

Chemistry of μ - η^1 : $\eta^2_{\alpha,\beta}$ -Butadiynyls: Chain Extension on C_4 Polycarbon Ligands

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The binuclear butadiynyl compounds $Ru_2(CO)_6(\mu-\eta^1, \eta^2_{\alpha,\beta}-C\equiv C-C\equiv CR)(\mu-PPh_2)$ ($R = Bu^t$ **1a** or Ph **1b**), with one π -coordinated and one free triple bond, synthesised *via* thermolysis of $Ru_3(CO)_{11}(PPh_2C\equiv C-C\equiv CR)$, react with NEt_2H to generate the novel diethylaminobutatriene complexes $Ru_2(CO)_6[\mu-\eta^1, \eta^1-Et_2N-C\equiv C-C(H)R](\mu-PPh_2)$ ($R = Bu^t$ **2a** or Ph **2b**) in high yields: the molecular structures of **1a** and **2a** are determined.

Transition metal diynyls ($M-C\equiv C-C\equiv CR$) are members of a rapidly expanding family of organometallic molecules bearing a carbon-rich, extended chain hydrocarbyl ligand.¹ Interest in such molecules stems from the favourable electronic and structural features of ynyl [$C\equiv CR$, $(C\equiv C)_x$, $(C\equiv C)_yR$] ligands for linking metal centres *via* σ - or σ/π networks and for the unusual material properties of designed ynyl-based oligomers and polymers.² By comparison with complexes of its lower homologue, the $C\equiv CR$ ligand, for which an extensive coordination chemistry and reactivity profile is established,³ relatively few organometallic diynyls have been prepared⁴ and their chemistry remains virtually unexplored. Here we describe the synthesis, characterisation and initial reactivity studies of two new binuclear diynyls, $Ru_2(CO)_6(\mu-\eta^1, \eta^2_{\alpha,\beta}-C\equiv C-C\equiv CR)(\mu-PPh_2)$ ($R = Bu^t$ **1a** or Ph **1b**). The butadiynyl ligands in **1** are bound to one metal centre *via* a σ -bond and to the other *via* a π -interaction of the inner triple bond, the outer alkyne functionality remaining uncoordinated. With the secondary amine Et_2NH , **1a** and **1b** undergo exclusive nucleophilic attack at the coordinated triple bond, generating novel diethylaminobutatriene ligands *via* C_4 chain extension.

The phosphinodiyne ligands $PPh_2C\equiv C-C\equiv CR$ ($R = Bu^t, Ph$) were prepared by sequential addition of $BuLi$ and PPh_2Cl at $-78^\circ C$ to $HC\equiv C-C\equiv CR$, obtained from the Cadiot–Chodkiewicz coupling of $RC\equiv CBr$ and $HC\equiv CCH_2OH$.⁵ This allowed convenient access to the monosubstituted clusters $Ru_3(CO)_{11}(PPh_2C\equiv C-C\equiv CR)$,[†] which under conditions of thermolysis in refluxing THF, afforded the μ - $\eta^1, \eta^2_{\alpha,\beta}$ -butadiynyl complexes **1a** and **1b**. Column chromatography on silica gel allowed the isolation of the dinuclear products $Ru_2(CO)_6(\mu-\eta^1, \eta^2-C\equiv C-C\equiv CR)(\mu-PPh_2)$ in moderate yields ($R = Bu^t$, 31%; $R = Ph$, 24%).[‡] The precise nature of the diynyl ligand and its interaction with the phosphido-bridged $(OC)_3Ru-Ru(CO)_3$ unit was of particular interest and an X-ray crystal structure determination of **1a** was undertaken, Fig. 1. § This revealed a μ - $\eta^1, \eta^2_{\alpha,\beta}$ -bonding mode of the hydrocarbyl ligand, with a σ -bond between C(7) and Ru(1) [2.031(3) Å] and π -coordination to Ru(2) *via* C(7) [2.284(3) Å] and C(8) [2.408(3) Å]. The C–C

bond distances are consistent with an acetylenic designation of C(7)–C(8) [1.227(5) Å] and C(9)–C(10) [1.172(6) Å] and form an approximately linear polycarbon chain [C(7)–C(8)–C(9) 164.9(4), C(8)–C(9)–C(10) 179.2(4), C(9)–C(10)–C(11) 174.3(8)°]. Hence the metal atoms are bridged by a phosphido group and by C_α and C_β of the butadiynyl ligand, leaving the second alkyne unit, $C_\gamma\equiv C_\delta$, unattached. As expected, the structural data for the ynyl-coordinated part of **1a** closely resemble those obtained for the corresponding acetylide complex $Ru_2(CO)_6(\mu-\eta^1, \eta^2-C\equiv CBu^t)(\mu-PPh_2)$,⁶ [C $\equiv$ C 1.218(4) Å; Ru–Ru 2.7523(3) *vs.* 2.769(1) Å in **1a**; Ru–P–Ru 72.03(1), 71.9(1)° in **1a**]. A decrease in the magnitude of J_{PC} coupling constants from C_α to C_δ allows ready assignment of the diynyl ^{13}C NMR signals in **1a** and **1b**. In each case, C_α resonates downfield of the other quaternary carbons, presumably reflecting its coordination to both metal centres.

Molecules **1a** and **1b** provide an interesting opportunity to test the preference for nucleophilic attack at a free or coordinated triple bond. Treatment of a heptane solution of **1a** or **1b** with excess diethylamine at room temp. effects a smooth and quantitative conversion to bright yellow **2a,b**, Scheme 1. The new organic ligand is the result of exclusive nucleophilic addition at C_α of the original butadiynyl group and an unusual hydrogen migration from nitrogen to C_δ of the hydrocarbyl, as determined by an X-ray diffraction of **2a**, Fig. 2. § Evidently C–N bond formation at C_α is associated with a new C_δ –H bond, generating a 1,4-addition product which may be best described as a diethylaminobutatriene. A short single carbon–carbon bond links the bridging carbon atoms of the Ru_2C_2 metallacyclic frame [C(7)–C(8) 1.470(5) Å], while C(7) is also attached to the diethylamine moiety with a C=N bond length [1.315(4) Å] typical of iminium ion salts.⁷ The three-carbon fragment C(8)C(9)C(10) is almost linear, giving an angle of 171.9(4)°, and thus resembles an allene unit with representative C–C bond lengths [C(8)–C(9) 1.303(5), C(9)–C(10) 1.306(5) Å]. The zwitterionic nature of **2** may alternatively be depicted by its neutral resonance form featuring a carbene-type interaction between Ru(1) and C(7). Such a contribution is in part confirmed by a shortened Ru(1)–C(7) [2.121(3) Å] bond relative to Ru(2)–C(8) [2.158(4) Å] and also by the low-field shift of C(7) in the ^{13}C NMR spectrum at δ 220.4. ‡

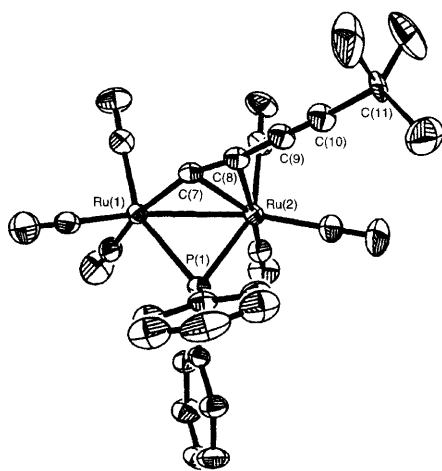
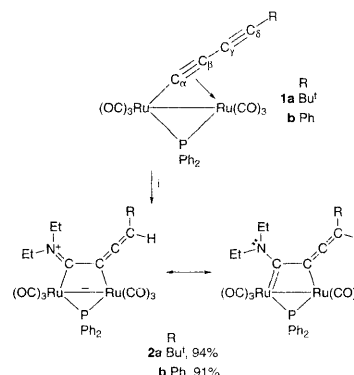


Fig. 1 Molecular structure of **1a**. Relevant bond parameters are discussed in the text



Scheme 1 Reagents and conditions: i, 2 NEt_2H , heptane, room temp., 1 h

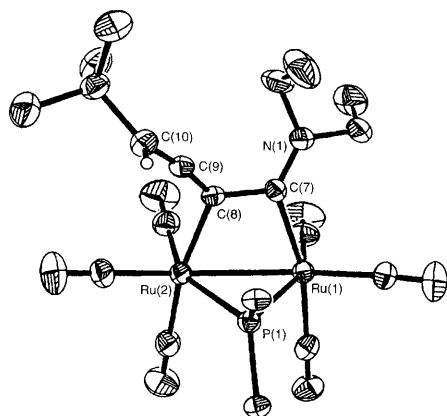


Fig. 2 Molecular structure of **2a**. For clarity, only the *ipso* carbons of the phenyl rings are drawn. Selected interatomic distances (Å) and angles (°): Ru(1)–Ru(2) 2.792(1), Ru(1)–P(1)–Ru(2) 73.4(1), C(7)–C(8)–C(9) 131.3(3), N(1)–C(7)–C(8) 120.9(3).

The regioselectivity of secondary amine addition to C_{α} of **1a,b** generating a coordinated diethylaminobutatriene ligand contrasts sharply with the formation of both μ -alkylidene and μ - η^1, η^1 -aminophenethylidene complexes *via* C_{β} and C_{α} attack, respectively, in the corresponding mononuclear complexes.⁸

Complexes containing aminopolysaturated C_n ligands are rare in group 8 chemistry,⁹ although the related mononuclear aminocarbene and vinylaminocarbene complexes of group 6 metals are coming to the fore because of their potential utility in organic synthesis.¹⁰ Further studies of the chemical reactivity of **1** are currently in progress.

We are grateful to the NSERC of Canada for financial support of this work.

Received, 16th May 1995; Com. 5/03112E

Footnotes

† Treatment of a THF solution of $Ru_3(CO)_{12}$ with one molar equiv. of phosphinodiyne $PPh_2C\equiv C-C\equiv CR$ ($R = Bu^t, Ph$), in the presence of a catalytic amount of sodium benzophenone ketyl, provides quantitative yields of $Ru_3(CO)_{11}(PPh_2C\equiv C-C\equiv CR)$.

‡ Spectroscopic data for **1a** and **1b**: IR (C_6H_{14}) $\nu(CO)/cm^{-1}$ **1a** 2085s, 2057s, 2021s, 2010m, 2002s, 1990mw; **1b** 2085s, 2058s, 2022s, 2012m, 2003s, 1992mw. NMR (J/Hz): 1H ($CDCl_3$) δ **1a** 7.48–7.20 (m, 10 H, Ph), 1.10 (s, 9 H, Bu^t); **1b** 7.61–7.21 (m, Ph); ^{13}C (1H) **1a** ($CDCl_3$) δ 197.4 (d, J_{PC} 12.6, CO), 195.0 (d, J_{PC} 72.5, CO), 193.6 (d, J_{PC} 4.5, CO), 138.9 (d, J_{PC} 28.7, PC_{ipso}), 134.2–128.0 (m, Ph), 100.2 (d, J_{PC} 27.7, C_{α}), 88.1 (s, C_{β}), 74.5 (d, J_{PC} 7.5, C_{β}), 66.8 (d, J_{PC} 3.5, C_{γ}), 30.6 (s, CMe_3), 28.0 (s, CMe_3); **1b** (CD_2Cl_2) δ 197.7 (d, J_{PC} 11.6, CO), 195.2 (d, J_{PC} 72.0, CO), 193.8 (d, J_{PC} 5.0, CO), 139.0 (d, J_{PC} 29.0, PC_{ipso}), 133.6 (d, J_{PC} 33.2, PC_{ipso}), 135.5–128.5 (m, Ph), 122.3 (s, PC_{ipso}), 109.0 (d, J_{PC} 27.7, C_{α}), 78.2 (d, J_{PC} 2.5, C_{β}), 77.4 (d, J_{PC} 4.5, C_{γ}), 74.0 (d, J_{PC} 8.2, C_{β}); ^{31}P (1H) ($CDCl_3$) δ **1a** 124.6 (s); **1b** 123.8 (s). For **2a** and **2b**: IR (C_6H_{14}) $\nu(CO)/cm^{-1}$ **2a** 2065vs, 2033vs, 2000vs, 1979s, 1961m; **2b** 2067vs, 2037vs, 2002vs, 1985s, 1965m. NMR: 1H (CD_2Cl_2 , 273 K) δ **2a** 7.80–7.18 (m, 10 H, Ph), 4.28 (sxt, J_{H_aMe} 7.0, $J_{H_bH_c}$ 13.5, 1 H, CH_aCH_bMe), 3.83 (spt, J_{H_aMe} 7.0, $J_{H_bH_c}$ 12.8, J_{H_bMe} 7.0, $J_{H_cH_d}$ 12.8, 2 H, CH_cCH_dMe), 3.41 (sxt, J_{H_bMe} 7.0, $J_{H_bH_c}$ 13.5, 1 H, CH_aCH_bMe), 3.01 (d, J_{PH} 9.1, 1 H, =CH), 1.38 (t, J_{HH} 7.0, 3 H, $MeCH_2$), 0.86 (s, 9 H, Bu^t), 0.81 (t, J_{HH} 7.0, 3 H, $MeCH_2$); **2b** 7.82–6.86 (m, 15 H, Ph), 4.37 (sxt, J_{H_aMe} 6.8, $J_{H_bH_c}$ 13.4, 1 H, CH_aCH_bMe), 3.91 (d, J_{PH} 8.8, 1 H, =CH), 3.68 (spt, J_{H_aMe} 6.5, $J_{H_bH_c}$ 13.2, J_{H_bMe} 6.5, $J_{H_cH_d}$ 13.2, 2 H, CH_cCH_dMe), 3.11 (sxt, J_{H_bMe} 6.8, $J_{H_bH_c}$ 13.4, 1 H, CH_aCH_bMe), 1.33 (t, J_{HH} 7.1, 3 H, $MeCH_2$), 0.88 (t, J_{HH} 6.9, 3 H, $MeCH_2$); ^{13}C (1H) (CD_2Cl_2 , 223 K) δ **2a** 220.4 (s, C_{α}), 203.9 (d, J_{PC} 52.8, CO), 203.3 (d, J_{PC} 63.9, CO), 200.1 (d, J_{PC} 9.2, CO), 199.8 (d, J_{PC} 11.3, CO), 196.6 (s, CO), 196.2 (d, J_{PC} 4.2, CO), 194.9 (d, J_{PC} 5.9, C_{γ}), 141.8 (d, J_{PC} 26.2, PC_{ipso}), 136.0 (d, J_{PC} 40.0,

PC_{ipso}), 133.6–128.0 (m, Ph), 93.6 (d, J_{PC} 12.9, C_{β}), 86.3 (d, J_{PC} 3.1, C_{δ}), 54.5 (s, $MeCH_2$), 45.5 (s, $MeCH_2$), 31.6 (d, J_{PC} 2.7, CMe_3), 29.9 (s, CMe_3), 13.6 (s, $MeCH_2$), 13.5 (s, $MeCH_2$); **2b** 218.9 (s, C_{α}), 203.2 (d, J_{PC} 52.8, CO), 202.9 (d, J_{PC} 62.9, CO), 199.8 (d, J_{PC} 9.1, CO), 199.3 (d, J_{PC} 11.6, CO), 195.7 (s, CO), 195.7 (d, J_{PC} 5.5, CO), 194.2 (d, J_{PC} 5.5, C_{γ}), 141.2 (d, J_{PC} 28.2, PC_{ipso}), 135.7 (d, J_{PC} 30.7, PC_{ipso}), 135.0 (d, J_{PC} 3.0, C_{ipso}), 133.5–125.0 (m, Ph), 95.1 (d, J_{PC} 11.9, C_{β}), 79.2 (br s, C_{δ}), 54.1 (s, $MeCH_2$), 45.9 (s, $MeCH_2$), 13.7 (s, $MeCH_2$), 13.0 (s, $MeCH_2$); ^{31}P (1H) ($CDCl_3$) δ **2a** 153.3 (s); **2b** 153.1 (s). Satisfactory elemental analyses were obtained for each compound.

§ Crystal data for **1a**: pale yellow polyhedra, $C_{26}H_{19}O_6PRu_2$, $M = 660.6$; monoclinic, space group $P2_1/n$, $a = 9.849(2)$, $b = 9.886(2)$, $c = 28.368(9)$ Å, $\beta = 95.18(2)^\circ$, $U = 2751.1(12)$ Å³, $Z = 4$, $T = 295$ K, $D_c = 1.595$ g cm⁻³, $F(000) = 1304$, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 11.92$ cm⁻¹. Intensity data were collected on a crystal of dimensions $0.60 \times 0.36 \times 0.25 \times 0.36$ mm mounted on a Siemens R3m/V diffractometer by the ω scan method ($2\theta < 50^\circ$). A total of 5169 reflections were collected of which 3886 were observed [$F > 6.0\sigma(F)$]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to yield final R and R_w values of 0.0243 and 0.0253 respectively. For **2a**: pale yellow polyhedra, crystal dimensions $0.44 \times 0.43 \times 0.58 \times 0.49$ mm, $C_{30}H_{30}NO_6PRu_2$, $M = 733.7$; orthorhombic, space group $P2_12_12_1$, $a = 10.796(2)$, $b = 16.375(2)$, $c = 17.664(2)$ Å, $U = 3122.8(7)$ Å³, $Z = 4$, $T = 200$ K, $D_c = 1.560$ g cm⁻³, $F(000) = 1472$, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 10.59$ cm⁻¹. The structure was solved and refined as for **1a** on the basis of 2951 observed reflections [$F > 6.0\sigma(F)$] (6032 measured). The final R and R_w values were 0.0190 and 0.0207 respectively. Refinement of the structure using the unmerged Friedels (5231 obs.) yielded $R = 0.0204$, $R_w = 0.0222$ and refinement of the opposite enantiomorph gave $R = 0.0238$, $R_w = 0.0264$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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