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Preliminary communication

Synthesis of linked metal acetylide complexes for nonlinear optics

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Abstract

Treatment of [Mn(CO)$_5$Br] (1) with a slight excess of Me$_3$SnC≡CPh affords the known species [(CO)$_5$Mn(C≡CPh)] (2), whereas reaction between 1 and Me$_3$SnC≡CRC≡CSnMe$_3$ (R = p-C$_6$H$_4$–C$_6$H$_4$) gives the bimetallic complex [(CO)$_5$MnC≡CRC≡CSnMe$_3$] (3). This latter species is a good precursor for other syntheses, and treatment of 3 with a further equivalent of 1 gives [(CO)$_5$MnC≡CRC≡CMn(CO)$_5$] (4), while 3 with *trans*-[Pd(PBu$_3$)$_2$Cl$_2$] affords [(CO)$_5$MnC≡CRC≡CPd(PBu$_3$)$_2$Cl] (5).

Organic molecules and polymers which exhibit second- and third-order nonlinear optical properties continue to attract great interest [1]. One particular class of compound which has been much investigated recently is donor–acceptor substituted diphenyl acetylenes 4-D-C$_6$H$_4$C≡CC$_6$H$_4$-4-A and their higher oligomers 4-D-C$_6$H$_4$(C≡C)$_n$C$_6$H$_4$-4-A, which show large χ^2 values [2]. It has also been demonstrated that transition metal σ-acetylide complexes, when suitably substituted, may show large second-order optical nonlinearities [3,4]. We have recently described new synthetic routes to monomeric and oligomeric σ-acetylide species [5], and in this paper we show how our synthetic precedents may be used to obtain compounds of the type D-C≡CRC≡C-A, where D and A are electron donating and accepting transition metal fragments, respectively. The obvious relationship between such species and the donor–acceptor acetylenes suggests that such transition metal containing species may also show interesting nonlinear optical behaviour.

A suitable choice for the electron accepting metal fragment would involve an early transition metal centre with associated π-acid ligands, such as Mn(CO)$_5$, whereas the donor fragment should contain an electron rich metal ligated by Lewis base type ligands, such as Rh(PR$_3$)$_4$ or Pt(PR$_3$)$_2$Cl. A preliminary study indicated that treatment of [Mn(CO)$_5$Br] (1) with a slight excess of Me$_3$SnC≡CPh afforded, after appropriate work up, the known complex [Mn(CO)$_5$(C≡CPh)] (2) [6,7], in 42% yield (Scheme 1). This result is in contrast with the reported reaction between 1 and AgC≡CPh which yields only decomposition products [7], and the relatively high yield make this reaction an attractive route to compound 2. In a similar manner the diacetylide reagent Me$_3$SnC≡CRC≡CSnMe$_3$ (R = p-C$_6$H$_4$) reacts with 1 to give the

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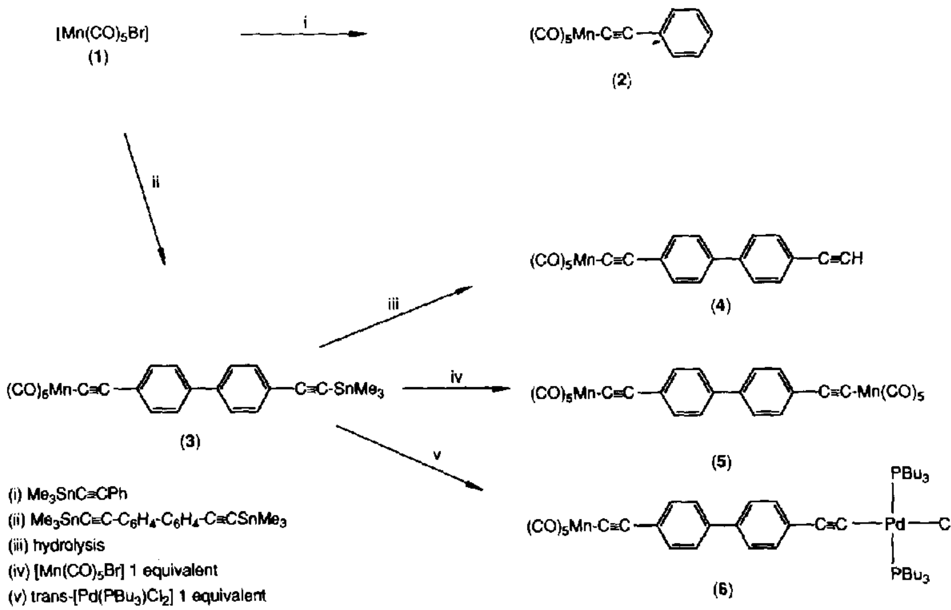

Scheme 1. The formation of linked metal acetylide complexes.

species [(CO)$_5$MnC≡CRC≡CSnMe$_3$] (**3**), when a slight excess of the tin reagent is employed (Scheme 1). The compound **3** is fully characterised by its spectroscopic data [8*]. In the IR spectrum an absorption is observed at 2137 cm^{-1} for the C≡C stretch associated with the trimethyltin acetylide functionality; the corresponding stretch in the free ligand occurs at 2135 cm^{-1}, in addition to the other expected carbonyl and acetylide stretches. The presence of a Me$_3$Sn group is clearly seen in the ^{1}H NMR spectrum of **3**.

Compound **3** has reactivity associated with its Me$_3$Sn group and so may be used as a precursor to other compounds. Hydrolysis of the trimethylstannyl group occurs readily and simply filtering a CH$_2$Cl$_2$ solution of **3** through a pad of silica gel affords the compound [(CO)$_5$MnC≡CRC≡CH] (**4**), which shows a ≡CH stretch in its IR spectrum, and two (AB)$_2$ patterns in its ^{1}H NMR spectrum, both observations being consistent with the proposed formulation. Treatment of **3** with one equivalent of **1** results in loss of the trimethylstannyl moiety and the formation of [(CO)$_5$MnC≡CRC≡CMn(CO)$_5$] (**5**), which may be purified by chromatography and crystallisation. The species **5** is again well characterised by its spectroscopic data [8]. The ^{1}H NMR spectrum of **5** is particularly informative as the aromatic protons appear as a simple (AB)$_2$ system, confirming the symmetrically substituted nature of the acetylene grouping. Compound **3** may also be used to synthesise the required donor–acceptor molecules. Treatment of **3** with one equivalent of *trans*-[Pd(PBu$_3$)$_2$Cl$_2$], followed by low temperature column chromatography and recrys-

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* Reference number with asterisk indicates a note in the list of references.

tallisation afforded the species [(CO)$_5$MnC≡CRC≡CPd(PBu$_3$)$_2$Cl] (**6**), in moderate yield (Scheme 1).

We are currently trying to extend our methodology to the incorporation of other transition metal fragments in similar donor–acceptor complexes, and to investigation of the properties of the species obtained.

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8 Spectroscopic data for **3**: IR (hexane) cm^{-1}, ν(CO), 2144sh, 2044s, 2009s, ν(C≡C), 2137m, 2117m, ^{1}H NMR (CD$_2$Cl$_2$), δ 0.36 (s, 9H, Me$_3$Sn), 7.04–7.92 (m, 8H, C$_6$H$_4$). **4**: IR (hexane) cm^{-1}, ν(CO), 2138w, 2043s, 2008s. ν(C≡C) 2114m; ν(≡CH) 3314 s. ^{1}H NMR (CD$_2$Cl$_2$) δ 3.23 (s, 1H, ≡CH), 7.40, 7.42 [(AB)$_2$, 4H, C$_6$H$_4$, *J*(AB) 8], 7.49, 7.51 [(AB)$_2$, 4H, C$_6$H$_4$, *J*(AB) 8]. **5**: IR (hexane) cm^{-1}, ν(CO), 2144w, 2044s, 2009s; ν(C≡C), 2117m. ^{1}H NMR (CD$_2$Cl$_2$), δ 7.38, 7.48 [(AB)$_2$, 8H, C$_6$H$_4$, *J*(AB) 7]. **6**: IR (hexane) cm^{-1}, ν(CO) 2141w, 2044s, 2009s; ν(C≡C) 2113m. ^{1}H NMR (CD$_2$Cl$_2$) δ 0.93, 1.45, 1.53, 1.77 (18H, PBu$_3$), 7.2–7.8 (m, 8H, C$_6$H$_4$). ^{31}P NMR (CD$_2$Cl$_2$), δ 11.8.