

SUPPORTED TRANSITION METALS AND METAL OXIDES AS CATALYSTS FOR THE METAL CARBONYL SUBSTITUTION REACTION

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Summary

A range of supported transition metals and metal oxides have been investigated as catalysts for the metal carbonyl substitution reaction $M-CO + L \rightarrow M-L + CO$ (L = isocyanide (RNC), Group V donor ligand). The use of model substitution reactions reveals the metals Pd, Pt, Ru and Rh and the oxides PdO and PtO₂ to be efficient catalysts for substitution reactions of mono-, di- and polynuclear metal carbonyl complexes, and, while there are observable effects which relate to the nature of the catalyst support, catalyst dispersion, catalyst activation and catalyst poisoning, the generally observed orders of activity are $Pd > Pt > Ru > Rh$ and $PdO > PtO_2$. The radical traps hydroquinone and galvinoxyl have an inhibiting effect on catalysis, while light has a mild promotional effect. These observations are consistent with a catalytic mechanism similar to that observed for $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, namely a radical non-chain process. The metal and metal oxides display considerable potential for the synthesis of substituted metal carbonyl complexes including $[Fe(CO)_{5-n}(CNR)_n]$ ($n = 1-5$), $[M(CO)_{6-n}(CNR)_n]$ ($M = Cr, Mo, W; n = 1-3$), $[M_3(CO)_{12-n}(CNR)_n]$ ($M = Ru, n = 1-3; M = Os, n = 1-4$), and $[Fe(CO)_4(L)]$ (L = Group V donor ligand). Certain catalyst supports (zeolites, activated carbon) have themselves been found to possess mild activity for the catalytic carbonyl substitution reaction.

Introduction

The metal carbonyl substitution reaction is of fundamental importance in synthetic organometallic chemistry, organic synthesis and catalysis [1,2]. In most cases

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carbonyl labilization is achieved simply by heating [3], but in others, photochemical procedures [4] have been employed to bring about the desired substitution process. More recently, alternative methods for inducing carbonyl substitution, namely the use of chemical reagents (e.g. trimethylamine-*N*-oxide [5,6]) or catalysts [6] have been successfully employed. These procedures contrast with the more traditional practices in that they are usually characterized by mild reaction conditions, multiple stepwise carbonyl ligand replacement, high yields of the desired product, and short reaction times [6].

Our recent study on the use of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ as a substitution catalyst [7] suggested to us that materials possessing electron transfer properties e.g. heterogeneous hydrogenation catalysts [8] should also catalyze the carbonyl substitution reaction. On the basis of this reasoning we considered several transition metals (in bulk form and dispersed on supports) as catalysts for a variety of substitution reactions, each offering a differing degree of difficulty. Herein we report on these studies which serve to establish that a range of Platinum Group metals (and their oxides) display remarkable catalytic activities for these reactions, and further, that certain catalyst supports, generally considered to be inert for most catalytic purposes, also exhibit some surprising catalytic properties. A preliminary account featuring some of this work has been published [9].

Experimental

All substitution reactions were routinely performed under nitrogen or argon in a round-bottomed flask, which was fitted with a rubber septum for convenient sample withdrawal for the purpose of monitoring the reaction solution by IR spectroscopy or thin layer chromatography. Operations such as filtration and recrystallization were carried out in air. All solvents were routinely dried and distilled under an inert atmosphere immediately before use. The activation of catalysts was achieved by heating the solid at 300°C for 13 h under a steady flow of argon. This was followed by a 2 h period of heating at 300°C under a flow of hydrogen. The catalyst was subsequently stored under an inert atmosphere of argon.

The metal carbonyls $[\text{Fe}(\text{CO})_5]$, $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $[\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Mn}, \text{Re}$) and $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) were used as purchased from Strem Chemicals Inc. The isocyanides 2,6-Me₂C₆H₃NC, Bu^tNC, and C₆H₁₁NC were obtained from Fluka AG, Switzerland, while C₆H₅CH₂NC was purchased from Aldrich Chemical Co. The following catalysts were obtained from the indicated sources: PdO, PtO₂ (Merck Chemicals); Pd metal (Johnson-Matthey); 10% Pd/C, 5% Pd/C(A), 5% Pd/C(B), 5% Pd/C (unreduced), 5% Pd/C (50% moisture), 5% Pd/C (50% moisture, sulfided), 0.5% Pd/C (granular), 5% Pd/Al₂O₃, 0.5% Pd/Al₂O₃, 0.1% Pd/Al₂O₃, 5% Pd/BaSO₄, 5% Pt/C, 5% Pt/C (50% moisture, sulfided), 1% Pt/C (50% moisture), 5% Pt/Al₂O₃, 0.5% Pt/Al₂O₃, 5% Rh/C, 5% Rh/Al₂O₃, 5% Ru/C, 5% Ru/Al₂O₃ (Engelhard Industries).

The complexes $[\text{Fe}(\text{CO})_4(\text{CNR})]$ ($\text{R} = \text{Bu}^t, \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5\text{CH}_2, 2,6\text{-Me}_2\text{C}_6\text{H}_3$) [10] and $[\text{Mn}(\text{CO})_5\text{Br}]$ [11] were prepared by the published procedures. The aluminosilicates 3d–3v and the corresponding analytical data were provided by Dr I.R. Leith of the Chemical Engineering Research Group, CSIR. The ZSM-5 zeolite was provided by Dr D.O. Hughes, AECI Ltd, and the activated carbon samples by Dr G.J. McDougall, Department of Chemistry, University of the Witwatersrand.

All infrared spectra were recorded using either a Perkin–Elmer 521 or a Jasco IRA 1 instrument. All ^1H NMR spectra were recorded using a Bruker WP80 FTNMR spectrometer. Melting points were determined using a Kofler micro-hot-stage apparatus and are uncorrected. Microanalyses, unless otherwise stated, were performed by the microanalytical section of the Analytical Division, NCRL.

A. The standard substitution reaction $[\text{Fe}(\text{CO})_4(\text{CNBu}')] + \text{Bu}'\text{NC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNBu}')_2] + \text{CO}$ [10]

$[\text{Fe}(\text{CO})_4(\text{CNBu}')] (1.0 \text{ mmol})$, the appropriate amount of catalyst, and benzene (10 ml) were combined in a two-necked round-bottomed flask. The mixture was heated to reflux by means of a thermostat controlled oil bath pre-set at 100°C and then $\text{Bu}'\text{NC}$ (1.0 mmol) was added. Samples were withdrawn at appropriate time intervals (the reaction rate may be qualitatively judged by the rate of CO evolution), and the course of the reaction monitored by IR spectroscopy ($2200\text{--}1900 \text{ cm}^{-1}$ region of the spectrum). The end of the reaction was taken to correspond to complete conversion of $[\text{Fe}(\text{CO})_4(\text{CNBu}')]$ to $[\text{Fe}(\text{CO})_3(\text{CNBu}')_2]$.

B. Other substitution reactions

(i) $[\text{Fe}(\text{CO})_4(\text{CNR}) + \text{RNC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNR})_2] + \text{CO}$ ($\text{R} = \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5\text{CH}_2, 2,6\text{-Me}_2\text{C}_6\text{H}_3$)

The procedures used for these experiments were identical to those outlined in A above.

(ii) $[\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)] + n \text{ 2,6-Me}_2\text{C}_6\text{H}_3\text{NC} \rightarrow [\text{Fe}(\text{CO})_{4-n}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_{n+1}] + n\text{CO}$ ($n = 1\text{--}4$)

The procedures used in these experiments have been detailed [10] for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ as catalyst. The only difference here was that $[\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]/2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ratios of $1.0/n \text{ mmol}$ ($n = 1.0, 2.0, 3.0, 4.0$) were used, together with 0.020 g of the appropriate catalyst.

(iii) $[\text{Fe}(\text{CO})_5] + \text{PPh}_3 \rightarrow [\text{Fe}(\text{CO})_4(\text{PPh}_3)] + \text{CO}$

The procedures used in this experiment have been described elsewhere [12]. The amount of catalyst used was 0.030 g.

(iv) $[\text{M}(\text{CO})_6] + \text{Bu}'\text{NC} \rightarrow [\text{M}(\text{CO})_5(\text{CNBu}')] + \text{CO}$ ($\text{M} = \text{Mo}, \text{W}$)

Procedures similar to those outlined in A above have been used except that a $[\text{M}(\text{CO})_6]/\text{Bu}'\text{NC}$ ratio of $1.0/1.2 \text{ mmol}$ and 0.030 g of catalyst was employed in each case.

(v) $[\text{Fe}(\text{CO})_5] + \text{RNC} \rightarrow [\text{Fe}(\text{CO})_4(\text{CNR})] + \text{CO}$ ($\text{R} = \text{Bu}', 2,6\text{-Me}_2\text{C}_6\text{H}_3$)

A procedure similar to that given in A above was used. The amount of catalyst used in each experiment was 0.030 g.

C. The catalyzed synthesis of the complexes $[\text{M}(\text{CO})_{6-n}(\text{CNCH}_2\text{C}_6\text{H}_5)_n]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; n = 1\text{--}3; 2a\text{--}2i$)

A mixture of $[\text{M}(\text{CO})_6]$ (2.0 mmol), catalyst (PdO , 0.020 g) and benzene (15 ml) was heated under reflux using a thermostat controlled oil-bath pre-set at 100°C .

Benzyl isocyanide (2.05, 4.1 or 6.15 mmol, depending on the required level of substitution) was then added, and the mixture heated under reflux until completion of the reaction as determined by IR spectroscopy (see Table 5). The solution was then cooled and filtered to remove the catalyst, and the solvent removed on a rotary evaporator to give the required product in typically > 90% yield. Recrystallization (pentane or hexane/dichloromethane mixtures) gave the required products in analytical purity.

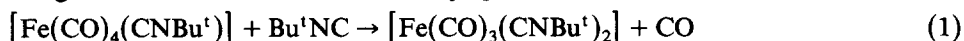
Results and discussion

Metal and metal oxide catalysts

An extensive range of catalysts for the metal carbonyl substitution reaction has been established [6]. These include transition metal salts, most notably cobalt(II) chloride [10,13,14], complexes of transition metals including $[\text{RhCl}(\text{PPh}_3)_3]$ [15,16] and $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}_2$ [7,12], and electron transfer agents e.g. sodium diphenylketyl [6,17]. In most cases the mechanisms of catalysis have not been unequivocally determined, but in two cases, catalysis by metal-metal bonded dimers (typified by $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}_2$), and catalysis by sodium diphenylketyl and related species, all available evidence supports the intermediacy of substitution labile, odd-electron intermediates [7,17]. Similar mechanisms have been considered for other carbonyl substitution systems, but to date supporting evidence has not been forthcoming and their mode of functioning remains obscure [10].

On the basis of these considerations we were led to consider other approaches to the problem of catalytically initiating carbonyl substitution processes. It is known that materials such as metallic palladium and platinum and various metal oxides, heterogeneous hydrogenation catalysts [8], possess electron transfer properties. We thus anticipated that these materials might possess catalytic activity similar to that observed for $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}_2$. (In support of this supposition it is interesting to note that supported palladium, and other materials such as metallic platinum and nickel, Fe_3O_4 and Al_2O_3 had previously been reported to catalyze carbonyl ligand exchange in metal carbonyl complexes [18,19]).

A range of transition metals (in bulk form and dispersed on various supports) and metal oxides were thus subjected to an initial screening for catalytic activity using a standard substitution reaction [10]:



A summary of the results is presented in Table 1. It is clear from these experiments that on the level of activity under consideration here, only palladium, platinum, ruthenium and rhodium (the qualitative order of activity being $\text{Pd} > \text{Pt} > \text{Ru} > \text{Rh}$) and the oxides PdO and PtO_2 (the qualitative order of activity being $\text{PdO} > \text{PtO}_2$), display measurable effects. Other metals e.g. rhenium, tungsten, cobalt, and metal oxides e.g. Co_2O_3 , NiO , Main Group metal oxides (see below) were, however, found to be catalytically inactive in (1).

In a more detailed study, a range of different supports, catalyst loadings and related variables for these metals have been considered (Table 2). As indicated by entries **1a–1g** there is, in general, very little variation in the observed reaction time with catalyst loading and selective catalyst poisoning (**1e**, **1f**) for palladium as catalyst. This is probably a consequence of the relatively high catalytic activity of

TABLE 1

THE EFFECT OF METAL AND METAL OXIDE CATALYSTS ON THE REACTIONS
 $[\text{Fe}(\text{CO})_4(\text{CNBu}^t)] + \text{Bu}^t\text{NC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNBu}^t)_2] + \text{CO}^a$

	Reaction time ^b (min)
MgO, CaO, Al ₂ O ₃ , SiO ₂ , P ₄ O ₁₀ , TiO ₂ , W, MoO ₃ , WO ₃ , MnO ₂ , Co, Ni/Al alloy, Fe ₂ O ₃ , Co ₂ O ₃ , NiO, Ni ₂ O ₃ , OsO ₄ , PtO ₂	nc ^a
5% Ru/Al ₂ O ₃	15
5% Rh/Al ₂ O ₃	60
5% Pd/Al ₂ O ₃	2
5% Pt/Al ₂ O ₃	5
PdO	2

^a Standard reaction conditions, see Experimental. ^b As estimated by IR spectroscopy. ^c nc = no catalysis.

metallic palladium (see below) towards this relatively facile substitution reaction. This is further illustrated by the results obtained for the varying dispersion of palladium on alumina (1h–1j) and the lack of any noticeable effect in varying

TABLE 2

THE EFFECT OF SUPPORTED TRANSITION METAL CATALYSTS ON THE REACTION
 $[\text{Fe}(\text{CO})_4(\text{CNBu}^t)] + \text{Bu}^t\text{NC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNBu}^t)_2] + \text{CO}^a$

		Reaction time ^b (min)
1a	10.0% palladium on carbon	2
1b	5.0% palladium on carbon (A) ^c	2
1c	5.0% palladium on carbon (B) ^c	2
1d	5.0% palladium on carbon, unreduced	2
1e	5.0% palladium on carbon, 50% moisture	4
1f	5.0% palladium on carbon, 50% moisture, sulphided	2
1g	0.5% palladium on carbon, granular	4
1h	5.0% palladium on alumina	2
1i	0.5% palladium on alumina	2
1j	0.1% palladium on alumina	4
1k	5.0% palladium on barium sulphate	2
1l	5.0% palladium on calcium carbonate	2
1m	0.5% palladium on zeolite Y ^d	4
1n	5.0% platinum on carbon	5
1o	5.0% platinum on carbon, 50% moisture, sulphided	30
1p	1.0% platinum on carbon, 50% moisture	8
1q	5.0% platinum on alumina	5
1r	0.5% platinum on alumina	30
1s	5.0% rhodium on carbon	45 (50) ^e
1t	5.0% rhodium on alumina	60
1u	5.0% ruthenium on carbon	nc ^f (35) ^e
1v	5.0% ruthenium on alumina	15 (2) ^e
1w	0.5% ruthenium on alumina	75 (2) ^e

^a Standard reaction conditions, see Experimental. ^b As estimated by IR spectroscopy. ^c Different catalyst surface area, A > B. ^d Union Carbide SK-120; catalyst support a rare earth de-cationised zeolite Y. ^e Reaction time following activation; 13 h at 300°C under argon followed by 2 h at 300°C under hydrogen. ^f nc = no catalysis.

TABLE 3

THE EFFECT OF CATALYSTS ON THE REACTION $[\text{Fe}(\text{CO})_4(\text{CNR})] + \text{RNC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNR})_2] + \text{CO}$ ($\text{R} = \text{C}_6\text{H}_{11}$, Bu^t , $\text{C}_6\text{H}_5\text{CH}_2$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$)^a

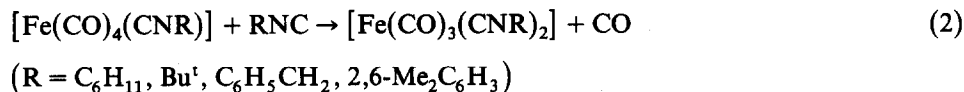
	Reaction time ^b (min)			
	C_6H_{11}	Bu^t	$\text{C}_6\text{H}_5\text{CH}_2$	$2,6\text{-Me}_2\text{C}_6\text{H}_3$
palladium metal	2	4	4	3
5.0% palladium on carbon	2	2	2	2
5.0% palladium on calcium carbonate	2	2	2	2
5.0% platinum on carbon	2	4	8	6
PdO	2	2	2	2
PtO ₂	4	20	16	8

^a $[\text{Fe}(\text{CO})_4(\text{CNR})]/\text{RNC}/\text{catalyst}$, 1.0 mmol/1.0 mmol/0.020 g; benzene (10 ml, 80°C). ^b As determined by IR spectroscopy.

surface area (**1b**, **1c**) and support (e.g. **1b**, **1c**, **1h**, **1k**, **1l**). This high activity may also be gauged by the remarkably small amounts of palladium metal required to effect these reactions. Thus, in the case of a 5.0% loading on carbon this represents only 0.59% palladium by mass (or 1.4 mole %), and in the case of 0.1% palladium on alumina, only 0.12% palladium by mass or 0.028 mole % catalyst.

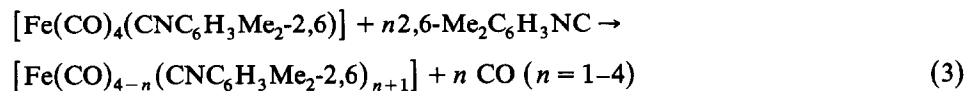
In general, platinum is indicated to possess a lower catalytic activity for reaction (1) when compared to palladium (compare **1r**, **1i**) and is thus more susceptible to catalyst poisoning (compare **1f**, **1o**). Metallic rhodium is, in general, only a poor catalyst for (1) and activation * has been found to have no advantageous effect (see for instance **1s**). Ruthenium also shows poor catalytic activity, but on activation * shows markedly improved catalytic properties (see **1u–1w**).

Further studies with metallic palladium and platinum, and the oxides PdO and PtO₂, have generalized these studies in terms of the variation in the isonitrile ligand viz.



The results (Table 3) confirm that the relative catalytic activities are again, in general, $\text{Pd} > \text{Pt}$ and $\text{PdO} > \text{PtO}_2$. Effects due to differing catalyst support (or lack of it) for the catalyst palladium are not detectable under these conditions.

In order to more fully assess the synthetic utility of these catalysts for the substitution of CO by isonitrile on iron pentacarbonyl [10], the reaction



was investigated by the stepwise addition of 2,6-dimethylphenyl isocyanide to $[\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]$ in the presence of metallic palladium (bulk and dispersed on carbon and CaCO_3), platinum (dispersed on carbon) and the oxides PdO and

* The catalyst was heated at 300°C for 13 h under a steady flow of argon. This was followed by a 2 h period of heating at 300°C under a flow of hydrogen. The catalyst was subsequently stored under an inert atmosphere of argon.

TABLE 4

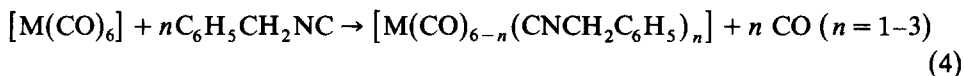
THE EFFECT OF CATALYSTS ON THE REACTION $[\text{Fe}(\text{CO})_{5-n}(\text{CNR})_n] + \text{RNC} \rightarrow [\text{Fe}(\text{CO})_{4-n}(\text{CNR})_{n+1}] + \text{CO}$ ($n = 1-4$, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$)^a

	Reaction time ^b (min)			
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
palladium metal	3	7	45	60
5.0% palladium on carbon	2	2	10	40
5.0% palladium on calcium carbonate	2	2	10	25
5.0% platinum on carbon	6	75	nc ^c	—
PdO	2	15	nc	—
PtO ₂	6	20	nc	—

^a $[\text{Fe}(\text{CO})_{5-n}(\text{CNC}_6\text{H}_3\text{Me}_2,6)_n]/2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}/\text{catalyst}$, 1.0 mmol/1.0 mmol/0.020 g; benzene (10 ml, 80°C). ^b As determined by IR spectroscopy. ^c nc = no catalysis observed.

PtO₂. The results are summarized in Table 4 and generally indicate $\text{Pd} \gg \text{Pt}$ in activity for multiple CO substitution in this system, and also that PdO approximates PtO₂ in activity. The expected difference in catalytic activity between bulk palladium metal and the catalyst dispersed on various supports is also evident, although in accordance with the high activity of palladium for such substitution reactions it is possible to obtain $[\text{Fe}(\text{CNC}_6\text{H}_3\text{Me}_2,6)_5]$ even with the bulk palladium metal catalyst. It is, however, interesting to contrast qualitatively the relative activities of cobalt(II) chloride [10] and palladium as catalysts for the multiple substitution of CO on iron pentacarbonyl. Thus the results with metallic palladium reflect the increasing difficulty of each step of the reaction, an effect not apparent with cobalt(II) chloride and aryl isonitriles (i.e. $[\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2,6)] + \text{isonitrile} \rightarrow [\text{Fe}(\text{CNC}_6\text{H}_3\text{Me}_2,6)_5]$, approximately 2 min per step under the same reaction conditions).

Palladium catalysts, and PdO and PtO₂, readily catalyze the substitution of CO by isonitrile on the Group VI metal hexacarbonyls. Thus, substitution of CO by benzyl isonitrile on $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)



have been carried out in boiling benzene in the presence of palladium on carbon, PdO and PtO₂ to give the products $[\text{M}(\text{CO})_{6-n}(\text{CNCH}_2\text{C}_6\text{H}_5)_n]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $n = 1-3$; **2a-2i**). Yields of the new products **2a-2i** and reaction times for their formation are listed in Table 5.

The relative ordering of catalyst activity for these reactions is $\text{PdO} > \text{Pd/C} > \text{PtO}_2$, and in contrast to the substitution of CO by isonitrile on $[\text{Fe}(\text{CO})_5]$, these catalysts possess qualitatively greater activity than cobalt(II) chloride for the replacement of CO by isonitrile on $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [14]. Thus, although product purity and yields are comparable to those generally obtained for instance for the compounds $[\text{M}(\text{CO})_{6-n}(\text{CNBu}^t)_n]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $n = 1-3$) using cobalt(II) chloride as catalyst [14], reaction conditions are milder, and, qualitatively, reaction times are considerably shorter, thereby suggesting considerable potential for the synthesis of higher substituted derivatives viz. $[\text{M}(\text{CO})_{6-n}(\text{CNR})_n]$ ($n = 4-6$) [20] using these catalysts. A further advantage of these catalysts relates to their

TABLE 5

REACTION CONDITIONS FOR THE CATALYSED SYNTHESIS OF THE COMPLEXES $[M(CO)_{6-n}(CNCH_2C_6H_5)_n]$ ($M = Cr, Mo, W$; $n = 1-3$)

		Pd/C ^a		PdO		PtO ₂	
		Reaction time ^b (min)	Yield (%)	Reaction time ^b (min)	Yield (%)	Reaction time ^b (min)	Yield (%)
$[Cr(CO)_5(CNCH_2C_6H_5)]$	(2a)	4	89	2	86	50	85
$[Mo(CO)_5(CNCH_2C_6H_5)]$	(2b)	2	87	2	94	2	91
$[W(CO)_5(CNCH_2C_6H_5)]$	(2c)	2	93	2	91	2	87
$cis-[Cr(CO)_4(CNCH_2C_6H_5)_2]$	(2d)	15	98	2	93	nc ^c	—
$cis-[Mo(CO)_4(CNCH_2C_6H_5)_2]$	(2e)	2	96	2	95	8	95
$cis-[W(CO)_4(CNCH_2C_6H_5)_2]$	(2f)	4	92	2	98	60	31
$fac-[Cr(CO)_3(CNCH_2C_6H_5)_3]$	(2g)	60	98	10	98	—	—
$fac-[Mo(CO)_3(CNCH_2C_6H_5)_3]$	(2h)	6	98	2	96	nc	—
$fac-[W(CO)_3(CNCH_2C_6H_5)_3]$	(2i)	15	93	2	96	—	—

^a 5.0% palladium on carbon. ^b As determined by IR spectroscopy. ^c nc = no catalysis observed.

TABLE 6

ANALYTICAL DATA FOR THE COMPLEXES $[M(CO)_{6-n}(CNCH_2C_6H_5)_n]$ ($M = Cr, Mo, W$; $n = 1-3$)

		Colour	M.p. ^a (°C)	Elemental analysis (Found (calc) (%))		
				C	H	N
$[Cr(CO)_5(CNCH_2C_6H_5)]$	(2a)	white	76–77	50.47(50.49)	2.07(2.27)	4.48(4.53)
$[Mo(CO)_5(CNCH_2C_6H_5)]$	(2b)	white	71–72	44.35(44.19)	1.87(1.98)	4.00(3.97)
$[W(CO)_5(CNCH_2C_6H_5)]$	(2c)	white	80–81	35.03(35.37)	1.45(1.58)	3.81(3.18)
$cis-[Cr(CO)_4(CNCH_2C_6H_5)_2]$	(2d)	white	85–86	59.75(60.30)	3.37(3.52)	7.00(7.04)
$cis-[Mo(CO)_4(CNCH_2C_6H_5)_2]$	(2e)	white	95–96	54.88(54.30)	3.20(3.16)	6.48(6.33)
$cis-[W(CO)_4(CNCH_2C_6H_5)_2]$	(2f)	white	117–119	45.15(45.28)	2.47(2.64)	5.33(5.28)
$fac-[Cr(CO)_3(CNCH_2C_6H_5)_3]$	(2g)	cream	99–101	65.94(66.53)	4.40(4.31)	8.63(8.62)
$fac-[Mo(CO)_3(CNCH_2C_6H_5)_3]$	(2h)	cream	110–111	61.04(61.02)	4.12(3.95)	7.89(7.91)
$fac-[W(CO)_3(CNCH_2C_6H_5)_3]$	(2i)	cream	117–118	52.03(52.34)	3.36(3.39)	6.74(6.79)

^a Uncorrected.

TABLE 7

SPECTROSCOPIC DATA FOR THE COMPLEXES $[M(CO)_{6-n}(CNCH_2C_6H_5)_n]$ ($M = Cr, Mo, W$; $n = 1-3$)

		IR ^a (cm ⁻¹)					¹ H NMR ^b	
		ν (NC)		ν (CO)			δ (CH ₂)	
[Cr(CO) ₅ (CNCH ₂ C ₆ H ₅)]	(2a)	2155		2060	1985	1959	1903	4.84
[Mo(CO) ₅ (CNCH ₂ C ₆ H ₅)]	(2b)	2158		2063	1086	1961	1933	4.87
[W(CO) ₅ (CNCH ₂ C ₆ H ₅)]	(2c)	2161		2062	1983	1958	1930	4.91
<i>cis</i> -[Cr(CO) ₄ (CNCH ₂ C ₆ H ₅) ₂]	(2d)	2162	2120	2018	1957	1943	1928	4.78
<i>cis</i> -[Mo(CO) ₄ (CHCH ₂ C ₆ H ₅) ₂]	(2e)	2157	2118	2020	1964	1948	1935	4.81
<i>cis</i> -[W(CO) ₄ (CNCH ₂ C ₆ H ₅) ₂]	(2f)	2159	2109	2013	1957	1944	1929	4.86
<i>fac</i> -[Cr(CO) ₃ (CHCH ₂ C ₆ H ₅) ₃]	(2g)	2158	2111	1943	1883			4.86
<i>fac</i> -[Mo(CO) ₃ (CNCH ₂ C ₆ H ₅) ₃]	(2h)	2165	2120	1947	1883			4.72
<i>fac</i> -[W(CO) ₃ (CNCH ₂ C ₆ H ₅) ₃]	(2i)	2178	2118	1938	1873			4.82

^a $[M(CO)_5(CNR)]$ recorded in hexane, $[M(CO)_{6-n}(CNR)_n]$ ($n = 2,3$) recorded in CHCl₃. ^b Recorded in CDCl₃ relative to TMS.

completely heterogeneous nature. Facile catalyst separation is thus achieved simply by filtration, which, followed by recrystallization, readily gives the analytically pure substitution products.

The new compounds $[M(CO)_{6-n}(CNCH_2C_6H_5)_n]$ ($M = Cr, Mo, W$; $n = 1-3$; **2a-2i**) have been characterized by elemental analysis (Table 6) and by IR and 1H NMR spectroscopy (Table 7). The IR data are consistent with that expected for the complexes $[M(CO)_{6-n}(CNR)_n]$ ($n = 1-3$) [14] and the 1H NMR spectra all show singlets for the methylene resonances.

The main disadvantage associated with the use of transition metal salts (e.g. $CoCl_2$, $NiCl_2$) as catalysts for the carbonyl substitution reaction is that all attempts at applying them to the substitution reactions of di- and polynuclear metal carbonyl complexes have failed [21]. Thus, for instance, cobalt(II) chloride has been found to be incapable of catalyzing the substitution of CO by isonitrile on the complexes $[M_2(CO)_{10}]$ ($M = Mn, Re$) as well as on $[M_3(CO)_{12}]$ ($M = Fe, Ru, Os$). In fact, unexpectedly, $CoCl_2 \cdot 2H_2O$ and related catalysts ($MX_2 \cdot nH_2O$, $M = Co, Ni$; $X = Br, I, NO_3$) retard the normally observed, limited, thermal substitution of CO by isonitrile in these systems. Also, on occasion, these salts have been found to promote the formation of mixtures of substituted products, including substituted mononuclear complexes obtained by metal-metal bond cleavage in the cluster complex.

For the purpose of establishing and investigating catalytic CO substitution in di- and polynuclear metal carbonyl complexes the model substitution reaction



has been monitored in the presence of a range of potential catalysts. These results have been discussed elsewhere [22], but briefly, palladium, platinum, ruthenium, and rhodium, dispersed on various supports, and PdO , were found to be active catalysts.

In the light of these results, we have attempted to extend the use of metallic palladium and platinum, and of palladium oxide as catalysts to the substitution of CO by isonitriles on carbonyl complexes of metal atom nuclearity > 2 . The addition of Bu^iNC to a solution of $[Fe_3(CO)_{12}]$ (3.0/1.0 mmol) in benzene at room temperature in the presence of palladium (5% dispersed on carbon, barium sulfate, and barium carbonate) and PdO , results in cleavage of the metal framework giving the substituted mononuclear complexes $[Fe(CO)_4(CNBu^i)]$ and $[Fe(CO)_3(CNBu^i)_2]$ (as identified by IR spectroscopy [10]). Thus the major pathway involved in these reactions appears to be cluster breakdown, with only small quantities of the substituted trinuclear complexes $[Fe_3(CO)_{12-n}(CNBu^i)_n]$ ($n = 1, 2$) [23] being observed. The reason for cluster fragmentation in these systems has not been established but it could be related to the effects observed in the presence of cobalt(II) chloride (see above), or simply to a thermodynamic effect arising from relatively high levels of substitution by bulky ligands, as observed for instance in the reactions of PPh_3 with $[Fe_3(CO)_{12}]$ [24].

Substitution with retention of the metal framework has, however, been found to be the favoured pathway for the catalyzed reactions between $[M_3(CO)_{12}]$ ($M = Ru, Os$) and isonitrile. Thus, Bu^iNC has been found to react readily with $[Ru_3(CO)_{12}]$ in the presence of 5.0% palladium on carbon (benzene, $35^\circ C$) to give good yields of the products $[Ru_3(CO)_{12-n}(CNBu^i)_n]$ ($n = 1-3$) [25], and with $[Os_3(CO)_{12}]$ in boiling benzene to give the products $[Os_3(CO)_{12-n}(CNBu^i)_n]$ ($n = 1-4$) [26]. These results are supported by the reported [27] use of palladium on carbon as a catalyst

TABLE 8

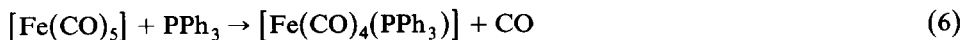
THE EFFECT OF LIGHT AND RADICAL INHIBITORS ON THE PALLADIUM, AND PALLADIUM AND PLATINUM OXIDE CATALYSED REACTIONS $[\text{Fe}(\text{CO})_4(\text{CNR})] + \text{RNC} \rightarrow [\text{Fe}(\text{CO})_3(\text{CNR})_2] + \text{CO}$ ^a (PdO, PtO₂, R = 2,6-Me₂C₆H₃; Pd/CaCO₃, R = Bu^t)

	Reaction time ^b (min)			
	Thermal reaction	Galvinoxyl ^c	Hydroquinone ^c	Light ^d
PdO	10	20	70	5
PtO ₂	12	30	70	9
Pd/CaCO ₃	35	nc ^e	nc	20

^a $[\text{Fe}(\text{CO})_4(\text{CNR})]/\text{RNC}/\text{catalyst}$, 1.0 mmol/1.0 mmol/0.020 g; PdO, PtO₂, R = 2,6-Me₂C₆H₃, benzene 65°C; Pd/CaCO₃, R = Bu^t, benzene 25°C. ^b As determined by IR spectroscopy. ^c 10% by mass based on catalyst. ^d 500 W light bulb. ^e nc = no catalysis.

for the enrichment of polynuclear metal carbonyl complexes in ¹³CO i.e. the catalytic replacement of ¹²CO by ¹³CO under mild reaction conditions.

We have made other attempts to broaden the use of metal and metal oxide catalysts to include substitution of CO by phosphine ligands. Thus, palladium (supported on carbon and calcium carbonate) and PtO and PtO₂ have been investigated as catalysts for the reaction



Heating of $[\text{Fe}(\text{CO})_5]$, PPh₃ and the catalyst in toluene under reflux gave the required product $[\text{Fe}(\text{CO})_4(\text{PPh}_3)]$, free from contamination by $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$, in 2.5 h (92% yield, 10.0% Pd/C catalyst), 3 h (90%, 10.0% Pd/CaCO₃), 10 h (96%, PdO), and 15 h (42%, PtO₂). While the principle is established, none of these reactions, however, compare favourably with the cobalt(II) halide or $\{(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\}_2$ (R = H, Me) catalyzed procedures reported previously [12,13]. Similar attempts to achieve the substitution of CO by phosphine ligands on $[\text{Mn}_2(\text{CO})_{10}]$ (to give as product $[\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2]$ [28]), and on $[\text{Re}_2(\text{CO})_{10}]$ [29], $[\text{Mn}(\text{CO})_5\text{Br}]$ [30], and $[\text{Ru}_3(\text{CO})_{12}]$ [31] have all met with little success.

The substitution reactions



(R = 2,6-Me₂C₆H₃, PdO, PtO₂, benzene, 65°C; R = Bu^t, Pd/CaCO₃, benzene 25°C)

were used to determine the effect of the radical inhibitors galvinoxyl* and hydroquinone, and of light, on the catalyzed reactions. The results are summarized in Table 8. For all three catalysts inhibition is observed on addition of galvinoxyl and hydroquinone. It is possible that the added inhibitor interacts either with the surface of the catalyst or with reactive intermediates produced by the catalyst. Also, a slight rate enhancement is observed in the presence of light (500 W light bulb), although the use of UV radiation in the case of PdO as catalyst did not produce any greater effect than noted with visible light.

No difficulties with catalyst reproducibility [6] have been noted in the present study experienced. In accordance with this, we have not observed transition metals

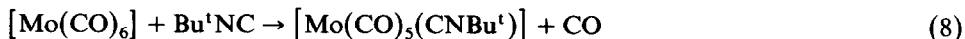
* 2,6-Di-*t*-butyl- α -(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-diene-1-ylidene)-*p*-tolyl-oxo.

and metal oxides to act as catalysts for the polymerization of isonitriles [32]. Sustained catalytic activity, even with long reaction times and high boiling solvents was found consistently. Furthermore, the investigation of a used catalyst (PtO_2) by IR spectroscopy and by X-ray powder diffraction showed no evidence for a modification of the catalyst during the course of the catalytic reaction.

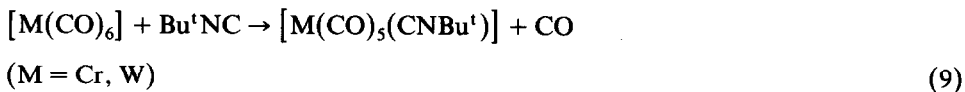
The mechanism of catalysis must involve a substrate-catalyst interaction, which would appear to be possible even in the absence of a definitive catalyst–ligand interaction (as usually observed for instance in most other catalytic carbonyl substitution systems except sodium benzophenone ketyl [6,17]). The actual substitution reaction may thus occur on the surface of the catalyst, or via catalyst generated, reactive metal carbonyl intermediates. The former alternative may be envisaged to occur via either associative or dissociative pathways (similar to those suggested by Webb and Mitchell [18] for the catalyzed replacement of ^{12}CO in $[\text{Fe}(\text{CO})_5]$ by ^{14}CO). The latter alternative could operate by means of formal one-electron transfer from the substrate (i.e. the metal carbonyl complex) to the catalyst, thereby generating substitution labile radical cations which would be expected [33] to interact rapidly with available ligands in either an associative or dissociative manner. On the basis of the results presented in the above discussion which all suggest a strong ligand dependence, an associative pathway would seem to be indicated. Further, on the basis of the similarity between these catalyst systems and the performance of the $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$ class of catalysts [7,12] it would thus seem reasonable that a largely similar reaction mechanism is involved, namely a radical non-chain process [7].

The role of the catalyst support

In order to delineate more fully the properties of the supported catalysts discussed above, we also investigated any possible activities of the catalyst supports by using of the substitution reaction (1). The materials barium sulfate, barium carbonate, calcium carbonate and alumina (Gibbsite) were found to be completely inactive for this reaction. However, initial studies using commercially available activated carbon and alumino-silicates, suggested that mild catalytic effects were observable. These effects were slight, and consequently erratic results were very often obtained. In order to overcome these limitations, another, thermally more facile reaction was used to study these catalysts:



This reaction, carried out in benzene at 80°C , requires 60 min to reach completion in the absence of added catalyst. An advantage of this system is that the more active catalysts can also be tested using the related but progressively more difficult reactions



(The observed relative reactivities are $\text{Mo} > \text{W} > \text{Cr}$)

The results of a study of a series of zeolites and metal exchanged zeolites using the reactions (8) and (9) are listed in Table 9. Generally the readily available zeolite

TABLE 9

THE EFFECT OF ALUMINOSILICATES ON THE REACTION $[M(CO)_6] + Bu^1NC \rightarrow [M(CO)_5(CNBu^1)] + CO$ ($M = Mo, W$) ^{a,b}

	Reaction time ^c (min)	
	$[Mo(CO)_5(CNBu^1)]$	$[W(CO)_5(CNBu^1)]$
3a 3Å molecular sieve	2	60 (~ 20%)
3b 4Å molecular sieve	2	60 (~ 30%)
3c 13X molecular sieve	4	nc ^d
3d NaY	2	60
3e NH ₄ NaY	> 60	—
3f MgNaY ^e	4	nc
3g LaNaY	30	—
3h CeNaY	> 60	—
3i NaZ	2	60 (~ 30%)
3j NH ₄ NaZ	25	—
3k MgNaZ ^f	4	nc
3l LaNaZ	2	nc
3m KL ^g	8	nc
3n RuNaY(1) ^h	60 (~ 50%)	—
3o RuNaY(2) ⁱ	4	nc
3p NiNaY ^j	45	—
3q NiNH ₄ Y ^k	60 (~ 80%)	—
3r CoNaY ^l	60 (~ 80%)	—
3s CoNH ₄ Y ^m	60 (~ 50%)	—
3t PdCoNaY ⁿ	2	2
3u PdNiNaY ^o	20	40
3v PdRuNaY ^p	2	2
3w ZSM-5	2	60

^a $[M(CO)_6]/Bu^1NC/catalyst$, 1.0 mmol/1.2 mmol/0.030 g; benzene (10 ml, 80 °C). ^b Thermal blank: 60 min ($M = Mo$), no reaction in 60 min ($M = W$). ^c As estimated by IR spectroscopy. ^d nc = no catalysis. ^e 2.8% Mg²⁺, ^f 1.6% Mg²⁺, ^g 14.7% K₂O, ^h 1.44% Ru³⁺, ⁱ 0.68% Ru³⁺, ^j 2.52% Ni²⁺, ^k 4.76% Ni²⁺, ^l 5.25% Co²⁺, ^m 5.09% Co²⁺, ⁿ 3.20% Co²⁺, 3.14–3.22% Pd²⁺, ^o 3.55% Ni²⁺, 2.67–2.82% Pd²⁺, ^p 0.71% Pd²⁺, 0.60%, Ru³⁺.

molecular sieves **3a–3c** are good catalysts for the substitution of CO by Bu¹NC in $[Mo(CO)_6]$, but lack activity for the more demanding substitution of $[W(CO)_6]$. Similarly the parent zeolites NaY and NaZ (**3d** and **3i**) show good activity for the substitution of CO on $[Mo(CO)_6]$, little activity for the corresponding reaction with $[W(CO)_6]$, and have considerably reduced catalytic properties on cation exchange e.g. to NH₄⁺, Mg²⁺ etc. Zeolites containing Ru³⁺ and Co²⁺ also show only mild catalytic effects. Further, at this stage there is no apparent correlation between the composition of the aluminosilicates (e.g. SiO₂/Al₂O₃ ratio or the pore size [34]), and the catalytic effects.

It should be noted that the catalysts **3a–3w** have been used in this study without any form of pre-treatment and were not protected from oxygen or moisture. However, activation * of selected, representative, catalysts has been carried out.

* Activation was carried out by heating of the catalyst at 300 °C for 13 h under a steady flow of argon, followed by heating at 300 °C for a 2 h period under a flow of hydrogen.

TABLE 10

THE EFFECT OF ACTIVATED ^a ALUMINOSILICATE CATALYSTS ON THE REACTION
 $[M(CO)_6] + Bu^1NC \rightarrow [M(CO)_5(CNBu^1)] + CO$ ($M = Mo, W$) ^b

	Reaction time ^c (min)	
	$[Mo(CO)_5(CNBu^1)]$	$[W(CO)_5(CNBu^1)]$
NaY	5	1 h (~ 60%)
MgNaY	30	nc ^d
NaZ	2	1 h (~ 60%)
KL	8	1 h (~ 50%)
RuNaY(1)	2	2
RuNaY(2)	2	2
NiNaY	nc	nc
NiNH ₄ Y	nc	nc
CoNaY	2	incomplete ^e
CoNH ₄ Y	incomplete	nc

^a 13 h heating at 300 °C under argon, 2 h heating at 300 °C under hydrogen. ^b $[M(CO)_6]/Bu^1NC/catalyst$, 1.0 mmol/1.2 mmol/0.030 g; benzene (10 ml, 80 °C). ^c As estimated by IR spectroscopy. ^d nc = no catalysis. ^e incomplete = reaction stopped without going to completion; catalyst deactivation is suspected.

These materials were protected from oxygen and moisture and re-tested for catalytic activity using the described reactions. The results are summarized in Table 10.

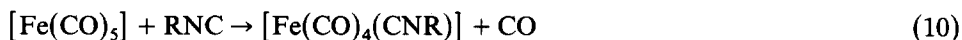
The zeolites NaY, NaZ, KL and MgNaY illustrate the undefined effect of the activation/dehydration procedure i.e. NaY and MgNaY were found to have a reduced catalytic activity, while NaZ and KL show slightly enhanced activity (as evidenced by the results for the reactions on $[W(CO)_6]$). The remaining zeolite catalysts (Table 10) were observed to undergo various physical changes during activation i.e. the Co^{2+} exchanged zeolites changed colour from pink to blue, the Ni^{2+} catalysts from yellow to grey and the Ru^{3+} exchanged catalysts to a pale grey colour. These changes may to a certain extent be correlated with the observed catalytic effects listed in Tables 9 and 10.

Thus, dehydration of the Co^{2+} exchanged zeolites (as indicated by the pink to blue colour change) led to enhanced catalytic activity. It is, however, questionable whether this catalyst functions as a cation exchanged zeolite or as a supported Co^{II} catalyst (cf. $CoCl_2 \cdot 2H_2O$ [10]). The experimental results presented in Tables 9 and 10 would indicate probably the latter. In this regard it is interesting to note that this is the first evidence we have found that water may adversely affect the catalyzed CO substitution reaction. For instance, cobalt(II) chloride functions effectively whether as the hexaqua salt, or as a partially dehydrated form (typically $CoCl_2 \cdot 2H_2O$) [10]. The colour changes observed for the Ni^{2+} exchanged zeolite may be correlated with the reduction of Ni^{II} to the metallic state by hydrogen i.e. the formation of a zeolite Y supported nickel catalyst. In keeping with earlier observations (Table 1) this catalyst (essentially metallic nickel) is inactive for carbonyl substitution. Similarly, the activation of the Ru^{3+} exchanged zeolite probably results in reduction of Ru^{III} to metallic ruthenium, which then, in accordance with earlier observations concerning activated ruthenium catalysts (see Table 2) shows a high degree of activity.

Exposure of the activated catalysts CoNaY and RuNaY(2) to air and moisture for 72 h results in catalyst deactivation. Thus CoNaY returned to its original pink

colour (and gave only approximately 90% $[\text{Mo}(\text{CO})_5(\text{CNBu}^t)]$ after the reaction time, benzene 80°C), and $\text{RuNaY}(2)$ became dark grey in colour and when tested gave no result in the reaction between $[\text{W}(\text{CO})_6]$ and Bu^tNC (benzene 80°C , 1 h).

Aluminosilicates have been screened for catalysis using a number of other reaction systems. Thus, only mild and erratic effects were observed in the standard substitution reaction (1) (e.g. type 13X molecular sieve, 90 min/reaction time). Good activity was, however, found for the thermally more facile [10] substitution reaction



(e.g. $\text{R} = \text{Bu}^t$, 2,6- $\text{M}_2\text{C}_6\text{H}_3$, type 3Å, 4Å molecular sieves, reaction times < 2 min, benzene 80°C). The substitution of CO by PPh_3 on $[\text{Fe}(\text{CO})_5]$ was, however, as anticipated, found to be unaffected by the addition of various zeolites, both in boiling benzene and toluene as reaction solvents. Similarly the substitution of CO by Bu^tNC on $[\text{Mn}_2(\text{CO})_{10}]$ (benzene, 80°C) and $[\text{Ru}_3(\text{CO})_{12}]$ (benzene, 35°C) was not catalyzed by either NaY or NaZ, although slight effects were observed on addition of the activated $\text{RuNaY}(2)$ (viz. Ru on NaY) catalyst.

Four commercially available activated carbons * (**4a–4d**), and one derived from a high ash South African coal (**4e**) have been screened for catalysis using the standard substitution reaction (1). Only **4c** showed any potential as a catalyst giving a reaction time of ca. 40 min for complete conversion of $[\text{Fe}(\text{CO})_4(\text{CNBu}^t)]$ to $[\text{Fe}(\text{CO})_3(\text{CNBu}^t)_2]$. A granular form of **4c** ** gave a reaction time of 50 min under the same conditions probably reflecting the surface area difference between these two.

In order to determine the origin of the catalytic effects, the ash content of **4a–4e** was determined (5.0, 4.0, 2.4, < 0.1 , 12.6% respectively) and analyzed. **4d**, an activated carbon derived from high purity polystyrene beads, is essentially ashless while the remainder of the carbons reflect the ash content of the parent coals used in their manufacture. Samples of the parent coals for carbons **4c** and **4e** were investigated for catalytic activity, but without success. Further, the ash derived from the respective carbons was also tested using reaction (1), but with no success. Similarly the individual components of the ash (e.g. SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO_2 , MgO , CaO , Na_2O , K_2O) were catalytically inactive. On this basis, it may be deduced that the catalytic effects noted for **4c** are not attributable to the ash content (or ash constituents) alone, nor is catalytic activity an inherent property of the parent coal from which this particular carbon is manufactured.

Owing to the mild and consequently erratic effects observed with **4c**, this material was further investigated using the thermally more facile substitution reaction (8) in order to estimate more reliably the magnitude of the catalytic effect.

Mild catalysis (15 min reaction time) was observed for **4c**, however, more importantly, catalytic effects were also found for **4b** (25 min reaction time) and the ashless activated carbon **4d** (40 min reaction time). These results suggest that “pure” activated carbon does possess mild catalytic properties for the replacement of carbon monoxide on metal carbonyl complexes in its own right, but that the ash content of the carbon plays a role, possibly in some form of cooperative manner.

* Norit W20 (**4a**), Le Carr G210 (**4b**), Bergwerksverband PK221 (**4c**), Amborsorb XE348 (**4d**).

** Bergwerksverband Type 47/2.

On the basis of these results a series of activated carbons, artificially enriched in particular components such as Fe_2O_3 and TiO_2 and also prepared in different manners, were investigated in reaction (1). However, despite extensive testing, no activated carbon could be prepared that showed even a mild catalytic effect [21].

Conclusions

The use of model substitution reactions has revealed that palladium, platinum, ruthenium and rhodium, and the oxides PdO and PtO_2 are efficient catalysts for the metal carbonyl substitution reaction. Particularly metallic palladium and PdO recommend themselves as catalysts for the substitution of CO by isocyanide and phosphine ligands in mono-, di- and polynuclear metal carbonyl complexes establishing synthetic routes alternative to the traditional thermal or photoactivated procedures.

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