dried in vacuo at 56°C to obtain 0.24 g (67%) of $(C_9H_6COOH)Re(CO)_3$ (the mixture of isomers 1 and 2). IR (KBr): 1678, 1692 (ν(C=O)), 1932, 1955, 2025 (ν(C≡O)), 2500–3100 (OH) cm^{-1} Mass spectrum, *m/z*: 430 $(M)^+$, 402 $(M-CO)^+$, 386 $(M-CO_2)^+$, 374 $(M-2CO)^+$, 356 $(M-3CO)^+$. Anal. Found: C, 36.41; H, 1.68; Re, 43.11. $C_{13}H_7O_3Re$ calcd.: C, 36.36; H, 1.64; Re, 43.36%.

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