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Preliminary communication

CHEMICAL SYNTHESES WITH METAL ATOMS

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Summary

Metal evaporation syntheses of $[Cr(C_7H_7)(C_7H_{10})]$, $[Cr(C_7H_8)(PF_3)_3]$, metal carbonyls, and anhydrous metal acetylacetonates are described.

The metal evaporation technique has now reached the stage of development and sophistication which allows it to be considered as a practical alternative synthetic tool [1]. We briefly report here some of our latest developments using the laser/thermal metal evaporation procedure [2]; this enables evaporation of e.g. chromium to take place in glass or steel reactors at a rate of 0.5—15 $g\,h^{-1}$ at 10^{-5} torr pressure.

The direct reaction of metals with acetylacetone to give the metal acetylacetonates has long been restricted to only a small number of metals [3]. We find that by evaporating and cocondensing the desired metal at −196°C, warming up, filtering through Kieselguhr and then removing solvent and excess of ligand in vacuo, the metal acetylacetonates can be obtained in good yields (Table 1). Recrystallization from toluene/ether mixtures give the pure salts which were characterized by microanalysis, ^1H NMR and mass spectroscopy. This direct route to anhydrous metal acetylacetonates with its minimum purification requirements contrasts strongly with classical procedures which are often complicated by purification steps and a necessity for stringent anhydrous conditions. Thus, e.g. bis(pentanedionato)tin(II) was only reported in 1973 [4]. In particular, rare earth elements are converted into the corresponding tris(acetylacetonates) and this represents an attractive new route to NMR shift reagents.

In contrast to the oxidative addition reactions of 2,4-pentadione with metals which proceed in acceptable yields, cocondensation of metal vapour with tetrahydrofuran and intermittent carbon monoxide matrix trapping, gave only small yields of the corresponding metal carbonyls (Table 2) which were characterized

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TABLE 1

SYNTHESIS OF METAL ACETYLACETONATES [M(acac)$_n$] BY COCODENSATION OF METAL ATOMS WITH 2,4-PENTANEDIONE (Yields are based on evaporated metal^b)

M	n	Yield (%)
Mn	2	30
Cr	3^a	32
Fe	2	25
Fe	3^a	24
Ni	2	36
Cu	2	10
Zn	2	28
Al	3	14
Sn	2	11
Pb	2	10
Er	3	20
Dy	3	35
Ho	3	30

^{a}Work up in air. ^{b}Only 60% of vessel surface can be coated.

TABLE 2

DIRECT SYNTHESIS OF METAL CARBONYLS FROM METAL ATOMS

Evaporated metal	mmol	THF (ml)	CO (mmol)^a	Products	Yield (%)^b
Cr	18	250	45	$Cr(CO)_6$	2.3
Mn	9	140	45	$Mn_2(CO)_{10}$	1.0
Fe	2	220	27	$Fe(CO)_5$	0.4
				$Fe_3(CO)_{12}$	0.2
				$Fe_2(CO)_9$	traces

^{a}Addition during evaporation; warming up of the THF matrix in the presence of 3 mol CO. ^{b}Yields based on evaporated metal (as determined where appropriate by UV spectroscopy).

by mass, IR (ν(CO)) and UV spectroscopy. In the case of Mn and Fe, the polynuclear carbonyls are probably produced by diffusion together of solvent stabilized [$Mn(CO)_5$] or [$Fe(CO)_4$] units rather than from the evaporation of polynuclear metal aggregates [5]. We conclude that the reaction of metal atoms with carbon monoxide and tetrahydrofuran is an inappropriate substitute for the normal high pressure synthesis of these commonly used starting materials. This may be due in part to the difficulties of condensing carbon monoxide at liquid nitrogen temperatures.

Cocondensation of chromium atoms with cycloheptatriene onto a hexane matrix at −196°C gives a brown material which upon warming to −20°C undergoes a transformation to produce a red-brown solid. Purification by column chromatography [Woelm Al_2O_3, 6% H_2O; eluant hexane (98)/methanol (2)] followed by recrystallization at −78°C gave a microcrystalline solid (4.2% yield, based on metal evaporated) which was characterized by mass spectroscopy, microanalysis and molecular weight determinations in benzene as the previously reported paramagnetic compound [6], [$Cr(C_7H_7)(C_7H_{10})$]. The properties of our sample agree completely with those reported by Fischer and although there is little difference in yields we believe the metal evaporation route to be more direct.

There was evidence to suggest that the low temperature (−196°C) brown intermediate contained only coordinated cycloheptatriene [7] and thus after cocondensation of chromium with the triene, excess PF_3 gas was introduced and the mixture allowed to warm up to −20°C. Filtration, column chromatography [silica gel, Merck 7734; eluant pentane (98)/Et_2O (2)] and recrystallization gave a yellow air sensitive solid (41 mg from 600 mg of evaporated Cr; 1%) which was characterized by low temperature mass spectroscopy, microanalysis and ^1H NMR (almost identical to that of $[Cr(C_7H_8)(CO)_3]$) as $[Cr(C_7H_8)(PF_3)_3]$.

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