

COBALT CHLORIDE: AN INEXPENSIVE CATALYST FOR THE SUBSTITUTION OF CO BY ISONITRILES ON $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$)

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Summary

$\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ has been found to catalyse the substitution of CO on Group VI metal carbonyls by isocyanides to yield $M(\text{CO})_{6-n}(\text{RNC})_n$ [$M = \text{Cr}, \text{Mo}, \text{W}$, $n = 1-3$, $\text{RNC} = t\text{-BuNC}$; $M = \text{Cr}, \text{Mo}, \text{W}$, $n = 1$, $\text{RNC} = \text{MeNC}$, XNC (2,6-dimethylphenylisocyanide); $M = \text{Mo}$, $n = 2$, $\text{R} = \text{MeNC}$, XNC ; *fac*- $\text{Mo}(\text{CO})_3(\text{MeNC})_3$ and *cis*- $\text{Mo}(\text{CO})_2(t\text{-BuNC})_4$]. The reactions occur by stepwise replacement of the CO groups and mixed isocyanide derivatives can readily be prepared e.g. $\text{Mo}(\text{CO})_4(\text{MeNC})(t\text{-BuNC})$. All the reported reactions are facile and product yields typically 80–95%.

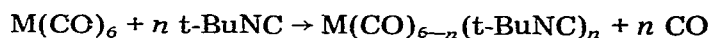
Introduction

The reaction of Group VI metal carbonyls and metal carbonyl derivatives with isocyanides is well documented [1–3]. It has been found that direct replacement of the carbonyls on the metal hexacarbonyls $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) by isocyanides can rarely be achieved and even then high temperatures and long reaction times give only poor yields of $M(\text{CO})_5(\text{RNC})$ and $M(\text{CO})_4(\text{RNC})_2$ [1,2]. As far as we are aware, in only one instance has the direct reaction between a Group VI metal carbonyl and isocyanide led to the replacement of three CO groups; in this study it was shown that reaction of $\text{W}(\text{CO})_6$ with *t*-BuNC (as solvent) yielded 80% $\text{W}(\text{CO})_3(t\text{-BuNC})_3$ but after 4 days reaction time [4].

Rather, the method of choice is to prepare metal carbonyl derivatives containing ligands which may readily be displaced by isocyanides [1–3]. e.g. *cis*- $\text{Mo}(\text{CO})_4(\text{NBD}) + 2 t\text{-BuNC} \rightarrow \text{cis-Mo}(\text{CO})_4(t\text{-BuNC})_2 + \text{NBD}$ (NBD = norborna-

diene). This method does yield the isocyanide products in moderate to good yields but requires the preparation and purification of the substituted metal carbonyl starting materials.

Our recent findings on the facile substitution of CO on $\text{Fe}(\text{CO})_5$ by isonitriles in the presence of $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ as catalyst [5] suggested that the reaction could be generalized to other metal carbonyls. We thus chose to systematically study the reaction of isocyanides with Group VI metal carbonyls in the presence of catalyst viz.



($\text{M} = \text{Cr}, \text{Mo}, \text{W}; n = 1-3$) to test our predictions. We chose to use t-BuNC as the isocyanide since the products are all stable in air and have been well characterized [2]. Herein we report the results of our findings. Also included are our results on the reaction of $\text{M}(\text{CO})_6$ with MeNC and XNC (2,6-dimethylphenylisocyanide) to emphasize the generality of this reaction.

Experimental

$\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ (Strem Chemicals), and t-butyliisocyanide (t-BuNC) and 2,6-dimethylphenylisocyanide (XNC) (Fluka A.G.), were used as purchased. Methylisocyanide (MeNC) was prepared by the method of Casanova et al. [6]. The catalyst $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ was obtained by heating $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (Riedel-de Haen A.G.) in vacuo at $\sim 50^\circ \text{C}$ for 5–10 hours. Toluene was refluxed under nitrogen over sodium prior to distillation. Silica gel 60 (Merck) was used for both product purification (vide infra) and column chromatography.

IR spectra were recorded on a Perkin Elmer 521 spectrophotometer, the NMR spectra on a Hitachi Perkin Elmer R20 (60 MHz) instrument and mass spectra on a Varian Mat CH5 spectrometer (operating at 70 eV). Melting points were recorded on a Koffler hot stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories, C.S.I.R. and are reported in Table 2.

All reactions were routinely carried out under nitrogen in a 2-necked round bottom flask, one neck of which was fitted with a rubber septum to allow for the monitoring of the reaction via sample removal after appropriate time intervals.

Reaction of $\text{M}(\text{CO})_6$ and isonitrile

Method 1: Preparation of $\text{M}(\text{CO})_{6-n}(\text{RNC})_n$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, n = 1-3$, $\text{RNC} = \text{t-BuNC}$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}, n = 1$, $\text{RNC} = \text{MeNC}$; $\text{M} = \text{Mo}, n = 2, 3$, $\text{R} = \text{MeNC}$). The catalyst $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ (0.2 mmol) and metal hexacarbonyl (3.0 mmol) were added to a reaction flask containing toluene (10 ml). The stirred heterogeneous solution was heated at reflux by means of an oil-bath pre-set at 125°C (2–5 min). The appropriate isonitrile (3.6, 6.6 or 9.6 mmol) was then added to the hot reactants to give an immediate blue solution. Continued reflux resulted in the solution turning bright green. Upon completion of the reaction (which may conveniently be monitored by changes in the $\nu(\text{CN})$ and $\nu(\text{CO})$ region of the IR) silica gel (10–20 g) was added to the cold reaction

solution and the product extracted with 5–10, 10 ml portions of benzene. Subsequent removal of the solvent on a rotary evaporator yielded the product in >95% purity. Recrystallisation (hexane/CH₂Cl₂) or elution through a silica gel column (eluent: hexane) gave the pure product.

Method 2: Preparation of $M(\text{CO})_{6-n}(\text{XNC})_n$ ($M = \text{Cr}, \text{Mo}, \text{W}$, $n = 1$; $M = \text{Mo}$, $n = 2$). XNC (3.6 or 6.6 mmol), CoCl₂ · 2 H₂O (0.2 mmol) and the metal hexacarbonyl (3 mmol) were added to toluene (10 ml). The solution was heated to reflux in an oil-bath pre-set at 125°C for the appropriate time (Table 1). The product was purified as in Method 1.

Method 3: Preparation of $\text{cis-Mo}(\text{CO})_2(\text{t-BuNC})_4$. CoCl₂ · 2 H₂O (0.2 mmol), t-BuNC (6 mmol) and *fac*-Mo(CO)₃(t-BuNC)₃ (3 mmol) were added to toluene (10 ml) and the solution refluxed for 6 hours. The reaction was monitored by IR and at the end of this time no significant changes were to be detected in the IR spectrum. The reaction mixture was cooled, the solvent removed and the impure product placed on a silica column. Gradient elution commencing with CH₂Cl₂/hexane (4/1) and ending with CH₂Cl₂ yielded two yellow bands. The first product eluted was characterized as starting material and the second as the required complex *cis*-Mo(CO)₂(t-BuNC)₄.

Method 4: Preparation of $\text{cis-Mo}(\text{CO})_4(\text{t-BuNC})(\text{RNC})$ ($\text{RNC} = \text{MeNC}$, t-BuNC). Catalyst (0.2 mmol) and Mo(CO)₅(RNC) (RNC = MeNC, t-BuNC)

TABLE 1

ISOCYANIDE DERIVATIVES OF GROUP VI HEXACARBONYLS

q	Method ^a	Reaction time (min)	Yield (%)	M.p. (°C) ^b
Cr(CO) ₅ (t-BuNC)	1	30	75	104–105
Mo(CO) ₅ (t-BuNC)	1	3	84	115–116
W(CO) ₅ (t-BuNC)	1	30	82	131–132
Cr(CO) ₅ (MeNC)	1	120	40	71–72
Mo(CO) ₅ (MeNC)	1	20	89	72–73
W(CO) ₅ (MeNC)	1	180	71	90–91
Cr(CO) ₅ (XNC) ^c	2	60	90	159–162
Mo(CO) ₅ (XNC) ^c	2	5	91	149–152
W(CO) ₅ (XNC) ^c	2	45	91	170–173
<i>cis</i> -Cr(CO) ₄ (t-BuNC) ₂	1	40	80	127–128
<i>cis</i> -Mo(CO) ₄ (t-BuNC) ₂	{ 1 4	3 3	93 90	129–131
<i>cis</i> -W(CO) ₄ (t-BuNC) ₂	1	40	90	145–147
<i>cis</i> -Mo(CO) ₄ (MeNC) ₂	1	90	95	149–150
<i>cis</i> -Mo(CO) ₄ (XNC) ₂ ^{c, d}	2	15	96	125–127
<i>cis</i> -Mo(CO) ₄ (MeNC)(t-BuNC)	4	10	95	130–132
<i>fac</i> -Cr(CO) ₃ (t-BuNC) ₃	1	180	80	170–171
<i>fac</i> -Mo(CO) ₃ (t-BuNC) ₃	{ 1 5	3 3	88 90	179–182
<i>fac</i> -W(CO) ₃ (t-BuNC) ₃	1	50	84	201–202
<i>fac</i> -Mo(CO) ₃ (MeNC) ₃	1	210	86	177–178
<i>fac</i> -Mo(CO) ₃ (MeNC)(t-BuNC) ₂	6	25	85	decomp.
<i>cis</i> -Mo(CO) ₂ (t-BuNC) ₄	3	360	40	>130 135–136

^a See experimental. ^b All values are in agreement with previously reported literature values unless otherwise stated. ^c XNC = 2,6-dimethylphenylisocyanide. ^d Lit. [10] 148–151°C (decomp).

TABLE 2

ANALYTICAL DATA FOR THE NEW ISONITRILE COMPLEXES

	Colour	Analyses (%) Found (calcd.)		
		C	H	N
Cr(CO) ₅ (XNC)	Cream	51.39(52.01)	2.80(2.79)	4.28(4.33)
Mo(CO) ₅ (XNC)	Cream	43.79(45.78)	2.33(2.45)	3.58(3.82)
W(CO) ₅ (XNC)	Cream	37.94(36.94)	2.14(1.98)	3.10(3.08)
<i>cis</i> -Mo(CO) ₄ (MeNC)(<i>t</i> -BuNC)	Cream	38.57(39.77)	3.52(3.62)	8.30(8.44)
<i>fac</i> -Mo(CO) ₃ (MeNC)(<i>t</i> -BuNC) ₂	Yellow	47.46(46.52)	5.86(5.43)	9.66(10.85)

(3.0 mmol) were added to toluene (10 ml). The solution was heated to reflux in an oilbath pre-set at 125°C (2–5 minutes). *t*-BuNC (3.6 mmol) was then added to the hot solution which turned blue and on continued reflux the solution rapidly changed colour to a bright green. The reaction was complete within 10 minutes (Table 1) as detected by IR spectroscopy. Product workup was carried out as in Method 1.

Method 5: Preparation of *fac*-Mo(CO)₃(*t*-BuNC)₃ from *cis*-Mo(CO)₄(*t*-BuNC)₂. Catalyst (0.2 mmol) and Mo(CO)₄(*t*-BuNC)₂ (3.0 mmol) were added to toluene (10 ml) and the solution heated to reflux in an oil-bath pre-set at 125°C (2–5 minutes). *t*-BuNC (3.6 mmol) was then added to the hot solution which turned blue. Continued reflux resulted in the formation of a bright green solution. At the end of the reaction (<2 minutes as detected by IR spectroscopy, Table 1) the product was purified as in Method 1.

Method 6: Preparation of *fac*-Mo(CO)₃(MeNC)(*t*-BuNC)₂. Catalyst (0.2 mmol) and Mo(CO)₅(MeNC) (3.0 mmol) were added to toluene (10 ml). The solution was heated to reflux in an oil-bath pre-set at 125°C (2–5 minutes). *t*-BuNC (6.6 mmol) was then added to the hot solution which turned blue and eventually bright green. Product workup was carried out as in Method 1.

TABLE 3

IR AND NMR DATA FOR THE NEW ISONITRILE COMPLEXES

	IR (cm ⁻¹)					NMR (τ) ^a Methyl protons
	ν(NC)	ν(CO)				
Cr(CO) ₅ (XNC) ^{b, c}	2133	2052	1985	1963	1939	7.62
Mo(CO) ₅ (XNC) ^c	2132	2059	1987	1966	1940	7.64
W(CO) ₅ (XNC) ^c	2133	2052	1981	1958	1935	7.61
<i>cis</i> -Mo(CO) ₄ (XNC) ₂ ^{d, e}	2130	2085	2010	1940		7.65
<i>cis</i> -Mo(CO) ₄ (MeNC)(<i>t</i> -BuNC) ^e	2154	2130	2007	1941	1931	8.54 6.71
<i>fac</i> -Mo(CO) ₃ (MeNC)(<i>t</i> -BuNC) ₂ ^f	2149	2109	1938	1869		8.56 6.71

^a Recorded in CDCl₃ against TMS. ^b XNC = 2,6-dimethylphenylisocyanide. ^c IR recorded in hexane.

^d Preparation previously reported [10] but IR and NMR data not recorded; ^e IR recorded in CHCl₃.

^f ν(NC) recorded in CHCl₃, ν(CO) recorded in hexane.

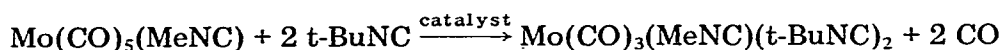
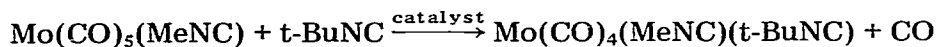
Discussion

Addition of *t*-BuNC to $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) in ratios varying from approximately 1/1 to 3/1, and catalyst in refluxing toluene gives the products $M(\text{CO})_{6-n}(\text{t-BuNC})_n$ ($n = 1-3$) in 80–95% yield. The general method involves the addition of $M(\text{CO})_6$ and $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ to toluene at room temperature. The solution is then stirred at reflux in an oil-bath pre-set at 125°C for 2–5 minutes. The reaction flask is then removed from the oil-bath and *t*-BuNC added to the hot solution which turns blue due to the formation of a cobalt chloride-isonitrile complex (vide infra). Continued reflux results in the solution turning bright green. It is important that this sequence of events is followed otherwise a competing reaction, the polymerization of the isocyanide by CoCl_2 occurs (vide infra) [7].

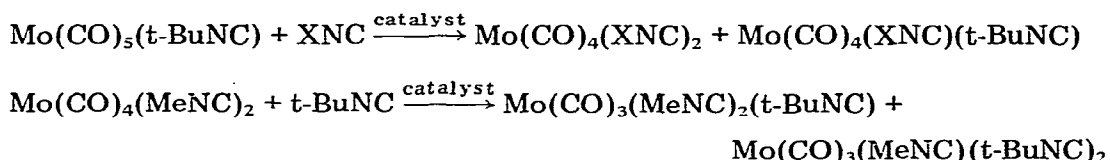
The reaction is monitored by following the changes in the $\nu(\text{CO})$ and $\nu(\text{NC})$ region of the IR spectrum. If the reaction comes to a stop before the required product has formed completely (as detected by IR) further small amounts of isocyanide are added to the reaction solution. This arises from either volatility losses of the *t*-BuNC which occurs in the refluxing toluene (b.p. *t*-BuNC = $90-92^\circ\text{C}$) or due to the cobalt catalyst retaining some of the isocyanide. On completion of the reaction silica is added to the cold clear green solution. The filtrate obtained from repeated extraction with benzene ranges in colour from colourless to yellow, depending on the reaction, while the catalyst remains entrapped in the silica. Yields at this stage are in the range 80–95% based on hexacarbonyl (Table 1). The poor yield obtained for the reaction of $\text{Cr}(\text{CO})_6$ and MeNC ($\sim 40\%$) is due to hexacarbonyl sublimation. An attempt to use THF as co-solvent [8] to overcome this difficulty did not give an increased product yield. The purity of the isonitrile complexes is typically greater than 95% as detected by IR spectroscopy. In general we have found that contamination of a required product with more highly substituted members of the series occurs to the greatest extent for XNC derivatives. For example, the reaction of $\text{Mo}(\text{CO})_6$ and 2 moles of *t*-BuNC gives *cis*- $\text{Mo}(\text{CO})_4(\text{t-BuNC})_2$ with only 2–5% of *fac*- $\text{Mo}(\text{CO})_3(\text{t-BuNC})_3$ being detected. The reaction of $\text{Mo}(\text{CO})_6$ and 2 moles of XNC on the other hand gives 5–10% of *fac*- $\text{Mo}(\text{CO})_3(\text{XNC})_3$ mixed in the required product, *cis*- $\text{Mo}(\text{CO})_4(\text{XNC})_2$. Recrystallization or column chromatography was employed to remove the impurities and to remove final traces of catalyst which can otherwise impart a green colour to the required product.

The catalytic reaction between $M(\text{CO})_6$ and isonitriles is not restricted to *t*-BuNC; we have also prepared the complexes $M(\text{CO})_5(\text{RNC})$ ($M = \text{Cr}, \text{Mo}, \text{W}$; $\text{RNC} = \text{MeNC}, \text{XNC}$) and $\text{Mo}(\text{CO})_{6-n}(\text{MeNC})_n$ ($n = 2-3$) and $\text{Mo}(\text{CO})_4(\text{XNC})_2$ by our catalytic route (Table 1).

All reactions occur with distinct, stepwise replacement of carbonyl groups. Thus, we have prepared *cis*- $\text{Mo}(\text{CO})_4(\text{t-BuNC})_2$ from $\text{Mo}(\text{CO})_5(\text{t-BuNC})$ and *fac*- $\text{Mo}(\text{CO})_3(\text{t-BuNC})_3$ from *cis*- $\text{Mo}(\text{CO})_4(\text{t-BuNC})_2$. As can be expected, mixed isocyanide derivatives may also be prepared by this method, viz:



and again high yields of product have been obtained. It must, however, be mentioned that a correct combination of isocyanide is required if pure mixed derivatives are to be obtained. Thus the reactions



give a mixture of products as detected by a combination of IR and NMR spectroscopy.

Whereas three carbonyls can readily be replaced on Mo(CO)_6 by t-BuNC, removal of a fourth CO can only be achieved with difficulty. Thus, the reaction of *fac*- $\text{Mo(CO)}_3(\text{t-BuNC})_3$ with a twofold excess of t-BuNC in refluxing toluene gave only a moderate conversion (~40%) to *cis*- $\text{Mo(CO)}_2(\text{t-BuNC})_4$ even after 6 hours. (Extended reaction times, after addition of further quantities of catalyst and t-BuNC, increases the yield of the reaction.) An attempt to use a higher boiling solvent (e.g. xylene) only resulted in product (or reactant) decomposition as detected by a blackening of the reaction solution. The method still compares favourably with the alternate literature methods [2,9] presently available for the preparation of the tetrasubstituted complex.

The above compounds $\text{M(CO)}_{6-n}(\text{RNC})_n$ ($n = 1-3$) and $\text{Mo(CO)}_2(\text{t-BuNC})_4$, were characterized by IR and NMR and mass spectral analysis (Table 3). The results are in accord with earlier literature reports [1-3,10] and require no further comment. Only the expected kinetic products, the *cis*- $\text{M(CO)}_4(\text{t-BuNC})_2$ and *fac*- $\text{M(CO)}_3(\text{t-BuNC})_3$ isomers were obtained from the appropriate reaction. The reaction pattern followed the same order as found for the non-catalysed reaction [2,3], viz $\text{Cr} \sim \text{W} < \text{Mo}$, in their ability to undergo carbonyl replacement by isocyanide.

Transition metals are known to catalyse the polymerization of isocyanides [7]. This competing reaction was found to cause loss of chemical reactivity if experimental conditions different to those reported herein were used. Thus, sluggish and erratic results were obtained on occasion when experiments were carried out in which (a) the catalyst was not sufficiently solubilized e.g. by adding catalyst to a refluxing solution of t-BuNC and M(CO)_6 or (b) hexacarbonyl was added to a refluxing solution of t-BuNC and catalyst. At the end of a reaction of the above type we found that the reaction flask was covered in a blue complex (containing trapped catalyst) insoluble in water or hydrocarbon solvents. An IR (KBr) on the product indicated this product was similar to that expected for polymeric t-BuNC [11]. Further evidence for this competing side reaction arises from our attempts to use $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ as catalyst in these reactions. Erratic results were obtained. A blank run ($\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ /t-BuNC/toluene) gave a good yield of a pale yellow insoluble material. An IR (KBr) spectrum of this material [$\nu(\text{NC})$ 1630 cm^{-1} , strong absorption at 3400 cm^{-1}] is similar to that reported by Nolte et al. [11,12] for polymeric isocyanides prepared from NiCl_2 and t-BuNC in ethanol as solvent.

As we experienced no polymerization problems with XNC under our reac-

tion conditions a simpler method of preparing the XNC isonitrile derivatives was employed (Method 2).

We have as yet not been able to establish the mechanism of this catalytic reaction conclusively. However, the following observations have been made:

(1) The reaction between $\text{Mo}(\text{CO})_6$ and $t\text{-BuNC}$ in toluene is not catalysed by the addition of water.

(2) The gas evolved in the reaction is CO (detected qualitatively by reaction with I_2O_5 [13]).

(3) The initial blue solution obtained on addition of $t\text{-BuNC}$ to the reaction mixture $[\text{M}(\text{CO})_6/\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}]$ is thought to be due to the formation of a $\text{CoCl}_2(t\text{-BuNC})_n$ ($n \leq 4$) complex [UV spectrum (acetone): 584 nm ($\epsilon = 209$), 594(204), 640(198), 661(238), 677(251)]. The formulation is supported by our studies on the reaction of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ with $t\text{-BuNC}$. Addition of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and $t\text{-BuNC}$ (1 : 4 ratio) to acetone followed by cooling (-20°C) gives a high yield of a blue-black crystalline material. By analogy with our preparation of $\text{CoCl}_2(\text{XNC})_4$ [5] this is thought to be $\text{CoCl}_2(t\text{-BuNC})_4$ [14]. A UV spectrum recorded on the blue-black complex (in toluene) is identical to that of our catalytic reaction solutions indicating the formation of similar cobalt chloride-isonitrile complexes in the catalytic reaction. This blue-black material also catalysed the reaction between $\text{Mo}(\text{CO})_6$ and $t\text{-BuNC}$.

(4) A reaction carried out between $\text{Mo}(\text{CO})_6$ and $\text{CoCl}_2(t\text{-BuNC})_4$ (4 : 1 ratio) in refluxing acetone (in which the catalyst is completely soluble) yielded exclusively $\text{Mo}(\text{CO})_5(t\text{-BuNC})$ and cobalt chloride as detected by IR and UV spectroscopy respectively.

(5) If the blue reaction solution [containing RNC , CoCl_2 and $\text{M}(\text{CO})_6$] is refluxed it turns green. The UV spectrum of this reaction solution showed no change in the region associated with the catalyst absorptions (400–800 nm). Thus the colour change from blue to green appears to correspond to the formation of the yellow $\text{M}(\text{CO})_{6-n}(\text{RNC})_n$ complexes rather than the formation of some novel intermediate involving cobalt.

We suspect that the predominant effect of the catalyst is to destabilize the metal–CO bond. This could occur via catalyst attack at CO, rather than at the metal centre, and is consistent with both electronic (non violation of the 18 electron rule [15]) and steric arguments. As we have also achieved facile catalytic substitution of CO on $\text{M}(\text{CO})_6$ by amines (e.g. the reaction of $\text{Mo}(\text{CO})_6$ and $\text{NH}_2(\text{C}_6\text{H}_{11})$ readily gives products of the type $\text{Mo}(\text{CO})_{6-n}[\text{NH}_2(\text{C}_6\text{H}_{11})]_n$ ($n = 1-3$)) [16] an intramolecular exchange of RNC between catalyst and metal carbonyl seem unlikely [5]. An intermolecular process consistent with our data is shown in Fig. 1. We believe that this catalytic reaction has implications for the study of the use of co-catalyst in organic synthesis [17] and we

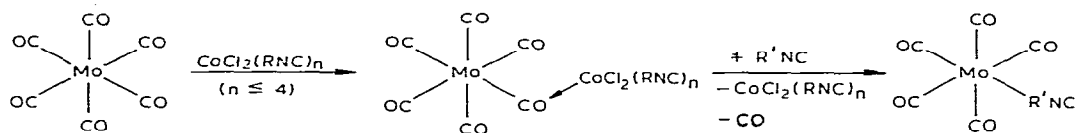


Fig. 1. Possible mechanism for the catalysed substitution reaction.

are currently exploring the potential of this type of reaction, e.g. the hydrogenation of olefins by $\text{Fe}(\text{CO})_5$ with CoCl_2 as co-catalyst [18].

Acknowledgments

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References

- 1 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, London, 1969.
- 2 R.B. King and M.S. Saran, *Inorg. Chem.*, **13** (1974) 74.
- 3 J.A. Connor, E.M. Jones, G.K. McEwen, M.K. Lloyd and J.A. McCleverty, *J. Chem. Soc., Dalton. Trans.*, (1972) 1246.
- 4 E.B. Dreyer, C.T. Lam and S.J. Lippard, *Inorg. Chem.*, **18** (1979) 1904.
- 5 M.O. Albers, N.J. Coville, T.V. Ashworth, E. Singleton and H.E. Swanepoel, *J. Chem. Soc., Chem. Commun.*, in press.
- 6 J. Casanova, R.E. Schuster and N.D. Werner, *J. Chem. Soc.* (1963) 4280.
- 7 F. Millich, *Chem. Rev.*, **72** (1972) 101.
- 8 C.A.L. Mahaffy and P.L. Pauson, *Inorg. Synth.*, **19** (1979) 154.
- 9 P.M. Treichel, D.W. Firsich and G.P. Essenmacher, *Inorg. Chem.*, **18** (1979) 2405.
- 10 Y. Yamamoto and H. Yamakazi, *J. Org. Chem.*, **42** (1977) 4136.
- 11 R.J.M. Nolte, R.W. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas.*, **92** (1973) 83.
- 12 R.J.M. Nolte and W. Crenth., *Recl. Trav. Chim. Pays-Bas*, **92** (1973) 788.
- 13 C.R.N. Strouts, H.N. Wilson and R.T. Parry-Jones, *Chemical Analysis*, Vol. I, (1962) 299.
- 14 Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc., Japan*, **42** (1969) 2077.
- 15 C.A. Tolman, *Chem. Soc. Rev.*, **1** (1972) 337.
- 16 M.O. Albers and N.J. Coville, unpublished results.
- 17 B.L. Booth, H. Goldwhite and R.N. Haszeldine, *J. Chem. Soc(C)* (1966) 1447.
- 18 E.N. Frankel, H.M. Peters, E.P. Jones and H.J. Dutton, *J. Amer. Oil. Chem. Soc.*, **41** (1964) 186.