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A novel methodology for the synthesis of complexes containing long carbon chains linking metal centres: molecular structures of $\{Ru(dppe)Cp^*\}_2(\mu\text{-}C_{14})$ and $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-}C_{16})$†

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Elimination of $AuX(PR_3)$ (X = halogen, R = Ph, tol) occurs readily in reactions between compounds containing C(sp)– or C(sp²)–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 $M–C_n–M$ chain may adopt a variety of electronic configurations.[3]

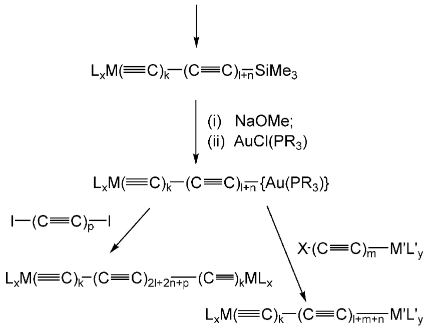
There has been little development of the chemistry of species containing ten carbons or more in the chain, these presently being limited to complexes of rhenium,[4] iron,[5] ruthenium[6,7] and platinum.[8] The longest carbon-chain complex reported is $\{Pt(C_6F_5)[P(Tol)_3]_2\}_2\{\mu\text{-}(C{\equiv}C)_{12}\}$, 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 $Co_3\{\mu_3\text{-}CC(O)NMe_2\}(CO)_9$ are formed,[9,10] while in the presence of alcohols, ruthenium complexes often afford alkoxycarbene or carbonyl derivatives.[11]

We sought an alternative route to complexes of this type and, guided by the isolobal analogy between H and $Au(PR_3)$,[12] we have discovered a novel elimination of $AuX(PR_3)$ (X = Cl, Br, I) in reactions between compounds containing C(sp)–X or C(sp²)–X bonds (X = 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 Pd(0)/Cu(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 $AuCl(PAr_3)$ (Ar = Ph, Tol). Examples of products we have characterised in initial studies of the scope of the reaction include $PhC{\equiv}CC{\equiv}CFc$ [**1**; 55% yield, from $PhC{\equiv}CAu(PPh_3)$ and $FcC{\equiv}CI$[13]], and $FcC{\equiv}CC(O)Ph$ [**2**; 77% yield, from $FcC{\equiv}CAu(PPh_3)$[14] and PhC(O)Cl]. The rod-like $Co_3(\mu_3\text{-}CC{\equiv}CC_6H_4C{\equiv}CPh\text{-}4)(\mu\text{-dppm})(CO)_7$ (**3**; 39% yield)[13] was formed from $Co_3(\mu_3\text{-}CBr)(\mu\text{-dppm})(CO)_7$[15] and $4\text{-}PhC{\equiv}CC_6H_4C{\equiv}CAu(PPh_3)$.[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 $R'C{\equiv}CAu(PR_3)$ and molecules such as $I(C{\equiv}C)_nR$, $I(C{\equiv}C)_nSiMe_3$ or $I(C{\equiv}C)_nML_x$, together with organometallic mononuclear or cluster complexes containing CX groups, such as $M({\equiv}CX)(CO)_2Tp$ (M = Mo, W) or $\{ML_x\}_3(\mu_3\text{-}CX)$ [ML_x = $Co_3(CO)_9$, $Co_3(\mu\text{-dppm})(CO)_7$, $Ru_3(\mu\text{-}H)_3(CO)_9$, $Os_3(\mu\text{-}H)_3(CO)_9$; X = 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 $I(C{\equiv}C)_nI$ (n = 1–4)[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 $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ with $Fc(C{\equiv}C)_2Au(PPh_3)$, carried out in thf in the presence of $Pd(PPh_3)_4$/CuI (r.t., 1 h), gave $Os_3(\mu\text{-}H)_3\{\mu_3\text{-}C(C{\equiv}C)_2Fc\}(CO)_9$ (**4**; 86% yield). Similarly, the reaction between $Ru\{(C{\equiv}C)_2Au[P(Tol)_3]\}(PPh_3)_2Cp$ and $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ afforded red crystals of $Ru_3(\mu\text{-}H)_3\{\mu_3\text{-}C(C{\equiv}C)_2[Ru(PPh_3)_2Cp]\}(CO)_9$ (**5**; 95% yield), while $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4[Ru(dppe)Cp^*]\}(\mu\text{-dppm})(CO)_7$ [**6**; 61% yield, from $Co_3(\mu_3\text{-}CBr)(\mu\text{-dppm})(CO)_7$ and $Ru\{(C{\equiv}C)_4Au(PPh_3)\}(dppe)Cp^*$] 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

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† Electronic supplementary information (ESI) available: synthetic procedures and characterisation data for $Fc(C{\equiv}C)_2Au(PPh_3)$, **4** and **6**–**9**. See http://www.rsc.org/suppdata/cc/b3/b315854n/

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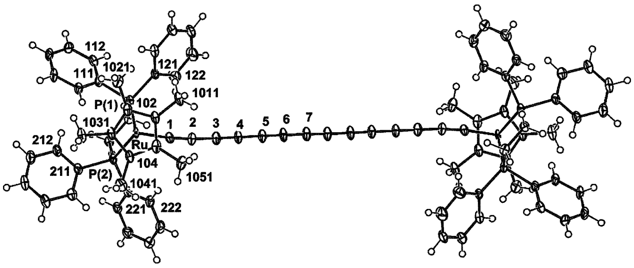

Fig. 1 Plot of a molecule of $\{Ru(dppe)Cp^*\}_2\{\mu\text{-}(C\equiv C)_7\}$ (**8**). Significant bond distances and angles: Ru–C(1) 1.958(5), C(1)–C(2) 1.236(7), C(2)–C(3) 1.354(7), C(3)–C(4) 1.226(7), C(4)–C(5) 1.351(7), C(5)–C(6) 1.218(7), C(6)–C(7) 1.357(7), C(7)–C(7′) 1.222(7) Å; Ru–C(1)–C(2) 173.8(5),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

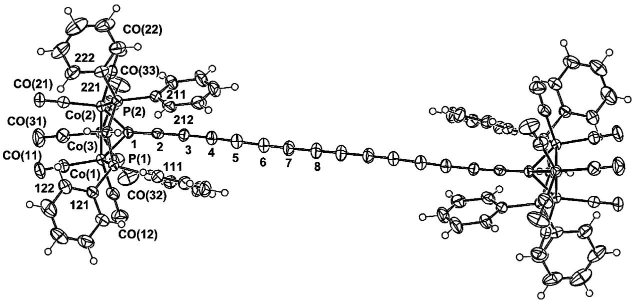

Fig. 2 Plot of a molecule of $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_7C\}$ (**9**). Significant bond distances and angles: C(1)–C(2) 1.371(6), C(2)–C(3) 1.221(8), C(3)–C(4) 1.336(8), C(4)–C(5) 1.228(8), C(5)–C(6) 1.339(8), C(6)–C(7) 1.221(8), C(7)–C(8) 1.343(9), C(8)–C(8′) 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)°.

organometallic nuclei in the product obtained from the reaction between $Fe\{\eta\text{-}C_5H_4C\equiv CAu(PPh_3)\}_2$[14] and $Co_3(\mu\text{-}CBr)(\mu\text{-}dppm)(CO)_7$, which afforded $Fe\{\eta\text{-}C_5H_4C\equiv C\text{-}\mu_3\text{-}C[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**7**; 96% yield). The X-ray structure of **7** will be described elsewhere.

The Pd(0)/Cu(I)-catalysed reaction of $Ru\{(C\equiv C)_2Au(PPh_3)\}(dppe)Cp^*$ with $I(C\equiv C)_3I$ afforded $\{Ru(dppe)Cp^*\}_2\{\mu\text{-}(C\equiv C)_7\}$ (**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 ($C\equiv C$) 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 $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ with $Me_3Si(C\equiv C)_2Au(PPh_3)$ to give $Co_3\{\mu_3\text{-}C(C\equiv C)_2SiMe_3\}(\mu\text{-}dppm)(CO)_7$, followed by a second auration as described above, afforded $Co_3\{\mu_3\text{-}C(C\equiv C)_2Au(PR_3)\}(\mu\text{-}dppm)(CO)_7$. Reaction with $I(C\equiv C)_3I$ then gave the bis(cluster) C_{16} derivative $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_7C\}$ (**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**: $\{Ru(dppe)Cp^*\}_2\{\mu\text{-}(C\equiv C)_7\}\cdot 7C_6H_6 \equiv C_{86}H_{78}P_4Ru_2\cdot 7C_6H_6$, M = 1984.04; triclinic, space group $P\bar{1}$, a = 14.108(3), b = 14.438(3), c = 15.051(3) Å, α = 75.371(3), β = 88.083(3), γ = 60.879(3)°, V = 2577 Å^3, Z = 1; 22 528 (= N_{tot}) absorption-corrected CCD diffractometer reflections (monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å; $2\theta_{max}$ = 53°, $T \approx$ 153 K) merged to N unique = 10 149 (R_{int} = 0.057), N_{obs} [$F > 4\sigma(F)$] = 7823; R = 0.062, R_w = 0.078. For **9**: $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_7C\} \equiv C_{80}H_{44}Co_6O_{14}P_4$, M = 1706.71; monoclinic, space group $P2_1/n$, a = 9.170(1), b = 19.914(3), c = 20.221(3) Å, β = 97.901(3)°, V = 3657 Å^3, Z = 2; N_{tot} = 36 221, N = 7475 (R_{int} = 0.041), N_{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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