Polycarbon ligand chemistry. Novel behaviour of μ-η^1,$\eta^2_{\alpha,\beta}$-butadiynyls towards metal fragment additions

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Reaction of [$Ru_2(CO)_6(\mu$-$PPh_2)(\mu$-$\eta^1,\eta^2_{\alpha,\beta}$-C≡C–C≡CR)] (R = Bu^t 1a, Ph 1b) with the labile complexes [$Pt(PPh_3)_2(\eta$-$C_2H_4)$], [Pt(dppb)(η-C_2H_4)] and [$Ni(cod)_2$] or [$Ni(CO)_4$] leads to the heteronuclear derivatives [$Ru_2Pt(CO)_7(PPh_3)(\mu_3$-$\eta^1,\eta^1,\eta^1$-C=C–C≡CR)($\mu$-$PPh_2$)] 2a,b, [$Ru_2Pt(CO)_6$(dppb)($\mu_3$-$\eta^1,\eta^1,\eta^1$-C=C–C≡CBu^t)($\mu$-$PPh_2$)] 2c and [$Ru_4Ni(CO)_{12}(\mu$-$PPh_2)_2(\mu_4$-$\eta^1,\eta^1,\eta^2,\eta^4$-Bu^{t}C≡CC$_4$C≡C-Bu^t)] 3 resulting from addition of a PtL$_2$ fragment and Ni-assisted stoichiometric coupling of two molecules of 1a respectively; the X-ray crystal structures of 2a and 3 are described.

The ability of ynyl and polyynyl [–C≡CR, –(C≡C)$_x$–] ligands to link metal centres into linear arrays bearing extended carbon–carbon unsaturation has stimulated the designed synthesis of molecular wires and rod-like new materials.[1] These highly unsaturated, carbon-rich chains possess even greater potential for the construction of two- and three-dimensional multimetallic arrays if the full coordinating capacity of the π systems can be exploited.[2,3] Here, we describe the addition of the reactive Pt and Ni reagents [$Pt(PPh_3)_2(\eta$-$C_2H_4)$], [Pt(dppb)(η-C_2H_4)] [dppb = 1,4-bis(diphenylphosphino)butane], [$Ni(cod)_2$] and [$Ni(CO)_4$] to the butadiynyl complexes [$Ru_2(CO)_6(\mu$-$PPh_2)(\mu$-$\eta^1,\eta^2_{\alpha,\beta}$-C≡C–C≡CR)] (R = Bu^t **1a**, Ph **1b**).

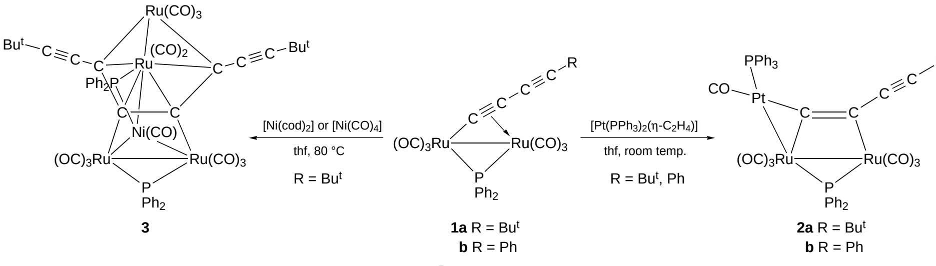
The σ–π butadiynyl complexes **1a** and **1b** react with [$Pt(PPh_3)_2(\eta$-$C_2H_4)$] in thf to give the trinuclear mixed-metal species [$Ru_2Pt(CO)_7(PPh_3)(\mu_3$-$\eta^1,\eta^1,\eta^1$-C=C–C≡CR)($\mu$-$PPh_2$)] **2** (**2a** 18%, **2b** 22%) (Scheme 1).† The molecular structure of **2a** (Fig. 1)‡ suggest that **2a,b** are formed from the addition of a Pt(CO)(PPh_3) fragment across the Ru–C$_\alpha$ bond of **1**. Thus **2a** contains the $Ru_2(CO)_6(\mu$-$PPh_2)$ unit found in **1** and is connected to Pt *via* Ru(1) to give a bent three-metal atom chain [Pt–Ru(1)–Ru(2) 105.837(17)°; Ru(1)–Pt 2.7725(13) Å]. The hydrocarbyl ligand is bound to all three metal atoms [Pt–C(38) 1.969(6), Ru(1)–C(38) 2.266(5), Ru(2)–C(39) 2.151(5) Å] and may be viewed as a metallated, alkynyl-functionalised μ-vinylidene bridging the Ru(1)–Pt bond *via* C(38) [C(38)–C(39) 1.284(8) Å]. The Pt centre is also ligated by a CO group [Pt–C(1) 1.905(7) Å] evidently scavenged from the reaction mixture and a PPh_3 ligand [Pt–P(2) 2.2884(13) Å] *trans* disposed to the Ru–Pt bond. The coordination environment about the Pt is approximately square planar and this moiety serves as a 16-electron fragment giving an overall count of 48 valence electrons for **2**, as found for other linear or bent M$_2$Pt complexes.[4] The transition from a σ–π bonding mode in **1a** to 3σ attachment in **2a** effects a distortion in the C$_4$ ligand [C(38)–C(39)–C(40) 136.3(5)° *cf.* 164. 9(4)° for the corresponding angle in **1a**[5]], although the outer triple bond length is essentially unchanged at 1.170(9) [*cf.* 1.172(6) in **1a**].

A competing process in the reaction of **1** with [$Pt(PPh_3)_2(\eta$-$C_2H_4)$] is phosphine substitution to give [$Ru_2(CO)_{6-n}(PPh_3)_n(\mu$-$PPh_2)(\mu$-$\eta^1,\eta^2_{\alpha,\beta}$-C≡C–C≡CR)] [$n$ = 1 (R = Bu^t, 29%), n = 2 (R = Bu^t, 13%)].§ Substitution is inhibited by using the chelating Pt complex [Pt(dppb)(η-C_2H_4)] which reacts rapidly at 293 K with a thf solution of **1a** to give the addition product [$Ru_2Pt(CO)_6$(dppb)(μ_3-η^1,η^1,η^1-C=C–C≡CBu^t(μ-PPh_2)] **2c** in 54% yield. X-Ray analysis confirmed **2c** as the analogue of **2a** and **2b**.

An isolobal analogy can be drawn between the reaction of **1** with the 14e moiety Pt(CO)(PPh_3) and the well documented addition of d^{10} ML$_2$ fragments to M=C bonds in mono- and poly-nuclear carbene and vinylidene complexes.[6] The Ru(1)=C$_\alpha$ unsaturation in **1a** presumably derives from a contribution of the canonical form Ru$^-$=C=C=C=C$^+$Bu^t to the bonding in **1**.[5]

1a also reacted smoothly with the naked nickel precursor [$Ni(cod)_2$]. After 2 h in refluxing thf, work-up gave a single major product [$Ru_4Ni(CO)_{12}(\mu$-$PPh_2)_2(\mu_4$-$\eta^1,\eta^1,\eta^2,\eta^4$-Bu^{t}C≡CC$_4$C≡CBu^t)] **3**.

The pentanuclear cluster **3** (Fig. 2) originates from the stoichiometric coupling of two molecules of **1a**, together with the incorporation of a single nickel atom which links the two Ru$_2$ units [Ru(2)–Ni 2.6910(16), Ru(3)–Ni 2.7042(17), Ru(4)–Ni 2.6957(16) Å]. The most outstanding feature of **3** is the head-to-head coupling of two butadiynyl ligands to create a C$_8$ chain which is attached to all four Ru atoms. This gives rise to a ruthenole unit formed from the π coordination of the Ru(1)–C(14)–C(13)–C(18)–C(19) ruthenacyclopentadiene ring to Ru(2). Although terminal, mononuclear butadiynyl ligands have been linked *via* oxidative coupling to generate linear C$_8$ chains,[1a,7] we are unaware of any examples of transition-metal mediated synthesis of C$_8$ ligands from binuclear or polynuclear C$_4$ precursors. The metallacyclopentadiene ring contains one long and two short C–C bonds [C(13)–C(14) 1.411(12), C(13)–C(18) 1.457(11), C(18)–C(19) 1.399(11) Å] in common with other crystallographically characterised examples from group 8, with the long bond bridging the Ru(3)–Ru(4) unit. This limited delocalisation extends to the exocyclic C(14)–C(15)



Scheme 1

[1.428(13) Å] and C(19)–C(20) [1.441(12) Å] bonds. Interestingly however, no elongation is apparent in the pendant alkynyl groups which exhibit typical C_{sp}–C_{sp} bond distances [C(15)–C(16) 1.182(13), C(20)–C(21) 1.186(13)].

Clearly a key step in the formation of **3** is the incorporation of a Ni(CO) moiety. Thus refluxing a thf solution of **1a** with excess $Ni(CO)_4$ indeed gave **3** as the major product, albeit in slightly lower yield {15% *cf.* 20% with $[Ni(cod)_2]$}, possibly suggesting the role of free nickel [*vs.* Ni(CO)] as an intermediate in the assembly of **3**.

It is perhaps surprising that both **2** and **3** contain uncoordinated triple bonds derived directly from the outer alkyne unit of precursor **1**, particularly considering the propensity of Pt^0 and Ni^0 reagents to form η^2-coordination complexes with free alkynes. Since sterically congested alkynes form η^2-coordination complexes with Pt^0 and Ni^0, it is unlikely that the presence of Bu^t or Ph substituents on the outer alkyne units of **1** account for the lack of complexation at these sites. However, while we believe this to be the first report detailing metal fragment additions to σ–π-butadiynyl complexes, there is evidence that metal aggregation ('clustering') occurs when fragments such as PtL_2 ($L = PR_3$, L_2 = cod) add to vinylidene and other hydrocarbyl-ligated species.[6] We suggest therefore that while **2a–c** are likely thermodynamic products and would not rearrange to the expected η^2-alkyne products, reaction at C_α may be driven by activation associated with μ-η^1,η^2 coordination. Such activation also accounts for recently observed regiospecificity in directing nucleophilic attack exclusively at the C_α–C_β sites[2a,8] in μ-η^1,η^2-butadiynyl complexes. These results suggest that metal activation of polyynyl ligands *via* μ-η^1,η^2-coordination can direct site specific metal fragment electrophilic attack and new patterns of C–C coupling.

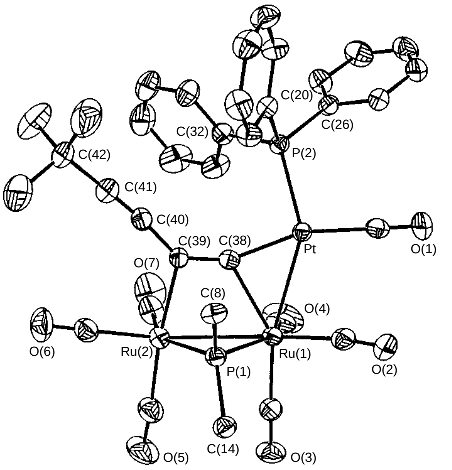


Fig. 1 Molecular structure of **2a**. For clarity, only the *ipso* carbons of the μ-PPh_2 phenyl rings are drawn. Relevant bond parameters: Ru(1)–Ru(2) 2.8407(6), C(39)–C(40) 1.400(8) Å; Ru(1)–P(1)–Ru(2) 74.56(4), Ru(2)–Ru(1)–Pt 105.837(17), Ru(1)–C(38)–Pt 81.46(20), Pt–C(38)–C(39) 153.9(5), C(39)–C(40)–C(41) 172.1(6), C(1)–Pt–C(38) 162.00(24), P(2)–Pt–Ru(1) 149.38(4)°.

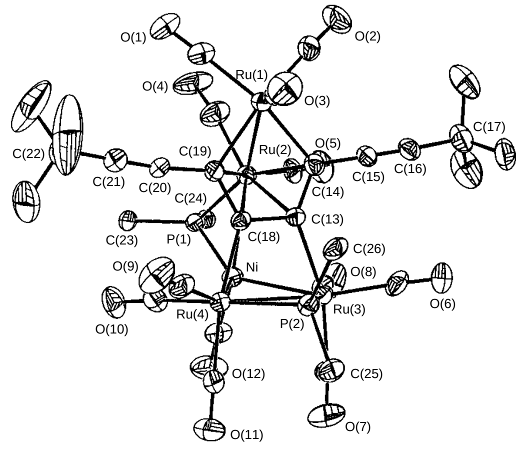


Fig. 2 Molecular structure of **3**. Relevant bond parameters: Ru(1)–Ru(2) 2.6860(11), Ru(3)–Ru(4) 2.8981(10), Ru(1)–C(14) 2.114(9), Ru(1)–C(19) 2.097(9), Ru(2)–C(13) 2.300(8), Ru(2)–C(14) 2.269(9), Ru(2)–C(18) 2.379(8), Ru(2)–C(19) 2.270(8), Ru(3)–C(13) 2.139(8), Ru(4)–C(18) 2.119(8) Å; Ru(2)–Ni–Ru(3) 91.73(5), Ru(2)–Ni–Ru(4) 100.46(5)°.

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Footnotes

† Experimental and spectroscopic data will be made available on the World Wide Web at http://chemistry.rsc.org/rsc/cccpub.htm

‡ *Crystallographic data*: **2a**: crystal grown from CH_2Cl_2–*n*-hexane (1 : 4) at –20 °C; $C_{45}H_{34}O_7P_2PtRu_2$, M = 1145.9; monoclinic, space group $P2_1/n$, a = 9.2369(6), b = 23.0550(11), c = 20.7034(8) Å, β = 97.596(5)°, U = 4370.3(4) Å^3, Z = 4, T = 295 K, D_c = 1.742 g cm^{-3}, $F(000)$ = 2211, λ = 1.54056 Å, μ(Cu-Kα) = 12.70 mm^{-1}. Intensity data were collected on a crystal of dimensions 0.25 × 0.25 × 0.20 mm mounted on an Enraf-Nonius CAD4 diffractometer using the θ–2θ scan method. The structure was solved (direct methods) and refined (full-matrix least squares) using 6526 observed [$I > 2.5\,\sigma(I)$] reflections to final R and R_w values of 0.031 and 0.041 respectively.

3: crystal grown from *n*-hexane at −20 °C; $C_{52}H_{38}O_{12}NiP_2Ru_4$, M = 1379.8; monoclinic, space group $P2_1/c$, a = 11.4833(19), b = 12.460(3), c = 38.055(4) Å, β = 91.016(14)°, U = 5444.3(17) Å^3, Z = 4, T = 295 K, D_c = 1.683 g cm^{-3}, $F(000)$ = 2717, λ = 1.54056 Å, μ(Cu-Kα) = 10.43 mm^{-1}. Intensity data were collected on a crystal of dimensions 0.03 × 0.20 × 0.20 mm as for **2a**. The structure was solved (direct methods) and refined (full-matrix least squares) using the 5211 observed [$I > 2.5\,\sigma(I)$] reflections to final R and R_w values of 0.043 and 0.049 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/338.

§ Performing the reaction with **1a** under a purge of CO gas inhibited the formation of substitution products but gave exactly the same yield of **2a**. For **1b** using a CO purge, **2b** (22%) and the monophosphine complex $[Ru_2(CO)_5(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{–}C{\equiv}CPh)]$ (36%) were produced.

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