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

Peter Blenkiron, Didier Pilette, John F. Corrigan, Nicholas J. Taylor and Arthur J. Carty*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The binuclear butadiynyl compounds $Ru_2(CO)_6(\mu$-$\eta^1,\eta^2_{\alpha,\beta}$-C≡C–C≡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 $Ru_2(CO)_6[\mu$-η^1,η^1-$Et_2N{=}C{=}C{=}C{=}C(H)R](\mu$-$PPh_2)$ (R = Bu^t **2a** or Ph **2b**) in high yields: the molecular structures of **1a** and **2a** are determined.

Transition metal diynyls (M–C≡C–C≡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≡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≡CR ligand, for which an extensive coordination chemistry and reactivity profile is established,[3] relatively few organometallic diynyls have been prepared[4] 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≡C–C≡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 °C to HC≡C–C≡CR, obtained from the Cadiot–Chodkiewicz coupling of RC≡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 $Ru_2(CO)_6(\mu$-η^1,η^2-C≡C–C≡CR)(μ-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 dibridged 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 $Ru_2(CO)_6(\mu$-η^1,η^2-C≡CBu^t)(μ-PPh_2),[6] [C≡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.

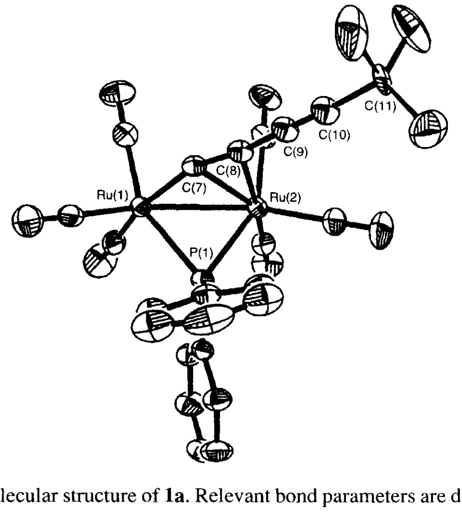
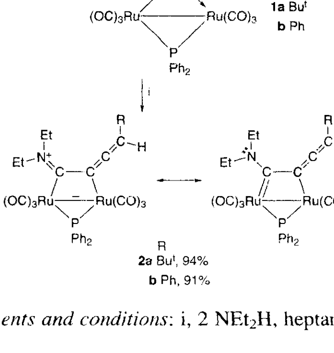


Fig. 1 Molecular structure of **1a**. Relevant bond parameters are discussed in the text

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.‡



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

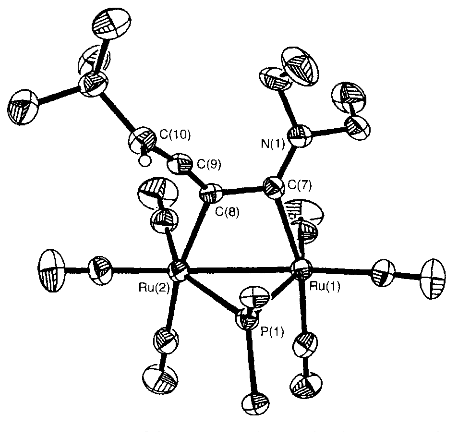


Fig. 2 Molecular structure of **2a**. For clarity, only the *ipso* carbons of the phenyl rings are drawn. Selected interatomic distances (Å) and angles (°): Ru(1)–Ru(2) 2.792(1), Ru(1)–P(1)–Ru(2) 73.4(1), C(7)–C(8)–C(9) 131.3(3), N(1)–C(7)–C(8) 120.9(3).

The regiospecificity 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 mononynl compounds.[8]

Complexes containing aminopolyunsaturated 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}) ν(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_δ), 74.5 (d, J_{PC} 7.5, C_β), 66.8 (d, J_{PC} 3.5, C_γ), 30.6 (s, C*Me*$_3$), 28.0 (s, *C*Me$_3$); **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_δ), 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}) ν(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, $J_{H_aH_b}$ 13.5, 1 H, CH_aCH_bMe), 3.83 (spt, J_{H_aMe} 7.0, $J_{H_cH_d}$ 12.8, J_{H_dMe} 7.0, $J_{H_dH_c}$ 12.8, 2 H, CH_cCH_dMe), 3.41 (sxt, J_{H_bMe} 7.0, $J_{H_bH_a}$ 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, *Me*CH_2), 0.86 (s, 9 H, Bu^t), 0.81 (t, J_{HH} 7.0, 3 H, *Me*CH_2); **2b** 7.82–6.86 (m, 15 H, Ph), 4.37 (sxt, J_{H_aMe} 6.8, $J_{H_aH_b}$ 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, $J_{H_cH_d}$ 13.2, J_{H_dMe} 6.5, $J_{H_dH_c}$ 13.2, 2 H, CH_cCH_dMe), 3.11 (sxt, J_{H_bMe} 6.8, $J_{H_bH_a}$ 13.4, 1 H, CH_aCH_bMe), 1.33 (t, J_{HH} 7.1, 3 H, *Me*CH_2), 0.88 (t, J_{HH} 6.9, 3 H, *Me*CH_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, *C*Me$_3$), 29.9 (s, C*Me*$_3$), 13.6 (s, *Me*CH_2), 13.5 (s, *Me*CH_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, *Me*CH_2), 13.0 (s, *Me*CH_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, β = 95.18(2)°, U = 2751.1(12) $Å^3$, Z = 4, T = 295 K, D_c = 1.595 g cm^{-3}, $F(000)$ = 1304, λ = 0.71073 Å, μ(Mo-Kα) = 11.92 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.60 × 0.36 × 0.25 × 0.36 mm mounted on a Siemens R3m/V diffractometer by the ω scan method ($2\theta < 50°$). 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 × 0.43 × 0.58 × 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) $Å^3$, Z = 4, T = 200 K, D_c = 1.560 g cm^{-3}, $F(000)$ = 1472, λ = 0.71073 Å, μ(Mo-Kα) = 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 Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

References

1 See for example: D. Touchard, P. Haquette, A. Daridor, L. Toupet and P. H. Dixneuf, *J. Am. Chem. Soc.*, 1994, **116**, 11157; M. Brady, W. Weng and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 1994, 2655; T. Rappert, O. Nürnberg and H. Werner, *Organometallics*, 1993, **12**, 1359; M. I. Bruce, P. Hinterding, E. R. T. Tiekink, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **450**, 209; J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend and A. E. Dray, *J. Organomet. Chem.*, 1992, **425**, 165.

2 A. J. Hodge, S. L. Ingham, A. K. Kakkar, M. S. Khan, J. Lewis, N. J. Long, D. G. Parker and P. R. Raithby, *J. Organomet. Chem.*, 1995, **488**, 205; H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1991, 188; S. Takahashi, Y. Takai, H. Morimoto and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3; Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller, K. Scott, L. Koch, N. J. Taylor and T. B. Marder, *J. Organomet. Chem.*, 1993, **452**, 115.

3 E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219; M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.

4 N. Pirio, D. Touchard, P. H. Dixneuf, M. Fettouhi and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 651; Y. Sun, N. J. Taylor and A. J. Carty, *Organometallics*, 1992, **11**, 4292; H. Werner, O. Gevert, P. Steinert and J. Wolf, *Organometallics*, 1995, **14**, 1786; A. Wong, P. C. W. Kang, C. D. Tagge and D. R. Leon, *Organometallics*, 1990, **9**, 1992; W. Weng, T. Bartik and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2199.

5 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988.

6 A. A. Cherkas, L. H. Randall, S. A. MacLaughlin, G. N. Mott, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 969.

7 R. Merenyi, *Adv. Org. Chem.*, 1976, **9**, 90.

8 A. A. Cherkas, L. H. Randall, N. J. Taylor, G. N. Mott, J. E. Yule, J. L. Guinamant and A. J. Carty, *Organometallics*, 1990, **9**, 1677; A. A. Cherkas, G. N. Mott, R. Granby, S. A. Maclaughlin, J. E. Yule, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 1115.

9 E. Cabrera, J.-C. Daran, Y. Jeannin and O. Kristiansson, *J. Organomet. Chem.*, 1986, **310**, 367.

10 J. Barluenga, F. Aznar and A. Martín, *Organometallics*, 1995, **4**, 1429, and references cited therein.