

A novel methodology for the synthesis of complexes containing long carbon chains linking metal centres: molecular structures of $\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2(\mu\text{-C}_{14})$ and $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2(\mu_3\text{-}\mu_3\text{-C}_{16})^\dagger$

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Elimination of $\text{AuX}(\text{PR}_3)$ ($\text{X} = \text{halogen}$, $\text{R} = \text{Ph}$, tol) occurs readily in reactions between compounds containing $\text{C}(\text{sp})\text{-}$ or $\text{C}(\text{sp}^2)\text{-X}$ bonds and alkynyl or polyynyl gold(I) complexes; this reaction has been applied to the syntheses of complexes containing a variety of metal centres linked by C_n chains (n up to 16).

The chemistry of compounds containing two or more transition metal centres linked by chains of carbon atoms has excited researchers for a decade or more,¹ both on account of their intrinsic interest and, more recently, their potential as components or models of nanoscale electronic and optical devices.² In these complexes, the $\text{M-C}_n\text{-M}$ chain may adopt a variety of electronic configurations.³

There has been little development of the chemistry of species containing ten carbons or more in the chain, these presently being limited to complexes of rhenium,⁴ iron,⁵ ruthenium^{6,7} and platinum.⁸ The longest carbon-chain complex reported is $\{\text{Pt}(\text{C}_6\text{F}_5)[\text{P}(\text{ToI})_3]_2\}_2\{\mu\text{-}(\text{C}\equiv\text{C})_{12}\}$, so far obtained only in trace amounts.^{8c} These symmetrical complexes contain identical metal-ligand end-caps and have been made by either (i) oxidative coupling using Eglinton–Glaser or the milder Hay conditions or (ii) growth methodologies involving silylated derivatives, fluoride-induced desilylation and subsequent coupling. Combination of two different chains is often accompanied by competing side-reactions which involve the basic solvent; for example, in the case of cobalt cluster complexes, amido derivatives of the form $\text{Co}_3\{\mu_3\text{-CC}(\text{O})\text{N-Me}_2\}(\text{CO})_9$ are formed,^{9,10} while in the presence of alcohols, ruthenium complexes often afford alkoxy-carbene or carbonyl derivatives.¹¹

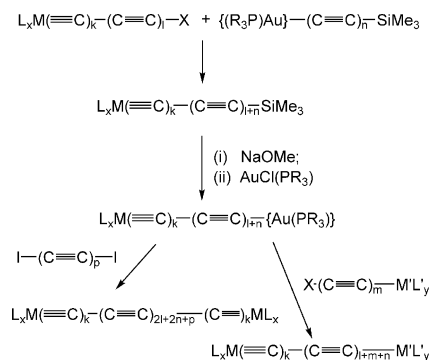
We sought an alternative route to complexes of this type and, guided by the isolobal analogy between H and $\text{Au}(\text{PR}_3)$,¹² we have discovered a novel elimination of $\text{AuX}(\text{PR}_3)$ ($\text{X} = \text{Cl}$, Br , I) in reactions between compounds containing $\text{C}(\text{sp})\text{-X}$ or $\text{C}(\text{sp}^2)\text{-X}$ bonds ($\text{X} = \text{Cl}$, Br , I) and alkynyl or polyynyl gold(I) complexes. This elimination takes place at r.t. in Et_2O or thf and is catalysed by $\text{Pd}(\text{O})/\text{Cu}(\text{I})$; in the absence of either or both of the latter, the reaction either did not proceed or was much slower. One-pot syntheses of the desired gold complexes, which are generally easier to obtain than the analogous Cu or Ag derivatives, from analogous SiMe_3 derivatives can be achieved by sequential reactions of the latter with base (NaOEt/EtOH) and $\text{AuCl}(\text{PAR}_3)$ ($\text{Ar} = \text{Ph}$, ToI). Examples of products we have characterised in initial studies of the scope of the reaction include $\text{PhC}\equiv\text{CC}\equiv\text{CFc}$ [**1**; 55% yield, from $\text{PhC}\equiv\text{CAu}(\text{PPh}_3)$ and $\text{FcC}\equiv\text{Cl}$]¹³, and $\text{FcC}\equiv\text{CC}(\text{O})\text{Ph}$ [**2**; 77% yield, from $\text{FcC}\equiv\text{CAu}(\text{PPh}_3)$ ¹⁴ and $\text{PhC}(\text{O})\text{Cl}$]. The rod-like $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh-4}(\mu\text{-dppm})(\text{CO})_7$ (**3**; 39% yield)¹³ was formed

from $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ ¹⁵ and $4\text{-PhC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CAu}(\text{PPh}_3)$.¹⁴

This reaction is the key step in a sequence of reactions capable of wide application to afford complexes containing odd- or even-numbered carbon atom chains linking two end-caps that may be either the same or different (Scheme 1). Evidently, construction of even-numbered carbon chains requires coupling between two smaller fragments, each bearing a σ -bonded polyynyl ligand ($k = 0$). In contrast, the synthesis of an odd-numbered carbon ligand with its M-C multiple bond requires a similarly multiply-bonded precursor, such as a metal carbyne complex ($k = 1$).

We have shown that facile coupling can be achieved between $\text{R}'\text{C}\equiv\text{CAu}(\text{PR}_3)$ and molecules such as $\text{I}(\text{C}\equiv\text{C})_n\text{R}$, $\text{I}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ or $\text{I}(\text{C}\equiv\text{C})_n\text{ML}_x$, together with organometallic mononuclear or cluster complexes containing CX groups, such as $\text{M}(\equiv\text{CX})(\text{CO})_2\text{Tp}$ ($\text{M} = \text{Mo}$, W) or $\{\text{ML}_x\}_3(\mu_3\text{-CX})$ [$\text{ML}_x = \text{Co}_3(\text{CO})_9$, $\text{Co}_3(\mu\text{-dppm})(\text{CO})_7$, $\text{Ru}_3(\mu\text{-H})_3(\text{CO})_9$, $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9$]; $\text{X} = \text{Cl}$, Br , I]. Products have been isolated in high yield and characterised by the usual analytical and spectroscopic methods and, in many cases, by single-crystal X-ray studies. A key to this success was the finding that symmetrical diiodopolyynes $\text{I}(\text{C}\equiv\text{C})_n\text{I}$ ($n = 1\text{--}4$)^{16,17} also react rapidly and completely, allowing chain elongation by between 2 and 8 carbons.

The sequence is applicable to the synthesis of complexes containing different end-groups and odd- or even-numbered carbon chains. As an example of the former, the coupling of $\text{Os}_3(\mu\text{-H})_3(\mu_3\text{-CBr})(\text{CO})_9$ with $\text{Fc}(\text{C}\equiv\text{C})_2\text{Au}(\text{PPh}_3)$, carried out in thf in the presence of $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ (r.t., 1 h), gave $\text{Os}_3(\mu\text{-H})_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_2\text{Fc}\}(\text{CO})_9$ (**4**; 86% yield). Similarly, the reaction between $\text{Ru}\{\text{C}(\text{C}\equiv\text{C})_2\text{Au}[\text{P}(\text{ToI})_3]\}(\text{PPh}_3)_2\text{Cp}$ and $\text{Ru}_3(\mu\text{-H})_3(\mu_3\text{-CBr})(\text{CO})_9$ afforded red crystals of $\text{Ru}_3(\mu\text{-H})_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_2[\text{Ru}(\text{PPh}_3)_2\text{-Cp}]\}(\text{CO})_9$ (**5**; 95% yield), while $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_4[\text{Ru}(\text{dppe})\text{-Cp}^*]\}(\mu\text{-dppm})(\text{CO})_7$ [**6**; 61% yield, from $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ and $\text{Ru}\{\text{C}(\text{C}\equiv\text{C})_4\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$] contains the longest (to our knowledge) odd-numbered carbon chain linking two metal centres. A further example results in the linking of three



Scheme 1

[†] Electronic supplementary information (ESI) available: synthetic procedures and characterisation data for $\text{Fc}(\text{C}\equiv\text{C})_2\text{Au}(\text{PPh}_3)$, **4** and **6–9**. See <http://www.rsc.org/suppdata/cc/b315854n/>

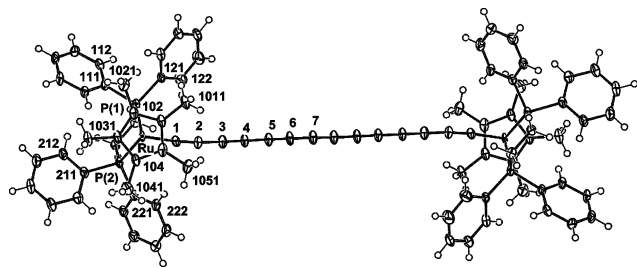


Fig. 1 Plot of a molecule of $\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-(C}\equiv\text{C)}_7\}$ (**8**). Significant bond distances and angles: Ru–C(1) 1.958(5), C(1)–C(2) 1.236(7), C(2)–C(3) 1.354(7), C(3)–C(4) 1.226(7), C(4)–C(5) 1.351(7), C(5)–C(6) 1.218(7), C(6)–C(7) 1.357(7), C(7)–C(7') 1.222(7) Å; Ru–C(1)–C(2) 173.8(5), C(1)–C(2)–C(3) 176.0(5), C(2)–C(3)–C(4) 178.6(6), C(3)–C(4)–C(5) 178.5(6), C(4)–C(5)–C(6) 177.5(7), C(5)–C(6)–C(7) 178.1(6), C(6)–C(7)–C(7') 178.7(6)°.

organometallic nuclei in the product obtained from the reaction between $\text{Fe}\{\eta\text{-C}_5\text{H}_4\text{C}\equiv\text{CAu}(\text{PPh}_3)\}_2^{14}$ and $\text{Co}_3(\mu\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$, which afforded $\text{Fe}\{\eta\text{-C}_5\text{H}_4\text{C}\equiv\text{C-}\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2$ (**7**; 96% yield). The X-ray structure of **7** will be described elsewhere.

The Pd(0)/Cu(I)-catalysed reaction of $\text{Ru}\{(\text{C}\equiv\text{C})_2\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ with $\text{I}(\text{C}\equiv\text{C})\text{I}$ afforded $\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-(C}\equiv\text{C)}_7\}$ (**8**; 36% yield), the first C_{14} complex to be structurally characterised.† A centrosymmetric molecule of **8** is shown in Fig. 1, with selected bond parameters given in the caption. As can be seen, the C_{14} chain is essentially straight, with deviations from linearity at the carbon atoms of between 1.3 and 6.2°; whilst the sum of deviations amounts to 37.6° and the separation of the two Ru centres [20.560(5) Å] is only 0.06 Å shorter than the sum of the Ru–C and C–C distances. The C–C separations alternate [ranges 1.211–1.228(8) and 1.336–1.371(8) Å for the short (C≡C) and long (C–C) distances, respectively] as expected for a conjugated polyyne system, with the longer bonds being in the middle of the C_{14} chain.

A sequence involving coupling of $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ with $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_2\text{Au}(\text{PPh}_3)$ to give $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_2\text{SiMe}_3\}(\mu\text{-dppm})(\text{CO})_7$, followed by a second auration as described above, afforded $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_2\text{Au}(\text{PR}_3)\}(\mu\text{-dppm})(\text{CO})_7$. Reaction with $\text{I}(\text{C}\equiv\text{C})\text{I}$ then gave the bis(cluster) C_{16} derivative $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2\{\mu_3\text{-}\mu_3\text{-C}(\text{C}\equiv\text{C})_7\text{C}\}$ (**9**; 86%), also structurally characterised.‡ Fig. 2 shows a plot of a centrosymmetric molecule of **9**, with selected bond parameters collected in the caption. There are no unusual features in the Co_3 clusters, while the C_{16} chain is also close to linear, with a maximum deviation of 10.3° from linearity at C(3) and a C(1)⋯C(1') separation of 19.176(8) Å, which is 0.15 Å shorter than the sum of the C–C distances.

In conclusion, we have devised and demonstrated a novel reaction sequence with the power to generate a wide range of new complexes containing odd- or even-numbered carbon chains with up to (so far) 16 carbon atoms, with either identical or dissimilar metal–ligand end-caps on the chains. These new materials have interesting redox, optical and electronic properties, which will be detailed elsewhere.

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Notes and references

† Crystal data for **8**: $\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-(C}\equiv\text{C)}_7\}\cdot 7\text{C}_6\text{H}_6 \equiv \text{C}_{86}\text{H}_{78}\text{P}_4\text{Ru}_2\cdot 7\text{C}_6\text{H}_6$, $M = 1984.04$; triclinic, space group $P\bar{1}$, $a = 14.108(3)$, $b = 14.438(3)$, $c = 15.051(3)$ Å, $\alpha = 75.371(3)$, $\beta = 88.083(3)$, $\gamma = 60.879(3)^\circ$, $V = 2577$ Å³, $Z = 1$; 22 528 (= N_{tot}) absorption-corrected CCD diffractometer reflections (monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å; $2\theta_{\text{max}} = 53^\circ$, $T \approx 153$ K) merged to N unique = 10 149 ($R_{\text{int}} = 0.057$), $N_{\text{obs}} [F > 4\sigma(F)] = 7823$; $R = 0.062$, $R_w = 0.078$. For **9**: $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2\{\mu_3\text{-}\mu_3\text{-C}(\text{C}\equiv\text{C})_7\text{C}\} \equiv \text{C}_{80}\text{H}_{44}\text{Co}_6\text{O}_{14}\text{P}_4$, $M = 1706.71$; monoclinic, space group $P2_1/n$, $a = 9.170(1)$, $b = 19.914(3)$, $c =$

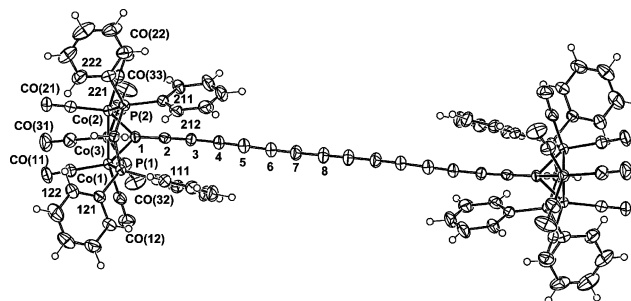


Fig. 2 Plot of a molecule of $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2\{\mu_3\text{-}\mu_3\text{-C}(\text{C}\equiv\text{C})_7\text{C}\}$ (**9**). Significant bond distances and angles: C(1)–C(2) 1.371(6), C(2)–C(3) 1.221(8), C(3)–C(4) 1.336(8), C(4)–C(5) 1.228(8), C(5)–C(6) 1.339(8), C(6)–C(7) 1.221(8), C(7)–C(8) 1.343(9), C(8)–C(8') 1.211(9) Å; C(1)–C(2)–C(3) 176.4(5), C(2)–C(3)–C(4) 169.7(6), C(3)–C(4)–C(5) 176.2(6), C(4)–C(5)–C(6) 178.9(6), C(5)–C(6)–C(7) 178.4(6), C(6)–C(7)–C(8) 178.6(6), C(7)–C(8)–C(8') 179.6(7)°.

20.221(3) Å, $\beta = 97.901(3)^\circ$, $V = 3657$ Å³, $Z = 2$; $N_{\text{tot}} = 36 221$, $N = 7475$ ($R_{\text{int}} = 0.041$), $N_{\text{obs}} = 5206$; $R = 0.057$, $R_w = 0.067$. CCDC 223663 and 223664. See <http://www.rsc.org/suppdata/cc/b3/b315854n/> for crystallographic data in CIF or other electronic format.

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