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Unexpected formation of [Z-PhCF=CFRe$_2$(CO)$_9$]Na in the reaction of [Re(CO)$_5$]Na with α,β,β-trifluorostyrene

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Abstract

The reaction of [Re(CO)$_5$]Na with α,β,β-trifluorostyrene follows two concurrent pathways: nucleophilic vinylic substitution forming Z-PhCF=CFRe(CO)$_5$ and radical-chain process producing Z-[PhCF=CFRe(CO)$_4$Re(CO)$_5$]Na. The intermediacy of metal carbonyl radicals in the radical process is evident from the fact that tertiary phosphines or an 'electron trap' inhibit, and Re$_2$(CO)$_{10}$, induce the production of Z-[PhCF=CFRe(CO)$_4$Re(CO)$_5$]Na. © 1998 Elsevier Science S.A. All rights reserved.

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Continuing interest in the chemistry of transition metal carbonyl anions, carbonylmetallates, arises from the extremely versatile reactivity of these species. Carbonylmetallates can act not only as nucleophiles [1–4], but also as reductants or halogen abstracters in the reactions with vinyl (aryl) halides, dimeric metal carbonyls usually coming as by-products [3,4]. The actual reaction pathway is controlled by a subtle balance of many factors such as the nature of organic substrate, leaving group and counterion, as well as solvent and temperature [3,4]. In this paper we propose a novel radical-chain mechanism to account for the formation of unusual product in the reaction of [Re(CO)$_5$]Na with α,β,β-trifluorostyrene.

Nucleophilic vinylic substitution with carbonylmetallates in activated vinyl halides is a well known route to σ-vinyl metal complexes [1,4]. With α,β,β-trifluorostyrene, the fluorine in *trans*-position to the phenyl group is preferentially substituted by [Re(CO)$_5$]Na, yielding Z-PhCF=CFRe(CO)$_5$ (**1**, 40–60%) as the major reaction product. However, the other substitution product, arising from the coupling of two rhenium carbonyl fragments, [Z-PhCF=CFRe$_2$(CO)$_9$]Na, (**2**, 20–30%) is of a kind never observed previously in similar reactions (Table 1 Scheme 1). Small amounts of PhC≡CRe(CO)$_5$ and Re$_2$(CO)$_{10}$ ($<6\%$, usually 1–4%) were also found in product mixtures. They could result from the decomposition of unstable complex **2**, as well as from the initial reaction.

The structure of **2** is unambiguously assigned on the basis of IR and ^{13}C- and ^{19}F-NMR spectra[1], which are in good agreement with those of the known anionic Re$_2$(CO)$_9$ complexes [5,6]. Unfortunately we failed to obtain complex **2** in crystalline form, even when the sodium counterion was exchanged for [PPN]$^{+}$[2]. FAB MS spectra of both sodium and [PPN]$^{+}$ salts of **2** gave

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[1] Spectral properties of **2**; IR ν_{CO} (THF): 1903s, 1942s, 1984vs, 2032s, 2096m. ^{19}F-NMR (376.3 MHz, THF-d$_8$) δ: -88.16 (d, $J=114.2$ Hz, $=$CFRe), -140.94 (d, $J=114.2$ Hz, $=$CFPh). ^{13}C-NMR (100.58 MHz, THF-d$_8$) δ: 201.24 (t, J_{CF} 6.8 Hz, 2C, CO), 199.9 (s br, 4C, CO), 197.14 (d, $J_{CF}=9.5$ Hz, 1C, CO), 192.24 (d, $J_{CF}=4.5$ Hz, 1C, CO), 189.4 (s br, 1C, CO), 176.37 (dd, $^1J_{CF}=295.1$, $^2J_{CF}=99.9$ Hz, $=$CFRe), 159.60 (dd, $^1J_{CF}=199.9$, $^2J_{CF}=40.9$ Hz, $=$CFPh), 134.35 (dd, $^2J_{CF}=30.3$, $^3J_{CF}=2.5$ Hz, C$_{ipso}$), 128.03 (d, $J_{CF}=3$ Hz, C$_m$), 125.07 (d, $J_{CF}=2.3$ Hz, C$_p$), 124.69 (dd, $J_{CF}=11.2$, $J_{CF}=7.7$ Hz, C$_o$).

[2] [PPN]$^{+}$ = bis(triphenylphosphine)nitrogen (1+).

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Table 1
Product yields in the reaction of $[Re(CO)_5]Na$ with α,β,β-trifluorostyrene—effect of solvent, added phosphine, 'electron trap' (3) and $Re_2(CO)_{10}^{a}$

Solvent	Initial concentration of $[Re(CO)_5]Na$, mol l^{-1}	Additive, mol per mole of $[Re(CO)_5]Na$	Product yields,%[b]	
			1	**2**
THF	0.27	—	58	20
THF	0.016	—	38	30
Ether	0.13	—	65	<3
Acetonitrile	0.22	—	72	12
THF	0.15	PEt_3, 1	68	2
THF	0.14	**3**, 0.25	65	4
THF	0.17	$Re_2(CO)_{10}$, 0.5	30	54

[a] $[Re(CO)_5]Na$ prepared by a standard technique [7] was purified by crystallisation. All reactions were carried out with an excess of trifluorstyrene at room temperature.

[b] The reaction products were isolated. The yields were determined by ^{19}F-NMR spectroscopy relative to the internal standard, benzotrifluoride.

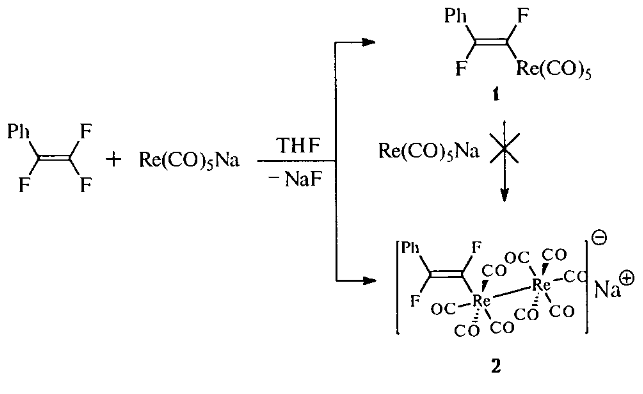
no additional information corroborating its structure, as only fragmentary ion peeks of low intensity were observed.

Tetrahydrofuran (at lower concentrations) proved to be an optimum solvent for the synthesis of complex **2**. Both less polar ether and more polar acetonitrile increased the rate of nucleophilic substitution producing **1**, thus decreasing the yield of **2** (Table 1).

The reaction of $[Re(CO)_5]Na$ with **1**, which might seem the simplest route to complex **2**, in fact proved to be inadequately slow, giving only 3% of **2** after 7 days. It is also noteworthy that no intermediates were detected by ^{19}F-NMR spectroscopy, and the maximum product ratio **2**/**1** was observed in the beginning of the reaction of $[Re(CO)_5]Na$ with trifluorostyrene.

The yield of **2** decreases (to 7%) when the reaction is carried out with $[Re(CO)_5]Na$ not purified beforehand, but obtained by the usual method [7]. This observation prompted us to examine the possibility of a radical-chain mechanism, that was further confirmed by our experiment as well as with literature data.

The initiation of the radical-chain process by spontaneous single electron transfer (SET) from $[Re(CO)_5]Na$ to trifluorostyrene is feasible in accordance with the known redox potentials of the reactants [8]. When triethylphosphine or 4-(diphenylmethyliden)-2,5-di-tert-butilcyclohexa-2,4-dienone (**3**) is added to the reaction mixture, the production of **2** stops (Fig. 1 and Table 1). Compound **3** could act both as an 'electron trap' and 'radical trap' terminating the propagation sequence described in Scheme 2. The effect of triethylphosphine provides compelling evidence for carbonylrhenium radicals participation in the reaction since interception of metal carbonyl radicals by phosphines is well known [9].



Scheme 1. Reaction demonstrating the coupling of two rhenium carbonyl fragments.

Radical anion, $[Re_2(CO)_9]^{-\bullet}$, is presumed to play an important role as a nucleophile in the radical-chain process leading to complex **2**. Unlike radical anions of other metal carbonyl dimers $[Re_2(CO)_{10}]^{-\bullet}$, is known to undergo facile CO dissociation (Reaction B, Scheme 2) instead of Re–Re bond cleavage [10]. The radical anion can be produced by degenerate electron transfer, recently demonstrated between the metal carbonyl anion and dimer [11] (Reaction C, Scheme 2). The initial production rate of complex **2** increased almost tenfold with the addition of $Re_2(CO)_{10}$ (Fig. 1 and Table 1)[3]. One should also consider direct coupling of $[Re(CO)_5]Na$ with $Re(CO)_5^{-\bullet}$ as another source of $[Re_2(CO)_{10}]^{-\bullet}$ (Reaction A, Scheme 2). The highest production rate of **2** is observed in the beginning of the reaction while $Re_2(CO)_{10}$ was proved to be absent in the starting carbonylmetallate.

The exact sequence of stages D and E (Scheme 2) is not really evident from the available data, it could not be ruled out that second electron transfer (E) precedes nucleophilic substitution (D), i.e. $[Re_2(CO)_9]^{2-}$ [5] actually is the nucleophile.

Radicals derived from organic substrate ($PhCF{=}CF_2^{-\bullet}$, $PhCF{=}CF^{\bullet}$) are not involved in chain propagation, that is carried out by metal carbonyl radicals, i.e. radicals derived from the nucleophile. Here lies a significant difference from the known $S_{RN}1$ mechanism

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[3] This experiment was suggested by Professor A.N. Kashin (MSU).

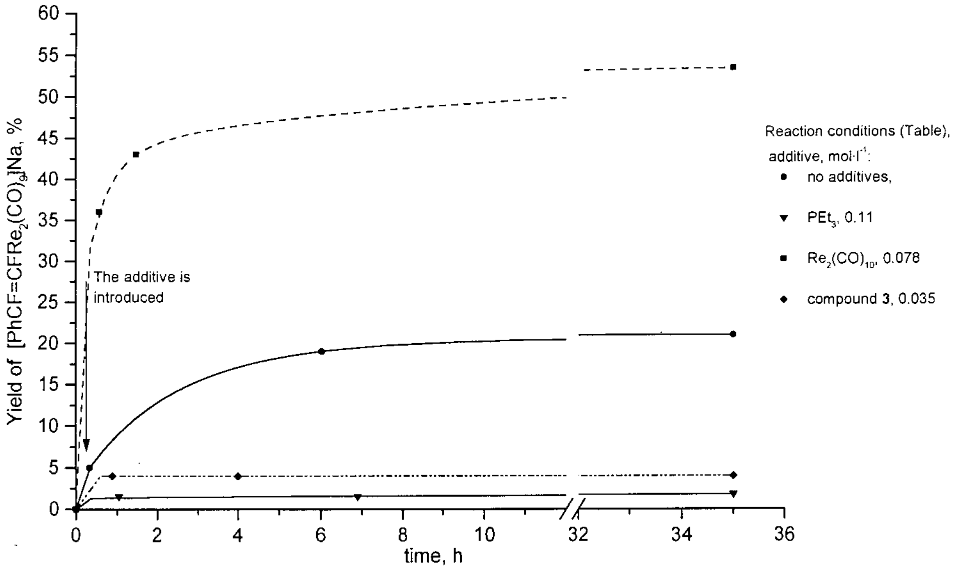
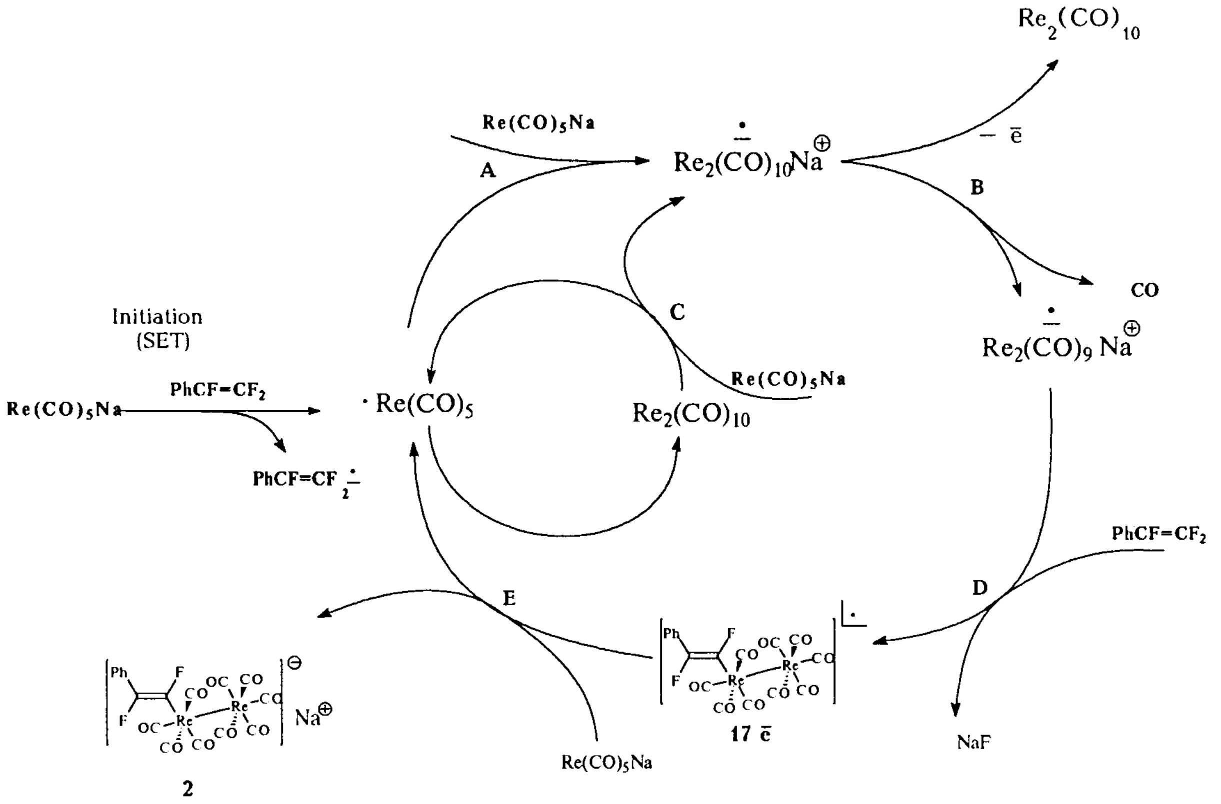


Fig. 1. Rate profiles of the reaction of $[Re(CO)_5]Na$ with α,β,β-trifluorostyrene, THF, 21–24°C.



Scheme 2. Propagation sequence demonstrating the route taken to produce **2**.

[12] supported by the fact that Z-β-chloro-α,β-difluorostyrene, much less reactive towards $Re(CO)_5Na$ in a separate experiment, does not participate in the reaction in the presence of trifluorostyrene.

Acknowledgements

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