Radical Chain Ligand Substitution of [(η5-RC5H4)2Fe2(CO)4] with Isocyanides induced by Et3B

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Reaction of [(η5-RC5H4)2Fe2(CO)4] with isocyanides in the presence of a catalytic amount of triethylborane results in the selective monosubstitution of the CO ligand with the isocyanide; a radical chain process is proposed for the reaction.

The ligand substitution reaction is one of the most fundamental reactions of organometallic compounds.[1] Much attention has been focused on the reaction intermediates which involve radical species [Fe(η5-C5H5)(CO)2] and dinuclear species [(η5-C5H5)Fe(μ-CO)3Fe(η5-C5H5)] in the photochemical and thermochemical reactions of [(η5-C5H5)2Fe2(CO)4].[2–6] For the ligand substitution of [(η5-C5H5)2Fe2(CO)4] with isocyanides, thermal and photochemical processes are generally used.[7] However, radical initiated processes have been little reported.[8] In this communication we report the first example of radical chain ligand substitution reaction of [(η5-RC5H4)2Fe2(CO)4] with isocyanides induced by triethylborane.

A mixture of 1a and 2a (2 equiv.) in benzene was stirred in the presence of a catalytic amount of Et3B (0.01–0.1 equiv.) under argon at room temperature in the dark to give an isocyanide monosubstituted complex 3a as the sole product in good yield. The other complexes, except for 1b reacted similarly with the isocyanides, yielding the corresponding isocyanide monosubstituted complexes. Tetrahydrofuran (THF) and acetonitrile can also be used as a solvent for the reaction. The results are shown in Table 1; the structures of the products were assigned from their spectroscopic data.†

No isocyanide substituted complex was produced when the reaction was conducted in the absence of Et3B in the dark, but the substitution reaction proceeded slowly on exposure to room light. Replacement of the CO ligand in 1a with isocyanides can be achieved by thermal and photochemical reactions[7] which afford generally polysubstituted complexes such as [(η5-C5H5)2Fe2(CO)2(C=NR)2] and [(η5-C5H5)2Fe2-(CO)(C=NR)3] in addition to [(η5-C5H5)2Fe2(CO)3(C=NR)]. However, the present reaction resulted in selective monosubstitution reaction.

Table 1 Et3B-induced ligand substitution of 1 with 2 in the dark

Complex 1	Isocyanide 2	Et3B/ equiv.	Solvent	t/h	Product 3 (%)[a]	Recovery of 1 (%)[a]
a	a	0	Benzene	2	0	95
a	a	0.1	Benzene	2	94	3
a	a	0.01	Benzene	17	71	0
a	a	0.1	THF	2	54	20
a	a	0.1	MeCN	2	73	Trace
a	b	0.1	Benzene	2	85	0
a	b	0.1	MeCN	2	88	0
b	a	0	Benzene	2	0	96
b	a	0.1	Benzene	2	0	86
b	a	0.1	THF	2	0	88
c	a	0	Benzene	2	0	95
c	a	0.1	Benzene	2	86	2
c	a	0.1	THF	2	64	15
d	a	0	Benzene	2	0	92
d	a	0.1	Benzene	2	85	7
d	a	0.1	THF	2	63	15

[a] Isolated yields.

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† Selected spectroscopic data for 3c: IR (neat) v/cm⁻¹ 2120 (terminal C=N), 1943 (terminal CO), 1754 (bridged CO); ¹H NMR (CDCl3) δ 4.71 (4H, s, C5H4), 4.40 (4H, s, C5H4), 1.16 (9H, s, Buᵗ), 0.35 (9H, s, CH3Si), 0.34 (9H, S, CH3SI); MS (70 eV) m/z 553 (M⁺).
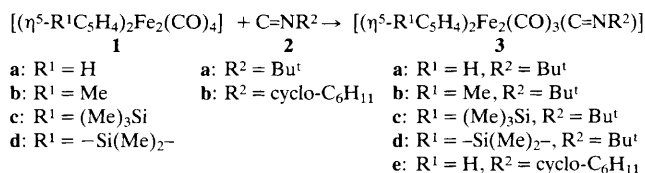
3d: IR (neat) v/cm⁻¹ 2118 (terminal C=N), 1941 (terminal CO), 1744 (bridged CO); ¹H NMR (CDCl3) δ 4.50–4.20 (8H, m, C5H4), 1.16 (9H, s, Buᵗ), 0.35 (6H, s, CH3Si): ¹³C NMR (CDCl3 at −20 °C) δ 282.1, 212.8, 159.6 97.8, 97.1, 86.2, 85.4, 57.1, 30.5, −3.75; MS (70 eV) m/z 465 (M⁺).

$[(\eta^5\text{-}R^1C_5H_4)_2Fe_2(CO)_4]$ $+ C=NR^2 \rightarrow$ $[(\eta^5\text{-}R^1C_5H_4)_2Fe_2(CO)_3(C=NR^2)]$

$\quad\quad\quad$ **1** $\quad\quad\quad\quad\quad\quad$ **2** $\quad\quad\quad\quad\quad\quad\quad\quad$ **3**

a: $R^1 = H$ $\quad\quad\quad$ **a**: $R^2 = Bu^t$ $\quad\quad\quad$ **a**: $R^1 = H, R^2 = Bu^t$

b: $R^1 = Me$ $\quad\quad$ **b**: $R^2 = $ cyclo-C_6H_{11} $\quad$ **b**: $R^1 = Me, R^2 = Bu^t$

c: $R^1 = (Me)_3Si$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ **c**: $R^1 = (Me)_3Si, R^2 = Bu^t$

d: $R^1 = -Si(Me)_2-$ $\quad\quad\quad\quad\quad\quad\quad\quad$ **d**: $R^1 = -Si(Me)_2-, R^2 = Bu^t$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ **e**: $R^1 = H, R^2 = $ cyclo-C_6H_{11}

Scheme 1

The other notable features of the reaction were as follows: (*i*) An induction period was observed in the reaction. (*ii*) The ligand substitution reaction was completely inhibited by the addition of radical inhibitors such as 1,4-benzoquinone. (*iii*) When traces of O_2 in the reaction mixture were rigorously removed using vacuum line technique, the substitution reaction did not proceed. On exposing the above reaction mixture to an equivalent amount of O_2 to Et_3B, the substitution reaction took place, while a large amount of O_2 inhibited the reaction. (*iv*) No cross-coupling reaction between **1a** and **1c** occurred under similar reaction conditions, but irradiation of a mixture of **1a** and **1c** with UV light in the absence of Et_3B gave the cross-coupled product [(η^5-C_5H_5)(Me$_3$SiC$_5$H$_4$)Fe$_2$(CO)$_4$]. From these results, we propose a radical chain mechanism as shown in Scheme 2 for the ligand substitution reaction. Organoboranes are known to be sources of free radicals[9] which initiate organic radical reactions.[10] The initial step is the formation of free radicals such as ethyl radical and ethylperoxyl radical by the reaction of Et_3B with traces of O_2 which exists adventitiously in the solvent. However, it is not clear which radical is necessary for the radical chain ligand substitution. Scheme 2 illustrates the ethyl radical as one of the free radicals. It is noteworthy that ligand substituted product was not obtained in the reaction of **1b**, and

$Et_3B + O_2 \longrightarrow Et^{\boldsymbol{\cdot}} + Et_2BO_2{}^{\boldsymbol{\cdot}}$

$[(\eta^5\text{-}C_5H_5)Fe_2(CO)_4] + Et^{\boldsymbol{\cdot}} \longrightarrow [(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3COEt]^{\boldsymbol{\cdot}}$

$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3COEt]^{\boldsymbol{\cdot}} \longrightarrow [(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3] + EtCO^{\boldsymbol{\cdot}}$

$[(\eta^5\text{-}C_5H_5)Fe_2(CO)_3] + C=NR \longrightarrow [(\eta^5\text{-}C_5H_5)Fe_2(CO)_3(C=NR)]$

$\quad\quad\quad EtCO^{\boldsymbol{\cdot}} \longrightarrow Et^{\boldsymbol{\cdot}} + CO$
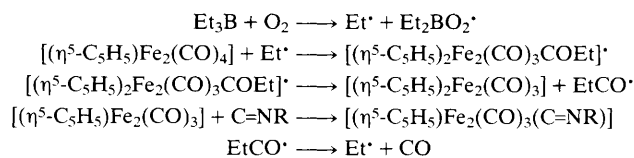
Scheme 2

the starting material was recovered. The ethyl radical may be captured by the methylcyclopentadienyl ligand of **1b**.

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