Michael Reaction Catalysed by Polymer-Anchored Metal Acetylacetonates

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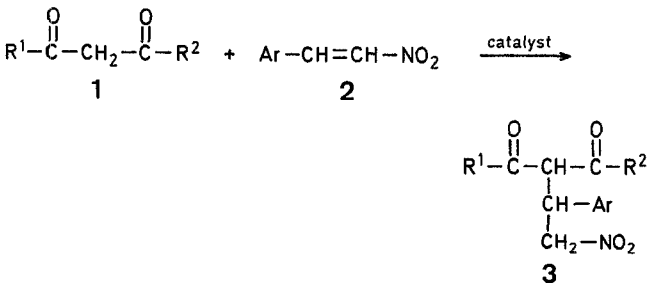
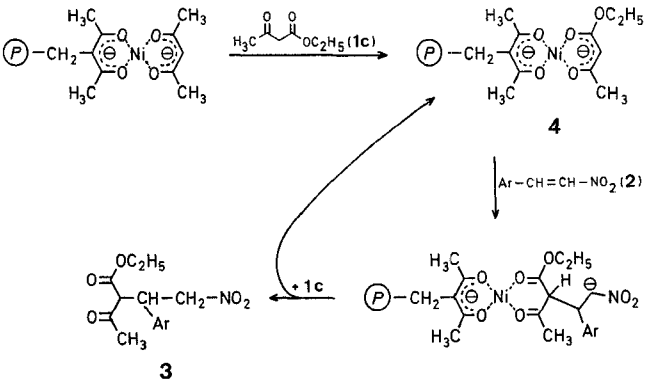
The use of polymer-anchored metal catalysts for chemical reactions has been a subject of intense investigation in the last decade[1]. However, much of the attention is focused on reactions such as hydrogenation, oxidation, carbonylation etc. involving the interaction of small molecules with organic substrates. Recently, we become interested in the possibility of activating fairly complicated organic compounds with polymer-bound catalysts. We report here the use of metal acetylacetonates anchored to polystyrene polymer as catalysts for Michael reactions.

The catalyst is prepared in the following manner. Chloromethylated macroporous polystyrene (cross-linked with 6% divinylbenzene) is reacted with nickel acetylacetonate in dimethylformamide to give in one step the blue polymer-anchored nickel acetylacetonate. The corresponding polymer-bound iron(III) catalyst can be obtained by washing the nickel-containing resins with acid to generate the free ligand [Ⓟ—CH_2—(acac)]. Subsequent exchange with iron(III) acetylacetonate in acetone gives the deep red polymer-anchored iron(III) acetylacetonate. Previously, polystyrene containing acetylacetone groups has been prepared by polymerisation of 3-*p*-vinylbenzylacetylacetone[2,3,4]. The present method appears to be simpler. The introduction of the acetylacetonate group is verified with I.R. spectroscopy by the diminuation of the peak at 1286 cm^{-1} (H—C—Cl bending) and the presence of new peaks at 1697 and 1720 cm^{-1}. The I.R. spectrum of 3-benzyl-2,4-pentanedione has been reported[5] to have carbonyl absorption bands at 1700 cm^{-1} and 1725 cm^{-1}. The metal ions are chelated to the polymer as acetylacetonates according to the difference spectra by Fourier-Transform I.R. spectroscopy. The characteristic bands at about 1580 and 1380 cm^{-1} for metal acetylacetonates can be clearly discerned after substracting the spectrum of Ⓟ—CH_2—(acac) from that of Ⓟ—CH_2—(acac)M (M = metal).

The results of the Michael condensations of β-diketones **(1)** with β-nitrostyrenes **(2)** are summarised in the Table. It is clear that in the absence of catalyst (entry 1), condensation does not take place. As reported, nickel acetylacetonate is effective in promoting the reaction to give the Michael adduct **3** (entry 2)[6]. Polymer-bound nickel(II) acetylacetonate is of comparable efficacy in catalysing the reaction when the amount of nickel(II) ion is present to the same extent as soluble nickel acetylacetonate (entry 3).



Lower concentration of polymer-bound catalyst gives poorer yield of the product (compare entries 3, 4, and 5). It is interesting to note that in the condensation of ethyl acetoacetate **(1c,** $R^2 = OC_2H_5$) with **2,** the polymer-bound catalyst is superior to soluble nickel acetylacetonate in giving a better yield (entries 14–17). This is explained on the basis of the mechanism shown below.



The formation of the mixed ligand complex **4** leads to the activation of ethyl acetoacetate solely, whereas in the case of nickel acetylacetonate, either the formation of the corresponding mixed ligand complex is less favorable or the acetylacetonate ligand competes in the subsequent step. The formation of **4** is evident from the I.R. spectrum of the recovered catalyst (from entry 15) which showed enhanced absorption at ~1725 cm^{-1}.

Polymer-anchored iron(III) acetylacetonate is found to be also effective as catalyst, albeit not as good as the nickel complex.

The polymer catalyst has the usual advantages associated with heterogeneous catalysts. The insoluble resin can be easily removed from the reaction mixture by filtration whereas the soluble catalyst has to be removed by column chromatography[6]. The polymer-anchored catalyst can be re-used (entries 6 and 9) with nearly the same efficiency.

We are now exploring the use of these catalysts for other organic reactions.

Polymer-Anchored Nickel Acetylacetonate:
To a three-necked 100 ml flask equipped with a magnetic stirrer and a condenser is added chloromethylated (20–21% Cl) macroporous polystyrene (5.0 g; cross-linked with 6% divinylbenzene, 16–20 mesh), nickel acetylacetonate (11.1 g), and dimethylformamide (50 ml). The mixture is heated for 18 h at 90–100°C. Potassium iodide (0.3 g) is added and the mixture is heated for another 33 h. The mixture is cooled, the polymer is filtered, washed with acetone (80 ml) and then chloroform (80 ml) until the solvent is colorless. The polymer-anchored nickel acetylacetonate is blue in color. The content of nickel is determined to be ~0.10 mmol Ni/g resin.

Polymer-Anchored Iron(III) Acetylacetonate:
The resin obtained above is washed with 5–10% hydrochloric acid (3 × 75 ml), each time immersing the resin in the aqueous acid for 8–10 h. The resin is then washed with distilled water until the solution is neutral in pH. The resin should be pale yellow in color when all the nickel has been removed. The resin (0.30 g) is suspended in acetone (10 ml) containing iron(III) acetylacetate (0.37 g) for two days. After filtration, the deep red resin is washed with acetone (30 ml), chloroform (10 ml), and dioxane (10 ml) successively until the washings contain no iron(III) acetylacetate. The content of iron is determined to be 0.26 mmol/g resin.

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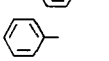
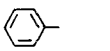
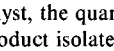
Table. Michael Reactions of **1** with **2** Catalysed by Metal Acetylacetonates

Entry	Product				Catalyst[a]	Reaction Conditions	Yield[b]	m.p.	Lit. m.p. or
	No.	R^1	R^2	Ar	(mmol)	Solvent/temp./time	[%]	[°C]	Molecular formula
1	**3a**	CH_3	CH_3		–	$CHCl_3$/60 °C/43 h	0	—	—
2		CH_3	CH_3		$Ni(acac)_2$ (0.10)	$CHCl_3$/60 °C/43 h	76	113–114°	114.5–116°[6]
3		CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.10)	$CHCl_3$/reflux/41 h	73		
4		CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.005)	$CHCl_3$/60 °C/43 h	59		
5		CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.016)	$CHCl_3$/reflux/49 h	55		
6		CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.016, recycled)	$CHCl_3$/reflux/49 h	43		
7		CH_3	CH_3		Ⓟ–CH_2–(acac)$Fe^{3\oplus}$ (0.09)	dioxan/reflux/48 h	63		
8		CH_3	CH_3		Ⓟ–CH_2–(acac)$Fe^{3\oplus}$ (0.03)	dioxan/reflux/48 h	40		
9		CH_3	CH_3		Ⓟ–CH_2–(acac)$Fe^{3\oplus}$ (0.03, recycled)	dioxan/reflux/48 h	45		
10	**3b**	CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.01)	$CHCl_3$/reflux/28 h	41	126–127.5°	128°[7]
11	**3c**	CH_3	CH_3		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.008)	dioxan/reflux/47 h	61	135.5–137°	$C_{13}H_{14}BrN_2O_6$ (374.2)[c]
12	**3d**	CH_3			$Ni(acac)_2$ (0.10)	dioxan/reflux/46 h	60	130–132°	131°[8]
13		CH_3			Ⓟ–CH_2–(acac)$Ni^{2\oplus}$	dioxan/reflux/46 h	47		
14	**3e**	CH_3	C_2H_5O		$Ni(acac)_2$ (0.10)	dioxan/90 °C/18 h	25	72–74°	76°[6]
15		CH_3	C_2H_5O		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.016)	dioxan/reflux/21 h	63		
16	**3f**	CH_3	C_2H_5O		$Ni(acac)_2$ (0.40)	$CHCl_3$/reflux/45 h	58	105.5–106°	$C_{14}H_{16}N_2O_7$ (324.3)[d]
17		CH_3	C_2H_5O		Ⓟ–CH_2–(acac)$Ni^{2\oplus}$ (0.005)	$CHCl_3$/reflux/41 h	65		

[a] For polymer-anchored catalyst, the quantity is based on nickel which is determined spectrophotometrically.

[b] Yield of pure crystalline product isolated.

[c] calc C 47.60 H 4.30 N 4.26 Br 24.3
found 47.6 4.17 4.01 23.7
^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.94$ (s, 3H); 2.25 (s, 3H); 4.2 (m, 1H); 4.29 (d, 1H, $J = 10$ Hz); 4.56 (d, 2H, $J = 7$ Hz); 7.05 (d, 2H, $J = 7$ Hz); 7.43 ppm (d, 2H, $J = 7$ Hz).

[d] calc C 51.85 H 4.97 N 8.64
found 52.1 5.03 8.65
^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.00$ (t, 3H, $J = 7$ Hz); 2.28 (s, 3H); 3.93 (q, 2H, $J = 7$ Hz); 4.07 (d, 1H, $J = 10$ Hz); 4.2 (m, 1H); 4.70 (d, 2H, $J = 7$ Hz); 7.32 (d, 2H, $J = 7$ Hz); 8.08 ppm (d, 2H, $J = 7$ Hz).

Catalysed Michael Reaction of 1 with 2; General Procedure:
To a mixture of the β-diketone **1** (10 mmol) and the β-nitrostyrene **2** (10 mmol) in solvent (10 ml) is added the indicated amount of catalyst (Table). The mixture is heated for the appropriate length of time. After the reaction is finished, the resin is removed by filtration. The solution is evaporated in vacuo and the product is recrystallised from ethanol.

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