Journal of Organometallic Chemistry, 414 (1991) C51–C53
Elsevier Sequoia S.A., Lausanne
JOM 22057PC

Preliminary communication

Synthesis of mononuclear and oligomeric ruthenium(II) acetylides

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(Received April 10th, 1991)

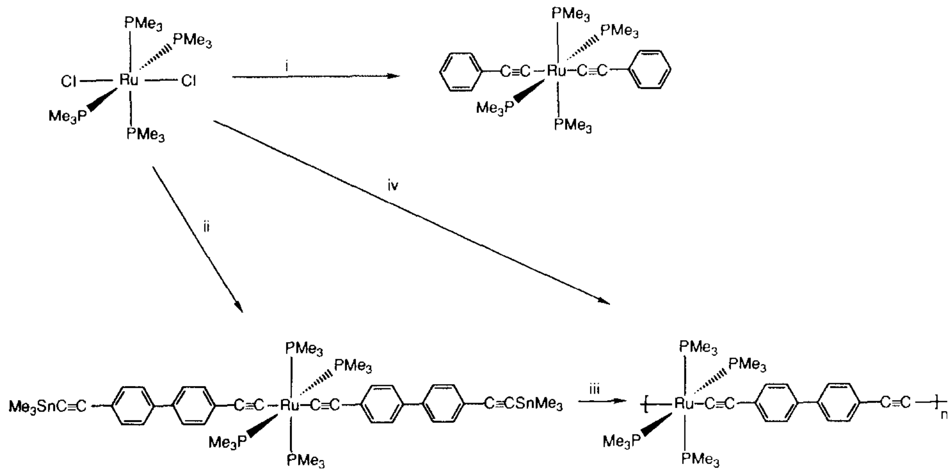
Abstract

The complexes *trans*-$[Ru(PMe_3)_4(C{\equiv}CPh)_2]$ and *trans*-$[Ru(PMe_3)_4(C{\equiv}CC_6H_4C_6H_4C{\equiv}CSnMe_3)_2]$ have been prepared from the reaction between *trans*-$[Ru(PMe_3)_4Cl_2]$ and an excess of either $Me_3SnC{\equiv}CPh$ or $Me_3SnC{\equiv}CRC{\equiv}CSnMe_3$ ($R = p\text{-}C_6H_4C_6H_4$), respectively. However, if only one equivalent of the latter reagent is used the rod-like polymeric species *trans*-$[-Ru(PMe_3)_4C{\equiv}CRC{\equiv}C-]_n$ can be isolated.

We have recently described [1] how trimethylstannyl(acetylide) complexes may be used as precursors to a variety of mononuclear and oligomeric transition metal σ-acetylide species. As part of our continuing investigation into the properties of metal poly-yne complexes, $[-ML_nC{\equiv}CRC{\equiv}C-]_n$, [2,3] we wished to synthesise examples of such compounds containing ruthenium. Two reasons for this were that it was anticipated that orbital overlap between metal *d*-orbitals and ligand π^*-orbitals would be greater for ruthenium than in the previously studied rhodium and platinum cases with a subsequent increase in the delocalisation along the polymer chains, and that the easily accessible Ru^{II}/Ru^{III} couple would allow electrochemical and ESR studies to be undertaken. Increased delocalisation along the polymer chains should improve the conductivity characteristics [3] of the materials produced and increase their nonlinear optical coefficients [4]. In this paper we wish to describe how our synthetic methodology may be applied to produce the first examples of ruthenium(II) *trans*-acetylide complexes and ruthenium poly-yne species.

Treatment of *trans*-$[Ru(PMe_3)_4Cl_2]$ (**1**) with an excess of $Me_3SnC{\equiv}CPh$ in refluxing THF results in the smooth loss of two equivalents of Me_3SnCl, and the formation of *trans*-$[Ru(PMe_3)_4(C{\equiv}CPh)_2]$ (**2**) in essentially quantitative yield (Scheme 1), as air sensitive yellow crystals. The presence of a $\nu(C{\equiv}C)$ stretch at 2055 cm^{-1} in the IR spectrum is indicative of a σ-bound acetylene monomer unit, and a preliminary X-ray crystallographic investigation of **2** indicated that the structure was isomorphous with the known iron complex *trans*-$[Fe(Me_2PCH_2CH_2PMe_2)_2(C{\equiv}CPh)_2]$ [5].

0022-328X/91/$03.50



Scheme 1. Reagents: i, $Me_3SnC{\equiv}CPh$ (excess); ii, $Me_3SnC{\equiv}CRC{\equiv}CSnMe_3$ (excess); iii, *trans*-$[Ru(PMe_3)_4Cl_2]$ (1 equiv.); iv, $Me_3SnC{\equiv}CRC{\equiv}CSnMe_3$ (1 equiv.).

When **1** is treated under analogous conditions with an excess of the bis(acetylide) species $Me_3SnC{\equiv}CRC{\equiv}CSnMe_3$ (**3**) only one trimethlytin group is lost from each molecule of **3** to give the complex *trans*-$[Ru(PMe_3)_4(C{\equiv}CRC{\equiv}CSnMe_3)_2]$ (**4**), which has been characterised from its NMR data *; in addition the mass peak for this species (1132 a.m.u.) was observed in its FAB mass spectrum. This result suggested that reaction of **1** with **3** in a 1 : 1 stoichiometry should yield rigid-rod linear polymers. Carrying out the reaction under these conditions does indeed afford the insoluble, orange, oligomeric species $[-Ru(PMe_3)_4-C{\equiv}CRC{\equiv}C-]_n$ (**5**) (Scheme 1). Compound **5** has been characterised from its microanalytical data, IR spectroscopy, and FAB mass spectrum *. The latter shows a major peak at 533 a.m.u. for the fragment $[Ru(PMe_3)_3(C{\equiv}CRC{\equiv}C)]$, which represents the "monomer unit" of the polymer minus one PMe_3 group. The IR $\nu(C{\equiv}C)$ stretch has moved to lower energy, by 9 cm^{-1}, compared to the value found for **2**, and the band is also much broader. This observation is consistent with the formation of the polymer. Treatment of **4** with one equivalent of **1** similarly affords the polymer **5**.

We have succeeded in our objective of synthesising ruthenium σ-acetylide complexes and poly-ynes. Subsequently we hope to produce polymeric materials which are soluble in organic solvents by varying the nature of the alkyl groups on the phosphine ligands. Studies are also underway to determine the physical, electrochemical and optical properties of the new species produced.

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* *Selected spectroscopic data*

2: IR (Nujol): 2055 cm^{-1} ($\nu(C{\equiv}C)$). ^1H NMR (CD_2Cl_2): δ 1.48 (s, 36H); 6.92 (m, 2H); 7.09 (m, 8H). ^{31}P NMR (CD_2Cl_2): δ −3.1. ^{13}C NMR (CD_2Cl_2): δ 135.4 ($Ru\mathit{C}{\equiv}C$); 130.2 ($RuC{\equiv}\mathit{C}$); 129.7, 129.6, 127.5, 122.2 (C_6H_5); 19.5 (PMe_3).

4: IR (Nujol): 2053 cm^{-1} ($\nu(C{\equiv}C)$). ^1H NMR (CD_2Cl_2): δ 0.35 (s, 18H); 1.58 (s, 36H); 7.10–7.60 (m, 8H). ^{31}P NMR δ −3.2.

5: IR (Nujol): 2046 cm^{-1}. FAB mass spectrum: 533 a.m.u.

Acknowledgements. We gratefully acknowledge the financial support of the S.E.R.C (S.J.D.).

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