Inorganica Chimica Acta, 150 (1988) 9–10

The Reactions of Cyclopentadienylhydridotricarbonylmolybdenum and -tungsten with Diorganomagnesium Reagents

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(Received April 29, 1988)

We are interested in preparing organomagnesium derivatives of the form $RMgML_n$, where ML_n represents an organotransition metal fragment. We report here the results of studies involving the use of the cyclopentadienyltricarbonylmetallates of molybdenum and tungsten, *i.e.* $ML_n = Mo(CO)_3(C_5H_5)$, $W(CO)_3(C_5H_5)$.

Various reductive routes have been applied to the synthesis of trimetallic compounds of the form $Mg[M(CO)_3(C_5H_5)]_2$ (M = Mo, W) [1–3]. However, bimetallic complexes $RMg[M(CO)_3(C_5H_5)]$ (R = hydrocarbyl; M = Mo, W) are unknown. We hoped to be able to synthesise such complexes by using a method based on elimination [4] rather than reduction. We chose to work initially on cyclopentadienylmagnesium derivatives, since (i) the d^6-cyclopentadienyltricarbonylmetallates are isolobal with the cyclopentadienyl anion [5]; (ii) use of the cyclopentadienyl ligand led to isolation of the first bimetallic organozinc complexes [6].

Addition of a toluene solution of cyclopentadienylhydridotricarbonylmolybdenum or -tungsten to one containing an equimolar amount of dicyclopentadienylmagnesium resulted in the immediate precipitation of an off-white solid. This was identified on the basis of elemental analysis and infrared spectroscopy as $Mg[M(CO)_3(C_5H_5)]_2$ (M = Mo, **1**; M = W, **4**).

$$(C_5H_5)_2Mg + 2HM(CO)_3(C_5H_5) \xrightarrow[20\ ^\circ C]{toluene} 2C_5H_6 + Mg[M(CO)_3(C_5H_5)]_2$$

Excess dicyclopentadienylmagnesium remained unreacted in solution. There was no evidence for the intermediate formation of a complex of the desired stoichiometry. Furthermore, the same product may be isolated from analogous reactions of bis(pentamethylcyclopentadienyl)magnesium and dimethylmagnesium.

The reaction between R_2Mg ($R = C_5H_5$, C_5Me_5, Me) and $HM(CO)_3(C_5H_5)$ (M = Mo, W) in tetrahydrofuran (thf) as solvent also resulted in the formation of an immediate precipitate. The products are thf complexes of the trimetallic species **1** and **4**, $(thf)_2Mg[M(CO)_3(C_5H_5)]_2$ (M = Mo, **2**; M = W, **5**). Similarly, carrying out the reaction in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) yielded the tmeda complexes $(tmeda)Mg[M(CO)_3(C_5H_5)]_2$ (M = Mo, **3**; M = W, **6**).

Compounds **1**–**6** are virtually insoluble in common organic solvents and pyrophoric on exposure to air. Though thermally stable below 150 °C they do not sublime at this temperature. Analytical data imply that the Lewis base adducts **2**, **3**, **5** and **6** contain tetrahedrally coordinated magnesium. This is in contrast with the octahedral structure of $(C_5H_5N)_4Mg[Mo(CO)_3(C_5H_5)]_2$, as determined by X-ray crystallography [1].

The infrared spectra of compounds **1**–**6** are reproduced in Fig. 1. The presence of low frequency carbonyl absorptions is well-established evidence for the existence of Mg–O–C–M bonding in these compounds. In **1** and **4** the magnesium atom is presumably only coordinated in this way.

Clearly, the driving force towards formation of trimetallic structures is very great in this system.

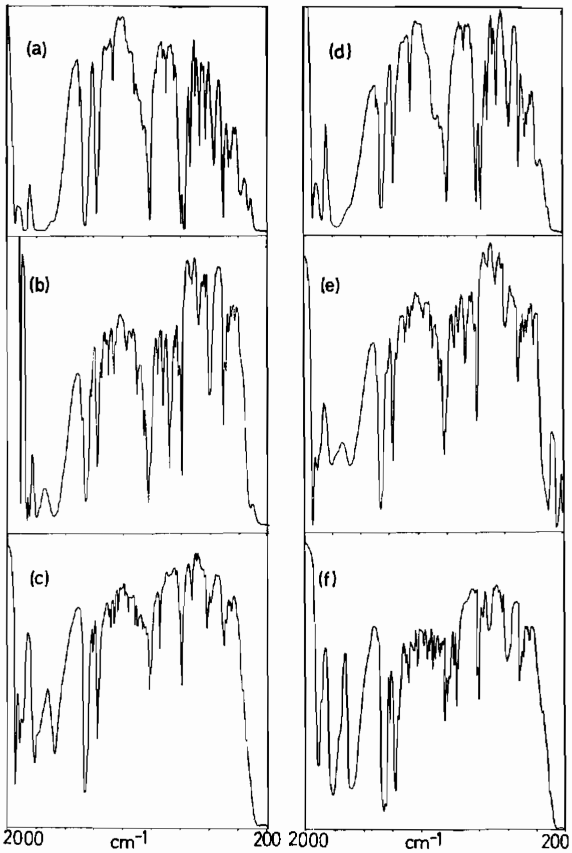

Fig. 1. Infrared spectra (2000–200 cm^{-1}) recorded as Nujol mulls between KBr discs of (a), **1**; (b), **2**; (c), **3**; (d), **4**; (e), **5**; (f), **6**.

0020-1693/88/$3.50

This may largely be associated with the very low solubility of the trimetallic species, as the hypothetical equilibrium

$$2RMg[M(CO)_3(C_5H_5)] \rightleftharpoons R_2Mg + Mg[M(CO)_3(C_5H_5)]_2$$

lies almost entirely over to the right even in the sterically (and possibly electronically) most favourable case, when R = C_5Me_5.

Further work is now in progress on more soluble systems.

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