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TRANSITION METAL CARBONYLATES IN NUCLEOPHILIC AROMATIC SUBSTITUTION

II *. MEDIUM EFFECTS FOR SUBSTITUTION IN 2-(PENTACARBONYLMANGANESE)-4,6-DIFLUORO-1,3,5-TRIAZINE

G.A. ARTAMKINA*, A. Yu. MIL'CHENKO, I.P. BELETSKAYA and O.A. REUTOV
Department of Chemistry, Moscow State University, 119899 GSP-3 Moscow V-234 (U.S.S.R.)

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Summary

Effects of counterion, solvent and solvating agents were studied for the reactions of transition metal carbonylates $CpFe(CO)_2^-$, ($Cp = C_5H_5$), $Re(CO)_5^-$, $Mn(CO)_5^-$, $CpW(CO)_3^-$, $CpMo(CO)_3^-$ with 2-(pentacarbonylmagnanese)-4,6-difluoro-1,3,5-triazine. The observed trends substantiate the hypothesis of enhanced reactivity of contact ion pairs as compared to solvent-separated ion pairs and free ions.

In the preceding article [1] we have demonstrated that in the reactions of $Re(CO)_5^-$, $Mn(CO)_5^-$ and $CpW(CO)_3^-$ ($Cp = C_5H_5$) with hexafluorobenzene and pentafluoropyridine contact ion pairs (further denoted as CIP) are markedly more reactive than both solvent-separated ion pairs (SSIP) and free ions. In order to verify the observed reactivity pattern we tried to extend kinetic studies to reactions of the same carbonylates and also of $CpFe(CO)_2^-$ and $CpMo(CO)_3^-$ with cyanuric fluoride. However, even at low temperatures (down to −40 °C) the reactions were too fast to enable rate measurements by the method used in our previous studies [1], even for the least reactive nucleophile in the series $CpMo(CO)_3^-$. Introduction of an electron-rich carbonylate group (e.g. $Mn(CO)_5$) in the molecule of cyanuric fluoride caused an essential retardation of the second metallation step (the third atom could not be substituted at all). Thus, here we discuss the kinetics of reactions between I and the following carbonylates $CpFe(CO)_2^-$ (a), $Mn(CO)_5^-$ (b), $Re(CO)_5^-$ (c), $CpW(CO)_3^-$ (d), $CpMo(CO)_3^-$ (e).

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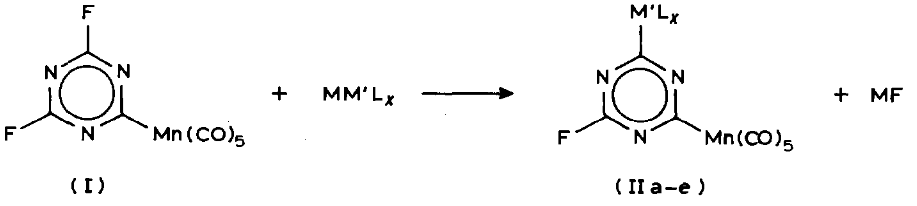

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[*] For part I see ref. 1.

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TABLE 1

THE KINETIC DATA FOR THE REACTION OF TRANSITION METAL CARBONYLATES WITH I

Num.	Carbonylate	Solvent	T (°C)	Other components, equiv. per mole of the carbonylate	Carbonylate ($\times 10^{-3}$), M	Substrate ($\times 10^{-3}$), M	k_2 ($\times 10^{-2}$), M^{-1} s^{-1}
1	$CpFe(CO)_2K$	THF	-52 ± 0.5		4.65	4.92	390
					6.0	6.2	405
2	$CpFe(CO)_2K$	THF	-52 ± 0.5	18-c-6, 2	5.2	5.6	110
					10.7	10.9	105
3	$CpFe(CO)_2K$	THF	-52 ± 0.5	HMPA, 20	5.0	5.54	89.5
					5.4	5.6	89
					4.1	4.53	87
4	$CpFe(CO)_2K$	ether	-52 ± 0.5		3.26	3.28	too high
5	$CpFe(CO)_2Li$	THF	-52 ± 0.5		4.3	4.32	600
					3.9	3.92	560
6	$CpFe(CO)_2Li$	THF	-52 ± 0.5	HMPA, 20	4.7	5.03	91
					5.4	5.60	87
7	$Re(CO)_5Na$	THF	-18 ± 1		4.59	5.11	810
					2.50	2.60	830
8	$Re(CO)_5Na$	THF	-18 ± 1	HMPA, 20	3.4	3.86	300
					5.6	5.75	297
9	$Re(CO)_5Na$	THF	-18 ± 1	Ph_4AsClO_4, 1	2.3	2.57	260
					5.0	5.20	273

10	$CpW(CO)_3K$	THF	−18 ± 1		9.4	10.35	7.3
					5.1	8.7	7.1
11	$CpW(CO)_3K$	THF	−12 ± 1		9.8	11.2	12.2
					7.2	15.0	11.5
12	$Mn(CO)_5K$	THF	−18 ± 1		20.5	26.4	1.30
					8.0	15.0	1.23
13	$Mn(CO)_5K$	THF	−12 ± 1		10.7	13.8	2.40
					5.0	12.0	2.32
14	$Mn(CO)_5K$	THF	0 ± 0.5		6.22	8.58	7.30
					10.5	15.0	7.15
15	$Mn(CO)_5K$	THF	0 ± 0.5	18-c-6, 1	6.7	9.45	5.58
					11.0	16.0	5.47
16	$Mn(CO)_5K$	THF	0 ± 0.5	18-c-6, 2	4.66	6.58	5.16
					8.70	10.60	5.13
17	$Mn(CO)_5K$	THF	0 ± 0.5	HMPA, 20	12.0	14.0	2.43
					8.7	12.0	2.40
18	$Mn(CO)_5K$	THF	0 ± 0.5	Ph_4AsClO_4, 1	14.5	17.7	2.14
					8.1	12.3	2.10
19	$Mn(CO)_5K$	ether	0 ± 0.5		4.8	5.23	54
					3.2	4.5	53
20	$Mn(CO)_5Li$	THF	0 ± 0.5		14.1	20.0	1.9
					19.5	25.1	1.9
21	$CpMo(CO)_3K$	THF	−18 ± 1		20.0	28.0	0.80
					8.0	26.0	0.76
22	$CpMo(CO)_3K$	THF	0 ± 0.5		12.0	25.0	2.85
					8.6	16.8	2.96

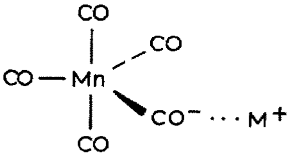
In all cases, the reactions at negative temperatures were fast and gave nearly quantitative yields. At room temperature the rates were too high to be measured, and the yields of II(a–e) decreased (probably owing to ring cleavage side reactions). The products II(a–e) are crystalline solids liable to degradation on heating or in solution. As solids II(a–e) can be stored in air from several days to several weeks; in an inert atmosphere or in vacuo II(a–e) are immensely stable. The products were characterized by their microanalyses, IR and ^{19}F NMR spectra (see Experimental section).

Table 1 lists the results of kinetic measurements. The overall trends in reactivity were essentially the same as those observed for the reactions with hexafluorobenzene and pentafluoropyridine. $CpFe(CO)_2^-$ is the most reactive species towards all the substrates, its reaction with the cyanuric fluoride derivative (I) being fairly fast even at −52°C (exp. 1). For all the other carbonylates kinetics were conveniently followed at a higher temperature (−18°C). According to the kinetic data the reactivity of carbonylates decreases in the following order: $CpFe(CO)_2^- \gg Re(CO)_5^-(1025) > CpW(CO)_3^-(9) > Mn(CO)_5^-(1,6) > CpMo(CO)_3^-(1)$.

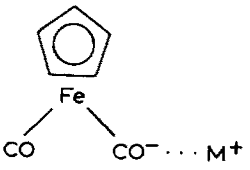
Iron and manganese carbonylates were selected for detailed investigation of the effects exerted by solvents, complexing agents and counterions (exp. 1–6, 12–20). The effects of added HMPA and tetraphenylarsonium perchlorate were also studied for rhenium carbonylate (exp. 7–9). Poor solubility of tetraphenylborates at low temperatures, unfortunately, interfered with elucidation of the common ion effect.

The addition of 18-crown-6 ether, HMPA or Ph_4AsClO_4 invariably caused a marked change in reaction rates, a 1.5–2-fold decrease for the crown ether to a 3–5-fold decrease for HMPA (exp. 2, 3, 6, 8, 9, 15, 18). Inasmuch as these agents are believed to induce conversion of CIP into SSIP and free ions [2–4], the supposition of the superior reactivity of CIP is consistent with the experimental facts. One more solid argument in favour of this hypothesis can be easily drawn from the sharp acceleration (more than 40-fold, exp. 4, 19) observed for the reactions run in ether, the only solvent in which CIP are known to occur.

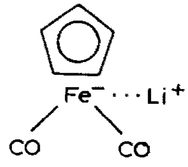
Furthermore, we have observed different responses in the reactivity of iron and manganese carbonylates to the changeover of the counterion from K to Li; the reaction with $Mn(CO)_5^-$ showed a 4-fold decrease in rate (exp. 14 and 20), while the corresponding iron compound reacted 1.5 times faster (exp. 1 and 5). It is very likely that this finding can be accounted for by a different structure of the lithium salts when in solution.



(III) M = Li, K



(IV)



(V)

Under experimental conditions, $LiMn(CO)_5$ predominantly occurs as SSIP. In CIP, which constitutes less than 10 percent of the total amount of $LiMn(CO)_5$, the lithium cation is bound to the oxygen atom of a carbonyl ligand (a similar structure was ascribed to CIP of $KMn(CO)_5$, formula III [2]). These suggestions could be used to reinforce our hypothesis of lower reactivity of SSIP as compared to CIP. For $LiFe(CO)_2Cp$ the amount of SSIP in solution is relatively small, while the abundant CIP occurs as a roughly equimolar mixture of species having structures IV and V [4]. Only CIP of type IV, were detected in THF solutions of $KFe(CO)_2Cp$ [4]. The specific features in the structures of CIP are most likely to account for their different reactivities (species of the type V might well be more reactive than those of the type IV in view of a more facile coordination of the counterion with the leaving fluoride). It is worth mentioning that on addition of HMPA to the solution of $LiFe(CO)_2Cp$ (exp. 6) the reaction rate decreased sharply and was equal to that for $KFe(CO)_2Cp$ measured in the presence of the same agent (exp. 3). Solvation of counterions, probably cancels out their effect on the reaction rates, making them solely dependent on the reactivities of the anions.

Thus, the evidence presented here substantially reinforces our recent suggestion that cationic assistance is a vital feature in aromatic nucleophilic substitution with the participation of transition metal carbonylates.

Experimental

^{19}F NMR spectra were recorded on a JEOL FX-100 spectrometer with $CFCl_3$ as an external standard in THF-d_8 solvent stored over 4 Å molecular sieves. IR spectra were recorded in THF on a UR-20 (Zeiss) instrument in CaF_2 cells of 0.11 mm path-length.

Purification of solvents and starting compounds, synthesis of carbonylates were done as in [1]. $LiFe(CO)_2Cp$ was prepared from $[CpFe(CO)_2]_2$ by reduction with 0.3% lithium amalgam [4]. The substrate I was prepared from cyanuric fluoride and $KMn(CO)_5$ at −18°C with 90% yield after purification by subliming in vacuum (50°C/0.01 Torr) with subsequent recrystallization from dry hexane. Physical constants of I were in good agreement with [5].

The general method used in the kinetic measurements can be found in ref. 1. Preparative-scale experiments were run at −30– −10°C in THF, the concentrations of the reagents were 5×10^{-2} *M* and the carbonylate: I ratio was 1 : 1. After removal of the solvent, the solid residue was twice recrystallized from a benzene : pentane (1 : 1) mixture and dried in vacuum. The rhenium and manganese compounds were further purified by sublimation (50–60°C/0.01 Torr). Reaction mixtures were kept at negative temperatures by the use of cold baths in Dewar flasks: −52°C, $CHCl_3$/dry ice; −18°C, CCl_4: ether (2 : 1)/liq. N_2; −12°C, n-butanol-water (4 : 1)/liq. N_2; 0°C, water/ice.

IIa: yield 91%, dark-yellow crystals, which darkened when heated to above 120°C; ^{19}F NMR, δ (ppm): 42.3; IR, $\nu(CO)$ (cm^{-1}): 2116w, 2055sh, 2036sh, 2024vs, 2015vs, 2000s; Found: C, 38.44; H, 1.10; N, 8.77; [Fe] : [Mn] 1 : 1. $C_{15}H_5FFeMnN_3O_7$ calc: C, 38.38; H, 1.07; N, 8.95%. [Fe] : [Mn] 1 : 1.

IIb: yield 93%, white crystals, which darkened when heated to above 155°C; ^{19}F NMR, δ (ppm): 38.5; IR, $\nu(CO)$ (cm^{-1}): 2135w, 2070w(sh), 2039vs, 2013vs; Found: C, 33.35; N 8.70; Mn 23.0. $C_{13}FMn_2N_3O_{10}$ calc: C, 32.7; N, 8.62; Mn, 22.59%.

IIc: yield 94%, white crystals, decomposed without melting above 100°C; ^{19}F NMR, δ(ppm): 38.4; IR, $\nu(CO)$(cm^{-1}): 2124w, 2116w, 2092sh, 2062sh, 2032sh, 2028vs, 2005vs; Found: C, 25.33; Mn, 9.0. $C_{13}FMnN_3O_{10}Re$ calc: C, 25.24; Mn 8.9%.

IId: yield 89%, yellow solid, darkened when heated to above 110°C; ^{19}F NMR, δ(ppm): 39.4; IR, ν(CO)(cm^{-1}): 2128w, 2120w, 2028vs, 2015sh, 1969s; Found: C, 30.64; N, 6.60; Mn, 8.7. $C_{16}H_5FMnN_3O_8W$ calc: C, 30.70; N, 6.72; Mn, 8.80%.

IIe: yield 88%, yellow crystals, decomposed above 130°C; ^{19}F NMR, δ(ppm): 39.1; IR, ν(CO)(cm^{-1}): 2128w, 2070sh, 2031vs, 2010sh, 1950w; Found: N, 7.83; Mn, 10.4. $C_{16}H_5FMnMoN_3O_8$ calc: N. 7.82; Mn, 10.24.

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