

Preliminary communication

Synthesis of novel rigid rod iron metal containing polyynes polymers

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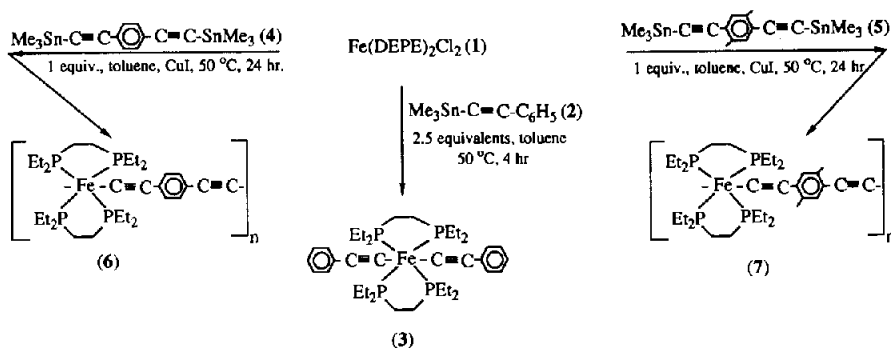
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Abstract

Treatment of the dihaloiron-chelating phosphine complex, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (**1**) with 2.5 equivalents of $\text{Me}_3\text{SnC}\equiv\text{C}_6\text{H}_5$ (**2**) gives the monomeric complex, *trans*- $\text{Fe}(\text{DEPE})_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ (**3**), whereas the reaction of equimolar quantities of **1** and $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ ($\text{R} = p\text{-C}_6\text{H}_4$ (**4**); $p\text{-(CH}_3)_2\text{C}_6\text{H}_2$ (**5**)) yields soluble and high molecular weight rigid rod polymeric species, *trans*- $[-\text{Fe}(\text{DEPE})_2(-\text{C}\equiv\text{CRC}\equiv\text{C}-)]_n$ (**6,7**).

Transition metal σ -acetylide polymers of the type $[-\text{ML}_n(-\text{C}\equiv\text{CRC}\equiv\text{C}-)]_n$ ($\text{ML}_n = d^6$ to d^8 metal fragment; $\text{R} = p\text{-C}_6\text{H}_4, p\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-}p$) continue to attract considerable attention. Extended back-bone conjugation through $d\pi\text{-}p\pi$ hybridization in these complexes imparts interesting physical properties with potential applications in the materials industry. Synthesis of such species has been mainly restricted to metals of group 10 (Ni, Pd, Pt) due to limitations of the synthetic approach firstly developed by Hagihara's group [1]. The design of new materials for specific applications by systematic variations of the metal centres and polyynes involved requires a general synthetic route to such polymers. Much effort is at present concentrated on the development of alternative syntheses [2–5]. Using a new synthetic route which employs bis-SnMe₃-acetylides, $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ ($\text{R} = p\text{-C}_6\text{H}_4$; $p\text{-(CH}_3)_2\text{C}_6\text{H}_2$) as precursors, we have now prepared the first examples of iron-metal containing rigid rod polymers, $[-\text{Fe}(\text{DEPE})_2(-\text{C}\equiv\text{CRC}\equiv\text{C}-)]_n$ (DEPE = 1,2-bis(diethylphosphino)ethane), in which the adjacent iron metal centres are joined by the delocalized π -system of the polyalkyne unit.

Treatment of the Fe-chelating phosphine dihalide complex, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (**1**)*, with 2.5 equivalents of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ (**2**)** in toluene at 50 °C for 4 h under nitrogen (Scheme 1) produces an orange solution from which the compound, *trans*- $\text{Fe}(\text{DEPE})_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ (**3***** can be isolated almost quantitatively by extraction with cold hexane. Reaction of compound **1** with equimolar quantities of the bifunctional tin reagents, $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ ($\text{R} = p\text{-C}_6\text{H}_4$ (**4**); $p\text{-(CH}_3)_2\text{C}_6\text{H}_2$ (**5**)) in the presence of a catalytic amount of CuI under similar conditions affords the desired polymeric species, *trans*- $[-\text{Fe}(\text{DEPE})_2(-\text{C}\equiv\text{CRC}\equiv\text{C}-)]_n$.



Scheme 1.

$\text{C}-)]_n$ ($\text{R} = p\text{-C}_6\text{H}_4$ (6); $p\text{-(CH}_3)_2\text{C}_6\text{H}_2$ (7)) in good yields. When an analogous reaction is attempted in diethylamine solvent (as required for Hagihara's synthesis method [1]), complete decomposition of compound 1 is observed even before the addition of acetylide ligands (4 or 5) and CuI. The polymeric complexes (6,7) can be purified by repeated crystallization from a 10:1 mixture of toluene/petroleum ether at $-40\text{ }^\circ\text{C}$ ($\sim 60\%$ yield). These complexes are fairly soluble in benzene, toluene, and dichloromethane, but only slightly soluble in hexane.

The monomeric iron- σ -acetylide species, $trans\text{-Fe}(\text{DMPE})_2(\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})_2$ [6] ($\text{R} = p\text{-C}_6\text{H}_4$; DMPE = 1,2-bis(dimethylphosphino)ethane) and $trans\text{-}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeC}\equiv\text{CC}\equiv\text{CFe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ [7] have been recently prepared, but to our knowledge, there have been no reports of Fe-polyynes oligomers or polymers. A single crystal structure determination [6] of $trans\text{-Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2(\text{DMPE})_2$ has shown that there is a linear arrangement of the acetylenic units at the metal centre, and there is a considerable delocalization of M-C and C-C bond distances in the molecule. This suggests a rigid rod-like structure for the corresponding Fe- σ -acetylide oligomers/polymers. The ^{31}P NMR spectra *** of the $trans$ -configurational complexes (6,7) contains a single peak, at ~ 69 ppm. The IR spectrum *** exhibits a single intense band at $\sim 2024\text{ cm}^{-1}$ in the acetylenic region. The weight average molecular weight (M_w) obtained by GPC method for the compound $trans\text{-}[\text{Fe}(\text{DEPE})_2(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_2)]_n$ ($\text{R} = p\text{-(CH}_3)_2\text{C}_6\text{H}_2$ (7)) was 173000, indicating a high degree of polymerisation ($n_w = 279$).

In an attempt to extend this methodology to other metals of group 8, we found [8] that the reaction of $\text{Ru}(\text{PMe}_3)_4\text{Cl}_2$ (8) with a slight excess of 2 leads to the

* 1,2-Bis(diethylphosphino)ethane (DEPE), and $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (1) were prepared by adaptation of the literature procedures [9,10].

** $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ (2) was prepared from phenylacetylene. Bis-SnMe₃ acetylides (4,5) were prepared by adaptation and modification of the literature procedures [11,12].

*** Selected data for $trans\text{-Fe}(\text{DEPE})_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ (3): IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2046 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) δ -68.8 ppm; ^1H NMR (C_6D_6 , 400 MHz) 1.14, 1.74, 2.44, 7.17, 7.59; high resolution mass spectrum m/z 671.4, M^+ .

$trans\text{-}[\text{Fe}(\text{DEPE})_2(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_2)]_n$ ($\text{R} = p\text{-(CH}_3)_2\text{C}_6\text{H}_2$ (7)): $M_w = 173,000$ ($n_w = 279$); IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2024 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) δ -69.0 ppm; ^1H NMR (C_6D_6 , 400 MHz) 1.13, 1.72, 2.27, 2.45, 7.41. Satisfactory analyses were obtained.

formation of Ru- σ acetylide complex, *trans*-(Ru(PMe₃)₄(C \equiv CC₆H₅)₂), which has been structurally characterized. The corresponding polymers, *trans*-[-Ru(PMe₃)₄-(C \equiv CRC \equiv -)]_n (R = *p*-C₆H₄-C₆H₄-*p*) prepared by the reaction of equimolar quantities of **8** and Me₃SnC \equiv CC₆H₄-C₆H₄C \equiv CSnMe₃ were found to be insoluble. We are currently investigating the analogous reactions of Ru(DEPE)₂Cl₂ with alkynyltrimethyltin reagents, which we believe should produce soluble polymers.

In conclusion, we have developed a good route to novel rigid rod Fe- σ -acetylide polymers. Detailed syntheses of monomeric, oligomeric, and polymeric group 8 metal- σ -acetylide complexes, [-M(DR'PE)₂(-C \equiv CRC \equiv -)]_n (M = Fe, Ru; R' = DEPE; 1,2-Bis(di-*n*-butylphosphino)ethane (DBPE)) and an investigation of their electronic structure, conductivity, magnetic and redox properties are currently in progress.

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