The Use of Supported Transition Metals and Metal Oxides as Catalysts for the Metal Carbonyl Substitution Reaction

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Supported transition metals (Pt, Pd, Ru, Rh) and PdO and PtO_2 catalyse the reaction M–CO + L → M–L + CO (L = isonitrile, group 5 donor ligand) and readily give complexes such as $Mo(CO)_2(PhCH_2NC)_4$, $Mn_2(CO)_9(C_6H_{11}NC)$, $Ir_4(CO)_6(Bu^tNC)_6$, and $Re_2(CO)_8(PMePh_2)_2$ in high yield; the catalyst supports also show mild catalytic behaviour.

The metal carbonyl substitution reaction is important in synthetic organometallic chemistry[1] and catalysis.[2] Thermal[3] and photochemical[4] procedures have been used to bring about the reaction M–CO + L → M–L + CO but more recently alternative procedures using chemical reagents (*e.g.* Me_3NO[5]) or catalysts[6] have also been used. Our recent study on the use of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as a catalyst[7] suggested to us that reagents capable of electron-transfer processes (*e.g.* heterogeneous hydrogenation catalysts)[8] should also catalyse the CO substitution raction. The model reaction $Fe(CO)_4(Bu^tNC) + Bu^tNC \rightarrow Fe(CO)_3(Bu^tNC)_2$[9] was used to explore this possibility and our results, indicating high catalytic activity for the Pt and Pd catalysts, are reported in Table 1. The use of Pd/C for the reaction $M(CO)_n + {}^{13}CO \rightarrow M(CO)_{n-1}({}^{13}CO)$ has been reported [10] but extension to ligand substitution reactions in general has not previously been considered.

Table 1. The effect of catalysts on the reaction $Fe(CO)_4(Bu^tNC) + (Bu^tNC) \rightarrow Fe(CO)_3(Bu^tNC)_2$[a].

Catalyst	Reaction time/min[b]	Catalyst	Reaction time/min[b]
Thermal blank	120	Pt/C (5%)	5
Pd	4	Pt/Al_2O_3 (5%)	5
Pd/C (5%)	2	Rh/C (5%)	45 (50)[c]
Pd/Al_2O_3 (5%)	2	Ru/C (5%)	[d] (35)[c]
Pd/Al_2O_3 (0·1%)	4	Ru/Al_2O_3 (5%)	15 (2)[c]
$Pd/BaSO_4$ (5%)	2	PdO	2
$Pd/CaCO_3$ (5%)	2	PtO_2	20

[a] Reaction conditions $Fe(CO)_4(Bu^tNC)$ (1 mmol); Bu^tNC (1 mmol), catalyst (20 mg), and benzene (reflux) (10 ml). [b] As determined by i.r. spectroscopy. [c] Reaction time after catalyst activation: 12 h at 300 °C under N_2 followed by 3 h at 300 °C under H_2. [d] No catalysis observed.

The substitution reaction can readily be extended to a wide range of isonitriles, RNC, *e.g.* with R = C_6H_{11}, $PhCH_2$, and 2,6-$Me_2C_6H_3$ and, further multiple CO substitution to give $Fe(CO)_{5-n}(2,6\text{-}Me_2C_6H_3NC)_n$[9] ($n$ = 1—5) has been achieved in the presence of Pd, Pd/C, and $Pd/CaCO_3$. The reaction between $Fe(CO)_5$ (20 mmol) and PPh_3 (10 mmol) in toluene (10 ml) is also catalysed by Pd and Pt catalysts to give $Fe(CO)_4(PPh_3)$[11] in typically $> 90\%$ yield (Pd/C, 2.5 h; $Pd/CaCO_3$, 3 h; PdO, 10 h; PtO_2, 15 h).

Extension of the use of Pt and Pd catalysts to other metal carbonyl systems has resulted in a significant breakthrough in the facile high-yield synthesis of substituted zerovalent isonitrile[12] and group 5 donor ligand complexes. This is exemplified by the complexes (mono- to tetra-metallic) listed in Table 2. All the new complexes have been characterized by i.r. and n.m.r. spectroscopy (Table 2) and elemental analyses. Reactions are reproducible and no evidence for isonitrile polymerization, as previously reported, *e.g.* in the synthesis of $Os_3(CO)_{12-n}(RNC)_n$[13] derivatives, has been observed.

The reaction $Fe(CO)_4(RNC) + RNC \rightarrow Fe(CO)_3(RNC)_2$ (R = 2,6-$Me_2C_6H_3$, Bu^t), in the presence of PdO, PtO_2, or $Pd/CaCO_3$ as catalyst, has been found to be inhibited by galvinoxyl and hydroquinone and enhanced by illumination (500 W lamp). We thus suspect that the mechanism is similar to that of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalysed reaction[7] (to be discussed further).

Control reactions, in the presence of the catalyst support only, have revealed that certain supports also show mild catalytic activity. For instance, the reaction between $M(CO)_6$ and Bu^tNC (1 mmol reactants, refluxing benzene) to give $M(CO)_5(Bu^tNC)$ (M = Mo, W) is catalysed by activated carbon obtained from a variety of sources. For M = Mo yields of $> 90\%$ product were obtained when the activated carbons Norit W20, Bergbau PK221, and Ambersorb XE348 were used. Although we have been unable to establish the

Table 2. Some representative examples of metal carbonyl substitution reactions catalysed by supported metals or metal oxides.

Reaction[a]	Catalyst	Solvent	Reaction time	Yield/%	Product I.r./cm^{-1}[b]	Product N.m.r. (δ)[c]
(1)[d]	Pd/C, PdO	Toluene (reflux)	3 h	> 60	2155, 2110(sh), 2096 2064, 1981, 1943	7.3 (Ph), 4·78, and 4.75 (CH_2)
(2)	$Pd/CaCO_3$, $Pd/BaSO_4$	Benzene (25 °C)	10 min	80	2175, 2088, 2028, 1995 1970, 1960[e]	1.3 and 1·1 (CH_2)[f]
(3)[d,g]	Pd/C	Benzene (45 °C)	10 min	70	2165, 2145, 2055, 2035 2014, 1988, 1973, 1955 1936[h]	1.5 (Me)
(4)[d,g]	Pd/C	Toluene (reflux)	10 min	60	2150, 1965, 1768	1.47 (Me)
(5)[d]	Pd/C	Xylene (reflux)	2 h	80	2064, 2009, 1976(sh) 1952, 1912(sh)[i]	7.4 (Ph), 2.47 (Me)[j]

[a] Typical reactions were carried out on a 1 mmol scale for reactants and *ca.* 20 mg catalyst (5—10% loading) in 10—20 ml of solvent. [b] Recorded in $CHCl_3$; 2200—1600 cm^{-1} region. [c] Recorded in $CDCl_3$ relative to tetramethylsilane. [d] The earlier members of the series can also be prepared in the presence of catalysts. [e] Recorded in hexane. [f] Recorded in C_6D_6. [g] 0.1 mmol of reactants. [h] Ref. 13. [i] Ref. 14. [j] J(P–H) 7.2 Hz.

$$Mo(CO)_3(PhCH_2NC)_3 + PhCH_2NC \rightarrow Mo(CO)_2(PhCH_2NC)_4 \tag{1}$$

$$Mn_2(CO)_{10} + C_6H_{11}NC \rightarrow Mn_2(CO)_9(C_6H_{11}NC) \tag{2}$$

$$Os_3(CO)_{11}(Bu^tNC) + 2Bu^tNC \rightarrow Os_3(CO)_9(Bu^tNC)_3 \tag{3}$$

$$Ir_4(CO)_7(Bu^tNC)_5 + Bu^tNC \rightarrow Ir_4(CO)_6(Bu^tNC)_6 \tag{4}$$

$$Re_2(CO)_{10} + 2PMePh_2 \rightarrow Re_2(CO)_8(PMePh_2)_2 \tag{5}$$

active component(s) in the carbon, *e.g.* by analysis of the ash content or preparation of activated carbons with added ingredients such as Fe and Ti, we have established that crystalline aluminosilicates also catalyse the substitution reaction, for example $Mo(CO)_6 + Bu^tNC \rightarrow Mo(CO)_5(Bu^tNC)$. Zeolites containing exchanged transition metals have also shown mild catalytic activity for the above reaction *e.g.* RuNaY (0.68% Ru) and NiNaY (2.52% Ni).

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