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DI- AND POLY-NUCLEAR TRANSITION METAL COMPLEXES AS CATALYSTS FOR THE METAL CARBONYL SUBSTITUTION REACTION. THE ROLE OF SUPPORTED METALS AND METAL OXIDES AS CATALYST PROMOTERS

MICHEL O. ALBERS* *, NEIL J. COVILLE,

Department of Chemistry, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg 2001 (Republic of South Africa)

and ERIC SINGLETON

National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001 (Republic of South Africa)

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Summary

Various di- and poly-nuclear transition metal complexes have been investigated as catalysts for the metal carbonyl substitution reaction. The complexes $[\{(\eta^5\text{-}C_5H_4R)Fe(CO)_2\}_2]$ (R = H, Me, CO_2Me, OMe, $O(CH_2)_4OH$) and $[\{(\eta^5\text{-}C_5H_5)\text{-}Ru(CO)_2\}_2]$ are active catalysts for a range of substitution reactions including the probe reaction $[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] + CO$. $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$ is catalytically active only on irradiation with visible light. For $[\{\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and a range of isocyanides RNC (R = Bu^t, $C_6H_5CH_2$, 2,6-$Me_2C_6H_3$), catalyst modification by substitution with isocyanide is a major factor influencing the degree of the catalytic effects observed, e.g. $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ is approximately 35 times as active as $[(\eta^5\text{-}C_5H_5)_2\text{-}Fe_2(CO)_3(CNBu^t)]$ for the $[Fe(CO)_4(CNBu^t)] \rightarrow [Fe(CO)_3(CNBu^t)_2]$ conversion. Mechanistic studies on this system suggest that the catalytic substitution step probably involves a rapid intermolecular attack of isonitrile, possibly on a labile catalyst-substrate radical intermediate such as $\{[Fe(CO)_4(CNR)][(\eta^5\text{-}C_5H_5)Fe\text{-}(CO)_2]\}^{\cdot}$, or on a reactive radical cation such as $[Fe(CO)_4(CNR)]^+$ generated via electron transfer between the substrate and the catalyst. Other transition metal complexes which also catalyze the substitution of CO by isocyanide in $[Fe\text{-}(CO)_4(CNR)]$ (and $[M(CO)_6]$ (M = Cr, Mo, W), $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$) include $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, $[M_4(CO)_{12}]$ (M = Co, Ir) and $[Co_2(CO)_8]$. These

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* Present address: National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001 (Republic of South Africa).

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reactions conform to the general mechanistic patterns established for $[\{(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2\}_2]$, suggesting a similar mechanism. A range of materials, notably PtO_2, PdO and Pd/C, act as promoters for the homogeneous di- and poly-nuclear transition metal catalysts, and can even be used to induce activity in normally inactive dimer and cluster complexes e.g. $[Os_3(CO)_{12}]$. This promotion is attributed to at least three possible effects: the removal of catalyst inhibitors, a catalyzed substitution of the homogeneous catalyst partner, and a possible homogeneous–heterogeneous interaction which promotes the formation of catalytic intermediates.

Introduction

Recent work [1–3] has established the importance of photo-induced radical catalysis in the substitution of metal carbonyl complexes e.g. $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ catalyze the substitution of CO by phosphorus donor ligands on $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$ [4] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$ [5], respectively. For these processes the reactions have been shown to proceed via a radical chain pathway [1,4,5]. It has also been observed that these catalysts may be used under thermal reaction conditions, and further, that in this mode of usage, they possess considerable utility in synthetic organometallic chemistry [1,6–9]. More particularly though, this work has raised the possibility of a second pathway involving radicals which requires electron transfer but not atom transfer. The mechanism can, under certain circumstances, be viewed as at least a competing reaction route with the established radical chain pathway [1,7,9]. On the basis of these results it was envisaged that transition metal complexes containing a metal–metal bond should quite generally be catalysts under thermal reaction conditions for the substitution of CO in a large variety of metal carbonyl systems. Preliminary evidence supports this expectation [1], and the limited studies to date have been directed towards the use of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ in the catalytic replacement of CO by isonitrile on $[Fe(CO)_4(CNBu^t)]$ [9] and by phosphorus donor ligands on $[Fe(CO)_5]$ [10]. Herein we report the first generalized study of the use of transition metal dimer and cluster complexes as catalysts for the metal carbonyl substitution reaction *, and also, studies which establish that these catalysts are promoted by transition metals and metal oxides. A preliminary account of some of this work has already appeared [11].

Experimental

All substitution reactions were performed under nitrogen or argon in an appropriate round-bottom flask. The reaction vessel 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. All solvents were dried and distilled under an inert atmosphere immediately prior to use. The metal carbonyls $[Fe(CO)_5]$, $[M(CO)_6]$, (M = Cr, Mo, W), $[M_2(CO)_{10}]$ (M = Mn, Re),

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* *Note added in proof*. The use of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ as a substitution catalyst for cluster carbonyl complexes has recently been reported (S. Aime, M. Botta, R. Gobetto and D. Osella, Inorg. Chim. Acta, 115 (1986) 129).

$[M_3(CO)_{12}]$ (M = Fe, Ru, Os), $[M_4(CO)_{12}]$ (M = Co, Ir), $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ were used as purchased from Strem Chemicals Inc. The isocyanides $2,6\text{-}Me_2C_6H_3NC$, $C_6H_5CH_2NC$ and Bu^tNC were obtained from Fluka AG, Switzerland. The catalysts PdO and PtO_2 were obtained from Merck Chemicals, while 10% Pd/C and 10% $Pd/CaCO_3$ were purchased from Engelhard Industries. The complexes $[Fe(CO)_4(CNR)]$ (R = Bu^t, $C_6H_5CH_2$, $2,6\text{-}Me_2C_6H_3$) [12], $[H_4Ru_4(CO)_{12}]$ [13], $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5H_4CO_2Me)Fe(CO)_2\}_2]$ [14], and $[\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2]$ [15] were all prepared by the published procedures or modifications thereof. The compounds $[\{(\eta^5\text{-}C_5H_4OMe)Fe(CO)_2\}_2]$ and $[\{(\eta^5\text{-}C_5H_4OCH_2CH_2CH_2OH)Fe(CO)_2\}_2]$ were provided by Dr A. Eisenstadt, Weizmann Institute, Israel.

Infrared spectra were recorded with a Perkin–Elmer 521 or a Jasco IRA 1 instrument. All ^1H NMR spectra were recorded with a Bruker WP80 FT NMR spectrometer.

A. The standard substitution reaction $[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] + CO$

$[Fe(CO)_4(CNBu^t)]$ (1.0 mmol), the appropriate amount of catalyst (typically 0.1 mmol, see Results and discussion), and benzene (10 ml), were combined in a two-necked, round-bottom flask. The mixture was heated to boiling in a thermostat-controlled oil bath pre-set at 100 °C and then Bu^tNC (1.1 mmol) was added. Samples were withdrawn at appropriate time intervals and the course of the reaction monitored by IR spectroscopy (2200–1900 cm^{-1} region of the spectrum). The end of the reaction was taken to correspond to the complete conversion of $[Fe(CO)_4(CNBu^t)]$ into $[Fe(CO)_3(CNBu^t)_2]$.

The substitution reactions $[Fe(CO)_4(CNR)] + RNC \rightarrow [Fe(CO)_3(CNR)_2] + CO$ (R = $2,6\text{-}Me_2C_6H_3$, $C_6H_5CH_2$) were carried out in a similar manner.

B. $[M(CO)_6] + Bu^tNC \rightarrow [M(CO)_{6-n}(CNBu^t)_n] + nCO$ *(M = Cr, Mo, W; n = 1–3)*

A procedure similar to that given in A above was used except that the complex/Bu^tNC ratios were 1.0/1.0, 1.0/2.0 and 1.0/3.0 in order to achieve mono-, di- and tri-substitution, respectively.

Results and discussion

$[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$, $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ *and related catalysts*

Addition of the complex $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ to the standard substitution reaction (1) [12] had no effect upon the rate of product formation. Instead, in both

$$[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] + CO \qquad (1)$$

boiling benzene, and also when the reaction was attempted at room temperature, the initially red reaction solution turned yellow. On the basis of IR spectroscopy (and previous studies [7]) it has been established that this effect is to be attributed to the formation of the salt $[(\eta^5\text{-}C_5H_5)Mo(CNBu^t)_4]^+[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ arising from the disproportionation of the added $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ with the excess of isocyanide [16]. Similar results are observed in the case of the reaction (2) carried

$$[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)] + 2,6\text{-}Me_2C_6H_3NC \rightarrow [Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2] + CO \qquad (2)$$

out in benzene at 80 °C, and also in the presence of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$, which gives as the only product $[(\eta^5\text{-}C_5H_5)Mo(CNC_6H_3Me_2\text{-}2,6)_4]^+[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ [7]. Both these complex salts may be independently synthesized in good yield by the addition of an excess of isocyanide to $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ in benzene at 80 °C [7,16]. This disproportionation has also been found to predominate when less than an excess of isocyanide is added to $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ (i.e. with the exclusion of simple substitution products of the type $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(CNR)_n]$ [7,16,17]). In accordance with the above observations, these independently synthesized salts $[(\eta^5\text{-}C_5H_5)Mo(CNR)_4]^+[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ (R = Bu^t, 2,6-$Me_2C_6H_3$) have been found to be catalytically inactive in (1) and (2), respectively.

In contrast, addition of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ to reaction (1) resulted in a moderate catalytic effect (75 min compared to the thermal, unassisted reaction time of 120 min). The added catalyst was observed (by IR spectroscopy and by comparative thin layer chromatography) to be modified via substitution of CO by isonitrile during the course of the catalyzed substitution reaction. On the basis of ^1H NMR and IR spectroscopy, and comparative TLC it has also been established that the only detectable product formed by the reaction of the catalyst $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ with Bu^tNC, under the conditions of the catalyzed substitution reaction (viz. benzene 80 °C), is the mono-substitution product $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ [18,19]. This material is formed rapidly (approximately 2–5 min reaction time) from $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and an excess of Bu^tNC in boiling benzene, and thus, on the basis of relative reaction rates, is presumed to be formed before the onset of catalytic CO substitution on the substrate $[Fe(CO)_4(CNBu^t)]$. In this regard, it has been reported previously [20], that in addition to the formation of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ as the major product under such conditions, further reaction does occur, although only with relative difficulty (6–12 h, benzene, 80 °C) to give small amounts of the complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ *. It is also possible that trace amounts of higher-substituted isonitrile derivatives, viz. $[(\eta^5\text{-}C_5H_5)_2Fe(CO)_{4-n}(CNBu^t)_n]$ (n = 3,4) and/or other products e.g. $[(\eta^5\text{-}C_5H_5)Fe(CNBu^t)_3]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ are also formed in this reaction [20] (and consequently also in the $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ catalyzed substitution reactions). The presence of such materials in the catalyzed substitution reactions has not, however, been established, and if indeed present, they are below the limits of detectability by IR and ^1H NMR spectroscopy. The addition of catalytic amounts of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ to reaction (1) (benzene, 80 °C) gives a result similar to that observed for $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$. This is also in keeping with the observation that $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ reacts rapidly with Bu^tNC at 80 °C to give predominantly the complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$. However, the addition of the complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ to (1) results in rapid catalysis (reaction time < 2 min), a result which suggests that little or none of this material is formed during the course of the catalyzed substitution of $[Fe(CO)_4(CNBu^t)]$.

Because of the apparent intimate relationship between the catalyst and the substituting ligand, we sought to establish the generality of the $[\{(\eta^5\text{-}$

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* The synthesis of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ may, however, be carried out with relative ease in toluene under reflux (approx. 2–3 h, yield $> 85\%$) [19,21].

$C_5H_5)Fe(CO)_2\}_2]$ catalyzed substitution of CO by isonitrile on mononuclear iron carbonyl complexes using the reactions

$$[Fe(CO)_4(CNR)] + RNC \rightarrow [Fe(CO)_3(CNR)_2] + CO \quad (3)$$

$$(R = C_6H_5CH_2, 2,6\text{-}Me_2C_6H_3)$$

as probes. The addition of isonitrile to $[Fe(CO)_4(CNR)]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (1.2/1.0/0.1 mole ratio, benzene, 80 °C) led to mild catalysis, viz. with $R = C_6H_5CH_2$ ca. 40% reaction in 2 h and with $R = 2,6\text{-}Me_2C_6H_3$, ca. 90% reaction in 2 h. Spectroscopy (IR and ^1H NMR) and comparative TLC in each case confirm the occurrence of a reaction between the catalyst and the isocyanide ligand. In eq. 3 $(R = C_6H_5CH_2)$ the formation of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNCH_2C_6H_5)]$ [18] was confirmed. However, owing to the small quantities of catalyst present, other possible products e.g. $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNCH_2C_6H_5)_n]$ $(n = 2\text{–}4)$ were not detected, although it is reportedly possible to synthesize the complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_2C_6H_5)\}_2]$ by extended heating of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ in the presence of an excess of isonitrile * in benzene [20]. Furthermore, on the basis of recent findings [22,23], $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ would be expected to participate in reaction (3) $(R = 2,6\text{-}Me_2C_6H_3)$ to give the fully substituted product $[\{\{\eta^5\text{-}C_5H_5)Fe(CNC_6H_3Me_2\text{-}2,6)_2\}_2]$ and this has been found to be the case. An independent study using the latter complex as the pre-formed catalyst has established that it shows identical catalytic effects for reaction (3), further supporting this contention.

A number of complexes related to $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ have been investigated for catalysis using the reaction (1). Thus $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5H_4CO_2Me)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5H_4OMe)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5H_4OCH_2CH_2\text{-}CH_2CH_2OH)Fe(CO)_2)\}_2]$ and $[\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2]$ gave reaction times of 30, 10, 4, 5 and 18 min, respectively. The complex $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$ was found to be catalytically inactive under the conditions used, although in the presence of visible light (500 W) a reaction time of 40 min for the complete conversion of $[Fe(CO)_4(CNBu^t)]$ to $[Fe(CO)_3(CNBu^t)_2]$ was recorded.

At room temperature and in the dark, $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ does not catalyze the conversion of $[Fe(CO)_4(CNBu^t)]$ to $[Fe(CO)_3(CNBu^t)_2]$ during a 4 h period, but in the presence of visible light (500 W, 4 h) approx. 20–30% conversion was found. A similar effect was found when $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ was used as catalyst.

The addition of the organic free radical scavengers galvinoxyl and hydroquinone (10 mole% based on catalyst) to the mixture $[Fe(CO)_4(CNBu^t)]/Bu^tNC/[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (1.0/1.2/0.1 mole ratio, benzene, 80 °C) resulted in an increase in the rate of the catalyzed reaction, thus on addition of galvinoxyl the substitution reaction was complete in 15 min, and in the presence of hydroquinone it was complete in 13 min (cf. the identical reaction in the absence of these additives requires 75 min to completion). These unexpected results could be related to similar promotional effects observed in the presence of metals and metal oxides (see below).

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* Recent studies carried out in these [21] and other laboratories [22] have shown the reaction between $C_6H_5CH_2NC$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ to be particularly complex, a number of products being formed, including $[(\eta^5C_5H_5)Fe_2(CO)_{4-n}(CNR)_n]$ $(n = 1\text{–}3)$ and $[(\eta^5\text{-}C_5H_5)Fe(CNR)_3]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$.

The crossover experiments

(i) $[\mathrm{Fe(CO)_4(CNBu^t)}] + 2{,}6\text{-}\mathrm{Me_2C_6H_3NC} + [(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Fe_2(CO)_3(CNBu^t)}]$ (1.0/0.5/0.5 mole ratio, benzene, 80 °C)

(ii) $[\mathrm{Fe(CO)_4(CNC_6H_3Me_2\text{-}2{,}6)}] + \mathrm{Bu^tNC} + [(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Fe_2(CO)_3(CNC_6H_3Me_2\text{-}2{,}6)}]$ (1.0/0./0.5 mole ratio, benzene 80 °C)

have been performed [9]. In each case the primary product formed was $[\mathrm{Fe(CO)_3(CNBu^t)(CNC_6H_3Me_2\text{-}2{,}6)}]$ (in reaction (i) <2 min and in reaction (ii) approx. 45 min). The subsequent transfer of isonitrile from the catalyst occurred in only trace amounts upon extended heating (2 h) after the initial formation of the complex $[\mathrm{Fe(CO)_3(CNBu^t)(CNC_6H_3Me_2\text{-}2{,}6)}]$. These results suggest that the catalytic substitution of the metal carbonyl substrate by isonitrile occurs via a rapid intermolecular attack of isonitrile on the activated substrate [9], and that the intramolecular transfer of isonitrile from the catalyst to the substrate is only a slower, secondary step.

The results show that the interaction of the isonitrile with the catalyst affects the course of the catalytic reaction. Thus by electronic and/or steric effects the interaction may have a beneficial (e.g. $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)(CNBu^t)}\}_2]$) or detrimental (e.g. $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mo(CNR)_4}]^+[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mo(CO)_3}]^-$) effect on the catalysis. Further, the transfer of isonitrile coordinated to the catalyst has been shown for $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}\}_2]$ and $\mathrm{Bu^tNC}$ or $2{,}6\text{-}\mathrm{Me_2C_6H_3NC}$ to be a relatively slow step when compared to the catalyzed reaction of the substrate with isonitrile derived from the reaction solution. In fact, there is not even a necessity for such a transfer mechanism to be operative. For example, certain catalysts react only extremely slowly with isonitrile under the conditions of the catalyzed substitution reaction (1) (e.g. $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ru(CO)_2}\}_2]$) yet are capable of catalyzing the substitution of CO by isonitrile on the metal carbonyl substrate. Also, the catalysts $[\{(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{Fe(CO)_2}\}_2]$ (R = H, Me) catalyze the substitution of CO on $[\mathrm{Fe(CO)_5}]$ by $\mathrm{PR_3}$ ligands, for which no transfer mechanisms can be operative [10].

The mechanism by which $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}\}_2]$ and related complexes catalyze the substitution of CO by isonitrile on metal carbonyl complexes such as $[\mathrm{Fe(CO)_4(CNR)}]$ is at present unknown. However, on the basis of the reported findings on the use of $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}\}_2]$ as a catalyst for the substitution of $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}(\eta^1\text{-alkyl})]$ [5,24], it would be reasonable to assume that substitution catalysis is brought about by transition metal radicals generated by thermally and/or light induced homolytic metal–metal bond cleavage viz.

$$[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}\}_2] \rightleftharpoons 2[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]^{\cdot} \qquad (4)$$

The interaction of such radicals with metal carbonyl complexes like $[\mathrm{Fe(CO)_5}]$ and $[\mathrm{Fe(CO)_4(CNR)}]$ can conceivably occur in two ways: (i) to produce a radical intermediate of the type $\{[\mathrm{Fe(CO)_5}][(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]\}^{\cdot}$ where the substrate and the activating radical remain together during the CO substitution reaction, or (ii) to produce a radical cation such as $[\mathrm{Fe(CO)_5}]^{+}$ arising from an electron transfer process between the substrate and the catalyst radical [9]. Both these processes can be envisaged to lead to the labilization of coordinated CO which may then be displaced upon ligand attack (in an associative process) or lead to the substituted product via dissociative loss of CO.

The complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ has been investigated as a catalyst for the substitution of CO by isonitrile on $[M(CO)_6]$ (M = Cr, Mo, W) (only mild catalysis was observed) and on $[Mn_2(CO)_{10}]$ and $[M_3(CO)_{12}]$ (M = Fe, Ru) [21]. In the latter case, mild catalysis was also observed, although particularly with $[Fe_3(CO)_{12}]$, this manifested itself as an increase in product selectivity rather than as a large increase in the rate of the substitution reaction.

The remarkable catalytic effects shown by the complexes $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2\}_2]$ (R = H, Me) for the catalyzed replacement of CO by Group 5 donor ligands on $[Fe(CO)_5]$ have been documented elsewhere [10]. The complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO_2\}_2]$ has also been successfully employed as a catalyst for the substitution of CO by PPh_3 on $[Mn_2(CO)_{10}]$:

$$[Mn_2(CO)_{10}] + 2PPh_3 \rightarrow [Mn_2(CO)_8(PPh_3)_2] + 2CO \qquad (5)$$

Thus, the addition of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ to $[Mn_2(CO)_{10}]$ and PPh_3 (0.1/3.0/6.0 mmol, toluene, 100 °C) gave $[Mn_2(CO)_8(PPh_3)_2]$ [25] in 98% yield in 90 min (cf. the thermal unassisted reaction, 90% yield of the product in 7 h reaction time).

Similarly, $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ (96% yield of the product, 60 min reaction time) and $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$ (95%, 3 h) were also found to catalyze (5). However, an attempted catalytic substitution of CO by PPh_3 on $[Re_2(CO)_{10}]$ [26] using the above catalysts (toluene, 100 °C) was not successful even with 5 h reaction time. Similarly, the attempted direct reaction between $[Fe(CO)_5]$ and maleic anhydride (to give the complex $[(\eta^2\text{-maleic anhydride})Fe(CO)_4]$ [27], benzene, 80 °C) failed, as did the attempted synthesis of *trans*-$[Mo(CO)_4(PPh_3)_2]$ [28] from $[Mo(CO)_6]$ and PPh_3 (toluene, 100 °C), both utilizing $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ as catalyst.

Di- and poly-nuclear metal carbonyl complexes as catalysts

On the basis of the studies involving $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ as a carbonyl substitution catalyst described above, other readily available di- and poly-nuclear metal carbonyl complexes have also been investigated as CO substitution catalysts. Thus the complexes $[M_3(CO)_{12}]$ (M = Fe, Ru, Os), $[H_4Ru_4(CO)_{12}]$, $[M_4(CO)_{12}]$ (M = Co, Ir), $[Co_2(CO)_8]$ and $[M_2(CO)_{10}]$ (M = Mn, Re) have all been tested for activity using the standard substitution reaction (1). All, except $[Re_2(CO)_{10}]$, $[Fe_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$, possessed varying, moderate to good catalytic activity, under the conditions employed.

$[Fe_3(CO)_{12}]$ was catalytically inactive in reaction (1), and was simply converted into the mononuclear complexes $[Fe(CO)_{5-n}(CNBu^t)_n]$ (n = 1–3), as shown by IR spectroscopy [12]. This reaction was evidenced by a gradual change in colour of the reaction solution from green to yellow, with the corresponding formation of the fragmentation products $[Fe(CO)_{5-n}(CNBu^t)_n]$. At room temperature $[Fe(CO)_4(CNBu^t)]$ and traces of $[Fe(CO)_3(CNBu^t)_2]$ were obtained, whereas in boiling benzene (80 °C) $[Fe(CO)_3(CNBu^t)_2]$ and varying quantities of $[Fe(CO)_2(CNBu^t)_3]$ were formed [29]. $[Os_3(CO)_{12}]$ and $[Re_2(CO)_{10}]$ also proved to be completely inactive as CO substitution catalysts, and the attempted use of $[Os_3(CO)_{12}]$ as a catalyst under more forcing conditions, for instance for reaction (2) in boiling toluene, was not successful, inhibition of the thermal reaction in fact being observed.

The active catalysts $[Ru_3(CO)_{12}]$, $[Co_2(CO)_8]$, $[M_4(CO)_{12}]$ (M = Co, Ir)

$[Mn_2(CO)_{10}]$ and $[H_4Ru_4(CO)_{12}]$ were all found by comparative TLC and IR spectroscopy to react with isonitrile under the conditions of the catalytic experiments. The identities of the products thus formed have not been investigated in detail, but for the complexes $[Mn_2(CO)_{10}]$ and $[Ru_3(CO)_{12}]$ the products were shown by comparative TLC not to correspond to the, perhaps expected, compounds $[Mn_2(CO)_{10-n}(CNBu^t)_n]$ ($n = 1$–3) [29] and $[Ru_3(CO)_{12-n}(CNBu^t)_n]$ ($n = 1$–3) [30]. As further support for ruling out these species as possible catalytic intermediates it has been established that a simple transfer of isonitrile from such products ($[Mn_2(CO)_9(CNBu^t)]$, $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Ru_3(CO)_{10}(CNBu^t)_2]$) to the substrate $[Fe(CO)_4(CNBu^t)]$ does not occur under the conditions used for catalysis (benzene, 80 °C), as shown by both IR and ^1H NMR spectroscopy.

The actual mechanism of catalysis, as for $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and related catalysts, is at present still obscure. However, it has been established for reaction (1) and the catalysts $[Ru_3(CO)_{12}]$ (benzene, 45 °C) and $[Co_4(CO)_{12}]$ (benzene, 25 °C) that visible light (500 W light bulb) has a moderate positive effect on catalysis (approximately 20–30% increase in the rate of the catalyzed substitution). Also, the presence of radical inhibitors (galvinoxyl and hydroquinone), and of the radical initiator benzoyl peroxide, in the above reactions results in mild inhibition of the catalyzed substitution reaction. These observations support the possible intermediacy of thermally (and photochemically) generated metal carbonyl radicals as the catalytic intermediates. Such species would be obtained (as for $[\{(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2\}_2]$ as catalyst) by the homolytic cleavage of a metal–metal bond in the catalyst. The generation of such radicals would clearly depend upon the strength of the metal–metal bond in question, which possibly accounts for the lack of catalytic activity of $[Os_3(CO)_{12}]$ and $[Re_2(CO)_{10}]$ [31].

The general performance of di- and poly-nuclear metal carbonyl catalysts has been further investigated using the reaction

$$[Mo(CO)_6] + Bu^tNC \rightarrow [Mo(CO)_5(CNBu^t)] + CO \tag{5}$$

($[Mo(CO)_6]/Bu^tNC$/catalyst, 1.0/1.0/0.1 mmol, benzene)

Thus, $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ (2 min reaction time at room temperature) and $[Ru_3(CO)_{12}]$, $[Ir_4(CO)_{12}]$, $[Mn_2(CO)_{10}]$ and $[H_4Ru_4(CO)_{12}]$ (2 min reaction time at 80 °C) were all found to be active catalysts. The catalysts $[Co_2(CO)_8]$ and $[Ir_4(CO)_{12}]$ were also tested for a more demanding reaction viz.

$$[Mo(CO)_6] + 2Bu^tNC \rightarrow [Mo(CO)_4(CNBu^t)_2] + 2CO \tag{6}$$

($[Mo(CO)_6]/Bu^tNC$/catalyst, 1.0/2.0/0.1 mmol, benzene 80 °C)

Rapid substitution to give the complex $[Mo(CO)_5(CNBu^t)]$ occurred with both catalysts, followed by the very slow formation of small amounts of *cis*-$[Mo(CO)_4(CNBu^t)_2]$ before the reactions were observed to stop completely. These observations are attributed to the competing substitution (by isonitrile) and subsequent decomposition of the catalyst under the reaction conditions.

In addition, the reaction

$$[Mn_2(CO)_{10}] + Bu^tNC \rightarrow [Mn_2(CO)_9(CNBu^t)] + CO \tag{7}$$

($[Mn_2(CO)_{10}]/Bu^tNC$/catalyst 1.0/1.2/0.1 mmol, benzene 80 °C) has been investigated with the aim of testing the feasibility of using such polynuclear metal carbonyl complexes as catalysts for the substitution of CO on other complexes containing a metal–metal bond. Indeed, $[Ru_3(CO)_{12}]$ (reaction time 7 min), $[Ir_4(CO)_{12}]$ (8 min), $[Co_4(CO)_{12}]$ (10 min) and $[Co_2(CO)_8]$ (10 min) were all found to catalyze the reaction (cf. the thermal unassisted substitution of CO by Bu^tNC on $[Mn_2(CO)_{10}]$ giving $[Mn_2(CO)_9(CNBu^t)]$ requires 35 min to reach completion).

Similarly, the formation of $[Re_2(CO)_9(CNBu^t)]$

$$[Re_2(CO)_{10}] + Bu^tNC \rightarrow [Re_2(CO)_9(CNBu^t)] + CO \tag{8}$$

($[Re_2(CO)_{12}]/Bu^tNC$/catalyst 1.0/1.2/0.1 mmol, benzene, 80 °C)

was catalyzed by $[Mn_2(CO)_{10}]$ (reaction time 10 min), $[Ru_3(CO)_{12}]$ (10 min), $[Ir_4(CO)_{12}]$ (5 min), $[Co_4(CO)_{12}]$ (5 min) and $[Co_2(CO)_8]$ (5 min). These results are to be considered in the light of the fact that under thermal reaction conditions alone (benzene, 80 °C, 2 h) there is no evidence for the formation of either $[Re_2(CO)_9(CNBu^t)]$ or other substitution products.

Transition metals and metal oxides as promoters for dimer and cluster carbonyl substitution catalysts

Transition metals and metal oxides have been shown [32] to be efficient catalysts for the substitution of CO by isonitriles on di- and poly-nuclear metal carbonyl complexes [33,34]. In an effort to synthesize highly substituted isonitrile derivatives of the complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ for use as potential CO substitution catalysts (see above) materials such as metallic palladium, PdO and PtO_2 were considered as possible catalysts for the substitution of CO by isonitriles on this, and related complexes. During our investigation we discovered that transition metals, metal oxides, and other related materials function as promoters for metal carbonyl substitution catalysts containing a metal–metal bond. The experiments discussed here were aimed at establishing the nature of the promotional effects observed for the catalyst combination transition metal or metal oxide/$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and exploring the generality of these observations.

In investigating the utility of the compounds $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNBu^t)_n]$ as catalysts for reaction (1), it was observed that $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ obtained from the reaction $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2] + Bu^tNC + PtO_2$ (1.0/1.0/0.1 mmol ratio, benzene, 80 °C) *, gave a catalytic effect superior to that observed for either $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ or $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ as catalysts. Thus, a reaction time of approximately 20 min was observed, compared to the normally observed 75 min for the complexes $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[(\eta^5\text{-}C_5H_5)_2\text{-}Fe_2(CO)_3(CNBu^t)]$ (see Table 1).

This material was characterized by means of IR and ^1H NMR spectroscopy. The spectra obtained were identical to those of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ synthesized under thermal conditions i.e. in the absence of any catalyst, and there was no evidence for the presence of impurities, which could account for the enhanced

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* $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ was the sole product obtained from this reaction. Product purification was achieved using a short cellulose column to effect the removal of PtO_2 prior to the use of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ as catalyst.

TABLE 1

THE EFFECT OF PROMOTED CATALYSTS ON THE STANDARD SUBSTITUTION REACTION $[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] + CO$ [a]

	Reaction time [b] (min)
Control	120
PtO_2	20
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$	75
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$	75
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$	2
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (PtO_2 activated)	20
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ (PtO_2 activated)	20
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2] + PtO_2$	2
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)] + PtO_2$	2

[a] See Experimental for details. [b] As determined by IR spectroscopy.

catalysis in reaction (1). This improved catalytic effect was also found not to be associated with a simple, thermally induced activation of the complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$. Thus, heating of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ alone in benzene (80 °C, 2 h) followed by the use of the material as catalyst for reaction (1) did not show improved catalysis. Similarly, heating of PtO_2 with Bu^tNC in benzene (80 °C, 2 h) failed either to improve upon the normally observed catalytic properties of PtO_2 [33,34] or to produce in any other way (e.g. via a reaction between PtO_2 and isonitrile) a species that could account for the high degree of catalytic activity observed in the reaction discussed above.

It was found, however, that heating $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ (synthesized independently via the thermal reaction between $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and Bu^tNC), with PtO_2 in benzene (80 °C, 2 h) prior to use of the catalyst gave a reaction time of 20 min for (1). Further, the use of the catalyst combination $PtO_2/[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ (1.0/1.0 mmole ratio, total 10 mole% catalyst) in reaction (1) resulted in a reaction time of < 2 min. These results thus indicate that the "activation" of the catalyst $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ by heating with PtO_2, or alternatively, the use of the catalyst combination $PtO_2/[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ gives rise to a catalytic effect larger than that observed for $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ or PtO_2 alone. More specifically, these results imply the occurrence of a catalyst promoting effect between the two materials PtO_2 and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$.

Subsequent studies have shown that this catalyst promotion may be attributed to at least three possible effects:

(a) the removal of catalyst inhibitors;

(b) a possible catalyzed substitution effect on the homogeneous catalyst partner;

(c) a third as yet uncharacterized effect, thought to be a homogeneous–heterogeneous interaction which promotes the formation of catalytic intermediates.

The following discussion has been subdivided so as to emphasise these effects. The standard substitution reaction (1) has been used extensively in the following investigations, and catalytic effects, unless otherwise stated, have always been determined making use of this reaction.

As expected observations similar to those noted above for the catalyst $[(\eta^5\text{-}$

$C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ concerning the use of the PtO_2 promoter have also been made for the catalyst $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$. Thus, the use of the combination $PtO_2/[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (1.0/1.0 mole ratio, total 10 mole % catalyst) in (1) gave a reaction time of 2 min (Table 1). Also, heating $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ with PtO_2 (1.0/0.1 mole ratio) in benzene (80 ° C, 2 h) followed by removal of PtO_2 by means of a cellulose column, resulted in an activated $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ catalyst which gave a reaction time of 20 min for (1). The heating of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ alone in benzene (80 ° C, 2 h) did not produce a catalyst that gave an improved substitution reaction as compared to commercially available $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ viz. 75 min (Table 1).

The use of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and thermally synthesized $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ as catalysts for reaction (1) (reaction conditions: benzene, 25 ° C, 4 h) in the presence of visible light and in the dark has been discussed above. Similar experiments carried out with $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ heated for 2 h with PtO_2 in benzene * showed approximately 50% conversion of $[Fe(CO)_4(CNBu^t)]$ to $[Fe(CO)_3(CNBu^t)_2]$ when the reaction was carried out in the dark, and an 80% conversion in the presence of visible light (both experiments were carried out at room temperature and monitored for a 4 h period). Thus, although a rate increase in the presence of light is observed for both PtO_2 activated, and unactivated $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$, the activated catalyst shows an overall greater activity than standard i.e. unactivated $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ under conditions of both light and dark.

Reaction 1 carried out in the presence of PtO_2 activated $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ as catalyst has been found to be inhibited by the organic radical scavenger galvinoxyl and hydroquinone (10 mole % based on catalyst). Reaction times for the complete conversion of $[Fe(CO)_4(CNBu^t)]$ into $[Fe(CO)_3(CNBu^t)_2]$ were found to be 50 and 60 min respectively. These reaction times should be compared with that of 20 min for the PtO_2 activated $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ catalyst, and that of 75 min observed in the presence of standard (i.e. unactivated) $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$, both performed in the absence of added radical inhibitors **.

Catalyst promotion – the removal of catalyst inhibitors

The heating of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ with PtO_2 followed by the removal of the heterogeneous catalyst by means of a short cellulose column has been found to result in an activated $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ catalyst (Table 1). The use, however, of a silica gel or neutral alumina column to effect removal of PtO_2 and purification of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ has been found to result in some measure of catalyst deactivation. Thus, $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and PtO_2 (1.0/0.1 mmol ratio) were heated in benzene (80 ° C, 2 h). One half of the reaction mixture was then eluted through a short cellulose column, and the other half through a similar silica gel column. The two catalysts, comprising $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ obtained by solvent removal from the two portions,

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* The PtO_2 was removed by use of a cellulose column prior to catalysis.

** It should be noted that the presence of galvinoxyl and hydroquinone in reaction (1) with commercial $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ as catalyst resulted in promotion of the catalyzed substitution reaction (see above).

were tested using reaction 1, gave reaction times for the complete conversion of $[Fe(CO)_4(CNBu^t)]$ to $[Fe(CO)_3(CNBu^t)_2]$ of 20 and 40 min, respectively.

An equimolar combination of these two catalysts (total 10 mole% catalyst) in reaction 1 gave a reaction time of 38 min. Similarly, the use of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (activated by heating with PtO_2 in benzene for 2 h) in an equimolar combination with commercial $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (total 10 mole% catalyst) in reaction 1 resulted in a reaction time of 60 min (cf. for activated $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ a reaction time of 20 min was observed, and for unactivated $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$, a reaction time of 75 min, Table 1).

These results strongly suggest that the activation achieved by heating $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ or $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ with PtO_2 in benzene involves the removal (or partial removal) of a catalyst inhibitor. This (or a similar) catalyst inhibitor is at least partly restored (possibly via decomposition of the catalyst) on contact with silica gel, and is also present in commercially available $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ *. It is conceivable that both light and oxygen are also partially responsible for the deactivation of these catalysts.

Given that materials such as $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ catalyze CO substitution reactions via the intermediacy of thermally and/or photochemically generated radicals [1], the catalyst inhibitors present in these materials would be expected to be paramagnetic in nature. Thus, interaction with the metal oxide surface may result in the removal (via for instance adsorption) or destruction (via for instance a redox reaction) of the paramagnetic impurity.

The effect of catalyst inhibitors is further emphasized by the "purification" of commercial $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ on a silica gel column. The use of the material so obtained as a catalyst in reaction 1 resulted in a reaction time corresponding to complete conversion of $[Fe(CO)_4(CNBu^t)]$ to $[Fe(CO)_3(CNBu^t)_2]$ in excess of 2 h, thus indicating an even further deterioration of the catalyst on silica gel.

In contrast to the above observations for the catalyst $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$, the treatment of the related complex $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ with PtO_2 in benzene (80 ° C, 2 h) followed by the removal of the platinum oxide activator using either a cellulose or a silica gel column, gave two samples of catalyst that both gave identical reaction times (17 min) in reaction 1. These results indicate that there is no appreciable deactivation of this catalyst on silica gel. However, equimolar amounts of activated $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ and commercial $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ (total 10 mole% catalyst) resulted in a reaction time of 26 min (cf. commercial $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ gives a reaction time of 30 min) thus indicating the presence of small amounts of catalyst inhibitor in the unactivated catalyst.

A number of other transition metal oxides have been investigated as potential, less expensive, agents for the removal of inhibitors from the catalysts $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$. In all cases, the complexes $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and the metal oxide (1.0/0.1 mmol ratio) were heated in benzene (80 ° C, 2 h). At the end of this period, the removal of the metal oxide was effected using a short cellulose column, and the

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* Several samples from differing sources were tested for activity – erratic results were obtained with reaction times varying between 35 and 75 min. The latter batch (obtained from Strem Chemicals) was used consistently throughout these studies.

TABLE 2

THE EFFECT OF METAL OXIDES ON THE HOMOGENEOUS CATALYSIS $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ AND $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ [a]

	Catalyst [b]	
	$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$	$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$
Control	75	75
PtO_2	15	23
PdO	20	4
Fe_2O_3	90	45
MnO_2	50	80
CuO	90	30
Cu_2O	90	30
Co_2O_3	45	90

[a] Judged using the standard substitution reaction $[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] +$ CO – see text for details. [b] Reaction time (min) for the homogeneous catalysts.

respective homogeneous catalysts investigated using reaction 1. The results of these experiments are summarized in Table 2.

From these results it is clear that the heating of either $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ or $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ with the listed metal oxides has different effects with respect to catalysis. Thus, as is shown for the heating of the metal oxides CuO and Cu_2O with these materials, both activating and deactivating effects may be achieved. The latter effect probably arises in a similar manner (i.e. via metal or metal oxide assisted decomposition of the catalyst) as observed for silica gel. Generally, though, only PdO has a consistent positive activating effect similar to that observed for PtO_2 (Table 1). As in the case of the PtO_2 activated catalysts described above, the elution of either PdO activated $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ or $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ through a silica gel column results in catalyst deactivation.

Catalyst promotion – the effect of catalyst substitution

The heating of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ with Bu^tNC and PtO_2 (1.0/2.0/0.1 mole ratio, benzene 80 °C, 2 h) gives a reaction mixture that consists primarily of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ (approximate mole ratio 3/1). Solvent removal from this reaction mixture (without prior removal of PtO_2) has been found to give a catalyst for the substitution of CO by Bu^tNC in reaction 1 more active than the catalysts $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$, and their combinations with the heterogeneous catalyst PtO_2. Due to the high catalytic activity shown by these catalyst combinations for the substitution reaction (1), the reactions

$$[M(CO)_6] + nBu^tNC \rightarrow [M(CO)_{6-n}(CNBu^t)_n] + nCO \quad (9)$$

$$(M = Cr, Mo, W;\ n = 1\text{–}3)$$

were utilized in order to obtain some measure of catalyst differentiation.

Thus the catalyst mixture (containing both $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$) was investigated using reaction 9 and the results are summarized in Tables 3 and 4. Further, for purposes of comparison, reactions

TABLE 3

THE EFFECT OF THE $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNBu^t)_n]$ (n = 1, 2) CATALYST MIXTURE ON THE REACTION $[M(CO)_6] + n\,Bu^tNC \rightarrow [M(CO)_{6-n}(CNBu^t)_n]$ (M = Cr, Mo, W; n = 1–3) [a]

	Cr		Mo		W	
	Reaction time [b] (min)	Yield (%)	Reaction time [b] (min)	Yield (%)	Reaction time [b] (min)	Yield (%)
$[M(CO)_5(CNBu^t)]$	4	94	2	95	2	95
$[M(CO)_4(CNBu^t)_2]$	22	87	4	96	4	93
$[M(CO)_3(CNBu^t)_3]$	180	10 [b]	6	96	15	93

[a] Reaction conditions; $[M(CO)_6]/Bu^tNC$, 2.0/n mmol, catalyst 0.030 g, benzene 10 ml, 80 °C. [b] As determined by IR spectroscopy.

between $[M(CO)_6]$ (M = Cr, Mo, W) and three molar equivalents of Bu^tNC were carried out in the presence of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$, $[\{(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(CNBu^t)\}_2]$, PtO_2, and the combination $PtO_2/[\{(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}(CNBu^t)\}_2]$ as catalysts. The results of these investigations are listed in Table 4.

On the basis of the products formed and the reaction times listed in Tables 3 and 4 it is clear that the most efficient is the combination $PtO_2/[\{(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(CNBu^t)\}_2]$. Further, on the basis of relative reaction times, it may be deduced that the active catalyst containing both $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ functions primarily as a result of the latter material in the presence of PtO_2. More importantly, however, there is increased substitution catalysis in the presence of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ as catalyst as compared to $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ [7].

Thus, assuming the participation of $\{(\eta^5\text{-}C_5H_5)FeL_2\}^{\cdot}$ radicals (L = CO or isonitrile) in the catalyzed substitution process, it would appear that the presence of two Bu^tNC ligands (as opposed to one or none at all) on the catalyst favours radical formation. It is conceivable that the two isonitrile ligands on the complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$, both remaining terminally bonded as opposed to bridge bonded, affect (via either steric or electronic parameters) the strength of the iron–iron bond in the catalyst. Such a labilization could result in increased radical formation and hence increased catalysis.

These results thus establish the importance of the modification of the homogeneous catalyst via an initial ligand substitution process. It should, however, be noted that although the formation of the complexes $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNBu^t)_n]$ (n = 3, 4) under purely thermal reaction conditions appears unlikely in substitution reactions catalyzed by $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$, the presence of such materials (and hence their possible effects on catalysis), cannot be excluded, particularly in reactions involving the combination catalyst transition metal oxide/$[\{(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2\}_2]$. Thus it is possible (particularly in the light of the known catalytic properties of transition metal oxides [33,34]) that the increased catalysis noted for homogeneous complex catalysts in the presence of certain heterogeneous catalyst promoters may be attributed to an initial rapid transition metal oxide catalyzed substitution of the homogeneous catalyst partner. On the basis of the above findings, this would be expected to result in overall improved catalysis on the metal carbonyl substrate. However, it should also be noted that the relative reaction rates (i.e. when compared to those of the catalyzed substitution of the metal carbonyl substrate) such a prior metal oxide mediated modification must be an extremely rapid process. Such an interaction might well be operative for certain catalyst combinations, but, such a process appears unlikely for the catalyst combinations PtO_2 and $PdO/[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$. PdO and PtO_2 have been found to be only poor catalysts for the substitution of CO by Bu^tNC on the complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ i.e. both materials give only an approximately 20–30% increase in the formation of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$, monitored during a 4 h period (benzene, 80 ° C) *.

On the basis of these only moderate substitution effects, the enhanced catalysis observed in the case of the catalyst combinations $PtO_2/[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $PtO_2/[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ (see for instance Table 1) therefore cannot be satisfactorily explained. Thus, it may be deduced that a heterogeneous catalyst mediated substitution of the homogeneous catalyst partner and the removal of catalyst inhibitors cannot be the sole effects contributing to the observed catalyst promotion. No doubt, for such catalyst combinations the metal oxide exerts an activating effect by the removal of catalyst inhibitors, and possibly also a substitutional effect on the homogeneous catalyst partner, but it also appears to increase the reactivity of the homogeneous catalyst.

Catalyst promotion - other effects

The additional interaction postulated to occur between heterogeneous catalysts and homogeneous catalyst partners is illustrated by the use of transition metals and metal oxides in combination with other di-, and also poly-nuclear metal carbonyl catalysts.

Thus, the catalyst combinations generated from heterogeneous catalysts (i.e. PtO_2, PdO, Pd/C, $Pd/CaCO_3$ and activated carbon) and the homogeneous catalyst partners $[M_2(CO)_{10}]$ (M = Mn, Re), $[Co_2(CO)_8]$, $[M_4(CO)_{12}]$ (M = Co, Ir), $[M_3(CO)_{12}]$ (M = Ru, Os), and $[H_4Ru_4(CO)_{12}]$ have been investigated using the substitution reaction (1). The results of these studies are summarized in Table 5. For the purposes of comparison, results for the homogeneous catalysts $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$, $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}_2]$ and $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$ and the above heterogeneous catalyst partners have also been included.

Generally, these studies indicate the ability of a heterogeneous catalyst partner to improve upon, or even induce, catalytic activity in a homogeneous complex catalyst. Thus for instance, the activity of $[Mn_2(CO)_{10}]$ or $[Ru_3(CO)_{12}]$ as substitution catalysts is greatly enhanced (at room temperature) by the presence of metallic palladium. More importantly, however, the presence of a catalyst partner such as PdO or metallic palladium may be used to induce catalytic activity in both $[Re_2(CO)_{10}]$ and $[Os_3(CO)_{12}]$, even at room temperature. It should be noted, however, that catalyst substitution effects are to be expected in certain instances e.g. $[Mn_2(CO)_{10}]$, in the presence of palladium on carbon, undergoes a rapid substitu-

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* Bergwerksverband Type PK221 activated carbon, and zeolites (e.g. type 3A, 4A, 5A, 13X) have also been utilized as promoters for the homogeneous catalyst $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$. These materials have, however, been found to give no detectable rate increase in the formation of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ from $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and Bu^tNC (benzene, 80 ° C) monitored over a 4 h period.

TABLE 4

THE EFFECT OF CATALYSTS ON THE REACTION $[M(CO)_6] + 3Bu^tNC \rightarrow [M(CO)_{6-n}(CNBu^t)_n]$ (M = Cr, Mo, W; $n \leq 3$) [a]

	Cr		Mo		W	
	Time [b] (min)	Reaction product	Time [b] (min)	Reaction product	Time [b] (min)	Reaction product
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$	20 [c]	$[M(CO)_5(CNR)]$	90	$[M(CO)_3(CNR)_3]$	240	$[M(CO)_3(CNR)_3]$
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$	10 [c]	$[M(CO)_5(CNR)]$	25	$[M(CO)_3(CNR)_3]$	60	$[M(CO)_3(CNR)_3]$
PtO_2	60	nr [d]	60	$[M(CO)_5(CNR)]$	60	$[M(CO)_5(CNR)]$
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2] + PtO_2$	7 [e]	$[M(CO)_4(CNR)_2]$	6	$[M(CO)_3(CNR)_3]$	7	$[M(CO)_3(CNR)_3]$
Mixed catalyst [f]	22 [g]	$[M(CO)_4(CNR)_2]$	6	$[M(CO)_3(CNR)_3]$	15	$[M(CO)_3(CNR)_3]$

[a] Reaction conditions as described in Table 3. [b] As determined by IR spectroscopy. [c] No further reaction in 60 min. [d] nr = no reaction. [e] Approximately 10% $[M(CO)_3(CNR)_3]$ formed in 60 min reaction time. [f] Mixtures of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ and $[\{(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)\}_2]$ (~ 3/1) in presence of PtO_2 - see Table 3. [g] Approximately 10% $[Cr(CO)_3(CNBu^t)_3]$ formed in 3 h reaction.

TABLE 5

THE EFFECT OF PROMOTED CATALYSTS ON THE REACTION $[Fe(CO)_4(CNBu^t)] + Bu^tNC \rightarrow [Fe(CO)_3(CNBu^t)_2] + CO$ [a]

Homogeneous catalyst	Control		Promoter				
	A [b]	B [c]	PtO_2 [b]	PdO [b]	Pd/C [b]	$Pd/CaCO_3$ [b]	activated carbon [c]
$[Mn_2(CO)_{10}]$	nr [d]	30	30 (~ 30%) [f]	30 (~ 20%)	15	25	12
$[Re_2(CO)_{10}]$	nr	nc [e]	nr	nr	nr	60	nc
$[Co_2(CO)_8]$	nr	6	nr	nr	15	38	–
$[Co_4(CO)_{12}]$	nr	4	nr	nr	15	32	–
$[Ir_4(CO)_{12}]$	nr	8	40	nr	60 (~ 60%)	42	–
$[Ru_3(CO)_{12}]$	nr	8	30 (~ 30%)	70	23	22	10
$[Os_3(CO)_{12}]$	nr	nc	nr	35	12	23	nc
$[H_4Ru_4(CO)_{12}]$	nr	35	nr	nr	25	22	20
$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$	nr	75	30 (~ 10%)	nr	50	60 (~ 40%)	6
$[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2\}]$	nr	30	nr	nr	25	45	8
$[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2]$	nr	nc	30 (~ 15%)	nr	0	60	40

[a] Standard conditions, as described in the Experimental. [b] Room temperature reaction (20 ° C). [c] Reaction carried out at 80 ° C. [d] nr = no reaction. [e] nc = no catalysis. [f] Approximately 30% reaction in 30 min.

tion of CO by isonitrile at room temperature [32] *. On the other hand, however, both PtO_2 and activated carbon show little or no detectable activity for the substitution of CO by isonitrile on $[Mn_2(CO)_{10}]$ [35], yet show a promotional effect in combination with $[Mn_2(CO)_{10}]$ in reaction (1). Conversely, PdO rapidly substitutes CO by isonitrile on $[Mn_2(CO)_{10}]$ at room temperature, but shows only a mild ability to promote the catalyst $[Mn_2(CO)_{10}]$. Thus, the use of both PdO and activated carbon as a catalyst promoter for $[Mn_2(CO)_{10}]$ excludes in this case, the possibility of substitution on the homogeneous catalyst partner being the dominant factor in the catalyst promotion effect.

At this stage, however, it is possible only to speculate about the nature of any additional interactions between the catalyst and the promoter. An interaction between the homogeneous catalyst and the heterogeneous surface clearly favours catalysis, and thus could conceivably be a process that results in the formation of catalytic intermediates. That such intermediates are radical species, formed for instance via a surface induced metal–metal bond cleavage of the homogeneous catalyst complex, has not been substantiated. Such a process would, for instance, be expected to result in the formation of the mixed metal dimer $[(\eta^5\text{-}C_5H_5)_2FeMo(CO)_5]$ [36] from a mixture of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ and $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ in the presence of PdO or PtO_2, but this has not been observed. Similar observations have been made with the dimers $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$; no evidence for the formation of the heterometallic species $[MnRe_2(CO)_{10}]$ [37] was forthcoming. Other possible catalytic intermediates generated by the surface could include the species $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]^+$ which may then catalyze CO substitution via either a chain or a non-chain radical process.

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* Bergwerksverband Type PK221.

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