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Preliminary communication

SUPPORTED METALS AND METAL OXIDES AS PROMOTERS FOR THE METAL DIMER AND CLUSTER CATALYSED CO SUBSTITUTION REACTION

MICHEL O. ALBERS, NEIL J. COVILLE*,
Department of Chemistry, University of the Witwatersrand, Johannesburg 2001 (Republic of South Africa)
and ERIC SINGLETON
National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001 (Republic of South Africa)

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Summary

Promotional effects due to PtO_2, PdO, Pd/C and $Pd/CaCO_3$ on the metal dimer or cluster (e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$) catalysed reaction between metal carbonyls and isonitriles are shown to lead to enhanced reaction rates for the metal carbonyl substitution reaction.

The use of promoters or cocatalysts to enhance the catalytic activity of transition-metal catalysts is a well known and studied phenomenon in heterogeneous catalysis [1]. Similar examples of catalyst promotion are also known in homogeneous catalysis [2] but this reaction type has not been explored in the non-patent literature in any detail. Herein we report on our investigations on the use of promoters (e.g., metal oxides or supported metals) to enhance the activity of homogeneous catalysts (e.g. metal carbonyl dimers, trimers, tetramers) in the metal carbonyl substitution reaction.

For example, the reaction between $Cr(CO)_6$ (1 mmol) and Bu^tNC (3 mmol) in benzene (10 ml, reflux) is catalysed by $[(\eta^5\text{-}C_5H_5)Fe(CO)(Bu^tNC)]_2/PtO_2$ mixtures (0.05 mmol/0.5 mmol) and readily leads to $Cr(CO)_4(Bu^tNC)_2$ [3] (quantitative yield, 7 min) and more slowly to $Cr(CO)_3(Bu^tNC)_3$ [3] (10%, 60 min). In contrast, the above reaction is not catalysed by PtO_2, and yields only $Cr(CO)_5(Bu^tNC)$ [3] (60 min) in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)(Bu^tNC)]_2$ [4], (0.1 mmol). Similar results have been obtained for the catalysed reaction between $M(CO)_6$ (M = Mo, W) and Bu^tNC.

Use of the model reaction shown in eq. 1 [5] has allowed us to extend our

$$Fe(CO)_4(Bu^tNC) \longrightarrow Fe(CO)_3(Bu^tNC)_2 + CO \qquad (1)$$

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TABLE 1

THE EFFECT OF PROMOTED CATALYSTS OF THE REACTION[a]

$Fe(CO)_4(Bu^tNC) + Bu^tNC \rightarrow Fe(CO)_3(Bu^tNC)_2 + CO$

Catalyst	Reaction time (min)[b]			
	Promoter			
	PdO_2	PdO	Pd/C (5%)	$Pd/CaCO_3$ (5%)
$Mn_2(CO)_{10}$	30 (~30%)[c]	30 (~20%)	15	25
$Re_2(CO)_{10}$	n.r.[d]	n.r.	n.r.	60
$Ir_4(CO)_{12}$	40	n.r.	60 (~60%)	42
$Ru_3(CO)_{12}$	30 (~30%)	70	23	22
$Os_3(CO)_{12}$	n.r.	35	12	23
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	30 (~10%)	n.r.	50	60 (~40%)
$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$	30 (~15%)	n.r.	60	60

[a] Reaction conditions: 1 mmol reactants; 0.05 mmol promoter + 0.05 mmol metal carbonyl catalyst; benzene (10 ml). [b] For complete reaction unless otherwise indicated. [c] Extent of reaction. [d] n.r. = no reaction.

studies to other potential catalyst mixtures. Addition of mixtures of metal carbonyl dimer (or cluster) and promoter (Table 1) to $Fe(CO)_4(Bu^tNC)$ and Bu^tNC in benzene at 25°C results in catalysed product formation, the reaction time and yield varying with the catalyst composition (vide infra). Addition of either the metal carbonyl dimer (or cluster) or the promoter separately gives no product formation (60 min) under similar reaction conditions (in refluxing benzene reaction (I) is catalysed by $Mn_2(CO)_{10}$ (30 min), $Ir_4(CO)_{12}$ (8 min), $Ru_3(CO)_{12}$ (8 min) and even the promoters; thermal blank, 120 min). Results are reproducible within the limits of detectability (5—10%; IR spectroscopy). Re-use of the catalyst combination either by addition of further quantities of reagents or by recovery and subsequent reuse of the catalyst in a new reaction has also been successful.

Pertinent observations relating to the mechanism of reaction (I) in the presence of catalyst and promoter have been made. (1) When $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$-Pd/C} is used as a catalyst, the iron dimer is recovered unchanged at the end of the reaction. (2) Modification of the catalyst is, however, possible. Thus the reaction $Mn_2(CO)_{10} + Bu^tNC \rightarrow Mn_2(CO)_9(Bu^tNC) + CO$ is catalysed by Pd/C (5%) [6] (>70% isolated yield; <5 min) and the catalyst observed (TLC and IR spectroscopy) during the reaction consists of mixtures of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(Bu^tNC)$. Although isonitrile substituted dimers (or cluster) carbonyls have been shown to be superior to the unsubstituted carbonyl complexes in their catalytic behavior [7], this effect cannot account for the total promotional effect being observed; see (1) above. (3) The different degree to which the metal carbonyl dimer or cluster can undergo substitution in the presence of a promoter precludes the possibility of making a rigorous comparison between the catalyst efficiency and the physical properties, e.g., metal—metal bond strengths of the catalysts noted in Table 1. (4) Table 1, and data to be reported, suggest that the promoters (equimolar in metal) can in general be ordered Pd/C (5%) > $Pd/CaCO_3$ (5%) > PtO_2 > PdO in their promotional effect. (The surface area and consequently the number of active sites on these metals is, however, unknown.) (5) No reaction occurs between the substituted metal carbonyl catalyst (e.g. $Mn_2(CO)_9(Bu^tNC)$) and $Fe(CO)_4(Bu^tNC)$ to give $Fe(CO)_3(Bu^tNC)_2$, thus ruling out possible ligand exchange between catalyst and reactant. (6) Studies (e.g. on $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(Bu^tNC)$ [8]/PtO_2 as catalyst) have shown that reaction (1) is enhanced by light (500 W lamp) and inhibited by galvinoxyl and hydroquinone. Thus, a radical mechanism involving the promotion of the metal dimer (or cluster) by PtO_2 to yield metal carbonyl radicals is possible.

Although the actual mechanism of the promotional effect is not yet understood, the methodology has allowed us to synthesize thermally a range of isonitrile complexes of Cr [9] and Mn [10] which have previously only been accessible by photochemical procedures. Thus, reaction of (Arene)$Cr(CO)_3$ (Arene = $C_6H_5Cl, C_6H_5COOMe, C_6H_6, C_6H_5Me, C_6H_3Me_3$) with Bu^tNC in heptane in the presence of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(Bu^tNC)/PtO_2$ as catalyst allows for the thermal synthesis of (Arene)$Cr(CO)_2(Bu^tNC)$ (50—90%). Similar results have been obtained for the catalysed reaction between $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, Me) and R'NC (R' = Bu^t [11], $PhCH_2$, 2,6-$Me_2C_6H_3$) to give $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(R'NC)$. These new isonitrile complexes have been completely characterized by IR and NMR spectroscopy and elemental analyses.

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