THE CATALYTIC SUBSTITUTION OF METAL CARBONYLS AND SUBSTITUTED METAL CARBONYLS BY ISONITRILES IN THE PRESENCE OF RHODIUM(I) AND POLYMER-SUPPORTED RHODIUM(I) COMPLEXES

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Summary

Metal carbonyls and substituted metal carbonyls, under relatively mild reaction conditions, in the presence of isonitriles, undergo catalytic CO substitution by rhodium(I) and polymer-supported rhodium(I) complexes. The reaction provides a facile route to the synthesis of transition metal isonitrile complexes.

Wilkinson's catalyst, $RhCl(PPh_3)_3$, I, has been found to be an effective reagent for the mild CO substitution of metal carbonyls [1—3]. However, the reactions are not catalytic as the $RhCl(CO)(PPh_3)_2$, II, produced cannot, under the reaction conditions employed, lose CO to reform an active reagent to complete a catalytic cycle. Catalytic decarbonylation reactions using II have only been achieved at high temperatures ($\sim 200°C$) on organic carbonyl-containing substances [4].

In a continuation of our investigations into the use of transition metals as catalysts in synthetic organometallic chemistry [5,6] we have found that I or II in the presence of isonitriles, RNC, brings about catalytic CO substitution of metal carbonyls and substituted metal carbonyls. Thus, reaction of $Fe(CO)_5$ (1 mmol) and 2,6-dimethylphenylisocyanide (XyNC) (1—5 mmol) in benzene at 35°C, in the presence of catalytic amounts of I or II readily yields the products $Fe(CO)_{5-n}(XyNC)_n$ ($n = 1—5$) [5] in high yield. In a similar way, we have prepared (a) $M(CO)_{6-n}(t\text{-BuNC})_n$ (M = Cr, Mo, W; $n = 1—3$) [6] from $M(CO)_6$, t-BuNC and I in refluxing toluene, and (b) $Fe(CO)_{4-n}(RNC)_nL$ (L = maleic or

TABLE 1

IR DATA [a, b] FOR THE NEW Fe(CO)$_{4-n}$(t-BuNC)$_n$(MA) [c] (n = 1—3) COMPLEXES

Complex	ν(NC)		ν(CO)
Fe(CO)$_4$MA [d]	—	2117, 2052, 2022	1826, 1765(br)
Fe(CO)$_3$(t-BuNC)MA	2198	2073, 2023, 2008	1813, 1745
Fe(CO)$_2$(t-BuNC)$_2$MA	2180w, 2160	2033m, 1976	1802, 1781w, 1831
Fe(CO)(t-BuNC)$_3$MA	2181w, 2136	1953	1793m, 1778m, 1722, 1703ms

[a] Recorded in CHCl$_3$ (cm^{-1}). [b] All bands strong unless otherwise stated; m = medium, w = weak, s = strong, br = broad. [c] MA = maleic anhydride. [d] Ref. 8.

citraconic anhydride, n = 1—3) [7] from the stepwise addition of XyNC or t-BuNC to Fe(CO)$_4$L [8] in toluene (50—100°C). All new compounds have been completely characterised by IR, NMR, and elemental analysis (Table 1).

There are, however, two problems associated with the use of I and II as catalyst in the above reactions, namely the generation of uncoordinated PPh$_3$, (which results in metal-phosphine complex formation) and the difficulty experienced in separating the rhodium species from the reaction products. These problems have been overcome by attaching I to a polymer support. Polystyrene, cross-linked with 2% divinylbenzene (Dow Chemicals) was brominated, phosphinated (15% ring functionalization) and then reacted with RhCl(PPh$_3$)$_3$ [10] to yield the required polymer (containing 5.2% Rh). The use of this polymer as a catalyst gave results similar to those obtained from identical reactions with I. Thus, no difficulty was experienced in the preparation and separation of the Fe(CO)$_{5-n}$(XyNC)$_n$ (n = 1—5) and M(CO)$_{6-n}$(t-BuNC)$_n$ (n = 1—3) derivatives.

Subsequent re-use of the catalyst in further reactions indicated sustained but reduced activity. Although elution of catalyst from a support is a serious problem [11] we have found that washing the polymer-supported catalyst in the reaction solvent (soxhlet extractor) before use results in minimal catalyst leaching and does not account for our observed reduced activity. As yet, we are unable to account satisfactorily for this loss of activity. The above catalytic reaction solvent (Soxhlet extractor) before use results in minimal catalyst of organometallic complexes [11] and the above examples indicate some of the advantages (and disadvantages) that can be expected with this synthetic method.

Mechanistic information on the catalytic reaction has been obtained from the reaction between Fe(CO)$_5$ and XyNC. The first step in the reaction involves the conversion of I to II in a non-catalytic process [1]. This was confirmed when II precipitated from benzene in high yield from the equimolar reaction between I, XyNC and Fe(CO)$_5$. The identity of II was confirmed by IR and elemental analysis. Addition of catalytic amounts of II (either prepared as above or from RhCl$_3$/PPh$_3$ [12]) to Fe(CO)$_4$XyNC gave Fe(CO)$_3$(XyNC)$_2$ in quantitative yield. However, II was found to react rapidly with XyNC in benzene at ambient temperature to yield RhCl(XyNC)(PPh$_3$)$_2$, II, (m.p. 167—168°C) and [Rh(XyNC)$_2$(PPh$_3$)$_2$]Cl, IV, [13] (m.p. 157—159°C); and these complexes were completely characterized by IR, NMR (Table 2) and elemental analysis. Both III and IV (as well as RhCl(MeNC)(PPh$_3$)$_2$ and RhCl(t-BuNC)(PPh$_3$)$_2$

TABLE 2

SPECTROSCOPIC DATA FOR THE Ru AND Rh ISONITRILE COMPLEXES

Complex	$\nu(NC)$ [a]	NMR (δ, ppm) [b, c]		
		Ph(PPh$_3$) [d]	Ph(RNC)	Me
RhCl(XyNC)(PPh$_3$)$_2$	2080	7.7, 7.2	6.7	1.61
[Rh(XyNC)$_2$(PPh$_3$)$_2$]Cl	2120	7.6, 7.4	6.9	1.66
trans-RuCl$_2$(MeNC)$_2$(PPh$_3$)$_2$	2150	7.8, 7.3	—	2.90
trans-RuCl$_2$(t-BuNC)$_2$(PPh$_3$)$_2$	2125	7.8, 7.3	—	0.99
trans-RuCl$_2$(XyNC)$_2$(PPh$_3$)$_2$	2090	7.8, 7.1	6.9	2.05
trans-RuCl$_2$(PhCH$_2$NC)(PPh$_3$)$_2$	2150	7.8, 7.2	7.2 [e]	—

[a] Recorded in CHCl$_3$ (cm^{-1}). [b] Recorded in CDCl$_3$ vs. TMS. [c] The predicted ratio of absorption intensities was observed in all the complexes. [d] Phenyl resonances broad and complex. [e] δ(CH$_2$) = 4.32 ppm.

[14,15]) were found to be active catalysts for the reactions between Fe(CO)$_4$-RNC and RNC. Competitive reactions carried out between Fe(CO)$_4$XyNC, XyNC and either III or IV favour III as the active catalysts for the substitution reaction.

We have also observed a slower secondary reaction between III and Fe(CO)$_4$-XyNC (equimolar, 80°C, benzene) which results in ligand exchange between reactants to eventually give II and Fe(CO)$_3$(XyNC)$_2$ in near quantitative yield. Simultaneous pairwise exchange of CO and XyNC between metal centres has thus occurred. The overall fate of the rhodium in the catalytic substitution reaction is outlined in Scheme 1.
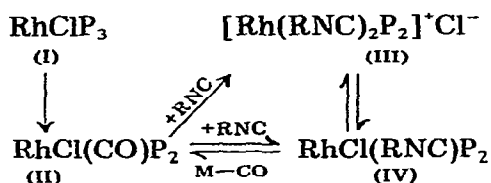
SCHEME 1

Interconversion of rhodium(I) complexes involved in the catalytic substitution reactions (P = PPh$_3$, M—CO = transition metal carbonyl)

RuCl$_2$(PPh$_3$)$_3$ and IrCl(CO)(PPh$_3$)$_2$ have also been found to be active CO-substitution catalysts for metal carbonyls: e.g., the Fe(CO)$_5$ + XyNC → Fe(CO)$_4$-XyNC reaction (benzene, 45°C) takes <5 min (Ru) and <3 min (Ir), respectively (cf. blank, <5%, 30 min). The Ru catalyst has, however, been found to have limited applicability. For instance, the catalysed reaction between Fe-(CO)$_4$RNC and RNC is found to give variable amounts of Fe(CO)$_3$(RNC)$_2$ (0—100%), depending on the method of reagent addition and the reaction temperature. This arises from a competing reaction in which the catalyst preferentially reacts with RNC to give trans-RuCl$_2$(RNC)$_2$(PPh$_3$)$_2$ [16]. These isonitrile

complexes were isolated from our reaction mixtures, characterized by IR, NMR (Table 2) and elemental analyses, and found to be completely inactive as CO substitution catalysts.

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