

Metal Carbonyl Substitution Reactions catalysed by Transition Metal Complexes

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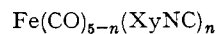
Summary The reaction of $\text{Fe}(\text{CO})_5$ with isonitriles RNC in the presence of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ as catalyst to give $\text{Fe}(\text{CO})_{5-n}(\text{RNC})_n$ ($n = 1-5$) is reported.

A common problem associated with the use of metal carbonyls as synthetic reagents is the drastic conditions required to induce CO dissociation and replacement, especially multiple CO replacement. Such drastic conditions often cause decomposition of reactants and products, prevent detection of intermediates, and give rise to mixtures which complicate isolation procedures. For example, $\text{Fe}(\text{CO})_5$ (usually contaminated with $\text{Fe}(\text{CO})_4\text{L}$) is, in general, the ultimate product from substitution reactions of $\text{Fe}(\text{CO})_5$, even when using u.v. irradiation, long reaction times, and elevated temperatures.^{1,2}

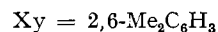
We have discovered that catalytic amounts of a variety of transition metal complexes readily induce stepwise CO

substitution of monomeric and cluster carbonyls under mild conditions. In this communication we illustrate our method with the CO substitution reactions of $\text{Fe}(\text{CO})_5$ with isonitriles to give successively $\text{Fe}(\text{CO})_{5-n}(\text{RNC})_n$ ($n = 1-5$).

$\text{Fe}(\text{CO})_5$ (10 mmol), 2,6-dimethylphenyl isocyanide (XyNC) (2 mmol), and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol) in benzene at 45 °C gives >90% yield of $\text{Fe}(\text{CO})_4(\text{XyNC})_3$ (**1**) within 15 min. The corresponding reaction in the absence of catalyst gives <5% yield of (**1**).



- | | |
|--------------------|--------------------|
| (1) $n = 1$ | (4) $n = 4$ |
| (2) $n = 2$ | (5) $n = 5$ |
| (3) $n = 3$ | |



In a similar manner, addition of further $XyNC$ to (1) and catalyst in refluxing benzene leads successively to $Fe(CO)_3(XyNC)_2$, (2), $Fe(CO)_2(XyNC)_3$, (3), $Fe(CO)(XyNC)_4$, (4), and $Fe(XyNC)_5$, (5).⁴ All reactions are essentially complete within 5–10 min. For comparison the non-catalytic reaction between (1) and $XyNC$ gives (2) in <5% yield after 90 min. The products were characterized by i.r.² and n.m.r. spectroscopy (Table), and elemental analyses. The oxidative stability of these isonitrile complexes decreases with isonitrile substitution and (4) and (5) must be handled under a nitrogen atmosphere at all times. Similar reactions were also carried out using $MeNC$ and Bu^tNC .

TABLE. I.r.^a and n.m.r.^b spectroscopic data for the iron-isonitrile complexes.

	ν_{CO}/cm^{-1}	ν_{NC}/cm^{-1}	τ^c
(1)	2052, 1993, 1960	2155	8.07
(2)	1995, 1934	2103	7.92
(3)	1949, 1908	2070	7.83
(4)	1900	2050, 1985	7.69
(5)	—	2028, 1960, 1920	7.61

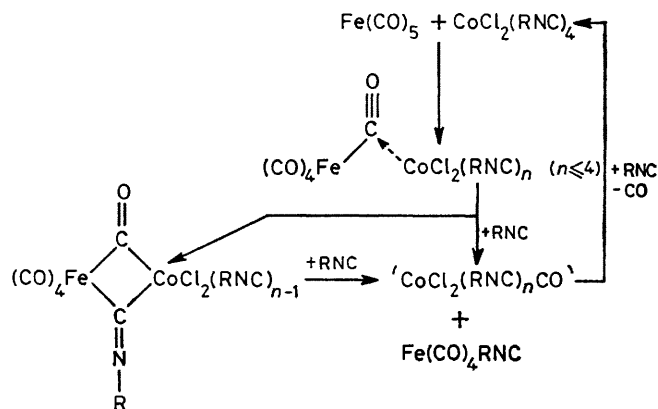
^a I.r. recorded in C_6H_6 . ^b In C_6D_6 relative to Me_4Si . ^c Methyl protons.

During the substitutions of $Fe(CO)_5$ by $XyNC$ the cobalt catalyst turns from pink to green. The green complex, (6), can be prepared independently in good yield from $CoCl_2 \cdot 6H_2O$ and $XyNC$ in acetone. Elemental analyses, a magnetic moment measurement (μ_{eff} 2.05 B.M. at 293 K; Gouy method), and i.r. data [$\nu_{NC}(CHCl_3)$ 2183 cm^{-1}] are consistent with the green complex being formulated as the β -modification of the cobalt chloride complex, *viz.* $CoCl_2 \cdot (XyNC)_4$.⁵ Complex (6) was found to catalyse the CO substitution reactions and is thought to be the true catalyst in these reactions.

We have attempted to elucidate the mechanism of this novel catalytic reaction and pertinent observations are as follows. (a) Neither $NaCl$ nor H_2O catalyse the reaction. (b) CO is evolved in the reaction. (c) Complexes (1) and (6) in the absence of free $XyNC$ give a near quantitative yield of (2). (d) Reaction of either (1), (6) and Bu^tNC or the reaction of (1), $CoCl_2[Bu^tNC]_4$, and $XyNC$ in equimolar ratio yields (2) exclusively in the early stages of the reaction. (e) Minimal exchange takes place between co-ordinated and unco-ordinated isonitrile under the reaction

conditions. (f) Addition of PPh_3 , a non-bridging ligand, to $Fe(CO)_5$ and $CoCl_2 \cdot 2H_2O$ gives $Fe(CO)_4PPh_3$ ⁶ in high yield.

These data, together with the 18-electron rule, are consistent with initial attack of $Fe(CO)_5$ by catalyst occurring at the CO group. Subsequent steps could involve attack of iron by isonitrile either in an intramolecular (*via* a bridging isonitrile)⁷ or intermolecular manner to produce $Fe(CO)_4RNC$ with catalyst regeneration in the presence of isonitrile (Scheme). Our preliminary data favour the intermolecular reaction pathway.



SCHEME. Possible reaction paths for the catalysed reaction between $Fe(CO)_5$ and RNC .

The replacement of CO on metal carbonyls in the presence of suitable transition metals appears to be of a general nature. Thus we have achieved replacement of CO, catalysed by $CoCl_2 \cdot 2H_2O$ on (a) $Fe(CO)_5$ by Group 5 ligands [*e.g.* PPh_3 , $SbPh_3$, $AsPh_3$, $P(OPh)_3$, $P(OMe)_3$, $P(C_6H_{11})_3$, and PPh_2Me], (b) $M(CO)_6$ (Cr, Mo, W) by RNC [$RNC = MeNC, Bu^tNC, or XyNC$], (c) $M_3(CO)_{12}$ ($M = Fe, Ru, Os$) and $Ir_4(CO)_{12}$ by Bu^tNC and $XyNC$. Further, the reaction between $Fe(CO)_5$ and RNC is catalysed by a wide variety of transition metals *e.g.* $NiX_2 \cdot xH_2O$ ($X = Cl, Br, I, MeCO_2, NO_3$), $CoX_2 \cdot xH_2O$ ($X = NO_3, MeCO_2$), $CoSO_4 \cdot 7H_2O$, $RuCl_2(PPh_3)_3$, and $RhCl(PPh_3)_3$.⁸

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