Titanium-promoted Allyl Transfer to Carbon Monoxide and Other Unsaturated Molecules

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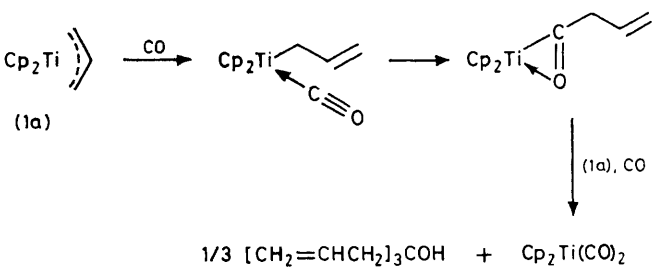
Summary Carbonylation of Cp_2Ti-(π-allyl) yields $Cp_2Ti(CO)_2$ and triallylmethanol; reactions of Cp_2Ti-(π-allyl) and Cp_2Ti-(π-1-methylallyl) with other ligands proceed *via* insertion or allyl-elimination pathways.

OUR interest in the reactivity of co-ordinatively unsaturated, paramagnetic compounds Cp_2TiR (R = aryl, alkyl) towards unsaturated substrates such as carbon monoxide, isocyanides, carbon dioxide, pyridines, *etc.*[1-4] prompted us to investigate the reactivity of the π-allyl derivatives Cp_2Ti-(π-allyl) (**1a**) and Cp_2Ti-(π-1-methylallyl) (**1b**)[5,6] towards a variety of unsaturated donor ligands.

Carbonylation of compound (**1a**) in pentane gives $Cp_2Ti(CO)_2$ (65%) and triallylmethanol (30—50%) (Scheme 1). The first two steps in this reaction are well established for other Cp_2TiR compounds.[1] Possibly the methanol is generated *via* diallyl-ketone formation by alkylation of the acyl intermediate by compound (**1a**). An interesting aspect of this reaction is that it shows, for the



SCHEME 1.

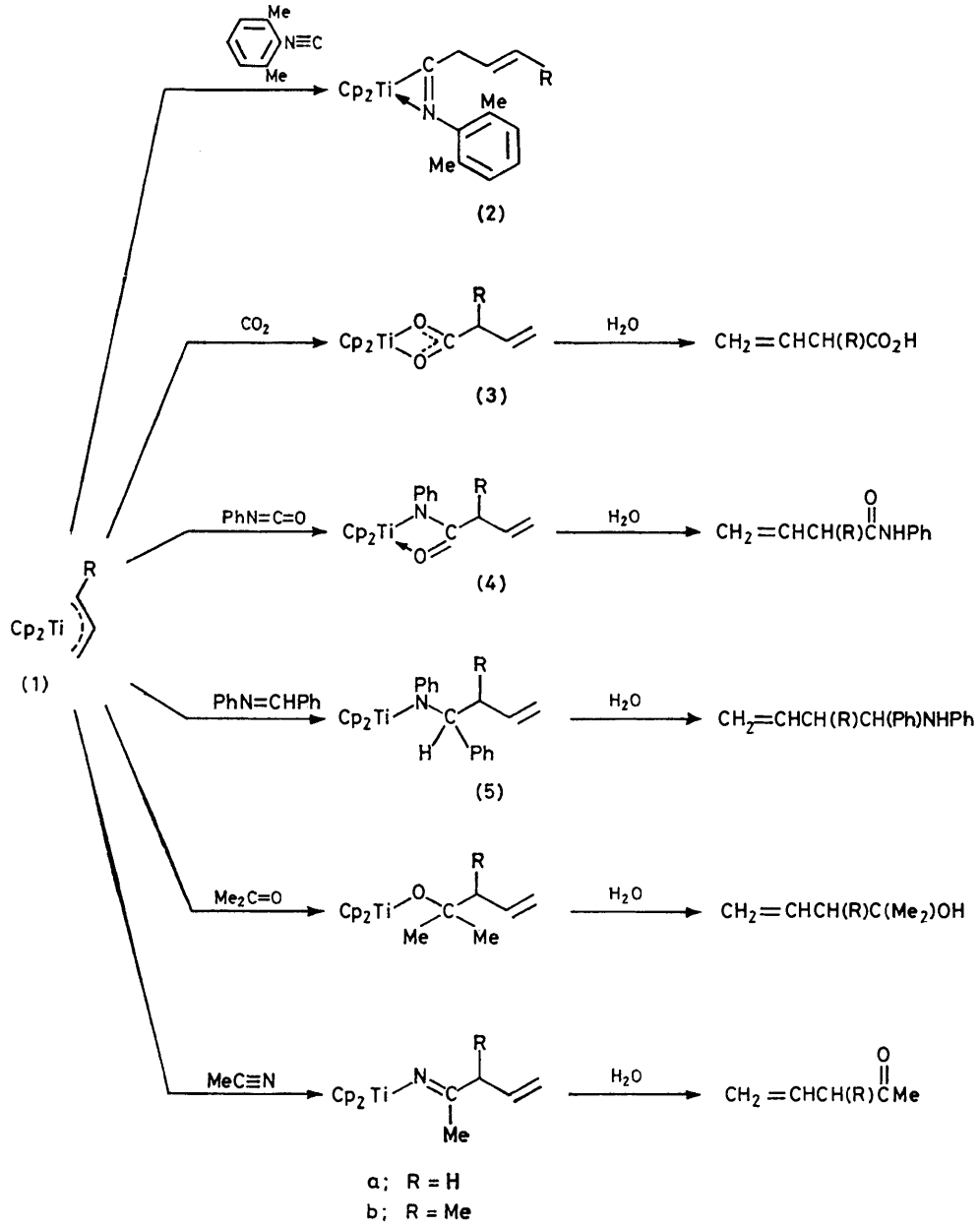
first time, insertion of CO into a Ti–C bond followed by reaction of the intermediate η^2-acyl with other Ti–C bonds resulting in C–C bond formation. The product formed is easily separated from the Ti-centre at which it is generated.

The formation of the triallylmethanol takes place without hydrolysis. The hydrogen needed may originate from the cyclopentadienyl rings (often occurring with Cp_2TiR[7]) or from the solvent. The system used here shows that it is possible to overcome the strongly oxophilic character of early transition metals, which is very important in relation to studies on reductive alkylation of CO with early transition metals.[8]

Since this reaction also indicates the useful synthetic potential of compounds (**1a**) and (**1b**), reactions with other unsaturated donor ligands were performed. The reactions observed can be divided in two classes, *viz.* insertion and allyl-elimination reactions. They are highly regioselective and proceed essentially quantitatively.

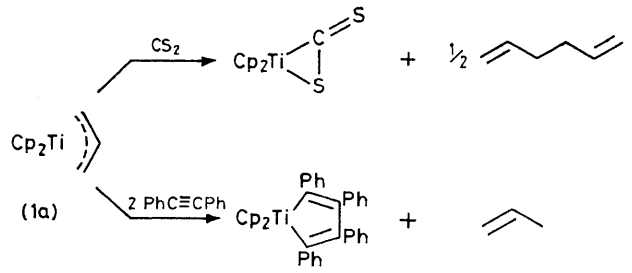
Insertion into the Ti–allyl bond of compounds (**1a**) and (**1b**) occurs with 2,6-xylyl isocyanide to give the red–purple paramagnetic η^2-iminoacyl complexes (**2a**) and (**2b**) (Scheme 2). For compound (**1b**) insertion takes place in the unsubstituted part of the allyl moiety.

Insertions with ligands such as CO_2, PhNCO, and PhN=CHPh proceed differently since, for compound (**1b**), insertion takes place in the most substituted part of the allyl moiety (Scheme 2). Hydrolysis of the blue paramagnetic carboxylato-derivatives (**3a**) and (**3b**) yields the



SCHEME 2.

corresponding carboxylic acids CH_2=CHCH(R)CO_2H; the blue amido-derivatives (**4a**) and (**4b**) yield the corresponding amides CH_2=CHCH(R)C(O)NHPh and the brown amido-derivatives (**5a**) and (**5b**) give the corresponding amines CH_2=CHCH(R)CH(Ph)NHPh (Scheme 2). Reactions with ligands such as Me_2CO and MeCN are analogous since after hydrolysis, the methanols CH_2=CHCH(R)C(Me_2)-OH and the ketones CH_2=CHCH(R)C(O)Me, respectively, are formed (Scheme 2).



SCHEME 3.

The other type of reaction is *via* allyl-elimination which occurs between compound (**1a**) and ligands like CS_2 and PhC≡CPh (Scheme 3). The ligand CS_2 induces allyl coupling to hexa-1,5-diene to give Cp_2Ti-(η^2-CS_2)[9] whereas diphenylacetylene is reductively coupled to $Cp_2TiC_4Ph_4$[10] with formation of propene.

All the paramagnetic organometallic compounds which formed were characterised by elemental analysis, molecular weight determination, and e.s.r. and i.r. spectroscopy. The organic products formed were analysed by ^{1}H n.m.r., i.r., and g.c.–mass spectrometry.

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