Synthesis of Monomeric and Oligomeric Bis(acetylide) Complexes of Platinum and Rhodium

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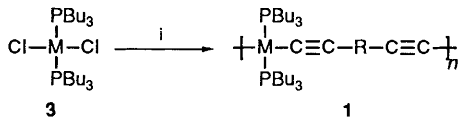
Treatment of the complexes *trans*-[M(PBu$_3$)$_2$Cl$_2$] (M = Ni, Pd or Pt) with one equivalent of the reagent Me$_3$SnC≡C–R–C≡CSnMe$_3$ (R = *p*-C$_6$H$_4$) affords the polymeric species *trans*-[–M(PBu$_3$)$_2$-C≡C–R–C≡C–]$_n$, whereas if two equivalents of the tin reagent are used in this reaction, when M = Pt, the complex *trans*-[Me$_3$SnC≡C–R–C≡C–Pt(PBu$_3$)$_2$–C≡C–R–C≡CSnMe$_3$] may be isolated, a precursor for further syntheses; the complex *mer-trans*-[Rh(PMe$_3$)$_3$(SnMe$_3$)(C≡CPh)$_2$] has been prepared by the addition of Me$_3$SnC≡CPh to [Rh(PMe$_3$)$_4$][Cl], and this latter species, when treated with Me$_3$SnC≡C–R′–C≡CSnMe$_3$ (R′ = *p*-C$_6$H$_4$–C$_6$H$_4$–*p*), affords the oligomeric compound *mer-trans*-[–Rh(PMe$_3$)$_3$(SnMe$_3$)–C≡C–R′–C≡C–]$_n$.

There is continuing interest in the synthesis and reactivity of transition metal σ-acetylide complexes. In particular polymeric species of the type [–M(PBu$_3$)$_2$–C≡C–R–C≡C–]$_n$ **1** (M = Ni, Pd or Pt), first developed by Takahashi and coworkers,[1] are now attracting attention because of their nonlinear optical[2] and liquid crystal properties.[3] However, synthetic methods for these polymeric compounds are limited in that the initial synthetic precedents[1] require amine solvents, in which many transition metal complexes are unstable. This limitation is presumably one of the major reasons why polymeric species of the type **1** have only been isolated for the Group 10 metals.

We have now found that the bis-trimethylstannyl(acetylide) species Me$_3$SnC≡C–R–C≡CSnMe$_3$ (R = *p*-C$_6$H$_4$) **2** is a very good precursor for the synthesis of a variety of linked transition metal σ-acetylide complexes. When the compounds *trans*-[M(PBu$_3$)$_2$Cl$_2$] **3a–c** are treated with one equivalent of **2** the metal poly-yne species **1** are produced (Scheme 1), in yields comparable to those reported for literature methods.[1]

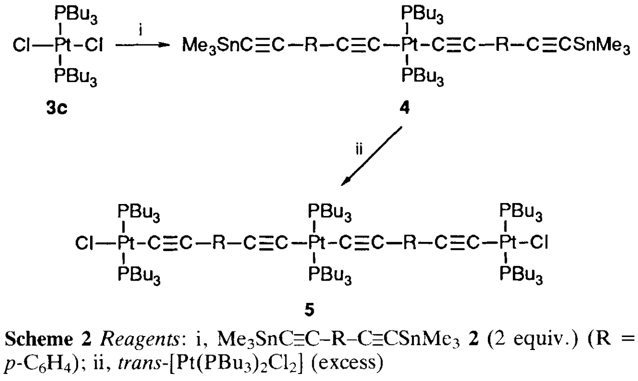
Electron microscopy studies have shown that the morphology of the polymeric complexes produced in this way is identical to that of samples produced by literature routes.[4] However, the weight-average molecular weights for the polymeric species produced by this new route, which have been determined by a variety of methods,[4] are found to be *ca.* 100 000, which is somewhat higher than those reported for samples synthesised previously (*ca.* 70 000).[1]



3 **1**

a M = Ni
b M = Pd
c M = Pt

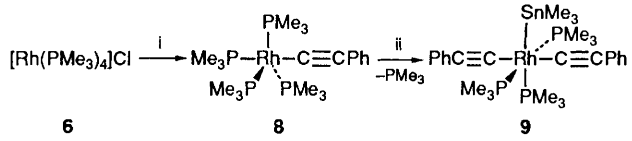
Scheme 1 *Reagents*: i, Me$_3$Sn–C≡C–R–C≡CSnMe$_3$ **2** (1 equiv.) (R = *p*-C$_6$H$_4$); M = Ni (**3a**), Pd (**3b**) or Pt (**3c**)



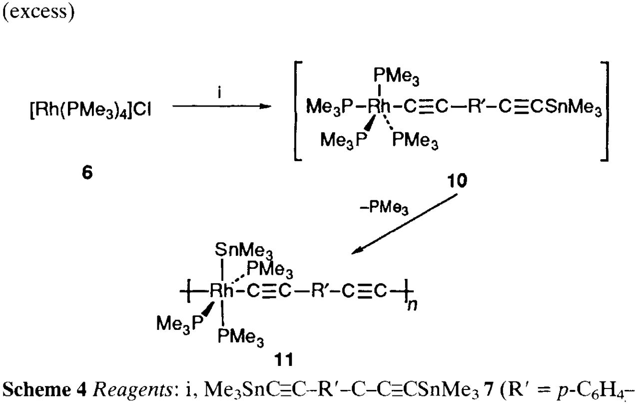
Scheme 2 *Reagents*: i, Me$_3$SnC≡C-R-C≡CSnMe$_3$ **2** (2 equiv.) (R = *p*-C$_6$H$_4$); ii, *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] (excess)

By varying the stoichiometry of these reactions a family of complexes containing different numbers of metal atoms may be synthesised (Scheme 2), and the polymerisation reactions put on a more rational basis. Treatment of *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] with two equivalents of the bis(acetylide) **2** affords the species **4** containing one platinum atom ligated by two *trans*-acetylide groups and trimethylstannyl acetylide moieties. Compound **4** decomposes during any attempted purification procedures and so this species is best used *in situ*. The trimethyltin groups in **4** are sites of further reactivity, and addition of an excess of *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] to **4** results in the loss of two equivalents of trimethyltin chloride and the production of complex **5** containing three platinum atoms linked together by two di-acetylide units. Alternatively treatment of compound **4** with only one equivalent of *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] gives the polymer [–Pt(PBu$_3$)$_2$–C≡C–R–C≡C–]$_n$ in good yield.

To determine whether the methodology that we have developed is applicable for the synthesis of complexes containing transition metals from other groups of the periodic table, the reaction between trimethylstannylacetylide species and [Rh(PMe$_3$)$_4$]Cl **6** was investigated. In order to identify the 'monomer unit' of any oligomer produced, the first reaction undertaken was between the mono-acetylide species Me$_3$SnC≡CPh **7** and compound **6**, which proceeds as shown in Scheme 3. Treatment of **6** with only one equivalent of **7** affords the known compound [Rh(PMe$_3$)$_4$(C≡CPh)] **8**.[5] However, when an excess of **7** is used in this reaction the new complex *mer-trans*-[Rh(PMe$_3$)$_3$(SnMe$_3$)(C≡CPh)$_2$] **9** is produced in high yield, presumably *via* oxidative addition of a second molecule of **7** to compound **8**. The complex **9** is well



Scheme 3 *Reagents*: i, Me$_3$SnC≡CPh (1 equiv.); ii, Me$_3$SnC≡CPh (excess)



Scheme 4 *Reagents*: i, Me$_3$SnC≡C-R′-C-C≡CSnMe$_3$ **7** (R′ = *p*-C$_6$H$_4$–C$_6$H$_4$-*p*)

characterised by its spectroscopic and analytical data,† and is related to the compound *mer-trans*-[Rh(PMe_3)$_3$(H)C≡CPh)$_2$] synthesised by Marder and coworkers.[6]

When **6** is instead treated with one equivalent of the bis(acetylide) $Me_3SnC{\equiv}C{-}R'{-}C{\equiv}CSnMe_3$ (R′ = *p*-C_6H_4–C_6H_4-*p*), in an attempt to synthesise the dimetallic species [$Me_3SnC{\equiv}C{-}R'{-}C{\equiv}CRh(PMe_3)_4$] **10** (Scheme 4) the species **10** may be detected in solution by spectroscopic means, but slowly oligomerises by oxidative addition of the Me_3Sn group of one molecule to the rhodium centre of another. The resulting polymeric species *mer-trans*-[–Rh(PMe_3)$_3$-($SnMe_3$)(C≡C–R′–C≡C)–]$_n$ **11** has been characterised by its IR spectrum and analytical data.† The FAB mass spectrum of **11** is also very diagnostic as it shows a major peak for the 'monomer unit' of the polymer [Rh(PMe_3)$_3$($SnMe_3$)-(C≡C–R′–C≡C)], minus the trimethyltin group, at *m*/*z* 533.

In conclusion we have developed a new flexible synthetic route to a variety of linked transition metal σ-acetylide complexes, which also allows the incorporation of a main group element at the transition metal centre in certain cases. We are currently further investigating the generality of this methodology and the physical properties of the new complexes produced.

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† *Selected spectroscopic data*: for **5** IR (Nujol) 2118s cm^{-1} ($\nu_{C\equiv C}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 5.2 (J_{Pt-P} 1184 Hz, 2 PBu_3) and 3.1 (J_{Pt-P} 1506 Hz, PBu_3); ^1H NMR δ 7.06 (C_6H_4); 1.98, 1.54, 1.43 and 0.91 (PBu_3); FAB MS, *m*/*z* 2118.

9: IR (Nujol) 2093s cm^{-1} ($\nu_{C\equiv C}$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −8.8 (dd, J_{Rh-P} 91, $^2J_{P-P}$ 31 Hz) and −26;8 (dt, J_{Rh-P} 84, $^2J_{P-P}$ 31 Hz); ^1H NMR (CD_2Cl_2) δ 7.16, 7.04 (2 pH), 1.63 (virtual t, $^2J_{P-H}$ 3 Hz, 2 PMe_3), 1.54 (d, $^2J_{P-H}$, 8 Hz, PMe_3) and 0.23 (J_{Sn-H} 19 Hz, Me_3Sn).

11: IR (Nujol) 2086s br. cm^{-1} ($\nu_{C\equiv C}$); the low solubility of this species in common NMR solvents has frustrated attempts to obtain NMR spectra of this compound.