

TRANSITION METAL CARBYNOLATES IN NUCLEOPHILIC AROMATIC SUBSTITUTION

I. INFLUENCE OF IONIC ASSOCIATION ON THE RATES OF REACTIONS WITH PERFLUOROAROMATIC SUBSTRATES

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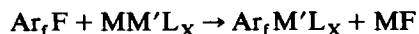
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Summary

Quantitative yields of monosubstituted products were obtained from the reactions between $\text{CpFe}(\text{CO})_2^-$ ($\text{Cp} = \text{C}_5\text{H}_5$), $\text{Re}(\text{CO})_5^-$ and C_6F_6 , $\text{C}_5\text{F}_5\text{N}$; and $\text{CpW}(\text{CO})_3^-$, $\text{Mn}(\text{CO})_5^-$ and $\text{C}_5\text{F}_5\text{N}$. The kinetics of the reactions of $\text{Re}(\text{CO})_5^-$ with C_6F_6 , and of $\text{CpW}(\text{CO})_3^-$ and $\text{Mn}(\text{CO})_5^-$ with $\text{C}_5\text{F}_5\text{N}$ were studied with respect to solvent, counterion, complexing agents and common ion effects. In all of the reactions studied, contact ion pairs were observed to be more reactive than solvent-separated ion pairs or free ions.

Although both neutral and anionic metal carbonyls have been extensively used in various organic preparations, there is only scarce kinetic and mechanistic evidence as to how their reactions proceed. Rate constants, solvent and counterion effects have been investigated for the reactions of $\text{MCo}(\text{CO})_4$ with substituted benzyl chlorides [1], $\text{MMn}(\text{CO})_5$ with benzyl and allyl halides [2], and $\text{MCpMo}(\text{CO})_3$ ($\text{Cp} = \text{C}_5\text{H}_5$) with n-butyl and benzyl halides [3,4]. Counterion effects for the reactions of $\text{MCpFe}(\text{CO})_2$ with epoxides [5], and $\text{MCpW}(\text{CO})_3$ with $\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_4\text{I}$ [6], along with the effects of solvent polarity on the interaction between $\text{Na}_2\text{Fe}(\text{CO})_4$ and n- $\text{C}_{10}\text{H}_{21}\text{Br}$, have also been discussed [7]. However, there is little evidence of the reaction kinetics of transition metal carbonylates with halogen-substituted aromatics, in the literature. Furthermore, only a few of such reactions have been reported hitherto, poor yields not being infrequent. Therefore, we have undertaken an investigation of the kinetics of nucleophilic aromatic substitution in perfluorobenzene and perfluoropyridine effected by the carbonylates of metals of Groups VI, VII and VIII.



The choice of these perfluoroaromatic substrates arose from their high reactivity

and symmetric structure, as well as from their reluctance to exchange fluorine for an alkali metal with successive transmetallation, that enabled us to neglect this pathway of product formation.

The reactions of $\text{NaCpFe}(\text{CO})_2$ with C_6F_6 and $\text{C}_5\text{F}_5\text{N}$ were reported [8,9] to require prolonged refluxing to yield 49 and 60% of substitution products, respectively; $\text{NaRe}(\text{CO})_5$ reacted with the same substrates to yield 16% of $\text{C}_6\text{F}_5\text{Re}(\text{CO})_5$ and 60% of $\text{NC}_5\text{F}_4\text{Re}(\text{CO})_5$ [10–12]. In the case of $\text{NaCpW}(\text{CO})_3$ and $\text{NaMn}(\text{CO})_5$, only the more reactive $\text{C}_5\text{F}_5\text{N}$ underwent substitution, the yields not exceeding 11 and 46%, respectively, on prolonged refluxing [8,13]. $\text{CpMo}(\text{CO})_3^-$ was reported to be unreactive towards these substrates [9,13]. In all cases, the substitution in $\text{C}_5\text{F}_5\text{N}$ was selectively directed in the γ -position.

Since the yields of substitution products have usually been reported to be moderate to low, we have carried out an optimization of the reaction conditions. In vacuo or under thoroughly purified argon, all the reactions of the carbonylates under study with the perfluoroaromatic substrates were found to proceed rapidly with close to quantitative yields (90–94%) even at low concentrations of the reagents.

Kinetic measurements were done at anion concentrations in the range 3×10^{-3} – 6×10^{-2} M, concentrations of Ar_rF in the range 5×10^{-3} – 6×10^{-1} M, in THF or ether at 25°C. The kinetics were followed by quantitatively determining the liberated fluoride ion by means of a fluoride-selective electrode. We have confirmed that $\text{CpMo}(\text{CO})_3^-$ is unreactive towards these fluoroaromatic substrates. For example, on exposing a mixture of $\text{KCpMo}(\text{CO})_3$ and substrate for 3–4 h at 35–40°C in vacuo, no fluoride anion could be detected while the recovery of the starting carbonylate amounted to 90–93%. On the other hand, the reactions of $\text{KCpFe}(\text{CO})_2$ with both $\text{C}_5\text{F}_5\text{N}$ and C_6F_6 were too fast to enable kinetic measurements by common methods (e.g. by spectrophotometric monitoring of the increase of the products absorption band with λ_{max} 350 nm at an initial anion concentration of 1×10^{-3} M). Although the reaction of $\text{NaRe}(\text{CO})_5$ with $\text{C}_5\text{F}_5\text{N}$ is also extremely fast, we have succeeded in measuring the rate of the reaction with less reactive C_6F_6 (Table 3). On the contrary, $\text{MMn}(\text{CO})_5$ ($M = \text{K}, \text{Li}$) and $\text{KCpW}(\text{CO})_3$ reacted at a reasonable rate only with $\text{C}_5\text{F}_5\text{N}$ (Tables 1 and 2). Depending on the reactivity of the carbonylate, kinetic runs were carried out either in excess of the perfluoroaromatic to secure pseudo-first-order conditions, or at comparable concentrations of both reagents. In all cases of second-order kinetics, no considerable deviations from linearity of the kinetic plots in appropriate coordinates (see Experimental section) were observed up to near completion. The rate constants obtained in runs with different initial concentrations were in good agreement.

We shall now consider separately the results obtained for each of the carbonylates.

$\text{Mn}(\text{CO})_5^-$. In dilute THF solutions, $\text{NaMn}(\text{CO})_5$ is known [2] to be a mixture of contact and solvent-separated ion pairs; at concentrations of the order of 10^{-2} M, contact ion pairs become predominant. In the presence of complexing agents, such as HMPA or 15-crown-5 ether (10–20 equiv. per mole) in THF solutions of $\text{NaMn}(\text{CO})_5$, solvent-separated ion pairs and free ions occur. In ether solutions of $\text{NaMn}(\text{CO})_5$, only contact ion pairs are detected. For $\text{LiMn}(\text{CO})_5$ in THF, the dissociation equilibrium is shifted towards solvent-separated ion pairs and free ions [2].

TABLE 1
RATE CONSTANTS FOR THE REACTION OF $\text{MMn}(\text{CO})_5$ WITH $\text{C}_5\text{F}_5\text{N}$ AT 25°C

Nr.	M	Solvent ^a	Other components ^b	c ($\times 10^{-2}$) (M)	$[\text{C}_5\text{F}_5\text{N}]$ ($\times 10^{-1}$) (M)	K_1 ($\times 10^{-4}$) (s^{-1})	K_2 ($\times 10^{-3}$) ($\text{M}^{-1} \text{s}^{-1}$)
1	K	THF		1.48	1.46	13.0	8.90
				1.50	1.51	13.5	8.95
				0.510	0.533	4.7	8.82
2	K	THF	18-c-6 (1)	2.0	2.51	16.5	6.6
				2.51	4.27	28.7	6.7
				2.02	2.00	12.8	6.4
3	K	THF	18-c-6 (2)	1.01	1.00	4.1	4.1
4	K	THF	18-c-6 (4)	1.03	1.20	4.7	3.9
5	K	THF	HMPA (20)	0.987	1.22	1.4	1.1
				2.05	2.04	2.8	1.3
6	K	THF	Ph_4AsCl (1)	0.455	4.14	2.9	0.7
			$\text{Ph}_4\text{AsClO}_4$ (1)	0.497	3.01	1.8	0.6
7	K	ether		1.04	1.00	> 800	
				0.730	0.225		134
				0.915	0.129		127
8	Li	THF		3.60	4.10	2.5	0.61
				6.0	5.9	3.7	0.63
9	Li	THF	Ph_4BLi (10)	1.00	1.0	6.3	6.3
			Ph_4BLi (15)	1.13	1.23	8.0	6.5

^a In THF, all the experiments were run under pseudo-first-order conditions. ^b The number of equiv. per one equiv. of carbonylate is given in parentheses.

In the reaction under study, we used the potassium salt $\text{KMn}(\text{CO})_5$, preparation of which can be fulfilled by reduction of the corresponding dimer with NaK alloy not only faster but with better yields (96–98%) as compared to the reduction with $\text{Na}(\text{Hg})$ yielding 81–83% of the sodium salt contaminated with $\text{Hg}[\text{Mn}(\text{CO})_5]_2$. The constitution of the solutions of the potassium salt can be expected to resemble that of $\text{NaMn}(\text{CO})_5$. Kinetic measurements for the reactions between $\text{MMn}(\text{CO})_5$ and $\text{C}_5\text{F}_5\text{N}$ were carried out in THF and ether, and in the case of the potassium salt some of the runs were planned to elucidate the effects of 18-crown-6 ether, HMPA and tetraphenylarsonium salts (Ph_3AsCl , $\text{Ph}_4\text{AsClO}_4$). The common ion effect was studied for the lithium salt (with Ph_4BLi added).

TABLE 2
RATE CONSTANTS FOR THE REACTION OF $\text{KCpW}(\text{CO})_3$ WITH $\text{C}_5\text{F}_5\text{N}$ AT 25°C

Nr.	Solvent	Other components ^a	c ($\times 10^{-2}$) (M)	$[\text{C}_5\text{F}_5\text{N}]$ ($\times 10^{-2}$) (M)	K_2 ($\times 10^{-2}$) ($\text{M}^{-1} \text{s}^{-1}$)
1	THF		1.85	2.92	8.4
			1.76	3.0	8.5
2	THF	HMPA (20)	1.62	2.46	3.4
		HMPA (55)	1.49	2.24	3.3
3	ether		1.01	0.75	46.7
			0.92	1.65	47.1

^a The number of equiv. per one equiv. of carbonylate is given in parentheses.

All the runs were carried out in an excess of the aromatic substrate, under pseudo-first-order conditions (Table 1). The Li salt turned out to be less reactive than the K salt. An intriguing conclusion can be drawn from this experimental fact, that is, there is a decrease in reactivity on going from ion pairs to free ions (cf. runs 1 and 8). This supposition gains additional support from the rate retardation caused by 18-crown-6 ether, HMPA and Ph_4AsX , of which the latter exerts the most striking influence (cf. runs 1 to 2-6), as well as the rate enhancement in ether (cf. runs 1 to 8) or caused by the common ion (cf. 8 to 9).

It is noteworthy that the largest rate constant was obtained for $M = \text{K}$ in ether (k_2 $0.13 \text{ M}^{-1} \text{ s}^{-1}$), 15 times that measured for the K salt in THF or with the Li salt in THF with Ph_4BLi added.

Thus, an inverted order of reactivity is evident in the reactions under investigation; in our case, ion pairs proved to be more reactive than free ions. Some kind of assistance provided by the counterion is usually believed to account for such deviant behaviour. Depending on which stage is rate-determining, we suggest that $\text{F}^- \cdots \text{M}^+$ (or $\text{N}^- \cdots \text{M}^+$) coordination can either assist stabilization of the σ -anionic type transition state or facilitate the elimination of fluoride anion. In this respect we might expect the lithium cation to be the most efficient species, but this was not the case. The superior reactivity of the potassium salt in ether has revealed that not only contact ion pairs, but even higher ionic associates similar to those reported in [2] might play an important role.

It is usually taken for granted that the nucleophilicity of anions in ion pairs is lower than that of free ions, even in the specific case of carbonylates, in which the cation is bound to the CO ligand. It is probably such coordination that suppresses the usually marked effect of crown ethers on the rates of reactions of carbanions.

In addition, we studied the kinetics of the reaction between $\text{C}_5\text{F}_5\text{N}$ and $\text{KMn}(\text{CO})_4\text{PR}_3$ ($R = \text{Ph}, \text{Et}$) obtained by reduction of the corresponding dimers. The introduction of strongly electron-releasing phosphinic ligands causes a substantial increase in the nucleophilicity of the anions and results in a sharp acceleration of the substitution. As can be deduced from the failure to follow the kinetics under pseudo-first-order conditions, $\text{Mn}(\text{CO})_4\text{PR}_3^-$ resembles $\text{CpW}(\text{CO})_3^-$ closely in reactivity, at comparable initial concentrations of the reagents, K $6.3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $1.55 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for $R = \text{PPh}_3$ and $R = \text{PEt}_3$, respectively (the latter value even exceeds that measured for $\text{KMn}(\text{CO})_5$ in ether; Table 1, expt. 7). Nevertheless, the reactivity of these species is still not sufficient to effect substitution in C_6F_6 .

$\text{CpW}(\text{CO})_3^-$. Contact ion pairs were reported to prevail in solutions of $\text{NaCpW}(\text{CO})_3$ and $\text{KCpW}(\text{CO})_3$ in THF at concentrations of the order of 10^{-2} M , whereas on addition of 20 equiv. of HMPA per mole of carbonylate, a mixture of solvent-separated ion pairs and free ions occurred [4]. $\text{KCpW}(\text{CO})_3$ is seen from the evidence of Table 2 to interact with $\text{C}_5\text{F}_5\text{N}$ in THF with a rate approximately one order of magnitude larger than that for $\text{KMn}(\text{CO})_5$. Therefore, the kinetics could be followed only under second-order conditions. The general regularities were essentially the same, although much less pronounced, as compared to the reactions of manganese carbonylates. Change of the solvent THF for ether resulted in 6-fold acceleration (as against 15-fold for $\text{Mn}(\text{CO})_5^-$ (cf. 2 to 3); addition of HMPA caused 3-fold retardation (as against 8-fold for $\text{Mn}(\text{CO})_5^-$ (cf. 1 to 2)).

$\text{Re}(\text{CO})_5^-$. Of all the rhenium carbonylates, the sodium salt $\text{NaRe}(\text{CO})_5$ is the

TABLE 3
RATE CONSTANTS FOR THE REACTION OF $\text{NaRe}(\text{CO})_5$ WITH C_6F_5 AT 25°C

Nr.	Solvent	Other components ^a	$c (\times 10^{-2})$ (M)	$[\text{C}_6\text{F}_6] (\times 10^{-2})$ (M)	$K_2 (\times 10)$ ($\text{M}^{-1} \text{s}^{-1}$)
1	THF		1.01	5.7	2.1
			1.00	1.14	2.2
2	THF	HMPA (20)	1.06	1.15	1.25
		HMPA (55)	1.02	1.14	1.30
3	THF	$\text{Ph}_4\text{AsClO}_4$ (1)	0.367	1.17	1.03
		Ph_4AsCl (1)	0.401	1.16	1.12
4	THF	NaBF_4 (10)	0.263	1.07	3.05
			0.323	1.29	3.06
5	ether		1.00	1.24	10.8
			0.462	0.574	10.3

^a The number of equiv. per an equiv. of carbonylate is given in parentheses.

easiest to prepare by the reduction of $\text{Re}_2(\text{CO})_{10}$ with sodium amalgam. Preparation of Li or K salts by reduction with Li amalgam or NaK alloy gives unsatisfactory results because of the unreasonably slow rate and the formation of coloured by-products (e.g. $\text{Re}_2(\text{CO})_9^{2-}$ [14]), which interfere with the kinetic measurements. Any evidence concerning the constitution of $\text{MRe}(\text{CO})_5$ solutions is lacking in the literature probably because of the complexity of their IR spectra.

We have mentioned that the high reactivity of $\text{NaRe}(\text{CO})_5$ presented an obstacle for direct measurement of the rate for the reaction with $\text{C}_5\text{F}_5\text{N}$; therefore, only the reaction with C_6F_6 was studied (Table 3). Despite the change of substrate and the high rates, all the general regularities remained the same. They were: retardation caused by HMPA (expt. 2) or by tetraphenylarsonium salts (expt. 3), and acceleration by the common ion (addition of NaBPh_4 , expt. 4) or in Et_2O (expt. 5) in place of THF. However, all the effects were even more suppressed than in the case of the reaction between $\text{CpW}(\text{CO})_3^-$ and $\text{C}_5\text{F}_5\text{N}$ (see above). Two reasonable explanations can be given: either complexing agents and solvents exert a slight influence on the constitution of the solution of rhenium carbonylates, or the high nucleophilicity of the reagent averages out all the differences in the constitution of the reactive species. Similar effects have been reported for the reactions of $\text{Co}(\text{CO})_4^-$, $\text{Mn}(\text{CO})_5^-$ and $\text{CpMo}(\text{CO})_3^-$ with benzyl chloride, where the reaction with the weakest nucleophile, $\text{Co}(\text{CO})_4^-$, was retarded 420-fold by crown ether, while the stronger nucleophiles $\text{Mn}(\text{CO})_5^-$ and $\text{CpMo}(\text{CO})_3^-$ caused 10-fold and 3-fold decreases of the rates on addition of crown ether and HMPA, respectively [2,4].

Thus, we have shown that the reactivity order of anions of transition metal carbonylates in aromatic nucleophilic substitution



corresponds in general to that established for nucleophilic aliphatic substitution [10,13,15,16]. Meanwhile, polar opinions concerning the relative reactivities of $\text{CpW}(\text{CO})_3^-$ and $\text{Mn}(\text{CO})_5^-$ towards different substrates can be found in the literature. In our case, tungsten carbonylate was more reactive towards perfluoro-aromatic compounds than manganese carbonylate.

Experimental

The products were identified by their elemental analyses, NMR and IR spectra. ^{19}F NMR spectra were recorded on a Varian XL-100 instrument, with CFCl_3 as the external standard; ^1H NMR spectra were recorded on a Bruker WM-250 instrument, with HMDSO as the internal standard. Spectra were taken in THF- d_8 and benzene- d_6 dried over 4\AA molecular sieves. IR spectra were recorded in THF on a UR-20 (Zeiss) instrument in CaF_2 cells of 0.11 mm path length.

THF and ether were refluxed and distilled successively over KOH, sodium and LiAlH_4 ; the purified solvents were stored in vacuo over benzophenone ketyl.

HMPA was kept in vacuo (1 Torr) at $50\text{--}60^\circ\text{C}$ for 10–12 h over thoroughly powdered CaH_2 , then distilled in vacuo ($50^\circ\text{C}/0.5$ Torr), and redistilled over CaH_2 prior to use. C_6F_6 and $\text{C}_5\text{F}_5\text{N}$ were distilled three times over 4\AA molecular sieves.

$\text{Mn}_2(\text{CO})_{10}$, $[\text{Mn}(\text{CO})_4(\text{PR}_3)_2]$, $\text{Re}_2(\text{CO})_{10}$, $[\text{CpMo}(\text{CO})_3]_2$ and $[\text{CpW}(\text{CO})_3]_2$ were dissolved in dry hexane and eluted under argon through a column packed with silica (L 40/100), dried and sublimed in vacuo ($80\text{--}90^\circ\text{C}/10^{-2}$ Torr). $[\text{CpFe}(\text{CO})_2]_2$ was dissolved in dry CH_2Cl_2 under argon and reprecipitated with hexane at -72°C to yield a glittery dark-violet solid, which was dried thoroughly in a high vacuum ($10^{-3}\text{--}10^{-4}$ Torr).

Transition metal carbonylates were obtained by reduction of the corresponding dimers in THF or in ether by NaK alloy [14]; in the case of $\text{Re}_2(\text{CO})_{10}$, sodium amalgam was used [16]. Li wire was used to prepare $\text{LiMn}(\text{CO})_5$ [2].

Typical procedure of the kinetic measurements

All the runs were carried out in a device similar to that shown in Fig. 1. The required quantities of starting dimer and reducing agent were immersed in bulb A; other solid reagents were immersed in bulb B through the neck (C), which was sealed off immediately afterwards. The device was evacuated through the vacuum stopcocks, D and E (residual pressure 10^{-4} Torr). The solvent was measured in a calibrated vessel and vacuum-transferred to A. At room temperature the reduction

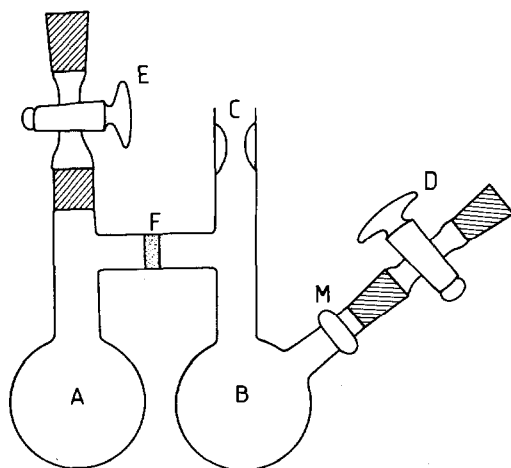


Fig. 1. The device used in the experiments.

took ca. 1–2 h of vigorous stirring by a magnetic stirrer for completion. Next, the solution of carbonylate was filtered through the glass frit F into B, and the device was filled with argon dried by bubbling it through an ethereal solution of benzophenone ketyl. The initial concentrations of carbonylate were determined by changes of the pH value of aqueous acetic acid on quenching an aliquot of the reaction mixture in it. The yields of anions $\text{Mn}(\text{CO})_5^-$, $\text{CpFe}(\text{CO})_2^-$, $\text{CpW}(\text{CO})_3^-$ and $\text{CpMo}(\text{CO})_3^-$ were close to quantitative (95–98%), but $\text{Re}(\text{CO})_5^-$ was obtained in a lower yield (85–87%).

Additional liquid components (HMPA and substrates, or their solutions) were added through the rubber membrane M by a syringe, which had been preflushed with dry argon. Samples of the reaction mixture were withdrawn at appropriate times by a syringe and quenched in 9 ml of "TISAB" buffer solution prepared by the standard method [18]. The fluoride-selective electrode, calibrated under similar conditions in the presence of THF, was used to follow the concentration of fluoride anion (electrodes supplied by Crytur (Czechoslovakia) and Radelkis (Hungary) were used). The electrode potentials were measured by an EV-74 universal ionmeter with an accuracy of about ± 1 mV or 1–2% of the maximum changes of the electrode potential in a typical run (50–100 mV). Pseudo-first-order rate constants were calculated from the equation

$$\ln(X/X_0) = -kt$$

while second-order kinetics were treated according to the equation

$$\ln\left[\frac{X_0}{Y_0}\left(1 + \frac{Y_0 - X_0}{X}\right)\right] = K(Y_0 - X_0)t$$

where X_0 is the initial concentration of the anion, Y_0 is the initial concentration of the substrate and X is the concentration at time t .

All synthetic preparations were carried out in the same device at concentrations 3–4 times higher than those taken for the kinetic runs and by the same procedure. On completion, the inorganic residue was filtered off; the solvent was removed under reduced pressure. The remaining solid was recrystallized under argon from a benzene/hexane (1/1) mixture and dried in vacuo. Additional purification of the Re and Mn derivatives for analytical purposes was achieved by sublimation at 80–90°C/0.1 Torr.

$\text{C}_6\text{F}_5\text{Fe}(\text{CO})_2\text{Cp}$. Yield 92%*, yellowish-orange substance, m.p. 143–143.5°C (lit. 142–143°C [8]); ^{19}F NMR, δ (ppm) (THF- d_8): 107.5 (2), 163.8 (2), 160.5 (1); ^1H NMR, δ (ppm) (C_6D_6): 4.98 (5H, s); IR, $\nu(\text{CO})$ (cm^{-1}): 2048s, 1998s.

$p\text{-NC}_5\text{F}_4\text{Fe}(\text{CO})_2\text{Cp}$. Yield 93%*, yellowish-orange crystals, m.p. 209°C (lit. 209°C [9]); ^{19}F NMR, δ (ppm) (THF- d_8): 114.5 (2), 102.3 (2); ^1H NMR, δ (ppm) (C_6D_6): 5.02 (5H, s); IR, $\nu(\text{CO})$ (cm^{-1}): 2048s, 2001s.

$\text{C}_6\text{F}_5\text{Re}(\text{CO})_5$. Yield 81.5%*, white crystals, m.p. 152–153°C (lit. 152°C [10]); ^{19}F NMR, δ (ppm) (C_6D_6): 103.2 (2), 160.5 (2), 167.8 (1); IR, $\nu(\text{CO})$ (cm^{-1}): 2145w, 2046vs, 2007s.

$p\text{-NC}_5\text{F}_4\text{Re}(\text{CO})_5$. Yield 83.0%*, white crystals, m.p. 124–125°C (lit. 123–125°C [9]); ^{19}F NMR, δ (ppm) (C_6D_6): 111.0 (2), 98.6 (2); IR, $\nu(\text{CO})$ (cm^{-1}): 2146m, 2064sh, 2036s, 2008s.

* The yield of the recrystallized product is given based on the initial dimer.

p-NC₅F₄Mn(CO)₅. Yield 92% *, white crystals, m.p. 95–96°C (dec.) (lit. 94°C (dec.) [9]); ¹⁹F NMR, δ(ppm) (C₆D₆): 113.4 (2), 100.2 (2); IR, ν(CO) (cm⁻¹): 2131m, 2072sh, 2038s, 2015s.

p-NC₅F₄W(CO)₃Cp. Yield 90% *, yellow crystals, m.p. 184–185°C (dec.) (lit. 184°C (dec.) [13]); ¹⁹F NMR, δ(ppm) (C₆D₆): 104.7 (2), 98.4 (2); IR, ν(CO) (cm⁻¹): 2036vs, 1960vs, 1934vs.

The NMR and IR spectra were in good agreement with the published data [8,9,10,13].

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