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Synthesis of monomeric, oligomeric and polymeric σ -acetylide complexes of platinum, palladium, nickel and rhodium

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Abstract

Reaction of equimolar quantities of $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ [$\text{R} = p\text{-C}_6\text{H}_4$; $p\text{-C}_6\text{H}_2(\text{CH}_3)_2$; $p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$] with the group 10 metal dihalide complexes, $[\text{M}(\text{X}^n\text{Bu}_3)_2\text{Cl}_2]$ ($\text{M} = \text{Pt}, \text{Pd}, \text{Ni}$; $\text{X} = \text{P}, \text{As}$; $\text{Bu} = \text{butyl}$) affords the polymeric species $\text{trans-}[\text{-M}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})]_n$ in excellent yields. By varying the stoichiometry of these reactions, complexes of the type $\text{trans-}[\text{M}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{CSnMe}_3)_2]$ and $\text{trans-}[\text{ClM}(\text{X}^n\text{Bu}_3)_2\text{C}\equiv\text{CRC}\equiv\text{CM}(\text{X}^n\text{Bu}_3)_2\text{Cl}]$, which are precursors to higher oligomers, can be prepared. Treatment of the former with an excess of $\text{trans-}[\text{M}(\text{X}^n\text{Bu}_3)_2\text{Cl}_2]$ affords the trimetallic compound $\text{trans-}[\text{ClM}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})\text{M}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})\text{M}(\text{X}^n\text{Bu}_3)_2\text{Cl}]$, while reaction of the latter with two equivalents of $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ followed by two equivalents of $\text{trans-}[\text{M}(\text{X}^n\text{Bu}_3)_2\text{Cl}_2]$ gives the complex $\text{trans-}[\text{ClM}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})\text{M}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})\text{M}(\text{X}^n\text{Bu}_3)_2\text{Cl}]$. Treatment of the complex $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ ($\text{Ph} = \text{Phenyl}$) with one equivalent of $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ [$\text{R} = p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$] gives the polymeric species $[\text{-Rh}(\text{PPh}_3)_2(\text{SnMe}_3\text{X-C}\equiv\text{CRC}\equiv\text{C-})]_n$. Model compounds for other rhodium-containing σ -acetylide complexes have been obtained from the reaction between the complex $[\text{Rh}(\text{PMe}_3)_4\text{Cl}]$ ($\text{Me} = \text{CH}_3$) and $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$, which yields the compound $\text{mer,trans-}[\text{Rh}(\text{PMe}_3)_3(\text{SnMe}_3\text{X-C}\equiv\text{CC}_6\text{H}_5)_2]$ via the intermediate $[\text{Rh}(\text{PMe}_3)_4(\text{-C}\equiv\text{CC}_6\text{H}_5)]$. Reaction of $[\text{Rh}(\text{PMe}_3)_4\text{Cl}]$ with one equivalent of $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ [$\text{R} = p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$] yields the polymer $\text{mer,trans-}[\text{-Rh}(\text{PMe}_3)_3(\text{SnMe}_3\text{X-C}\equiv\text{CRC}\equiv\text{C-})]_n$.

Introduction

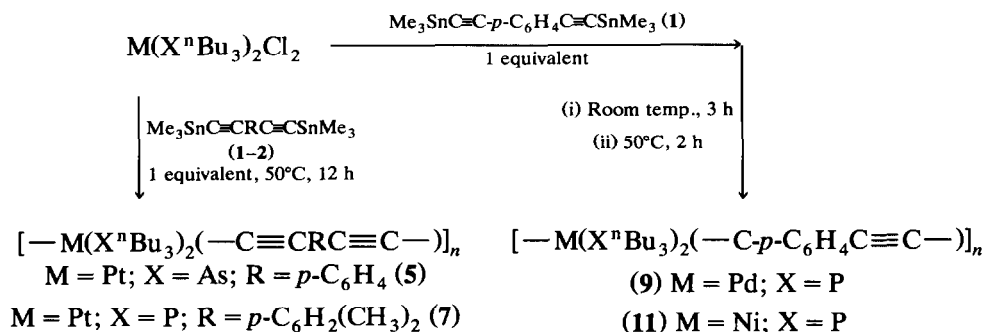
Polymeric materials containing transition metal centres joined by delocalizable π -system of a polyene continue to attract considerable attention. The soluble organometallic polyene polymers of the type, $\text{trans-}[\text{M}(\text{X}^n\text{Bu}_3)_2(\text{-C}\equiv\text{CRC}\equiv\text{C-})]_n$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{X} = \text{P}$; $\text{R} = p\text{-C}_6\text{H}_4$; $p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$), first developed by Hagihara's group [1], have been of particular interest. The overlap of the metal $d\pi$ -orbitals with the alkyne $p\pi^*$ -orbitals in these complexes should give rise to a partially delocalized π -system along the polymer chain, the extent of which depends on the degree of orbital overlap. This delocalization imparts interesting physical properties such as nonlinear optical effects. The rigid rod type structure of these polymers means that they form liquid crystalline phases.

Despite this interest, there have been to our knowledge no examples of rigid rod metal acetylide polymers containing metals other than those of group 10. This is possibly because the reaction conditions required to form these species involve amine solvents in which many of the other transition metal halide complexes are unstable. However, it would be of great interest to obtain such systems containing other metals in order to vary the degree of orbital overlap along the polymer chains, in order to see how this affects the properties of the resulting materials. We have recently reported [2–5] that bis-trimethylstannyl(acetylide) complexes, $\text{Me}_3\text{SnC}\equiv\text{CRC}\equiv\text{CSnMe}_3$ [$\text{R} = p\text{-C}_6\text{H}_4$; $p\text{-C}_6\text{H}_2(\text{CH}_3)_2$; $p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$] are important precursors for a variety of linked metal acetylide complexes. Using this new approach, we have prepared a number of platinum, palladium, nickel and rhodium containing monomeric, oligomeric and polymeric σ -acetylide complexes.

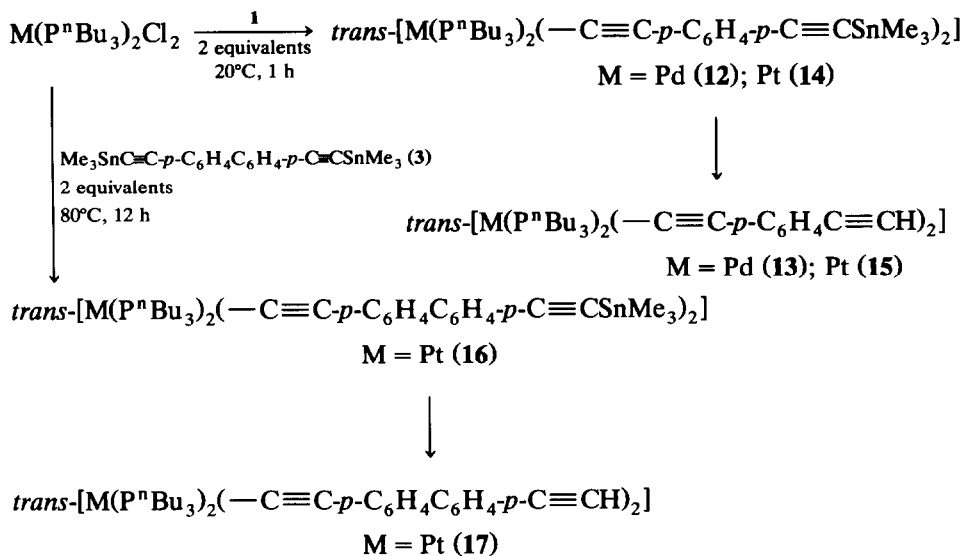
Results and discussion

A general synthetic route to the desired complexes is shown in Schemes 1–3. The bis(trimethylstannyl)acetylide complexes 1–3 were prepared from the corresponding alkynes ($\text{HC}\equiv\text{CRC}\equiv\text{CH}$ ($\text{R} = p\text{-C}_6\text{H}_4$; $p\text{-C}_6\text{H}_2(\text{CH}_3)_2$; $p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4$)) by treatment with $n\text{BuLi}$ followed by SnMe_3Cl . The polymeric species are obtained by the reaction of 1–3 with one equivalent of the transition metal dihalide. In a typical procedure for the preparation of the Pt-metal containing polymers, one equivalent of $\text{Pt}(\text{As}^n\text{Bu}_3)_2\text{Cl}_2$ (**4**) was treated with one equivalent of **1** and a catalytic amount of CuI in toluene at 50°C for 12 h. The mixture obtained after evaporation of toluene was filtered through a column of alumina with dichloromethane as an eluant and the pale yellow product purified by repeated precipitation from dichloromethane by addition of methanol. Polymer **5** was obtained as a pale yellow solid in very high yield. The weight average molecular weight obtained by gel permeation chromatography (GPC) was found to be 120000. The polymer $[-\text{Pt}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_2(\text{CH}_3)_2\text{-}p\text{-C}\equiv\text{C-})]_n$ (**7**) was similarly obtained (mol. wt. = 82000) by the reaction of equimolar quantities of $\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2$ (**6**) and **2**.

In a similar experiment, when one equivalent of $[\text{Pd}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2]$ (**8**) was treated with one equivalent of **1** and a catalytic amount of CuI in toluene at room temperature, the originally yellow solution became brown in ca. 3 h. The IR spectra indicated that all of **1** had been consumed. The product mixture was then



Scheme 1. Synthesis of σ -acetylide polymeric complexes of group 10.

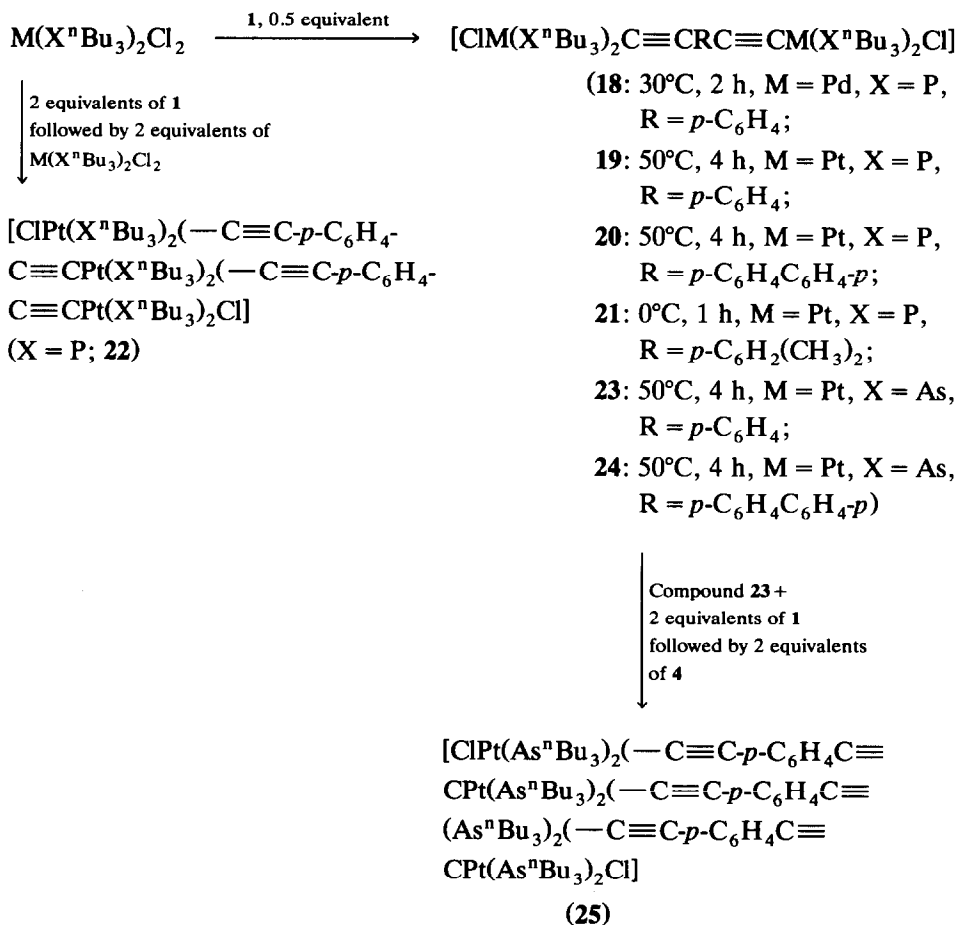


Scheme 2. Synthesis of bis-acetylide complexes of platinum and palladium.

chromatographed on alumina to give the yellow polymeric species *trans*-[Pd(PⁿBu₃)₂-C≡C-*p*-C₆H₄-*p*-C≡C-]_n (**9**). This compound was previously prepared by Hagihara and coworkers by a different route but the weight average molecular weight determined for **9** (30000) was found to be higher than that they reported [6] (22000). The polymer, [-Ni(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-)]_n (**11**) was prepared by the reaction of equimolar quantities of Ni(PⁿBu₃)₂Cl₂ (**10**) and **1** in toluene at 50°C for 2 h.

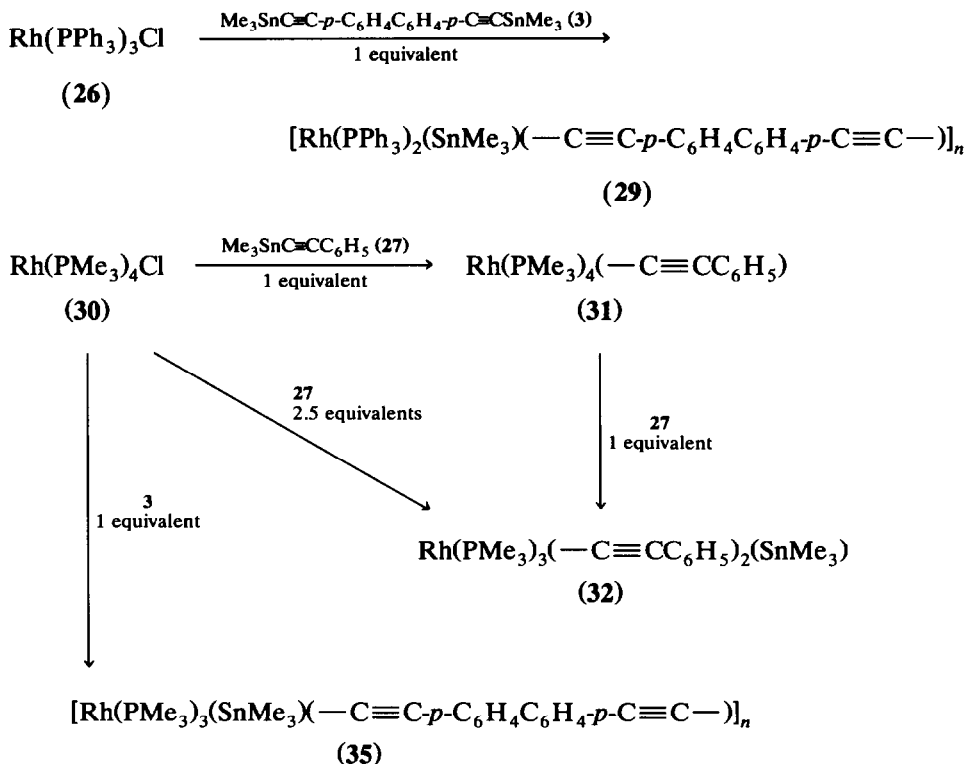
By varying the stoichiometry of these reactions, monomeric and oligomeric complexes can be prepared in good quantities. When *trans*-Pd(PⁿBu₃)₂Cl₂ (**8**) is treated with two equivalents of Me₃Sn-C≡C-*p*-C₆H₄-*p*-C≡C-SnMe₃ (**1**) the species *trans*-[Pd(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-SnMe₃)₂] (**12**) is formed. The latter is quite sensitive to moisture and was not characterized directly; instead the reaction mixture containing **12** was passed through an alumina column, leading to hydrolytic removal of the trimethylstannyl groups to give the known [6] compound *trans*-[Pd(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡CH)₂] (**13**). A similar reaction sequence gave the platinum containing analogues of **12**, *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-SnMe₃)₂] (**14**) and *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-SnMe₃)₂] (**16**); in each case these compounds were characterized by conversion into their known [1,7] terminal H derivatives, *trans*-[Pt(PⁿBu₃)₂(-C≡C-RC≡CH)₂] (**15** and **17**).

When the reaction between **8** and **1** was carried out with an excess of the palladium complex the known species *trans*-[ClPd(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-C≡C-)-Pd(PⁿBu₃)₂Cl] (**18**) was isolated in high yields. Similarly, the platinum containing species, *trans*-[ClPt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-C≡C-)-Pt(PⁿBu₃)₂Cl] (**19**) and *trans*-[ClPt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-C₆H₄-*p*-C≡C-)-Pt(PⁿBu₃)₂Cl] (**20**) were obtained from the reaction of [Pt(PⁿBu₃)₂Cl₂] (**6**) with **1** or **3** respectively. Reaction of 2.5 equivalents of [Pt(PⁿBu₃)₂Cl₂] (**6**) with **2** gives *trans*-[ClPt(PⁿBu₃)₂(-C≡C-*p*-C₆H₂(CH₃)₂-*p*-C≡C-)-Pt(PⁿBu₃)₂Cl] (**21**). The trimetallic species, *trans*-[ClPt(PⁿBu₃)₂-

Scheme 3. Synthesis of monomeric and oligomeric platinum σ -acetylide complexes.

$(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{C-})\text{Pt}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{C-})\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}$ (22) was obtained by the reaction of 14 with 2 equivalents of 6. The arsine-substituted analogues of 19, *trans*-[ClPt(AsⁿBu₃)₂(-C≡CRC≡C-)Pt(AsⁿBu₃)₂Cl] (R = *p*-C₆H₄ (23); *p*-C₆H₄C₆H₄-*p* (24)) were made by treating Pt(AsⁿBu₃)₂Cl₂ (4) with 0.5 equivalents of 1 or 3. When 23 was treated with a further 2 equivalents of 1 and then with 2 equivalents of 4, the tetrametallic complex, *trans*-[ClPt(AsⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-)Pt(AsⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-)Pt(AsⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡C-)Pt(AsⁿBu₃)₂Cl] (25) was obtained.

In an attempt to demonstrate the generality of our synthetic procedure, we also prepared some complexes containing linked rhodium centres (Scheme 4). Reaction of two equivalents of [Rh(PPh₃)₃Cl] (26) with one of Me₃Sn-C≡C-*p*-C₆H₄C₆H₄-*p*-C≡C-SnMe₃ (3) at room temperature resulted in an initial darkening of the solution followed by separation of a dark red powder after 3 h. The precipitate was separated, and subsequent work up of the remaining solution indicated the presence of only [Rh(PPh₃)₃Cl]. The nature of the precipitate, which was found to

Scheme 4. Synthesis of rhodium σ -acetylide complexes.

be insoluble in common organic solvents, was determined by reference to observations by Lappert et al. [8]. They showed that when **26** was treated with an excess of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ (**27**) two acetylide groups were added to the rhodium centre to give the complex $[\text{Rh}(\text{PPh}_3)_2(-\text{C}\equiv\text{CC}_6\text{H}_5)_2(\text{SnMe}_3)]$ (**28**); the IR spectrum of **28** shows two $\nu(\text{C}\equiv\text{C})$ stretching frequencies ($\nu(\text{C}\equiv\text{C})$ 2082, 2073 cm^{-1}) [8], which indicates a *cis*-configuration for the acetylide units in **28**. Comparison of their data with those for the precipitate obtained in the reaction of **26** and **3** indicated that the precipitate should be formulated as $[-\text{Rh}(\text{PPh}_3)_2(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{C-})(\text{SnMe}_3)-]_n$ (**29**). A single broad absorption is observed in the $\nu(\text{C}\equiv\text{C})$ stretching region (2080 cm^{-1}) of the IR spectrum of **29**, only slightly shifted from the major band in the IR spectrum of **28**. Microanalytical data correspond to the repeat unit $[-\text{Rh}(\text{PPh}_3)_2(-\text{C}\equiv\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{C-})(\text{SnMe}_3)-]$, while the FAB mass spectrum of **29** has its major peak at 991 amu, which also corresponds to the repeat unit of the polymer.

The reaction between **26** and **3** was repeated under a variety of reaction conditions and with various reactant ratios; however, the only species isolated on work up were unchanged starting material and the polymeric species **29**. This somewhat surprising result implies that the polymerization must be strongly favoured.

The extent to which the above polymer could be characterized was limited by its insolubility in all common organic solvents. This insolubility presumably also

means that **29** has a relatively low molecular mass. The solubility of these polymeric complexes could be enhanced by varying the substituents on the phosphine ligands. Complexes with alkyl-substituted phosphine ligands in general are more soluble than those with aryl phosphine ligands. A readily available alkyl phosphine complex is $[\text{Rh}(\text{PMe}_3)_4\text{Cl}]$ (**30**) [9]. The reaction between this species and bis-trimethylstannyl(acetylide) complexes appears to proceed in much the way outlined above for $\text{Rh}(\text{PPh}_3)_3\text{Cl}$. Careful treatment of **30** with one equivalent of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ (**27**) results in the formation of $[\text{Rh}(\text{PMe}_3)_4(-\text{C}\equiv\text{CC}_6\text{H}_5)]$ (**31**), a known complex [10]. Further treatment of **31** with an excess of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ causes loss of one phosphine ligand from the metal centre of **31** with subsequent oxidative addition of a further molecule of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ to the metal centre to give *mer,trans*- $[\text{Rh}(\text{PMe}_3)_3(-\text{C}\equiv\text{CC}_6\text{H}_5)_2(\text{SnMe}_3)]$ (**32**). Interestingly this molecule adopts a *trans*-configuration in contrast to the compound **28** in which the acetylide ligands are in a *cis*-configuration. The identity of **32** was confirmed by its NMR data. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two signals, a doublet of doublets and a doublet of triplets which is consistent with the proposed *mer,trans* geometry. The equivalence of the phenylacetylide ligands is apparent from the observation of only one $\nu(\text{C}\equiv\text{C})$ stretch in the IR spectrum of **32**. The presence of terminal Me_3Sn groups is clearly indicated by the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Compound **32** is closely related to the species *mer,trans*- $[\text{Rh}(\text{PMe}_3)_3(-\text{C}\equiv\text{CC}_6\text{H}_5)_2(\text{H})]$ (**33**) which differs from **32** only in the replacement of a trimethylstannyl moiety by a proton [11]. This species is produced by the oxidative addition of $\text{HC}\equiv\text{CC}_6\text{H}_5$ (**34**) to the compound **31**, whereas **32** is obtained by the addition of $\text{Me}_3\text{SnC}\equiv\text{CC}_6\text{H}_5$ to the latter.

As **32** contains a *trans*-arrangement of phenylacetylide ligands, it is again a suitable repeat unit for rigid rod oligomers. Treatment of $[\text{Rh}(\text{PMe}_3)_4\text{Cl}]$ with one equivalent of $\text{Me}_3\text{SnC}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{CSnMe}_3$ did indeed produce the expected oligomer *mer,trans*- $[\text{Rh}(\text{PMe}_3)_3(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{C-})(\text{SnMe}_3)]_n$ (**35**) as an insoluble white powder. The reaction presumably proceeds through the intermediate, $\text{Rh}(\text{PMe}_3)_4(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p\text{-C}\equiv\text{CSnMe}_3)]$ (**36**) which oligomerises by oxidative addition of the $\text{Me}_3\text{SnC}\equiv\text{C-}$ bond to the rhodium centre. Many unsuccessful attempts were made to isolate the intermediate **36**. The oligomer **35** was characterized in the usual way; again FAB mass spectroscopy proved to be a useful tool since it showed a major peak for the repeat unit of the polymer at 695 amu. The low solubility of **35** was disappointing, and indicates that production of soluble polymeric species may only be possible when larger chain alkyl phosphines, such as tri-*n*-butylphosphine, are present. Similar properties of this oligomer prepared by a different route were reported by Marder et al. [11].

We have demonstrated that a series of group 9 or 10 metal σ -acetylide complexes are now accessible in good quantities by use of bis(trimethylstannyl) acetylide complexes as precursors. A detailed investigation of their physical properties is currently in progress.

Experimental

General. NMR spectra were recorded on a Bruker AM-400 spectrometer. ^{31}P NMR spectra were referenced to external trimethylphosphite and the ^1H NMR spectra were referenced to solvent resonances. The IR spectra were recorded on a

Perkin Elmer-1710 Fourier Transform spectrometer. The molecular weights were determined by GPC methods [12].

Synthesis. The platinum metal dihalide complexes $\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2$ (**6**) and $\text{Pt}(\text{As}^n\text{Bu}_3)_2\text{Cl}_2$ (**4**) were prepared by published methods [13–14]. Alkyne ligands (**1–3**) were prepared by published procedures [15–18] with some minor modifications.

$\text{trans-}[-\text{Pt}(\text{As}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{C-})]_n$ (**5**). To a stirred solution of $\text{Pt}(\text{As}^n\text{Bu}_3)_2\text{Cl}_2$ (0.302 g, 0.4 mmol) and the bis-SnMe₃ acetylide **1** (0.180 g, 0.4 mmol) in toluene (30 ml) under nitrogen was added a catalytic amount (~ 3 mg) of CuI. The yellow solution was stirred at 50°C for 12 h and toluene was then removed under vacuum. The residue was dissolved in dichloromethane and the solution passed through a short alumina column. The solvent was removed *in vacuo* and the pale yellow product was purified by repeated precipitation from dichloromethane by addition of methanol. Yield 90% (0.3 g). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2096 cm⁻¹. Anal. Found: C, 50.52; H, 7.16. C₃₄H₅₈As₂Pt calc.: C, 50.30; H, 7.20%. Mw = 120000 ($n_w = 148$). The other platinum-containing polymeric complexes were prepared by following this general synthetic procedure.

$[-\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{C}\equiv\text{C-p-C}_6\text{H}_2(\text{CH}_3)_2\text{C}\equiv\text{C-}]_n$ (**7**). Pale yellow solid, 90% yield. IR (dichloromethane) $\nu(\text{C}\equiv\text{C})$ 2091 cm⁻¹. Anal. Found: C, 57.13; H, 7.96. C₃₆H₆₂P₂Pt calc.: C, 57.35; H, 8.29%. Mw = 82000 ($n_w = 109$).

$\text{trans-}[-\text{Pd}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{C-})]_n$ (**9**). To a stirred solution of $\text{Pd}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2$ (0.582 g, 1 mmol) and the bis-SnMe₃ acetylide (**1**) (0.450 g, 1 mmol) in toluene (60 ml) under nitrogen, catalytic amounts (~ 8 mg) of CuI and PⁿBu₃ (40 mg) were added. The yellow solution was stirred at 30°C for 3 h and the mixture was passed through a short alumina column. The solvent was removed *in vacuo* and the yellow product was purified by repeated precipitation from toluene by addition of methanol. Yield 91% (0.577 g). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2096 cm⁻¹. Anal. Found: C, 63.98; H, 9.34; P, 9.63. C₃₄H₅₈P₂Pd calc.: C, 64.28; H, 9.20; P, 9.75%. Mw = 30000 ($n_w = 47$).

$[-\text{Ni}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{C-})]_n$ (**11**). A mixture of *trans*-dichloro-bis(tri-*n*-butylphosphine)nickel(II), NiCl₂(PⁿBu₃)₂, (0.533 g, 1 mmol), bis(trimethylstannylethynyl)benzene (0.450 g, 1 mmol) and CuI (5 mg) was placed in a 100 cm³ Schlenk flask containing 50 cm³ of dry toluene. The solution was stirred at 50°C for 2 h under nitrogen. The reaction mixture was cooled to room temperature and passed through an alumina column with toluene as eluant. The yellow product obtained after removing toluene *in vacuo* was purified by repeated precipitation from toluene by addition of methanol. The product was obtained as a yellow solid in 90% yield (0.530 g). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2075 cm⁻¹. Anal. Found: C, 69.98; H, 10.09; P, 10.45. C₃₄H₅₈P₂Ni calc.: C, 69.51; H, 9.95; P, 10.54%. Mw = 21000 ($n_w = 36$).

$\text{trans-}[\text{Pd}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{CSnMe}_3)]$ (**12**), $\text{trans-}[\text{Pd}(\text{P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{CH})_2]$ (**13**). A solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)palladium(II) (0.116 g, 0.2 mmol) in toluene (20 cm³) was added dropwise to a solution of bis(trimethylstannylethynyl)-*p*-benzene (**1**) (0.180 g, 0.4 mmol) in toluene (25 cm³). The solution was stirred at 20°C for 1 h under nitrogen and then passed through a short alumina column with toluene as eluant. The bright yellow product obtained after removal of toluene *in vacuo* was purified by chromatography on alumina with toluene/hexane (1:2) mixture. The bis-SnMe₃ derivative **12**

was hydrolysed during the chromatography on alumina to the terminal-H complex, *trans*-[Pd(PⁿBu₃)₂(-C≡C-*p*-C₆H₄-*p*-C≡CH)₂] (**13**). Compound **13**: Yellow solid, 0.140 g, 90% yield. IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2096 cm⁻¹; $\nu(\text{C}\equiv\text{H})$ 3280 cm⁻¹. Anal. Found: C, 69.08; H, 8.51; P, 7.94. C₄₄H₆₄P₂Pd calc.: C, 69.41; H, 8.47; P, 8.13%. Mass spectrum (+FAB) 761. The platinum σ -bisacetylide complexes **14** and **15** were obtained by this route as well.

trans-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C≡CSnMe₃)₂] (**14**), *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C≡CH)₂] (**15**). The bis-SnMe₃ derivative **14** was also hydrolysed during the purification process on alumina to the terminal-H complex, *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C≡CH)₂] (**15**). Compound **15**: Bright yellow solid, 90% yield. IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2098; $\nu(\text{C}\equiv\text{H})$ 3285 cm⁻¹. Anal. Found: C, 62.10; H, 7.61; P, 7.19. C₄₄H₆₄P₂Pt calc.: C, 62.17; H, 7.59; P, 7.29%. Mass spectrum (+FAB) 850.

trans-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C₆H₄-*p*-C≡CSnMe₃)₂] (**16**), *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C₆H₄-*p*-C≡CH)₂] (**17**). A solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)platinum(II) (0.134 g, 0.2 mmol) in toluene (20 cm³) was added dropwise to a solution of bis(trimethylstannylethynyl)-*p*-biphenyl (**3**) (0.210 g, 0.4 mmol) in toluene (25 cm³). The solution was stirred at 80°C for 12 h under nitrogen and then passed through a short alumina column with toluene as eluant. The bright yellow product obtained after removal of the toluene *in vacuo* was purified by chromatography on alumina with toluene/hexane (1:2) mixture. The bis-SnMe₃ derivative was hydrolysed during the chromatography process on alumina to the terminal-H complex, *trans*-[Pt(PⁿBu₃)₂(-C≡C-*p*-C₆H₄C₆H₄-*p*-C≡CH)₂] and hence it was not possible to isolate the bis-SnMe₃ derivative. (Yield: Compound **17**: 0.170 g, 85%.) IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2097; $\nu(\text{C}\equiv\text{H})$ 3287 cm⁻¹. Anal. Found: C, 66.97; H, 7.27; P, 6.14. C₅₆H₇₂P₂Pt calc.: C, 67.11; H, 7.24; P, 6.18%.

trans-[ClPd(PⁿBu₃)₂C≡C-*p*-C₆H₄C≡CPd(PⁿBu₃)₂Cl] (**18**). A solution of bis(trimethylstannyl-ethynyl)-*p*-benzene (0.045 g, 0.1 mmol) in toluene (10 cm³) was added dropwise to a solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)palladium (II) (0.116 g, 0.2 mmol) in toluene (25 cm³) containing PⁿBu₃ (5 mg). The mixture was stirred at 30°C for 2 h under nitrogen, then passed through a short alumina column. The yellow product obtained after removal of the toluene *in vacuo* was purified by chromatography on alumina with toluene/hexane (1:2) mixture as eluant. The solid product was then recrystallized from ethanol to give compound **18** as bright yellow crystals (0.100 g, 85% yield). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2117 cm⁻¹. Anal. Found: C, 56.89; H, 9.37; Cl, 5.98; P, 10.57. C₅₈H₁₁₂Cl₂P₄Pd₂ calc.: C, 57.23; H, 9.28; Cl, 5.83; P, 10.18%. Mass spectrum (+FAB) 1217.

trans-[ClPt(PⁿBu₃)₂C≡C-*p*-C₆H₄C≡CPl(PⁿBu₃)₂Cl] (**19**). A solution of bis(trimethylstannylethynyl)-*p*-benzene (0.045 g, 0.1 mmol) in toluene (10 cm³) was added dropwise to a solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)platinum(II) (0.134 g, 0.2 mmol) in toluene (25 cm³). The solution was stirred at 50°C for 4 h under nitrogen then cooled to room temperature and passed through a short alumina column with toluene as eluant. The yellow product obtained after removal of the toluene *in vacuo* was purified by chromatography on alumina with toluene/hexane (1:2) as eluant. It was then recrystallized from ethanol to give compound **19** as yellow crystals (0.125 g, 90% yield). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2118 cm⁻¹. Anal. Found: C, 50.13; H, 8.02; Cl, 5.12; P, 8.84. C₅₈H₁₁₂Cl₂P₄Pt₂ calc.: C, 49.96; H, 8.10; Cl, 5.08; P, 8.88%. Mass spectrum (+FAB) 1394.

$\text{trans-[ClPt(P}^n\text{Bu}_3)_2\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-p-C}\equiv\text{C}]\text{Pt(P}^n\text{Bu}_3)_2\text{Cl}]$ (**20**). Compound **20** was prepared on a similar scale by the method as described above. It was obtained as bright yellow crystals in 90% yield. IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2118 cm^{-1} . Anal. Found: C, 51.85; H, 7.89; Cl, 4.93; P, 8.56. $\text{C}_{64}\text{H}_{116}\text{Cl}_2\text{P}_4\text{Pt}_2$ calc.: C, 52.27; H, 7.95; Cl, 4.82; P, 8.42%. Mass spectrum (+ FAB) 1470.

$\text{trans-[ClPt(P}^n\text{Bu}_3)_2\text{C}\equiv\text{C-p-C}_6\text{H}_2(\text{CH}_3)_2\text{C}\equiv\text{C}]\text{Pt(P}^n\text{Bu}_3)_2\text{Cl}]$ (**21**). To a solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)platinum(II) (0.353 g, 0.528 mmol) in toluene (20 cm^3), a solution of $\text{Me}_3\text{SnC}\equiv\text{C-p-C}_6\text{H}_2(\text{CH}_3)_2\text{C}\equiv\text{CMe}_3\text{Sn}$ (**2**) (0.101 g, 0.211 mmol) in toluene (20 cm^3) was added dropwise at 0°C. The solution was stirred for 1 h at 0°C then warmed to room temperature and the toluene removed *in vacuo*. The residue was dissolved in dichloromethane and the solution passed through a column of alumina then concentrated to ca. 5 ml and a large excess of methanol (200 cm^3) was added. The cloudy solution was filtered through Celite to give a clear yellow solution. It was precipitated from dichloromethane by addition of methanol at -78°C, and isolated as an off-white solid in 69% yield. IR (dichloromethane) $\nu(\text{C}\equiv\text{C})$ 2114 cm^{-1} . Anal. Found: C, 50.96; H, 7.93. $\text{C}_{60}\text{H}_{116}\text{Cl}_2\text{P}_2\text{Pt}$ calc.: C, 50.68; H, 8.22%. Mass spectrum (+ FAB) 1423.

$\text{trans-[ClPt(P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-p-C}\equiv\text{C-})\text{Pt(P}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}\equiv\text{C-})\text{Pt(P}^n\text{Bu}_3)_2\text{Cl}]$ (**22**). A solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)platinum(II) (0.134 g, 0.2 mmol) in toluene (20 cm^3) was added dropwise to a solution of bis(trimethylstannyl-ethynyl)-*p*-benzene (0.180 g, 0.4 mmol) in toluene (25 cm^3). The solution was stirred at 20°C for 1 h under nitrogen. The reaction mixture was then added dropwise to a solution of *trans*-dichloro-bis(tri-*n*-butylphosphine)-platinum(II) (0.268 g, 0.4 mmol) in toluene (20 cm^3) and was heated to 50°C for 4 h. After cooling to room temperature, it was passed through a short alumina column. The yellow solid obtained after the evaporation of toluene *in vacuo* was further purified on alumina using dichloromethane/hexane (1:2) mixture as an eluant. The pale yellow solid obtained was recrystallized from ethanol. Yield 0.3 g (70%). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2114 cm^{-1} . Anal. Found: C, 51.94; H, 8.01; Cl, 3.39; P, 8.81. $\text{C}_{92}\text{H}_{170}\text{Cl}_2\text{P}_6\text{Pt}_3$ calc.: C, 52.16; H, 8.09; Cl, 3.35; P, 8.77%. Mass spectrum (+ FAB) 2118.

$\text{trans[ClPt(As}^n\text{Bu}_3)_2\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-p-C}\equiv\text{C}]\text{Pt(As}^n\text{Bu}_3)_2\text{Cl}]$ (**23**). Compound **23** was prepared by the method as described above for compound **19**. It was obtained as bright yellow crystals in 90% yield. IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2119 cm^{-1} . Anal. Found: C, 43.92; H, 7.09; Cl, 4.41. $\text{C}_{58}\text{H}_{112}\text{Cl}_2\text{As}_4\text{Pt}_2$ calc.: C, 44.36; H, 7.18; Cl, 4.51%. Mass spectrum (+ FAB) 1570.

$\text{trans-[ClPt(As}^n\text{Bu}_3)_2\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-p-C}\equiv\text{C-Pt(As}^n\text{Bu}_3)_2\text{Cl}]$ (**24**). Compound **24** was prepared by the method as described above for compound **19**. It was obtained as yellow crystals in 90% yield. IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2119 cm^{-1} . Anal. Found: C, 45.91; H, 7.02; Cl, 4.35. $\text{C}_{64}\text{H}_{116}\text{Cl}_2\text{As}_4\text{Pt}_2$ calc.: C, 46.69; H, 7.10; Cl, 4.31%.

$\text{trans-[ClPt(As}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-p-C}\equiv\text{C-})\text{Pt(As}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-p-C}\equiv\text{C-})\text{Pt(As}^n\text{Bu}_3)_2(-\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-p-C}\equiv\text{C-})\text{Pt(P}^n\text{Bu}_3)_2\text{Cl}]$ (**25**). A solution of *trans*-[ClPt(AsⁿBu₃)₂C≡C-*p*-C₆H₄-*p*-C≡C]Pt(AsⁿBu₃)₂Cl] (0.314 g, 0.2 mmol) in toluene (20 cm^3) was added dropwise to a solution of bis(trimethylstannyl-ethynyl)-*p*-benzene (0.180 g, 0.4 mmol) in toluene (25 cm^3). The mixture was stirred at 20°C for 2 h under nitrogen then added dropwise to a solution of *trans*-dichloro-bis(tri-*n*-butylarsine)platinum(II) (0.302 g, 0.4 mmol) in toluene (20 cm^3). The mixture

was heated to 50°C for 4 h then allowed to cool to room temperature, and the solution passed through a short alumina column. The yellow solid obtained was further chromatographed on alumina with dichloromethane/hexane (1:2) mixture as eluant. The pale yellow solid obtained was recrystallized from ethanol. Yield 0.45 g (70%). IR (toluene) $\nu(\text{C}\equiv\text{C})$ 2110 cm^{-1} . Anal. Found: C, 47.62; H, 7.01; Cl, 2.27. $\text{C}_{126}\text{H}_{228}\text{Cl}_2\text{As}_8\text{Pt}_4$ calc.: C, 47.38; H, 7.20; Cl, 2.22%. Mass spectrum (+ FAB) 3193.

trans-[*-Rh*(PPh₃)₂(SnMe₃)(-C≡C-*p*-C₆H₄-C₆H₄-*p*-C≡C-)]_n (**29**). To a solution of Rh(PPh₃)₃Cl (0.250 g, 0.27 mmol) in toluene (10 cm³) was added a solution of Me₃SnC≡C-*p*-C₆H₄-*p*-C₆H₄-*p*-C≡CSnMe₃ (0.14 g, 0.27 mmol) in toluene (5 cm³). The mixture was stirred for 12 h at 30°C during which a dark red precipitate separated. The solid was filtered off and washed repeatedly with toluene and ether then dried *in vacuo*. Compound **29** was obtained as a dark red solid (0.19 g, 72%). IR (Nujol) $\nu(\text{C}\equiv\text{C})$ 2080 cm^{-1} . Anal. Found: C, 66.9; H, 4.4; P, 6.0. $\text{C}_{55}\text{H}_{47}\text{P}_2\text{RhSn}$ calc.: C, 66.6; H, 4.7; P, 6.3%.

mer,trans-[*-Rh*(PMe₃)₃(SnMe₃)(-C≡CC₆H₅)₂]_n (**32**). To a suspension of Rh(PMe₃)₄Cl (0.25 g, 0.31 mmol) in THF (10 cm³), a solution of Me₃SnC≡CC₆H₅ (0.20 g, 0.77 mmol) in THF (5 cm³) was added over a period of 10 min. The mixture was then refluxed for 3 h then allowed to cool to room temperature and filtered. The filtrate was evaporated *in vacuo* and the residue recrystallized from THF-hexane (5 cm³, 1:5) at -30°C to afford white crystals of compound **32** (0.18 g, 84%). IR (Nujol) $\nu(\text{C}\equiv\text{C})$ 2093 cm^{-1} . Anal. Found: C, 48.7; H, 6.8; P, 13.5. $\text{C}_{28}\text{H}_{46}\text{P}_3\text{RhSn}$ calc.: C, 48.2; H, 6.6; P, 13.3%. ³¹P{¹H} (CD₂Cl₂): δ -8.8 (dd, *J*(Rh-P) 91, *J*(P-P) 31 Hz), 26.8 (dt, *J*(Rh-P) 84, *J*(P-P) 31 Hz). ¹H NMR (CD₂Cl₂): 7.16, 7.04 (m, C₆H₅), 1.63 (vt, *J*(P-H) 3 Hz, 2 PMe₃), 1.54 (d, *J*(P-H) 8 Hz, PMe₃), 0.23 (d, *J*(Sn-H) 19 Hz, SnMe₃).

trans-[*-Rh*(PMe₃)₃(SnMe₃)(-C≡C-*p*-C₆H₄-*p*-C₆H₄-*p*-C≡C-)]_n (**35**). To a solution of Rh(PMe₃)₄Cl (0.250 g, 0.31 mmol) in THF (10 cm³), Me₃SnC≡C-*p*-C₆H₄-C₆H₄-*p*-C≡CSnMe₃ (0.16 g, 0.31 mmol) in THF (5 cm³) was added during 10 min. The mixture was refluxed for 3 h during which a pale orange precipitate separated. The solid was filtered off, was washed repeatedly with THF and ether then dried *in vacuo*. Compound **35** was obtained as a pale orange powder (0.17 g, 77%). IR (Nujol) $\nu(\text{C}\equiv\text{C})$ 2086 cm^{-1} . Anal. Found: C, 48.1; H, 6.6; P, 13.1. $\text{C}_{28}\text{H}_{44}\text{P}_3\text{RhSn}$ calc.: C, 48.4; H, 6.4; P, 13.4%.

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